

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

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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 nine sites. 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

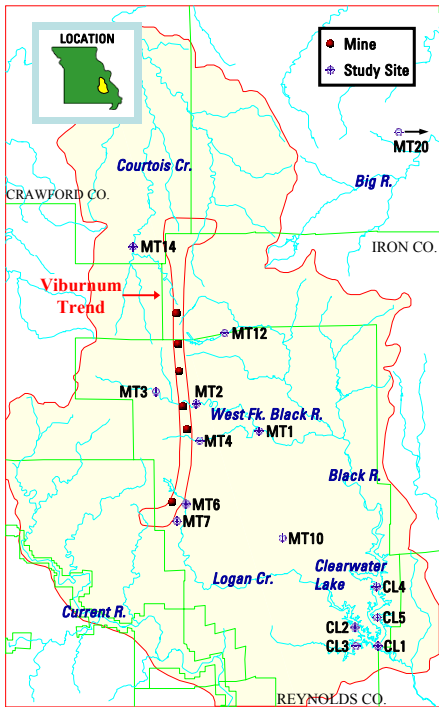


Figure 1. Location of sediment collection sites and mines of the Viburnum Trend Mining District in southeast Missouri.

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	<i>H. azteca</i> - site sediments	<i>C. dubia</i> - site pore waters
1. Test type	Whole sediment (May 2003)	Pore water (May 2003)
2. Duration	72 (42 survival, 14 d growth, 14 d reproduction)	72
3. Endpoints	Survival (May 20/24/42), Growth (May 28/42), Reproduction (May 28/42)	Survival (daily), Reproduction (daily)
4. Temperature	22 °C	25 °C
5. Lighting	48 hr dark, White spectrum fluorescent light, about 100 µmol photons m ⁻² s ⁻¹ , 16 hr light, 8 hr dark	16 hr light, 8 hr dark
6. Exposure	Control and site sediments	Control, site pore waters
7. Water	Hard: CDR, well water (approx. 200 mg/L)	Hard: CDR, well water (approx. 200 mg/L)
8. Water volume (chamber volume)	100 ml (500 ml)	10 ml (50 ml)
9. Water renewal	0 volume addition of site water (CL1-CL5)	50% (renewal of site water)
10. Substrate	Site sediment (CL1-CL5) sand layer (0-20-42)	Na ₂ SO ₄ (less than 1% by wt. of <i>C. dubia</i> , 1% (control))
11. Test Organism	Juvenile <i>H. azteca</i> (about 7 d old), 10/replicate	10/replicate
12. Number of replicates	12 (8 after day 28)	10
13. Feeding	YEL 1.5 ml/d	YEL 0.1 ml/d
14. Water quality	Temperature, B.O., pH, conductivity (weekly), alkalinity, hardness, DOC (weekly), Dissolved trace metals Pb (initial, day 0, 4, 7)	Temperature, B.O., pH, conductivity (daily), alkalinity, hardness, DOC (initial, day 7), Dissolved trace metals Pb (initial, day 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 $p \leq 0.05$. Nonlinear regression and correlation analysis was analyzed using SAS (2000).

RESULTS AND DISCUSSION

Hyalella 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).

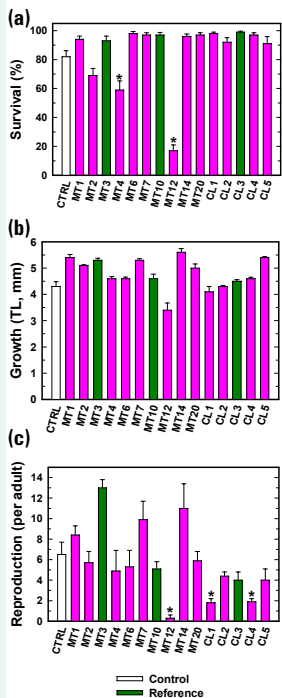


Figure 2. Toxicity of sediments to *H. azteca* (survival (a), growth (b), reproduction (c)).

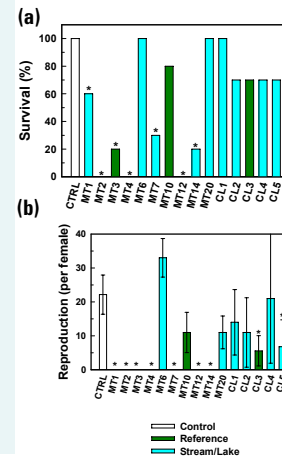


Figure 3. Toxicity of sediments to *C. dubia* (survival (a) and reproduction (b)).

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

Site ID	Temp (°C)	pH	Cond (µg/cm)	DO (mg/L)	Alk (mg/L CaCO ₃)	Hard (mg/L CaCO ₃)	Amn (mg/L)	DOC (µg/L)
MT1	23.4	8.14	1012	2.60	580	932	8.71	544
MT2	23.4	8.33	1067	7.02	458	860	27.4	307
MT3	22.9	8.21	1323	6.81	516	644	6.64	332
MT4	23.0	8.64	1057	5.72	600	456	26.6	469
MT6	23.4	8.40	686	7.96	154	200	2.25	7.9
MT7	22.6	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	884	9.14	248	506	14.7	171
MT14	22.9	8.35	970	7.65	420	512	6.88	218
MT20	22.9	8.38	460	5.44	290	350	2.17	79.3
CL1	23.0	8.85	462	9.39	259	250	3.01	6.99
CL2	23.4	8.6	359	8.29	186	184	0.96	4.50
CL3	23.4	8.62	389	8.16	212	210	1.61	4.36
CL4	23.2	8.53	312	8.21	160	164	0.84	3.42
CL5	23.4	8.63	407	8.12	248	236	2.16	7.47

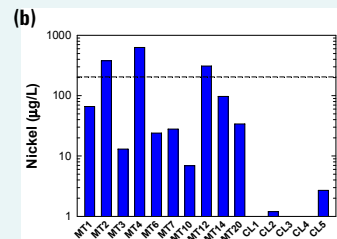
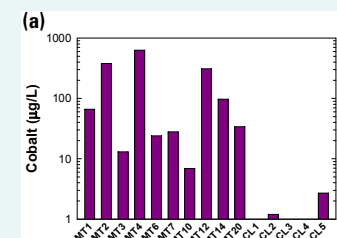


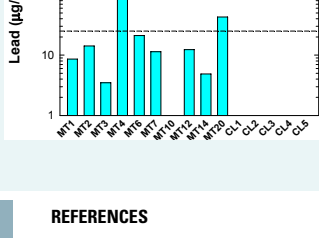
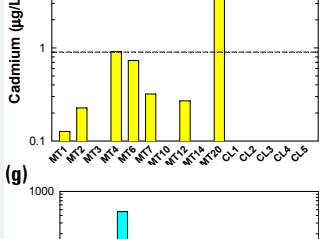
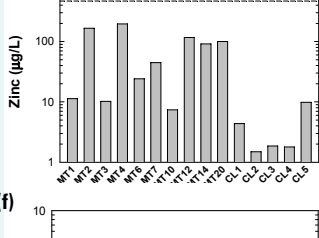
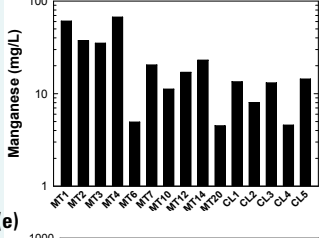
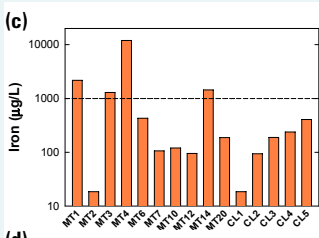
Figure 4. Average metal concentrations in pore waters from *C. dubia* test. Chronic water quality criteria (WQC) assume hardness of 500 mg/L (USEPA 2002). (a) cobalt; (b) nickel; (c) iron; (d) manganese; (e) zinc; (f) cadmium; (g) lead.

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.



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.

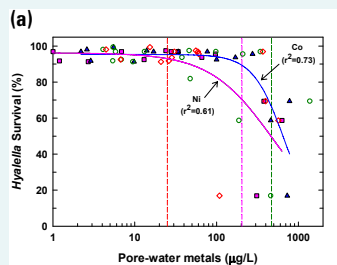


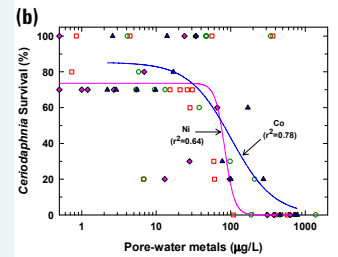
Figure 5. Relationships between survival of *H. azteca* (a) and *C. dubia* (b) during 28-d sediment toxicity and dissolved metal concentrations in sediment pore water. Regression lines and R^2 values refer to nonlinear (logistic) regression; vertical dashed lines indicate USEPA (2002) chronic water quality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

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

Parameter	<i>H. azteca</i> Survival	<i>H. azteca</i> Growth	<i>H. azteca</i> 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	0.57	0.48
PW Cond	-0.30	0.57	0.48
PW Alk	0.11	0.77	0.72
PW Ammonia	-0.49	0.31	0.20

Parameter	<i>C. dubia</i> Survival	<i>C. dubia</i> Reproduction
PW Fe	-0.52	-0.50
PW Mn	-0.77	-0.58
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	-0.78	-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



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