PT110

Sediment toxicity and metal bioavailability in streams downstream of lead mining areas in the Missouri Ozarks

John M. Besser, William G. Brumbaugh, Chris D. Ivey, Christopher G. Ingersoll. U.S. Geological Survey, Columbia MO, and Lopaka Lee, U.S. Geological Survey, Denver, CO

ABSTRACT

Proposals to expand lead mining activity in the Ozarks of southeast Missouri have raised concerns about possible adverse effects of current and proposed mining activities on stream ecosystems. During 2004, we studied longitudinal trends in sediment toxicity and metal bioavailability in three stream reaches downstream of mining in the Black River watershed. Survival, growth, and reproduction of the amphipod, *Hyalella azteca*, were significantly reduced after 28-d exposures to sediments from several sites downstream of mining, relative to sediments from reference streams. Toxic effects and concentrations of lead, zinc, nickel, and cadmium in pore water were greatest in sediments from sites closest to mining areas and generally decreased with distance downstream. Toxic effects and elevated metal concentrations were evident at sites as far as 14 km downstream of mining areas. Concentrations of zinc, nickel, and cadmium in pore waters were significantly correlated with toxic effects on *H. azteca.* Concentrations of free metal ions in equilibrium with organic and inorganic ligands, modeled with PHREEQC and WHAM thermodynamic models, had strong concentration-response relationships with toxicity endpoints. Sediment toxicity and high metal concentrations in sediments and pore waters from streams downstream of mining areas are consistent with findings of alterations of resident fish and invertebrate communities.

BACKGROUND

- Since the 1970's, the Viburnum Trend mining district of southeast Missouri has been the leading producer of lead in the United States. Ores are extracted by deep shaft mining and processed tailings are deposited in large tailings ponds, located in the headwaters of the Black River and Meramec River drainages (Figure 1).
- Recent studies have documented toxic effects of fine sediments from streams draining the Viburnum Trend (Besser et al. 2003) and apparent impacts of mining on stream fish and invertebrate communities (Allert et al., poster TP105, this session).
- During 2004, we studied longitudinal trends in toxicity, metal concentrations, and modeled metal speciation of sediments from three stream reaches downstream of active mining areas: Strother Creek/Middle Fork Black River; West Fork Black River; and Bee Fork (Figure 1; Table 1).

Figure 1. Sediment collection sites near Viburnum Trend mining district, Missouri USA, August 2004.

METHODS

Collection of sediment and pore water

- Sediments were collected from 14 stream sites downstream of mines and from two reference sites with no known upstream mining activity (Figure 1, Table 1).
- Fine sediment (<1 mm particle diameter) was extracted from stream gravels using a diaphragm pump with a stainless steel intake manifold. Sediment slurries were held in conical polyethylene settling tanks for 30 min before overlying water was decanted. Sediments were stored at 4°C for 13-20 d before testing and analysis.
- Pore waters were centrifuged for 30 min at 3500g and filtered through polypropylene syringe filters (0.45 um pore diameter). Samples for metal analysis were preserved with 1% v/v ultrapure nitric acid. Other samples were analyzed immediately or refrigerated for analysis of DOC and anions.

Toxicity Testing

- Chronic sediment toxicity tests with the amphipod, *Hyalella azteca*, were conducted according to the method of ASTM (2005) and USEPA (2000). Tests included evaluation of survival and growth after a 28-d sediment exposure, followed by a 14-d reproduction period.
- Sediments were tested in two batches, started one week apart. Each batch included one reference sediment and a control sediment (Kemble et al. 1994). Survival of amphipods in control sediment exceeded 90% in both tests.

Physical and chemical characterization

- Metals (Pb, Zn, Cd, Ni, and Co) in sediment and pore water were determined by ICP-MS (May et al. 1997). Total recoverable metals in sediments were analyzed following microwave digestion with HNO_3 (5.5%) and HCl (0.5%). Filtered and acidified pore waters were analyzed without digestion.
- Sediments were also analyzed for moisture content, particle-size distribution, and total organic carbon (TOC; by combustion and coulometric titration)
- Other analyses of pore waters included major cations and anions, dissolved organic carbon (DOC; automated colorimetric method); conductivity; pH; alkalinity; hardness; and ammonia.

Geochemical modeling

- Speciation of metals in pore waters was modeled using the thermodynamic modeling program PHREEQC (Parkhurst and Appelo 1999) with the LLNL thermodynamic database (Delany and Lundeen 1990) and the Windermere Humic Aqueous Model (Tipping 1994).

Statistical analysis

- Data were analyzed using SAS/STAT software (version 10). Toxicity data were rank-transformed and analyzed by analysis of variance, with differences from reference sediments determined by Dunnett's one-tailed test. Relationships between toxicity endpoints and log-transformed chemical parameters were evaluated with Pearson's correlation analysis.

Table 1. Sites near the Viburnum Trend mining area sampled in summer 2004. Pink shading indicates sites closest to tailings deposits; yellow indicates sites further downstream from mining; and green shading indicates reference sites with no upstream mining activity.

Site	Stream	Latitude (deg. N)	Longitude (deg. W)	Dist. from tailings (km)	Sediment components (%)				Pore-water constituents (mg/L)						
					Water	Sand	Fines	TOC	pH	Cond.	Alk.	Hard.	Mn	Sulfate	DOC
SC1	Strother Creek	37.5900	91.0540	2.6	65	47	53	0.73	8.41	1300	230	640	11	320	48
SC2	Strother Creek	37.6020	91.0280	3.9	36	79	21	0.15	8.19	1200	230	620	12	310	63
SC3	Strother Creek	37.6040	91.0010	6.7	42	73	27	0.48	8.13	1000	320	560	6	170	66
MF1	M. Fork Black R.	37.5990	90.9570	11.2	30	87	13	0.22	7.44	1100	450	600	21	10	160
MF2	M. Fork Black R.	37.5240	90.9350	22.4	40	76	24	0.55	7.62	1049	490	590	15	2	150
WF1	W. Fork Black R.	37.5110	91.1620	NA	25	80	20	0.10	7.95	810	360	450	9	3	110
WF2	W. Fork Black R.	37.5000	91.1200	6.2	42	69	31	0.38	7.67	1020	410	630	17	3	160
WF3	W. Fork Black R.	37.4970	91.0870	2.2	38	82	18	0.15	8.23	630	290	340	13	8	90
WF4	W. Fork Black R.	37.4870	91.0510	10.1	31	84	16	0.23	7.92	690	350	370	12	6	43
WF5	W. Fork Black R.	37.4760	91.0090	16.5	31	70	30	0.21	7.45	1100	460	580	5	2	180
WF6	W. Fork Black R.	37.4580	90.9790	14.4	45	5	95	0.54	7.13	1800	690	1000	40	3	480
BF1	Bee Fork	37.4440	91.1060	NA*	29	88	12	0.11	8.00	520	220	240	13	14	26
BF2	Bee Fork	37.4420	91.0830	1.4	49	68	32	0.32	7.72	1200	430	610	24	16	210
BF3	Bee Fork	37.4600	91.0250	9.8	24	90	10	0.09	7.82	520	190	240	3	60	8
BF4	Bee Fork	37.4550	90.9900	13.7	26	88	12	0.08	7.70	1000	400	290	20	10	140
BC	Blair Creek	37.2600	91.2150	NA	33	85	15	0.07	7.65	980	440	600	14	3	145

* BF1 has upstream mine water settling pond, but no tailings

RESULTS AND DISCUSSION

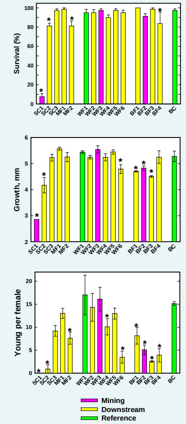

Figure 2. Chronic toxicity of stream-bed sediments from mining sites, downstream sites, and reference sites to *H. azteca*. Asterisks indicate means that are significantly less than those for reference sediments.

Toxicity and metal concentrations of sediments downstream from mining areas

- **Survival of *H. azteca* was significantly reduced at four of 14 sites downstream of mining areas, relative to reference sites, but survival was 80% or greater in all sediments except SC1 (Figure 2).**
- **Sublethal responses were also significantly affected by sediments collected downstream from mining areas: six sediments for growth and nine sediments for reproduction (Figure 2).**
- **Sediments from Strother Creek were most toxic, with significant effects on all three endpoints at the two sites closest to mining (2.6 km and 3.9 km downstream of tailings). None of these endpoints were significantly affected at site SC3, 6.7 km downstream of mining.**
- **Toxic effects of sediments from Bee Fork were less severe, with no reductions in survival at sites closest to mining, but sediments from all four Bee Fork sites (up to 14 km downstream) caused significant effects on one or more test endpoint.**
- **Sediments from the West Fork Black River caused the fewest toxic effects, with no toxicity observed at WF3, the site closest to mining activities.**
- **For all three stream segments, sediments from one or more sites well downstream of mining areas (e.g., MF2, WF6, BF4) caused significant toxic effects.**
- **Total recoverable metal concentrations in stream sediments followed similar longitudinal trends with respect to mining areas (Figure 3). Sediments from Strother Creek had highest metal levels.**
- **Concentrations of dissolved metals in pore waters followed similar trends, with highest concentrations of all metals in sediments from sites nearest mining areas (Figure 4).**
- **Concentrations of several metals in pore waters showed secondary peaks at downstream sites, notably WF6, 15-17 km downstream of mining areas in the West Fork and Bee Fork drainages (Table 1).**

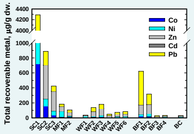

Figure 3. Concentrations of total recoverable metals in fine (<1 mm diam.) stream-bed sediments.

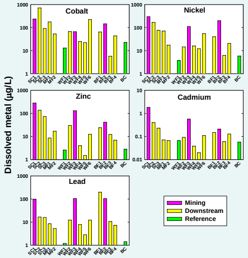

Figure 4. Concentrations of dissolved metals in pore waters of sediments from sites close to mining areas, sites further downstream, and reference sites.

Association of toxicity with metals in pore water

- **Toxicity endpoints had significant negative correlations with concentrations of dissolved zinc, nickel, cadmium, and cobalt, but not lead, in pore water.**
- **Toxicity was also significantly correlated with concentrations of sulfate, consistent with mobilization of metals by oxidation of sulfide in tailings or stream sediments.**
- **Models of complexation with inorganic ligands indicated that almost all pore-water lead would be complexed as $PbCO_3$ (mean across sites: 95% of total) and $PbOH^-$ (2.0%), with only 1.6% occurring as free Pb^{2+}.**
- **Models of inorganic complexation predicted that several metals would occur predominantly as free ions: 63% for Cd^{2+}, 68% for Zn^{2+}, and 97% for Ni^{2+}.**
- **Models using the WHAM algorithm to describe complexation to dissolved organic compounds predicted much lower concentrations of Zn^{2+} (mean 1.6% of dissolved Zn; Figure 5) and Cd^{2+} (13%).**
- **Despite the predominance of complexed zinc and cadmium species, modeled Zn^{2+} and Cd^{2+} had strong concentration-response relationships with amphipod survival and growth, and significant negative correlations with reproduction (Figure 6).**
- **Although WHAM modeling of nickel speciation is incomplete, we expect that free Ni^{2+}will also be strongly associated with observed toxicity.**

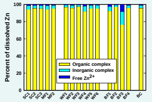

Figure 5. Distribution of zinc among complexed and free-ion species in sediment pore waters.

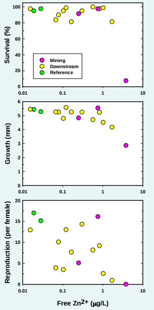

Figure 6. Relationships between free zinc ion concentrations of in pore water and responses of *H. azteca* in sediment toxicity tests.

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SUMMARY AND CONCLUSIONS

1. **Fine sediments from streams draining lead-mining areas of southeast Missouri were toxic to the amphipod, *Hyalella azteca,* and had elevated concentrations of lead and other metals. Toxicity and metal concentrations decreased with distance downstream of mining, but significant toxicity was observed in sediments collected as far as 14 km downstream from deposits of mine tailings.**
2. **Geochemical models suggested that lead and cobalt would have a stronger affinity for formation of inorganic complexes in pore waters than would cadmium, nickel, and zinc. Models of organic complexation indicated that a high percentages of zinc and cadmium would be bound to dissolved organic ligands in pore water.**
3. **Despite model predictions that dissolved metals in pore waters would be complexed with inorganic or organic ligands, toxic effects on amphipods had strong concentration-response relationships with measured concentrations of dissolved nickel, zinc, and cadmium, and with modeled concentrations of free metal ions, in pore water.**
4. **Our results indicate that metals in sediments from Ozark streams downstream of mining areas can be bioavailable and toxic to aquatic biota. This finding is consistent with results of laboratory toxicity tests with metal mixtures based on our study (Kunz et al., poster TP111, this session) and with field studies of fish and invertebrate communities of these streams (Allert et al., poster TP105, this session).**

John M. Besser, Ph.D.
Research Fisheries Biologist (Toxicology)
USGS Columbia Environmental Research Center
4200 New Haven Rd., Columbia MO 65201
phone, (573) 876-1818; fax (573) 876-1896
jbesser@usgs.gov