TOXICITY OF SEDIMENT AND PORE WATER FROM STREAM AND RESERVOIR SITES DOWNSTREAM OF LEAD MINING AREAS

Allert, A.L., Besser, J.M., Fairchild, J.F., Kunz, J.L., Schmitt, C.J., Ingersoll, C.G., and May, T.W., U.S. Geological Survey, Columbia Environmental Research Center, Columbia, MO

ABSTRACT

The Viburnum Trend mining district of southeast Missouri is one of the world's largest producers of lead ore. The possibility of mining operations expanding into the adjacent Mark Twain National Forest and the Ozark National Scenic Riverways has raised concerns about contamination of aquatic resources and risks of toxicity to aquatic biota. We assessed potential impacts of mining on aquatic invertebrates using laboratory toxicity tests. Sediments collected from 15 stream and reservoir sites, including two reference sites with no known upstream mining activity, were tested with the amphipod, *Hyalella azteca* (42-d survival, growth, and reproduction) and pore waters from these sediments were tested with *Ceriodaphnia dubia* (7-d survival and reproduction). Sediment and pore water samples were analyzed for metals, major elements, and other constituents that may affect metal bioavailability, including acid volatile sulfide, dissolved organic carbon, and ammonia. Pore water of sediments from six sites caused significant mortality of *C. dubia*, and sediment from two sites caused significant mortality of *H. azteca*. Reproduction of *C. dubia* was reduced by pore waters from nine sites. Growth of *Hyalella* was not significantly affected by any of the sediments, but amphipod reproduction was reduced by sediments from three sites. Effects on survival and reproduction were associated with pore-water concentrations of lead or zinc above the chronic water quality criteria (12.9 and 265 µg/L, respectively) at sites with impacted survival or reproduction of these species. These results indicate that current mining practices result in significant metals exposure and potential ecological effects on aquatic biota. We will attempt to validate these findings using community surveys of benthic invertebrate and fish communities.

INTRODUCTION

❖Recent proposals to expand areas of prospecting for deposits of lead ore in the Mark Twain National Forest (MTNF) of southeast Missouri raised concerns about potential surface and ground-water quality degradation due to lead mining. In response to concerns about potential impacts in Federal lands (MTNF and the Ozark National Scenic Riverways), the USGS is evaluating the effects of current and proposed mining activities on surface and ground waters in the Missouri Ozarks.

❖These investigations have found elevated concentrations of lead and other elemental contaminants associated with lead mining. Biochemical effects indicate exposure of fish to environmental lead from sites closest to mines and tailings (Whyte 2001).

STUDY AREA

❖We selected 15 sites (Figure 1 and Table 1) to characterize the influence of mining activities on metals and other constituents of aquatic sediment in water sheds with mining activity. Ten sites were located in wadable streams and 5 sites were located in Clearwater Lake, a reservoir located on the mainstem of the Black River.

❖Three sites are designated as 'reference' sites. These sites were either upstream of mining activity (MT3) or in watersheds without mining activity (MT10, CL3).

❖MT20 was selected in the Big River which is a stream where stream sediment are extensively contaminated with mine tailings from historic mining in the Old Lead Belt.

OBJECTIVES

❖Determine concentrations of lead and associated metals in sediment and pore waters.

❖Conduct laboratory toxicity tests to determine if lead and associated metals in sediment and pore water are significantly impacting survival, growth and reproduction of test organisms

METHODS

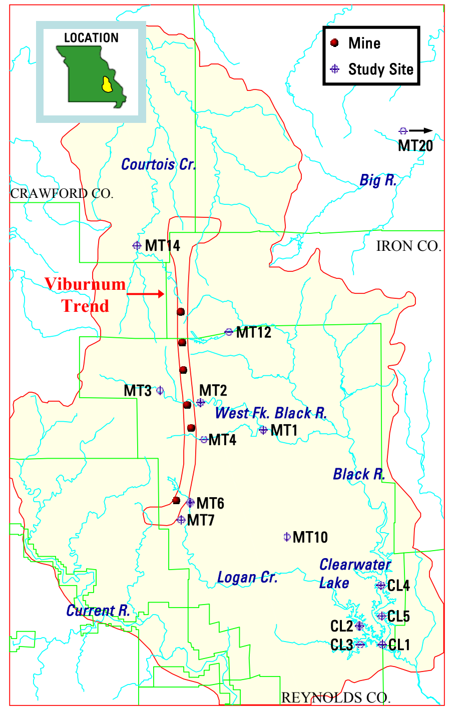


Figure 1. Location of sediment collection sites and mines of the Viburnum Trend Mining District in southeast Missouri.

Table 1. Study site locations and types.

Site ID	Site Description	Type of Site
MT1	West Fork Black River at Sutton Bluff	Stream
MT2	West Fork Black River at West Fork	Stream
MT3	West Fork Black River at Greeley	Stream - Reference
MT4	Bee Fork Creek	Stream
MT6	Logan Creek	Stream
MT7	Sweetwater Creek	Stream
MT10	Sinking Creek	Stream - Reference
MT12	Strother Creek	Stream
MT14	Courtois Creek	Stream
MT20	Big River	Stream
CL1	Clearwater Lake - Near dam	Lake
CL2	Clearwater Lake - Logan Creek arm	Lake
CL3	Clearwater Lake - Webb Creek arm	Lake - Reference
CL4	Clearwater Lake - Lower Black River arm	Lake
CL5	Clearwater Lake - Upper Black River arm	Lake

SEDIMENT COLLECTION

See Besser, et al. 2003, poster PM050, this session for sediment collection methods.

METAL ANALYSIS

Analyses of metals in pore water were conducted by ICP-mass spectroscopy (May et al. 1997).

Pore waters were filtered and acidified to 1% v/v with ultra-pure nitric acid and analyzed without digestion. See Table 2 for sampling schedule.

TOXICITY TESTS

Test conditions for sediment and pore water toxicity tests are listed in Table 2 (ASTM 2002a,b; USEPA 1993, 2000).

Table 2. Test conditions and water quality sampling schedule.

Parameter	*H. azteca* – site sediments	*C. dubia* – site pore waters
1. Test type	Whole sediment (flow-through)	Pore water (static/renewal)
2. Duration	28 d (sediment); 14-d (water only)	7 d
3. Endpoints	Survival (days 28/35/42) Growth (days 28/42) Reproduction (days 35/42)	Survival (daily) Reproduction (daily)
4. Temperature	23 °C	25 °C
5. Lighting	All tests: Wide spectrum fluorescent light, about 400 lux; 16 hr light: 8 hr dark	
6. Exposure	Control and site sediments	Control; site pore waters
7. Water	Hard: CERC well water (hardness 280 mg/L)	Hard: CERC well water (hardness 280 mg/L)
8. Water volume (chamber volume)	150 ml (300 ml)	15 ml (30 ml)
9. Water renewal	6 volume additions/ d	100% renewal/ d
10. Substrate	Site sediment (28 d); sand layer (d 28-42)	NA
11. Test Organism	Juvenile H. azteca (about 7-d old); 10/ replicate	Less than 12-hr old C. dubia; 1/replicate
12. Number of replicates	12 (8 after day 28)	10
13. Feeding	YCT, 1.8 ml/d	YTC, 0.1 ml/d; *Selenastrum capricornatum*, 0.1 ml/d
14. Water quality	Temperature, D.O., pH, conductivity (weekly), alkalinity, hardness, DOC (weekly); filtered porewater Pb (initial, d 28)	Temperature, D.O., pH, conductivity (daily); alkalinity, hardness, DOC (initial d 7); filtered porewater Pb (initial, days 0, 4, 7)

STATISTICAL ANALYSIS

H. azteca: Survival, growth and reproduction data were rank-transformed and analyzed by one-way ANOVA. Differences from controls were determined by one-way Dunnett's test. Significance (asterisks on charts) refers to $p \leq 0.05$. Nonlinear regression and correlation analysis was analyzed using SAS (2000).

C. dubia: Survival data was analyzed using Fisher's Exact Test. Significance from controls (asterisks on charts) refers to $p \leq 0.05$. Reproduction data were tested for normality and analyzed using the Bonferroni test. Significance from controls (asterisks on charts) refers to $p \leq 0.05$. Nonlinear regression and correlation analysis was analyzed using SAS (2000).

RESULTS AND DISCUSSION

Hyallela Toxicity Test

❖Survival and reproduction of *Hyalella* were significantly reduced relative to the controls by exposure to sediments from several stream and lake sites downstream of mining activities (Figure 2). *Hyalella* performance in sediments from reference sites did not differ significantly from controls.

❖Survival was greatly reduced (17%) in sediments from MT12 and was also significantly reduced in sediments from MT4. A smaller, non-significant reduction occurred in sediments from MT3. Survival in other sediments was equal to or greater than that in the control sediments. Reproduction was significantly reduced by sediments from stream sites MT12 and two of the lake sediments (CL1 and CL4).

❖*Hyalella* growth (Figure 2) was not significantly affected by sediment exposure, although there was a small depression of growth in sediments from the most toxic site, MT12.

Ceriodaphnia Toxicity Test

❖Survival of *Ceriodaphnia* was significantly reduced relative to the controls by exposure to pore water from several stream sites downstream of mining activities (Figure 3a). There were no survival at MT2, MT4 and MT12, which are the sites most impacted by mining activity.

❖Survival was also significantly reduced at MT3, a reference site, and at MT1, MT7 and MT14, which are not directly downstream of mining activities.

❖There was a significant reduction in reproduction at the same stream sites where survival was significantly reduced (Figure 3b), as well as two lake sites, CL3 and CL5.

Water Quality of Pore Waters

❖Water quality from stream sites were generally higher in conductivity, alkalinity, hardness, DOC and ammonia relative to lake sites (Table 3). Parameters were higher at the West Fork Black River sites and sites (MT 4, MT12) directly below mining areas.

❖Metal concentrations also were generally higher from stream sites, but concentrations varied widely between the sites (Figure 4).

❖Concentrations of Pb, Zn and Cd exceeded water quality criteria (USEPA 2002).

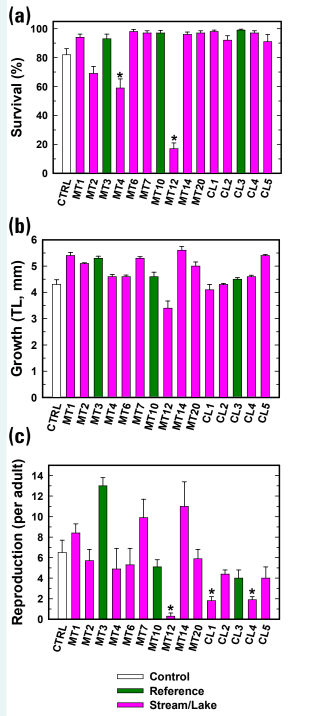


Figure 2. Toxicity of sediments to *H. azteca* [survival (a), growth (b), reproduction (c)].

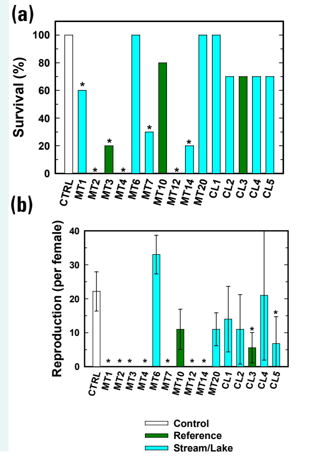
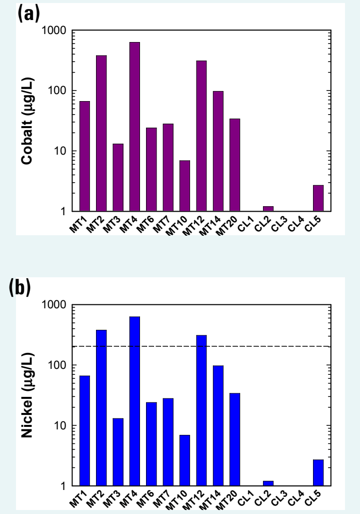


Figure 3. Toxicity of sediments to *C. dubia* [survival (a) and reproduction (b)].

Table 3. Average water quality of pore water of *C. dubia* toxicity test.

Site ID	Temp (°C)	pH	Cond (µs/cm)	DO (mg/L)	Alk (mg/L $CaCO_3$)	Hard (mg/L $CaCO_3$)	Amm (mg/L)	DOC (µg/L)
MT1	23.4	8.14	1612	2.60	580	932	8.71	544
MT2	23.4	8.33	1667	7.02	456	860	27.4	307
MT3	22.9	8.21	1323	6.81	516	644	6.64	332
MT4	23.0	8.04	1657	5.72	660	456	26.6	466
MT6	23.4	8.40	606	7.96	154	260	2.25	7.9
MT7	22.8	8.40	775	7.29	370	460	1.04	196
MT10	23.4	8.54	425	7.67	242	284	1.04	26.0
MT12	22.3	8.20	984	9.14	248	506	14.7	171
MT14	22.9	8.35	970	7.65	420	512	6.68	218
MT20	23.5	8.38	683	5.44	290	350	2.17	79.3
CL1	23.5	8.65	452	8.20	258	250	2.01	6.99
CL2	23.4	8.6	359	8.29	186	184	0.96	4.50
CL3	23.4	8.63	389	8.18	212	210	1.61	4.38
CL4	23.2	8.53	312	8.21	160	164	0.84	3.42
CL5	23.4	8.63	437	8.12	248	236	2.16	7.47



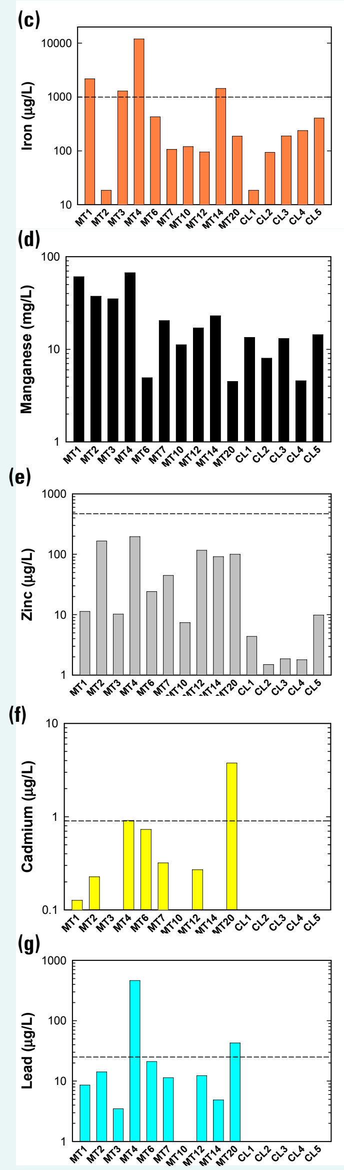


Figure 4. Average metal concentrations in pore waters from *C. dubia* test. Chronic water quality criteria (WQC) assume hardness of 500 mg/L (USEPA 2002). (a) cobalt; (b) nickel; (c) iron; (d) manganese; (e) zinc; (f) cadmium; (g) lead.

Relationship of *Hyalella* and *Ceriodaphnia* Survival to Pore-water Metals

❖*Hyalella* survival was not strongly associated with concentrations of lead or zinc in sediment or pore waters. The absence of toxic effects on amphipods exposed to concentrations of lead substantially greater than water quality criteria (USEPA 2002) or chronic toxicity thresholds (Besser et al. 2003) for lead suggests that the bioavailability of lead and perhaps other metals was substantially reduced under conditions in some sediments tested.

❖In contrast, survival of *Hyalella* survival corresponded closely to concentrations of other metals in pore waters, notably nickel and cobalt. Nonlinear regression with survival produced significant for nickel (R^2=0.61) and cobalt (R^2=0.73), but not for lead (R^2=0.19) or zinc (R^2=0.34) (Figure 5).

❖*Hyalella* reproduction was not strongly associated with metal concentrations in sediment or pore waters, but had significant positive correlations with DOC and alkalinity (Table 4), suggesting high level of organic and inorganic ligands ameliorated metal bioavailability.

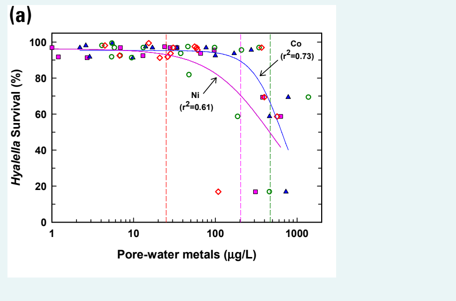
❖Survival of *Ceriodaphnia* also corresponded closely to concentrations of nickel (R^2=0.64) and cobalt (R^2=0.78) (Figure 5). Survival and reproduction of *Ceriodaphnia* was negatively correlated with several metal (Fe and Mn) as well as most water quality variables (Table 5), therefore determining the specific variable(s) that caused the effects will be difficult.

Table 4. Correlations ('r' values) of *Hyalella* and *Ceriodaphnia* endpoints with sediment and pore-water variables.

Parameter	*H. azteca* Survival	*H. azteca* Growth	*H. azteca* Reproduction
SED-Fe	0.29	-0.37	-0.51
SED-Ni	-0.69	-0.43	-0.53
SED-SUM-PEQ	-0.04	0.10	-0.08
SED-SEM-AVS	-0.23	0.19	0.14
PW Ni	-0.73	-0.10	-0.15
PW Co	-0.84	-0.09	-0.11
PW TU	-0.22	0.08	-0.09
PW DOC	-0.30	0.52	0.49
PW Cond	-0.30	0.52	0.48
PW Alk	0.11	0.77	0.72
PW Ammonia	-0.49	0.31	0.20

Parameter	*C. dubia* Survival	*C. dubia* Reproduction
PW Fe	-0.52	-0.50
PW Mn	-0.77	-0.59
PW Co	-0.81	-0.55
PW Ni	-0.72	-0.45
PW DOC	-0.72	-0.60
PW Cond	-0.71	-0.56
PW Alk	-0.79	-0.67
PW Hard	-0.60	-0.58
PW Ammonia	-0.61	-0.46

LEGEND:	
Red	=highly significant negative correlation (p<0.001)
Yellow	=significant negative correlation (p<0.05)
Green	=significant positive correlation (p<0.01)
Blue	=highly significant positive correlation



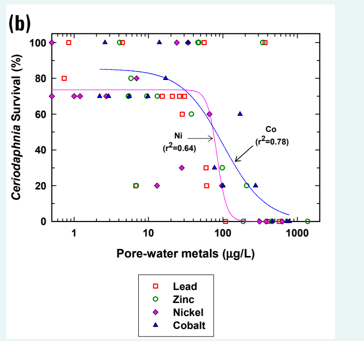


Figure 5. Relationships between survival of *H. azteca* (a) and *C. dubia* (b) during 28-d sediment toxicity and dissolved metal concentrations in sediment pore water. Regression lines and R^2 values refer to nonlinear (logistic) regression; vertical dashed lines indicate USEPA (2002) chronic water quality criteria for nickel (pink), zinc (green) and lead (red) at a hardness of 500 mg/L).

CONCLUSIONS

❖Water quality and metal concentrations from stream sites near mining activities were elevated above reference sites.

❖Toxicity was greater than stream sites near mining activities. Survival and reproduction of *Hyalella* and *Ceriodaphnia* were significantly reduced at sites near mining areas.

❖Results from *Hyalella* and *Ceriodaphnia* tests were similar. *Ceriodaphnia* were more sensitive, however their sensitivity may be more correlated with water quality parameters than dissolved metals.

REFERENCES

ASTM 2002a Standard guide for conducting acute toxicity tests on test materials with fishes, macroinvertebrates, and amphibians, E 729-96. American Society for Testing and Materials, West Conshohocken, PA.
ASTM 2002b. Standard test methods for measuring the toxicity of sediment-associated contaminants with freshwater invertebrates, E1706-00. American Society for Testing and Materials, West Conshohocken, PA.
Besser, J.M., Brumbaugh, W.G., Brunson, E.L, Allert, A.L., Schmitt, C.J. 2003. Metal bioavailability in stream and reservoir sediments downstream of lead-mining areas. Poster presented at the 24th Annual Meeting of SETAC, November 2003, Austin, TX. (Poster PM050; this session).
May, TW, Wiedmeyer, RH, Brumbaugh, WG, and Schmitt, CJ. 1997. The determination of metals in sediment pore waters and in 1N HC l-extracted sediments by ICP-MS. Atomic Spectroscopy 18: 133-139.
Statistical Analysis System Institute (SAS). 2000. SAS/STAT Guide for Personal Computers, Version 6, 4th ed., Volumes 1 & 2. SAS Institute, Cary, North Carolina.
USEPA 1993. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms, Fourth Edition, EPA/600/4-90/027F. U.S. Environmental Protection Agency, Washington, DC.
USEPA 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates, EPA/600/R-99/064. U.S. Environmental Protection Agency, Washington, DC.
Whyte, J., C.J. Schmitt, W.G. Brumbaugh, M. Annis, and D.E. Tillitt . 2002. Biomarkers of metal exposure in fish from existing and proposed mining area of Missouri. Presentation at the 23rd Annual Meeting of SETAC, November 2002, Salt Lake City, UT.

ACKNOWLEDGEMENTS

We thank Jesse Arms, Bill Brumbaugh, Eric Brunson, Robin Calfee, Duane Chapman, Doug Hardesty, Brooks Hill, Chris Ivy, Lynne Johnson, Sarah Koppi, Ben Lakish, Steve Olson, Angie Pestka, Linda Sappington, Abe Smith, Chris Witte and Chad Vishy for their technical assistance. We also thank Lynne Johnson for her assistance with the preparation of this poster. This study is part of a congressionally-funded project involving all scientific disciplines within USGS.