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Assessment of Elemental Concentrations in Streams of the New Lead Belt in Southeastern Missouri, 2002–05

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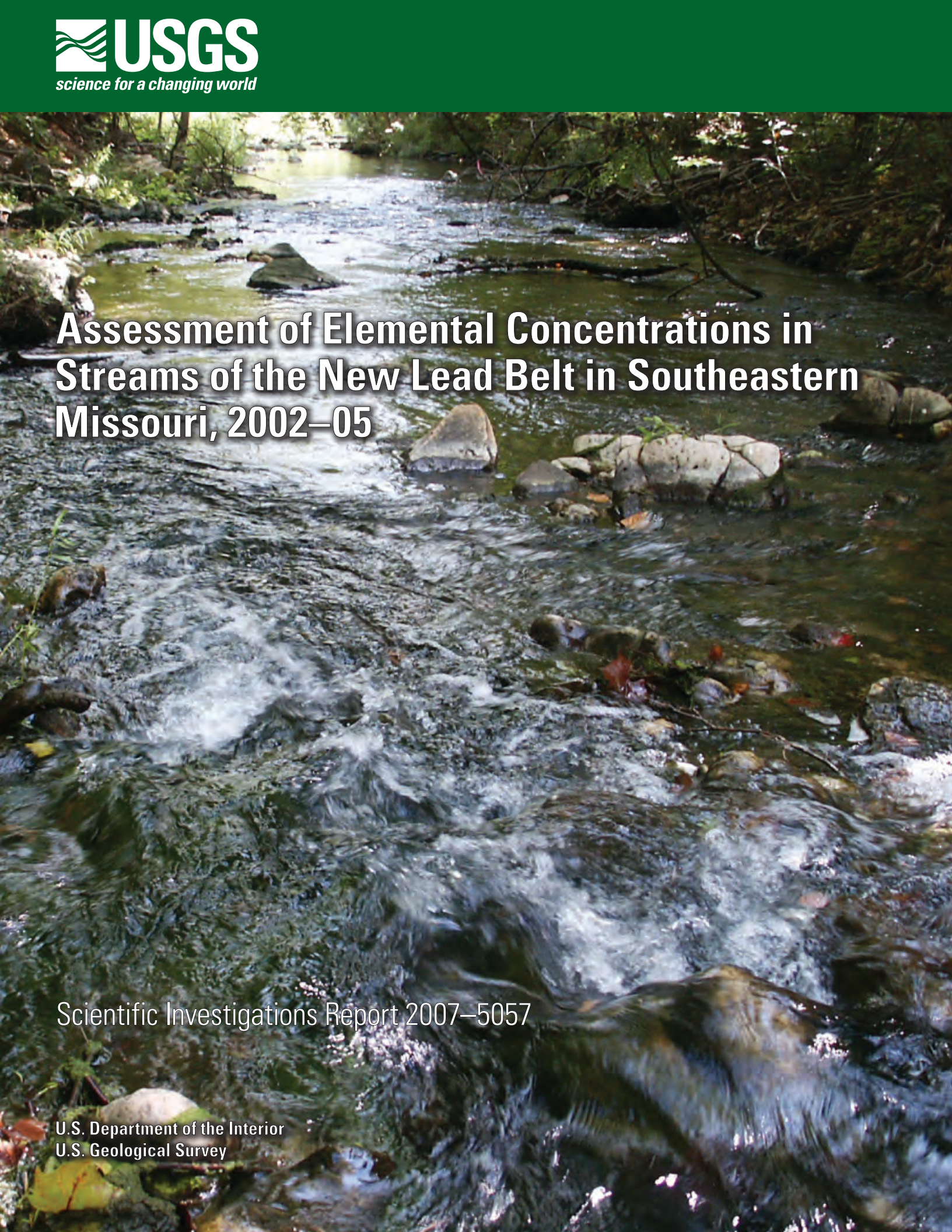
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**Assessment of Elemental Concentrations in
Streams of the New Lead Belt in Southeastern
Missouri, 2002–05**

Scientific Investigations Report 2007–5057

Cover photograph: Strother Creek in Iron County, Missouri, 2004 (photograph by J.M. Besser, U.S. Geological Survey).

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Contents

Abstract.....	1
Introduction.....	1
Purpose and Scope	2
Materials and Methods.....	2
Chronology of Sites and Sampling Matrices.....	2
Field Procedures.....	5
Sediment and Surface Water	5
Pore Water.....	5
Passive Sampler Deployment.....	5
Laboratory Procedures.....	8
Peeper Preparation	8
Sediment Toxicity Testing Sampling	8
Chemical Treatment Procedures.....	8
Instrumental Analysis	9
Quality Assurance.....	9
Results and Discussion.....	10
2002 Samples.....	10
Total Recoverable Metals in Sediments	10
SEM Versus Total Recoverable Metals.....	11
Pore Water.....	11
SEM-AVS.....	14
2003 Samples.....	14
Pore Water.....	14
Surface Water	15
2004 Samples.....	16
Sediments and Pore Water	16
Sediment Probes.....	19
2005 Samples.....	20
Surface and Pore Water	20
Passive Integrative Water Samplers.....	20
Summary and Conclusions.....	23
Acknowledgments.....	24
References.....	24

Figures

1–2. Maps showing—	
1. Sampling locations for biological studies conducted between 2001 and 2005.....	3
2. Sampling locations near the Viburnum Trend.....	4
3–4. Photographs showing—	
3. Sampling fine sediments from streams	6
4. In-stream, passive sampling apparatus	7
5–12. Graphs showing—	
5. Total recoverable concentrations of selected metals in 2002 sediment samples....	12
6. Comparison of filterable concentrations of selected metals in laboratory- produced pore water to differences between simultaneously extracted metals and acid-volatile sulfide for 2002 sediment samples.....	13
7. Filterable concentrations of cobalt, lead, nickel, and zinc in 2003, in-stream pore water	15
8. Total recoverable concentrations of selected metals in 2004 sediment samples....	17
9. Filterable concentrations of selected metals in laboratory-produced pore water of 2004 sediment samples.....	18
10. Comparison of filterable concentrations of cobalt, nickel, and lead in pore water to the mass of each metal recovered from sections of probes used to passively sample pore water in selected 2004 sediment samples	19
11. Filterable concentrations of cobalt, lead, nickel, and zinc in 2005, in-stream pore water	21
12. Mass of selected metals recovered from stabilized liquid membrane devices used for passive, integrative water sampling at three sites, July 2005.....	22

Tables

1. Sampling sites and sampling matrices collected for determination of elemental concentrations, by watershed.....	28
2. Descriptive features of sampling sites potentially affected by mining activities	30
3. Total recoverable concentrations of selected metals in 2002 sediment samples.....	32
4. Percent water, loss on ignition, total organic carbon, and particle size distribution in 2002 sediment samples.....	33
5. Concentrations of acid-volatile sulfide and simultaneously extracted metals in 2002 sediment samples	34
6. Filterable concentrations of selected metals in pore-water samples from 2002 sediment toxicity tests	36
7. Filterable concentrations of selected metals in water samples from 2002 pore-water toxicity tests	38
8. Filterable concentrations of cadmium, lead, and zinc in overlying water samples from 2002 sediment toxicity tests.....	39
9. Filterable concentrations of selected major and minor elements in water samples from 2002 pore-water toxicity tests	40
10. Change in acid-volatile sulfide, and ratios and differences between the sum of simultaneously extracted metals and acid-volatile sulfide in sediment samples from 2002 sediment toxicity tests.....	41

11. Filterable concentrations of cobalt and nickel in pore water, and cadmium, lead, and zinc in pore water and surface water, September 2003	42
12. Concentrations of selected major and minor elements in pore water, September 2003.....	43
13. Filterable concentrations of selected major and minor elements in surface water, September 2003.....	44
14. Percent water and total organic carbon, particle size distribution, and total recoverable metal concentrations in sediment samples from 2004 sediment toxicity tests.....	45
15. Filterable concentrations of selected metals in pore-water samples from 2004 sediment toxicity tests	46
16. Filterable concentrations of selected major and minor elements in pore-water samples from 2004 sediment toxicity tests	48
17. Filterable concentrations of selected anions in pore-water samples from 2004 sediment toxicity tests	49
18. Mass of selected metals in sections of pore-water sampling probes placed in selected test chambers of 2004 sediment toxicity tests	50
19. Filterable concentrations of selected metals in pore water and surface water, June and July 2005	51
20. Filterable concentrations of selected major and minor elements in pore water, July 2005.....	53
21. Filterable concentrations of selected major and minor elements in surface water, June and July 2005	54
22. Filterable concentrations of selected anions in pore water and surface water, July 2005.....	56
23. Mass of selected metals in passive integrative water samplers deployed for up to 22 days at three stream locations, July 2005	57

Conversion Factors, Abbreviations, and Datum

Multiply	By	To obtain
Length		
micrometer (μm)	0.00003937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
kilometer (km)	0.6214	mile (mi)
Area		
square kilometer (km^2)	0.3861	square mile (mi^2)
Volume		
milliliter (mL)	0.03382	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)
Flow rate		
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)
Pressure		
torr	133.3	Pascal (Pa)
Chemical constituents		
nanogram per milliliter	1.0	part per billion
microgram per liter	1.0	part per billion
milligram per liter	1.0	part per million
microgram per gram	1.0	part per million
milligram per kilogram	1.0	part per million

Temperature in degrees Celsius ($^{\circ}\text{C}$) may be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Vertical coordinate information is referenced to World Geodetic System,1984 (WGS 84).

Horizontal coordinate information is referenced to World Geodetic System,1984 (WGS 84).

Assessment of Elemental Concentrations in Streams of the New Lead Belt in Southeastern Missouri, 2002–05

By William G. Brumbaugh, Thomas W. May, John M. Besser, Ann L. Allert, and Christopher J. Schmitt

Abstract

Concerns about possible effects of lead-mining activities on the water quality of federally protected streams located in southeastern Missouri prompted a suite of multidisciplinary studies to be conducted by the U.S. Geological Survey. As part of this investigation, a series of biological studies were initiated in 2001 for streams in the current mining region and the prospecting area. In this report, results are examined for trace elements and other selected chemical measurements in sediment, surface water, and sediment interstitial (pore) water sampled between 2002 and 2005 in association with these biological studies.

Compared to reference sites, fine sediments collected downstream from mining areas were enriched in metals by factors as large as 75 for cadmium, 62 for cobalt, 171 for nickel, 95 for lead, and 150 for zinc. Greatest metal concentrations in sediments collected in 2002 were from sites downstream from mines on Strother Creek, Courtois Creek, and the West Fork Black River. Sediments from sites on Bee Fork, Logan Creek, and Sweetwater Creek also were noticeably enriched in lead. Sediments in Clearwater Lake, at least 75 kilometers downstream from mining activity, had metal concentrations that were 1.5 to 2.1 times greater than sediments in an area of the lake with no upstream mining activity. Longitudinal sampling along three streams in 2004 indicated that sediment metal concentrations decreased considerably a few kilometers downstream from mining activities; however, in Strother Creek some metals were still enriched by a factor of five or more as far as 13 kilometers downstream from the Buick tailings impoundment. Compared with 2002 samples, metals concentrations were dramatically lower in sediments collected in 2004 at an upper West Fork Black River site, presumably because beneficiation operations at the West Fork mill ceased in 2000.

Concentrations of metals and sulfate in sediment interstitial (pore) waters generally tracked closely with metal concentrations in sediments. Metals, including cobalt, nickel, lead, and zinc, were elevated substantially in laboratory-produced pore waters of fine sediments collected near mining operations in 2002 and 2004. Passive diffusion samplers (peepers) buried 4 to 6 centimeters deep in riffle-run stream sediments during 2003 and 2005 had much lower pore-water metal concentra-

tions than the laboratory-produced pore waters of fine sediments collected in 2002 and 2004, but each sampling method produced similar patterns among sites. The combined mean concentration of lead in peeper samples from selected sites located downstream from mining activities for six streams was about 10-fold greater than the mean of the reference sites. In most instances, metals concentrations in surface water and peeper water were not greatly different, indicating considerable exchange between the surface water and pore water at the depths and locations where peepers were situated.

Passive sampling probes used to assess metal lability in pore waters of selected samples during 2004 sediment toxicity tests indicated that most of the filterable lead in the laboratory-prepared pore water was relatively non-labile, presumably because lead was complexed by organic matter, or was present as colloidal species. In contrast, large percentages of cobalt and nickel in pore water appeared to be labile. Passive integrative samplers deployed in surface water for up to 3 weeks at three sites in July 2005 confirmed the presence of elevated concentrations of labile metals downstream from mining operations on Strother Creek and, to a lesser extent, Bee Fork. These samplers also indicated a considerable increase in metal loadings occurred for a few days at the Strother Creek site, which coincided with moderate increases in stream discharges in the area.

Introduction

Southeastern Missouri has been a primary producer of lead (Pb) since the early 1700s (Mining and Quarry World, 2004). Mining ceased in 1972 in the Old Lead Belt (fig. 1, inset) where large quantities of metal-enriched tailings eroded into area streams. Contamination of fish and other aquatic biota, alteration of fish and invertebrate communities, and public health advisories against human consumption of lead-contaminated fish have resulted (Czarneski, 1985; Schmitt and others, 1993).

Since the 1960s, most lead mining in Missouri shifted to a new district, the Viburnum Trend, also known as the New Lead Belt. This area remains a primary producer of lead, and a secondary producer of zinc (Zn); copper (Cu) and silver (Ag) also are produced in small quantities (Missouri Department of Natural Resources, 2004). Viburnum Trend deposits also

contain considerable quantities of cobalt- (Co) and nickel- (Ni) bearing minerals (Jessey, 1981), but there is no production of those metals (Shedd, 2004; Kuck, 2004). In fact, lead production in Missouri has been identified as a primary loss pathway in the materials flow of cobalt in the United States (Shedd, 1993).

Mining in the Viburnum Trend has developed concurrently with increased environmental regulation and improved technology for metal recovery and pollution control. Studies conducted in the 1970s reported amelioration of adverse biological effects on stream biota, and attributed these changes to processes such as recycling wastewater from mining and beneficiation (milling and flotation concentration) and the development of passive wastewater treatment systems with increased retention time (Ryck and Whitley, 1974; Wixson, 1977). However, mining in the Viburnum Trend has not necessarily proceeded without environmental questions (Duchrow, 1983). Through the early 1980s, most instances of water-quality degradation associated with active lead-zinc mines in Missouri were attributed to catastrophic or intermittent releases from tailings or settling ponds during heavy rainfall events (U.S. Environmental Protection Agency, 1994). Limited U.S. Geological Survey (USGS) investigations conducted during the 1990s suggested that lead and/or zinc concentrations in sediments were potentially harmful to aquatic organisms at some locations (Petersen and others, 1998).

With time, mining activity in the Viburnum Trend has progressed from north to south as ore deposits were depleted and new mines opened. Most of these mines have been developed on lands adjacent to the Mark Twain National Forest, federally-owned lands that are managed for forestry, mining, and recreation (U.S. Department of Agriculture, 2005). Beginning in the late 1970s, prospecting for new ore was conducted primarily in two exploration areas about 30 kilometers south of the Viburnum Trend (Kleeschulte and Seeger, 2003). This activity has raised concerns about possible adverse environmental effects of mining on the water quality and aquatic biota of nearby high-quality streams that are federally protected and managed as National Parks, National Scenic Rivers, and National Forests. In the karst landscape of southeastern Missouri, metals and other substances associated with mining activities potentially could enter surface streams and subsurface waterways that recharge springs (Kleeschulte, 2000). Consequently, concerns about possible effects of mining activities on the water quality of federally-protected streams located in this region of Missouri prompted a series of multidisciplinary studies conducted by the USGS that began in October, 2000 (Kleeschulte, 2003).

Purpose and Scope

This report presents results of chemical measurements performed on surface-water, sediment, and sediment pore-water samples collected between 2002 and 2005 in association

with USGS biological studies conducted at sites near mining and exploration regions in southeastern Missouri. Biological studies are described in part by Besser and others (2006), and Schmitt and others (2007a, 2007b). The primary objectives of this report are to assess the magnitude, geographic range, temporal variation, and bioavailability of mining-related metals in water and sediment, and to provide baseline data for locations in exploration areas.

Materials and Methods

Chronology of Sites and Sampling Matrices

Biologic sampling was initiated in 2001, sampling of sediment and water began in 2002, and sampling of all matrices continued through July 2005. Sampling sites are shown in figures 1 and 2; the sampling matrices that were collected for each year and site are summarized in table 1. Descriptions of sampling sites potentially affected by mining activities are listed in table 2. Sampling conducted from 2001 to 2003 included a broad geographic area, whereas sampling conducted in 2004 and 2005 was limited to a few streams, but with more sampling locations in each stream. A brief summary of the chemical measurements performed on the abiotic components associated with these biological studies follows.

Fine sediment samples were collected from Clearwater Lake (fig. 1) in July 2002, and from streams in the Black River Basin upstream from Clearwater Lake in July 2002, and August 2004. Composite samples of these sediments were transported to the laboratory for toxicity testing with sediment (2002 and 2004) and sediment interstitial (pore) water (2002). Sediments from the 2002 collection were analyzed for total recoverable metals of cadmium (Cd), Cu, Ni, Pb, Zn, thallium (Tl), acid-volatile sulfide (AVS), and simultaneously extracted metals (SEM) including Cd, Cu, Ni, Pb and Zn. Overlying water and pore water also were sampled periodically during the toxicity tests and analyzed for selected metals. For 2004 sediments, analyses included Cd, Co, Ni, Pb and Zn in sediments, laboratory-prepared pore waters, and in pore-water sampling probes. Pore waters obtained from the 2004 sediments also were analyzed for selected major and minor elements including aluminum (Al), barium (Ba), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), silicon (Si), and strontium (Sr). Anions, including chloride, nitrate, sulfate, and fluoride also were measured. In-stream samples of surface and pore water were collected at selected locations in September 2003, and June and July 2005. These water samples were analyzed for Cd, Co, Ni, Pb, Zn and the selected major and minor elements; the 2005 samples also were analyzed for anions. Passive integrative samplers, which were deployed for up to 22 days in surface waters at three sampling sites in July 2005, also were analyzed for Cd, Co, Ni, Pb, and Zn.

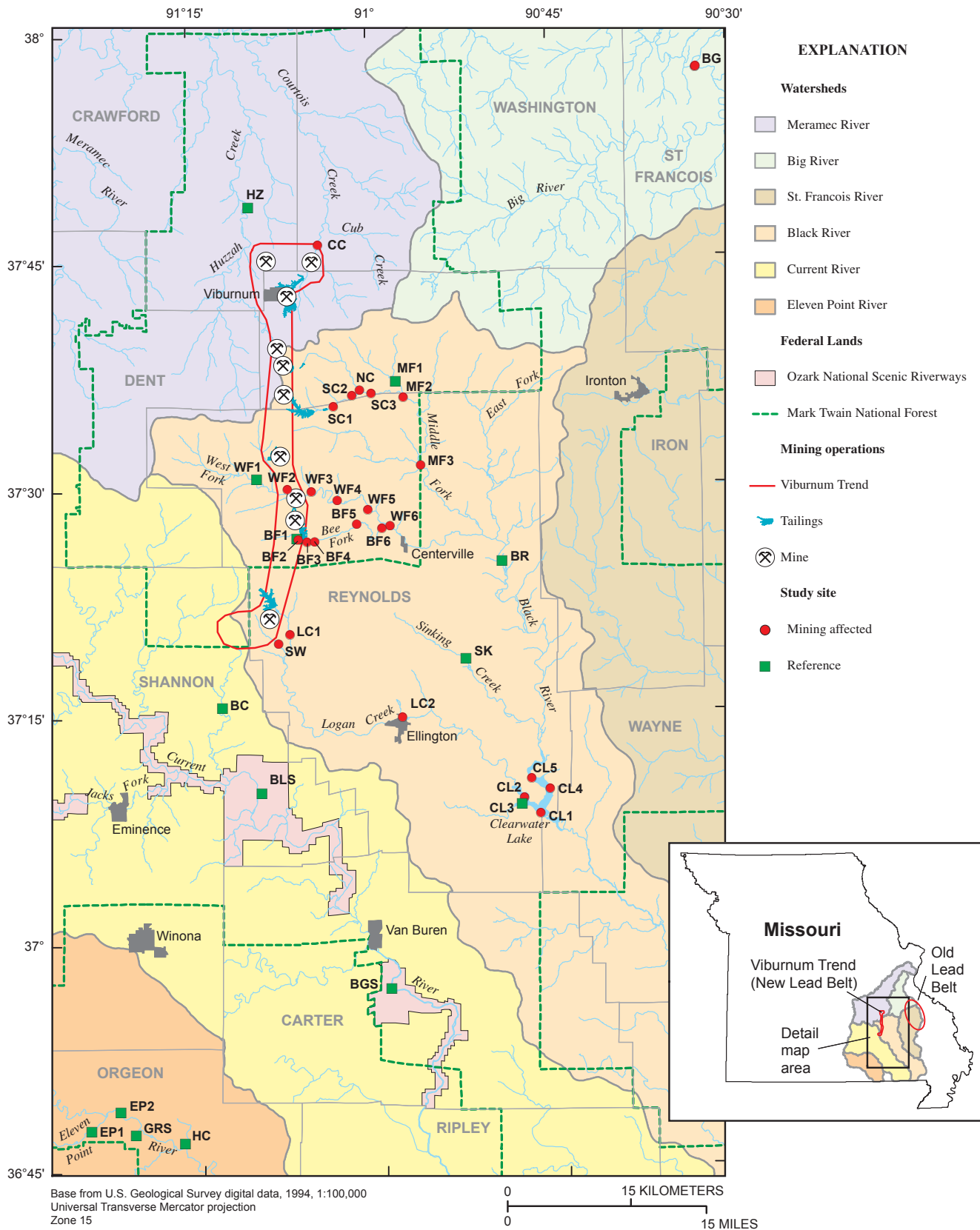


Figure 1. Sampling locations for biological studies conducted between 2001 and 2005.

4 Assessment of Elemental Concentrations in Streams of the New Lead Belt in Southeastern Missouri, 2002–05

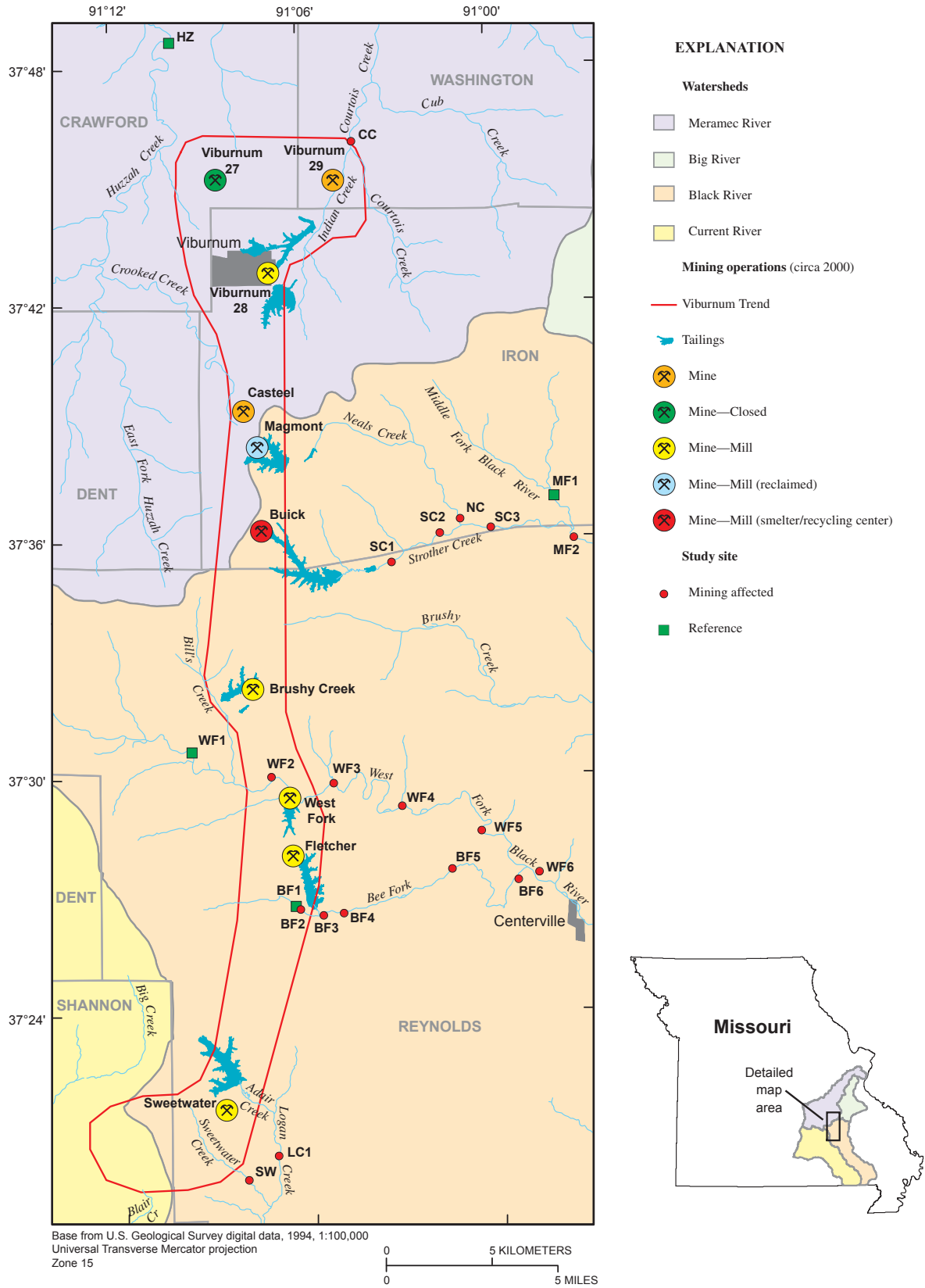


Figure 2. Sampling locations near the Viburnum Trend.

Field Procedures

Field procedures are described separately for sediment and surface-water sampling, passive pore-water sampling, and passive surface-water sampling. All sediment samples were transported to the laboratory for homogenization, sub-sampling, and collection of pore water. Surface water was sampled by grab method and sub-samples were filtered immediately on site. Passive sampling was conducted using in-stream methods (samplers were situated in the stream for several days before retrieval).

Sediment and Surface Water

Fine sediments were extracted from gravel-bottom streams using a mechanized wet-sieving apparatus. A sediment slurry was pumped from the streambed using a gas-powered diaphragm pump equipped with a polyvinyl chloride (PVC) suction hose and a stainless steel intake manifold wrapped with a 2-mm (millimeter) mesh stainless steel screen (fig. 3A; Schmitt and others, 1987). The intake manifold was raked through stream gravels in depositional habitats to extract embedded fine sediments (fig. 3B). The slurry was pumped to a large conical polyethylene settling tank (fig. 3C), where the sediment was allowed to settle for 30 minutes. Clear overlying water was decanted via an upper drain valve. The sediment was transferred into an acid-washed, 20-L (liter) polyethylene bucket via the lower drain valve. This process was repeated until the desired volume of wet sediment (20 L in 2002; 4 L in 2004) was obtained. The pump assembly was flushed with site water before and after sample collection. The settling tanks were scrubbed to remove visible sediment and rinsed with site water after each use. Lake sediments were sampled with a Ponar dredge and immediately transferred to 20-L polyethylene buckets; the dredge was rinsed thoroughly with lake water between sites. All sediment samples were sealed and transported to the laboratory, and kept refrigerated until analysis and toxicity testing.

Surface-water grab samples were collected in mid-stream by submersing collapsible 1-L polyethylene containers that had been purchased pre-cleaned to meet U. S. Environmental Protection Agency (USEPA) guidelines for sampling ambient water for trace metals (U.S. Environmental Protection Agency, 1996). The grab sample was transported immediately to the stream bank where a 25-mL (milliliter) sub-sample was extracted with a polypropylene syringe fitted with a short piece of fluoroethylene-perfluoropropylene tubing. A 0.45- μm (micrometer) polypropylene filter cartridge was attached, 5 mL of sample was expelled to waste, and the remaining 20 mL of filtrate was collected in a pre-cleaned 30-mL polyethylene bottle, sealed, and placed into a zip-seal plastic bag. The syringe, tubing, and filter cartridge were pre-cleaned at the laboratory by drawing and filtering a dilute mixture of nitric acid (HNO_3) and hydrochloric acid (HCl) followed by two rinses with de-ionized, ultra-pure water having a specific resistivity greater than 10 $\text{M}\Omega/\text{cm}$ (million ohms per centimeter).

For the determination of anions, a second sub-sample of water was collected in a similar manner using a non acid-cleaned syringe and filter cartridge. All samples were stored on ice or refrigerated for 1 to 2 days before return to the laboratory; those designated for elemental analysis were then preserved by adding 0.2 mL 16 M (molar) HNO_3 .

Pore Water

Field sampling of pore water was conducted in 2003 and 2005 with in-stream diffusion samplers or “peepers” (Serbst and others, 2003) fabricated at the USGS laboratory in Columbia, Missouri (fig. 4A; see laboratory procedures later in this report). The peepers were buried about 4 to 6 cm (centimeters) deep in riffle-run stream sediments for about 2 weeks. Field tests conducted at USGS indicated that peeper equilibration in fine stream sediments was complete after 5 days. Peepers were buried using a “dibble” digging tool, similar to that used to plant tree saplings. Facing the current, the dibble was forced at a 45-degree angle downward and upstream until the top of the blade was even with the sediment surface. The handle was then pushed forward to create a small trench behind the dibble blade. The peeper was situated horizontally in the trench and the dibble was slowly removed, allowing the surrounding sediment to cover the peeper. During burial, a short strip of bright-colored vinyl flagging was secured to the body of each peeper with a 30-cm long nylon wire tie. The flagging strip and tag end of the wire tie were positioned above the sediment surface to provide a visible indicator of the peeper location, and to serve as a handle to facilitate removal.

After 2 weeks in the sediment, peepers were removed and gently agitated in the stream water to remove any attached particles. The lid and membrane were inspected for the presence of any visible particles; if particles were present, they were removed using a de-ionized water stream. The membrane and perforated cap were then carefully removed and replaced with a pre-labeled non-perforated cap. Each peeper was individually sealed in a small zip-seal bag and placed on ice within 20 minutes of retrieval. Upon return to the laboratory, the contents of each peeper were acidified to an effective concentration of 0.16 M HNO_3 .

Passive Sampler Deployment

Experimental passive integrative metals samplers (stabilized liquid membrane devices or SLMDs) were prepared according to Brumbaugh and others (2002). Three 15-cm by 2.5-cm SLMD strips were deployed at three locations for up to 22 days in July 2005. The SLMDs were transported to the field on ice in a 1-L polyethylene bottle filled with ultra-pure water. At the stream site, each SLMD was transferred with plastic forceps to a 15-cm by 2.5-cm diameter, PVC tubular housing fitted with press-on end caps (fig. 4B). Each housing was pre-drilled with a few evenly spaced, 1-mm diameter



Photographs by
Douglas K. Hardesty,
U.S. Geological Survey,
July, 2002.

Figure 3. Sampling fine sediments from streams: *A*, diaphragm pump with hose and sieve attachment; *B*, sampling operation; *C*, settling tanks.



Photographs by
Douglas K. Hardesty,
U.S. Geological Survey,
July, 2005.

Figure 4. In-stream, passive sampling apparatus: *A*, "peeper" (pore-water diffusion sampler); *B*, opened housing containing stabilized liquid membrane device (passive integrative water sampler); *C*, outer canister containing three sampler housings.

holes (3 in each cap, 15 in the tube) to allow water exchange, but minimize potential effects of variable water flows on the sampling rate (Brumbaugh and others, 2002). Three housings containing individual SLMDs were then placed into a larger, 25-cm by 10-cm, tubular PVC canister pre-drilled with several evenly spaced 1.5-cm holes, and fitted with a solid cap on one end and a threaded cap on the other, each with four 0.5-cm holes (fig. 4C). A nylon tether cord was attached to the threaded cap through one of the holes. The canister was placed on the stream bottom about 0.5 m deep, and the tether cord secured to the bank. All PVC components were pre-cleaned by submerging in a 70 °C (degrees Celsius) bath of 4 M HNO₃, 2 M HCl for 1 hour, followed by overnight soaking in a bath of ultra-pure water. One sampler/housing combination was removed from each of the three sites after 7, 13, and 22 days of stream-water exposure. Upon removal, each housing was sealed in a zip-lock bag and placed on ice for transport to the laboratory, where it was stored frozen until ready for processing.

Laboratory Procedures

Laboratory procedures are described separately for preparation of passive pore-water samplers (peepers), sampling methods for sediments and pore water during sediment toxicity testing, chemical treatment procedures, and instrumental analysis. Some of the procedures were non-standardized techniques developed or modified at the USGS; therefore, these procedures are described in detail.

Peeper Preparation

Peepers (fig. 4A) were fabricated from 50-mL polypropylene snap-cap vials. The lid of each vial was punched with five, 6-mm diameter holes; an equivalent number of non-punched lids were removed from additional vials to seal the peepers after retrieval. Vials and lids were cleaned by soaking in a bath of dilute HNO₃ and HCl for 1 hour, followed by a rinse with ultra-pure water. Within 4 days of deployment the vials were fitted with membranes and filled with de-oxygenated, ultra-pure water. Wearing powder-free latex gloves, each vial was submerged in a bath of de-oxygenated, ultra-pure water with the top edge just below the water surface. A 47-mm diameter, 0.45- μ m pore-size, polyether-sulfone filter membrane was placed above the vial and the lid was seated slowly (beginning at the hinged side) to seal the membrane in place. The vial was inspected for air bubbles or rupture of the membrane and the peeper was inverted to check for leaks. Peepers were placed in a 2-L polyethylene bottle filled completely with de-oxygenated, ultra-pure water, which was capped and stored in a refrigerator for 1 to 2 days before transportation on ice to the field.

Sediment Toxicity Testing Sampling

Pore waters associated with 28-day sediment toxicity tests were prepared in the laboratory by centrifugation of 100

to 250 mL sub-samples of wet sediment (Besser and others, 2004). Separate sub-samples of sediment were used to produce pore water on days 0 and 27 of the tests. The day-0 sample was extracted from a sub-sample of the bulk sediment; the day-27 sample was obtained from a sediment sub-sample that was held in a simulated test chamber for 27 days. Separate samples of pore water were prepared using a “squeezing” method (Carr and Chapman, 1995) for use with 7-day pore-water toxicity tests because large volumes were needed. Briefly, samples of homogenized sediment were transferred to a PVC pore-water extracting chamber fitted with a micro-porous membrane. Using nitrogen gas, the chamber was subjected to a positive pressure up to 1,550 torr to displace pore water, which was collected in a 250-mL polypropylene centrifuge bottle. The pore water was centrifuged for 30 minutes at 5,000 revolutions per minute (RPM), after which it was decanted into a 2-L polyethylene bottle. Pore water obtained from similarly processed replicate samples of sediment were combined to produce a 2-L bulk sample. The bulk pore water was stored at 4 °C before and during the toxicity test, and was used for water renewal in the toxicity test chambers and for periodic sampling for metals. Filtered samples for metals determinations were collected on day 0 (immediately after centrifugation), and on days 4 and 7 of the toxicity test. All samples of laboratory-prepared pore water and overlying water were filtered for metals determinations in the same manner as the field sub-sampling of surface waters.

During sediment toxicity tests conducted in 2004, sampling probes that incorporate the diffusion gradient in thin film (DGT) technique (Zhang, 2002) were inserted into selected test chambers to sequester labile metals from sediment pore water during the final 48 hours of the 28-day toxicity test. The DGT probe consists of a flat sheet of polypropylene backing, a layer of a metal chelating resin imbedded in hydro gel, another layer of hydro gel, all which are sealed behind a micro-porous membrane sheet. After removal, each probe was disassembled and the bottom part of the gel was sliced with a scalpel into three 2-cm sections for measurement. The three sections represented exposures from roughly the lower and upper 2-cm layers of the test sediment, and the overlying water layer nearest the sediment surface. Metals bound by the DGT resin from each 2-cm gel section were extracted with 1 mL of 1.6 M HNO₃ for 24 hours and diluted to 10 mL with ultra-pure water.

Chemical Treatment Procedures

No chemical treatments were necessary before analysis of peeper water, filtered surface water, or filtered-pore water. For sediments, two separate chemical treatment schemes were performed for the characterization of AVS and SEM, and total recoverable metals. The AVS and SEM extraction was performed using an adaptation of the method of Brumbaugh and Arms (1996). Each sediment sample was homogenized in its collection container by stirring with a plastic scoop. A 5-mL aliquant was transferred to a nitrogen-purged, 250-mL round-bottom glass flask containing a tetra-fluoroethylene coated

magnetic stirring bar. Fifty mL of de-oxygenated, ultra-pure water was added, the flask was sealed with a ground glass stopper fitted with a 3-way valve, and 50 mL de-oxygenated 2 M HCl was added. The sample was reacted with stirring for 1 hour during which a nitrogen gas flow of 60 mL per minute was used to purge the resultant hydrogen sulfide into a pH 12, anti-oxidant buffer trapping solution. The sulfide ion concentration in the buffer solution was then measured with a sulfide-specific ion electrode. During the extraction, a second aliquant of wet sediment was weighed for the determination of percent moisture by drying at 95 °C to constant weight in a convection oven. Afterwards, the loss on ignition was determined by heating the dried sample in a muffle furnace at 450 °C for 4 hours, and then reweighing.

A SEM sample was generated from each AVS sediment extraction. After the 1-hour extraction was completed, the sediment/acid mixture was allowed to settle for about 10 minutes. A 40-mL portion was then filtered through a 0.45- μ m polypropylene membrane for analysis by inductively coupled plasma-mass spectrometry (ICP-MS). An evaporative digestion was performed on the extract to reduce the high chloride concentration, which is detrimental for the analysis of certain elements. For this, a 10-mL portion of each filtered extract was combined with 1 mL of 16 M HNO₃ in a 50-mL glass tube fitted with a 1-mL lower reservoir. The mixture was slowly evaporated to 1 mL with microwave heating and diluted to a final volume of 50 mL to produce a solution consisting of 0.32 M HNO₃ and less than 0.012 M HCl.

For the analysis of total recoverable metals, a 0.25-g subsample of the freeze-dried sediment was digested with 5.5 mL of 16 M HNO₃ and 0.5 mL 12 M HCl in a tetrafluoroethylene-lined vessel. Each vessel was sealed and heated to 190 \pm (plus or minus) 10 °C in a temperature-programmed microwave oven. The digestate was transferred to a low-density polyethylene bottle, and diluted to 100 mL with ultra-pure water to produce a final acid matrix of 0.88 M HNO₃ and 0.12 M HCl. The digestion procedure is similar to USEPA method 3051A, which is termed "total-recoverable" because it does not yield a complete dissolution of all elements, particularly those bound within lattices of refractory minerals (U.S. Environmental Protection Agency, 1998). However, the recovery for this method typically is at least 90 percent for most of the priority pollutant metals, including Cd, Co, Cu, Pb, Ni, and Zn.

Preparation of SLMDs for analysis of the sequestered metals was performed by extraction with dilute HNO₃ in a heated ultrasonic water bath. Each SLMD strip was transferred with plastic forceps to a 60-mL pre-cleaned borosilicate glass jar with a tetrafluoroethylene-lined polypropylene lid; 50 mL of 3.2 M HNO₃ was added, and the jar was sealed and placed in an ultrasonic bath pre-heated to 50 °C for 20 minutes. The extract was cooled for 10 minutes, and the liquid was transferred to a 60-mL pre-cleaned polyethylene bottle using an acid-rinsed, disposable polyethylene transfer pipette. A 2-mL portion of the cooled extract was filtered through a 0.45- μ m pore-size, polypropylene cartridge, and the filtered extract was diluted to 20 mL with ultra-pure water.

Instrumental Analysis

All samples were analyzed for trace elements by ICP-MS that was set up and optimized according to manufacturer specifications. Samples were analyzed using quantitative methods using at least four individual standard concentrations for calibration with periodic monitoring of the instrumental response and baseline for each element. Samples were delivered automatically to the instrument by means of a software-controlled auto-sampler and auto-diluter system (May and others, 1997). All sediment digestates (total recoverable and SEM), filtered pore waters, and DGT extracts were analyzed with 10-fold auto-dilution to reduce concentrations of chloride and other potential interfering matrix ions. Filtered surface waters (field sampled) and overlying waters associated with whole-sediment laboratory toxicity tests were analyzed without dilution. For all analyses, any sample with a concentration exceeding the upper calibration standard for any element was diluted automatically an additional 10-fold in a serial fashion until all concentrations were within the range of the calibration standards.

The ICP-MS quantitative method was set up to determine the following masses: Co⁵⁹, Ni⁶⁰ and Ni⁶², Zn⁶⁶ and Zn⁶⁸, Cd¹¹¹ and Cd¹¹⁴, and Pb as the sum of three masses (Pb²⁰⁶ + Pb²⁰⁷ + Pb²⁰⁸). An internal standard mixture providing an effective concentration of 50 ng/mL (nanograms per mL) of germanium, and 10 ng/mL of rhodium and bismuth, was metered into the sample line via peristaltic pump to correct for instrumental drift and sample matrix effects. Calibration standards used for analyses were as follows: Co and Ni - 5, 10, 20, and 40 ng/mL; Zn - 50, 150, 300 ng/mL; Cd and Pb - 1.5, 3.0, 6.0, and 12 ng/mL. For analysis of sediment SEM extracts concentrations of Ni, Cu, Zn, Cd, and Pb were determined with germanium (50 ng/mL) and rhodium (10 ng/mL) as the internal standards. Calibration standards (ng/mL) were as follows: Ni and Cu - 5, 10, 20, 40; Zn - 75, 150, 300; Cd and Pb - 3, 6, 12. Masses monitored included Ni⁶⁰ and Ni⁶², Cu⁶³ and Cu⁶⁵, Zn⁶⁶ and Zn⁶⁸, Cd¹¹¹ and Cd¹¹⁴, and Pb²⁰⁶ + Pb²⁰⁷ + Pb²⁰⁸. Masses reported, based on quality control performance and less interferences, were Ni⁶⁰, Cu⁶³, Zn⁶⁶, Cd¹¹⁴, and Pb²⁰⁶ + Pb²⁰⁷ + Pb²⁰⁸. Total recoverable and SEM metals in sediments were reported as dry weight concentrations.

Water samples were analyzed for selected major elements by inductively-coupled plasma atomic emission spectrophotometry (ICP-AES) and for selected ions by ion chromatography (IC) according to USEPA and USGS protocols. Particle-size distribution of sediments was determined by the hydrometer method (American Society of Testing and Materials, 2005a) and total organic carbon of sediments was determined by combustion and coulometric titration (American Society of Testing and Materials, 2005b).

Quality Assurance

Quality assurance (QA) measures associated with field sampling included replicate sampling (most water samples),

field container blanks, and field filtration blanks. There were no instances of unacceptably high blanks or abnormal variation between replicates. Agreement between field replicates was quite good for the majority of surface-water and pore-water samples, in spite of the low concentrations (0.01 to 0.10 ng/mL) that were measured in many instances.

For each group of samples analyzed, QA measures incorporated at the digestion stage included blanks, certified reference materials, replicate samples, and fortified samples (spikes). During the analysis, blank verification, calibration verification, and laboratory control solutions were determined after every 10 samples; duplicates, post-digestion spikes, and interference checks (dilution checks and a synthetic interference solution) also were determined. The method detection limit (MDL) was estimated for each element and analytical run according to the following formula:

$$MDL = 3.3(SD_b^2 + SD_s^2)^{1/2}$$

where

SD_b is the standard deviation of three or more digestion blanks; and

SD_s is the standard deviation of a triplicate analysis of a low concentration sample.

Target criteria for QA parameters were as follows: digestion blanks less than or equal to 5 times the MDL; certified reference materials within ± 10 percent of certified range; replicate samples within ± 20 percent relative standard deviation (RSD) for triplicates or ± 25 relative percent difference (RPD) for duplicates; pre-digestion spike recovery at 100 ± 20 percent; post-digestion spike recovery at 100 ± 10 percent; calibration checks within ± 10 percent of actual; and dilution percent difference within ± 10 percent.

Results for the vast majority of QA measurements met target criteria and in most instances, the recovery and precision values were within ± 5 percent of optima. The QA parameter for which the target criteria was exceeded most frequently was the repeatability of measurements between replicate analyses of sediment (including the extraction or digestion) by either SEM method (2002 samples) or the total recoverable method (2002 and 2004 samples). Among those samples, the results for copper and nickel were the most variable. For example, the RPD of duplicate SEM measurements for 2002 sediments (all 16 samples were analyzed in duplicate) ranged from 25 to 32 percent in four samples for copper and from 25 to 60 percent in seven samples for nickel. Three of the 2002 sediment samples were analyzed in triplicate for total recoverable metals; the RSD for one of these was 71, 57, and 38 for copper, nickel, and zinc, respectively. Similarly, the RSD for one 2004 sediment sample analyzed in triplicate for total recoverable metals was 45, 60, 99, 31 and 29 for Co, Cd, Ni, Pb and Zn, respectively. Thus, variability exceeded the target of ± 25 percent for some of the replicate sediment-sample analyses. However, sample heterogeneity among these sediments is the suspected cause of the variability, because the repeatability

was excellent for replicate analyses of reference sediments and individual sediment and pore-water digestates.

The only other notable exceptions of target exceedances were results for a small number of spikes, dilution checks, and interference checks. Spike recoveries exceeding target criteria represented less than 5 percent of all spikes performed. There were some instances in which target criteria were exceeded for serial dilution of samples for zinc (110 to 115 percent recovery); and for the interference check sample for cadmium (up to 140 percent), lead (up to 119 percent), or zinc (up to 132 percent). However, the interference check sample is considered a “worst-case” because it contains extraordinarily high concentrations of many potentially interfering elements that generally were not observed in the unknown samples. Overall, QA results indicated satisfactory accuracy and precision; complete QA results are available upon request.

Results and Discussion

2002 Samples

The results of chemical analyses performed in 2002 are summarized in tables 3–10. Samples included sediment and pore water from 15 field-collected sediments, and one control sediment used for either sediment or pore-water toxicity testing. Because the method of sampling and the elapsed time between sediment manipulation and sampling potentially affected some of the measurements, particularly for pore water, details of these aspects are described below.

For the 2002 sediment toxicity tests, total recoverable metals (table 3), selected physical characteristics (table 4), AVS and SEM in sediments (table 5), and filterable metals in pore water (table 6) were each determined in separate sub-samples collected both at the beginning (day 0) and near the end (day 27). All day-27 samples had been transferred to an exposure chamber on day 0 and were treated in the same manner as those used for toxicity testing. Filterable cadmium, lead, and zinc were determined in overlying water of exposure chambers on days 0 and 16 for the sediment toxicity tests (table 8). Concentrations of AVS, SEM, and pore water metals were determined in duplicate for all day-0 sediment samples. For the pore-water toxicity tests, filterable cadmium, lead, and zinc were determined in samples collected on days 0, 4, and 7 from the bulk pore water (table 7) that was used to renew the exposure water chambers, but major and minor elements (table 9) were determined only in the day-0 samples.

Total Recoverable Metals in Sediments

Excluding the Big River site (BG, fig.1, upper right) near the Old Lead Belt (fig.1, inset), site means (two samples per site) of total recoverable metals measured in fine sediments in $\mu\text{g/g dw}$ (micrograms per gram dry weight) ranged as fol-

lows: Cd, 0.045–4.7; Cu, 2.3–38.7; Ni, 4.5–122; Pb, 4.3–381; Tl, 0.038–0.83; Zn, 9.0–1,202 (table 3). Concentrations of iron and manganese (table 3), which typically are present at percent levels in sediments, were included primarily to aid interpretation of trace metal concentrations. As illustrated in figure 5, samples from sites CC, SC2, and WF3, had the greatest concentrations of most metals. Samples from LC1 and Clearwater Lake had the next greatest concentrations, but these had considerably lower metal concentrations (particularly lead and zinc) than did samples from CC, SC2, and WF3. The lake sediments had the greatest concentrations of copper and thallium, but none of the samples had particularly elevated concentrations of these two elements, so they were not a focus of subsequent investigations. With the exception of nickel in samples from WF3 and SC2, and thallium in samples from the Clearwater Lake, metal concentrations were considerably lower in samples from the New Lead Belt sites as compared to the Old Lead Belt site (BG), which evidently reflects improved metal recovery and waste containment realized with modern era (1970–2005) mining processes.

For comparative purposes, a sediment enrichment factor for each stream site and metal was calculated as the mean concentration divided by the mean for the two stream reference sites. Sites for which sediment enrichment factors were greater than 5.0 included WF3 (Cd, 75; Ni, 16; Pb, 47; Zn, 124), SC2 (Cd, 11; Ni, 19; Pb, 28; Zn, 58), CC (Cd, 36; Cu, 7.3; Ni, 5.1; Pb, 24; Zn, 33), LC1 (Cd, 12; Pb, 11; Zn, 7.4), and SW (Pb, 5.3). Thus, among the 2002 samples, concentrations of lead and zinc were about twice as great at WF3 as compared with the next greatest concentrations (SC2). Concentrations of lead and zinc reported by Petersen and others (1998) for composite sediment samples collected in 1995 from reaches of Strother Creek and West Fork Black River that were in proximity to sites SC2 and WF3, respectively, appeared to be of a similar range to the 2002 samples. However, in 1995, samples from Strother Creek had greater zinc concentrations than samples from the West Fork Black River.

Samples from the four sites located within the Black River or Logan Creek arms of Clearwater Lake, which were at least 75 kilometer (km) downstream from mining operations, had average sediment enrichment factors of between 1.5 and 2.1 when compared to the reservoir reference site in the Webb Creek arm (CL3). However, the water level of Clearwater Lake periodically rises several meters, which could result in some mixing of suspended sediments throughout the reservoir. Metals concentrations were considerably greater in the sample from CL3 as compared with samples from the two stream reference sites (fig. 5), suggesting that metal-enriched suspended sediment originating from mining sources has been distributed, to some extent, into the reference arm. Thus, site CL3 may not represent absolute reference conditions; however, enrichment factors for Clearwater Lake sediments cannot be determined reasonably by comparison to reference stream sediments because lake sediments were considerably finer in texture (table 4).

SEM Versus Total Recoverable Metals

Extraction of sediment with dilute HCl at room temperature (essentially the SEM procedure) is one approach historically used to approximate “potentially bioavailable” or “labile” metals (Luoma and Bryan, 1982). Accordingly, a comparison of the SEM concentration to the total recoverable concentration (SEM divided by total recoverable) can provide an indication of the percentage of potentially bioavailable metals in a sediment sample. When averaged for the two reference stream sites (WF1 and SK), the fraction of the total recoverable concentration (table 3) measured as SEM (table 5) ranged from 24 percent (zinc) to 54 percent (lead). In comparison, the same values calculated as an average across the remaining seven stream sites ranged from 47 percent (copper) to 89 percent (lead). Thus, based on these measurements, the percentages of potentially bioavailable metals in sediments of non-reference streams were considerably greater than for the nearby reference streams. Clearwater Lake sediments were intermediate in this respect; corresponding values averaged across all five lake sites ranged from 21 percent (nickel) to 79 percent (lead).

Pore Water

Metals and organic chemical concentrations are often measured in pore water as part of a comprehensive sediment toxicity assessment (U.S. Environmental Protection Agency, 2005). However, variability between measurements and between different preparation methods can be considerable (Bufflap and Allen, 1995) and this was true for some of the 2002 samples (fig. 6, top). Filterable metal concentrations in pore water obtained by centrifugation (table 6) generally were greater than in bulk pore water produced by squeezing and centrifugation (table 7), especially for samples obtained from sediment collected at WF3. Lower concentrations obtained by the squeezing method might have been caused in part by losses of dissolved metals by adsorption to fine sediment particles during pressurized pore-water extraction, or from differences in redox conditions potentially affected by each preparation method (U.S. Environmental Protection Agency, 2005). Variability of measured concentrations was small between duplicate preparations and samplings of pore water on day 0 or day 27 for the centrifugation method (table 6), and for repeated sampling of bulk (squeezed and centrifuged) pore water on days 0, 4, and 7 (table 7). However, there were some considerable differences between replicate samples that were collected at different times during the sediment toxicity tests. Most notably, iron and lead concentrations were markedly higher in pore-water samples obtained on day 27 from sediments collected at WF3 and SC2, but considerably lower in samples obtained from sediment collected at BF4 (table 6). Concentrations of lead decreased substantially in overlying waters of test chambers sampled on day 16 as compared to day 0 (table 8). This was expected to some extent because of par-

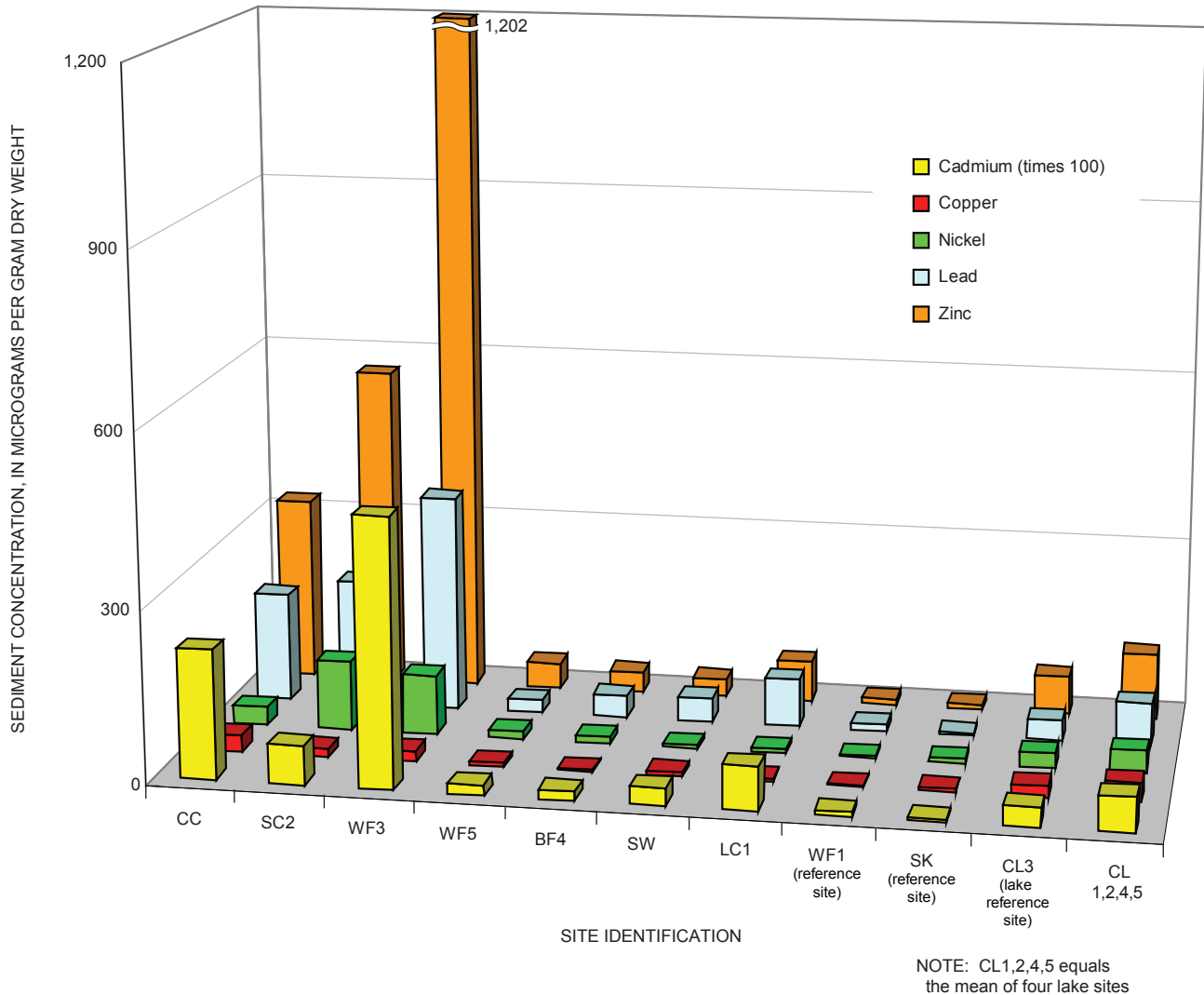


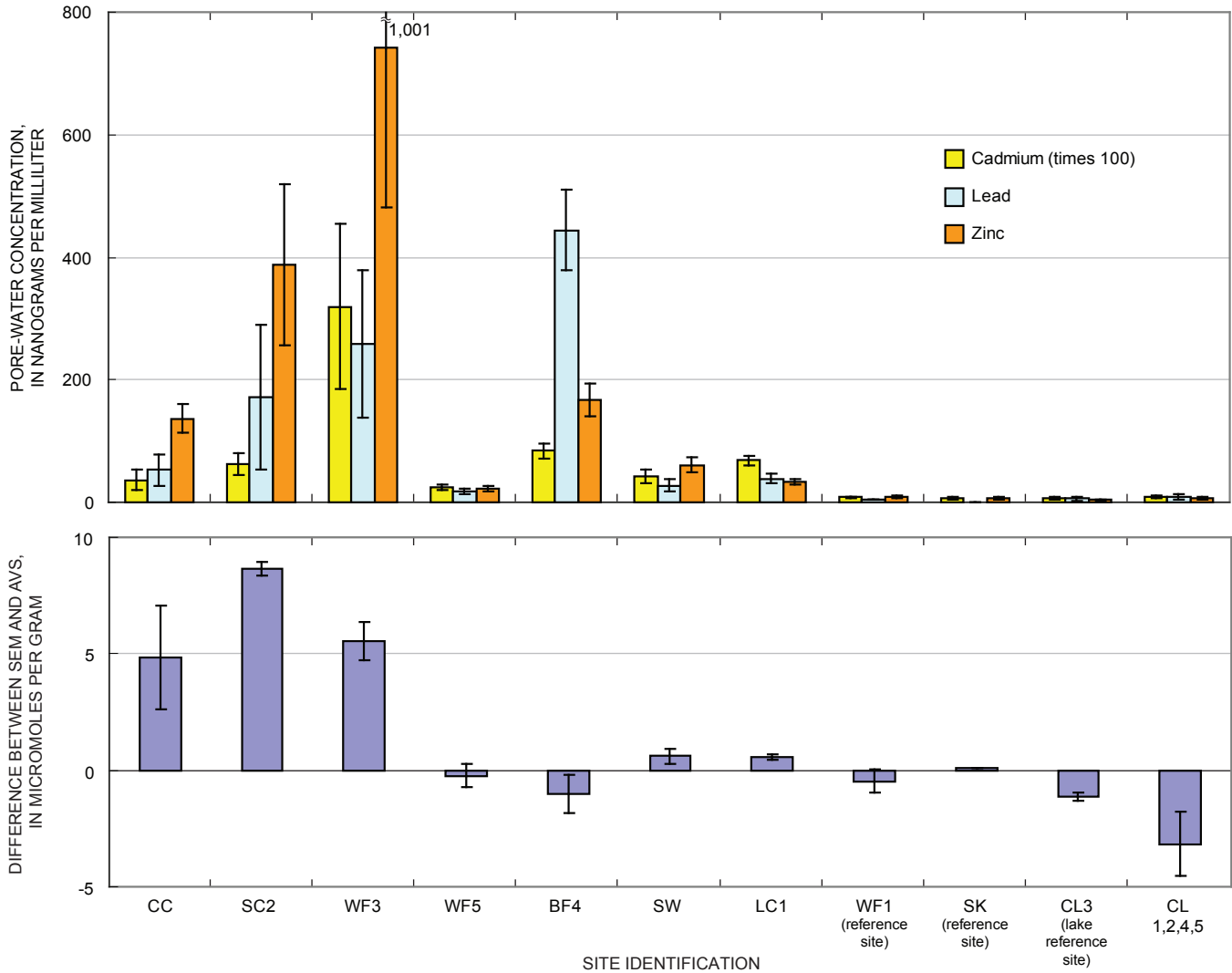
Figure 5. Total recoverable concentrations of selected metals in 2002 sediment samples.

tial flushing that occurs during periodic renewal of test waters. Despite large variability among replicate measurements for some samples, mean pore water concentrations generally tracked closely with total recoverable sediment concentrations (fig. 5; fig. 6, top). Samples from site BF4 were an exception because pore-water concentrations of cadmium, lead, and zinc were greater in proportion to sediment concentrations as compared with corresponding sediment and pore-water samples from other sites.

For the selected major and minor elements determined in the bulk pore water by ICP-AES (table 9), the greatest differences among sites were between lake and stream sediments. Pore-water samples from Clearwater Lake sediments had the lowest concentrations of K, Na and Sr, and among the lowest concentrations of some of the other elements. Some of these differences may correlate with differences in texture (table 4) and redox conditions; however, detailed statistical analyses of these data are beyond the scope of this report. The sample

from site BF4 had the greatest concentration of Fe, K, Mn, Na, Si, and Sr. Notably, iron and manganese concentrations determined by ICP-AES in the day-0 bulk pore water (table 9) were in good agreement with those determined by ICP-MS (table 7).

Some of the apparent temporal differences among centrifuged pore-water samples might have been caused by sample heterogeneity, but increases in pore water metal concentrations for some sediment samples probably resulted from remobilization of these metals in association with reductive dissolution of oxyhydroxide particles of iron and manganese. This can occur when organic-rich, chemically-reduced particles are mixed with overlying oxidized particles; for example, during fall turnover in seasonally-anoxic water bodies (Hamilton-Taylor and others, 1999). In aquatic sediments, ferric oxyhydroxides can undergo reductive dissolution (Van Cappellen and Gaillard, 1996) that can be coupled directly to the microbial oxidation of organic matter (DiChristina and Delong, 1993).



NOTE: SEM, Simultaneously Extracted Metals; AVS, Acid-Volatile Sulfide; Error bars are \pm one standard error ($n=3$ for SEM/AVS; $n=6$ for pore water metals) which includes two preparation methods and multiple sampling times; CL1,2,4,5 equals the mean of four lake sites

Figure 6. Comparison of filterable concentrations of selected metals in laboratory-produced pore water to differences between simultaneously extracted metals and acid-volatile sulfide for 2002 sediment samples.

In sediment pore waters, the supply of organic material is reportedly the limiting factor and the dissolution of iron and manganese oxides can be highly localized (Shuttleworth and others, 1999).

Some of the fine sediments that were collected from depositional habitats might have included oxic and anoxic sediment horizons. In addition, sediments were collected in late summer when biological productivity was presumably near its peak, and it is likely that this collection method mixed fine organic detritus and biofilm from the sediment surface

with metal-rich fine sediments. Consequently, storage of the sediments in the dark and without oxygen could have led to increasingly reducing (anoxic) conditions before the pore-water samples were obtained. Furthermore, sulfate reducing bacteria and microbial growth in general might have promoted localized anoxia within sediment layers in some of the test chambers. Consistent with this hypothesis is the fact that AVS, which is associated with anoxic conditions (discussed later in this report), appeared to increase between day 0 and day 27 for some of the stream sediment samples, particularly in those

obtained from sites WF1, WF3, WF5 and BF4 (table 10). In contrast, AVS decreased during toxicity tests for three of the five lake sediments, which appeared to consist primarily of anoxic sediment layers at the time of collection. Presumably, when fine sediments are redistributed among depositional pools after large rainfall events, metals potentially could be released from oxyhydroxide particles of iron and manganese in a manner analogous to that described above. Thus, although in some instances pore-water metal concentrations were variable and appeared to depend on the method and time of sampling, these results overall could be considered indicative of potentially available metal concentrations during certain conditions.

SEM-AVS

AVS is an important sediment-binding phase for cationic metals because it represents the most chemically reactive form of reduced sulfur. In the solid phase, AVS consists primarily of monosulfides of iron and manganese (Morse and Rickard, 2004). AVS occurs primarily in anoxic sediments, but considerable AVS also may be present in association with weathered shales (Ogendi and others, 2007) or fine-grained, sulfide-bearing minerals in sediments associated with mine tailings (Brumbaugh and others, 1994). Consistent with these observations, AVS concentrations in the 2002 samples were greatest in the bottom sediments of Clearwater Lake and from sites that were near mining activities (CC, WF3, BF4; table 5).

The difference between the molar sum of certain SEM metals and AVS (SEM-AVS) can be a useful parameter for assessing the potential for toxicity from elevated metal concentrations in pore water (U.S. Environmental Protection Agency, 2005). For the 2002 samples, SEM-AVS (table 10) generally was a good predictor of elevated metals in pore water as three of the four sediments exhibiting the greatest pore-water metal concentrations also had the greatest (positive) SEM-AVS values (fig. 6). The one exception was the sediment sample from BF4, which had considerable concentrations of lead and to a lesser extent, cadmium and zinc in the pore water despite a negative SEM-AVS value. Interestingly, samples from BF4 also had the greatest pore-water concentrations of iron and manganese using either pore-water preparation method, and sediment from BF4 was the only one in which samples of pore water produced by either method had extraordinarily high concentrations of lead (tables 7 and 9). As noted previously, sediment from BF4 also had comparatively high pore water metal concentrations relative to total recoverable sediment concentrations.

Greater concentrations of iron and manganese in pore-water samples obtained from BF4 sediment suggests metals were released by reduction of oxyhydroxides to a greater extent in that sediment sample as compared to other samples. The texture and organic carbon content of the sediment sample from BF4 were not remarkably different from other samples (table 4). Perhaps that sample had unusual biochemical

characteristics, or a unique combination of oxic and anoxic sediment layers, which promoted the dissolution of lead and other metals despite the apparent excess of AVS. Pore-water concentrations of all metals in samples obtained from BF4 sediment decreased greatly between day 0 and day 27 of the test (table 6), while AVS increased considerably (table 10), indicating that pore-water metals were not in equilibrium with AVS in the sediment.

2003 Samples

Results of chemical analyses performed on water samples collected in 2003 are summarized in tables 11–13. Analyses include selected trace metals and other elements from field-collected surface- and pore-water samples from 12 stream riffle-run sites where biological communities and habitats were assessed. Metal concentrations in selected biota and numerous water quality parameters also were measured, but those data are not presented in this report. Diffusion samplers were buried in riffle-run stream sediments for the in-stream sampling of pore waters. Surface water and pore water were sampled in triplicate and analyzed for cadmium, lead, and zinc; pore waters also were analyzed for cobalt and nickel. Because the selection of 2003 locations was guided primarily by stream habitat considerations, sampling was not conducted at site BG (near the Old Lead Belt) or in Clearwater Lake. In addition, one site on the Middle Fork Black River (MF3) and two additional reference sites (HZ and BC) were sampled (fig. 2).

Pore Water

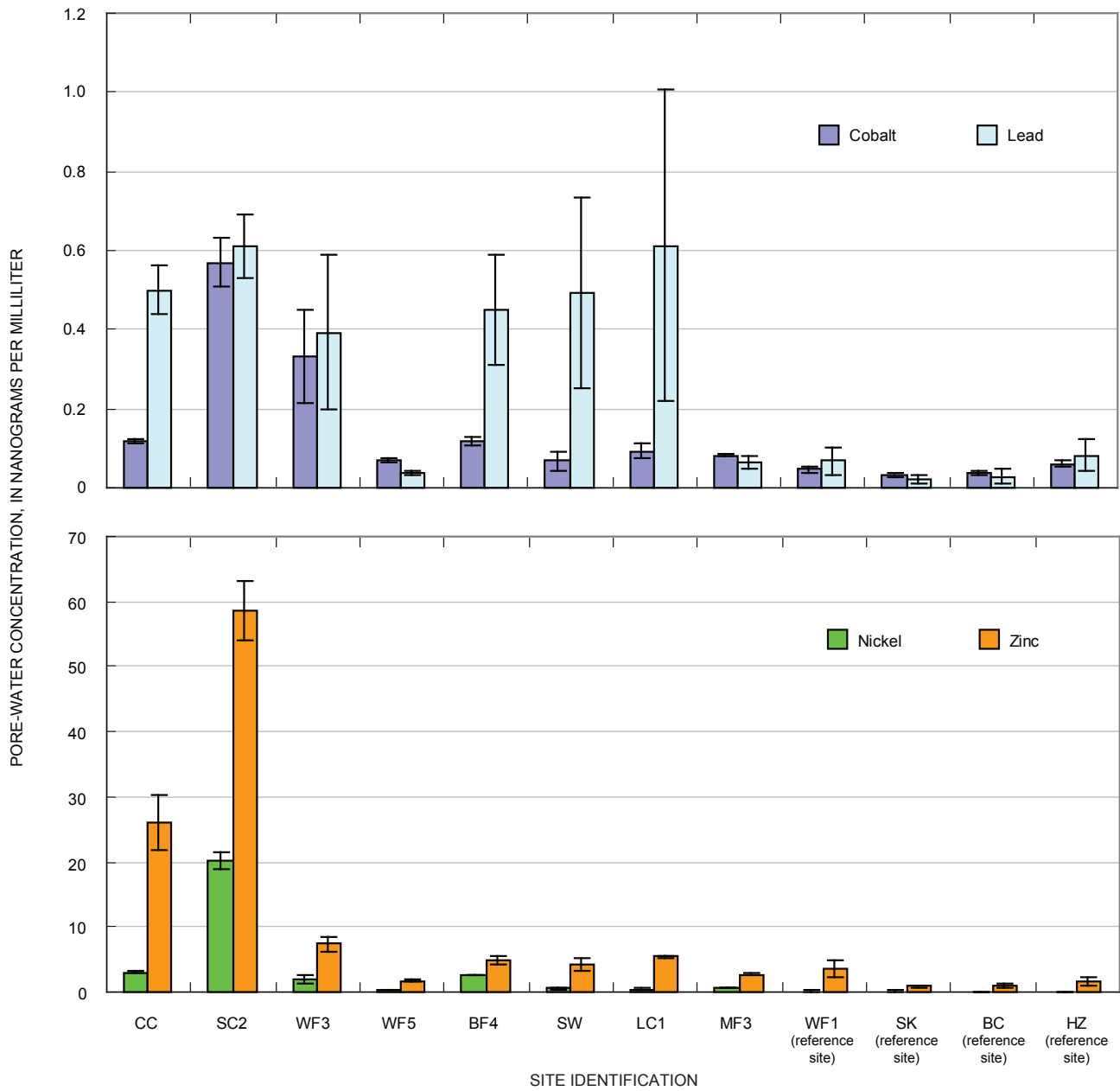
Metals concentrations in riffle-run sediment pore waters (table 11) are summarized graphically in figure 7, with the exception of cadmium because it was near the MDL (0.01 $\mu\text{g/L}$) for all samples except those from sites CC (mean, 0.18 $\mu\text{g/L}$) and SC2 (mean, 0.11 $\mu\text{g/L}$). Metal concentrations in the 2003 in-stream, pore-water samples were much lower than concentrations in 2002 pore waters produced in the laboratory. This is not surprising because leaching of metals from weathered mine wastes typically is greatest in the smaller-sized particles (Smith and others, 2000). Despite much lower concentrations, the pattern among sites for 2003 in-stream pore water was similar to the 2002 laboratory-prepared pore water. The greatest concentrations of all metals were measured at sites CC and SC2, but WF3, BF4, SW, and LC1 also had noticeably elevated lead concentrations. The mean lead concentration in pore waters averaged across these six sites was 0.51 $\mu\text{g/L}$, or about 10-fold greater than the mean of the four reference sites (0.05 $\mu\text{g/L}$). The greatest concentrations of cobalt (not measured in 2002) were measured at SC2 and WF3, which also were about 10-fold greater than the reference sites. The greatest concentration of nickel in pore water also was at SC2 (mean, 20 $\mu\text{g/L}$), whereas the mean of the four reference sites was 0.13 $\mu\text{g/L}$. Only two sites (CC and SC2) had markedly

elevated concentrations of zinc, and those concentrations were about 20- to 30-fold greater than the reference sites.

Selected major and minor element concentrations of did not differ greatly between sites (table 12) and in many instances, in-stream concentrations were lower than in corresponding laboratory-produced pore waters of sediment samples collected in 2002. For example, none of the 2003 in-stream pore-water samples had detectable concentrations of iron and manganese.

Surface Water

Surface water (not analyzed for cobalt and nickel) tended to have lower metal concentrations than pore water, but surface water and pore water had similar concentrations in many instances (table 11). Mean concentrations of lead were greatest at sites CC and BF4 (each 0.39 $\mu\text{g/L}$) followed by site SC2 (0.22 $\mu\text{g/L}$). Filterable concentrations of zinc were greatest in surface water at sites CC (mean, 45 $\mu\text{g/L}$) and SC2 (mean,



NOTE: Error bars are \pm one standard error ($n=3$ for each)

Figure 7. Filterable concentrations of cobalt, lead, nickel, and zinc in 2003, in-stream pore water.

55 µg/L). The only site with a cadmium concentration clearly above the 0.01 µg/L MDL was CC (mean, 0.08 µg/L). In comparison, the mean filterable surface-water concentrations averaged across the four reference sites were less than 0.01 µg/L for cadmium, 0.01 µg/L for lead, and 1.8 µg/L for zinc. Concentrations were less variable in surface waters than in pore waters, which had highly variable lead concentrations (fig. 7, top). This probably reflects localized variation of stream sediment constituents and associated localized differences in pore-water metal concentrations, which can be quite large (Shuttleworth and others, 1999). Concentrations of selected major and minor elements measured in surface water (table 13) closely matched the corresponding in-stream pore-water concentrations (table 12). These results indicate that exchange between surface water and pore water was considerable for the 4 to 6 cm sediment depths in which the peepers were buried.

Surface-water concentrations previously reported for multiple samplings conducted in Strother Creek and West Fork Black River in 1995 appeared to be greater than for samples collected at common locations in 2003. For example, 1995 filterable surface-water concentrations at a site near SC2 were reported as <1 (less than 1) to 3 µg/L for lead, and from 33 to 148 µg/L for zinc (Petersen and others, 1998). The 1995 concentrations at a site near WF3 were reported as <1 to 11 µg/L for lead and from 13 to 33 µg/L for zinc. Thus, samples collected in 1995 had greater maximum lead and zinc concentrations than those in 2003 (table 11). Milling operations at the West Fork Mine ceased in 2000 (Thomas Yanske, Doe Run Company, written commun., 2006), which might be one reason why metal concentrations were lower in 2003 at the WF3 site. In addition, the 1995 samples were collected during high and low stream discharges, whereas 2003 samples were collected only during low discharge. Based on the 1995 data, Peterson and others (1998) concluded that, compared with reference streams, concentrations of zinc, but not lead were significantly elevated in surface waters of mining-affected streams, but both metals were elevated significantly in bed sediment and biota. In contrast, and although concentrations in surface waters appeared to be lower in 2003 than in 1995, both lead and zinc were noticeably greater at mining-affected streams in 2003 as compared with reference streams (table 11, fig. 7).

Femmer (2003) compared the 1995 surface water concentrations of three reference stream locations in the Viburnum Trend region to those of 2001 samples collected from four sites in the un-mined exploration region. In this assessment, only samples collected in August or September and during low-flow conditions were compared, and one of the sites was the same WF1 location used for the current study. Concentrations at site WF1 in 1995 were reported as <1 µg/L for lead and 13 µg/L for zinc, whereas mean 2003 concentrations were 0.01 µg/L for lead and 1.2 µg/L for zinc (table 11). Thus, based on a limited comparison with data from two previous reports, surface-water concentrations of lead and zinc at reference and mining-affected sites seemed to be lower in

2003 than in 1995; however, lower analytical detection limits for the 2003 data might have contributed to the apparent differences.

2004 Samples

Results of chemical analyses performed on 2004 sediment samples, which were collected to characterize longitudinal trends in sediment toxicity and metals concentrations downstream from mining activities in three streams, are summarized in tables 14–18. Sites included three locations on Strother Creek (SC1, SC2, SC3), two on the Middle Fork Black River (MF2, MF3) downstream of Strother Creek, five on the West Fork Black River (WF2, WF3, WF4, WF5, WF6), and four on the Bee Fork (BF2, BF4, BF5, BF6). Also included were samples from four reference stream locations and one control sediment. Analyses included total recoverable metals in sediments; metals, selected major and minor elements, and anions in laboratory-prepared pore water; and metals in sediment pore-water probes (selected sediments only).

Sediments and Pore Water

Total recoverable metals concentrations in sediments are indicated in table 14 and figure 8. Concentrations of all metals except iron and manganese were by far the greatest in the sample from SC1, which was located about 3.2 km downstream from the Buick tailings impoundment, and 0.9 km downstream from the Buick tailings secondary settling basin (fig. 2, center). Concentrations of cobalt, nickel, and zinc in the sediment sample from SC1 were more than 10-fold greater than those of any of the samples from the Bee Fork or West Fork (fig. 8). Compared to the average of the concentrations in samples from the four reference sites, the sediment sample from SC1 was enriched by factors of 13, 62, 171, 95 and 150 for Cd, Co, Ni, Pb and Zn, respectively. The sediment sample from SC2, which was about 2.8 km downstream from SC1, had metal concentrations that were about 5-fold less than the sample from SC1. The sample from SC3 (about 2.6 km downstream from SC2) had concentrations that were about 2- to 3-fold less than the sample from SC2. However, compared to reference sites, metal concentrations remained elevated at site SC3; with the exception of cadmium, the sediment sample from that location was enriched by factors of between 6 and 18. At site MF2, about 13 km downstream from the Buick tailings impoundment, cadmium, lead, cobalt, and lead were enriched by a factor of 3 or less, but nickel and zinc were enriched by factors of 9 and 5, respectively.

Bee Fork sediment samples had lesser metals concentrations than samples from Strother Creek. The sample from BF2 (just downstream from the Fletcher mine water clarification pond) was enriched by a factor of 51 for lead, but only by factors of 2 to 9 for the other metals. The lead concentration of the sample from BF4, located just downstream from the Fletcher tailings impoundment and 3.8 km downstream from

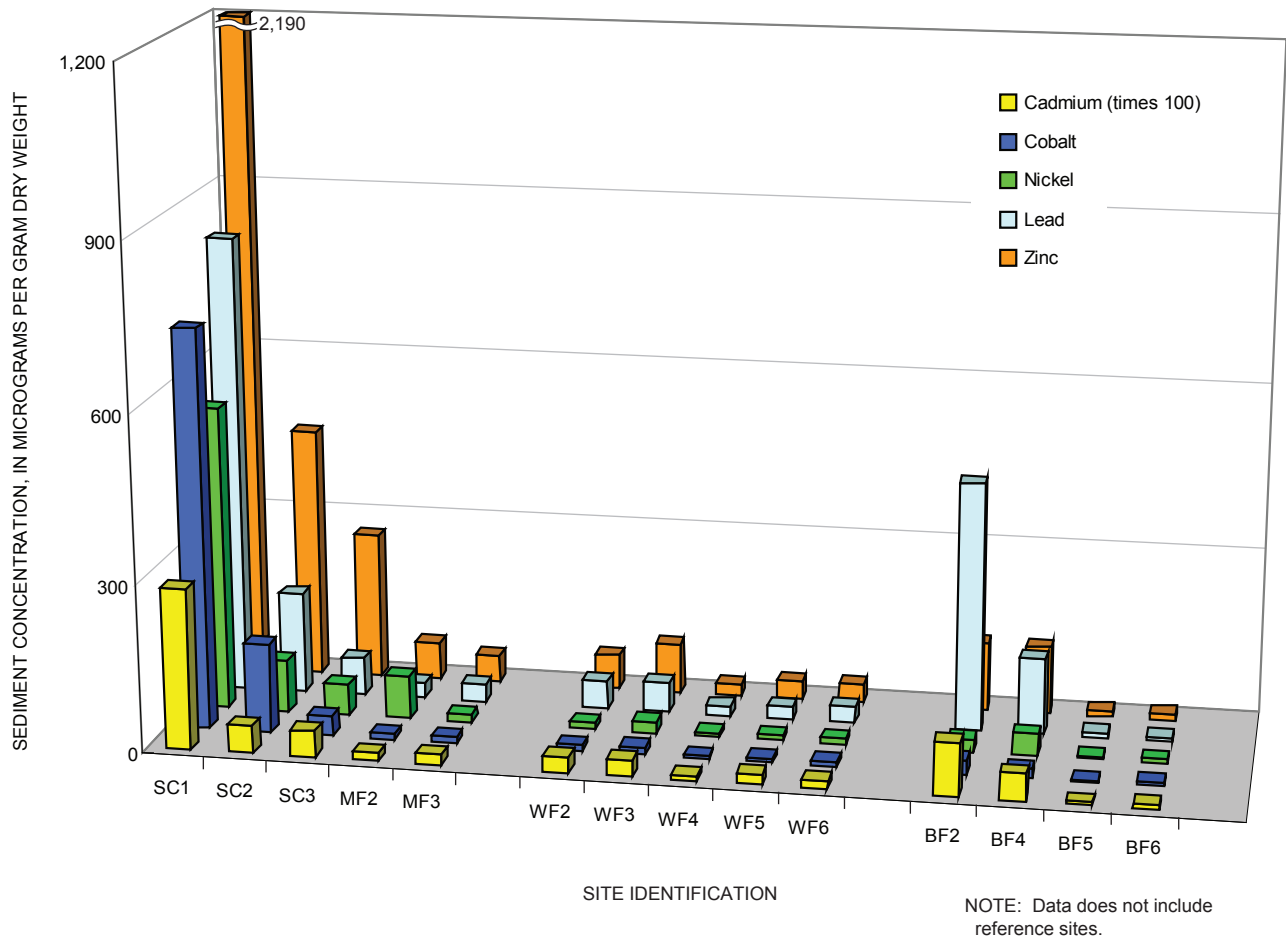


Figure 8. Total recoverable concentrations of selected metals in 2004 sediment samples.

BF2, was about 3-fold lower than the sample from BF2, whereas the concentrations of the other metals were not substantially different. Sediments collected at WF3, 2.2 km downstream from the West Fork tailings impoundment, were only moderately elevated. Cobalt, lead, nickel, and zinc concentrations in the sample from WF3 were about 2- to 6-fold greater than the concentrations in samples from reference streams. Concentrations of cadmium, lead, and zinc in the sediment sample from Huzzah Creek (site HZ) appeared to be slightly elevated compared to the other three reference sites (table 14). The HZ site was presumed to be a reasonable reference site for the Meramec River Basin because no tailings drain into that watershed (fig. 2, top left). However, this site may have been affected by the Casteel mine and/or historical effects from Viburnum Mine 27 (closed in 1978).

Among the four non-reference sites sampled in 2004 and 2002, sediment concentrations did not appear to change appreciably in 2004 at sites SC2 or WF5. However, 2004 concentrations were considerably higher at BF4, and dramatically lower at WF3 (figs. 5 and 8). Some of the changes in sediment concentrations might have occurred because mill-

ing operations at the West Fork Mine ceased in 2000; the ore mined there has since been transported to the Fletcher Mill for beneficiation (Thomas Yanske, Doe Run Company, written commun., 2006). In addition, the total organic carbon content of the sediment from WF3 was considerably lower in the 2004 sample (0.2 percent; table 14) as compared to 2002 (2.0 percent; table 4). Greater organic carbon content in the 2002 sample might have contributed indirectly to greater metal concentrations in the sediment from WF3 because of the strong binding affinity of many metal ions with natural organic matter (U.S. Environmental Protection Agency, 2005). However, as suggested by Besser and others (2006), temporal trends in metals concentrations also might be greatly affected by differences in the movement of metal-enriched sediments resulting from heavy rainfall events. The region experienced dry conditions for an extended period before 2001 sampling, excessive rainfall before 2002 sampling, and typical seasonal rainfall from 2003 to 2005.

Patterns of metal concentrations in 2004 pore-water samples (table 15; fig. 9) generally corresponded closely to total recoverable concentrations in sediments (fig. 8), including the

sample from BF4, which seemed anomalous in this respect in 2002. One notable exception was the high cobalt concentration in pore water obtained from sediments collected at SC2. Generally, cobalt concentrations in pore water corresponded less consistently with sediment concentrations than the other metals. There were no clear patterns evident among the major and minor elements measured in pore waters (table 16).

Metals concentrations were considerably lower and longitudinal trends less evident for West Fork as compared with Strother Creek and Bee Fork. Metal concentrations in sediments from WF2 (upstream from West Fork Mine and tailings) were similar to those from WF3 (downstream from tailings; fig. 8), but pore-water concentrations were lower in samples obtained from sediment collected at WF2 (fig. 9). Lead concentrations in sediment samples from WF2 and WF3 were about 12 times greater than in the sample from WF1 (table 14). Presumably, enrichment of metals at WF2 resulted in part from activities at the Brushy Creek Mine, which operates with a permit to discharge process water into a tributary of Bill’s Creek (fig. 2; Missouri Department of Natural Resources,

2003). Sediment- and pore-water metal concentrations (particularly cobalt) appeared to increase slightly in samples from WF6 as compared to those obtained from upstream locations at WF4 and WF5 (fig. 9). This increase might reflect an influence from Bee Fork, which joins the West Fork Black River just upstream from WF6. However, concentrations in pore waters did not appear elevated in samples from the two Bee Fork sites (BF5 and BF6) immediately upstream from the mouth, and sediment concentrations at WF6 were 2- to 3-fold greater than those at BF5 and BF6 for most metals (table 14). The sample from WF6 had a greater organic carbon content (table 14), which might have been a factor in the greater sediment concentrations because of the strong binding affinity of metal ions with natural organic matter (U.S. Environmental Protection Agency, 2005). The sample from WF6 also had the greatest day-0 pore-water concentrations of Ba, Fe, Mg, and Mn (table 16). In addition, cobalt and nickel concentrations were considerably greater in the day-0 sample of pore water obtained from WF6 sediment, than in the day-27 sample (table 15). Therefore, reductive dissolution of oxyhydroxides,

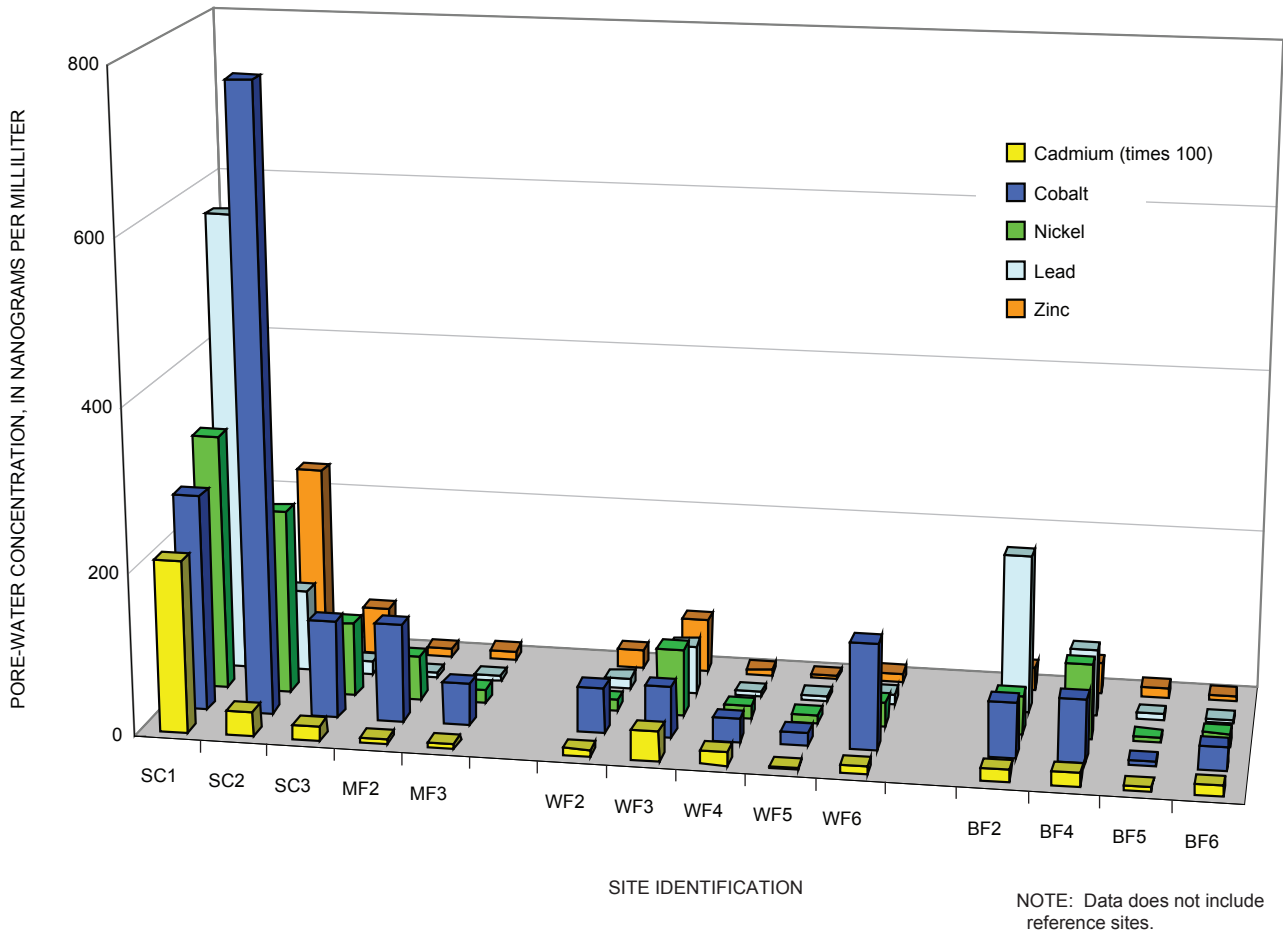


Figure 9. Filterable concentrations of selected metals in laboratory-produced pore water of 2004 sediment samples.

as previously discussed, might have been responsible for the comparatively greater concentrations of metals in the pore water of the sediment obtained at WF6.

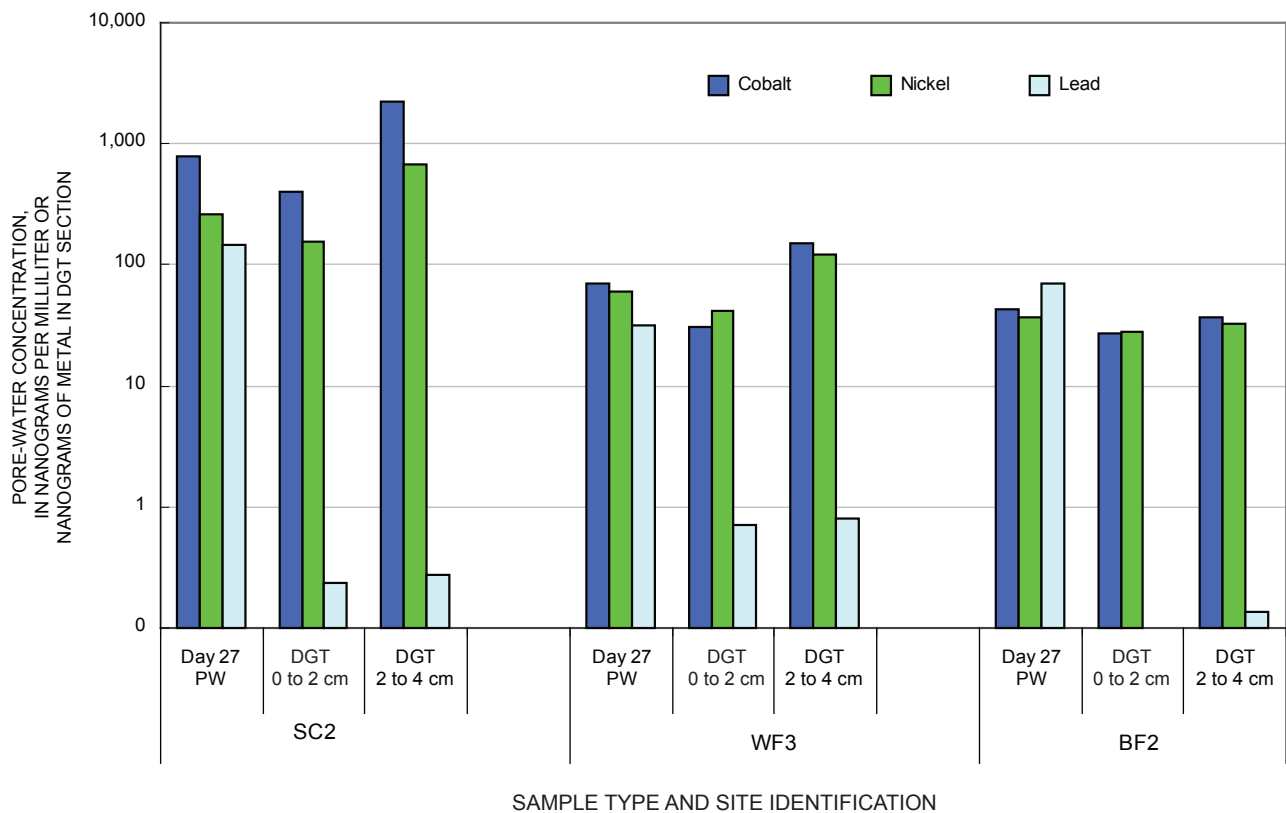
Sulfate concentrations in pore water (table 17) tracked closely with metals concentrations. The lone exception was the sample from BF5, which had a sulfate concentration that was about 5-fold greater than the other pore-water samples from Bee Fork. The greatest concentrations occurred in pore waters obtained from sediments at SC1 and SC2, which were about 100-fold greater than in reference site pore waters.

Sediment Probes

Probes that sequester ions from water by means of the diffusion gradient in thin film (DGT) technique (Zhang, 2002) were used to assess the relative lability and mobility of metals in pore water. Theoretically, metal-ion fluxes and pore-water concentrations can be estimated with the DGT method (Zhang and others, 1995). However, because of uncertainties in the

assumptions associated with the models used for those calculations (Dunn and others, 2003), the probes were used only for qualitative comparisons between sediments and depth horizons. Extra test chambers containing sediments from four sites were monitored with the DGT probes for 48 hours beginning on day 27 of the toxicity test. Complete results (mass of metal sampled from each horizon) are summarized in table 18. Most samples contained readily measurable amounts of iron, cobalt, nickel, and lead. In contrast, cadmium and zinc were below the MDL for most samples, but high DGT blanks greatly increased the MDL for zinc.

For all samples, loading of iron (assumed to be mostly ferrous ion) was considerably greater in the probe section exposed to the lower (2 to 4 cm) sediment horizon than in the 0 to 2 cm horizon, indicating that redox gradients had formed in the chambers during the first 27 days of the test. Presumably, this resulted from downward diffusion of oxygenated overlying water into the upper sediment horizon. Trends in cobalt and nickel concentrations mirrored those of iron.



NOTE: Day 27 PW, laboratory-prepared pore water obtained from sediment sample after 27 days in a toxicity test chamber. DGT, diffusion gradient in thin film passive sampling probe; 0 to 2 centimeter (cm) and 2 to 4 cm refer to sections of DGT probe corresponding to depths of sediment within a toxicity test chamber. Probes were placed in selected test sediments for 48 hours beginning on day 27 of toxicity test.

Figure 10. Comparison of filterable concentrations of cobalt, nickel, and lead in pore water to the mass of each metal recovered from sections of probes used to passively sample pore water in selected 2004 sediment samples.

In contrast, DGT loadings of lead were low and inconsistent, especially considering some of the high concentrations measured in the prepared pore waters. To illustrate this point, day-27 pore-water concentrations of cobalt, nickel, and lead (measured using sediment from a separate test chamber) are presented with DGT results for sediment samples from sites SC2, WF3, and BF2 (fig. 10). Compared to concentrations measured in prepared pore waters, DGT probes sampled proportionally lesser amounts of lead than cobalt or nickel. According to speciation modeling, carbonate complexes should have been the dominant soluble inorganic species of lead (Rob Lee, USGS, written commun., 2006), but carbonate complexes presumably would have been sampled effectively by the DGT method. Comparatively low sampling efficiency of lead by the DGT method indicates that lead was present primarily as an organically-complexed or colloidal species (Muller, 1996; Scoullou and Pavlidou, 2003).

2005 Samples

Results for 2005 samples, which included surface water, in-stream pore water, and in-stream passive water samplers are summarized in tables 19–23. Samples were collected in association with 28-day, in-stream crayfish exposures conducted at a site on Strother Creek, and three sites each on the West Fork Black River and Bee Fork. All samples were analyzed for Cd, Co, Ni, Pb and Zn; pore water and surface water also were analyzed for selected major and minor elements and anions.

Surface and Pore Water

Concentrations of Cd, Co, Ni, Pb, and Zn in pore water and surface water for sites sampled in 2005 are presented in table 19, and pore-water concentrations are depicted graphically in figure 11 (except cadmium, which was below the MDL in most samples). Concentrations of nickel and zinc were greatest at site SC2; lead was greatest at SC2 and BF3. Sites SC2 and WF3 were sampled in 2003 and 2005. For those two sites, concentrations of cobalt and lead measured in 2005 were greater at SC2, but lower at WF3 (tables 11 and 19); nickel and zinc concentrations were about the same in 2003 and 2005. As was observed in 2003, concentrations generally were lower in surface water than in pore water, except at site BF1, a reference site that was not sampled previously. At BF1, mean concentrations of cobalt and nickel were considerably greater in pore water than in surface water, and cobalt was greatest in the pore water obtained on day 28 (table 19).

Elevated metal concentrations at site BF1 were unexpected because it was located upstream from potential inputs from Fletcher mine water and mill tailings. However, this particular site was located relatively close to the mine and mill (fig. 2) because access farther upstream was limited. Historically, considerable quantities of cobalt associated with Mis-

souri lead ores have been lost during mining and milling and about 50 percent of that loss was attributed to waste tailings (Shedd, 1993). The Missouri Department of Natural Resources indicated in 2002 that windblown tailings leaving the designated waste-management area at the Fletcher tailings dam (including beyond highway TT, which lies immediately to the west) was an environmental concern; corrective measures were to be implemented in 2003 (Doe Run Company, 2003). Thus, historical transport of windblown tailings dust to nearby streambed sediments might explain the comparatively high concentration of cobalt in pore water at site BF1. Notably, unusually high concentrations of iron (1.9 mg/L) and manganese (1.5 mg/L) were measured in the peeper obtained from BF1 on day 28 (table 20). Field analysis for ferrous iron performed on sub-samples collected from a separate peeper at each site using the ferrozine method (Viollier and others, 2000) confirmed the presence of about 2 mg/L ferrous iron in a day-28 peeper at BF1 (data not shown). In contrast, ferrous iron was not detectable in any other peeper samples. These results indicate that the second set of peepers deployed at BF1 (retrieved on day 28) were buried into an anoxic sediment horizon (perhaps somewhat deeper than the first set), which might also have contributed to the greater overall concentrations of cobalt and nickel measured at site BF1 (per discussion of 2002 sediment results).

Concentrations of selected major and minor elements (tables 20 and 21) and anions (table 22) were nearly identical for surface- and pore-water samples, again indicating that exchange between surface water and pore water was considerable for sediment depths of 4 to 6 cm. Sulfate concentrations of pore water measured by in-stream (peeper) sampling at site SC2 in 2005 (table 22) were nearly identical to the sulfate concentration measured in laboratory prepared pore water from fine sediment collected in 2004 (table 17). The chloride concentrations also were similar, but nitrate was considerably greater in the 2005 peeper samples. Sulfate concentrations appeared to increase slightly at site SC2 in surface water and pore water on day 28 as compared with day 14, but no substantial differences were apparent between sampling days for the other sites.

Passive Integrative Water Samplers

Three SLMD passive, integrative water samplers were deployed at each of three sites (SC2, BF1, and BF3) from July 6 to July 28, 2005. One sampler was removed from each site after 7 days, the second after 13 days, and the third after 22 days. The deployment interval for the SLMDs corresponded roughly with days 7 through 28 of a 28-day, in-stream crayfish exposure. Results from these samplers are provided in table 23 and figure 12. Compared to reference site BF1 (upstream from Fletcher Mine and tailings), metal amounts sampled after 7 days were greater at site SC2 (downstream of Buick Mine and tailings) by factors of about 40, 100, 150, 350, and 600 for Cd, Co, Ni, Pb, and Zn, respectively (table 23). Amounts

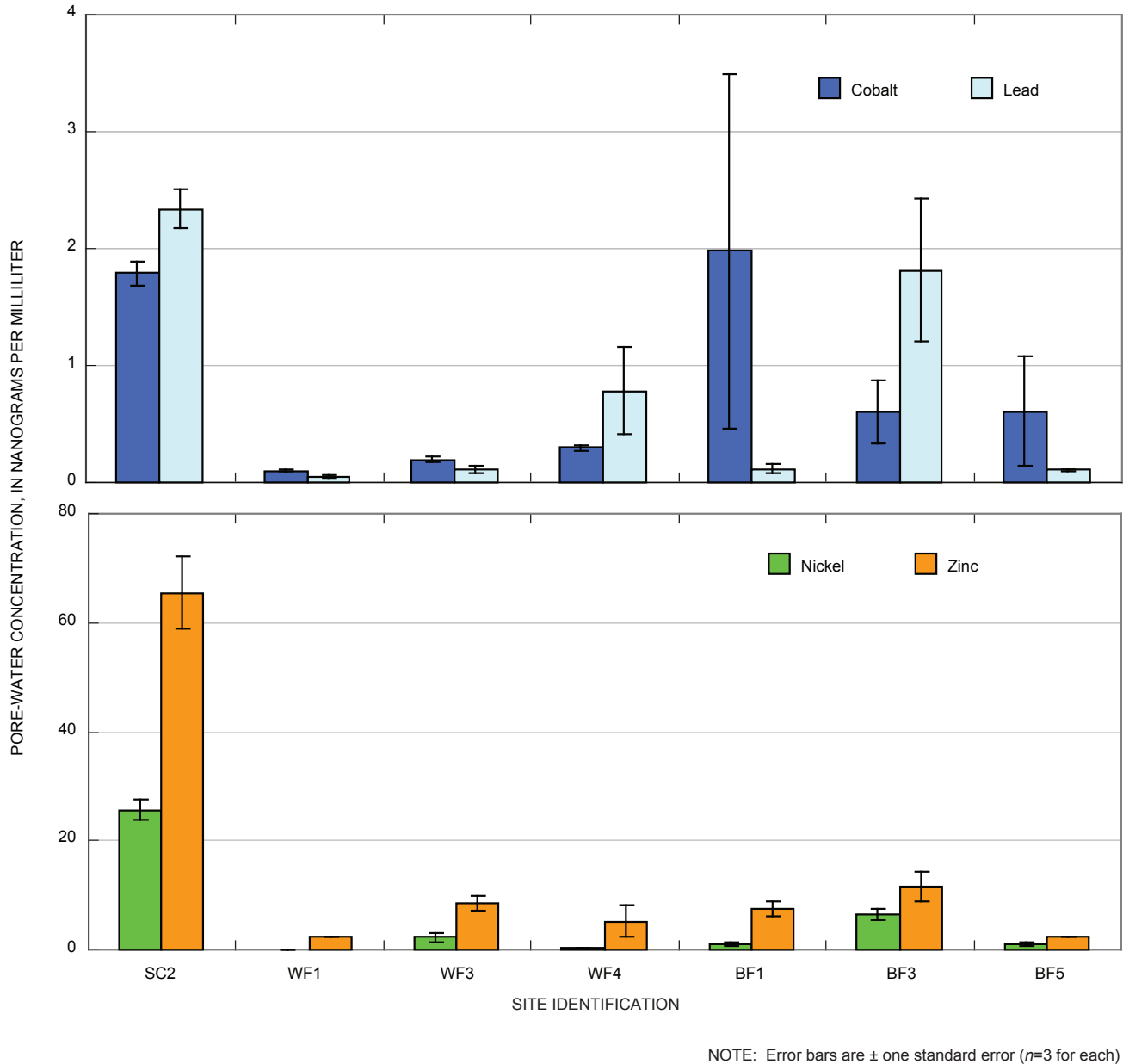


Figure 11. Filterable concentrations of cobalt, lead, nickel, and zinc in 2005, in-stream pore water.

sampled after 7 days at site BF3 (downstream from Fletcher Mine and tailings) ranged from about 10- to 60-fold greater for cadmium, nickel, and zinc, and were about 150-fold greater for lead, than the amounts sampled at BF1 (table 23). The proportion of metals sequestered after 13 days of sampling as compared to after 7 days, was much greater for site SC2 than it was for sites BF1 and BF3, as indicated by steeper line slopes for SC2 (fig. 12).

If labile metal concentrations and water conditions (temperature, flow, and pH) of streams had remained constant, a nearly 2-fold increase in passive-sampled metal would be expected for a 13-day sample as compared to a 7-day sample (Brumbaugh and others, 2002). However, two significant rain-

fall events occurred that might have affected the results during the 22 days of sampling. The first corresponded with day 6 of SLMD sampling and the second with day 13. Based on historic stream-gaging data for the nearby East Fork Black River (U.S. Geological Survey, 2001), mean daily discharge averaged for each of the three relevant sampling periods was 8.6, 18.0, and 19.8 ft³/s (cubic feet per second) for the 0 to 7, 7 to 13, and 13 to 22 day intervals, respectively. Thus, assuming all other parameters were equal, and assuming a 2.1-fold increase in discharge (18.0/8.6) and a linear relation between metal sequestration and discharge, the amount of metals sequestered would be about 2.1 x 13/7, or 3.9 times greater for the 13-day as compared with the 7-day deployment. Measured increases

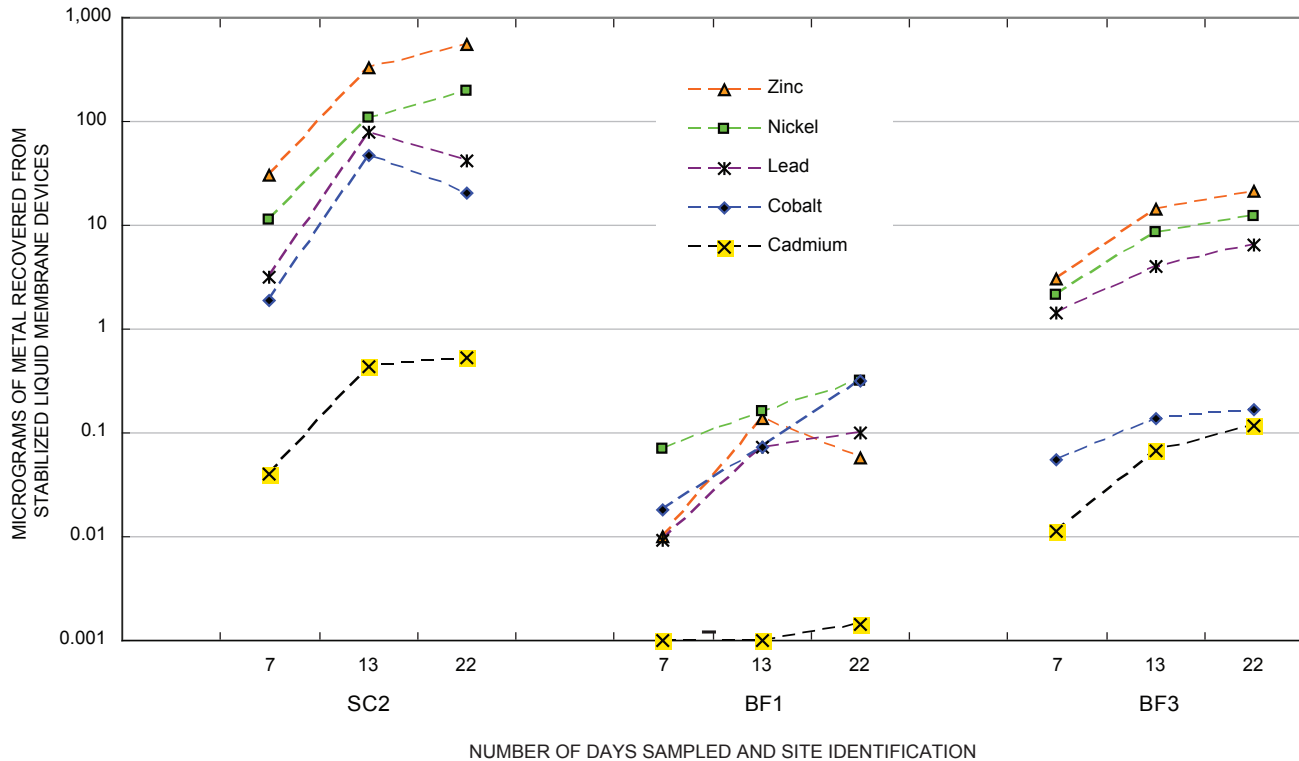


Figure 12. Mass of selected metals recovered from stabilized liquid membrane devices used for passive, integrative water sampling at three sites, July 2005.

in metal uptake by SLMDs for 13-day and 7-day deployments were in approximate agreement with the predicted 3.9 value for sites BF1 and BF3. However, at site SC2 there was about a 10-fold increase in uptake for cadmium, nickel, and zinc, and more than a 20-fold increase for cobalt and lead (7 day to 13 day line slopes; fig. 12). The rate of metal uptake appeared to decrease during the 13 day to 22 day sampling interval, especially at site SC2, and actually was negative in three instances (cobalt and lead at SC2; zinc at BF1); however, results for zinc at site BF1 were too near the MDL to be considered quantitative (table 23).

Greater than predicted metals uptake by the SLMD at site SC2 suggests that water-borne labile metals concentrations increased considerably there between days 7 and 13 (days 14 to 20 of the in-stream crayfish exposure). Apparent concentration increases at site SC2 correspond to factors of about 2.5 for cadmium, nickel, and zinc, and about 5 for cobalt and lead, when averaged over the 7- to 13-day sampling interval. However, it is likely that metal concentrations increased by factors of more than 2.5 to 5, but the increase occurred during a smaller time interval. Otherwise, a measurable change in water concentrations should have been observed in the grab-surface water samples obtained on days 0, 14, and 28 of the crayfish exposures, or the peepers retrieved on days 14 and 28 (table 19). Minimal temporal differences measured among the surface and peeper samples does not necessarily contradict

the SLMD data because of the timing of the grab sampling (surface water) and the peeper retrieval, and because the peepers require several days to equilibrate. Peepers function as equilibrium samplers, consequently, peeper concentrations slowly increase or decrease as a delayed response to surrounding concentrations. In contrast, SLMDs function as integrative (cumulative) samplers. Thus, despite the apparent exchange between surface water and sediment pore water, peepers only would reflect a temporary increase in surface-water concentrations if surface-water concentrations remained elevated for several days just before peeper retrieval. Collectively, these results indicate that surface water metal concentrations at site SC2 temporarily increased by factors of at least 2.5, and possibly much more, and that the increase in concentrations was associated with rainfall that occurred between July 12 and 13, 2005. Notably, a previous study indicated that the stream meander system in upper Strother Creek designed to remove metals immediately downstream from the Buick Mine and mill was less efficient with increased stream velocities (Erten, 1988).

This evidence for a temporary increase in surface-water metal concentrations at site SC2 is not entirely conclusive, because there are factors that can complicate the interpretation of SLMD results. For example, changes in water flow or other conditions during deployment can affect the uptake of metal ions differently, depending on each individual metal-SLMD

binding constant. For this study, an experimental housing was used to minimize flow effects on metal uptake rates (fig. 4), but the relation between metal uptake and flow has not been fully characterized for this housing, and actual stream flows were not monitored throughout the sampling period. In addition, the SLMD surface can become saturated under conditions of high metals loading, especially after long deployment intervals. This situation can cause reduced metal uptake rates and partial displacement of some metals with intermediate binding affinities by those with stronger binding affinities (Brumbaugh and others, 2002). Saturation and displacement may be the reason why the 22-day sampler at site SC2 appeared to contain lower amounts of lead and cobalt compared to the 13-day sampler (fig. 12). Thus, it cannot be concluded unequivocally that metals *concentrations* temporarily increased substantially in waters at site SC2 during the 7- to 13-day passive sampler deployment. However, it can be stated with reasonable certainty that average metal loads increased considerably at site SC2 between July 13 and July 20, 2005, and that waterborne loads of labile metals were much greater at site SC2 as compared to the other two sites.

Summary and Conclusions

This report describes results of measurements for trace elements and other parameters performed on sediment and water collected between 2002 and 2005 from streams in or near the Viburnum Trend mining district of southeastern Missouri. These measurements were conducted in association with studies designed to assess the extent of mining effects on stream habitat and biota, and to provide baseline data for stream locations in exploration areas south of the Viburnum Trend.

Compared to reference sites, fine sediments sampled at locations downstream from mining activities in 2002 were enriched in metals by factors as large as 75 for cadmium, 15 for nickel, 47 for lead, and 124 for zinc. Greatest metal concentrations in sediments collected in 2002 were from sites downstream of mines/mills on Strother Creek, Courtois Creek, and the West Fork Black River. Sediments in Clearwater Lake, at least 75 km downstream from mining activity, had metal concentrations that were 1.5 to 2.1 times greater than sediments in an area of the lake with no upstream mining activity. Metal concentrations in laboratory-prepared pore water generally tracked total recoverable sediment concentrations, and in some pore-water samples, concentrations of lead and zinc were greatly elevated. However, concentrations of lead in pore water were highly variable, which was attributed to the preparation method, conditions during sampling, and temporal variation in study streams. Sediment collected from a site on Bee Fork in 2002 was unusual because total recoverable concentrations of lead and other metals in that sediment were considerably less than in samples from other locations, but the pore water had among the greatest lead concentrations. In

addition, it was the only sediment that had elevated pore water metals and a negative SEM-AVS value.

In-stream, pore-water diffusion samplers (peepers) buried 4 to 6 cm deep in riffle-run sediments during 2003 had much lower metal concentrations, but indicated similar patterns among sites, when compared with laboratory-prepared pore waters obtained from fine sediments collected in 2002. Lower metal concentrations were expected for in-stream samples as compared to laboratory-prepared pore waters, because metals typically are greatly enriched in sediment fine particle fractions. In addition, homogenization and storage of 2002 sediment samples may have promoted the release of metals from sediment particle surfaces into the pore water as a result of reductive dissolution of iron and manganese oxyhydroxides. For 2003 sample collections, a site on Strother Creek and a site on Courtois Creek had the greatest concentrations of cobalt, nickel, lead, and zinc. Samples from sites on the West Fork Black River, Bee Fork, Logan Creek, and Sweetwater Creek also had noticeably elevated concentrations of lead. The combined mean lead concentration in peeper pore-water samples from selected sites on these six streams was about 10-fold greater than the mean of four reference sites. In most instances, peeper and surface-water metal concentrations were not remarkably different, indicating exchange between surface water and pore water was considerable at the depths and locations where peepers were placed.

Longitudinal sampling of sediments conducted in 2004 along Strother Creek, West Fork Black River, and Bee Fork indicated that metals concentrations decreased considerably over distances of a few kilometers from presumed mining sources. However, in Strother Creek some metals remained enriched by a factor of five or more as far as 13 kilometers downstream from the Buick tailings impoundment. Greatest metal concentrations overall were measured in sediments from an uppermost site on Strother Creek where Cd, Co, Ni, Pb and Zn were enriched by factors of 13, 62, 171, 95 and 150, respectively. Compared with sediment samples collected in 2002, concentrations in 2004 were similar for a Strother Creek site, much lower for a West Fork Black River site, and slightly higher for a Bee Fork site. Presumably, cessation of beneficiation operations in 2000 at the West Fork mill was a factor in the differences between 2002 and 2004 sediment metal concentrations. In addition, rainfall was unusually heavy during the spring and summer of 2002, which also might have been a factor because of effects on the transport of fine sediments. Passive sampling probes used for monitoring selected samples during 2004 sediment toxicity tests indicated that most of the filterable lead in the laboratory-prepared pore water was relatively non-labile, presumably because it was complexed by organic matter, or was present as colloidal species. In contrast, large percentages of cobalt and nickel in pore water appeared to be labile.

Peeper samplers buried in sediments at selected locations on Strother Creek, West Fork Black River, and Bee Fork during July 2005 had metal concentrations that were similar to 2003 field experiments, except that for 2005, concentrations

of cobalt and lead were higher at a site on Strother Creek and lower at a site on West Fork Black River. Metal concentrations tended to be slightly greater in pore water than in surface water, and sulfate concentrations tracked closely with metals in pore water and surface water. Pore-water concentrations of replicate peepers were most variable for lead, probably reflecting spatial heterogeneity and localized chemical and physical gradients in sediments. Passive integrative water samplers deployed for up to 22 days in July 2005 confirmed the presence of elevated concentrations of labile metals in surface waters downstream from mining activities on Strother Creek and, to a lesser extent, Bee Fork. These data also indicated that a considerable increase in metal loadings occurred at the Strother Creek location for a few days, which coincided with moderate increases in stream discharges in the area.

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Tables 1–23

Table 1. Sampling sites and sampling matrices collected for determination of elemental concentrations, by watershed.

[ID, identification; Latitude-Longitude as documented by global positioning receiver (plus or minus 10 meters); Letter codes A through F indicate study (sample types), as follows: A, Fish metals and biomarkers (metals in fish blood and liver); B, Food web metals (periphyton, algae, detritus, snails, crayfish, riffle benthos, fish); C, Sediment toxicity tests (sediment and pore water); D, Biological community assessment (surface water, pore water, fish, invertebrates, snails); E, Longitudinal toxicity and biological community assessment (sediment, pore water, fish, crayfish, riffle benthos); F, In-stream crayfish exposure (surface water, pore water, fish, crayfish, detritus, riffle benthos); --, not sampled; datum = World Geodetic System 1984 (WGS 84)]

Site ID	Water body	Location description; figure(s) where shown	County	Latitude (north)		Longitude (west)		Year, study, and sample types collected						
				(degrees, minutes, seconds)	(degrees, minutes, seconds)	(degrees, minutes, seconds)	(degrees, minutes, seconds)	2001	2002	2003	2004	2005		
Meramec River														
BG	Big River	St. Francois State Park (Old Lead Belt); 1	St. Francois	37	57	21.6	90	32	31.2	A,B	C	--	--	--
HZ	Huzzah Creek	Red Bluff campground; 1,2	Crawford	37	48	39.6	91	10	1.2	--	--	D	E	--
CC	Courtois Creek	Downstream from Indian Creek; 1,2	Washington	37	46	4.8	91	4	15.6	A,B	B,C	D	--	--
Middle Fork Black River														
NC	Neals Creek	Near mouth; 1,2	Iron	37	36	28.8	91	1	1.2	A,B	--	--	--	--
SC1	Strother Creek	Downstream from Buick Tailings; 1,2	Iron	37	35	24.0	91	3	14.4	--	--	--	E	--
SC2	Strother Creek	Upstream from Neals Creek; 1,2	Iron	37	36	7.2	91	1	40.8	A,B	C	D	E	F
SC3	Strother Creek	Downstream from Neals Creek; 1,2	Iron	37	36	14.4	91	0	3.6	--	--	--	E	--
MF1	Middle Fork Black River	State Highway 49; 1,2	Iron	37	37	1.2	90	58	1.2	A,B	--	--	--	--
MF2	Middle Fork Black River	Downstream from Strother Creek; 1,2	Reynolds	37	35	56.4	90	57	25.2	--	--	--	E	--
MF3	Middle Fork Black River	Near Black; 1	Reynolds	37	31	26.4	90	56	6.0	A,B	C	D	E	--
West Fork Black River														
WF1	West Fork Black River	Near Greeley; 1,2	Reynolds	37	30	39.6	91	9	43.2	A,B	B,C	D	E	F
WF2	West Fork Black River	Downstream from Bills Creek; 1,2	Reynolds	37	30	0.0	91	7	12.0	--	--	--	E	--
WF3	West Fork Black River	Downstream from West Fork Mine and tailings; 1,2	Reynolds	37	29	49.2	91	5	13.2	A,B	C	D	E	F
WF4	West Fork Black River	Downstream from Radford Hollow; 1,2	Reynolds	37	29	13.2	91	3	3.6	--	--	--	E	F
WF5	West Fork Black River	Sutton Bluff campground; 1,2	Reynolds	37	28	33.6	91	0	32.4	A,B	C	D	E	--
WF6	West Fork Black River	Downstream from Bee Fork; 1,2	Reynolds	37	27	28.8	90	58	44.4	--	--	--	E	--
BF1	Bee Fork Black River	Upstream from Highway TT; 1,2	Reynolds	37	26	43.4	91	6	29.4	--	--	--	--	F
BF2	Bee Fork Black River	Highway TT; 1,2	Reynolds	37	26	38.4	91	6	21.6	--	--	--	E	--
BF3	Bee Fork Black River	Downstream from Fletcher tailings; 1,2	Reynolds	37	26	28.7	91	5	38.0	--	--	--	--	F
BF4	Bee Fork Black River	Downstream from Grasshopper Hollow; 1,2	Reynolds	37	26	31.2	91	4	58.8	A,B	B,C	D	E	F
BF5	Bee Fork Black River	Downstream from South Branch; 1,2	Reynolds	37	27	36.0	91	1	30.0	--	--	--	E	F
BF6	Bee Fork Black River	Near mouth; 1,2	Reynolds	37	27	18.0	90	59	24.0	--	--	--	E	--

Table 1. Sampling sites and sampling matrices collected for determination of elemental concentrations, by watershed.—Continued

[ID, identification; Latitude-Longitude as documented by global positioning receiver (plus or minus 10 meters); Letter codes A through F indicate study (sample types), as follows: A, Fish metals and biomarkers (metals in fish blood and liver)¹; B, Food web metals (periphyton, algae, detritus, snails, crayfish, riffle benthos, fish)²; C, Sediment toxicity tests (sediment and pore water); D, Biological community assessment (surface water, pore water, fish, invertebrates, snails); E, Longitudinal toxicity and biological community assessment (sediment, pore water, fish, crayfish, riffle benthos); F, In-stream crayfish exposure (surface water, pore water, fish, crayfish, detritus, riffle benthos); --, not sampled; datum = World Geodetic System 1984 (WGS 84)]

Site ID	Water body	Location description; figure(s) where shown	County	Latitude (north)		Longitude (west)		Year, study, and sample types collected					
				(degrees, minutes, seconds)	(degrees, minutes, seconds)	(degrees, minutes, seconds)	(degrees, minutes, seconds)	2001	2002	2003	2004	2005	
Logan Creek													
SW	Sweetwater Creek	Downstream from Sweetwater Mine; 1,2	Reynolds	37	19	48.0	91	8	9.6	A,B	B,C	D	--
LC1	Logan Creek	Highway B; 1,2	Reynolds	37	20	24.0	91	7	12.0	A,B	C	D	--
LC2	Logan Creek	Ellington; 1	Reynolds	37	14	49.2	90	58	1.2	A,B	--	--	--
Main Stem Black River													
SK	Sinking Creek	Near Redford; 1	Reynolds	37	18	36.0	90	52	40.8	A,B	C	D	E
BR	Black River	Near Lesterville; 1	Reynolds	37	25	1.2	90	49	30.0	A,B	--	--	--
CL1	Clearwater Lake	Near Clearwater Dam; 1	Reynolds	37	8	18.8	90	46	47.0	--	C	--	--
CL2	Clearwater Lake	Logan Creek arm; 1	Reynolds	37	9	20.5	90	48	7.1	--	C	--	--
CL3	Clearwater Lake	Webb Creek arm; 1	Reynolds	37	8	55.5	90	48	17.8	--	C	--	--
CL4	Clearwater Lake	Black River arm south; 1	Reynolds	37	9	53.6	90	45	57.8	--	C	--	--
CL5	Clearwater Lake	Black River arm north; 1	Reynolds	37	10	37.4	90	47	28.4	--	C	--	--
Current River													
BC	Blair Creek	Near Midridge; 1	Shannon	37	15	36.0	91	12	54.0	--	--	D	E
BGS	Big Spring	Spring branch (Current River); 1	Carter	36	56	52.8	90	59	24.0	B	--	--	--
BLS	Blue Spring	Spring branch (Current River); 1	Shannon	37	9	57.6	91	9	46.8	B	--	--	--
Eleven Point River													
GRS	Greer Spring	Spring branch (Eleven Point River); 1	Oregon	36	47	27.6	91	20	38.4	B	--	--	--
HC	Hurricane Creek	Near mouth (Eleven Point River); 1	Oregon	36	46	51.6	91	16	37.2	B	--	--	--
EP1	Eleven Point River	Cane Bluff access; 1	Oregon	36	47	45.6	91	24	18.0	A,B	--	--	--
EP2	Eleven Point River	Downstream from Spring Creek; 1	Oregon	36	49	1.2	91	21	50.4	--	--	E	--

¹ Schmitt and others, 2007a, 2007b; sites were identified numerically as follows: 1 = WF3, 2 = WF5, 3 = WF1, 4 = BF4, 5 = LC2, 6 = LC1, 7 = SW, 8 = BR, 9 = MF3, 10 = SK, 11 = MF1, 12 = SC2, 13 = NC, 14 = CC, 15 = EPI, 16 = BG.

² Besser and others, 2006; site ID's same except BF2 was identified as 'BF' and WF3 as 'WF2'.

Table 2. Descriptive features of sampling sites potentially affected by mining activities.

[ID, identification; km², square kilometers; km, kilometer]

Water body	Site ID	Location description; figure(s) where shown	Upstream		Stream order	Prominent mining features in watershed	Years of operation	Site stream distance from tailings or mine (km)	Tailings area (km ²)	Total tailings area for watershed (km ²)	Tailings area/ water- shed area
			water- shed area (km ²)	order							
Big River	BG	St. Francis State Park (Old Lead Belt); 1	1,016	4	4	Leadwood tailings	1915–1962	30.2	0.53		
Huzzah Creek	HZ	Red Bluff campground; 1, 2	290	3	3	St. Joe State Park tailings Viburnum Mine 27	1915–1972 1960–1978	22.1 20.0	1.11 none	1.64	0.002
Courtois Creek	CC	Downstream from Indian Creek; 1, 2	107	3	3	Casteel Mine Viburnum Mine 29 Viburnum Mine 28	1985–present 1964–present 1960–2003	30.0 2.5 5.0	none none none	0	0
Neals Creek	NC	Near mouth; 1, 2	47	1	1	Old Viburnum tailings New Viburnum tailings ¹	1960–1975 1975–2000	4.9 7.6	0.88 1.30	2.18	0.021
Strother Creek	SC1	Downstream from Buick Tailings; 1, 2	23	1	1	Magmont tailings (reclaimed) Effluent sedimentation pond	1962–1994 1972–present	10.9 0.9	0.42 0.66	0.42	0.009
Strother Creek	SC2	Upstream from Neals Creek; 1, 2	39	2	2	Buick tailings and smelter ² Effluent sedimentation pond	1969–present 1972–present	3.2 3.7	0.66 0.66	0.66	0.028
Strother Creek	SC3	Downstream from Neals Creek; 1, 2	92	2	2	Buick tailings and smelter ² Effluent sedimentation pond	1969–present 1972–present	6.0 6.3	0.66 0.66	0.66	0.017
Middle Fork Black River	MF2	Downstream from Strother Creek; 1, 2	169	3	3	Buick tailings and smelter ² Magmont tailings (reclaimed)	1969–present 1962–1994	8.6 12.8	0.66 0.42	1.08	0.012
Middle Fork Black River	MF3	Near Black; 1	377	3	3	Effluent sedimentation pond Buick tailings and smelter ²	1972–present 1969–present	11.0 13.3	0.66 0.66		
West Fork Black River	WF2	Downstream from Bills Creek; 1, 2	153	2	2	Magmont tailings (reclaimed) Buick tailings and smelter ²	1962–1994 1969–present	17.3 22.4	0.42 0.66	1.08	0.006
West Fork Black River	WF3	Downstream from West Fork Mine; 1, 2	199	2	2	Buick tailings and smelter ² Magmont tailings (reclaimed)	1962–1994 1973–present	28.5 6.2	0.42 0.77	0.77	0.003 0.005
West Fork Black River	WF4	Downstream from Radford Hollow; 1, 2	217	2	2	Brushy Creek tailings Brushy Creek tailings	1973–present 1973–present	10.3 2.2	0.77 0.50	1.27	0.006
West Fork Black River	WF5	Sutton Bluff campground; 1, 2	236	2	2	West Fork tailings ³ Brushy Creek tailings West Fork tailings Brushy Creek tailings	1985–2000 1973–present 1985–2000 1973–present	18.3 10.1 24.6 16.5	0.77 0.50 0.77 0.50	1.27 1.27 1.27 1.27	0.006 0.006 0.005 0.005

Table 2. Descriptive features of sampling sites potentially affected by mining activities.—Continued

[ID, identification; km², square kilometers; km, kilometer]

Water body	Site ID	Location description; figure(s) where shown	Upstream water- shed area (km ²)	Stream order	Prominent mining features in watershed	Years of operation	Site stream distance from tailings or mine (km)	Tailings area (km ²)	Total tailings area for watershed (km ²)	Tailings area/water- shed area
West Fork Black River	WF6	Downstream from Bee Fork; 1, 2	343	3	Brushy Creek tailings West Fork tailings ³	1973–present 1985–2000	28.6 20.5	0.77 0.50		
Bee Fork Black River	BF2	Hwy TT (downstream from Fletcher Mine); 1, 2	35	1	Fletcher clarification dam Fletcher tailings	1966–present 1966–present	17.1 14.6	0.08 1.26	2.60	0.008
Bee Fork Black River	BF3	Downstream from Fletcher tailings; 1, 2	39	1	Fletcher clarification dam	1966–present	2.8	0.08		
Bee Fork Black River	BF4	Downstream from Grasshopper Hollow; 1, 2	49	1	Fletcher clarification dam	1966–present	3.8	0.08		
Bee Fork Black River	BF5	Downstream from South Branch; 1, 2	80	2	Fletcher tailings Fletcher clarification dam	1966–present 1966–present	1.4 9.8	1.26 0.08	1.34	0.027
Bee Fork Black River	BF6	Near mouth; 1, 2	94	2	Fletcher tailings Fletcher clarification dam	1966–present 1966–present	7.4 16.1	1.26 0.08	1.34	0.017
Sweetwater Creek	SW	Downstream from Sweetwater Mine; 1, 2	21	1	Fletcher tailings Sweetwater Mine	1966–present 1968–present	13.7 2.6	1.26 none	1.34 0	0.014 0
Logan Creek	LC1	Hwy B (downstream from Sweetwater tailings); 1, 2	61	2	Sweetwater tailings	1968–present	4.4	1.29	1.29	0.021
Logan Creek	LC2	Ellington; 1	285	2	Sweetwater tailings	1968–present	31.3	1.29	1.29	0.005
Black River	BR	Near Lesterville; 1	1,181	4	Brushy Creek tailings West Fork tailings ³	1973–present 1985–2000	49.8 41.7	0.77 0.50		
					Buick tailings and smelter ²	1969–present	42.1	0.66		
					Magnont tailings (reclaimed)	1962–1994	48.2	0.42		
					Fletcher tailings	1966–present	35.7	1.26	3.69	0.003

¹ Viburnum mill operations after 2000 include only the primary crushing of ore rock.

² Buick smelter converted to recycling center in the late 1980s.

³ West Fork mill operations ceased in 2000.

Table 3. Total recoverable concentrations of selected metals in 2002 sediment samples.

[Metal concentrations in micrograms per gram dry weight. All samples consisted of particles smaller than 2 millimeter in diameter. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test. Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Italicized values are greater than detection limit but less than the method quantitation limit. ID, identification; Fe, iron; Mn, manganese; Cu, copper; Ni, nickel; Pb, lead; Tl, thallium; Zn, zinc; <, less than; (ref), reference site]

Sample ID	Fe		Mn		Cd		Cu		Ni		Pb		Tl		Zn	
	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27
CC	13,240	11,970	728	316	3.26	1.25	40.4	17.1	43.1	20.9	272	112	0.18	0.07	436	210
SC2	11,060	7,810	1,340	1,100	0.75	0.61	14.8	13.9	124	120	232	212	0.16	0.15	597	534
WF3	10,030	12,390	1,890	4,470	2.40	6.93	11.0	26.9	62.7	146	204	558	0.11	0.32	633	1,770
WF5	8,000	8,780	715	453	0.21	0.15	6.73	5.62	14.4	12.9	25.6	19.7	0.14	0.10	51	38
BF4	3,910	5,810	226	136	0.16	0.16	2.48	4.17	11.5	12.3	39.8	38.5	<0.03	0.07	36	36
SW	4,990	7,240	295	312	0.30	0.31	3.34	12.0	5.48	6.91	43.4	41.8	0.08	0.06	31	32
LC1	4,190	3,940	696	589	0.82	0.72	6.56	5.65	7.45	7.78	89.1	79.8	<0.03	0.04	76	69
WF1 (ref)	3,700	2,870	245	112	0.11	0.05	2.48	2.17	4.80	4.25	14.8	8.9	0.04	0.05	12	9
SK (ref)	4,160	3,910	356	258	0.04	0.05	8.49	2.69	11.7	4.55	5.0	3.5	0.04	0.04	11	7
CL3 (lake ref)	19,120	29,620	1,040	1,750	0.24	0.45	15.0	24.9	20.3	31.9	26.9	45.3	0.45	0.70	53	85
CL1	38,980	37,760	1,950	1,810	0.53	0.53	36.3	37.4	45.2	46.7	81.9	80.7	0.83	0.83	135	137
CL2	28,350	37,350	1,450	1,980	0.44	0.71	25.5	40.4	31.0	46.1	60.3	92.6	0.58	0.82	83	124
CL4	29,730	40,090	1,000	1,340	0.62	0.90	32.1	45.3	36.0	50.3	71.3	98.5	0.63	0.76	116	159
CL5	16,700	25,170	754	1,280	0.39	0.74	21.0	36.8	22.1	37.8	40.7	70.6	0.33	0.53	67	112
BG (Old Lead Belt)	27,350	27,960	3,210	2,610	17.1	28.0	57.3	94.5	31.7	51.8	2,130	2,870	0.21	0.36	1,160	1,970
Toxicity control	18,340	19,350	696	1,560	0.23	0.36	11.6	12.9	16.6	22.9	15.3	20.3	0.33	0.43	50	52
Range of site means																
Mining sites	4,060 – 12,600	181 – 3,180	0.16 – 4.7	3.3 – 28.8	6.2 – 122	23 – 381	0.043 – 0.22	31 – 1,202								
Stream reference sites	3,280 – 4,030	178 – 307	0.045 – 0.080	2.3 – 5.6	4.5 – 8.1	4.3 – 11.9	0.038 – 0.044	9.0 – 10.4								
Clearwater Lake sites	20,900 – 38,400	1,020 – 1,880	0.34 – 0.76	20.0 – 38.7	26.1 – 46.0	36.1 – 84.9	0.43 – 0.83	68 – 138								

Table 4. Percent water, loss on ignition, total organic carbon, and particle size distribution in 2002 sediment samples.

[All sediments consisted of particles smaller than 2 millimeter in diameter. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test; Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Replicate number represents separate chemical preparation and analysis. TOC and particle size measured in Day-0 samples only. LOI, loss on ignition; TOC, total organic carbon; --, not measured; (ref), reference site]

Sample ID	Replicate number	Water (percent)		LOI (percent)		TOC (percent)	Particle size distribution (percent)		
		Day 0	Day 27	Day 0	Day 27		Sand	Silt	Clay
CC	1	80.6	27.1	8.1	2.5	1.2	78	7	15
	2	79.7	--	8.9	--	--	--	--	--
SC2	1	41.8	24.1	1.9	1.5	1.5	77	7	16
	2	41.4	--	1.9	--	--	--	--	--
WF3	1	62.1	45.6	4.1	4.8	2.0	72	9	19
	2	60.4	--	3.9	--	--	--	--	--
WF5	1	30.5	22.0	1.3	1.2	0.8	74	2	24
	2	32.0	--	1.5	--	--	--	--	--
BF4	1	40.1	23.6	1.3	1.0	0.8	82	4	14
	2	40.1	--	1.4	--	--	--	--	--
SW	1	28.5	20.4	0.6	0.5	0.2	83	4	14
	2	27.2	--	0.6	--	--	--	--	--
LC1	1	25.4	21.6	0.5	0.5	0.2	84	4	12
	2	24.8	--	0.5	--	--	--	--	--
WF1 (ref)	1	33.3	21.8	1.0	1.1	0.4	82	4	14
	2	33.1	--	1.0	--	--	--	--	--
SK (ref)	1	28.4	22.9	0.6	0.3	0.1	83	3	14
	2	29.7	--	0.5	--	--	--	--	--
CL3 (lake ref)	1	51.1	44.1	3.7	7.5	1.7	10	66	24
	2	51.2	--	4.0	--	--	--	--	--
CL1	1	70.1	55.5	5.6	5.7	2.1	21	72	7
	2	69.7	--	5.4	--	--	--	--	--
CL2	1	56.9	34.9	4.1	3.8	1.7	16	54	30
	2	56.8	--	4.1	--	--	--	--	--
CL4	1	63.4	47.3	5.4	6.2	2.0	17	48	35
	2	63.3	--	5.4	--	--	--	--	--
CL5	1	50.1	47.2	4.2	8.9	1.9	5	71	24
	2	49.6	--	4.3	--	--	--	--	--
BG (Old Lead Belt)	1	54.5	36.9	3.3	3.9	5.1	47	33	19
	2	55.7	--	3.3	--	--	--	--	--
Toxicity test control	1	27.4	21.5	2.9	2.3	1.0	0	70	30
	2	27.1	--	2.9	--	--	--	--	--

Table 5. Concentrations of acid-volatile sulfide and simultaneously extracted metals in 2002 sediment samples.

[Concentrations of AVS in micromoles per gram dry weight. SEM concentrations in micrograms per gram dry weight. All sediments consisted of particles smaller than 2 millimeter in diameter. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test; Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Replicate numbers represent separate chemical preparations and analyses. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; AVS, acid-volatile sulfide; SEM, simultaneously extracted metal; Cd, cadmium; Cu, copper; Ni, nickel; Pb, lead; Zn, zinc; --, not measured; (ref), reference site; <, less than]

Sample ID	Replicate number	AVS		SEM Cd		SEM Cu		SEM Ni		SEM Pb		SEM Zn	
		Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27
CC	1	3.47	3.72	4.18	1.31	38.0	11.1	45.6	13.6	392	131	493	201
	2	3.32	--	3.63	--	34.9	--	39.5	--	335	--	469	--
SC2	1	0.26	0.45	0.44	0.37	6.73	6.19	95.3	86.0	187	164	435	405
	2	0.26	--	0.43	--	6.89	--	92.9	--	172	--	431	--
WF3	1	3.22	11.5	1.96	3.14	7.46	8.83	54.6	68.6	176	266	547	862
	2	3.03	--	1.78	--	5.38	--	42.5	--	157	--	438	--
WF5	1	0.23	1.75	0.11	0.11	2.12	2.22	4.68	4.43	15.3	16.3	18	23.6
	2	0.24	--	0.1	--	2.30	--	6.06	--	14.4	--	20	--
BF4	1	0.97	3.49	0.12	0.13	1.62	1.34	11.9	7.18	38.2	37.7	26	33.7
	2	0.96	--	0.13	--	1.21	--	7.25	--	36.4	--	28	--
SW	1	0.15	0.30	0.28	0.39	1.69	2.92	2.35	4.29	41.3	72.8	19	42.2
	2	0.14	--	0.27	--	2.30	--	2.32	--	37.5	--	21	--
LC1	1	0.01	0.65	0.34	0.26	2.43	2.17	4.25	2.28	64.2	41.5	35	22.2
	2	0.01	--	0.31	--	2.87	--	3.97	--	57.3	--	35	--
WF1 (ref)	1	0.12	1.53	0.03	0.04	1.14	0.85	2.90	0.89	5.75	5.16	<7	2.40
	2	0.11	--	0.04	--	1.15	--	3.05	--	5.69	--	<7	--
SK (ref)	1	0.02	<0.01	0.02	0.03	0.74	1.50	1.07	1.19	2.26	2.66	<7	2.25
	2	0.02	--	0.03	--	0.95	--	1.69	--	2.98	--	<7	--
CL3 (lake ref)	1	1.34	2.26	0.21	0.36	5.30	9.28	4.03	5.98	22.6	35.9	9	21.2
	2	1.38	--	0.20	--	5.00	--	3.30	--	20.7	--	12	--
CL1	1	9.20	5.17	0.42	0.44	11.9	12.6	10.5	9.90	68.1	66.3	30	35.4
	2	9.03	--	0.39	--	11.1	--	8.73	--	59.0	--	32	--
CL2	1	1.77	1.17	0.35	0.40	8.5	10.8	6.57	5.53	51.6	57.7	17	24.1
	2	1.86	--	0.34	--	8.3	--	8.55	--	47.7	--	20	--
CL4	1	6.28	2.88	0.56	0.61	12.0	14.7	12.1	9.75	68.5	69.3	35	42.1
	2	6.58	--	0.44	--	8.8	--	7.55	--	52.6	--	31	--

Table 5. Concentrations of acid-volatile sulfide and simultaneously extracted metals in 2002 sediment samples.—Continued

[Concentrations of AVS in micromoles per gram dry weight. SEM concentrations in micrograms per gram dry weight. All sediments consisted of particles smaller than 2 millimeter in diameter. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test; Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Replicate numbers represent separate chemical preparations and analyses. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; AVS, acid-volatile sulfide; SEM, simultaneously extracted metal; Cd, cadmium; Cu, copper; Ni, nickel; Pb, lead; Zn, zinc; --, not measured; (ref), reference site; <, less than]

Sample ID	Replicate number	AVS		SEM Cd		SEM Cu		SEM Ni		SEM Pb		SEM Zn	
		Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27
CL5	1	1.69	2.75	0.34	0.60	8.4	17.1	8.6	11.3	32.8	54.3	17	34.8
	2	1.73	--	0.31	--	8.2	--	5.7	--	29.6	--	19	--
BG (Old Lead Belt)	1	1.56	1.35	17.0	22.8	30.4	43.8	20.9	30.2	1,840	2,390	1,020	1,560
	2	1.67	--	16.0	--	31.3	--	23.6	--	1,820	--	1,050	--
Toxicity test control	1	<0.01	<0.01	0.19	0.20	4.42	4.40	4.07	4.77	9.24	9.43	7	7.64
	2	<0.01	--	0.18	--	4.12	--	3.79	--	8.48	--	8	--

Table 6. Filterable concentrations of selected metals in pore-water samples from 2002 sediment toxicity tests.

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test; Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Replicate numbers represent a separate sediment sub-sample centrifuged and filtered. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Fe, iron; Mn, manganese, Cd, cadmium; Pb, lead, Zn, zinc; --, not measured; (ref), reference site; <, less than]

Sample ID	Replicate number	Fe		Mn		Cd		Pb		Zn	
		Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27
CC	1	4,790	7,180	28,700	11,200	0.44	1.10	63.1	173	211	136
	2	4,510	--	28,200	--	0.46	--	57.8	--	208	--
SC2	1	473	6,770	17,700	21,100	0.75	1.41	107	755	452	955
	2	503	--	18,300	--	0.76	--	110	--	465	--
WF3	1	1,840	29,500	50,600	30,100	7.13	5.32	444	717	1,460	1,190
	2	1,660	--	50,700	--	6.04	--	352	--	1,300	--
WF5	1	7,170	3,580	75,200	10,800	0.40	0.29	28.4	25.0	41	16
	2	7,020	--	72,400	--	0.40	--	28.3	--	35	--
BF4	1	24,700	15,000	81,400	19,300	1.05	0.22	570	134	187	37
	2	25,000	--	76,500	--	1.02	--	570	--	189	--
SW	1	382	322	7,130	9,770	0.76	0.12	61.7	11.3	94	31
	2	448	--	7,050	--	0.71	--	56.9	--	102	--
LC1	1	462	281	6,420	5,160	0.80	0.28	53.7	55.6	43	35
	2	560	--	5,990	--	0.83	--	58.0	--	50	--
WF1 (ref)	1	7,600	5,140	48,600	14,500	0.13	0.04	7.52	2.56	9	3
	2	7,050	--	50,100	--	0.09	--	5.94	--	5	--
SK (ref)	1	156	157	12,800	8,360	0.03	0.02	0.69	0.47	5	3
	2	170	--	13,100	--	0.08	--	0.78	--	6	--
CL3 (lake ref)	1	10,500	11,300	13,400	14,400	0.14	0.07	15.3	5.28	6	3
	2	10,500	--	13,900	--	0.14	--	15.3	--	5	--
CL1	1	10,600	27,700	17,200	17,300	0.02	0.01	4.68	0.84	5	2
	2	10,800	--	16,400	--	< 0.01	--	4.22	--	3	--
CL2	1	6,130	5,710	11,400	12,100	0.12	0.08	26.6	5.79	5	13
	2	6,160	--	11,600	--	0.13	--	25.5	--	6	--
CL4	1	7,780	15,300	5,550	10,300	0.33	0.03	30.4	1.56	13	4
	2	7,760	--	5,050	--	0.21	--	30.6	--	13	--

Table 6. Filterable concentrations of selected metals in pore-water samples from 2002 sediment toxicity tests.—Continued

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test; Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Replicate numbers represent a separate sediment sub-sample centrifuged and filtered. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Fe, iron; Mn, manganese; Cd, cadmium; Pb, lead, Zn, zinc; --, not measured; (ref), reference site; <, less than]

Sample ID	Replicate number	Fe		Mn		Cd		Pb		Zn	
		Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27
CL5	1	11,600	27,700	15,300	16,800	0.23	0.35	20.5	25.8	8	17
	2	12,000	--	14,800	--	0.23	--	21.3	--	11	--
BG (Old Lead Belt)	1	887	3,350	8,970	8,000	7.50	7.63	357	621	335	382
	2	940	--	8,970	--	7.67	--	379	--	352	--
Toxicity test control	1	1,720	1,950	8,380	3,160	1.58	0.33	0.78	1.54	44	11
	2	1,970	--	8,310	--	1.69	--	0.91	--	51	--
Filtration blank	1	<10	<18	<2	<2	<0.01	<0.01	<0.02	0.04	<3	<1

Table 7. Filterable concentrations of selected metals in water samples from 2002 pore-water toxicity tests.

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Day 0, Day 4, and Day 7 indicate sampling day during a 10-day pore water toxicity test. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Fe, iron; Mn, manganese; Cd, cadmium; Pb, lead; Zn, zinc; dup, duplicate sample from a separate filtration of bulk pore water; --, not measured; <, less than; (ref), reference site]

Sample ID	Fe			Mn			Cd			Pb			Zn		
	Day 0	Day 4	Day 7	Day 0	Day 4	Day 7	Day 0	Day 4	Day 7	Day 0	Day 4	Day 7	Day 0	Day 4	Day 7
CC	1,560	1,450	1,170	22,300	23,990	22,000	0.07	0.07	0.04	8.43	6.94	5.75	96	90	80
CC dup	1,490	--	--	23,200	--	--	0.07	--	--	8.10	--	--	94	--	--
SC2	<66	38	91	17,500	17,730	16,880	0.30	0.29	0.25	21.9	22.5	11.7	96	277	81
SC2 dup	--	--	144	--	--	16,610	--	--	0.26	--	--	11.9	--	--	83
WF3	87	62	24	37,100	38,500	36,400	0.28	0.23	0.17	17.5	13.5	11.5	179	166	153
WF5	2,280	2,160	2,080	54,600	64,500	63,400	0.14	0.12	0.12	9.76	7.89	8.17	13	16	15
BF4	13,000	12,000	11,000	68,600	70,500	62,600	1.01	0.86	0.86	510	450	433	210	195	184
SW	<66	235	<17	21,400	21,100	18,700	0.41	0.28	0.27	21.0	8.41	4.71	49	43	42
LC1	525	574	190	5,490	4,920	4,420	0.82	0.70	0.67	31.4	17.5	14.5	26	24	23
WF1 (ref)	1,770	1,280	819	36,300	35,800	33,400	0.11	0.08	0.07	4.70	3.40	2.36	18	6	7
SK (ref)	109	252	76	12,300	11,600	9,680	0.08	0.06	0.17	0.95	0.19	0.93	<5	5	15
CL3 (lake ref)	223	198	147	14,200	12,400	12,700	0.03	0.03	0.03	0.39	0.29	0.23	<5	1	3
CL1	79	79	53	13,200	13,600	13,600	<0.03	<0.01	0.01	0.12	0.11	0.09	<5	7	3
CL2	167	116	132	7,740	7,940	8,360	0.03	0.03	0.03	0.86	0.59	0.57	<5	1	2
CL4	290	170	256	4,580	4,570	4,590	0.05	0.04	0.04	1.02	0.57	0.61	<5	1	3
CL5	447	348	428	13,500	14,500	15,200	0.05	0.06	0.08	0.98	0.66	0.77	<5	1	27
BG (Old Lead Belt)	300	260	<17	7,800	3,990	1,270	4.71	3.66	2.51	105	23.9	11.1	137	81	64
BG dup	361	--	49	7,810	--	1,470	5.06	--	2.76	103	--	14.4	143	--	71
Filtration blank	<66	--	--	<2	--	--	<0.03	--	--	<0.01	--	--	<5	--	--

Table 8. Filterable concentrations of cadmium, lead, and zinc in overlying water samples from 2002 sediment toxicity tests.

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Day 0 and Day 16 indicate sampling day during a 28-day sediment toxicity test. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Cd, cadmium; Pb, lead, Zn, zinc; dup, duplicate sample from a separate filtration of overlying water; <, less than; --, not measured; (ref), reference site]

Sample ID	Cd		Pb		Zn	
	Day 0	Day 16	Day 0	Day 16	Day 0	Day 16
CC	<i>0.05</i>	<i>0.06</i>	1.10	0.14	12	12
CC dup	<0.05	--	0.88	--	9	--
SC2	<0.05	<0.03	1.06	<0.02	34	<2
SC2 dup	<i>0.09</i>	--	2.46	--	39	--
WF3	<i>0.10</i>	<0.03	1.66	0.07	19	38
WF5	<i>0.08</i>	<0.03	0.33	<i>0.03</i>	6	11
BF4	<i>0.06</i>	<i>0.03</i>	24.5	<i>0.04</i>	18	<2
SW	<0.05	<0.03	0.26	<i>0.04</i>	4	<2
LC1	<i>0.09</i>	<0.03	0.72	0.12	5	4
WF1 (ref)	<0.05	<0.03	<0.05	<0.02	3	18
WF1 dup	<0.05	<0.03	<0.05	<i>0.02</i>	3	11
SK (ref)	<i>0.10</i>	<i>0.05</i>	<0.05	<i>0.04</i>	<2	4
CL3 (lake ref)	<0.05	<0.03	<0.05	<i>0.05</i>	3	4
CL1	<0.05	<0.03	<0.05	0.06	4	4
CL2	<0.05	<0.03	<0.05	<0.02	<2	<2
CL4	<0.05	<0.03	<i>0.06</i>	<i>0.03</i>	8	3
CL5	<0.05	<i>0.04</i>	<0.05	0.07	4	12
BG (Old Lead Belt)	0.32	0.11	0.87	0.21	15	6
BG dup	0.34	<i>0.04</i>	1.27	0.08	18	18
Toxicity test control	<i>0.07</i>	<i>0.04</i>	<i>0.05</i>	<0.02	<2	20

Table 9. Filterable concentrations of selected major and minor elements in water samples from 2002 pore-water toxicity tests.

[Concentrations in milligrams per liter. Water filtered through a 0.45 micrometer pore-size filter. All samples collected at beginning (Day 0) of toxicity test. Analysis performed using inductively coupled plasma atomic emission spectrophotometry; samples diluted 10-fold for analysis. ID, identification; Al, aluminum; Ba, barium; Ca, calcium; Fe, iron; K, potassium; Mg, magnesium; Mn, manganese; Na, sodium; Si, silicon; Sr, strontium; <, less than; dup, duplicate sample from a separate filtration of bulk pore water; (ref), reference site]

Sample ID	Al	Ba	Ca	Fe	K	Mg	Mn	Na	Si	Sr
CC	<0.05	0.46	143	1.7	6	96	23.8	5.9	16.4	0.19
CC dup	<0.05	0.46	143	1.6	7	96	24.3	6.0	16.6	0.19
SC2	0.37	0.27	77	0.3	10	76	18.4	15.0	4.6	0.20
WF3	0.10	0.61	94	0.1	13	76	40.3	10.0	16.3	0.22
WF5	<0.05	1.40	222	2.3	21	167	64.9	12.0	12.5	0.39
BF4	1.50	1.10	171	13.9	25	110	70.4	34.0	16.9	0.61
SW	<0.05	0.78	88	0.1	9	60	21.9	3.4	4.2	0.17
LC1	0.22	0.15	32	0.3	5	32	5.7	34.0	3.2	0.14
WF1 (ref)	0.27	0.78	177	1.6	11	91	36.6	4.3	12.8	0.18
SK (ref)	0.24	0.34	45	0.1	3	30	12.4	1.0	3.5	0.09
CL3 (lake ref)	<0.05	0.14	42	0.2	2	23	12.9	<0.6	10.4	0.05
CL1	<0.05	0.15	52	0.2	2	32	14.3	1.9	13.7	0.07
CL2	0.07	0.07	38	0.1	2	22	8.6	1.0	9.6	0.05
CL4	0.10	0.08	30	0.3	2	19	4.8	0.9	12.1	0.04
CL5	<0.05	0.15	54	0.5	3	27	15.0	0.8	13.8	0.08
BG (Old Lead Belt)	0.40	0.30	77	0.5	6	59	8.0	10.0	4.7	0.09
BG dup	0.10	0.30	77	0.2	6	60	7.9	10.0	4.3	0.10
Filtration blank	<0.05	<0.02	<0.6	<0.02	<1	<0.1	<0.05	<0.6	<0.1	<0.01

Table 10. Change in acid-volatile sulfide, and ratios and differences between the sum of simultaneously extracted metals and acid-volatile sulfide in sediment samples from 2002 sediment toxicity tests.

[All values calculated using concentrations in micromoles per gram dry weight. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test; Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Replicate samples represent a separate sediment sub-sample extracted and analyzed. ID, identification; AVS, acid-volatile sulfide; SEM, simultaneously extracted metal including cadmium, copper, nickel, lead, and zinc; δ AVS, difference of AVS concentration in micromoles per gram dry weight between Day 27 and Day 0 measurements; Σ SEM/AVS, molar sum of SEM concentrations divided by molar AVS concentration; Σ SEM-AVS, molar sum of SEM concentrations minus molar AVS concentration; --, not measured; (ref), reference site; ND, not determined because AVS was non detectable]

Sample ID	Replicate number	Change	Ratio		Difference	
		δ AVS	Σ SEM/AVS		Σ SEM-AVS	
		Day 27 - Day 0	Day 0	Day 27	Day 0	Day 27
CC	1	0.33	3.13	1.11	7.38	0.41
	2	--	3.03	--	6.73	--
SC2	1	0.19	35.7	19.0	9.03	8.10
	2	--	35.1	--	8.86	--
WF3	1	8.38	3.19	1.38	7.06	4.31
	2	--	2.73	--	5.25	--
WF5	1	1.52	1.99	0.31	0.23	-1.20
	2	--	2.12	--	0.27	--
BF4	1	2.53	0.83	0.24	-0.16	-2.65
	2	--	0.78	--	-0.21	--
SW	1	0.16	3.71	3.73	0.41	0.82
	2	--	4.13	--	0.44	--
LC1	1	0.64	107	0.95	0.95	-0.03
	2	--	103	--	0.92	--
WF1 (ref)	1	1.42	1.22	0.06	0.03	-1.44
	2	--	1.17	--	0.02	--
SK (ref)	1	-0.02	3.81	20.3	0.07	0.09
	2	--	3.90	--	0.07	--
CL3 (lake ref)	1	0.90	0.30	0.33	-0.93	-1.51
	2	--	0.30	--	-0.96	--
CL1	1	-3.95	0.13	0.24	-8.04	-3.94
	2	--	0.12	--	-7.92	--
CL2	1	-0.65	0.42	0.78	-1.02	-0.25
	2	--	0.44	--	-1.05	--
CL4	1	-3.55	0.20	0.48	-5.02	-1.50
	2	--	0.15	--	-5.58	--
CL5	1	1.04	0.42	0.46	-0.98	-1.49
	2	--	0.38	--	-1.07	--
BG (Old Lead Belt)	1	-0.27	16.3	27.3	23.91	35.46
	2	--	15.5	--	24.22	--
Toxicity test control	1	0.00	ND	ND	0.29	0.31
	2	--	ND	--	0.29	--

Table 11. Filterable concentrations of cobalt and nickel in pore water, and cadmium, lead, and zinc in pore water and surface water, September 2003.

[Concentrations in micrograms per liter. Surface water filtered through a 0.45 micrometer pore-size filter. Pore water sampled by in-stream diffusion samplers (peepers). Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Co, cobalt; PW, pore water; Ni, nickel; Cd, cadmium; SW, surface water; Pb, lead; Zn, zinc; dup, duplicate sub-sampling from peeper or grab surface water sample; <, less than; (ref), reference site]

Sample ID	Field replicate	Co PW	Ni PW	Cd		Pb		Zn	
				PW	SW	PW	SW	PW	SW
CC	1	0.11	2.78	0.20	0.10	0.46	0.30	21.4	17.2
	2	0.12	3.18	0.23	0.06	0.62	0.35	34.5	21.2
	3	0.13	3.28	0.10	0.08	0.42	0.51	22.3	96.4
SC2	1	0.45	19.3	0.12	<i>0.02</i>	0.53	0.21	52.1	54.5
	1 dup	0.53	18.8	0.11	<i>0.04</i>	0.58	0.22	55.2	55.5
	2	0.62	22.9	0.07	<i>0.02</i>	0.53	0.23	56.7	56.0
WF3	3	0.64	18.5	0.14	<i>0.03</i>	0.77	0.23	67.0	55.3
	1	0.33	2.23	0.04	<0.01	0.34	0.16	8.6	8.6
	1 dup	0.20	1.43	<0.01	<0.01	0.17	0.17	6.4	5.1
WF5	2	0.54	2.93	<i>0.03</i>	<0.01	0.76	0.19	8.3	5.7
	3	0.13	0.83	<0.01	<0.01	0.08	0.17	5.2	6.8
	1	0.07	<i>0.20</i>	<i>0.02</i>	<0.01	0.03	0.03	1.6	<i>1.0</i>
BF4	2	0.08	<i>0.21</i>	<i>0.02</i>	<0.01	0.05	0.02	2.0	1.2
	3	0.06	<i>0.17</i>	<i>0.02</i>	<0.01	0.04	0.03	1.6	1.5
	1	0.14	2.56	0.04	<i>0.02</i>	0.73	0.40	4.2	6.5
SW	1 dup	0.16	2.97	0.04	<0.01	0.86	0.34	7.9	5.5
	2	0.11	2.53	0.04	<i>0.02</i>	0.34	0.36	5.9	4.6
	3	0.10	2.77	<i>0.02</i>	<0.01	0.28	0.45	4.7	9.1
LC1	1	0.04	0.34	0.09	<i>0.02</i>	0.36	0.13	5.5	3.2
	2	0.05	0.49	0.03	<i>0.02</i>	0.16	0.14	2.3	3.3
	3	0.11	1.00	0.10	<i>0.04</i>	0.96	0.29	4.9	3.6
MF3	1	0.08	0.47	0.04	0.05	0.18	0.13	5.8	6.4
	2	0.13	0.51	0.06	<i>0.03</i>	1.40	0.15	5.4	6.0
	3	0.07	0.29	0.04	0.05	0.26	0.24	5.1	17.3
WF1 (ref)	1	0.08	0.70	<i>0.02</i>	<0.01	0.04	<i>0.02</i>	2.3	2.7
	2	0.09	0.67	<0.01	<0.01	0.07	<0.01	2.7	1.5
	3	0.08	0.58	<0.01	<0.01	0.09	<0.01	3.2	7.8
SK (ref)	1	0.04	<i>0.14</i>	<0.01	<0.01	0.04	<i>0.01</i>	2.2	<i>1.0</i>
	2	0.06	0.25	<i>0.03</i>	<0.01	0.14	<i>0.01</i>	6.1	<i>1.3</i>
	3	0.04	<i>0.09</i>	<i>0.02</i>	<0.01	0.02	<i>0.02</i>	2.8	<i>1.4</i>
BC (ref)	1	0.04	<i>0.19</i>	<i>0.02</i>	<0.01	0.05	<0.01	1.0	1.7
	2	0.03	<i>0.20</i>	<0.01	<0.01	0.02	<0.01	1.0	<0.5
	3	<i>0.02</i>	<0.07	<0.01	<0.01	0.01	<0.01	0.6	<0.5
HZ (ref)1	1	0.04	<0.07	<0.01	<0.01	<i>0.01</i>	<i>0.01</i>	0.5	5.4
	2	0.04	<i>0.15</i>	<0.01	<0.01	0.06	<0.01	1.6	4.1
	3	0.04	<i>0.09</i>	<0.01	<0.01	0.02	<0.01	1.0	<0.5
HZ (ref)1	1	0.07	<i>0.15</i>	<i>0.03</i>	<0.01	0.16	<i>0.02</i>	3.0	1.9
	2	0.05	<i>0.11</i>	<i>0.02</i>	<0.01	0.03	<i>0.02</i>	0.7	<i>0.7</i>
	3	0.07	<i>0.13</i>	<i>0.02</i>	<0.01	0.05	<0.01	1.0	<0.5

¹Nominal reference for Meramec River watershed; some mining effects possible.

Table 12. Concentrations of selected major and minor elements in pore water, September 2003.

[Concentrations in milligrams per liter. Pore water sampled by in-stream diffusion samplers (peepers). Analysis performed using inductively coupled plasma atomic emission spectrophotometry; samples diluted 10-fold for analysis. ID, identification; Al, aluminum; Ba, barium; Ca, calcium; Fe, iron; K, potassium; Mg, magnesium; Mn, manganese; Na, sodium; Sr, strontium; <, less than; dup, duplicate sub-sampling from peeper; (ref), reference site]

Sample	Field		Al	Ba	Ca	Fe	K	Mg	Mn	Na	Sr
	ID	replicate									
CC	1		<0.2	0.03	33	<0.5	<1	19.0	<0.02	<1	0.03
	2		<0.2	0.03	32	<0.5	<1	19.0	<0.02	<1	0.03
	3		<0.2	0.03	32	<0.5	<1	19.0	<0.02	<1	0.03
SC2	1		<0.2	0.05	45	<0.5	1	31.0	<0.02	5	0.06
	2		<0.2	0.04	45	<0.5	<1	29.7	<0.02	5	0.06
	3		<0.2	0.05	46	<0.5	1	30.0	<0.02	4	0.06
WF3	1		<0.2	0.03	37	<0.5	<1	23.7	<0.02	6	0.08
	1 dup		0.8	0.03	39	<0.5	1	26.8	<0.02	6	0.08
	2		<0.2	0.04	39	<0.5	2	25.3	<0.02	7	0.08
	3		<0.2	0.04	39	<0.5	2	25.4	<0.02	7	0.08
WF5	1		<0.2	0.03	35	<0.5	<1	23.1	<0.02	5	0.06
	2		<0.2	0.04	36	<0.5	1	23.1	<0.02	5	0.06
	3		<0.2	0.04	34	<0.5	1	22.2	<0.02	4	0.05
BF4	1		<0.2	0.04	34	<0.5	2	22.7	<0.02	15	0.12
	1 dup		<0.2	0.04	34	<0.5	2	23.3	<0.02	15	0.12
	2		<0.2	0.04	34	<0.5	1	23.1	<0.02	15	0.12
	3		<0.2	0.04	34	<0.5	2	23.3	<0.02	15	0.12
SW	1		<0.2	0.04	28	<0.5	<1	17.0	<0.02	1	0.04
	2		<0.2	0.05	18	<0.5	<1	11.0	<0.02	1	0.04
	3		<0.2	0.05	17	<0.5	<1	11.0	<0.02	1	0.04
LC1	1		<0.2	0.06	33	<0.5	4	24.2	<0.02	35	0.14
	2		<0.2	0.07	31	<0.5	3	24.5	<0.02	36	0.14
	3		<0.2	0.06	31	<0.5	3	23.7	<0.02	36	0.13
MF3	1		<0.2	0.05	20	<0.5	<1	12.0	<0.02	1	0.03
	2		<0.2	0.05	22	<0.5	<1	12.0	<0.02	1	0.04
	3		<0.2	0.04	23	<0.5	<1	13.0	<0.02	1	0.04
WF1 (ref)	1		<0.2	0.03	35	<0.5	<1	22.3	<0.02	1	0.04
	2		<0.2	0.03	36	<0.5	<1	21.5	<0.02	<1	0.04
	3		<0.2	0.03	36	<0.5	1	22.0	<0.02	1	0.04
SK (ref)	1		<0.2	0.04	79	<0.5	5	50.2	<0.02	18	0.16
	1 dup		<0.2	0.04	79	<0.5	4	51.2	<0.02	18	0.16
	2		<0.2	0.05	81	<0.5	4	51.5	<0.02	18	0.16
	3		<0.2	0.05	77	<0.5	4	49.8	<0.02	17	0.16
BC (ref)	1		<0.2	0.05	42	<0.5	<1	25.8	<0.02	5	0.06
	2		<0.2	0.05	42	<0.5	2	26.3	<0.02	5	0.06
	3		<0.2	0.06	43	<0.5	<1	26.3	<0.02	5	0.06
HZ (ref) ¹	1		<0.2	0.05	41	<0.5	<1	25.3	<0.02	15	0.05
	2		<0.2	0.05	42	<0.5	1	25.5	<0.02	15	0.05
	3		<0.2	0.05	42	<0.5	1	25.3	<0.02	15	0.05
Peeper blank	1		<0.2	<0.01	<1	<0.5	<1	0.2	<0.02	<1	<0.01
Peeper blank	2		<0.2	<0.01	<1	<0.5	<1	<0.2	<0.02	<1	<0.01
Peeper blank	3		<0.2	<0.01	<1	<0.5	<1	<0.2	<0.02	<1	<0.01

¹ Nominal reference for Meramec River watershed; some mining effects possible.

Table 13. Filterable concentrations of selected major and minor elements in surface water, September 2003.

[Concentrations in milligrams per liter. Water filtered through a 0.45 micrometer pore-size filter. Analysis performed using inductively coupled plasma atomic emission spectrophotometry. Al, aluminum; Ba, barium; Ca, calcium; Fe, iron; K, potassium; Mg, magnesium; Mn, manganese; Na, sodium; Sr, strontium; <, less than; dup, duplicate filtration of a grab water sample; (ref), reference site]

Sample ID	Field replicate	Element								
		Al	Ba	Ca	Fe	K	Mg	Mn	Na	Sr
CC	1	<0.02	0.047	42.9	<0.05	1.3	29.9	<0.002	4.4	0.06
	2	<0.02	0.048	43.6	<0.05	1.2	29.5	<0.002	4.3	0.06
	3	<0.02	0.047	40.9	<0.05	1.2	28.8	<0.002	3.9	0.06
SC2	1	<0.02	0.046	76.3	<0.05	4.9	55.5	<0.002	18.4	0.17
	1 dup	<0.02	0.045	76.0	<0.05	4.9	55.1	<0.002	18.3	0.17
	2	<0.02	0.045	76.2	<0.05	5.1	54.3	<0.002	18.5	0.17
WF3	3	<0.02	0.045	76.5	<0.05	5.0	53.9	<0.002	18.5	0.17
	1	<0.02	0.040	39.1	<0.05	1.5	25.5	0.013	6.9	0.08
	1 dup	<0.02	0.039	37.4	<0.05	1.4	25.0	0.012	6.6	0.08
WF5	2	<0.02	0.040	39.2	<0.05	1.6	25.6	0.018	7.2	0.08
	3	<0.02	0.039	38.9	<0.05	1.5	25.4	0.019	7.3	0.09
	1	<0.02	0.041	36.3	<0.05	1.3	23.1	<0.002	5.3	0.06
BF4	2	<0.02	0.042	36.7	<0.05	1.3	23.4	<0.002	5.3	0.06
	3	<0.02	0.041	35.1	<0.05	1.1	22.8	<0.002	5.1	0.06
	1 dup	<0.02	0.044	35.8	<0.05	1.9	25.2	<0.002	16.4	0.13
SW	2	<0.02	0.043	35.4	<0.05	2.0	25.0	<0.002	16.1	0.13
	3	<0.02	0.043	34.7	<0.05	2.0	24.5	<0.002	15.9	0.13
	3	<0.02	0.042	35.4	<0.05	2.1	24.5	<0.002	16.3	0.13
LC1	1	<0.02	0.052	18.7	<0.05	1.2	11.9	0.014	2.0	0.04
	2	<0.02	0.054	18.7	<0.05	1.1	12.0	0.012	2.0	0.04
	3	<0.02	0.054	19.0	<0.05	1.2	12.2	0.015	2.1	0.04
MF3	1	<0.02	0.068	32.4	<0.05	2.9	25.1	0.009	37.6	0.14
	2	<0.02	0.068	32.4	<0.05	2.9	25.4	0.010	37.8	0.15
	3	<0.02	0.068	33.5	<0.05	3.0	25.4	0.011	39.7	0.15
WF1 (ref)	1	<0.02	0.053	39.4	<0.05	1.8	25.9	<0.002	5.6	0.06
	2	<0.02	0.054	41.2	<0.05	1.8	26.6	<0.002	5.9	0.06
	3	<0.02	0.054	40.5	<0.05	1.9	26.0	<0.002	5.7	0.06
SK (ref)	1	<0.02	0.038	35.9	<0.05	0.8	22.4	<0.002	1.5	0.04
	2	<0.02	0.038	35.6	<0.05	0.8	23.5	<0.002	1.5	0.04
	3	<0.02	0.038	35.6	<0.05	0.8	23.1	<0.002	1.5	0.04
BC (ref)	1	<0.02	0.050	21.5	<0.05	1.0	13.2	<0.002	1.7	0.04
	2	<0.02	0.050	21.4	<0.05	1.0	13.0	<0.002	1.7	0.04
	3	<0.02	0.052	21.8	<0.05	1.1	14.2	<0.002	1.7	0.04
HZ (ref) ¹	1	<0.02	0.031	30.5	<0.05	0.6	19.2	<0.002	1.2	0.03
	2	<0.02	0.031	29.8	<0.05	0.7	18.9	<0.002	1.2	0.03
	3	<0.02	0.031	30.3	<0.05	0.6	19.3	0.003	1.2	0.03
Filtration blank	1	<0.02	0.051	42.3	<0.05	1.4	25.5	<0.002	16.0	0.04
	2	<0.02	0.049	39.3	<0.05	1.4	25.1	<0.002	14.7	0.04
	3	<0.02	0.051	39.3	<0.05	1.4	25.5	<0.002	14.8	0.04
Filtration blank	1	<0.02	<0.001	<0.1	<0.05	<0.1	<0.02	<0.002	<0.1	<0.01
	2	<0.02	<0.001	<0.1	<0.05	<0.1	<0.02	<0.002	<0.1	<0.01
	3	<0.02	<0.001	<0.1	<0.05	<0.1	<0.02	<0.002	<0.1	<0.01

¹ Nominal reference for Meramec River watershed; some mining effects possible.

Table 14. Percent water and total organic carbon, particle size distribution, and total recoverable metal concentrations in sediment samples from 2004 sediment toxicity tests.

[Metal concentrations in micrograms per gram dry weight. All sediments consisted of particles smaller than 2 millimeter in diameter. ID, identification; TOC, total organic carbon; Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Ni, nickel; Pb, lead, Zn, zinc; (ref), reference site]

Sample ID	Water		TOC (percent)	Particle size distribution (percent)				Fe	Mn	Cd	Co	Ni	Pb	Zn
	(percent)	(percent)		sand	silt	clay								
SC1	64.9	0.7	0.7	47	23	30	12,160	4,280	2.89	719	550	827	2,190	
SC2	35.8	0.2	0.2	79	6	15	6,210	894	0.49	159	93.0	182	453	
SC3	41.8	0.5	0.5	73	9	18	8,070	389	0.47	35.7	56.2	67.9	264	
MF2	29.6	0.2	0.2	88	2	11	6,910	191	0.14	10.5	77.3	28.3	66.3	
MF3	39.9	0.6	0.6	76	8	16	7,240	330	0.18	11.5	12.5	31.6	50.0	
WF2	42.1	0.4	0.4	69	12	20	7,890	354	0.28	10.7	12.5	50.2	63.1	
WF3	37.6	0.2	0.2	82	3	15	4,310	722	0.30	13.1	20.7	55.3	89.3	
WF4	30.6	0.2	0.2	84	5	11	4,490	173	0.09	4.65	6.66	18.2	20.6	
WF5	31.0	0.2	0.2	70	14	17	4,990	218	0.18	6.69	9.73	23.5	33.4	
WF6	44.7	0.5	0.5	86	3	11	5,870	332	0.15	8.72	10.6	29.8	34.1	
BF2	29.0	0.1	0.1	89	2	10	4,950	623	0.95	24.5	22.2	448	125	
BF4	48.6	0.3	0.3	69	10	22	6,530	495	0.48	16.6	39.4	137	123	
BF5	24.1	0.1	0.1	90	0	10	2,720	82	0.05	2.90	5.04	8.84	11.3	
BF6	26.4	0.1	0.1	88	1	12	3,090	233	0.08	5.72	7.11	6.87	12.2	
WF1 (ref)	24.7	0.1	0.1	81	7	12	3,360	270	0.05	5.42	16.6	4.38	10.9	
BC (ref)	33.3	0.1	0.1	85	4	11	5,540	258	0.08	4.92	6.93	5.02	12.7	
EP2 (ref)	27.1	0.2	0.2	86	2	12	3,350	208	0.06	1.96	3.71	5.24	13.3	
HZ (ref) ¹	37.6	0.2	0.2	78	6	16	8,610	169	0.69	4.54	8.32	20.3	21.5	
Toxicity test control	28.9	0.4	0.4	6	65	29	20,010	1,610	0.31	15.9	20.5	21.2	55.4	

¹ Nominal reference for Meramec River basin; some mining effects possible.

Table 15. Filterable concentrations of selected metals in pore-water samples from 2004 sediment toxicity tests.

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test; Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Replicate numbers represent a separate sediment sub-sample centrifuged and filtered. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Ni, nickel; Pb, lead, Zn, zinc; --, not measured; <, less than; (ref), reference site]

Sample ID	Replicate number	Fe		Mn		Cd		Co		Ni		Pb		Zn	
		Day0	Day27	Day0	Day27	Day0	Day27	Day0	Day27	Day0	Day27	Day0	Day27	Day0	Day27
SC1	1	1,150	1,240	11,200	5,980	1.82	2.40	234	302	299	338	98.8	1,050	281	652
SC2	1	280	3,330	11,700	13,720	0.40	0.31	713	791	168	270	16.8	177	138	343
	2	--	1,350	--	12,410	--	0.21	--	804	--	246	--	113	--	221
SC3	1	577	11,280	6,330	9,670	0.23	0.13	91.4	149	77.3	105	15.8	17.2	73	43
MF2	1	176	688	12,000	10,070	<0.15	<0.11	122	63.4	50.7	42.4	4.74	3.33	14	<1
	2	2,080	--	21,400	--	0.07	--	177	--	70.7	--	8.56	--	9	--
MF3	1	367	16,560	15,030	10,930	0.07	0.06	53.4	50.5	17.2	17.6	5.29	8.14	17	7
WF2	1	326	12,000	10,500	11,940	<0.15	<0.11	36.2	66.3	10.6	15.8	15.2	12.1	31	7
	2	165	--	17,100	--	0.09	--	67.7	--	14.6	--	12.3	--	30	--
WF3	1	469	3,860	9,610	11,340	0.38	<0.11	44.0	61.0	98.7	53.5	66.0	25.0	82	19
	2	790	5,180	12,800	11,830	0.57	0.16	66.2	79.5	11	66	106	38.9	131	37
WF4	1	59	1,150	7,100	9,780	0.31	<0.11	14.9	44.4	11.6	19.8	7.75	2.55	10	5
	2	144	--	12,000	--	0.04	--	25.1	--	16.0	--	7.82	--	4	--
WF5	1	2,850	20,290	5,410	3,830	<0.02	0.02	22.3	11.8	12.1	6.74	2.81	8.06	2	6
WF6	1	19,800	21,080	39,900	11,420	0.11	0.09	22.5	37.3	54.7	6.68	12.3	13.7	13	10
BF2	1	467	566	10,400	6,550	0.18	<0.11	47.6	96.1	37.9	67.7	36.1	25.3	49	12
	2	389	--	13,300	--	0.15	--	63.8	--	40.4	--	199	--	24	--
BF4	1	614	16,700	23,600	10,110	0.21	0.13	146	37.0	20.1	32.1	106	64.5	42	31
	2	--	27,130	--	14,660	--	0.19	--	48.2	--	42.0	--	76.9	--	44
BF5	1	152	37	2,350	4,780	<0.15	<0.11	4.80	8.74	5.24	6.86	9.6	1.05	13	13
	2	140	--	2,920	--	0.06	--	5.77	--	6.18	--	10.7	--	12	--
BF6	1	363	275	11,700	11,090	<0.15	<0.11	26.7	16.6	16.0	13.7	6.13	3.28	12	4
	2	327	--	20,200	--	0.13	--	43.5	--	20.8	--	7.27	--	7	--

Table 15. Filterable concentrations of selected metals in pore-water samples from 2004 sediment toxicity tests.—Continued

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Day 0 and Day 27 indicate sampling day during a 28-day sediment toxicity test; Day-27 samples were a separate sediment portion held in a toxicity test chamber for 27 days. Replicate numbers represent a separate sediment sub-sample centrifuged and filtered. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Ni, nickel; Pb, lead; Zn, zinc; --, not measured; <, less than; (ref), reference site]

Sample ID	Replicate number	Fe		Mn		Cd		Co		Ni		Pb		Zn	
		Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27	Day 0	Day 27
WF1 (ref)	1	119	3,420	8,950	13,580	0.07	0.05	12.9	31.4	3.77	7.73	1.2	1.37	3	3
BC (ref)	1	404	12,700	11,500	10,990	<0.15	<0.11	20.1	38.8	5.54	6.52	0.98	1.36	6	<1
	2	357	10,200	13,500	10,920	0.06	<0.11	22.6	33.3	5.86	6.32	1.43	1.56	3	<1
EP2 (ref)	1	239	--	12,000	--	0.04	--	4.90	--	3.13	--	2.34	--	2	--
HZ (ref)1	1	1,450	--	3,470	--	0.13	--	6.46	--	3.61	--	4.66	--	2	--
Toxicity test control	1	1,330	--	9,260	--	1.49	--	9.78	--	44.0	--	1.31	--	35	--
	2	699	--	8,760	--	1.23	--	8.29	--	34.4	--	0.76	--	24	--
Filtration blank	1	<8	<8	<0.2	0.2	<0.15	<0.11	<0.06	<0.02	<0.07	0.75	<0.15	<0.01	<2	<1
	2	<8	<6	<0.2	<0.2	<0.02	<0.02	<0.06	<0.12	<0.07	<0.09	<0.15	<0.05	<2	<1

¹ Nominal reference for Meramec River basin; some mining effects possible.

Table 16. Filterable concentrations of selected major and minor elements in pore-water samples from 2004 sediment toxicity tests.

[Concentrations in milligrams per liter. Water filtered through a 0.45 micrometer pore-size filter. Analysis performed using inductively coupled plasma atomic emission spectrophotometry; samples diluted 10-fold for analysis. ID, identification; Al, aluminum; Ba, barium; Ca, calcium; Fe, iron; K, potassium; Mg, magnesium; Mn, manganese; Na, sodium; Sr, strontium; <, less than; (ref), reference site]

Sample ID	Al	Ba	Ca	Fe	K	Mg	Mn	Na	Sr
SC1	<0.2	0.05	99.3	<0.5	8.9	79.8	11.1	24	0.21
SC2	<0.2	0.09	104	<0.5	9.7	78.8	11.8	22	0.22
SC3	0.3	0.13	93.1	<0.5	6.9	69.1	6.3	16	0.18
MF2	<0.2	0.40	136	2.0	6.3	87.2	21.1	10	0.20
MF3	<0.2	0.33	107	<0.5	5.8	62.1	14.8	2.9	0.12
WF2	<0.2	0.38	136	<0.5	5.6	85.3	16.9	6.4	0.20
WF3	1.2	0.26	62.7	0.9	6.3	48.6	12.7	5.7	0.12
WF4	<0.2	0.23	82.4	<0.5	3.5	54.1	11.8	6.7	0.14
WF5	<0.2	0.20	103	2.5	4.0	63.6	4.7	3.8	0.16
WF6	<0.2	0.81	185	17	11	104	36.8	12	0.32
BF2	<0.2	0.31	52.6	<0.5	3.5	39.7	13.6	10	0.15
BF4	0.7	0.36	97.4	0.6	12	70.2	24.2	20	0.34
BF5	<0.2	0.13	51.2	<0.5	2.0	34.7	2.9	12	0.13
BF6	<0.2	0.46	111	<0.5	7.9	69.2	19.2	12	0.25
WF1 (ref)	<0.2	0.25	82	<0.5	4.7	51.9	8.7	2.8	0.08
BC (ref)	<0.2	0.29	115	<0.5	3.5	72.2	13.8	3.0	0.11
EP2 (ref)	<0.2	0.19	60.7	<0.5	2.0	34.0	12.2	1.0	0.05
HZ (ref) ¹	<0.2	0.19	89.7	1.0	3.8	63.6	3.5	17	0.10
Toxicity test control	1.5	0.63	390	1.0	6.9	85.8	8.7	23	1.36
Filtration blank	<0.2	<0.01	<0.5	<0.5	<1	<0.1	<0.02	<0.5	<0.01
Filtration blank	<0.2	<0.01	<0.5	<0.5	<1	<0.1	<0.02	<0.5	<0.01

¹ Nominal reference for Meramec River basin; some mining effects possible.

Table 17. Filterable concentrations of selected anions in pore-water samples from 2004 sediment toxicity tests.

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Cl, chloride; F, fluoride; NO₃, nitrate; SO₄, sulfate; <, less than; (ref), reference site]

Sample ID	Cl	F	NO ₃	SO ₄
SC1	32.6	0.80	0.80	318
SC2	32.8	0.43	<0.08	312
SC3	20.6	0.32	<0.08	170
MF2	51.7	0.11	<0.08	10
MF3	7.1	0.09	<0.08	2
WF2	56.8	<0.08	0.17	3
WF3	13.8	0.20	<0.08	8
WF4	34.5	0.14	<0.08	6
WF5	6.8	0.11	<0.08	<2
WF6	18.0	<0.08	<0.08	3
BF2	50.2	0.24	<0.08	14
BF4	24.2	0.25	<0.08	16
BF5	58.0	0.20	0.15	60
BF6	55.0	0.18	0.11	10
WF1 (ref)	6.1	<0.08	<0.08	3
BC (ref)	16.2	<0.08	<0.08	3
Filtration blank	<0.08	<0.08	<0.08	<2

Table 18. Mass of selected metals in sections of pore-water sampling probes placed in selected test chambers of 2004 sediment toxicity tests.

[Values are mass of metal in nanograms. Probes were placed in sediment test chamber for 48 hours beginning on day 27 of sediment toxicity test. Each sampling horizon represents a 2-centimeter width section of the probe gel and resin. ID, identification; DGT, diffusion gradient in thin film (passive metals sampling probe); Fe, iron; Mn, manganese; Cd, cadmium; Co, cobalt; Ni, nickel; Pb, lead; Zn, zinc; <, less than; dup, duplicate sediment test chamber and probe; (ref), reference site]

Sample ID	DGT sampling horizon	Fe	Mn	Cd	Co	Ni	Pb	Zn
SC2	overlying water	320	168	<0.08	3	8	0.1	<115
	upper sediment	3,920	14,188	<0.08	207	99	0.3	<115
	lower sediment	11,610	30,158	<0.08	1,160	356	0.5	<115
SC2 dup	overlying water	<26	1,988	<0.08	34	12	1.9	<115
	upper sediment	10,510	28,888	<0.08	598	209	0.1	<115
	lower sediment	21,630	27,528	<0.08	3,240	1,013	<0.1	417
BF4	overlying water	<26	843	<0.08	2	3	0.5	<115
	upper sediment	8,530	10,398	<0.08	23	26	<0.1	<115
	lower sediment	23,880	7,058	<0.08	32	26	<0.1	<115
BF4 dup	overlying water	<26	2,328	<0.08	4	15	1.3	<115
	upper sediment	16,090	12,348	<0.08	32	30	0.1	<115
	lower sediment	26,550	3,718	<0.08	43	39	0.2	<115
WF3	overlying water	284	90	<0.08	1	5	0.1	164
	upper sediment	4,180	19,158	<0.08	43	52	0.6	144
	lower sediment	17,120	40,628	0.13	139	109	0.5	<115
WF3 dup	overlying water	160	132	<0.08	1	6	0.3	<115
	upper sediment	255	5,518	<0.08	18	32	0.8	<115
	lower sediment	8,520	31,428	<0.08	159	133	1.1	<115
BC (ref)	overlying water	250	1,208	<0.08	2	2	<0.1	<115
	upper sediment	50,650	16,148	<0.08	135	26	<0.1	<115
	lower sediment	66,180	12,028	<0.08	152	26	0.6	<115
BC dup	overlying water	194	883	<0.08	3	3	<0.1	<115
	upper sediment	54,370	16,658	<0.08	153	34	0.5	<115
	lower sediment	60,500	12,638	<0.08	144	29	<0.1	<115

Table 19. Filterable concentrations of selected metals in pore water and surface water, June and July 2005.

[Concentrations in micrograms per liter. Surface water filtered through a 0.45 micrometer pore-size filter. Pore water sampled with in-stream diffusion samplers (peepers). Exposure day refers to test day of in-stream crayfish study. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Cd, cadmium; Ni, nickel; Pb, lead; Zn, zinc; --, not measured; (ref), reference site; <, less than]

Sample ID	Replicate number	Sampling date	Exposure day	Cd		Co		Ni		Pb		Zn		
				PW	SW	PW	SW	PW	SW	PW	SW	PW	SW	
SC2	1	06/30/05	0	--	<i>0.06</i>	--	<i>0.80</i>	--	<i>21.7</i>	--	--	<i>0.67</i>	--	47
	1	07/14/05	14	<i>0.11</i>	<i>0.08</i>	1.78	0.59	23.8	23.4	2.50	0.68	59	49	49
	1	07/28/05	28	<i>0.16</i>	<i>0.07</i>	1.80	0.59	27.4	29.3	2.17	0.75	72	60	60
	2	07/28/05	28	--	<i>0.09</i>	--	<i>0.58</i>	--	<i>29.7</i>	--	<i>0.74</i>	--	--	66
WF1 (ref)	1	06/30/05	0	--	<0.06	--	<i>0.09</i>	--	<0.25	--	<0.06	--	--	9
	2	06/30/05	0	--	<0.06	--	<i>0.10</i>	--	<0.25	--	<0.06	--	--	<5
	1	07/14/05	14	<0.06	<0.06	<i>0.11</i>	<i>0.10</i>	<0.25	<0.25	<i>0.07</i>	<0.06	<5	<5	<5
	1	07/27/05	28	<0.06	<0.06	<i>0.09</i>	<i>0.08</i>	<0.25	<0.25	<0.06	<0.06	<5	<5	<5
WF3	1	06/30/05	0	--	<0.06	--	<i>0.42</i>	--	<i>2.12</i>	--	--	<i>0.10</i>	--	<5
	1	07/12/05	14	<0.06	<0.06	0.20	0.39	1.62	1.81	<i>0.10</i>	<i>0.11</i>	6	<5	<5
	2	07/12/05	14	--	<0.06	--	<i>0.42</i>	--	<i>2.07</i>	--	--	<i>0.15</i>	--	<5
	1	07/27/05	28	<0.06	<0.06	<i>0.15</i>	<i>0.32</i>	1.27	1.69	<i>0.07</i>	<i>0.11</i>	10	<5	<5
	2	07/27/05	28	<0.06	--	<i>0.24</i>	--	<i>3.99</i>	--	<i>0.16</i>	--	<i>10</i>	--	--
	1	06/30/05	0	--	<0.06	--	<i>0.14</i>	--	<i>0.34</i>	--	<0.06	--	<5	<5
WF4	1	07/14/05	14	<0.06	<0.06	0.27	0.17	0.46	0.44	0.42	0.07	<5	<5	<5
	1	07/27/05	28	<0.06	<0.06	0.32	0.14	0.47	0.42	1.15	<0.06	8	<5	<5
	1	06/30/05	0	--	<0.06	--	<i>0.18</i>	--	<0.25	--	<0.06	--	<5	<5
BF1 (ref)	1	07/13/05	14	<0.06	<0.06	0.48	0.12	0.76	<0.25	<i>0.16</i>	<0.06	6	<5	<5
	2	07/13/05	14	--	<0.06	--	<i>0.14</i>	--	<0.25	--	<0.06	--	<5	<5
	1	07/28/05	28	<0.06	<0.06	3.48	0.12	1.36	<0.25	<i>0.08</i>	<0.06	9	<5	<5
	1	07/28/05	28	<0.06	<0.06	3.48	0.12	1.36	<0.25	<i>0.08</i>	<0.06	9	<5	<5

Table 19. Filterable concentrations of selected metals in pore water and surface water, June and July 2005.—Continued

[Concentrations in micrograms per liter. Surface water filtered through a 0.45 micrometer pore-size filter. Pore water sampled with in-stream diffusion samplers (peepers). Exposure day refers to test day of in-stream crayfish study. Italicized values are greater than detection limit but less than method quantitation limit. ID, identification; Cd, cadmium; PW, pore water; SW, surface water; Co, cobalt; Ni, nickel; Pb, lead; Zn, zinc; --, not measured; (ref), reference site; <, less than]

Sample ID	Replicate number	Sampling date	Exposure day	Cd		Co		Ni		Pb		Zn		
				PW	SW	PW	SW	PW	SW	PW	SW	PW	SW	
BF3	1	06/30/05	0	--	<0.06	--	0.30	--	6.14	--	--	1.42	--	7
	2	06/30/05	0	--	<0.06	--	0.31	--	6.36	--	--	1.48	--	7
	1	07/13/05	14	0.07	<0.06	1.11	0.28	8.41	5.75	2.44	1.70	17	6	6
	2	07/13/05	14	--	<0.06	--	0.28	--	6.07	--	--	1.68	--	6
	1	07/28/05	28	<0.06	<0.06	0.48	0.25	5.00	5.67	2.38	1.65	10	7	7
	2	07/28/05	28	<0.06	--	0.22	--	5.97	--	0.61	--	8	--	--
BF5	1	06/30/05	0	--	<0.06	--	0.13	--	0.51	--	--	0.06	--	8
	1	07/14/05	14	<0.06	<0.06	1.07	0.12	1.48	0.48	0.10	<0.06	<5	<5	<5
	1	07/27/05	28	<0.06	<0.06	0.14	0.11	0.83	0.52	0.11	<0.06	<5	<5	<5
	2	07/27/05	28	--	<0.06	--	0.12	--	0.48	--	--	<0.06	--	<5
Blank ¹	1	06/30/05	0	--	<0.06	--	<0.05	--	<0.25	--	--	<0.06	--	<5
	1	07/12/05	14	<0.06	<0.06	<0.05	<0.05	<0.25	<0.25	<0.06	<0.06	<5	<5	<5
	2	07/12/05	14	<0.06	--	<0.05	--	<0.25	--	0.11	--	<5	--	--
	3	07/12/05	14	<0.06	--	<0.05	--	<0.25	--	0.14	--	<5	--	--
	1	07/27/05	28	<0.06	<0.06	<0.05	<0.05	<0.25	<0.25	0.08	<0.06	<5	<5	<5
	2	07/27/05	28	<0.06	--	<0.05	--	<0.25	--	0.12	--	<5	--	--
3	07/27/05	28	<0.06	--	<0.05	--	<0.25	--	0.07	--	<5	--	--	

¹ Blank refers to filtration blank (SW) or peeper blank (PW).

Table 20. Filterable concentrations of selected major and minor elements in pore water, July 2005.

[Concentrations in milligrams per liter. Pore water sampled with in-stream diffusion samplers (peepers). Analysis performed using inductively coupled plasma atomic emission spectrophotometry. Exposure day refers to test day of in-stream crayfish study. ID, identification; Al, aluminum; Ba, barium; Ca, calcium; Fe, iron; K, potassium; Mg, magnesium; Mn, manganese; Na, sodium; Sr, strontium; <, less than; (ref), reference site]

Sample ID	Replicate number	Exposure day	Sampling date	Al	Ba	Ca	Fe	K	Mg	Mn	Na	Sr
SC2	1	14	7/13/2005	<0.02	0.046	71.7	<0.05	4.8	50.6	0.006	24.6	0.158
WF1 (ref)	1	14	7/14/2005	<0.02	0.040	36.0	<0.05	0.8	21.6	0.002	1.4	0.035
WF3	1	14	7/12/2005	<0.02	0.045	41.1	<0.05	1.4	25.8	<0.002	6.2	0.076
WF4	1	14	7/14/2005	<0.02	0.045	38.5	<0.05	1.3	23.2	0.009	4.5	0.059
BF1 (ref)	1	14	7/13/2005	<0.02	0.055	29.1	<0.05	0.7	16.8	0.120	1.4	0.033
BF3	1	14	7/13/2005	<0.02	0.058	46.6	<0.05	2.9	31.3	0.059	24.9	0.184
BF5	1	14	7/14/2005	<0.02	0.072	42.3	<0.05	1.6	23.3	0.527	12.9	0.104
Blank	1	14	7/18/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001
Blank	2	14	7/18/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001
Blank	3	14	7/18/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001
SC2	1	28	7/28/2005	<0.02	0.048	78.4	<0.05	5.4	56.2	0.004	27.5	0.190
WF1 (ref)	1	28	7/27/2005	<0.02	0.047	37.8	<0.05	0.9	22.1	<0.002	1.4	0.037
WF3	1	28	7/27/2005	<0.02	0.045	36.3	<0.05	1.0	21.3	<0.002	3.3	0.052
WF3	2	28	7/27/2005	<0.02	0.048	37.4	<0.05	1.2	21.6	0.029	3.6	0.062
WF4	1	28	7/27/2005	<0.02	0.042	35.1	<0.05	1.0	20.8	0.011	3.3	0.047
BF1 (ref)	1	28	7/28/2005	<0.02	0.112	30.5	1.90	0.8	18.0	1.500	1.6	0.036
BF3	1	28	7/28/2005	<0.02	0.064	46.7	<0.05	2.8	33.0	0.016	25.3	0.188
BF3	2	28	7/28/2005	<0.02	0.057	45.3	<0.05	2.7	32.5	<0.002	24.8	0.186
BF5	1	28	7/27/2005	<0.02	0.057	39.5	<0.05	1.6	25.0	<0.002	12.6	0.103
Blank	1	28	7/29/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001
Blank	2	28	7/29/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001
Blank	3	28	7/29/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001

Table 21. Filterable concentrations of selected major and minor elements in surface water, June and July 2005.

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Exposure day refers to test day of in-stream crayfish study. Analysis performed using inductively coupled plasma atomic emission spectrophotometry. ID, identification; Al, aluminum; Ba, barium; Ca, calcium; Fe, iron; K, potassium; Mg, magnesium; Mn, manganese; Na, sodium; Sr, strontium; <, less than; (ref), reference site]

Sample ID	Replicate number	Exposure day	Sampling date	Al	Ba	Ca	Fe	K	Mg	Mn	Na	Sr
SC2	1	0	6/30/2005	<0.02	0.048	72.1	<0.05	4.9	52.1	0.003	24.8	0.159
	1	14	7/13/2005	<0.02	0.046	73.1	<0.05	5.0	55.6	<0.002	25.4	0.173
	1	28	7/28/2005	<0.02	0.047	81.8	<0.05	5.3	58.0	<0.002	28.6	0.196
	2	28	7/28/2005	<0.02	0.047	81.2	<0.05	5.6	56.0	<0.002	28.4	0.190
WF1 (ref)	1	0	6/30/2005	<0.02	0.044	38.3	<0.05	0.8	23.2	0.002	1.5	0.038
	2	0	6/30/2005	<0.02	0.043	38.6	<0.05	0.9	22.9	0.003	1.5	0.038
	1	14	7/14/2005	<0.02	0.041	37.2	<0.05	0.8	22.4	<0.002	1.5	0.037
	1	28	7/27/2005	<0.02	0.044	37.5	<0.05	0.8	22.0	0.003	1.5	0.037
WF3	1	0	6/30/2005	<0.02	0.046	42.3	<0.05	1.4	26.4	0.015	6.2	0.078
	1	14	7/12/2005	<0.02	0.044	40.9	<0.05	1.3	25.4	0.013	5.9	0.072
	2	14	7/12/2005	<0.02	0.045	41.4	<0.05	1.3	25.5	0.013	5.9	0.072
	1	28	7/27/2005	<0.02	0.045	41.3	<0.05	1.3	25.2	0.016	5.7	0.076
WF4	1	0	6/30/2005	<0.02	0.046	39.6	<0.05	1.3	25.0	<0.002	4.8	0.065
	1	14	7/14/2005	<0.02	0.044	39.4	<0.05	1.2	24.8	<0.002	4.9	0.065
	1	28	7/27/2005	<0.02	0.046	39.3	<0.05	1.3	24.0	<0.002	4.8	0.064
BF1 (ref)	1	0	6/30/2005	<0.02	0.054	29.7	<0.05	0.7	18.5	0.010	1.7	0.037
	1	14	7/13/2005	<0.02	0.050	28.6	<0.05	0.7	17.6	0.003	1.5	0.033
	2	14	7/13/2005	<0.02	0.049	28.9	<0.05	0.7	18.0	0.005	1.4	0.034
	1	28	7/28/2005	<0.02	0.050	29.7	<0.05	0.7	17.7	0.005	1.6	0.034

Table 21. Filterable concentrations of selected major and minor elements in surface water, June and July 2005.—Continued

[Concentrations in micrograms per liter. Water filtered through a 0.45 micrometer pore-size filter. Exposure day refers to test day of in-stream crayfish study. Analysis performed using inductively coupled plasma atomic emission spectrophotometry. ID, identification; Al, aluminum; Ba, barium; Ca, calcium; Fe, iron; K, potassium; Mg, magnesium; Mn, manganese; Na, sodium; Sr, strontium; <, less than; (ref), reference site]

Sample ID	Replicate number	Exposure day	Sampling date	Al	Ba	Ca	Fe	K	Mg	Mn	Na	Sr
BF3	1	0	6/30/2005	<0.02	0.056	46.1	<0.05	2.6	33.4	0.003	25.8	0.194
	2	0	6/30/2005	<0.02	0.056	45.7	<0.05	2.6	33.1	0.003	25.5	0.192
	1	14	7/13/2005	<0.02	0.051	42.8	<0.05	2.5	31.9	0.002	22.0	0.172
	2	14	7/13/2005	<0.02	0.050	43.0	<0.05	2.4	31.9	0.002	22.1	0.173
	1	28	7/28/2005	<0.02	0.056	47.6	<0.05	2.9	34.2	0.002	25.9	0.195
BF5	1	0	6/30/2005	<0.02	0.054	38.7	<0.05	1.5	24.3	<0.002	12.0	0.097
	1	14	7/14/2005	<0.02	0.054	39.9	<0.05	1.7	26.0	<0.002	13.5	0.104
	1	28	7/27/2005	<0.02	0.056	39.8	<0.05	1.6	25.3	<0.002	13.4	0.105
	2	28	7/27/2005	<0.02	0.055	38.3	<0.05	1.6	24.2	<0.002	13.0	0.101
Filtration blank	1	0	6/30/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001
Filtration blank	1	14	7/12/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001
Filtration blank	1	28	7/27/2005	<0.02	<0.001	<0.05	<0.05	<0.1	<0.02	<0.002	<0.05	<0.001

Table 22. Filterable concentrations of selected anions in pore water and surface water, July 2005.

[Concentrations in milligrams per liter. Surface water filtered through a 0.45 micrometer pore-size filter. Pore water sampled with in-stream diffusion samplers (peepers). Exposure day refers to test day of in-stream crayfish study. ID, identification; Cl, chloride; PW, pore water; SW, surface water; F, fluoride; NO₃, nitrate; SO₄, sulfate; (ref), reference site; dup, duplicate subsample from grab water sample or peeper; --, not measured]

Site ID	Exposure day	Sampling date	Cl		F		NO ₃		SO ₄	
			PW	SW	PW	SW	PW	SW	PW	SW
SC2	14	7/13/2005	26.0	27.3	0.50	0.50	4.3	4.5	308	312
WF1 (ref)	14	7/13/2005	2.6	2.5	0.15	0.04	0.5	0.4	4	4
WF3	14	7/13/2005	8.2	7.2	0.30	0.30	1.0	1.2	48	44
WF4	14	7/13/2005	5.7	5.6	0.20	0.20	0.8	0.6	31	33
BF1 (ref)	14	7/13/2005	2.3	2.5	0.04	0.04	0.4	0.5	4	4
BF3	14	7/13/2005	23.0	21.0	0.60	0.50	1.8	2.5	126	112
BF5	14	7/13/2005	14.0	14.0	0.30	0.40	0.6	1.1	66	68
SC2	28	7/28/2005	29.5	30.0	0.50	0.50	6.4	6.2	360	371
WF1 (ref)	28	7/28/2005	2.9	2.8	0.04	0.15	0.4	0.3	4	4
WF3	28	7/28/2005	5.2	7.3	0.24	0.30	0.6	0.8	22	40
WF3 dup	28	7/28/2005	5.1	--	0.30	--	0.4	--	23	--
WF4	28	7/28/2005	4.4	5.7	0.20	0.20	0.6	0.5	21	33
BF1 (ref)	28	7/28/2005	3.0	3.0	1.00	0.04	0.0	0.8	3	4
BF3	28	7/28/2005	26.0	25.6	0.70	0.70	2.2	2.0	130	133
BF3 dup	28	7/28/2005	25.6	29.6	0.70	0.50	2.2	6.2	130	164
BF5	28	7/28/2005	13.6	14.0	0.40	0.40	1.0	1.0	63	70
BF5 dup	28	7/28/2005	--	14.0	--	0.34	--	0.9	--	69

Table 23. Mass of selected metals in passive integrative water samplers deployed for up to 22 days at three stream locations, July 2005.

[Values represent total mass in nanograms of each metal recovered from sampling device after subtraction of mean of three extraction blanks. Italicized values are less than method detection limit and are included for informational purpose only. ID, identification; SLMD, stabilized liquid membrane device (passive integrative metals sampler); Cd, cadmium; Co, cobalt; Ni, nickel; Pb, lead; Zn, zinc; (ref), reference site]

Sample ID	Site deployment location	Sampling interval	nanograms of metal per SLMD					
			Cd	Co	Ni	Pb	Zn	
SC2	Strother Creek upstream from Neals Creek	7/6/05 – 7/13/05	40	1,920	11,370	3,200	30,990	
		7/6/05 – 7/19/05	435	46,110	110,200	78,950	328,600	
		7/6/05 – 7/28/05	540	20,080	194,500	41,310	548,800	
BF1	Bee Fork upstream from Highway TT (ref)	7/6/05 – 7/13/05	0	18	71	9	0	
		7/6/05 – 7/19/05	0	74	160	73	137	
		7/6/05 – 7/28/05	1	318	320	100	57	
BF3	Bee Fork downstream from Fletcher tailings	7/6/05 – 7/13/05	11	56	2,130	1,410	3,010	
		7/6/05 – 7/20/05	66	137	8,430	3,950	14,340	
		7/6/05 – 7/28/05	116	168	12,270	6,390	21,110	

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