Distribution of Mining-Related Trace Elements and Sulfide-Mineral Occurrence in Streambed Sediment of the Viburnum Trend Subdistrict and Non-Mining Areas, Southeastern Missouri, 1992–2002

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Distribution of Mining-Related Trace Elements and Sulfide-Mineral Occurrence in Streambed Sediment of the Viburnum Trend Subdistrict and Non-Mining Areas, Southeastern Missouri, 1992–2002

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Abstract

The Mississippi Valley Type deposits of the Viburnum Trend Subdistrict in southeastern Missouri are mined for lead and zinc sulfides containing the primary trace elements arsenic, cadmium, cobalt, copper, lead, nickel, and zinc (hereafter referred to as metals). The waste material produced during this mining is stored in headwater valleys of the area and thus can be transported downstream into larger streams and rivers. Streambed-sediment sampling at sites in non-mining basins, sites upstream, and sites at varying distances downstream from mining activities indicates streambed sediments are significantly enriched in Mississippi Valley Type-related metals. The degree of this enrichment depends on the constituent considered and the distance downstream from mining activities.

Statistical analysis indicated that the distribution of Mississippi Valley Type-related metals in the less than 63 micrometer fraction of streambed-sediment samples upstream from mining areas and in non-mining stream basins were similar. This indicated if Mississippi Valley Type-related metal enrichment was occurring in the Viburnum Trend, it was not caused by geographical location. Near-mining sites (mining activity within 7.5 miles upstream from the site) were enriched significantly in cobalt, lead, nickel, and zinc. Statistical analysis indicated the distribution of nickel and zinc in non-mining and distal-mining sites were similar, but these metals were significantly enriched in near-mining sites. This indicates concentrations of these metals in streambed sediment at sites within 7.5 miles of mining activity were elevated, but returned to baseline-like conditions at distal-mining sites (distances of 7.5 miles or more downstream from mining activity). However, cobalt and lead concentrations do not decrease to the lower non-mining concentrations at the distal-mining sites, but stay slightly elevated.

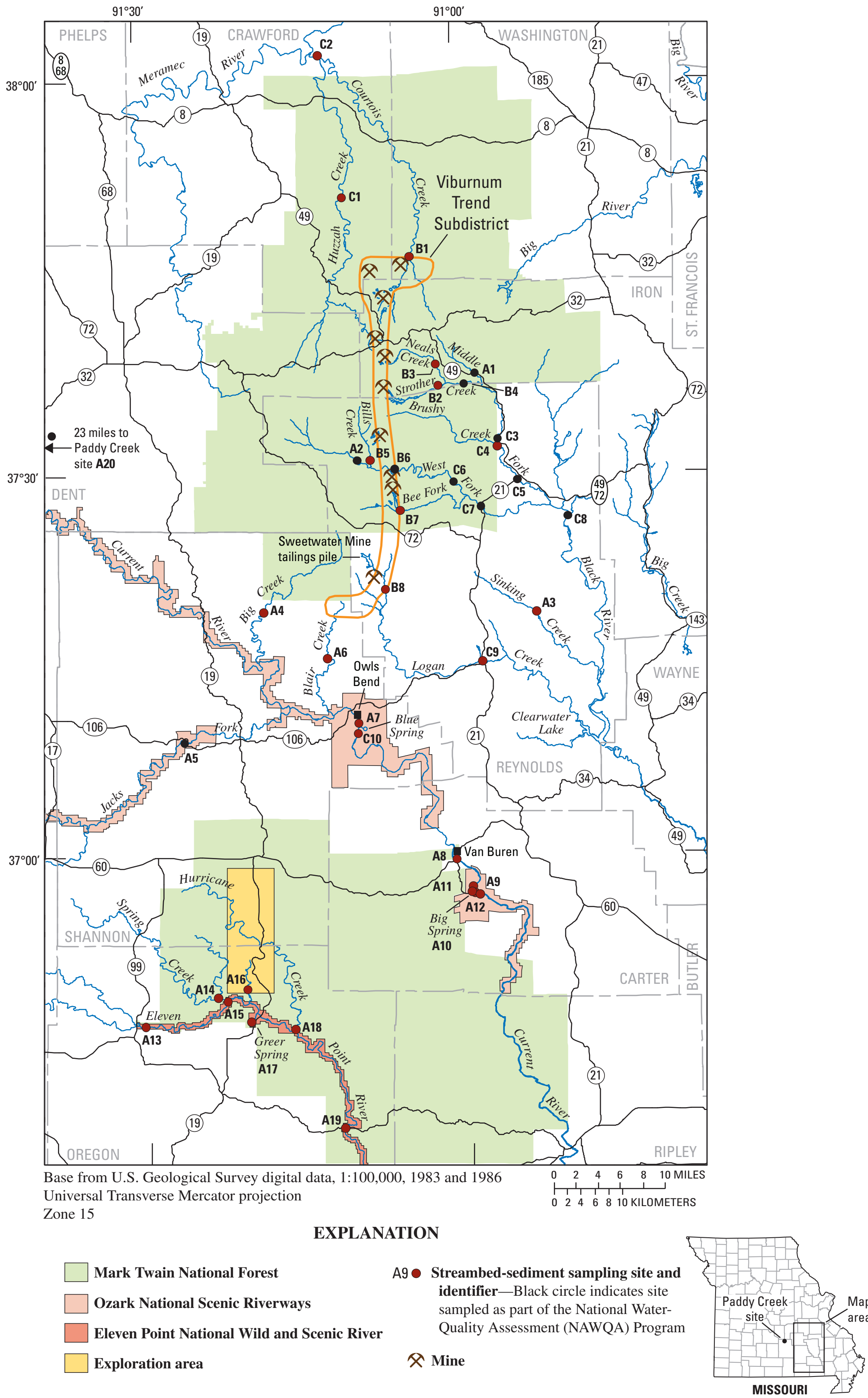
Median lead concentrations at near-mining sites were about 10 times greater than median lead concentrations observed at non-mining sites. Similarly, median zinc concentrations were elevated about seven times, cobalt about five times, and nickel about four times. Arsenic, cadmium, copper, and chromium median concentrations at near-mining sites were similar to non-mining sites.

At near-mining sites, every lead and nickel concentration, and all but one zinc concentration, exceeded their respective probable effects concentration thresholds, even though these same metals only exceeded these thresholds occasionally in the samples from non-mining sites. No distal-mining sites exceeded the probable effects concentration thresholds for copper or zinc, but three sites exceeded the lead probable effects concentration threshold, and two sites exceeded the nickel probable effects concentration threshold.

Pyrite and galena were the only sulfide minerals observed in the non-magnetic, heavy mineral fraction samples. Pyrite was the most commonly observed sulfide mineral, occurring in 55 percent (18 of 33) of all samples. Galena was observed far less frequently, occurring in 12 percent (4 of the 33) of all samples. The proportion of samples in which pyrite occurs increased from 33 percent at non-mining sites to 86 percent at near-mining sites, and then decreased to 75 percent at distal-mining sites. Pyrite is common in all Paleozoic rocks in this region and occurs in trace- and ore-grade mineralized areas. This may explain the increased occurrence rate of pyrite in areas upstream from mining and overall lower occurrence of galena.

Introduction

The lead and zinc ore deposits of the Viburnum Trend Subdistrict (hereafter referred to as Viburnum Trend in this chapter) in southeastern Missouri are a part of the largest known lead reserves within the United States (U.S. Geological Survey, 2008) (fig. 1). The genesis of these deposits is associated with regional mineralization (Leach, 1994) and the deposits are a class known as Mississippi Valley Type (MVT). Although MVT deposits are named for the region in the United States where they were first described and studied, they occur on every continent of the world (Leach and Sangster, 1993).



Base from U.S. Geological Survey digital data, 1:100,000, 1983 and 1986
Universal Transverse Mercator projection
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Figure 1. Study area and streambed-sediment sampling sites.

The MVT deposits of the Viburnum Trend are metal-sulfide deposits that are hosted in Paleozoic dolostone, limestone, and to a lesser extent sandstone. The primary metal-sulfide minerals of these deposits are pyrite–marcasite (FeS_2), galena (PbS), and sphalerite (ZnS). In localized areas, mixed-metal sulfides also occur in minor amounts. These include copper sulfides, such as bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$), and enargite (Cu_3AsS_4); nickel sulfides, such as millerite (NiS) and vaesite (NiS_2); and iron sulfides, such as arsenopyrite (FeAsS) (Rakovan, 2007). Arsenic, cadmium, cobalt, copper, lead, nickel, and zinc are the primary trace elements associated with the sulfide minerals of MVT ores and, therefore, are referred to as MVT-related metals in this chapter.

Mining in the northern part of the Viburnum Trend began in 1960, and mining began in the Black River Basin in 1966 and has continued uninterrupted since. As many as 10 mines have operated along the Viburnum Trend (fig. 1); presently (2008), 6 mines are in operation. These mines are large-scale underground workings that implement a room and pillar method of mining that has resulted in an extensive, interconnected system of underground workings. Ore material mined underground is brought to the surface and milled near the mine shafts. Wastes from the milling process are pumped as a slurry to large surface impoundments that fill headwater stream valleys.

Study Area Description

The study area includes streams in the Huzzah Creek and Black River Basins that drain the Viburnum Trend and streams draining non-mining areas to the south and west in the Current River, Eleven Point, and Paddy Creek Basins (fig. 1). The area lies within a large region of well-developed karst terrain that is characterized by the presence of caves, springs, sinkholes, and gaining and losing streams. The topography is characterized by deep, narrow valleys and narrow, steep-sided ridges that resulted from deep dissection of the carbonate bedrock by surface and karst drainage. More than 300 feet (ft) of relief is common between the ridge top and the adjacent valley.

Two federally designated scenic rivers, the Eleven Point River and the Current River, are immediately south of the Viburnum Trend. The Eleven Point River flows through the Mark Twain National Forest and contains the Eleven Point National Wild and Scenic River, which is managed by the U.S. Department of Agriculture, Forest Service. The adjacent Current River Basin contains the Ozark National Scenic Riverways, which is managed by the National Park Service. Additionally, these basins contain the two largest springs in Missouri, Big Spring and Greer Spring (Vineyard and Feder, 1982). As ore reserves are being depleted in the Viburnum Trend, exploration for new deposits is expanding south into the Mark Twain National Forest (fig. 1).

Purpose and Scope

The U.S. Geological Survey (USGS) collected 44 streambed-sediment samples between 1992 and 2002 from streams draining the Viburnum Trend and nearby non-mining basins to determine the distribution of mining-related trace metals and sulfide-mineral occurrence. The purpose of this chapter is to quantify the degree of trace-metal enrichment in the less than 63 micrometer (μm) fraction of streambed sediment as a result of mining in the Viburnum Trend and to determine if this enrichment is caused by geographical location or proximity-to-mining activity. Trace-metal enrichment is characterized with respect to baseline conditions as defined by sampling sites upstream from active mining within the Viburnum Trend and in non-mining river basins, which include streams in the exploration area. No time trends were investigated. Chromium is a metal not associated with MVT ores, but it is included in the analysis of trace metals as an indicator for alternative trace-metal sources in streambed sediment other than lead and zinc mining.

Methodology

The streambed-sediment data described in this chapter are a compilation of data that were collected as part of four different studies that investigated the effects of lead and zinc mining on southeastern Missouri streams. Each study had a different purpose; consequently, different reporting limits were used for some of the analyzed elemental concentrations.

All streambed-sediment data used in this analysis came from samples collected in a similar manner by USGS personnel, and all samples were analyzed by the same laboratory using the same analytical methods. For these reasons, all the data are considered comparable.

Sample Sites

Most of the data (26 samples) were collected from April through June 2002 at stream and spring sites in the Huzzah Creek and Black River Basins of the Viburnum Trend (fig. 1) and river basins to the south near the exploration area. The analyses of these data were performed to characterize streambed sediments along flow paths from lower-order, or smaller streams in headwater areas, to higher-order streams. In the Black River and Huzzah Creek Basins of the Viburnum Trend, the lower-order streams are used as containment areas for mine tailings.

The data collected in 2002 were supplemented with National Water-Quality Assessment (NAWQA) Program streambed-sediment data from 11 sites collected from 1992 through 1995. These data were collected as part of a reconnaissance investigation to evaluate, by using multiple lines of evidence, the effects of lead and zinc mining on area streams in the Viburnum Trend. Nine of the 11 sites sampled for the

NAWQA program were in the Black River Basin and 2 additional non-mining (baseline) sites were Paddy Creek (A20) and Jacks Fork (A5; fig. 1).

Also added to the data set were three streambed-sediment samples collected in June 1995 from two sites on the Current River near Owls Bend. The Current River sample collected upstream from Blue Spring (A7) is considered a baseline site, but the two samples collected downstream from Blue Spring (C10, east side and west side of the Current River) are considered to be from a distal-mining site. During 1977 and 1978, part of the Sweetwater Mine tailings pile upstream from site B8 (fig. 1) was breached on three occasions causing mine tailings to be released into Logan Creek (Duchrow and others, 1980). Increased turbidity caused by the tailings releases extended more than 40 miles (mi) downstream in Logan Creek, and Blue Spring also reportedly became turbid. A dye-trace investigation conducted by Feder and Barks (1972) verified the connection between Logan Creek downstream from the tailings pile and Blue Spring.

Four streambed-sediment samples collected in October 1997 from Big Spring and the Current River near Van Buren completes the data set (sites A9–A12). These data were collected to document baseline conditions in a non-mining area that has potential to be affected if future mining occurs in the exploration area.

Sample Collection

All streambed-sediment samples used for this study consisted of alluvium that was collected and composited from several dozen localities across each stream and spring sampling site to obtain a representative sample of available sediment. Samples from springs were collected at or near the spring orifice. About 20 individual subsamples at wadable sections were obtained from a hand-held sampler that used a 2-inch (in.) cup made of polyvinyl chloride (PVC) or Teflon. The sampling cup was scraped across the top 2 in. of the streambed and the collected sediment was deposited into a polyethylene container. In stream reaches that were too deep to wade, an epoxy-coated BMH-60 sampler was used (Radtke, 1997). This sampler contains an impact-activated scoop (stainless steel bucket) that penetrates into the streambed about 2 in.

The faster flowing sections of the stream were the most difficult to sample using the hand-held sampler because, in swift current, a part of the sample typically was flushed from the sampler as it was brought to the surface. Consequently, the resulting composite samples were more representative of the finer sediment from the slower current areas typically near the sides of the stream. However, because the silt and clay fraction (less than 63 µm) is the standard fraction for which to perform chemical analyses, these results are expected to be comparable to other streambed-sediment studies.

Sample Analyses

All samples used in this study were sent to the USGS mineralogic laboratory in Lakewood, Colorado, for further processing and were analyzed using the same analytical methods. The composited samples from each site were sieved to obtain the less than 2-millimeter (mm) fraction and oven dried at 105 degrees Fahrenheit (°F) before subsequent preparation or analyses. After drying, each sample was divided into two subsamples; one was analyzed for total elemental abundance and the other for selective concentration of heavy minerals.

Grain-size analyses of the streambed-sediment samples indicate the mass of coarse material (2 mm to 63 µm) ranged from 91.6 to 99.5 percent, the silt fraction (less than 63 to 2 µm) ranged from 0.1 to 7.0 percent, and the clay fraction (less than 2 µm) ranged from less than 0.1 to 1.4 percent (table 1, at the back of this chapter). However, only the silt and clay fraction (less than 63 µm) of samples was used to determine the total elemental abundances. This fraction was used to remove some of the large variability in sediment trace-element concentrations that is caused by analysis on bulk samples with differing grain size distribution (Horowitz, 1985). The samples were digested using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids at low temperature (Crock and others, 1983). The digested sample was then aspirated into the inductively coupled plasma-atomic emission spectrometry (ICP-AES) discharge where the elemental emission signals were measured simultaneously for 40 elements. Additional details about this method are documented in Briggs (2003). Chemical constituents detected at concentrations less than limits deemed reliable for reporting as numerical values were considered less than the reporting limit. This situation is indicated by a less than (<) symbol in front of the reporting limit value in table 1.

No stringent quality assurance or quality control measures were incorporated in any of the four studies for which these samples were collected; therefore, there were no duplicate or split samples for comparison or quality control. Whereas mining activity may have increased or diminished during this 10-year period, mining and milling practices probably changed little. Five sites (A2, A10, B6, C7, and C8; fig. 1) were sampled twice between 1992 and 2002; and these data provide an indication of temporal variability of the sediment released from mining facilities into area streams during the period.

Using the criterion of a greater than 50 percent difference in elemental concentration between the two samples, Big Spring orifice (A10) and West Fork Black River at West Fork (B6) were the two sites that exceeded the criterion most often (table 1). Compared to the other sites, A10 had more exceedances for the major elements (concentrations given in percent weight) and site B6 had more exceedances for the MVT-related metals. Site B6 was the closest of the five sites to active mining operations.

Sediment-Quality Guidelines

Consensus-based sediment-quality guidelines have been developed to measure the potential effects of sediment trace-element concentrations on freshwater ecosystems. Two guidelines are used to place the detected concentrations of arsenic, cadmium, copper, lead, nickel, zinc, and chromium (table 1) within the context of element toxicity. The threshold effects concentration (TEC) is the concentration below which adverse biological effects to sediment-dwelling organisms are not expected to occur or rarely occur. The probable effects concentration (PEC) is the concentration above which adverse biological effects to sediment-dwelling organisms are expected to usually or frequently occur (MacDonald and others, 2000).

Heavy Mineral Concentrate

The selective concentration of heavy minerals was performed on all of the streambed-sediment samples, except for the 11 NAWQA samples, to isolate sulfide ore minerals that may be present in streambed sediment. These minerals commonly are a small part of the total minerals in bulk material. The heavy-mineral fraction of streambed-sediment samples was used to determine if the occurrence of sulfide minerals changes downstream from mining operations.

To isolate the heavy-mineral fraction, the less than 2-mm fraction of sediments was wet panned until most of the quartz, feldspar, organic material, and clay-size sediment were removed. The samples were then sieved with a 0.5-mm (35 mesh) screen and floated through bromoform (specific gravity 2.85) to remove the remaining quartz, feldspar, and other light minerals. The remaining sediment was collected, air dried, and separated into three magnetic fractions using a modified Frantz Isodynamic Separator. The most magnetic fraction (primarily magnetite) and the moderately to weakly magnetic fraction (largely ferromagnesian silicates and oxides) were isolated and saved, but not analyzed for this study. The fraction that includes nonmagnetic sulfide minerals, such as galena, pyrite, and sphalerite, was retained and characterized. This fraction is referred to as the C3 fraction.

Sulfide minerals in the C3 fraction were identified using the standard methods of optical mineralogy that are based on morphology and optical properties of grains (table 2, at the back of this chapter). The absence or presence of sulfide minerals in samples was documented, and the relative proportions of detection or non-detection of sulfide minerals were used for characterizing spatial trends in sulfide occurrence.

Data Analysis

The computer software SYSTAT (SYSTAT Software Inc., 2002) was used for statistical hypothesis tests, summary statistics, and the preparation of boxplots. A level of significance (α-value) less than 0.05 caused rejection of the null hypothesis that states the streambed-sediment concentrations for compared areas were similar. The “attained significance level” (p-value) is a probability value determined from the data (Helsel and Hirsch, 1992) and measures the “believability” of the null hypothesis. The larger the p-value, the more likely is the observed test statistic when the null hypothesis is true and the weaker the evidence to reject the null hypothesis. Both logarithmic and linear scales were used to graphically present the concentration data. When a constituent concentration was less than the reporting limit, the reporting limit value was substituted for the “less than” value during the statistical calculations. A “less than” symbol was inserted before the appropriate calculated value listed in the summary statistics (table 3, at the back of this chapter).

Distribution of Mining-Related Trace Metals

The results of the entire 40-element ICP-AES are reported in table 1; however, only the total elemental abundances of the MVT–related metals and chromium are discussed here. A statistical summary of the MVT-related metals and chromium total elemental abundances are listed in table 3. The observed abundance of MVT-related metals in all samples ordered from largest to smallest median concentration is: zinc greater than (>) copper > lead > nickel > cobalt > arsenic > cadmium (fig. 2; table 3). The median concentrations of zinc, copper, lead, nickel, and cobalt equaled or exceeded 25 milligrams per kilogram (mg/kg). Median concentrations of arsenic (< 10 mg/kg) and cadmium (< 2 mg/kg) were equal to the reporting limit. The four largest maximum concentrations of MVT-related metals detected were zinc > lead > cobalt > nickel (fig.2; table 3). Using the interquartile range (IQR) as a robust measure of variability, lead concentrations are the most variable, followed by zinc, copper, nickel, cobalt, arsenic, and cadmium (table 3).

Data from the 20 non-mining sites (22 samples) were analyzed to determine if trace-metal enrichment is caused by geographical location. These baseline data were subgrouped based on drainage basin and included sites in the Huzzah Creek and Black River Basins upstream from active Viburnum Trend mining and sites in non-mining river basins to the south and west of the Viburnum Trend. The concentrations of MVT-related metals and chromium in the less than 63 µm fraction of streambed sediment in these two subgroups were analyzed using the non-parametric two-sample Kolmogorov-Smirnov test (SYSTAT Software Inc., 2002) to determine if concentrations in both areas were similar.

The results of this statistical test indicated that the MVT-related metals in the two areas have a similar distribution (p-values ranged from 0.272 to 0.992). This indicated if MVT-related metal enrichment was occurring in the Viburnum Trend, it was not caused by geographical location; therefore, data from both areas were combined to form a larger data set and improve the power of the statistical tests.

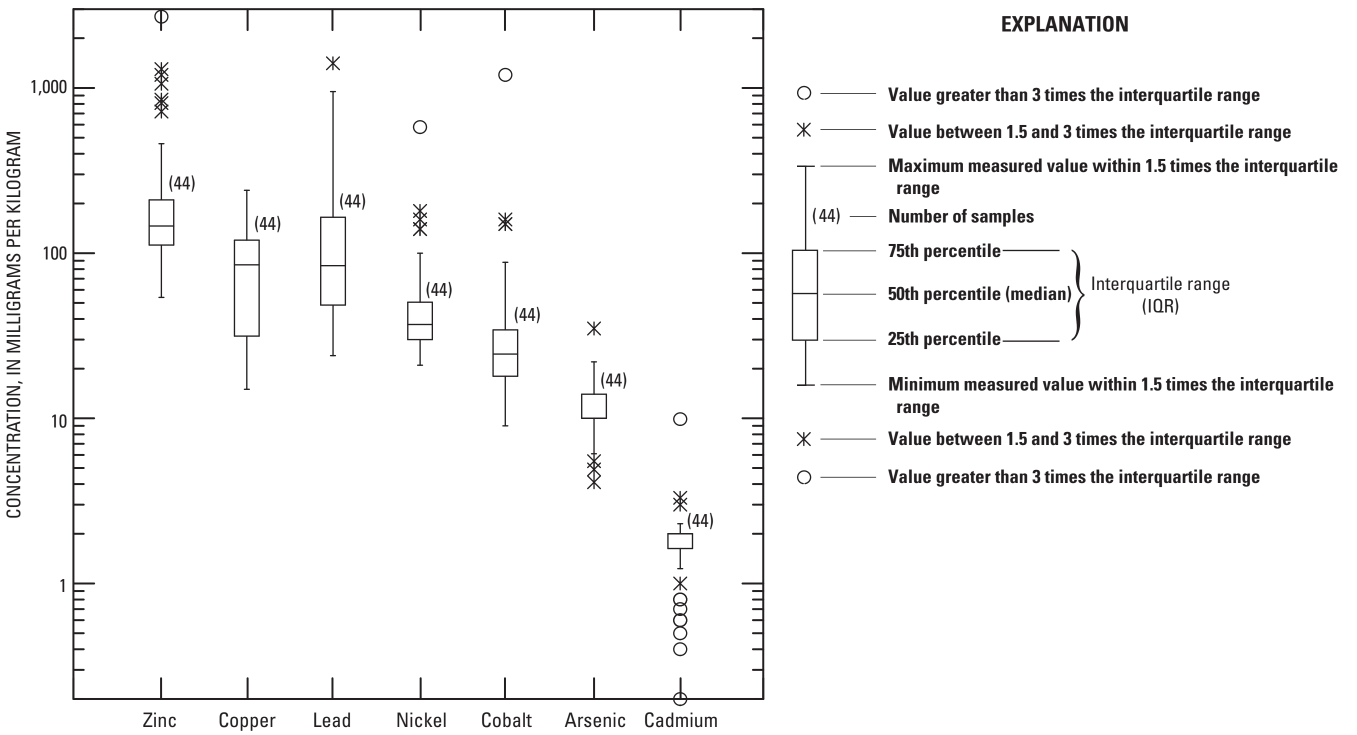

Figure 2. Observed abundance of Mississippi Valley Type-related metals in streambed-sediment samples, 1992–2002.

The distribution of the chromium concentrations, a trace metal not related to MVT deposits but included as an indicator for alternative sources of trace elements other than lead and zinc mining in the basins, was statistically different (p-value = 0.003) for the two subgroups. Chromium concentrations were significantly larger at sites in non-mining basins than at sites upstream from active mining in the Viburnum Trend. This indicates geographical location affects chromium concentrations.

Because the streambed-sediment concentrations for MVT-related metals from both non-mining areas were similar statistically, any statistical changes to these metal concentrations downstream from mines would be a result of activity at the mines. Therefore, all the sampling sites were classified into three groups based on the location and proximity of the sampling site to mining activity. The grouping was performed to determine if distance downstream from active mines or tailings piles affects the total elemental concentrations of the MVT-related metals. The three groups include: (A) non-mining sites; sampling sites upstream from mining activity or tailings ponds, or sites where no mining activity is present in the basin, (B) near-mining sites; mining activity or tailings ponds within 7.5 mi upstream from sampling site, and (C) distal-mining sites; mining activity greater than 7.5 mi upstream from the sampling site. The arbitrary 7.5-mi distance that was used as the criterion to separate near-mining and distal-mining sites was based on the distribution of the sampling sites.

The non-parametric Kruskal-Wallis statistical test (Helsel and Hirsch, 1992; SYSTAT Software Inc., 2002) was performed on the grouped data to determine if there was similar distribution between the three groups. Statistical analyses for cadmium were difficult because many cadmium concentrations were less than the reporting limit (28 of 44 values). Various reporting limits were used in the cadmium analysis (0.1, 2, and 3 mg/kg) and the substitution method was used to resolve the numerous less than reporting limit situation. The median values for the cadmium concentrations (fig. 3) indicate the distribution in the three proximity-to-mining groups to be similar; however, the statistical analysis indicated the three groups were different. This discrepancy was caused by the substitution of different reporting limits; therefore, the cadmium concentrations are considered to be similar in the three groups.

Arsenic, copper, and chromium concentrations had p-values greater than 0.05, which indicates these concentrations are similar statistically in all three proximity-to-mining groups. Although the boxplot of copper concentrations (fig. 3) appears to show a significant difference, the p-value for the copper analysis indicated marginal similarity (p-value = 0.053) between the three groups. Cobalt, lead, nickel, and zinc concentrations were different statistically for the three groups.

The Tukey method for multiple comparisons (SYSTAT Software Inc., 2002) was applied to the ranked data of cobalt, lead, nickel, and zinc to identify which groups were different statistically. The distribution of nickel and zinc concentrations in non-mining sites and distal-mining sites (groups A and C) were similar (p-value > 0.05), but concentrations of these trace metals in near-mining sites (group B) were significantly larger (p-value < 0.05) than the other two groups (fig. 3). Cobalt and lead concentrations were different statistically in all three groups, with the largest concentrations at near-mining sites

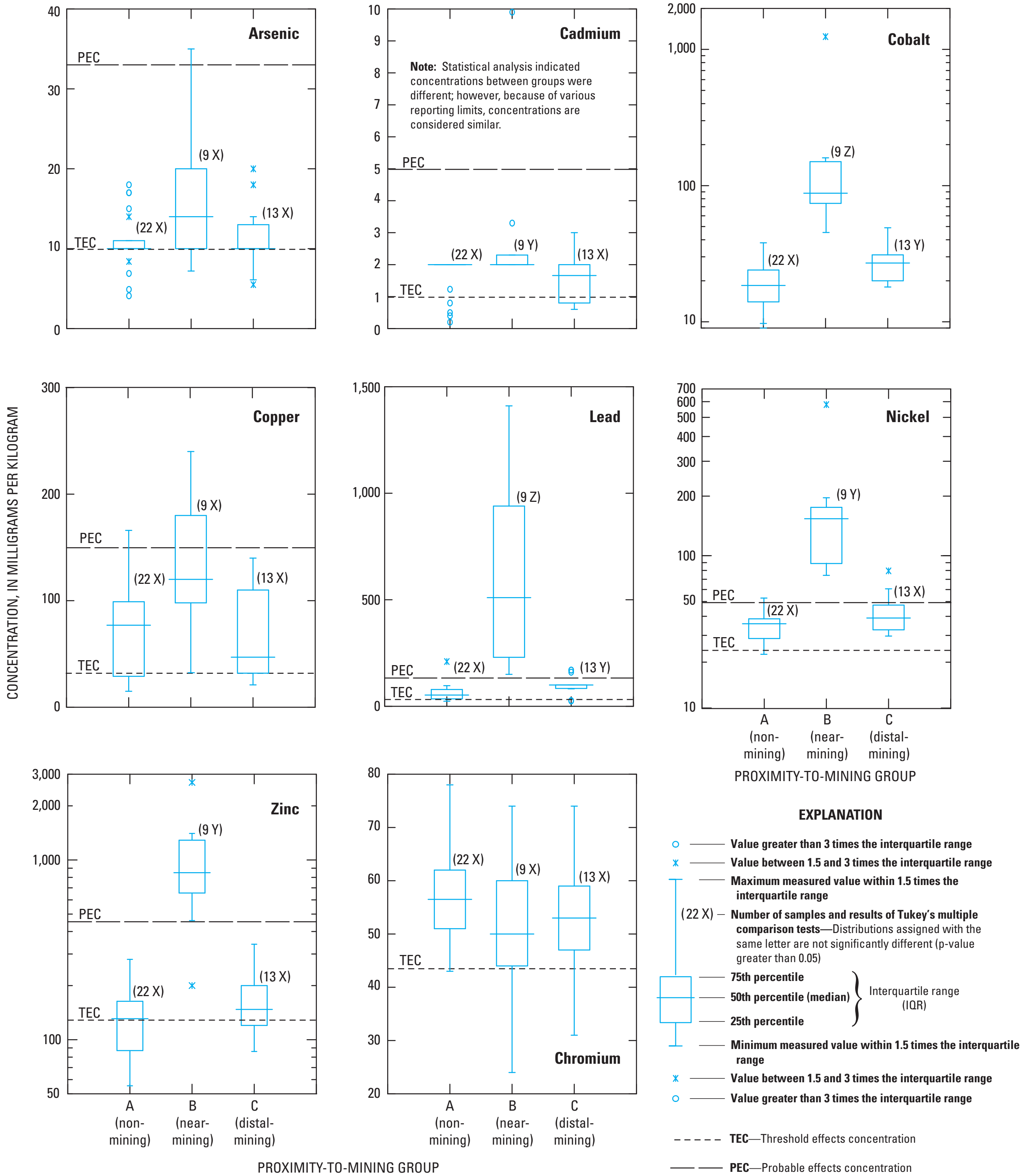

Figure 3. Concentrations of Mississippi Valley Type-related metals and chromium in streambed sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC).

and the smallest concentration at the non-mining sites. These concentrations at the distal-mining sites did not decrease to the smaller non-mining concentrations, but stayed slightly elevated.

Thus, for MVT-related metals in streambed-sediment samples, near-mining sites had significantly elevated cobalt, lead, nickel, and zinc concentrations when compared to baseline-like conditions in non-mining areas. Distal-mining sites (7.5 mi or more downstream from mining activity) had nickel and zinc concentrations that were not significantly different from sites with no mining activity; however, cobalt and lead concentrations were more persistent in the streambed-sediment samples, even at sites greater than 7.5 mi downstream from mining activities.

With the exception of one elevated arsenic concentration (35 mg/kg) at Strother Creek near Goodland (B2; fig. 1) and one elevated cadmium concentration (9.9 mg/kg) at Logan Creek near Corridon (B8; fig. 1), which were both near-mining sites, concentrations of these two metals were small in all samples (table 1). Although arsenic and cadmium concentrations increased in group B samples, these are minor constituents of Viburnum Trend sulfides when compared to cobalt, lead, nickel, and zinc (Hagni, 1983). This is perhaps the primary reason why these metals were detected in lower concentrations in streambed-sediment samples downstream from mining operations.

In contrast to the MVT-related metals discussed above, other metals were not expected to indicate a relation with the degree of mining activity upstream. For example, chromium is not associated with MVT ore minerals. Consistent with this, the distribution of chromium concentrations in streambed-sediment samples was similar between all three groups (p-value = 0.391) and not significantly elevated at sites downstream from mining activity (fig. 3).

Comparing median concentrations of MVT-related metals in streambed-sediment samples at near-mining sites (group B) to non-mining sites (group A) indicated the most enriched metals were lead and zinc followed by cobalt and nickel. Median lead concentrations at near-mining sites were about 10 times greater than the median lead concentrations detected at non-mining sites. Similarly, median zinc concentrations were elevated about seven times, cobalt about five times, and nickel about four times in samples from near-mining sites. In contrast, arsenic, cadmium, copper, and chromium median concentrations at near-mining sites were similar to median concentrations observed at non-mining sites (table 3; fig. 3).

Few samples in each of the three proximity-to-mining groups met the TEC for the MVT-related metals and chromium (table 1). No samples from any of the proximity-to-mining groups exceeded the PEC threshold for chromium. One sample (Strother Creek at Goodland, B2; fig. 1) exceeded the PEC for arsenic and one sample (Logan Creek at Corridon, B8; fig. 1) exceeded the PEC for cadmium (table 1). Both samples were from near-mining sites (group B). The percentage of near-mining samples that exceeded the PEC for copper, lead, nickel, and zinc was substantially greater as compared to the percentage of samples from non-mining sites (table 1; fig. 4). Four copper concentrations, all lead and nickel concentrations, and all but one zinc concentration exceeded their respective PEC threshold in near-mining sites. This occurred even though these same metals only occasionally exceeded these thresholds in samples from the non-mining sites. A trace of anthropogenic lead contamination (processed lead, such as lead shot or fishing sinkers, not galena) was contained in the sample from the non-mining site (A17, West Fork Black River near Greeley; table 2), which exceeded the lead PEC threshold. No distal-mining sites exceeded the PEC thresholds for copper or zinc, but three sites exceeded the lead PEC threshold and two sites exceeded the nickel PEC threshold.

Sulfide Mineral Occurrence

The selective concentration of heavy minerals indicated pyrite and galena were the only sulfide minerals observed in the C3 fraction samples (table 2). Pyrite was the most commonly observed sulfide mineral, occurring in 55 percent (18 of 33) of all samples (table 2). Galena was observed far less frequently, occurring in 12 percent (4 of the 33) of all samples. Pyrite occurrence increased from non-mining sites (group A) to near-mining sites (group B). The proportion of samples where pyrite occurs increased from 33 percent at non-mining sites to 86 percent at near-mining sites, and then decreased to 75 percent at distal-mining sites (group C). Because of the small number of sites where galena was detected, no trends will be inferred.

Pyrite is common in all Paleozoic rocks in this region and occurs in trace- and ore-grade mineralized areas (Erickson and others, 1978; Lee, 2001; Lee and Goldhaber, 2002). The occurrence of galena, however, is confined to ore-grade mineralization, which may explain the higher occurrence rate of pyrite in areas upstream from mining and overall lower occurrence of galena.

Summary and Conclusions

The Viburnum Trend Subdistrict (Viburnum Trend) in southeastern Missouri is part of the largest known lead reserve within the United States and is mined for lead and zinc sulfides containing the primary trace elements arsenic, cadmium, cobalt, copper, lead, nickel, and zinc (hereafter referred to as metals). The waste material produced during this mining is stored in headwater valleys of the area and thus may be transported downstream into larger streams and rivers.

Streambed-sediment samples were collected from sites along the Viburnum Trend and from non-mining areas to the south and west of the subdistrict. The samples were divided into three groups that included: (A) non-mining sites; sites upstream from mining activity or mine tailings ponds, or sites where no mining activity is present in the basin, (B) near-mining sites; mining activity or mine tailings ponds within

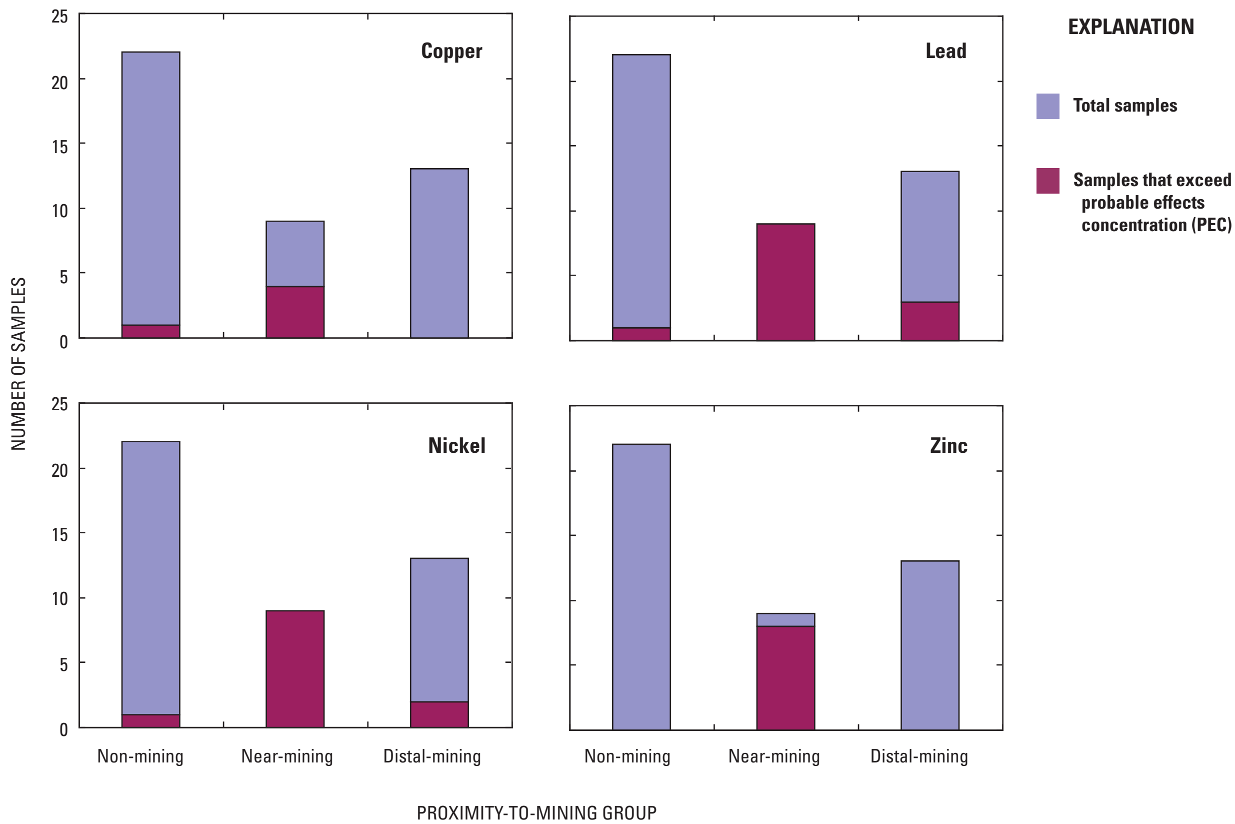

Figure 4. Exceedance of probable effects concentrations (PEC) of copper, lead, nickel, and zinc in streambed-sediment samples.

7.5 miles upstream from the site, and (C) distal-mining sites; mining activity distally upstream at distances greater than 7.5 miles. The total elemental concentrations in the less than 63 micrometer fraction of streambed sediment from the three groups were compared to quantify the degree of heavy metal enrichment that occurred as a result of mining. Chromium (a non-Mississippi Valley Type-related metal) concentrations also were analyzed as an indicator for alternative trace metal sources in streambed material other than lead and zinc mining in the basins.

Data from the 20 non-mining sites (22 samples) were analyzed to determine if trace-metal enrichment was caused by geographical location. These data were divided into two subgroups and compared. One group consisted of sites in the mining area, but upstream from any mining activity; the other group consisted of sites in stream basins outside of the Viburnum Trend where no mining has occurred. Statistical analysis indicated that the MVT-related metals in these two areas were distributed similarly in the streambed sediment. This indicated that if MVT-related metal enrichment was occurring in the Viburnum Trend, it was not caused by geographical location; therefore, data from both areas were combined to form a larger data set.

A comparison of concentrations of MVT-related metals in streambed sediment indicates a significant relation between the proximity-to-mining groups and the degree of metal enrichment. Near-mining sites were enriched significantly in the primary MVT-related metals—cobalt, lead, nickel, and zinc. Statistical analyses indicate that the distribution of nickel and zinc in non-mining and distal-mining sites were similar, but the concentrations of these metals in near-mining sites were significantly larger. This indicated the elevated nickel and zinc concentrations in streambed sediment at near-mining sites returned to near baseline conditions at distal-mining sites (7.5 miles or more downstream from mining activity). However, cobalt and lead concentrations did not decrease to the lower non-mining concentrations at the distal-mining sites but stayed slightly elevated.

When comparing median concentrations of MVT-related metals in streambed sediment at near-mining (group B) sites to non-mining (group A) sites, lead concentrations were about 10 times greater. Similarly, zinc concentrations were elevated about seven times, cobalt about five times, and nickel about four times. Arsenic, cadmium, and copper concentrations at near-mining sites were similar to non-mining sites. Chromium (a non-MVT related metal) concentrations also were similar at the two groups.

Consensus based sediment-quality guidelines were used as a means of measuring the potential effects of the sediment trace-metal concentrations of arsenic, cadmium, copper, lead, nickel, zinc, and chromium on freshwater ecosystems. The threshold effects concentration (TEC) is the level below which adverse biological effects to sediment dwelling organisms are not expected to occur or rarely occur; the probable effects concentration (PEC) is the level above which adverse biologic effects to sediment dwelling organisms are expected to usually or frequently occur. Few samples in each of the three proximity-to-mining groups met the TEC for the MVT-related metals and chromium. At near-mining sites, every lead and nickel concentration and all but one zinc concentration, exceeded their respective PEC threshold, even though these same metals only occasionally exceeded these thresholds in samples from the non-mining sites. No distal-mining sites exceeded the PEC thresholds for copper or zinc, but three sites exceeded the lead PEC threshold, and two sites exceeded the nickel PEC threshold.

Pyrite and galena were the only sulfide minerals observed in the non-magnetic, heavy mineral fraction (C3) samples. Pyrite was the most commonly observed sulfide mineral, occurring in 55 percent (18 of 33) of all samples. Galena was observed far less frequently, occurring in 12 percent (4 of the 33) of all samples. The proportion of samples that pyrite occurs increased from 33 percent at non-mining sites to 86 percent at near-mining sites, and then decreased to 75 percent at distal-mining sites. Pyrite is common in all Paleozoic rocks in this region and occurs in trace- and ore-grade mineralized areas. The occurrence of galena, however, is confined to ore-grade mineralization. This may explain the higher occurrence rate of pyrite in areas upstream from mining and overall lower occurrence of galena.

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Tables

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992–2002.

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier (fig. 1)	Date (mm/dd/yyyy)	Distance downstream from mining activity (miles)	Site name	Alumimun (% wt)	Calcium (% wt)	Iron (% wt)	Magnesium (% wt)	Phosphorous (% wt)
			Group A (Non-mining sites)					
A1	09/14/1995	NA	Middle Fork Black River at Redmondville[a]	4.7	4.9	2.1	0.83	0.07
A2	09/12/1995	NA	West Fork Black River near Greeley[a]	3.8	1.4	1.6	.40	.06
	05/06/2002			3.7	.91	1.9	.59	.05
A3	05/07/2002	NA	Sinking Creek near Redford	3.6	.52	2.8	.37	.07
A4	05/29/2002	NA	Big Creek at Mauser Mill	5.1	.68	2.6	.49	.07
A5	10/21/1993	NA	Jacks Fork at Alley Spring[a]	4.5	.50	1.9	.40	.06
A6	05/29/2002	NA	Blair Creek	4.9	1.10	3.1	.73	.07
A7	06/20/1995	NA	Current River upstream from Blue Spring	5.7	.79	2.7	.59	.08
A8	06/11/2002	NA	Current River at Van Buren	4.5	.52	2.4	.37	.06
A9	10/16/1997	NA	Current River upstream from Big Spring	4.7	.89	2.5	.47	.07
A10	10/16/1997	NA	Big Spring orifice	6.0	2.60	3.3	1.80	.13
	06/11/2002			4.7	.77	2.3	.53	.08
A11	10/16/1997	NA	Big Spring branch	4.2	1.80	2.2	1.20	.10
A12	10/16/1997	NA	Current River downstream from Big Spring	4.4	1.10	2.4	.59	.09
A13	06/10/2002	NA	Eleven Point River at Thomasville	3.5	.35	1.8	.27	.06
A14	06/12/2002	NA	Spring Creek tributary	5.2	.62	3.2	.44	.09
A15	06/25/2002	NA	Spring Creek	4.6	.55	2.4	.36	.09
A16	06/12/2002	NA	McCormack Spring	5.4	.70	2.4	.46	.08
A17	06/10/2002	NA	Greer Spring	4.6	1.40	2.6	.80	.09
A18	06/12/2002	NA	Hurricane Creek	3.9	.48	1.8	.30	.07
A19	06/10/2002	NA	Eleven Point River at Bardley	3.2	.66	1.6	.30	.05
A20	10/28/1992	NA	Paddy Creek near Slabtown Spring[a]	6.2	.47	1.7	.53	.04

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992–2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier (fig. 1)	Date (mm/dd/yyyy)	Distance downstream from mining activity (miles)	Site name	Alumimun (% wt)	Calcium (% wt)	Iron (% wt)	Magnesium (% wt)	Phosphorous (% wt)
Group B (Near-mining sites; within 7.5 miles downstream from mining activity)								
B1	04/29/2002	2.5	Courtois Creek near Courtois	5.4	2.10	3.8	1.20	0.07
B2	04/30/2002	4.0	Strother Creek near Goodland	4.2	3.00	2.5	1.80	.07
B3	04/30/2002	4.7	Neals Creek near Goodland	3.8	5.10	2.2	.77	.07
B4	09/18/1995	6.3	Strother Creek near Redmondville[a]	2.5	3.60	1.2	.39	.06
B5	05/06/2002	2.3	Bills Creek near Greeley	4.2	1.20	2.5	.54	.06
B6	09/11/1995	.6	West Fork Black River at West Fork[a]	4.2	.89	1.9	.52	.04
	05/06/2002			4.3	.87	2.5	.54	.07
B7	05/06/2002	.4	Bee Fork Black River near Reynolds	4.0	.96	2.9	.62	.08
B8	05/29/2002	2.7	Logan Creek near Corridon	3.4	2.00	3.0	1.20	.05
Group C (Distal-mining sites; more than 7.5 miles downstream from active mining)								
C1	04/29/2002	20.9	Huzzah Creek near Davisville	4.7	1.3	2.6	0.56	0.07
C2	04/29/2002	32.2	Huzzah Creek near Scotia	4.0	.96	2.6	.64	.07
C3	09/14/1995	15.7	Middle Fork Black River at Black[a]	5.6	.49	2.9	.48	.07
C4	04/30/2002	15.7	Middle Fork Black River near Black	4.9	.76	3.2	.57	.08
C5	10/27/1993	20.3	Middle Fork Black River near Lesterville[a]	4.6	.40	2.3	.35	.05
C6	09/13/1995	9.9	West Fork Black River near Centerville[a]	3.6	3.40	1.5	.44	.05
C7	09/13/1995	10.9	West Fork Black River at Centerville[a]	5.2	.60	2.2	.43	.04
	05/07/2002			3.7	.57	2.2	.38	.05
C8	10/26/1993	21.4	Black River near Lesterville[a]	3.7	.36	1.9	.29	.04
	05/07/2002			4.8	.55	3.1	.47	.06
C9	05/29/2002	21.8	Logan Creek at Ellington	3.8	.52	2.7	.39	.07
C10	06/20/1995	16.5	Current River downstream Blue Spring—es	5.3	1.28	2.3	.95	.09
	06/20/1995	16.5	Current River downstream Blue Spring—ws	4.9	1.44	2.6	.82	.10
TEC[c]				NA	NA	NA	NA	NA
PEC[c]				NA	NA	NA	NA	NA

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992-2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier	Potassium (% wt)	Sodium (% wt)	Titanium (% wt)	Arsenic (mg/kg)	Barium (mg/kg)	Beryllium (mg/kg)	Bismuth (mg/kg)	Cadmium (mg/kg)	Cerium (mg/kg)	Chromium (mg/kg)
Group A (Non-mining sites)										
A1	2.1	0.19	0.23	6.9	350	2.0	<10	0.8	61	43
A2	.88	.26	.25	4.9	340	1.0	<10	.5	61	32
	.85	.21	.24	<10	370	1.4	<10	<2	74	45
A3	.68	.14	.24	<10	420	1.5	<10	<2	88	51
A4	.82	.14	.29	14	390	2.2	<10	<2	91	63
A5	1.20	.20	.28	8.4	380	2.0	<10	.4	69	52
A6	.73	.10	.24	<10	315	2.7	<10	<2	74	73
A7	1.09	.19	.33	<10	386	2.3	<10	1.23	78	62
A8	.93	.17	.30	<10	406	2.0	<10	<2	78	58
A9	1.00	.19	.32	<10	370	2.0	<10	<2	84	60
A10	1.10	.09	.28	17	230	3.0	<10	<2	95	61
	1.00	.20	.31	11	402	2.2	<10	<2	85	54
A11	.86	.13	.23	11	220	2.0	<10	<2	77	54
A12	.89	.16	.29	10	310	2.0	<10	<2	78	60
A13	.84	.16	.28	10	360	1.4	<10	<2	74	47
A14	.86	.12	.30	18	362	2.2	<10	<2	90	67
A15	.85	.13	.31	<10	367	2.1	<10	<2	79	59
A16	.87	.14	.32	17	321	2.4	<10	<2	90	55
A17	1.00	.14	.33	15	438	2.2	<10	<2	97	66
A18	.78	.14	.31	11	355	1.8	<10	<2	84	54
A19	.83	.15	.25	<10	328	1.5	<10	<2	63	44
A20	1.20	.24	.36	4.1	410	2.0	<10	.2	84	78

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992-2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier	Potassium (% wt)	Sodium (% wt)	Titanium (% wt)	Arsenic (mg/kg)	Barium (mg/kg)	Beryllium (mg/kg)	Bismuth (mg/kg)	Cadmium (mg/kg)	Cerium (mg/kg)	Chromium (mg/kg)
Group B (Near-mining sites; within 7.5 miles downstream from mining activity)										
B1	0.95	0.18	0.28	22	580	1.8	<10	2.3	78	74
B2	.73	.14	.20	35	230	2.2	<10	<2	62	53
B3	.70	.15	.20	10	300	1.4	<10	<2	57	44
B4	.63	.23	.14	7.2	240	1.0	<10	2.2	38	24
B5	.79	.16	.24	17	300	1.7	<10	<2	78	60
B6	.93	.26	.29	10	310	2.0	<10	3.3	65	38
	.83	.17	.26	14	390	1.7	<10	<2	71	50
B7	.74	.16	.26	<10	470	1.9	<10	<2	83	50
B8	.60	.11	.20	<20	375	2.0	<20	9.9	76	60
Group C (Distal-mining sites; more than 7.5 miles downstream from active mining)										
C1	0.94	0.24	0.27	<10	400	1.5	<10	<2	78	51
C2	.91	.23	.27	10	450	1.3	<10	<2	72	72
C3	1.60	.20	.32	14	390	3.0	<10	.8	98	53
C4	1.30	.16	.26	18	370	2.1	<10	<2	89	61
C5	1.40	.25	.26	11	410	2.0	<10	.7	78	47
C6	.77	.22	.25	5.5	310	2.0	<10	1	59	31
C7	.84	.21	.29	6.1	290	2.0	<10	.6	79	45
	.71	.16	.24	<10	310	1.6	<10	<2	68	55
C8	.99	.26	.27	7.6	370	2.0	<10	.6	76	42
	1.10	.19	.30	13	400	2.0	<10	<2	87	52
C9	.68	.11	.22	<20	383	<2	<20	<3	74	59
C10	.99	.15	.25	<10	278	2.3	<10	1.60	64	58
	1.02	.19	.24	<10	369	2.1	<10	1.66	70	74
TEC[c]	NA	NA	NA	9.79	NA	NA	NA	0.99	NA	43.4
PEC[c]	NA	NA	NA	33.0	NA	NA	NA	4.98	NA	111

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992–2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier	Cobalt (mg/kg)	Copper (mg/kg)	Europium (mg/kg)	Gallium (mg/kg)	Gold (mg/kg)	Holmium (mg/kg)	Lanthanum (mg/kg)	Lead (mg/kg)	Lithium (mg/kg)	Manganese (mg/kg)
Group A (Non-mining sites)										
A1	15	26	<2	9	<8	<4	32	80	20	510
A2	16	17	<2	7	<8	<4	30	33	20	610
	20	130	<2	8.7	<8	<4	33	[b]210	21	660
A3	38	85	<2	10	<8	<4	32	53	22	2,000
A4	24	142	<2	11	<8	<4	42	97	30	1,740
A5	16	19	<2	10	<8	<4	37	24	31	760
A6	29	97	<2	11	<8	<4	36	61	29	1,760
A7	22	27	<2	14	<8	<4	45	24	37	843
A8	18	138	<2	10	<8	<4	40	85	26	1,480
A9	26	29	<2	12	<8	<4	42	33	31	1,600
A10	28	40	2	24	<8	<4	57	53	43	1,300
	16	61	<2	10	<8	<4	43	49	26	1,190
A11	19	39	<2	14	<8	<4	42	45	28	750
A12	31	31	<2	13	<8	<4	42	35	29	1,500
A13	12	166	<2	7.9	<8	<4	36	72	20	892
A14	20	85	<2	12	<8	<4	42	79	31	1,740
A15	14	108	<2	9.9	<8	<4	42	72	26	1,230
A16	10	89	<2	12	<8	<4	50	72	32	823
A17	20	99	<2	9.9	<8	<4	46	84	27	2,210
A18	12	74	<2	9	<8	<4	42	48	22	1,280
A19	10	80	<2	7.4	<8	<4	33	44	19	739
A20	9	15	<2	14	<8	<4	55	27	38	170

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992–2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier	Cobalt (mg/kg)	Copper (mg/kg)	Europium (mg/kg)	Gallium (mg/kg)	Gold (mg/kg)	Holmium (mg/kg)	Lanthanum (mg/kg)	Lead (mg/kg)	Lithium (mg/kg)	Manganese (mg/kg)
Group B (Near-mining sites; within 7.5 miles downstream from mining activity)										
B1	88	240	<2	13	<8	<4	37	510	32	1,500
B2	1,200	180	<2	6.6	<8	<4	30	860	28	4,200
B3	76	120	<2	8.2	<8	<4	28	150	22	1,400
B4	150	31	<2	5	<8	<4	21	200	20	910
B5	160	110	<2	10	<8	<4	34	940	29	1,500
B6	43	36	<2	8	<8	<4	34	950	30	490
	150	98	<2	12	<8	<4	33	420	27	4,700
B7	67	150	<2	11	<8	<4	36	230	26	4,300
B8	74	180	<4	8.8	<10	<7	32	1,410	24	6,470
Group C (Distal-mining sites; more than 7.5 miles downstream from active mining)										
C1	18	110	<2	12	<8	<4	37	100	27	950
C2	19	110	<2	10	<8	<4	34	[b]88	24	1,000
C3	31	37	<2	11	<8	<4	46	100	30	760
C4	49	120	<2	12	<8	<4	38	160	26	1,400
C5	29	32	<2	11	<8	<4	38	100	26	1,500
C6	18	22	<2	7	<8	<4	31	170	20	450
C7	20	29	<2	10	<8	<4	40	100	30	280
	30	120	<2	9.4	<8	<4	30	170	25	1,100
C8	25	21	<2	8	<8	<4	37	84	22	1,500
	31	87	<2	13	<8	<4	39	[b]82	26	1,700
C9	31	140	<3	9.1	<10	<6	29	93	23	2,330
C10	20	35	<2	13	<8	<4	40	27	40	388
	27	47	<2	11	<8	<4	38	25	32	1,580
TEC[c]	NA	31.6	NA	NA	NA	NA	NA	35.8	NA	NA
PEC[c]	NA	149	NA	NA	NA	NA	NA	128	NA	NA

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992–2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier	Molybdenum (mg/kg)	Neodybium (mg/kg)	Nickel (mg/kg)	Niobium (mg/kg)	Scandium (mg/kg)	Silver (mg/kg)	Strontium (mg/kg)	Tantalum (mg/kg)	Thorium (mg/kg)	Tin (mg/kg)
Group A (Non-mining sites)										
A1	<2	28	28	2	7	0.2	65	<40	7.0	5
A2	<2	28	21	12	5	.1	51	<40	10.0	5
	<2	31	27	14	5.9	<2	41	<40	9.0	11
A3	2.1	32	37	6.3	6.6	<2	34	<40	7.7	11
A4	2	41	40	8.4	9.2	<2	34	<40	7.3	17
A5	<2	34	30	9	8	.2	46	<40	9.0	<5
A6	2.6	36	45	8.3	9.5	<2	30	<40	8.9	16
A7	<2	41	36	16	9.7	<2	48	<40	11.9	<5
A8	<2	34	33	8.8	7.5	<2	36	<40	7.1	23
A9	<2	41	29	17	8	<2	43	<40	10.0	<5
A10	2	67	51	12	12	<2	40	<40	11.0	<5
	<2	40	35	11	8.5	<2	39	<40	6.5	7.3
A11	<2	49	35	10	8	<2	38	<40	6.0	<5
A12	<2	41	34	16	8	<2	40	<40	9.0	<5
A13	2.3	28	24	8.1	5.7	<2	36	<40	6.4	16
A14	3.1	36	41	9.4	8.8	<2	29	<40	6.8	12
A15	2	35	34	11	7.5	<2	34	<40	6.8	8.9
A16	<2	47	35	13	10	<2	33	<40	7.9	7.9
A17	2.9	38	42	5.7	7.6	<2	37	<40	7.3	18
A18	<2	35	27	7.1	6.8	<2	31	<40	6.7	12
A19	<2	28	24	7.5	5.4	<2	34	<40	4.9	8.6
A20	<2	46	23	11	10	.1	52	<40	15.0	<5

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992–2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier	Molybdenum (mg/kg)	Neodybium (mg/kg)	Nickel (mg/kg)	Niobium (mg/kg)	Scandium (mg/kg)	Silver (mg/kg)	Strontium (mg/kg)	Tantalum (mg/kg)	Thorium (mg/kg)	Tin (mg/kg)
Group B (Near-mining sites; within 7.5 miles downstream from mining activity)										
B1	2	34	100	14	8.6	<2	49	<40	14.0	18
B2	6.5	30	580	<4	7.4	<2	48	<40	11.0	15
B3	<2	27	140	10	6.1	<2	52	<40	9.1	6.8
B4	<2	19	160	8	3	.1	71	<40	2.0	5
B5	<2	32	140	9.3	6.6	<2	48	<40	11.0	16
B6	<2	30	73	7	6	.3	55	<40	9.0	5
	<2	28	180	<4	7	<2	43	<40	11.0	11
B7	2	36	76	<4	7.6	<2	42	<40	9.5	18
B8	4.1	29	91	<7	6.5	<4	36	<70	7.8	27
Group C (Distal-mining sites; more than 7.5 miles downstream from active mining)										
C1	<2	33	29	16	7.3	<2	47	<40	12.0	12
C2	<2	30	30	14	6.4	<2	48	<40	11.0	18
C3	<2	45	50	8	10	.2	55	<40	10.0	5
C4	2	40	78	18	9	<2	42	<40	12.0	19
C5	<2	39	37	9	9	.2	56	<40	12.0	<5
C6	<2	29	31	7	5	.2	61	<40	8.0	5
C7	<2	39	39	6	9	.2	50	<40	10.0	5
	<2	30	44	12	6.2	<2	38	<40	9.4	18
C8	<2	34	29	6	7	.2	51	<40	9.0	<5
	<2	37	42	18	8.5	<2	43	<40	12.0	11
C9	<3	26	38	<6	6.6	<3	28	<60	6.6	44
C10	<2	42	36	13	8.9	<2	45	<40	11.3	<5
	<2	34	47	12	7.9	<2	57	<40	9.1	<5
TEC[c]	NA	NA	22.7	NA	NA	NA	NA	NA	NA	NA
PEC[c]	NA	NA	48.6	NA	NA	NA	NA	NA	NA	NA

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992–2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier	Uranium (mg/kg)	Vanadium (mg/kg)	Ytterbium (mg/kg)	Yttrium (mg/kg)	Zinc (mg/kg)	Bulk grain size distribution Percentage		
						Coarse	Silt	Clay
Group A (Non-mining sites)								
A1	2.6	53	2.0	21	180	--	--	--
A2	3.4	53	2.0	20	150	--	--	--
	<100	58	2.2	20	100	96.8	2.5	0.6
A3	<100	69	2.7	26	83	98.7	1.0	.3
A4	<100	73	3.3	35	280	99.3	.4	.3
A5	4.4	63	3.0	29	64	--	--	--
A6	<100	81	3.2	33	159	99.2	.3	.4
A7	<100	81	3.0	30	81	97.7	1.1	1.2
A8	<100	63	2.5	28	134	99.1	.7	.2
A9	<100	70	3.0	28	74	98.5	1.0	.6
A10	<100	90	4.0	44	160	98.0	1.0	1.0
	<100	66	2.8	30	114	95.0	4.0	1.0
A11	<100	62	3.0	32	110	99.1	.4	.4
A12	<100	68	3.0	28	87	98.6	.8	.6
A13	<100	50	1.8	20	142	97.2	2.2	.5
A14	<100	80	2.4	27	166	98.8	.8	.3
A15	<100	64	2.5	28	127	97.8	1.5	.6
A16	<100	72	3.0	32	152	91.6	7.0	1.4
A17	<100	74	2.7	31	151	98.0	1.6	.5
A18	<100	51	2.4	27	128	98.0	1.6	.3
A19	<100	43	1.9	21	115	98.3	1.4	.3
A20	4.8	87	3.0	31	54	--	--	--

Table 1. Quantitative elemental analysis of the less than 63-micrometer fraction and bulk sample grain size distribution of streambed-sediment samples, threshold effects concentrations (TEC), and probable effects concentrations (PEC) for selected trace elements, 1992–2002.—Continued

[mm/dd/yyyy, month/day/year; % wt, percent by weight; NA, not applicable; es, east side; ws, west side; mg/kg, milligrams per kilogram; <, less than; shaded cells indicate PEC exceedance; --, no data]

Site identifier	Uranium (mg/kg)	Vanadium (mg/kg)	Ytterbium (mg/kg)	Yttrium (mg/kg)	Zinc (mg/kg)	Bulk grain size distribution Percentage		
						Coarse	Silt	Clay
Group B (Near-mining sites; within 7.5 miles downstream from mining activity)								
B1	<100	97	2.7	24	850	98.5	1.1	.4
B2	<100	74	3.0	29	2,700	97.1	1.9	1.0
B3	<100	63	2.0	18	810	97.3	1.7	1.0
B4	2.2	35	1.0	13	1,200	--	--	--
B5	<100	78	2.3	21	1,300	98.4	.8	.8
B6	3.6	63	2.0	24	460	--	--	--
	<100	74	2.6	24	720	98.4	1.1	.4
B7	<100	70	3.4	33	200	98.5	1.2	.3
B8	<200	66	2.5	26	1,060	99.4	.2	.4
Group C (Distal-mining sites; more than 7.5 miles downstream from active mining)								
C1	<100	78	2.2	20	120	96.4	3.4	.2
C2	<100	74	2.1	19	210	99.4	.4	.2
C3	4	79	4.0	38	210	--	--	--
C4	<100	83	3.4	32	340	98.9	.6	.4
C5	4.1	69	28	3	150	--	--	--
C6	2.7	52	2.0	22	200	--	--	--
C7	3.7	74	3.0	33	120	--	--	--
	<100	63	2.5	24	140	99.5	.5	<0.1
C8	3.9	56	2.0	24	91	--	--	--
	<100	84	3.1	30	140	98.0	1.3	.7
C9	<200	69	2.1	22	130	99.5	.1	.4
C10	<100	76	2.1	31	86	98.2	.6	1.2
	<100	72	2.5	26	86	99.5	.3	.3
TEC[c]	NA	NA	NA	NA	121	NA	NA	NA
PEC[c]	NA	NA	NA	NA	459	NA	NA	NA

[a] Sample collected as part of the National Water-Quality Assessment (NAWQA) Program.

[b] Anthropogenic lead (lead shot) contaminated sample.

[c] Concentrations from MacDonald and others, 2000.

Table 2. Optical mineralogy of non-magnetic fraction (C3) of heavy mineral concentrate for streambed-sediment samples, 1995–2002.

[All values are in percent; --, not detected; es, east side; ws, west side; contam, contaminated with man-made material]

Site identifier (fig. 1)	Sample name	Date	Dolomite	Limonite oxidized rock fragments	Zircon	Apatite	Rutile	Pyrite	Tourmaline	Anatase	Sphene	Barite	Cassiterite
				Group A (Non-mining sites)									
A2	West Fork Black River near Greeley	05/06/2002	5	50	--	5	--	25	--	Trace	5	--	--
A3	Sinking Creek near Redford	05/07/2002	30	40	Trace	25	--	--	--	5	--	--	--
A4	Big Creek at Mauser Mill	05/29/2002	5	80	5	5	--	--	--	5	--	--	--
A6	Blair Creek	05/29/2002	20	60	Trace	20	--	--	--	--	--	--	--
A7	Current River upstream from Blue Spring	06/20/1995	10	10	50	2	20	Trace	5	--	--	--	--
A8	Current River at Van Buren	06/11/2002	50	--	Trace	40	Trace	--	--	Trace	10	--	--
A9	Current River upstream from Big Spring	[a]10/16/1997	--	5	1	--	2	6	4	--	3	--	8
A10	Big Spring orifice	[a]10/16/1997	6	4	1	8	2	7	3	--	--	5	--
		06/11/2002	99	--	--	Trace	--	--	--	--	--	--	--
A11	Big Spring branch	[a]10/16/1997	2	3	1	--	7	5	4	--	--	6	--
A12	Current River downstream from Big Spring	[a]10/16/1997	7	4	1	11	2	6	3	10	--	5	--
A13	Eleven Point River at Thomasville	06/10/2002	35	30	Trace	35	--	--	--	--	--	--	--
A14	Spring Creek Tributary	06/12/2002	20	50	5	20	--	--	--	--	--	--	--
A15	Spring Creek	06/25/2002	--	5	--	90	2	--	--	3	--	--	--
A16	McCormack Spring	06/12/2002	90	--	--	10	Trace	--	--	Trace	--	--	--
A17	Greer Spring	06/10/2002	90	5	--	5	--	--	--	--	--	--	--
A18	Hurricane Creek	06/12/2002	15	--	2	80	--	--	--	--	2	--	--
A19	Eleven Point River at Bardley	06/10/2002	90	--	Trace	Trace	Trace	--	--	Trace	--	Trace	--
				Group B (Near-mining sites; within 7.5 miles downstream from mining activity)									
B1	Courtois Creek near Courtois	04/29/2002	30	60	--	--	--	Trace	--	--	--	--	--
B2	Strother Creek near Goodland	04/30/2002	90	10	--	--	--	--	--	--	--	--	--
B3	Neals Creek near Goodland	04/30/2002	70	25	Trace	Trace	--	Trace	--	--	--	--	--
B5	Bills Creek near Greeley	05/06/2002	20	75	--	Trace	--	Trace	--	Trace	--	Trace	--
B6	West Fork Black River at West Fork	[a]05/06/2002	--	--	--	4	5	3	--	2	--	--	--
B7	Bee Fork Black River near Reynolds	05/06/2002	40	20	5	20	--	10	--	Trace	Trace	--	--
B8	Logan Creek near Corridon	05/29/2002	--	99	--	--	--	Trace	--	--	--	--	--
				Group C (Distal-mining sites; more than 7.5 miles downstream from mining activity)									
C1	Huzzah Creek near Davisville	04/29/2002	30	60	--	10	--	--	--	Trace	--	--	--
C2	Huzzah Creek near Scotia	04/29/2002	20	--	--	60	Trace	5	--	5	3	--	--
C4	Middle Fork Black River near Black	04/30/2002	50	30	5	10	--	Trace	Trace	Trace	--	--	--
C7	West Fork Black River at Centerville	05/07/2002	20	75	--	Trace	--	Trace	--	Trace	--	Trace	--
C8	Black River near Lesterville	05/07/2002	20	60	--	20	--	--	--	--	--	--	--
C9	Logan Creek at Ellington	05/29/2002	Trace	98	--	Trace	--	Trace	--	--	--	--	--
C10	Current River downstream from Blue Spring—es	06/20/1995	40	5	40	1	4	Trace	10	--	--	Trace	Trace
	Current River downstream from Blue Spring—ws	06/20/1995	30	50	10	1	5	Trace	--	--	--	Trace	--

Table 2. Optical mineralogy of non-magnetic fraction (C3) of heavy mineral concentrate for streambed-sediment samples,1995–2002.—Continued

[All values are in percent; --, not detected; es, east side; ws, west side; contam, contaminated with man-made material]

Site identifier (fig. 1)	Galena	Pyroxene	Hematite	Amphibole	Mica	Lead contam	Zinc (silvery metal)	Brass	Glass
Group A (Non-mining sites)									
A2	5	--	--	--	--	Trace	--	--	--
A3	--	--	--	--	--	--	--	--	--
A4	--	--	--	--	--	--	--	--	--
A6	--	--	--	--	--	--	--	--	--
A7	--	--	--	--	--	--	--	--	--
A8	--	--	--	--	--	--	--	--	Trace
A9	--	--	--	--	--	--	7	--	--
A10	--	--	--	--	--	9	10	--	--
	--	--	Trace	--	--	--	--	--	Trace
A11	--	--	--	--	--	8	9	--	--
A12	--	--	--	--	--	8	9	--	--
A13	--	--	Trace	--	--	--	--	--	--
A14	--	--	5	--	--	--	--	--	--
A15	--	--	--	--	--	--	--	--	Trace
A16	--	--	Trace	--	--	--	Trace	--	--
A17	--	--	Trace	--	--	--	--	--	--
A18	--	--	1	--	--	--	--	--	--
A19	--	5	--	5	Trace	--	--	--	--
Group B (Near-mining sites; within 7.5 miles downstream from mining activity)									
B1	--	Trace	--	--	--	--	--	--	--
B2	--	--	--	--	--	--	--	--	--
B3	--	--	--	--	--	--	--	--	--
B5	--	--	--	--	Trace	--	--	--	--
B6	--	--	--	--	1	--	--	--	--
B7	Trace	Trace	--	--	Trace	--	--	--	--
B8	--	--	--	--	--	--	--	--	Trace
Group C (Distal-mining sites; more than 7.5 miles downstream from mining activity)									
C1	--	--	--	--	--	--	--	--	--
C2	5	--	--	--	--	Trace	--	--	--
C4	--	--	--	--	--	--	--	--	--
C7	--	--	--	--	--	--	--	--	--
C8	--	--	--	--	--	Trace	--	--	--
C9	--	--	--	--	--	--	--	--	--
C10	Trace	--	--	--	--	--	--	--	--

[a] No percentages given; numbers represent decreasing order of abundance.

Table 3. Summary statistics for Mississippi Valley Type-related metals and chromium in streambed-sediment samples, 1992–2002.

[All concentrations in milligrams per kilogram; proximity-to-mining group—A, non-mining sites; B, near-mining sites (less than 7.5 miles downstream from mining activity); C, distal-mining sites (more than 7.5 miles downstream from mining activity); Q5, 5th percentile; Q25, 25th percentile; Q50, 50th percentile; Q75, 75th percentile; Q95, 95th percentile; Interquartile range, difference between Q75 and Q25]

	Arsenic				Cadmium				Cobalt				Copper			
	All sites	Proximity-to-mining group			All sites	Proximity-to-mining group			All sites	Proximity-to-mining group			All sites	Proximity-to-mining group		
		A	B	C		A	B	C		A	B	C		A	B	C
Number of samples	44	22	9	13	44	22	9	13	44	22	9	13	44	22	9	13
Minimum	4.1	4.1	7.2	5.5	.2	.2	2.0	.6	9	9	43	18	15	15	31	21
Maximum	35.0	18.0	35.0	20.0	9.9	2.0	9.9	3.0	1,200	38	1,200	49	240	166	240	140
Range	30.9	13.9	27.8	14.5	9.7	1.8	7.9	2.4	1,191	29	1,157	31	225	151	209	119
Mean	12.0	10.8	16.1	11.2	1.9	1.7	3.1	1.5	63	19	223	27	83	73	127	70
Standard Deviation	5.4	3.5	8.7	4.2	1.4	0.6	2.6	.7	179	8	369	9	54	46	69	45
Q5	5.3	4.6	7.2	5.6	.5	.3	<2	.6	10	10	43	18	18	16	31	21
Q25	<10	<10	<10	<10	1.6	<2	<2	.8	18	14	72	20	32	29	83	31
Q50 median	<10	<10	14.0	<10	<2	<2	<2	1.7	25	19	88	27	85	77	120	47
Q75	14.0	11.0	20.5	13.3	<2	<2	2.6	2.0	35	24	153	31	120	99	180	113
Q95	20.6	17.4	35.0	19.7	3.1	2.0	9.9	2.9	153	34	1,200	46	180	152	240	137
Interquartile range	4.0	1.0	10.5	3.3	.4	0	.6	1.2	17	10	81	11	88	70	97	82

	Lead				Nickel				Zinc				Chromium			
	All sites	Proximity-to-mining group			All sites	Proximity-to-mining group			All sites	Proximity-to-mining group			All sites	Proximity-to-mining group		
		A	B	C		A	B	C		A	B	C		A	B	C
Number of samples	44	22	9	13	44	22	9	13	44	22	9	13	44	22	9	13
Minimum	24	24	150	25	21	21	73	29	54	54	200	86	24	32	24	31
Maximum	1,410	210	1,410	170	580	51	580	78	2,700	280	2,700	340	78	78	74	74
Range	1,386	186	1,260	145	559	30	507	49	2,646	226	2,500	254	54	46	50	43
Mean	190	63	630	100	64	33	171	41	321	128	1,033	156	54	56	50	54
Standard Deviation	296	40	432	46	88	8	158	13	481	49	714	70	12	10	14	12
Q5	25	24	150	25	24	22	73	29	71	60	200	86	32	39	24	33
Q25	49	35	223	84	30	27	87	31	112	87	655	113	47	51	43	47
Q50 median	84	53	510	100	37	34	140	38	146	128	850	140	54	57	50	53
Q75	165	79	943	115	51	37	165	45	210	152	1,225	203	61	62	60	60
Q95	943	142	1,410	170	166	47	580	74	1,230	220	2,700	321	74	75	74	74
Interquartile range	116	44	720	31	21	10	78	14	98	65	570	90	14	11	17	13