

Trace Elements and Lead Isotopes in Modern Streambed and Terrace Sediment—Determination of Current and Premining Geochemical Baselines

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Chapter E12 of

**Integrated Investigations of Environmental Effects of Historical
Mining in the Animas River Watershed, San Juan County, Colorado**

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Chapter E12

Trace Elements and Lead Isotopes in Modern Streambed and Terrace Sediment—Determination of Current and Premining Geochemical Baselines

By Stanley E. Church, David L. Fey, and Daniel M. Unruh

Abstract

The Animas River watershed study area, in southwestern Colorado, contains a Precambrian crystalline basement overlain by Paleozoic, Mesozoic, and Eocene-age sedimentary rock, and a Tertiary volcanic cover. An Oligocene volcanic sequence exceeding 1 kilometer in thickness was deposited by a now-eroded complex of volcanic calderas; it forms the majority of the rock exposed in the study area. This volcanic sequence was heavily faulted, hydrothermally altered, and mineralized in Oligocene and Miocene time with base and precious metals. The resulting sulfide mineral deposits in this region were exploited beginning in 1871.

Two primary drainages, the upper Animas River on the east and Mineral Creek on the west, follow the ring fractures of the Silverton caldera. The third primary drainage, Cement Creek, drains the center of the caldera. Assessment of the extent to which historical mining and milling practices have affected these stream reaches and their tributaries in the Animas River watershed has demonstrated that concentrations of copper, lead, zinc, arsenic, cadmium, silver, manganese, iron, and perhaps aluminum have been enriched in modern streambed sediment relative to those found prior to mining. Concentrations of a suite of deposit-related trace elements—copper, lead, zinc, arsenic, cadmium, and silver—are elevated downstream from major mining and milling sites.

The Sunnyside Eureka Mill, a large flotation mill, operated at a capacity of 500 tons per day or more from 1917 to 1930 on the Animas River upstream from Silverton. It discharged tailings either directly into the Animas River or in settling ponds on the flood plain immediately downstream of the mill. Mapping that compares concentration data from both the premining and postmining eras indicates that this mill still has a profound effect on modern streambed-sediment geochemistry. Contamination from historical mining and milling has affected the geochemistry of streambed sediment in the Animas River more than that of streambed sediment in either Cement Creek or Mineral Creek. These observations are confirmed by systematic changes with time of the $^{206}\text{Pb}/^{204}\text{Pb}$

value in streambed sediment in all the drainages downstream of historical mine and mill sites. The isotopic compositions of lead are systematically closer to that in the mill tailings than in premining streambed-sediment samples from terrace deposits throughout the basin.

Premining geochemical baseline data clearly show that there were local geochemical anomalies in streambed sediment. Downstream from Eureka, the premining geochemical baseline for zinc was about 1,000 ppm; that for lead was about 400 ppm. The mineral deposits were exposed at the time of their discovery in 1873. Other premining baseline geochemical anomalies occur in both Cement and Mineral Creeks.

In comparison with published sediment-quality guidelines, arsenic, copper, lead, and zinc exceed recommended values for toxicological effects in many of the major stream reaches. Prior to mining, both lead and zinc concentrations exceeded the recommended values in the Animas River downstream from Eureka to Elk Park. Lead exceeded the recommended value in both Cement and Mineral Creeks. However, concentrations of copper, cadmium, and silver in all three drainages and their tributaries did not exceed the recommended sediment-quality values.

Introduction

Acidic drainage, the result of either weathering of hydrothermally altered rock or of historical mining activities, has an adverse effect on streams (fig. 1). In particular, streams that have a pH less than 4 will not support most aquatic life. When acidic metal-bearing water mixes with more neutral water, iron and aluminum oxyhydroxides and oxysulfates precipitate, forming colloids that can coat the gills of fish and affect respiration. Upon precipitation to the streambed, this fine-grained chemical sediment coats the rock and fills the interstices, reducing or eliminating stream habitat for invertebrates (Besser and others, this volume, Chapter D; Besser and Brumbaugh, this volume, Chapter E18) and affecting spawning habitat for trout (Milhous, 1999). In this report, we examine the current state of selected



Figure 1. Streambed of upper Cement Creek showing iron-coated substrate caused by acidic drainage.

streams (1995–2000) to determine how much of an effect acidic drainage, whether from weathering of altered rock or from historical mining and milling, has had on the surface water and aquatic and riparian habitats of the Animas River watershed study area.

Streambed-sediment geochemical studies have been used in mineral exploration programs for more than 50 years, using the principle that the presence of elevated trace-element concentrations may be an indication of undiscovered mineral deposits upstream. Erosion of these mineral deposits or the altered rock surrounding them provides tangible evidence of their presence in the watershed. In the case of historical mining districts such as the Red Mountain, Eureka, and Animas districts discussed here, no historical data are available to indicate either what the concentrations of several important trace elements in water or streambed sediment might have been, or whether aquatic life was present near or downstream from these deposits prior to mining. For this report, we investigated the concentrations in and sources of deposit-related trace elements to streambed sediment in tributaries of the Animas River near Silverton in southwestern Colorado. We also used streambed-sediment data from terrace deposits to determine the amount of metals present in the streambed sediment prior to historical mining.

The mineral deposit type, its production history, and the geologic and climatic settings are important factors that determine the effect that a mineral deposit will have on the environment. Mineral deposit types that occur within the Animas River watershed study area are acid-sulfate epithermal vein, polymetallic vein, breccia-pipe or chimney deposits, and

at depth, porphyry copper-molybdenum deposits. The deposits have highly variable mineralogies that differ between deposit types. Ransome (1901), Burbank and Luedke (1968, 1969), Lipman and others (1976), Casadevall and Ohmoto (1977), and Bove and others (this volume, Chapter E3), as well as many others, described the vein deposits as quartz veins or stockworks that generally contain pyrite, galena, sphalerite, chalcopyrite, and arsenopyrite, with variable and generally minor amounts of free gold, tetrahedrite, tennantite, proustite, and some tungsten minerals. Gangue minerals include quartz, adularia, rhodochrosite, pyroxmangite, barite, ankerite, and fluorite. The breccia-pipe deposits contain pyrite, arsenopyrite, galena, enargite, tetrahedrite, and tennantite, in a matrix of quartz, highly altered rock and clays, barite, and fluorite (Burbank and Luedke, 1968). None of the porphyry copper-molybdenum deposits are exposed at the surface or have been developed, but they are known from studies of hydrothermal alteration (Ringrose, 1982; Yager and others, 2000) and from subsurface drilling (Bove and others, this volume). Weathering of sulfide minerals from the mineral deposits and the hydrothermal alteration zones that surround them, particularly pyrite, results in the release of sulfuric acid that subsequently dissolves the remaining sulfide minerals and releases potentially toxic trace elements into the near-surface environment. Trace elements derived from mineralized areas and inactive mines are concentrated in streambed sediment downstream within the Animas River watershed.

Yager and Bove (this volume, Chapter E1, pl. 1) and Bove and others (this volume) summarize the geology, alteration, age of mineralization, and deposit types that are present

in the watershed. The mineral deposits in the study area were emplaced by hydrothermal events that postdate the formation of the San Juan and later the Silverton calderas. These calderas are large volcanic centers that formed in Oligocene time and erupted large volumes of volcanic rock that now covers most of the study area. Church, Mast, and others (this volume, Chapter E5) summarize the distribution of mines, mills, and large tailings deposits in the watershed; that report is the source for the numbering of mine, mill, smelter, and tailings repository sites in the chapter. Nash and Fey (this volume, Chapter E6) present the effects of mine waste in the basin, and Jones (this volume, Chapter C) presents a historical account of the development of the mining districts and the effects of technological development on mine production. Different mineral deposit types have different suites of associated trace elements. For purposes of this report, we focus on the distribution of a subset of trace elements that are specifically associated with the mineral deposits: copper, lead, zinc, arsenic, cadmium, and silver. We refer to this trace-element suite as the deposit-related trace elements. The major elements iron, manganese, and aluminum are also important in some geologic settings. In contrast, trace elements that are neither associated with nor enriched in these deposits are herein referred to as rock-forming elements; they include chromium, cobalt, nickel, strontium, titanium, vanadium, and the rare-earth elements, as well as many others.

The upper Animas River and Mineral Creek follow the Silverton caldera ring fractures (fig. 2; Yager and Bove, this volume, pl. 1). The volcanic rock in this arcuate fracture zone was rapidly weathered and eroded as a result of the intense fracturing and hydrothermal alteration. Today, surficial deposits in the stream valleys are mostly glacial, fluvial, and colluvial. Although there have been multiple glacial episodes during the past 2 million years (Atwood and Mather, 1932; Gillam, 1998), only glacial deposits of the most recent glaciation are recognized in the watershed. Mineral Creek and the upper Animas River have classic U-shaped valleys and both contain morainal deposits (Blair and others, 2002).

Fundamental time-frame differences are present in the data obtained from different sample media collected in the Animas River watershed study. Water-quality data provide an instantaneous measure of the concentrations of constituents in the water column (Kimball and others, this volume, Chapter E9; Wright, Simon, and others, this volume, Chapter E10; Leib and others, this volume, Chapter E11). The concentrations of the trace elements in water can vary widely depending on streamflow conditions, pH, ground- and surface-water flow, vegetation uptake, and the interaction of these flows with the various sources of trace elements. Suspended-sediment samples provide data on the concentrations of trace elements in the finest grain-size fraction being transported in suspension in the water column and are dominated by colloidal sediment in watersheds affected by acidic drainage from historical mining activity (Kimball and others, 1995; Church, Holmes, and others, 1993; Church, Kimball, and others, 1997). In contrast, streambed-sediment samples integrate conditions

at a sample site over a longer time period because the streambed deposits are constructed of fine-grained colloidal material and detrital material derived from erosion. These materials accumulate at the sampling site under low-flow conditions for a period of several months following spring runoff.

Purpose and Scope

Major objectives of this study were four-fold. (They are listed here beginning with the primary goal.)

- Characterize the current aquatic environmental conditions in the Animas River watershed study area—that is, determine the present-day spatial distribution of deposit-related trace-element concentrations in streambed sediment throughout the area. This objective has been achieved through geochemical analysis of streambed-sediment samples collected at 50 sites throughout the area, from the headwaters where historical mining occurred south to the confluence with Elk Creek on the Animas River downstream from Silverton. Samples were collected during low flow (August–October) over a 5-year period from 1995 to 1999.
- Identify those sites that provide the major contributions of deposit-related trace elements to various stream reaches. This objective has been achieved through spatial analysis of contributions of the deposit-related trace elements from those sites to streambed sediment in specific stream reaches.
- Determine the premining geochemical baseline—that is, the concentrations of the deposit-related trace elements in streambed sediment that predate historical mining. This goal has been achieved by sampling premining fluvial deposits in old stream terraces (Church, Fey, and Blair, 2000). However, we were limited by the distribution, preservation, and recognition of, as well as the access to, these old stream-terrace deposits downstream from historical mining sites. Dendrochronology (Fey, Church, and Unruh, 2000), geomorphological data (Blair and others, 2002; Vincent and others, this volume, Chapter E16), historical records, and ^{14}C radiometric dating (Vincent and Elliott, this volume, Chapter E22; Verplanck and others, this volume, Chapter E15; Vincent and others, this volume) have been used to provide a chronology for the formation of these terrace deposits.
- Quantify the deposit-related trace-element contributions to modern streambed sediment from historical mine sites within the watershed. The data sets can then be used to evaluate the elevated deposit-related trace-element concentrations found in water and their potential detrimental effects on aquatic habitat in the Animas River study area (Besser and others, 2001; Besser and Brumbaugh, this volume; Besser and others, this volume; Wright, Simon, and others, this volume).

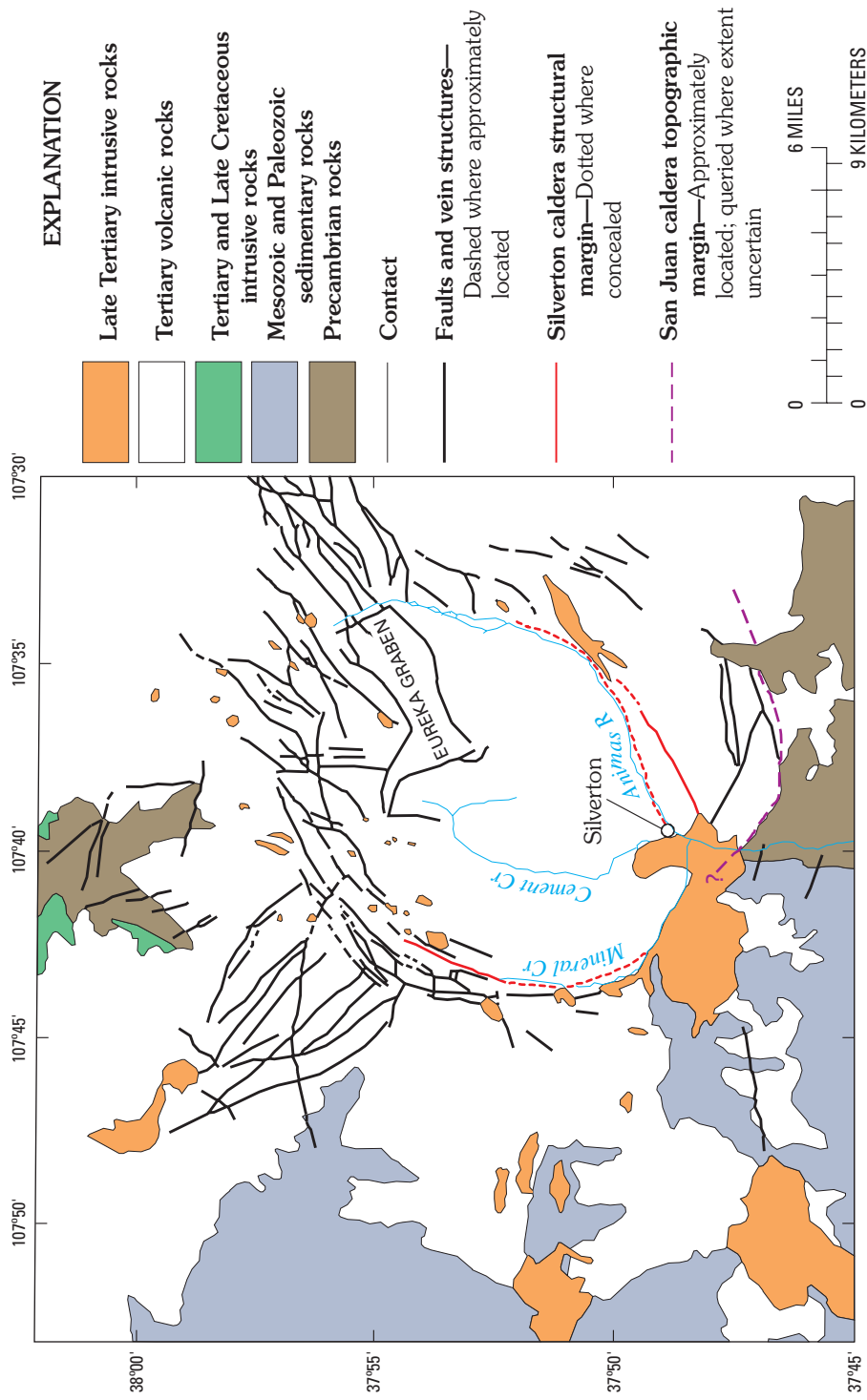


Figure 2. Generalized regional geology of the Animas River watershed study area, showing Animas River and Mineral Creek following the structural margin of Silverton caldera. In addition to the ring-fractures that were created when the Silverton and the earlier San Juan calderas formed, radial and graben faults, which hosted much of the subsequent vein mineralization, are shown schematically (modified from Casadevall and Ohmoto, 1977).

Previous Geochemical Investigations

Previous reconnaissance exploration streambed-sediment geochemical sampling of the watershed was conducted in the mid-1970s under the National Uranium Resource Evaluation (NURE) program (Shannon, 1980; Warren and others, 1981). NURE geochemical data (fig. 3) from small tributary streams (Hoffman and Buttleman, 1994) were used to prepare point-plot geochemical maps (not shown) of the Animas River watershed study area. These data were used to evaluate the sources of deposit-related trace elements in the small tributary drainage basins with areas of 1–4 mi² or more and to develop a sampling strategy for our subsequent geochemical work. The data were of adequate sample density and analytical quality to characterize the geochemistry of several tributary streams in our study area of the Animas River watershed. Geochemical graphs of the NURE data clearly show how the geology of the Animas River watershed study area controls the geochemistry of the streambed sediment in the Animas River. The NURE data also indicate the geochemical baseline at the time the samples were collected, the mid-1970s. The NURE geochemical maps of copper, lead, and zinc showed elevated concentrations of the deposit-related trace elements in streambed sediment collected from the Animas River watershed upstream of Silverton where metal concentrations exceed 20 times crustal abundance. Note that the maps did not give an indication of the premining geochemical baseline concentrations of the deposit-related trace elements in streambed sediment in the vicinity of Silverton, and no data for arsenic were available. However, the NURE geochemical maps provide a mid-1970s geochemical baseline that included the effects of historical mining on these stream reaches.

Sample Collection and Preparation

In order to meet the objectives of this study, we collected new streambed-sediment samples in Cement and Mineral Creeks, and the Animas River, as well as in their larger tributary streams. We used this suite of samples to evaluate stream reaches where major sources of deposit-related trace elements might be expected. It was also used to supplement and validate the previous (NURE) geochemical data set. The initial streambed-sediment sampling was conducted during the week of Oct. 16–20, 1995, during low-flow conditions. Supplementary sampling of the streambed sediment was done during late August and mid-October 1996, in mid- to late August or early September in 1997 and 1998, and in early October 1999 to evaluate annual and seasonal variability. Sample localities are in figure 3.

Streambed Sediment

Streambed-sediment samples were collected within selected stream reaches during low-flow conditions. At individual sites, the collector, using a plastic scoop, composited a streambed-sediment sample along 50–100 feet of the stream from several localities on both sides of the stream below the active water line. The composite sample was sieved through a minus-10-mesh stainless steel sieve (2 mm) into a plastic gold pan, and about 6.5 lb of fine-grained sediment sample was transported to the laboratory. The sample was air-dried at room temperature (about 20°C), split, and sieved to collect the minus-100-mesh (<150- μ m) size fraction. The sample material constitutes the very fine sand, silt, and clay-size fractions of the fluvial sediment in the active stream channel. The minus-100-mesh sample was used for all subsequent geochemical and lead-isotopic work.

Five samples of overbank sediment, composed of fine sand and silt deposited at high flow, were collected in the same manner from the sides of the stream channel to evaluate the effect of wetting and drying of the sediment on the availability of water-soluble trace elements. These samples were dry-sieved in the field and processed in the same manner in the laboratory; the data are discussed in Church, Kimball, and others (1997).

Terrace Deposits—Premining Sediment

Stream terraces¹ were sampled at a number of localities (fig. 4) in the study area by means of either trenches or cores through stream deposits preserved in cutbanks along the streams (Fey and others, 2000). Sediment samples collected for the determination of the premining geochemical baseline are from fluvial sand and gravel deposits preserved in the stream terraces (Blair and others, 2002). Fluvial deposits consist of gravel transported as bed load and deposited in the streambed and on bars, as well as finer grained sediment transported in suspension and deposited in overbank deposits. These sediments are found in the active stream channels and flood plains, and they are also found in stream terraces.

Terrace localities were selected on the basis of geomorphological mapping of unconsolidated deposits in the Animas River watershed study area. A surficial geologic strip map (Blair and others, 2002) of the major tributaries, representing an area about ½ mile in width and extending about 400 ft up the sides of the drainages above the active flood plain, has been completed for the upper Animas River and Cement and Mineral Creeks.

¹Stream terraces are former flood plains no longer constructed and maintained by the stream. They were abandoned because the stream became incised, because of changes in stream flow or climate, or for some other reason such as a landslide or tailings release that changed the stream dynamics and left these deposits elevated above the active channel and flood plain. An understanding of the geomorphic evolution of the stream valleys and these terraces is necessary to interpret the geochemical data (Church, Fey, and Blair, 2000).

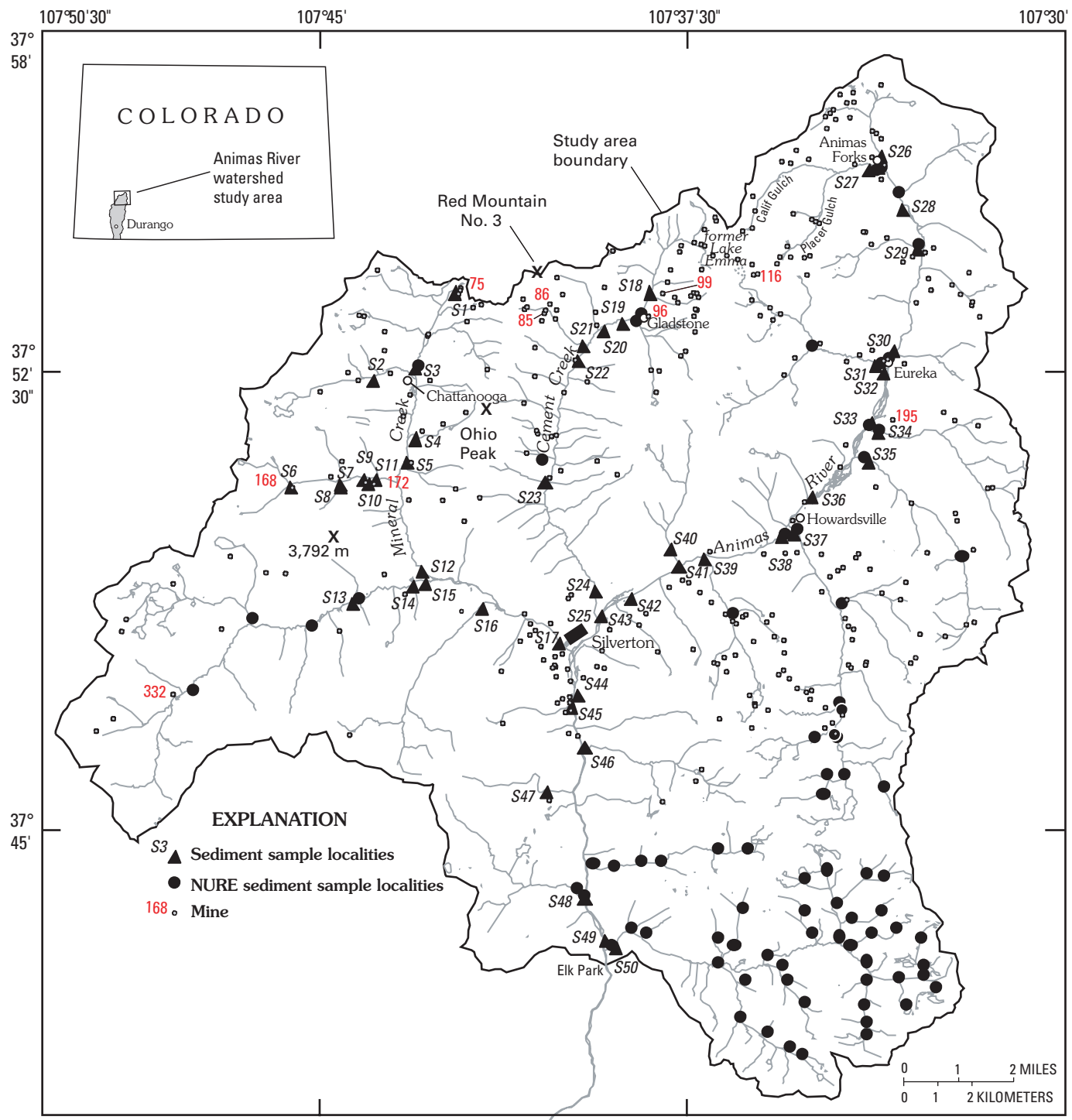


Figure 3. Sample localities of streambed-sediment samples collected in the NURE study and in this study. Mines discussed in text are from Church, Mast, and others (this volume): Koehler tunnel (mine # 75); Henrietta mine, level # 7 (mine # 85); Lark (mine # 86); American tunnel, Sunnyside (mine # 96); Red and Bonita (mine # 99); Sunnyside mine (mine # 116); Paradise portal (mine # 168); Bonner mine (mine # 172); Forest Queen mine (mine # 195); Bandora mine (mine # 332).

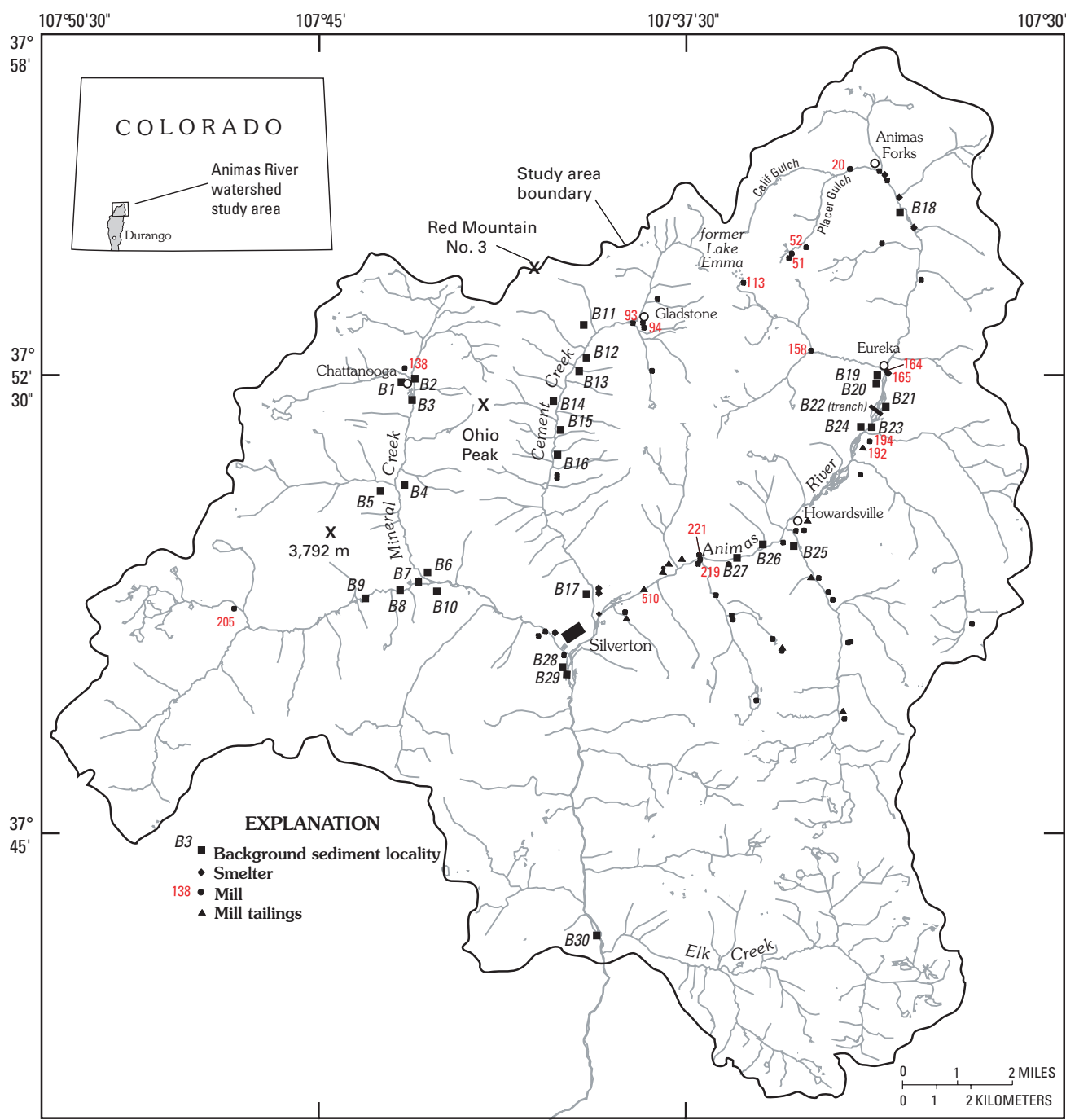


Figure 4. Sample localities of stream terraces sampled, some of which are used here to determine premining geochemical background in streambed sediment in the various basins of the Animas River watershed study area. Other sites are used to determine the present-day composition of contaminants in the watershed (table 1). Mills discussed in text are from Church, Mast, and others (this volume): Bagley Mill (site # 20); Hanson Mill (site # 51); Mastodon Mill (site # 52); Mogul Mill (site # 93); Gold King Mill (site # 94); Sunnyside-Thompson Mill (site # 113); Silver Ledge Mill (site # 138); Sunnyside Mill # 1 (also known as the Midway Mill, site # 158); Sunnyside Eureka Mill (site # 164); Sunnyside Mill # 2 (site # 165); Kittimack Mill and tailings (site # 194 and 192); Silver Lake Mill # 2 (site # 219); Mayflower Mill (site # 221); and the active Sunnyside tailings pond # 4 at the Mayflower Mill (site # 510).

The terrace deposits were generally composed of poorly sorted fluvial silt, sand, and gravel containing rock clasts as large as 12 in. (inches) in diameter. Because no discernible stratigraphy was preserved in the gravel deposits, samples were taken in 6- to 12-in. intervals throughout the exposed gravel section. We dug back into the terrace deposit at least 8 in., carefully removing any materials that might have been deposited on the surface or cutbank of the terrace by historical floods and that might have contaminated the sample of premining terrace deposits. We removed unvegetated sand and gravel deposited on top of the terrace deposits (unless they were in turn covered by a well-developed soil horizon) to prevent contamination by recently deposited gravel and silt. A minimum three samples at each site were taken to provide some measure of reproducibility of the analytical data, or to discern a geochemical trend in the data from the site. The gravel samples were dry-sieved in the field to pass a 2-mm stainless steel screen, and sent to the laboratory for further processing.

In the laboratory, the samples were air-dried if needed, sieved to minus-100 mesh (<150 μm), and mixed to ensure homogeneity. The sample material analyzed constitutes the very fine sand, silt, and clay-size fractions of the premining fluvial sediment. Sample descriptions are in Fey and others (2000).

Dendrochronology Samples

Dendrochronology of the trees growing on the stream terrace deposits was used to constrain the minimum age of the terrace. Live trees were cored using a standard tree coring device, and dead trees were slabbed. Samples were sent to the Laboratory for Tree Ring Research, University of Arizona in Tucson, Ariz., for age determinations.

Sample Analysis

Geochemical Analytical Methods

Geochemical data for the streambed-sediment and terrace samples were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES) from a mixed mineral-acid total digestion (Briggs, 1996; Church, 1981) and from a partial-digestion method using 2M HCl-1 percent H_2O_2 (Church, Fey, Unruh, and others, 2000). This partial digestion or leach was designed to dissolve the aluminum, iron, and manganese oxyhydroxide component of the streambed sediment and isolate the deposit-related trace elements contained in this component of the streambed sediment from those trace elements in the rock-forming phases of the streambed sediment found in the total digestions of the residual phases (Sole and others, this volume, Chapter G). Total-digestion data were used for the map presentations so that the data collected

in this study are comparable with those from previous studies, whereas the partial-digestion data have been used to make concentration versus distance diagrams that show the streambed-sediment geochemistry profiles. Unless otherwise noted, all analytical results are in Fey and others (2000) and Church, Fey, Unruh, and others (2000), and are available in the database (Sole and others, this volume).

Analytical precision of the total-digestion determinations was assessed by duplicate analyses of three standard reference materials (SRM) issued by the National Institute of Standards and Technology (SRM 2704, 2709, and 2711; NIST, 1993a, 1993b, and 1993c). These three standards were analyzed as unknown samples with each batch of 40 samples, and the results compiled over a 3-year period. Statistical data, including means, medians, standard deviations, and percent recoveries, for approximately 50 replicates of each standard are summarized in Fey and others (1999). The data show that analytical precision over 3 years was better than 5 percent for aluminum, calcium, iron, potassium, magnesium, and sodium. Precision for phosphorus and titanium was between 5 and 10 percent. Analytical variation for the trace elements (including the deposit-related elements) was generally between 5 and 10 percent. Analytical precision is affected by variability in both the sample digestion and the instrumental analyses, and by the ratio of the analyte concentration to the instrumental detection limits. The standard deviations determined from low concentrations of analytes in the reference materials are probably higher than would be derived from samples with higher concentrations, so the variations given are high estimates.

Lead Isotopic Methods

Lead isotopic analyses of all streambed sediment, sediment cores, and selected premining terrace sediment were completed to determine whether metals in modern streambed-sediment samples were derived from past mining activities. Four isotopes of lead exist in nature, three of which change as a function of time through the radioactive decay of uranium and thorium: ^{206}Pb is the daughter product of decay of ^{238}U , ^{207}Pb is the daughter product of decay of ^{235}U , ^{208}Pb is the daughter product of decay of ^{232}Th . However, ^{204}Pb has no radioactive parent. Thus, the isotopic composition of lead in rock in the Earth's crust (that is, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$) changes regularly with time as uranium and thorium undergo radioactive decay. During a mineral deposit-forming event, lead is separated from the parent uranium and thorium isotopes and the lead isotopic composition of the hydrothermal fluid is "frozen" into the sulfide minerals, usually in galena, within the mineral deposit. This mineral-deposit lead isotopic signature will eventually differ from that of the host rock underlying a watershed because the lead in the host rock continues to change with time whereas the lead in the mineral deposit remains fixed.

The isotopic composition of lead in streambed sediment reflects mixtures of lead from many discrete sources: the mineral deposits, unmined altered rock surrounding those deposits, the unmineralized rock underlying the watershed, mine waste dumps near mine adits, and mill tailings resulting from the processing of ore. Physical transport of detrital material derived from erosion and mixing of all of these materials makes up the streambed sediment. In addition, aqueous or colloidal transport of deposit-related trace elements from mined sites to the stream, and precipitation by mixing, sorption to colloids and grain coatings, and subsequent settling of the colloids to the streambed also contribute deposit-related trace elements to the streambed. Lead isotopic analyses of the streambed sediment were done on the partial-digestion solutions using standard lead isotopic methods (Church, Fey, Unruh, and others, 2000; Fey and others, 2000). Analytical methods and precision are in Unruh and others (2000). Analytical precision for the NBS standards 981 and 982 are 0.05–0.07 percent for the $^{206}\text{Pb}/^{204}\text{Pb}$ value over the 3-year period of analysis for these data depending upon the analytical instrument used. This means that the reported $^{206}\text{Pb}/^{204}\text{Pb}$ results for the unknown samples are thought to be accurate to about ± 0.01 (for example, 18.25 ± 0.01). Results are reported in terms of the lead isotope ratio to ^{204}Pb , the isotope of lead that has no radioactive parent. All analytical results are in the database (Sole and others, this volume).

Dendrochronology and the Historical Record

We used historical data and dendrochronology to constrain the ages of premining gravel in terrace deposits used to determine the premining geochemical baseline. The dendrochronological data provide minimum ages for the terrace deposits, whereas the historical data provide ages of structures or events within the mining districts. Some historical data for the mining history of the Animas River watershed study area are from Ransome (1901) and Jones (this volume). The history of construction of the railroads is from Sloan and Skowronski (1975).

Dendrochronological analysis was conducted in the Laboratory of Tree-Ring Research, University of Arizona; the results are in Fey and others (2000). Dates from live trees provided a minimum age of the terrace. Dates from dead standing trees sampled provided only a minimum age. Construction of a dendrochronological record from live trees to allow dating of dead trees was not achieved because the climate of the basin was sufficiently constant through time that a distinctive tree-ring structure versus time curve could not be constructed (Jeff Dean, Laboratory of Tree-Ring Research, University of Arizona, written commun., 1999). Results are presented in terms of the calendar year when growth began, or in the case of dead trees, the calendar date for the minimum age of the tree, assuming that it had died within the last year. Development of a mature soil horizon on terraces was used in a qualitative sense to estimate the relative age and maturity of stream terrace deposits.

Trace Elements in Streambed Sediment

Deposit-related trace elements derived from acidic drainage and mine waste as well as from mineralized but unmined sources typically accumulate in the streambed sediment downstream from inactive, historical mines. In the Animas River watershed study area, these trace elements were concentrated in the colloidal phase and the grain coatings of the streambed sediment (fig. 1). As seen from the data (Sole and others, this volume), the difference between the concentrations of the deposit-related trace elements in the total-digestion data from the streambed sediment and data from the residual silicates (that is, the rock-forming silicate mineral phases) clearly showed that the deposit-related trace elements were concentrated in and associated with the iron-oxyhydroxide component of the streambed sediment. In addition, we used these concentration data to evaluate the potential toxicity of deposit-related trace elements in streambed sediment to biota (Besser and Brumbaugh, this volume; Besser and others, this volume).

The measured concentrations of deposit-related trace elements in the streambed sediment vary with the velocity of the flow regime. The colloidal component and the suspended sediment, which contain most of the trace elements, tended to settle out of suspension in low-velocity reaches in the stream or river. Thus, the deposit-related trace-element concentrations were susceptible to temporal variability caused by deposition of the suspended sediment during low flow. The concentrations were also dependent upon the frequency of summer storms because the increased flow could mobilize some fraction of the colloidal component that had settled to the streambed. In general, barring a summer rainstorm immediately prior to or during the sample collection period, one would not expect temporal variability to affect spatial variation of the geochemical signal obtained from a streambed-sediment survey within a watershed as long as the entire sample suite was collected over a short time frame (on the order of several days). No such event occurred during the 1995 sampling of the watershed or during the short intervals when 11 monitoring sites within the watershed were resampled in subsequent years. However, significant differences in spring runoff did occur in the years between 1995 and 1999 (von Guerard and others, this volume, Chapter B, fig. 4).

This study identified systematic variations in the geochemical data collected at the 11 monitoring sites in different years. On a relative basis, the concentrations of the deposit-related trace elements in streambed-sediment data from 1995 and 1996 are in good agreement, whereas data from 1997 are systematically high and data from 1998 are systematically low. These differences are accentuated by the changes in concentrations of the deposit-related trace elements because these elements are partitioned into the colloid phase of the streambed sediment relative to the rock-forming trace elements. These variations represent primarily differences in sample variability from year to year. The highest concentrations occurred in 1997 following a wet late spring, whereas the lowest concentrations

occurred in 1998 following the lowest snow pack of the 5-year period of the study. From observation of the hydrograph (von Guerard and others, this volume, fig. 4), it is not apparent that these variations can be correlated with flow measured at the gauge downstream from Silverton, Colo.

From the preceding discussion on analytical precision, we showed that the analytical variation of the deposit-related trace elements was not as large as the year-to-year variation observed at the monitoring sites. The total-digestion data for the major and minor elements from the monitoring sites are reproducible within 5–10 percent and the partial digestion data for these elements are generally reproducible within 10–15 percent. In contrast, the variation in the concentration data for the deposit-related trace elements from the monitoring sites is greater than 20 percent. This indicates that annual site variability contributes a large part of the within-site variation from year to year. We attribute the within-site variation to the colloidal transport, settling, and mobilization processes discussed.

The systematic changes in concentration as a function of distance downstream provide useful diagnostic methods for evaluation of changes in stream chemistry and their effects on deposit-related trace-element concentrations in the streambed sediment. Some of the concentration data are presented in profile diagrams in subsequent figures and are plotted against downstream distance measured in river miles. Upstream is always to the left regardless of the direction of flow; the confluence of Mineral Creek with the Animas River has been assigned an arbitrary value of 15.5 mi. These graphs allow evaluation of the effect of single-point sources of metals and their relative impact on the stream reach. Arsenic, cadmium, copper, lead, silver, and zinc were concentrated in the leachable phase, indicating sorption to the hydrous aluminum, iron, and manganese grain coatings and colloids in streambed sediment. Concentrations of trace elements not associated with the mineral deposits (for example, chromium, cobalt, strontium, titanium, vanadium, and the rare earth elements) were similar throughout the watershed where underlain by the same rock type (Church, Kimball, and others, 1997; Wirt and others, 1999; Wirt and others, 2001). Vanadium has been used as a convenient measure of the rock component in mixtures of mill tailings with fluvial sediment at the Eureka mill site on the Animas River (Vincent and Elliott, this volume).

Upper Animas River Basin

Profile graphs of the geochemical data from streambed sediment from the upper Animas River basin are in figure 5 for the major elements aluminum, calcium, iron, magnesium, and manganese, and in figure 6 for the six deposit-related trace elements copper, arsenic, lead, silver, zinc, and cadmium. Values of pH are in the range of 5.5 at the headwaters; they quickly rise to near neutral from Eureka (figs. 5 and 6, mi 6.2) downstream to mi 7.5, upstream from the confluence

with Cement Creek (figs. 5 and 6, mi 14.6; Church, Kimball, and others, 1997, Wright, Simon, and others, this volume). Both iron and aluminum colloids precipitated, and most of the deposit-related trace elements, except zinc and cadmium (Schemel and others, 2000; Kimball and others, this volume), were partitioned into the colloidal phase as shown by the high concentrations of deposit-related trace elements throughout the entire reach (fig. 6). Manganese is significantly elevated in the streambed sediment of the Animas River; the values reflect the predominance of the manganese-rich Eureka graben deposits in the upper Animas River basin (Bove and others, this volume).

Major-element data from tributary streams (fig. 5) plot near the main trend of the Animas River upstream from the southern boundary of the Silverton caldera (fig. 2; dashed lines in figs. 5 and 6), although magnesium and manganese show larger variation in tributaries downstream of the Eureka graben (fig. 5, mi 6). Downstream of the caldera margin (mi 15.5), tributaries are depleted in aluminum, iron, and manganese and provide variable amounts of calcium and magnesium to the streambed sediment of the Animas River.

The deposit-related trace-element data in streambed sediment from tributary streams (fig. 6) show more variation than shown by data from the upper Animas River; they reflect the variation in the distribution of mineral deposits in the basin. Downstream from the Silverton caldera (mi 15.5), concentrations of the deposit-related trace elements approach crustal abundance values (Fortescue, 1992) in tributary streambed sediment where the tributary streams drain Precambrian rock. In the Animas River between mi 5 and mi 15.5, concentrations of deposit-related trace elements in modern streambed sediment (fig. 6) exceed crustal abundance values for copper by more than 40 fold, lead by more than 100 fold, silver by more than 50 fold, zinc by more than 20 fold, cadmium by more than 40 fold, and manganese by about 10 fold. Arsenic concentrations are only slightly elevated in streambed sediment of the upper Animas River basin, ranging from about 15 to 30 ppm with an enrichment of 8–15 fold.

Cement Creek Basin

Profile graphs of the geochemical data from streambed sediment from the Cement Creek basin are in figure 7 for the major elements aluminum, calcium, iron, magnesium, and manganese, and in figure 8 for the six deposit-related trace elements copper, arsenic, lead, silver, zinc, and cadmium. The data from the upper Animas River basin are also plotted for comparison. Major-element concentrations in streambed sediment of Cement Creek (fig. 7) are depleted for aluminum, calcium, magnesium, and manganese and enriched for iron relative to the streambed sediment in the upper Animas River. Arsenic concentrations in streambed sediment (fig. 8) are similar to those from the Animas River, but the other deposit-related trace elements have much lower concentrations

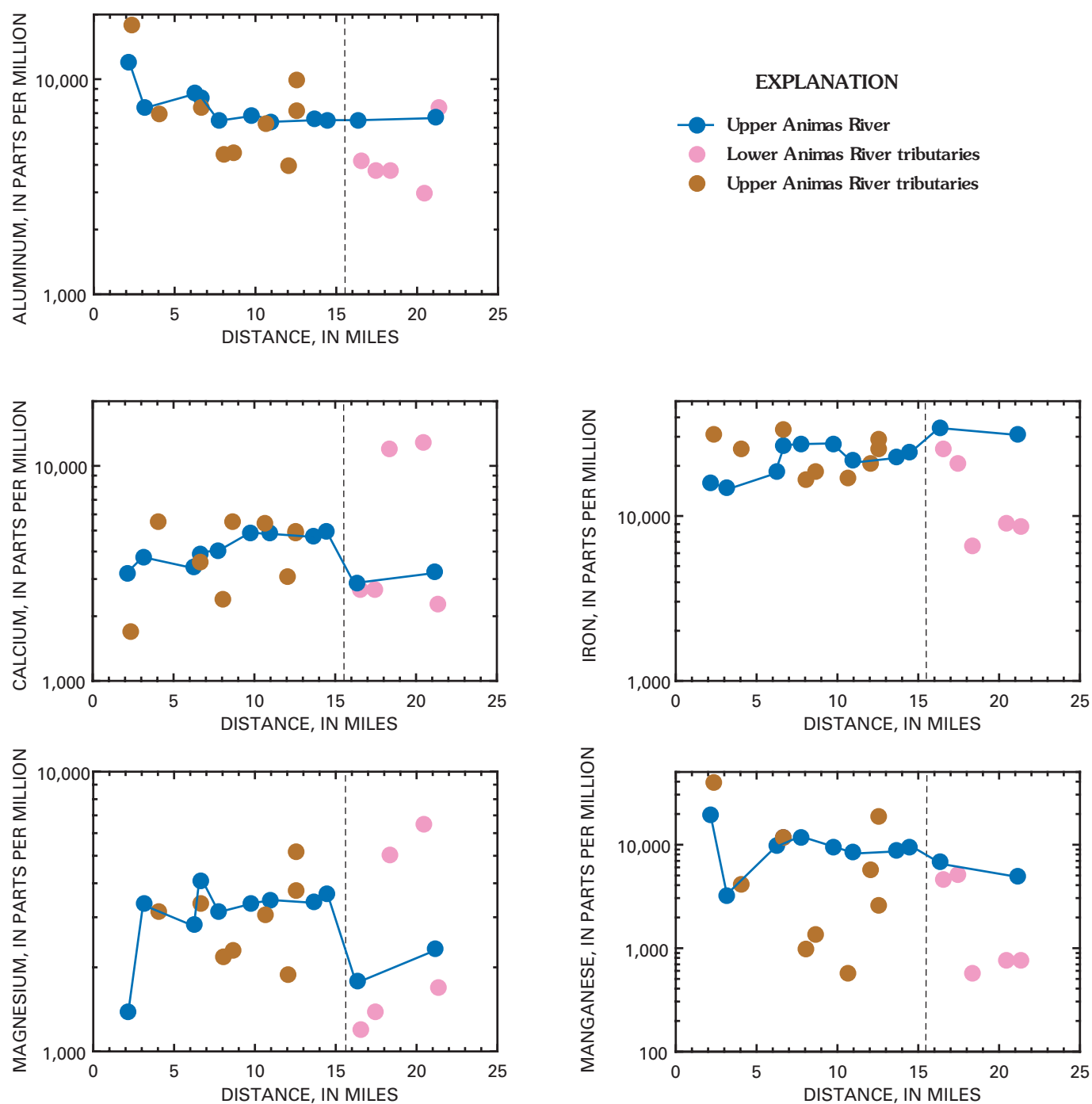


Figure 5. Profile graphs of leachable aluminum, calcium, iron, magnesium, and manganese from modern streambed sediment in upper Animas River. Data plotted against distance; upstream always to left regardless of actual direction stream flows. Samples that represent streambed sediment from active stream or river channel are indicated by discrete solid symbols and connected by tie lines. Data from tributary streams shown as discrete symbols. Confluence of Cement Creek is at mi 14.6 and Mineral Creek is at mi 15.5. All distances are defined relative to arbitrary value of 15.5 mi assigned for confluence of Mineral Creek with Animas River. Dashed line, approximate southern boundary of Silverton caldera margin (fig. 2).

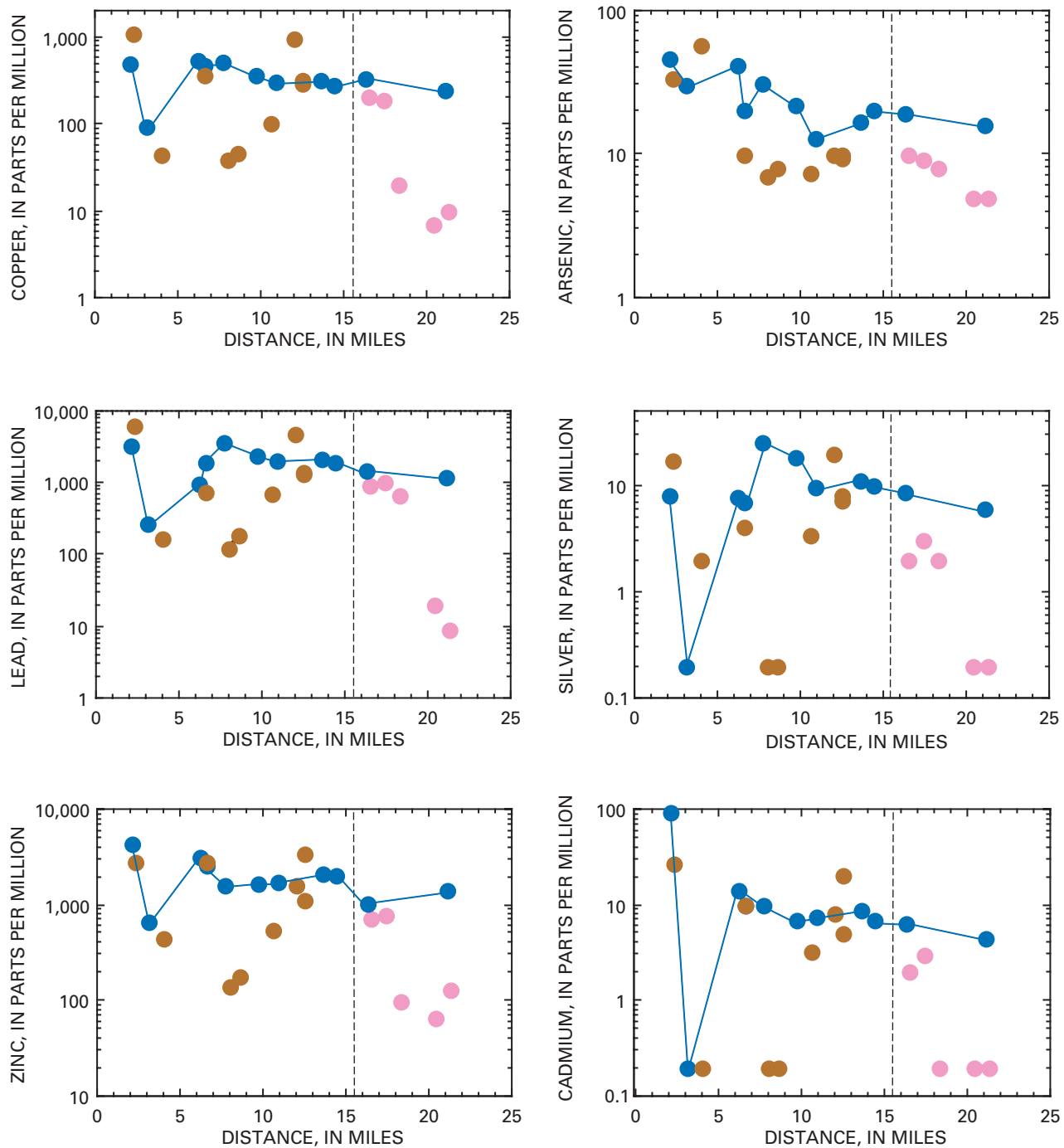


Figure 6. Profile graphs of leachable copper, arsenic, lead, silver, zinc, and cadmium from modern streambed sediment in upper Animas River basin. Data plotted against distance; upstream always to left regardless of actual direction stream flows. Samples that represent streambed sediment from active stream or river channel are indicated by discrete solid symbols and connected by tie lines. Blue, upper Animas River. Data from tributary streams shown as discrete symbols; brown, upper Animas River tributaries; pink, lower Animas River tributaries. Confluence of Cement Creek is at mi 14.6 and Mineral Creek is at mi 15.5. All distances are defined relative to arbitrary value of 15.5 mi assigned for confluence of Mineral Creek with Animas River. Dashed line, approximate southern boundary of Silverton caldera margin (fig. 2). Concentrations of cadmium and silver are censored, that is, less than the detection limit, at 2 ppm and for arsenic at 5 ppm. Crustal abundance values are: CA_{Cu} , 68 ppm; CA_{As} , 1.8 ppm; CA_{Pb} , 13 ppm; CA_{Ag} , 0.08 ppm, CA_{Zn} , 76 ppm; and CA_{Cd} , 0.16 ppm (Fortescue, 1992).

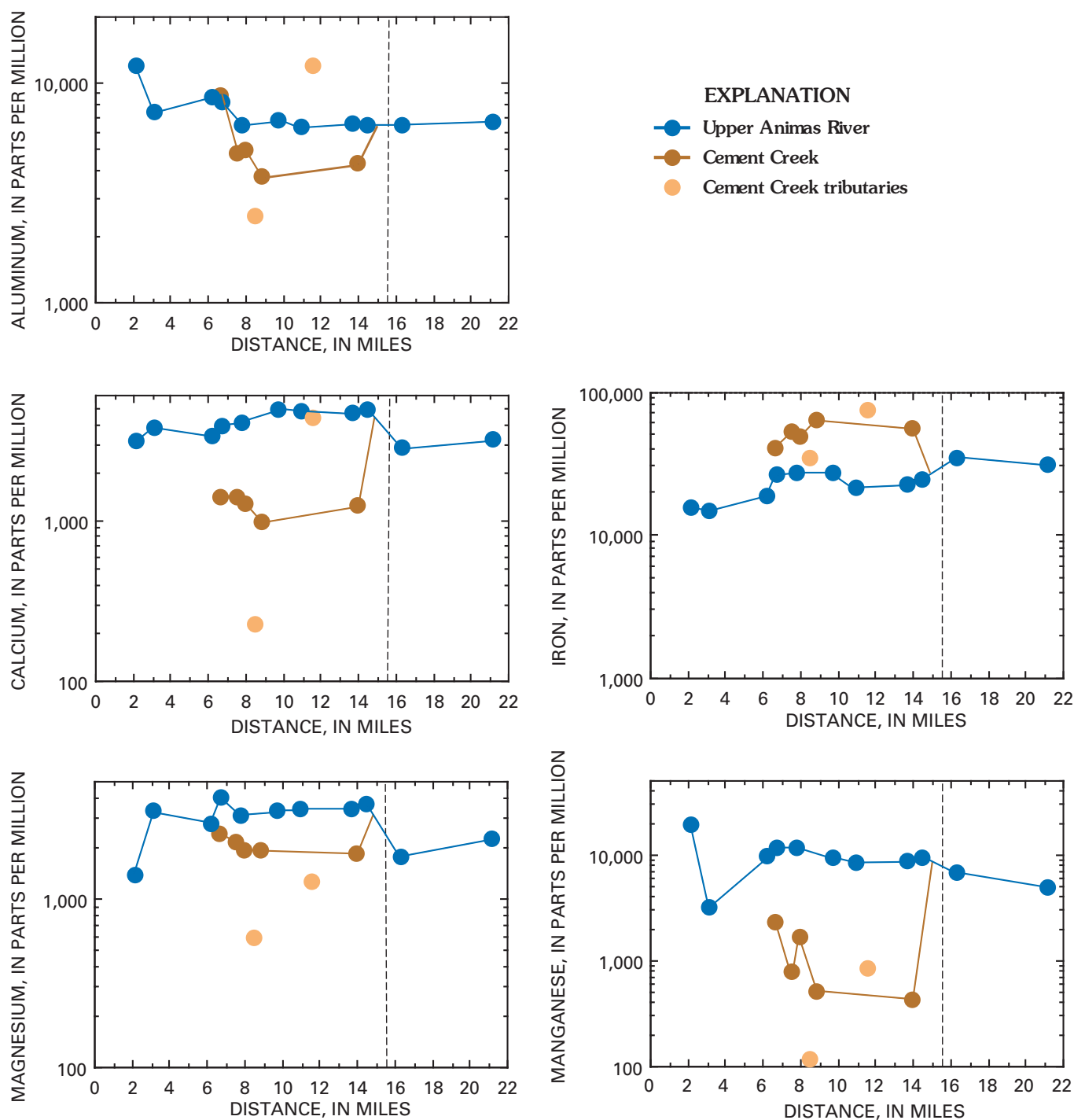


Figure 7. Profile graphs of leachable aluminum, calcium, iron, magnesium, and manganese from modern streambed sediment in Cement Creek basin. Data plotted against distance; upstream always to left regardless of actual direction stream flows. Samples that represent streambed sediment from active stream or river channel are indicated by discrete solid symbols and connected by tie lines. Data from tributary streams shown as discrete symbols. Confluence of Cement Creek is at mi 14.6 and Mineral Creek is at mi 15.5. All distances are defined relative to arbitrary value of 15.5 mi assigned for confluence of Mineral Creek with Animas River. The data from the Animas River are shown for comparison. Confluence of Cement Creek is at mi 14.6 and Mineral Creek is at mi 15.5. Dashed line, approximate southern boundary of Silverton caldera margin (fig. 2).

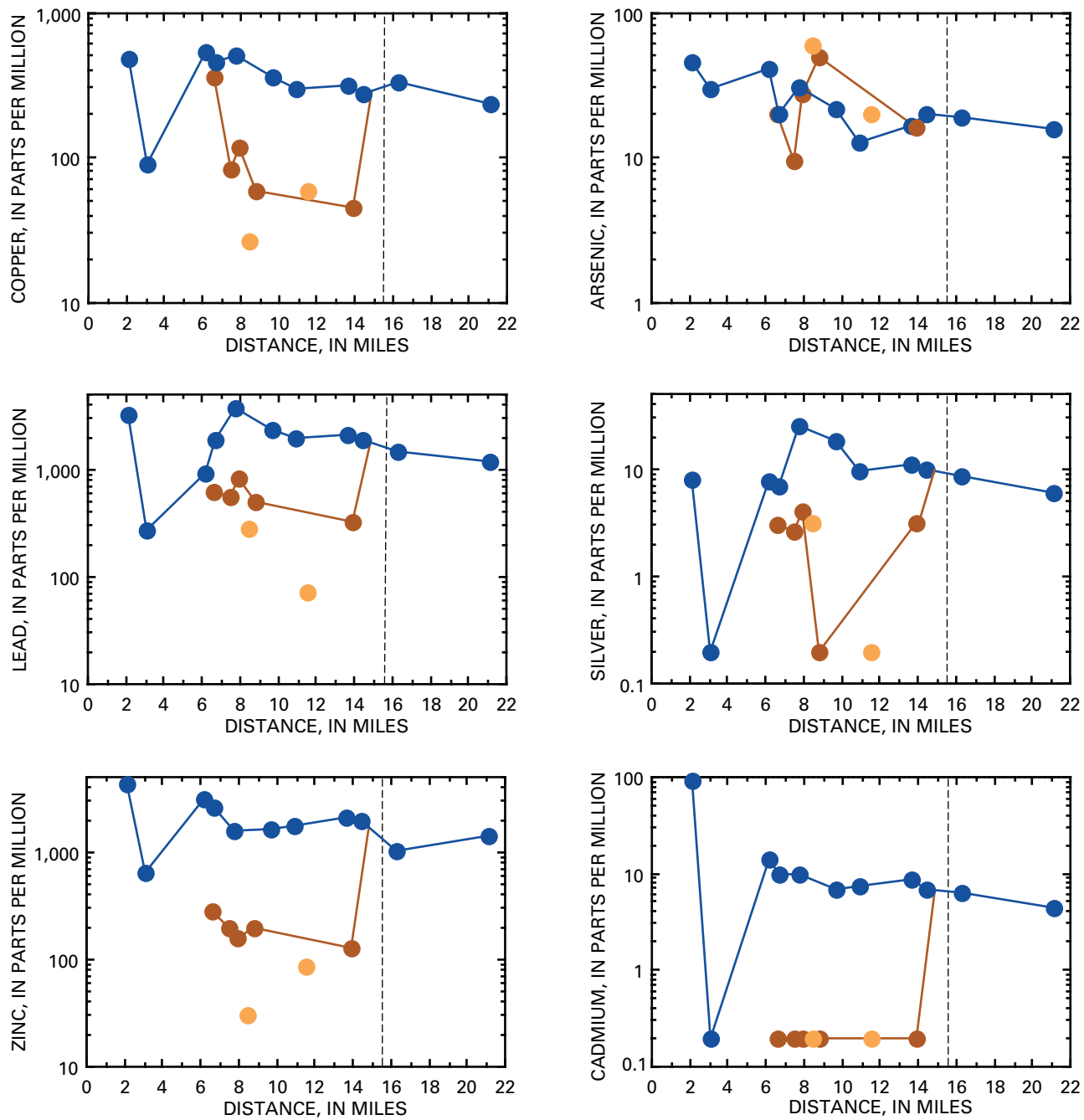


Figure 8. Profile graphs of leachable copper, arsenic, lead, silver, zinc, and cadmium from the Cement Creek basin. Data plotted against distance; upstream always to left regardless of actual direction stream flows. Samples that represent streambed sediment from active stream or river channel are indicated by discrete solid symbols and connected by tie lines. Data from tributary streams shown as discrete symbols. Confluence of Cement Creek is at mi 14.6 and Mineral Creek is at mi 15.5. All distances are defined relative to arbitrary value of 15.5 mi assigned for confluence of Mineral Creek with Animas River. Data from Animas River (blue) shown for comparison. Dark brown, Cement Creek; light brown, Cement Creek tributaries. Dashed line, approximate southern boundary of Silverton caldera margin (fig. 2). Concentrations of cadmium and silver are censored, that is, less than the detection limit, at 2 ppm and for arsenic at 5 ppm. Crustal abundance values are: CA_{Cu} , 68 ppm; CA_{As} , 1.8 ppm; CA_{Pb} , 13 ppm; CA_{Ag} , 0.08 ppm, CA_{Zn} , 76 ppm; and CA_{Cd} , 0.16 ppm (Fortescue, 1992).

in streambed sediment of Cement Creek. The paucity of deposit-related trace elements in the streambed sediment of Cement Creek is primarily a function of the low pH of the stream water in Cement Creek (Wright, Simon, and others, this volume). Iron is actively precipitating to form colloids, but only arsenic, lead, and silver are being actively sorbed to those colloids. Copper, zinc, and cadmium remain soluble and do not precipitate until the pH rises to near-neutral in iron-rich water (Smith, 1999; Schemel and others, 2000).

The pH of Cement Creek at low flow is in the range of 3.5–3.7. At this pH, aluminum is completely soluble (Furrer and others, 2002), and some of the iron has precipitated to form colloids (Schemel and others, 2000; Kimball and others, this volume). Desborough and others (2000) documented the presence of schwertmannite, a hydrous iron sulfate (Bigham and others, 1996) in streambed sediment at five localities on Cement Creek, which were sampled at low flow in 1997 and 1998, between sites *S19* and *S24* (fig. 3). The pH of the stream water ranged from 3.36 to 4.25, which is within the pH range of 2.8 to 4.5 that Bigham and others (1996) have shown is the most favorable pH range for schwertmannite-dominant precipitates to form in iron-rich streams. Goethite was also identified in X-ray patterns at sites sampled in 1998 (Desborough and others, 2000). Studies of ferricrete deposits and the ground water that forms them in this basin show that water draining from areas of altered rock in the upper part of the basin are naturally acidic (Wirt and others, 1999; Wirt and others, this volume, Chapter E17; Bove and others, this volume; Mast and others, this volume, Chapter E7). The lower concentrations of deposit-related trace elements in the streambed sediment of Cement Creek, as compared to the upper Animas River reach, are primarily a function of lower pH of Cement Creek stream water rather than a function of the different suites of altered rock or mineralized veins in the basin (Bove and others, this volume).

Mineral Creek Basin

Profile graphs of the geochemical data from streambed sediment from the Mineral Creek basin are in figure 9 for the major elements aluminum, calcium, iron, magnesium, and manganese, and in figure 10 for the six deposit-related trace elements copper, arsenic, lead, silver, zinc, and cadmium. The data from the upper Animas River reach are also plotted for comparison. Concentrations of aluminum are comparable with that in streambed sediment of the Animas River upstream from the Mineral Creek confluence, but concentrations of calcium, magnesium, and manganese are depleted, and iron enriched relative to that in streambed sediment of the Animas River reach. Similar results are found in the streambed sediment of Middle Fork Mineral Creek subbasin. Arsenic, and in one instance, copper concentrations are also elevated in the streambed sediment of Mineral Creek relative to that in the upper Animas River basin. The

breccia-pipe deposits exploited in this basin in the late 19th and early 20th centuries were both arsenic and copper rich. “Gray copper ore,” enargite (Ransome, 1901), and galena and tetrahedrite containing silver were the primary ore minerals. Near the headwaters, just downstream from site *S1* (fig. 3), Desborough and others (2000) reported schwertmannite precipitates in the streambed sediment of Mineral Creek. Like Cement Creek, Mineral Creek upstream from the confluence with the South Fork Mineral Creek (mi 12.3) is acidic, having a pH of 4 or less (Wright, Simon, and others, this volume). Tributary streams draining into Mineral Creek from the west lie outside the Silverton caldera margin and are affected by the porphyry copper-molybdenum deposit beneath peak 3,792 m (Yager and others, 2000; Mast and others, this volume). Very high concentrations of iron, aluminum, and manganese from the Middle Fork Mineral Creek subbasin (fig. 9, mi 10.45; Kimball and others, this volume) are associated with the quartz-sericite-pyrite alteration halo surrounding this unnamed peak (Ringrose, 1982; Yager and others, 2000; Bove and others, this volume). Mineralized rock in these tributary drainages has not been exploited to the extent that it has been in the upper part of the Mineral Creek basin, so all deposit-related trace-element concentrations except for lead and zinc are very low. Exploitation of mineral deposits at the Bonner mine (mine # 172) represents the major production from the Middle Fork Mineral Creek subbasin (Jones, this volume; Church, Mast, and others, this volume). Concentrations of deposit-related trace elements in many of these tributary streams are low in comparison with those in Mineral Creek (fig. 10). Concentrations of lead, silver, and zinc in streambed sediment of Mineral Creek are lower than those in the Animas River, and cadmium is quite a bit lower, as expected given the low pH of Mineral Creek upstream from the confluence with South Fork Mineral Creek.

South Fork Mineral Creek Basin

South Fork Mineral Creek is a large tributary stream that contributes about half the flow of Mineral Creek downstream from its confluence (Kimball and others, this volume). The creek drains a large area of Paleozoic rock that lies outside the margin of the Silverton caldera (Yager and Bove, pl. 1); it has a neutral pH, and it causes a significant rise in pH where it mixes with the water from Mineral Creek (mi 12.3). A few small mines exist in the South Fork Mineral Creek subbasin (Bandora mine, # 332; Church, Mast, and others, this volume; Nash and Fey, this volume). Mixing of the more neutral water of the South Fork Mineral Creek and Mineral Creek in the zone downstream (fig. 11) results in the precipitation of iron and aluminum colloids that sorb deposit-related trace elements from the water. Note the increase in aluminum, copper, zinc, and cadmium concentrations in streambed sediment of Mineral Creek downstream from mi 12.3 (figs. 9 and 10).

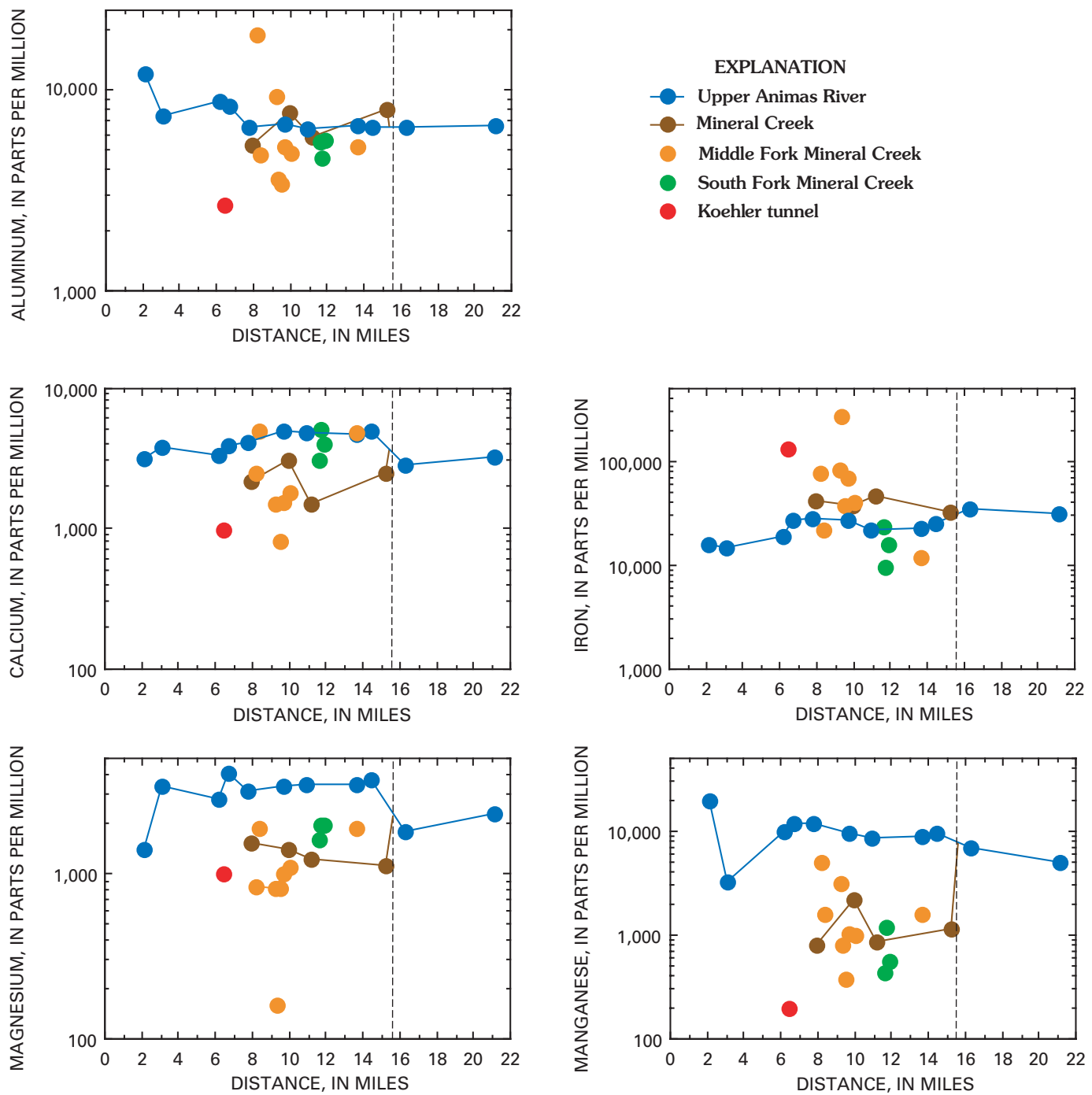


Figure 9. Profile graphs of leachable aluminum, calcium, iron, magnesium, and manganese from streambed sediment in Mineral Creek basin. Data plotted against distance; upstream always to left regardless of actual direction stream flows. Samples that represent streambed sediment from active stream or river channel are indicated by discrete solid symbols and connected by tie lines. Data from the tributaries include a large number of samples from Middle Fork Mineral Creek. The data from the Animas River are shown for comparison. Confluence of Mineral Creek is at mi 15.5; all distances are defined relative to arbitrary value of 15.5 mi assigned for confluence of Mineral Creek with Animas River. Dashed line, approximate southern boundary of Silverton caldera margin (fig. 2).

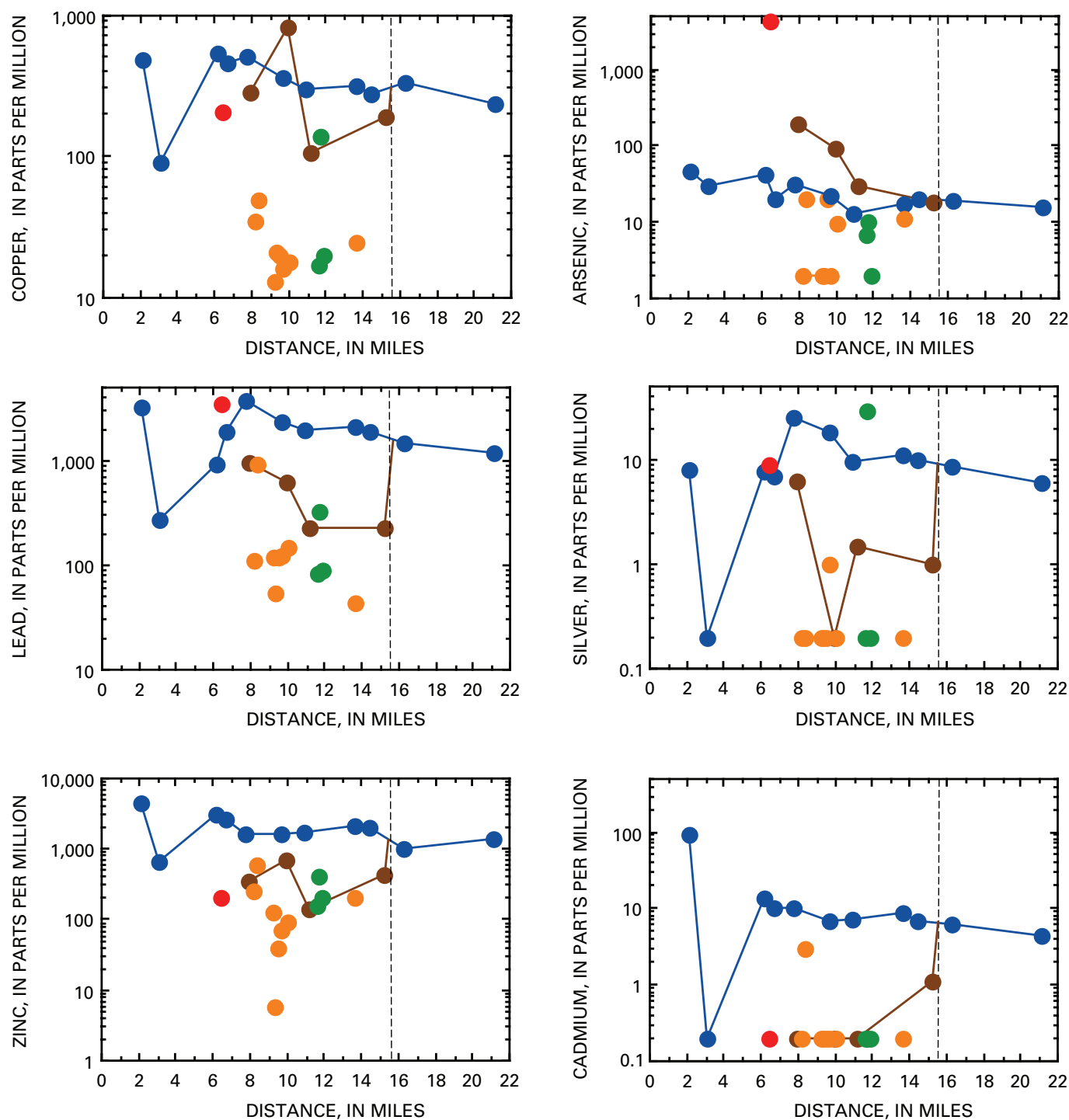


Figure 10. Profile graphs of leachable copper, arsenic, lead, silver, zinc, and cadmium from the Mineral Creek basin. Data plotted against distance; upstream always to left regardless of actual direction stream flows. Samples that represent streambed sediment from active stream or river channel are indicated by discrete solid symbols and connected by tie lines. Brown, Mineral Creek. Data from the tributaries include a large number of samples (orange) from Middle Fork Mineral Creek. Green, South Fork Mineral Creek; red, Koehler tunnel. Data from Animas River (blue) shown for comparison. Confluence of Mineral Creek is at mi 15.5; all distances are defined relative to arbitrary value of 15.5 mi assigned for confluence of Mineral Creek with Animas River. Dashed line, approximate southern boundary of Silverton caldera margin (fig. 2). Concentrations of cadmium and silver are censored, that is, less than the detection limit, at 2 ppm and for arsenic at 5 ppm. Crustal abundance values are: CA_{Cu} , 68 ppm; CA_{As} , 1.8 ppm; CA_{Pb} , 13 ppm; CA_{Ag} , 0.08 ppm, CA_{Zn} , 76 ppm; and CA_{Cd} , 0.16 ppm (Fortescue, 1992).



Figure 11. Photographs of the mixing zone at confluence of South Fork Mineral Creek with Mineral Creek. Brown precipitates on far shore of view *A* (north) are the iron colloids, which form when pH of the stream water rises above about 3.5. White precipitate visible in *A* and *B* is the hydrous aluminum colloids, which precipitate from acidic mine-impacted water above a pH of about 4.2 (Furrer and others, 2002). Both the iron and aluminum precipitates coat the streambed (fig. 1) resulting in loss of aquatic habitat. Water remains turbid for hundreds of feet downstream.

Mixing Zones

Changes in chemistry of the water and colloids resulting from the mixing of acidic water of Cement Creek with the Animas River are documented in Schemel and others (2000). This process is quite visible at the confluence of Mineral Creek with South Fork Mineral Creek (fig. 11). Because we did not collect streambed sediment in these mixing zones, the effects of mixing at the confluence of the Animas River both with Cement Creek (mi 14.6) and with Mineral Creek (mi 15.5) were most readily apparent in the decrease in manganese and a small increase in iron concentrations (fig. 9), and the decrease in zinc and the increase in copper concentrations (fig. 10) in streambed sediment of the Animas River downstream from the confluence of Mineral Creek. Downstream from the confluence with Mineral Creek, the increase in zinc concentration is the result of sorption of zinc by the suspended iron and aluminum colloids and settling to become part of the streambed-sediment load. This process of sorption of both copper and zinc, and probably of cadmium, continues downstream in the Animas River to Aztec, N. Mex., near the confluence of the San Juan River (Church and others, 1997). Dilution by sediment from unmineralized rock is the primary mechanism of the downstream decrease in deposit-related trace-element concentrations in streambed sediment downstream from the confluence with Mineral Creek.

Contaminants from Historical Mining and Milling in Stream Terrace Deposits

Church, Mast, and others (this volume) describe the distribution of mines and mills in the Animas River watershed study area, and Nash and Fey (this volume) provide site descriptions of mine waste at many of those sites. Jones (this volume) discusses the effects of government price supports and the demand for metals during World War II on mining practices in the area. These policies, as well as changes in mining practices, greatly affect the distribution of mill tailings in the streams. Jones (this volume) identifies four major periods of production in the watershed: the smelting era (1871–1889), the gravity milling era (1890–1913), the early flotation era (1914–1935), and the modern flotation era (1936–1991). The following is summarized from his chapter:

- During the smelting era, ore was hand sorted and most was shipped directly to smelters. A few small gravity or stamp mills were in operation. Total ore production was small and the amount of mill tailings released to streams was small, but unknown. There was no market for zinc, so sphalerite was left in the mines or on the mine waste dumps, because the smelters charged a penalty to process ores containing more than 10 percent sphalerite (Ransome, 1901).

- During the gravity milling era, many small mines had a stamp mill to prepare a concentrate for shipment to the smelter. Milling of ore occurred on site; trams transported ore to the mills or the railroad for shipment to smelters outside the watershed (Jones, this volume, fig. 3). Mill tailings were not impounded, but rather were dumped in the riparian zone or directly into the streams. Sulfide recovery was about 60 percent. Copper was not recovered, and zinc was still not a marketable commodity. An estimated 4.3 million short tons of mill tailings were discharged directly into the streams (Jones, this volume). The Animas River contained so much tailings that the town of Durango, Colo., had to construct a new reservoir and delivery system for public water supply (Durango Democrat, Nov. 15, 1902).
- During the early flotation era, a few mills dominated production in the basin. The Sunnyside Mill # 2 at Eureka (site # 165, fig. 4) was a leader in developing flotation technology. Ores were ground to finer grain size, and sphalerite and copper sulfide concentrates were recovered. The volume of tailings increased dramatically over the previous period. The gravity or stamp mills were all closed by 1921, and ore was processed at these large modern mills. In 1917, U.S. Smelting and Refining Co. completed a large flotation mill at Eureka (Sunnyside Eureka Mill, site # 164) to process ore from Sunnyside (mine # 116). This mill was by far the largest mill in the basin; it processed on the order of 2.5 million tons of ore from the period 1917–1930 (Bird, 1999). Sulfide recovery exceeded 80 percent. Tailings were impounded in retaining ponds on the flood plain immediately downstream. As evidenced by the dispersed mill tailings deposits present in the braided reach downstream from Eureka (Vincent and Elliott, this volume), floods periodically breached the tailings impoundments and released mill tailings to the Animas River. The mill closed in 1930 during the Depression and reopened briefly in 1937 (Bird, 1999). An estimated 4.2 million tons of ore was processed by the mills during this period (Jones, this volume). Most of the mill tailings were discharged into settling ponds in the riparian zone or directly into the streams.
- During the modern flotation era, the Mayflower Mill, built in 1929 (site # 221, fig. 4), was the primary mill operating in the watershed. This mill was designed not to release mill tailings to the Animas River. Although the tailings impoundment effort was not completely successful in the beginning, the majority of the mill tailings were retained after 1935 (Jones, this volume). Sulfide recovery using improved flotation technology was greater than 95 percent after 1940. Jones (this volume) estimates that only 200,000 tons of mill

tailings were released to the streams during this period. Furthermore, in support of both World War II and the Korean War, many of the old stamp mill tailings were reprocessed and the stamp mills were burned to recover scrap iron.

Nash and Fey (this volume) note that many of the old stamp mill sites contain little or no mill tailings. Given the historical mining practices just summarized, this is not surprising. As substantial amounts of mill tailings were released into the surface streams (an estimated 8.7 million short tons, Jones, this volume), we would expect to find evidence in the streambed of these discharges. Table 1 summarizes deposit-related trace-element concentrations from intervals of contaminated terrace deposits discussed herein that may be indicative of the composition of contaminants dumped directly into the streams. Most of the mills were concentrated along the Animas River (Church, Mast, and others, this volume, fig. 5; Jones, this volume), and most of our data were from abandoned mill sites along the Animas River upstream from Silverton (fig. 4).

In this study, we also evaluate what effect the Gladstone flood of 1911 had on the distribution of stamp mill tailings from the gravity milling era. We question whether the paucity of mill tailings from the gravity milling era in this watershed represents a scouring of those tailings by this flood event. On Oct. 5, 1911, the Gladstone flood devastated the Animas River valley. According to the Durango Evening Herald (Oct. 5–10, 1911), many stretches of the Denver and Rio Grande Railroad tracks between Silverton and Tacoma (about 25 mi downstream) were washed out. Osterwald (1995) stated that more than 22 mi of track were washed out, and rail service to Silverton was disrupted for 63 days. Bridges in the Animas River watershed upstream from Silverton were washed out, and most bridges in the Durango area, 45 mi downstream, were also damaged or washed out. We identified mill tailings in flood deposits at sites *B27* (about 2.5 ft above low-flow water level) and *B30* (about 6 ft above low-flow water level) at Elk Park (fig. 4). Do these fluvial deposits represent the 1911 Gladstone flood event?

The extent and distribution of contamination of the streams in the Animas River watershed study area by mine waste and mill tailings can be evaluated using our geochemical data. Geochemical plots of several elements can be used to discriminate the different contaminants from the Mineral Creek, Cement Creek, and upper Animas River basins (fig. 12). These graphs use elements that are concentrated in the different mineral deposit types to show that mill tailings can be traced downstream from the point of origin even though they have been diluted by uncontaminated sediment. Dilution with uncontaminated streambed sediment is a primary instream process that affects the geochemistry of the fluvial tailings deposits. To represent the composition of the contaminants and the mixing line formed when dilution takes place, we have plotted the minimum, median, 75th percentile, and maximum values determined where data exist from a number of contaminated intervals (table 1). Four different

Table 1. Statistical distributions for deposit-related trace elements in historical fluvial deposits, Animas River watershed study area.—Continued

Site No.	Sample No.	n	Al wt. pct.	Fe wt. pct.	Ti wt. pct.	As ppm	Cu ppm	Cd ppm	Zn ppm	Pb ppm	Ag ppm	Mn ppm	Mo ppm	Ba ppm	Sr ppm	V ppm	$\frac{206\text{Pb}}{204\text{Pb}}$	$\frac{207\text{Pb}}{204\text{Pb}}$	$\frac{208\text{Pb}}{204\text{Pb}}$
B22	Trench	9	2.0	1.4	0.00	28	530	9.0	1,300	3,800	37	22,000	14	200	44	30	18.310	15.539	37.862
	Stamp mill tailings		3.5	2.5	0.04	40	1,400	20	4,400	7,800	52	28,000	15	380	78	56	18.328	15.550	37.902
	Std. Dev.		0.99	0.61	0.04	10	450	12	3,200	3,100	14	4,300	1.5	110	25	17	0.012	0.012	0.036
	Median		3.8	2.6	0.05	40	1,500	16	3,200	7,800	50	28,000	15	410	83	64			
	75th percentile		4.0	2.9	0.06	42	1,700	23	5,400	9,200	64	31,000	16	450	100	66			
	Maximum		4.8	3.3	0.13	61	2,000	42	10,000	14,000	71	34,000	19	520	110	78	18.344	15.571	37.968
B24	96ABS118	5	1.5	2.0	0.04	30	820	2.0	750	7,300	17	25,000	12	280	42	23	18.327	15.566	37.948
	Minimum		2.5	2.7	0.07	50	1,400	8.8	1,400	13,000	41	31,000	22	370	56	37			
	Mean		0.90	0.49	0.02	12	730	5.8	570	3,900	20	5,100	7.7	60	11	14			
	Std. Dev.		2.4	2.8	0.08	52	1,200	7.0	1,300	13,000	44	32,000	24	360	60	37			
	Median		2.7	3.1	0.09	55	1,400	12	1,400	16,000	58	36,000	25	420	61	39			
	75th percentile		3.9	3.2	0.10	61	2,700	17	2,300	17,000	62	36,000	32	430	70	60	18.329	15.566	37.947
	Maximum		3.9	4.0	0.18	36	270	1.0	520	2,600	18	14,000	8.0	100	62	62	18.374	15.567	37.965
B27	98ABB234	3	3.9	4.2	0.23	42	327	2.0	663	3,200	28	17,000	10	113	73	73			
	Minimum		4.4	4.4	0.31	45	430	3.0	890	3,800	35	19,000	11	140	95	95			
	Mean		5.3	4.4	0.31	45	430	3.0	890	3,800	35	19,000	11	140	95	95			
	Std. Dev.		3.2	2.8	0.10	21	220	4.0	790	790	15	9,500	65	300	63	53	18.557	15.578	38.066
	Median		3.7	4.1	0.15	37	350	10	1,300	1,400	23	13,700	72	420	86	61			
B30	96ABS126	5	0.55	1.00	0.04	12	100	5.1	320	610	8.1	3,900	10	140	31	11			
	Minimum		3.6	4.1	0.14	37	370	10	1,400	1,300	21	13,000	66	370	80	58	18.559	15.582	38.073
	Mean		3.7	4.6	0.15	42	380	14	1,500	1,400	23	14,000	79	390	81	61			
	Std. Dev.		4.6	5.4	0.21	54	500	16	1,600	2,400	36	20,000	86	660	140	80	18.580	15.580	38.071
	Median		3.5	3.9	0.12	46	360	4.0	660	2,300	16	11,000	9.0	540	98	61	18.400	15.568	37.980
B30	98ABB225	4	4.7	4.8	0.23	54	530	5.5	980	3,800	24	14,000	15	660	160	79			
	Minimum		1.34	0.61	0.10	5.9	140	1.0	240	1,900	8.2	3,400	6.1	110	59	20			
	Mean		4.6	5.1	0.23	55	550	5.5	1,000	3,200	23	13,500	15	660	160	77			
	Std. Dev.		5.7	5.1	0.30	57	640	6.0	1,100	4,200	28	15,000	19	740	200	93			
	Median		6.1	5.2	0.33	60	650	7.0	1,200	6,500	35	19,000	22	770	210	100			
B30	02ABB-EP ²	6	1.6	1.3	0.00	25	530	6.0	1,700	1,900	24	11,000	14	200	44	25	18.333	15.542	37.877
	Minimum		2.8	3.5	0.10	41	675	12	3,050	3,483	32	19,500	18	382	86	50	18.338	15.550	37.897
	Mean		0.9	1.5	0.08	14	329	6.5	1,892	1,021	8.4	8,689	3.1	174	35	19	0.006	0.007	0.018
	Std. Dev.		2.7	3.5	0.10	38	550	8.9	2,050	3,500	29	17,500	19	355	89	51			
	Median		3.3	4.5	0.16	46	705	17	4,300	4,000	35	23,250	20	520	101	63			
	75th percentile		4.1	5.4	0.19	64	1,300	21	5,900	4,900	47	34,000	22	610	140	74	18.344	15.556	37.910
	Maximum																		

¹Sunnyside mine operated several mills at the Eureka site (Jones, this volume). The large flotation mill (Sunnyside Eureka Mill, site # 164, fig. 4) was put into operation in 1917.

²Data not included in database.

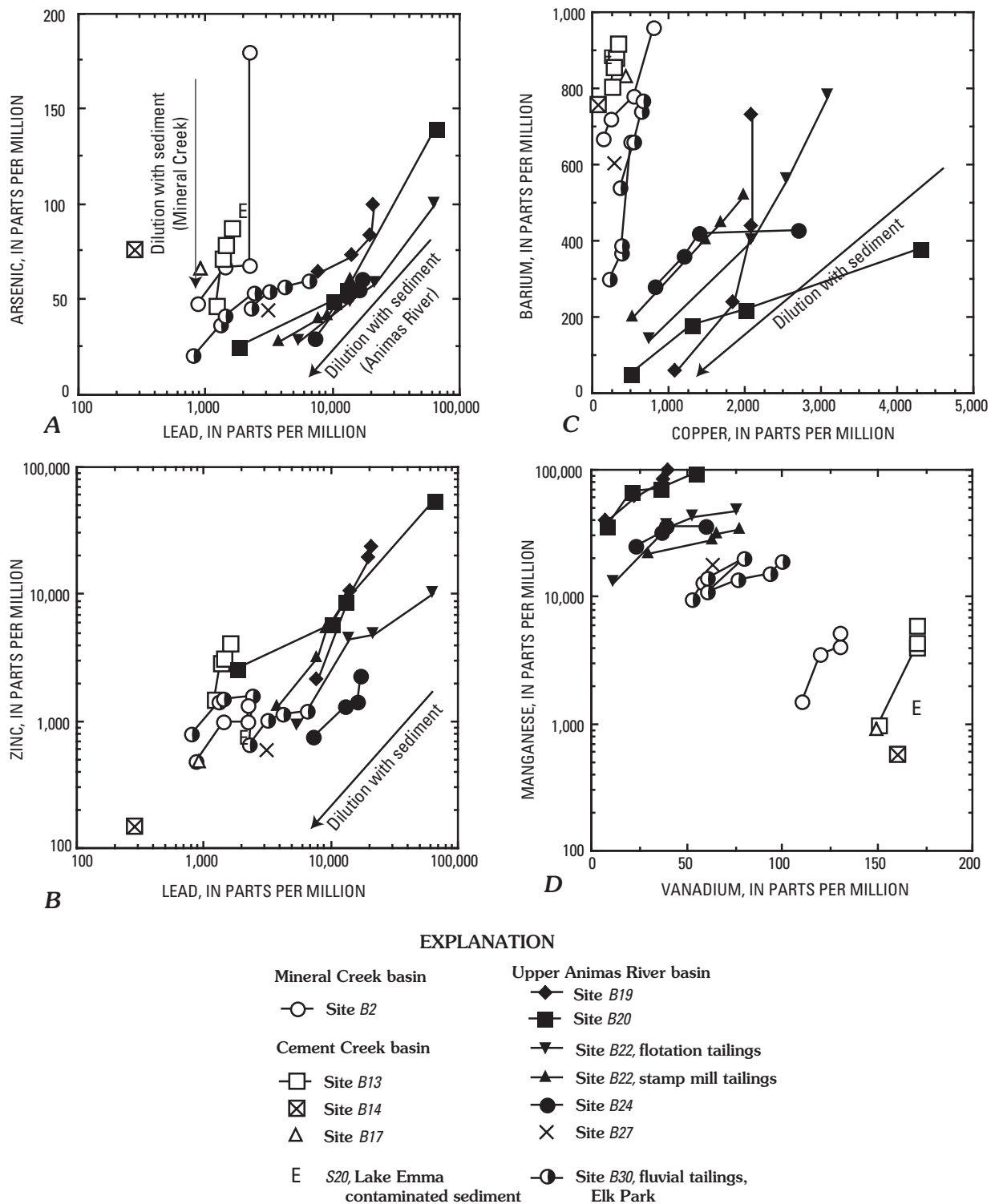


Figure 12. Geochemical data from contaminants from terrace deposits showing the different geochemical characteristics that are used to discriminate between various mill tailings from the Sunnyside mills at Eureka and other contaminated fluvial sediment. View letters A–D are used in discussion in text. Minimum, median, 75th percentile, and maximum value for each sample (table 1) are plotted and connected by a tie line to show the effect of dilution by mixing with streambed sediment. Open symbols are from reaches containing the breccia-pipe deposits; S20, Lake Emma blowout deposit from the 1978 flood. B19–B24, tailings or contaminated sediment from the Animas River downstream from Eureka; at site B22, both flotation and stamp mill tailings were sampled. B27, B30, sediment contaminated by tailings from Sunnyside mills at Eureka.

element graphs (fig. 12) demonstrate the effects of mixing of the mill tailings found in fluvial deposits with sediment. These deposit-related element graphs also can be used to discriminate sources of materials found in the terrace deposits because different mineral deposits within the watershed have different metal signatures. Because the primary ore minerals in the breccia-pipe deposits were galena, tetrahedrite, and enargite, fluvial tailings deposits in this mining district should contain high concentrations of arsenic, copper, lead, and silver (Ransome, 1901). Virtually all of the concentrate prepared by the early stamp mills would have been shipped to the smelters outside the study area, so the amount of tailings in the basin from this era would be small (Jones, this volume, fig. 3). Furthermore, mining in the Red Mountain district was essentially complete by 1900. The terrace deposits from sites in upper Mineral and Cement Creeks (*B2* and *B13*, fig. 4) should be considered contaminated gravel rather than fluvial tailings. Moderate concentrations of arsenic and barium, relatively low concentrations of lead, zinc, and copper, and concentrations of manganese and vanadium that are near crustal abundance characterize this gravel deposit (fig. 12).

In contrast, fluvial tailings from the upper Animas River do represent the deposits milled at the Sunnyside Mill # 2 (site # 165) and the Sunnyside Eureka Mill (site # 164) at Eureka (sites *B19*, *B20*, *B22*, and *B24*, fig. 4) and are characterized by high concentrations of lead, zinc, and manganese, moderately high concentrations of copper, and low concentrations of arsenic and barium. The primary ore minerals were galena and sphalerite. Zinc was not recovered as a commodity at the Sunnyside Mill # 2 (site # 165, fig. 4) until 1912. In 1915, a flotation process introduced at the Sunnyside Mill # 2 produced a copper, lead, zinc, gold, and silver concentrate. In 1917, a selective flotation process plant was added at the new Sunnyside Eureka Mill, which allowed the effective separation of a zinc concentrate (Bird, 1999). Manganese is present at high concentrations in this mill waste (table 1; Nash and Fey, this volume), as evidenced by the intimate intergrowth of rhodochrosite and pyroxmangite in the ore (Casadevall and Ohmoto, 1977). Both deposit types contain low concentrations of vanadium, whereas the concentration of vanadium in rock (and streambed sediment) from the Silverton caldera is on the order of 165 ppm (Yager and Bove, this volume). The decrease in vanadium content in the fluvial tailings is a measure of the amount of uncontaminated sediment in the fluvial tailings (Vincent and Elliott, this volume).

In figure 12A, sites that have been influenced by the breccia-pipe deposits from the upper reach of Mineral Creek basin (site *B2*) and from Cement Creek (*B13*) have relatively higher concentrations of arsenic and lower concentrations of lead, whereas the samples from the fluvial tailings in the Animas River from the Sunnyside Eureka Mill (1917–1930, site # 164, fig. 4, sites *B19*, *B20*, *B22*, and *B24*) show greatly enriched concentrations of lead: the flotation tailings contain more than 20,000 ppm lead and 9,000 ppm zinc. Stamp mill tailings from the Sunnyside Mill # 2 at Eureka (site # 165, 1899–1915 era) have only about 10,000 ppm lead and 5,000 ppm zinc. In figure 12, the effect of variability of the

mill feed on the lead- and zinc-rich tailings from flotation milling at the Sunnyside Mill at Eureka (sites *B20*, *B22F*, and *B24*) is apparent. Samples of flotation mill tailings contain high but variable amounts of lead, zinc, and manganese but low concentrations of vanadium, which is a measure of dilution by sediment. The lead to zinc ratios of the flotation mill tailings (fig. 12B) contrast with those of the gravity mill tailings (site *B22S*). The two samples contain comparable zinc concentrations, but the mill tailings from the early flotation era are enriched in lead by about a factor of two. They are also enriched in vanadium by a factor of two as well, but are not enriched in manganese.

In figure 12C and 12D we use barium, which is found in high concentrations in the mill waste from the breccia-pipe deposits, and manganese, which is found in high concentrations in mill waste from the Eureka district, as tracers of these deposits in the streambed sediment. Copper was not recovered at the Sunnyside Mill # 2 at Eureka until 1912, but it was a major commodity recovered from the ores in the breccia-pipe deposits. The copper versus barium plot (fig. 12C) provides a method to discriminate between mill waste from these two mineral deposit types. Likewise, manganese concentrations are greatly elevated in the ores from the Eureka graben (Bove and others, this volume). The graph of manganese versus vanadium (fig. 12D) shows the mixing of two populations. The first is manganese-poor with concentrations of vanadium near crustal abundance values found in the volcanic rock in the Silverton caldera. The second end member, manganese rich but vanadium poor, represents the mill tailings from the Eureka graben ores. Vincent and Elliott (this volume) use these relationships to calculate the dilution of streambed sediment by mill tailings in the upper Animas River flood plain downstream from the Sunnyside Eureka Mill.

Lake Emma was accidentally breached by the Sunnyside mine in 1978 (Jones, this volume) resulting in the draining of the lake through the American tunnel at Gladstone (mine # 96, fig. 3). A sample representing the Lake Emma blowout was collected from a terrace on Cement Creek near site *S20* (fig. 3). It contained high concentrations of lead, 2,200 ppm, but low concentrations of zinc and manganese, both of which were prominent in the ore. Historical records show that a small mill (Sunnyside-Thompson Mill, site # 113, fig. 4) was present on the shores of Lake Emma and processed ore from production at the Sunnyside mine (mine # 116) through 1899. However, much of the early hand-sorted and cobbled ore from the smelting era was shipped down in sacks (Jones, this volume, fig. 4) and much of the production from the gravity milling era was shipped by tram (Jones, this volume, fig. 2) to the Sunnyside Mill # 1 (also known as the Midway Mill, site # 158, fig. 4; Jones, this volume; Bird, 1999). Only a small amount of mine waste was probably present in Lake Emma when it collapsed into the mine. Galena is a brittle mineral with perfect cleavage, easily crumbled. We suspect that the high concentrations of lead in the 1978 flood deposit probably resulted from contamination by galena dust in the mine as the glacial mud flowed through the American tunnel at Gladstone

(site # 96, fig. 3; Jones, this volume, figs. 27–30). The geochemical and lead isotopic data (fig. 12 and table 1) support this hypothesis.

Samples of fluvial tailings from sites *B27* and *B30* (fig. 4) downstream from mills in the upper Animas River basin have been diluted by unmineralized sediment. Using the geochemical discriminators just discussed, we evaluate the hypothesis that the flood deposits from site *B27*, which is located on a bar in the upper Animas River in the narrow reach between Howardsville and Silverton (fig. 3) and which Pruess (1996) hypothesized to be remnants from the Gladstone flood, are a good match with stamp mill tailings from the Eureka district. In figure 12, manganese, lead, zinc, arsenic, and vanadium concentrations from site *B27* lie close to mixing lines of mill tailings diluted by streambed sediment. Concentrations of copper are less than those of the stamp mill tailings (*B22S*) from the Sunnyside Mill # 2 (site # 165), whereas arsenic and barium concentrations are elevated. Concentrations of lead and zinc lie along mixing lines between the stamp mill tailings and uncontaminated streambed sediment. The strongly elevated concentrations of manganese tie the fluvial tailings deposits from site *B27* to mill tailings contaminated material from the Eureka graben. The lead isotopic signature from site *B27* (table 1) also is a close match with that of the ore from the Sunnyside mine processed at the Sunnyside Mill # 2 (site # 165) prior to the 1911 Gladstone flood (table 1, site *B22*, stamp mill tailings).

Flood deposits at site *B30* at Elk Park (fig. 4) almost certainly represent the 1911 Gladstone flood because they were deposited about 6 ft above low-flow water level. Both arsenic and barium concentrations are elevated relative to the mill tailings from the Sunnyside Eureka Mill, but manganese and vanadium (fig. 12D) and barium and copper (fig. 12C) concentrations lie along a mixing line with uncontaminated sediment. Elevated concentrations of manganese implicate mill tailings from the Eureka graben ore; concentrations of both arsenic and barium are higher than those from the Sunnyside Eureka Mill (site # 165) and suggest that mill tailings from other sites in the watershed are also present at site *B30*. Lead isotopic data are a good match for the ores produced from Sunnyside mine (mine # 116) and an exact match with lead isotope signatures of the mill tailings from the Sunnyside Mill # 2 (table 1, site *B22*, stamp mill tailings). High copper concentrations and a more radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ signature from tailings from the Silver Lake Mill #2 (site # 219, fig. 4) do not implicate the latter mill as a source of the coarse mill tailings at site *B30*, but do show that they are present in the finer tailings deposits at this site in core 96ABS126 (table 1).

Premining Geochemical Baseline

As described previously, we collected stream-terrace gravel samples² in order to determine the premining baseline. These streambed-sediment samples, as preserved in premining terrace gravel deposits, represent the only measure of

aquatic conditions in the watershed prior to the occupation of the watershed by the early wave of miners in 1873. Using the geomorphological mapping of terrace deposits along the major stream channels in the Animas River watershed (Blair and others, 2002), we selected sample sites (fig. 4) and collected the minus-100-mesh sample material for analysis. We then calculated average concentrations for samples from the stratigraphic column that we interpret, using elemental abundances, within-stratigraphic section consistency, and lead isotopic data, to be unaffected by erosion and deposition in the last 150 years. Premining geochemical baseline data are summarized in table 2. Where possible, we selected sites where we could also provide dendrochronological age control by coring Engelmann spruce trees. The trees were cored if live, or sampled if dead, for dendrochronological determination of the minimum age of the terrace deposits, expressed as the calendar year when growth began. Not all sites shown in figure 4 were used to determine the premining geochemical baseline in streambed sediment. Those that were used are listed in table 2 with average premining geochemical baseline values for the deposit-related trace elements at each site. Details of site selection are in Church, Fey, and Blair (2000). We note that stream terrace deposits are not preserved everywhere within the study area, so the sample distribution is neither uniform nor ideal. Enrichment ratios are calculated for each sample interval for each of the deposit-related trace elements. Enrichment factors are calculated on the basis of the average value determined for the premining baseline from each basin. Thus the data used are not independent, but they do provide a useful visual criterion to evaluate contamination processes caused either by deposition of modern contaminated materials on the older terrace deposits or by infiltration of contaminated stream water into the terrace deposits as the height above low-flow water level decreases. Following sections present field observations and data for each site that document and support our interpretation that the sites selected do represent premining streambed sediment.

Upper Animas River Basin

Opportunities for sampling the premining geochemical baseline in terrace deposits (Blair and others, 2002; Church, Fey, and Blair, 2000) are numerous in the upper Animas River basin. The river valley is wide and in most places not incised, especially downstream from Eureka to Howardsville. Premining background samples were collected from sites *B18–B30* (fig. 4).³

²Fluvial deposits consist of gravel that was deposited as bed load in streams and bars or as flood deposits in the recent past. Stream terraces are former flood plains that are no longer active. They have been incised because of changes in stream flow or meandering of the stream within the flood plain and are now elevated above the active stream channel.

³Sites *B28–B30*, near and downstream from Silverton, are in localities of the Animas River but in an extension out of the specific area called upper Animas River basin (Animas River upstream from Silverton).

Table 2. Preming geochemical baseline data from terrace deposits, Animas River watershed study area.

[n, number of samples; <, less than concentration shown; --, data insufficient to warrant reporting a median value; values in italics calculated using data that follow consistent enrichment pattern that we interpret has not been affected by ground-water movement of those metals; sample localities in fig. 4]

Site No.	Sample No.	n	As ppm	Cu ppm	Cd ppm	Zn ppm	Pb ppm	Ag ppm	Mn ppm	Mo ppm	Ba ppm	Sr ppm	V ppm	$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{207}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{208}\text{Pb}}{^{204}\text{Pb}}$
Mineral Creek																
B1	97ABS312	7	38	63	<2	410	450	<2	2,300	10	800	230	120	18.852	15.595	38.236
B4	98ABB236	4	35	60	<2	200	150	<2	1,750	1	680	235	115	18.556	15.572	38.090
B5	98ABB233	4	24	35	3	120	75	<2	570	7	775	180	90	18.741	15.607	38.284
B6	98ABB221	3	37	80	4	180	210	<2	563	5	760	285	120	18.528	15.561	38.053
B8	98ABB230	3	31	32	2	160	58	<2	1,600	<1	720	260	110	18.966	15.621	38.288
B10	999292	10	15	35	<2	210	78	<2	210	5	260	220	56	18.838	15.601	38.217
Cement Creek																
B13	97ABS324A	24	45	130	2	400	420	2	830	6	810	280	150	18.390	15.569	37.998
B14	00ABFC-209	1	18	21	2	80	240	<2	550	7	860	260	180	18.438	15.575	38.054
B15	99-ABB-127	1	43	47	2	120	360	<2	1,200	3	870	400	220	18.441	15.556	38.014
B16	96ABS121 & 122	17	69	62	<2	160	235	<2	830	1	615	240	160	18.449	15.577	38.072
B17	98ABB241	1	65	150	<2	200	230	<2	780	2	740	260	160	18.539	15.578	38.116
Upper Animas River																
B18	98ABB237	5	60	100	4	610	210	3	2,700	7	825	160	110	18.600	15.568	38.136
B19	96ABS140	10	40	120	3	1,350	300	<2	3,900	4	850	205	145	18.416	15.583	38.072
B20	96ABS001B	6	35	160	4	590	320	<2	5,500	4	780	170	140	18.409	15.553	37.985
B21	96ABS131 & 132	19	68	120	2	820	450	<2	3,700	6	765	195	115	18.446	15.576	38.073
B22	Brown silt	19	55	120	2	1,000	360	<2	3,100	9	800	185	120	18.424	15.573	38.055
B22	Preming gravels	10	55	140	3	1,050	410	<2	--	10	820	195	140	18.402	15.555	37.991
B24	96ABS118 & 119	3	51	100	5	540	425	3	--	5	695	170	120	18.431	15.579	38.070
B25	98ABB232	3	26	110	3	300	370	<2	3,500	7	620	180	170	19.050	15.630	38.428
B26	97ABS313	1	21	100	<2	340	290	<2	1,800	4	680	210	130	18.764	15.588	38.216
B27	98ABB234	1	24	190	3	470	210	<2	--	3	740	190	120	18.685	15.576	38.152
B29	98ABB240	3	40	145	2	665	280	<2	2,100	4	720	260	140	18.586	15.572	38.102
B30	96ABS126	6	30	40	<2	800	120	<2	2,250	1	725	225	110	18.693	15.626	38.290
B30	96ABS127	6	33	46	<2	670	110	<2	3,300	1	620	300	160	18.677	15.598	38.199
B30	96ABS128 (soil)	4	26	48	<2	330	75	<2	1,250	1	745	240	100	18.808	15.636	38.385
B30	98ABB225	4	35	48	--	530	150	<2	--	1	760	240	110	18.665	15.600	38.193

Site *B18* (fig. 4) is located on a 6-ft gravel cutbank in the upper part of the Animas River upstream from Eureka. Dendrochronology on a stump on this terrace gave a minimum age of 78 years (the year 1920). Samples from two live trees on this terrace gave ages of 93 and 104 years (Jeff Dean, University of Arizona, written commun., 1999). Five samples from the upper 4 ft of the terrace gave very consistent geochemical results for the deposit-related trace elements. The lowest sample from 5 ft depth (1 ft above low-flow water level) showed the effects of contamination by infiltration of stream water (fig. 13). White coatings (fig. 13A) are aluminum precipitates on gravel in this interval and indicate the high-flow water level. Enrichment ratios (that is, the value measured in modern streambed sediment relative to that measured in the premining gravel) for arsenic and cadmium generally exceeded 2 (table 2), suggesting that the premining geochemical baseline from the Animas River basin upstream from Eureka may be different from that in the lower portion of this basin. Zinc concentrations were highly variable (fig. 13B); only the data from intervals 1, 2, and 4 were used to estimate the zinc concentration given in table 2. Values for arsenic and zinc are in italics in table 2, indicating that only some of the sample intervals from this site were used to calculate the premining geochemical baseline.

At sites *B19* and *B20* (fig. 4), we cored through the flotation mill tailings in the breached tailings dam immediately downstream from the Sunnyside Eureka Mill (site # 165). The upper 1 ft of this core is flotation tailings from the Sunnyside Eureka Mill (fig. 14A). The next 8–10 in. section of core represents a mixing zone. Below 1.7 ft, the core is premining sands and gravel. Crowns of dead willow, which were rooted in the premining silt and were buried by mill tailings, were dated by means of dendrochronology (Vincent and Elliott, this volume). These mill tailings were removed by Sunnyside Gold, Inc., and placed in their repository (site # 510) at the Mayflower Mill in 1998. Similar results were obtained from site *B20* (table 2). A core through mill tailings and contaminated gravel at site *B20* penetrated premining silt that also provided useful premining geochemical background data (table 2). These cores also provided concentrations for contaminants from the Sunnyside Eureka Mill (table 1).

At site *B21* (fig. 4), historical photographs taken of the Eureka town site in 1885 showed that the Animas River was cutting back the east bank of the valley during this period. Site *B21* is inside the railroad turnaround loop south of Eureka. The map of the Silverton Northern Railroad (Sloan and Skowronski, 1975) also shows the Animas River on the east side of the valley, but just west of the railroad tracks. We sampled gravel from a pit excavated at this site in September 1997 inside the railroad turnaround. As the Silverton Northern Railroad arrived in Eureka in 1896 (Sloan and Skowronski, 1975; Jones, this volume, fig. 2), these samples represent geochemical background between the time of the photograph and the time the railroad was built. During this time, milling of ore from the Sunnyside mine was still being done at the Sunnyside-Thompson Mill at Lake Emma (site # 113) and at the Sunnyside Mill # 1 (site # 158, fig. 4),

also known as the Midway Mill, on Eureka Gulch (Bird, 1999). Sunnyside Mill # 2 was not built at Eureka until 1899 (Jones, this volume, table 4 and fig. 19) after the arrival of the Silverton Northern Railroad. However, mining and milling upstream from Animas Forks at the Hanson Mill (site # 51) and the Mastodon Mill (site # 52, fig. 4) at the head of Placer Gulch were ongoing (Jones, this volume, table 2). We call this site an 1885 geochemical background site and recognize that streambed sediment from *B21* could have been contaminated by mining activity upstream from Eureka. The samples from below 4 ft depth in the pit are quite consistent, and enrichment values are generally less than 1.5 (fig. 15). We interpret these data to represent concentrations of deposit-related trace elements in premining streambed sediment.

At site *B22* (fig. 4), a trench about 1,000 ft long was dug across the flood plain of the Animas River (Vincent and Elliott, this volume), and the mapped stratigraphic intervals were sampled and analyzed. Two of those units, the premining silt and gravel, provided excellent data for concentrations of deposit-related trace elements in premining sediment (table 2). In figure 16, we compare the results of these two units with that from four contaminated units—the manganiferous gravels, the stamp mill tailings from the Sunnyside Mill # 2 (site # 165, fig. 4), the flotation mill tailings from the Sunnyside Eureka Mill (site # 164, fig. 4), and the postmining gravel. Note the large differences in concentrations of these two age classes of sediment for all of the deposit-related trace elements except arsenic. Arsenic is mobilized by the manganese oxidation couple and concentrated in the manganiferous gravel relative to all other stratigraphic units, although arsenic is also enriched in the postmining gravel. Concentrations of copper, lead, zinc, cadmium, and manganese are strongly enriched in the manganiferous gravel, the mill tailings, and the postmining gravel, whereas concentrations of vanadium are diluted by the mill tailings (fig. 16). Other aspects of the geochemistry and the details of the stratigraphy are in Vincent and Elliott (this volume). Premining geochemical baseline values for the deposit-related trace elements are in good agreement between premining silt and gravel; these, in turn, are in agreement with other samples from this reach. Manganese concentrations in particular showed large variation among samples in the premining gravel, and data from some sample intervals were rejected because of the large variations in concentration of mobile metals (such as copper, cadmium, manganese, and zinc). Manganese gangue minerals associated with the Sunnyside ore are rhodochrosite and pyroxmangite (Casadevall and Ohmoto, 1977). Manganese is particularly mobile in the ground water in the area as shown by the crosscutting relationship of the manganiferous gravel lenses (Vincent and Elliott, this volume). Reliable manganese values for premining geochemical background in this reach are tentative at best; concentrations of zinc, also very mobile in ground water at site *B22*, are also tentative. Our best estimate of the premining geochemical background value for manganese is about 3,000–3,500 ppm. The ¹⁴C ages from this site are discussed in Vincent and Elliott (this volume).

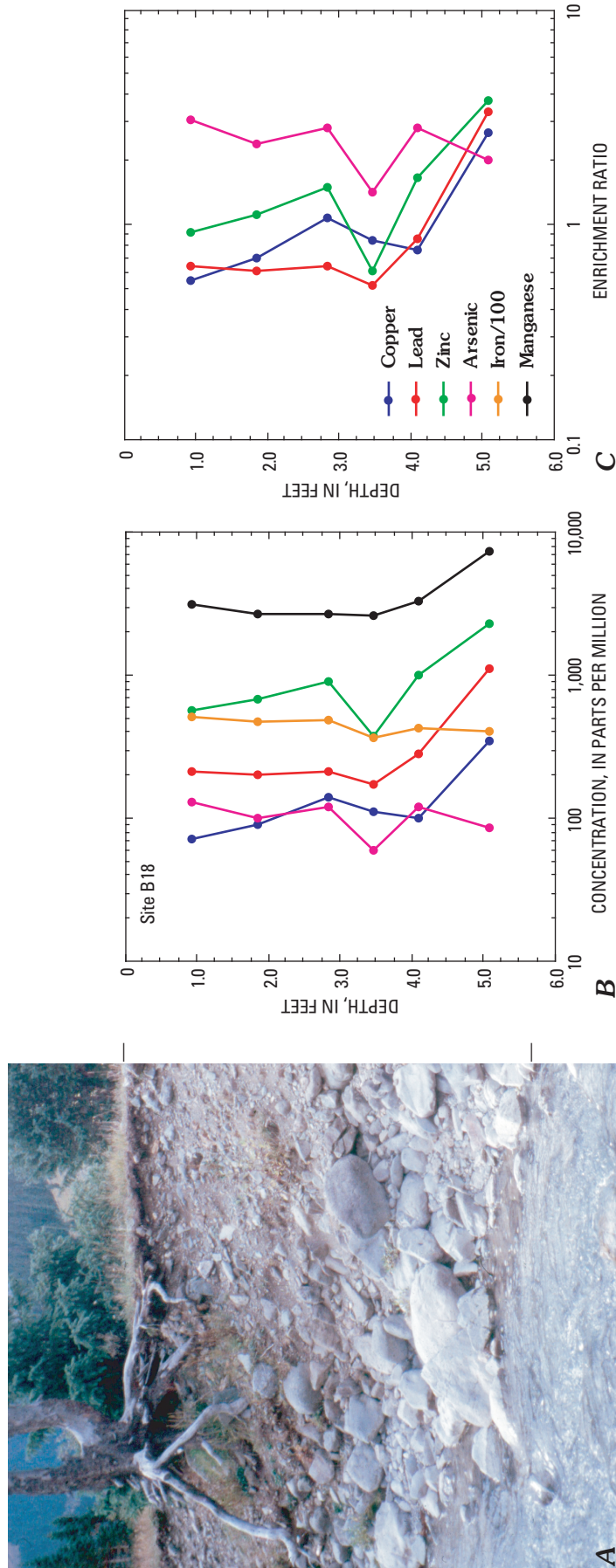


Figure 13. Site B18, downstream from Animas Forks. A, View of west bank of Animas River. B, Stratigraphic profile of geochemical data for copper, lead, zinc, arsenic, iron, and manganese; scaled to photograph. C, Enrichment ratios for copper, lead, zinc, and arsenic plotted against depth below surface of terrace. Enrichment ratios calculated relative to average value for background determined from upper Animas River basin (see data in table 2). In photograph, notice prominent high-water mark on lower boulders in section indicated by white precipitates; data from this interval are contaminated by infiltration of stream water at high flow. Dead tree on terrace gave a minimum date of formation of this terrace at 1920. Other live trees on this terrace were dated at 93 and 104 years, which would push minimum date of formation of this terrace back to 1894.

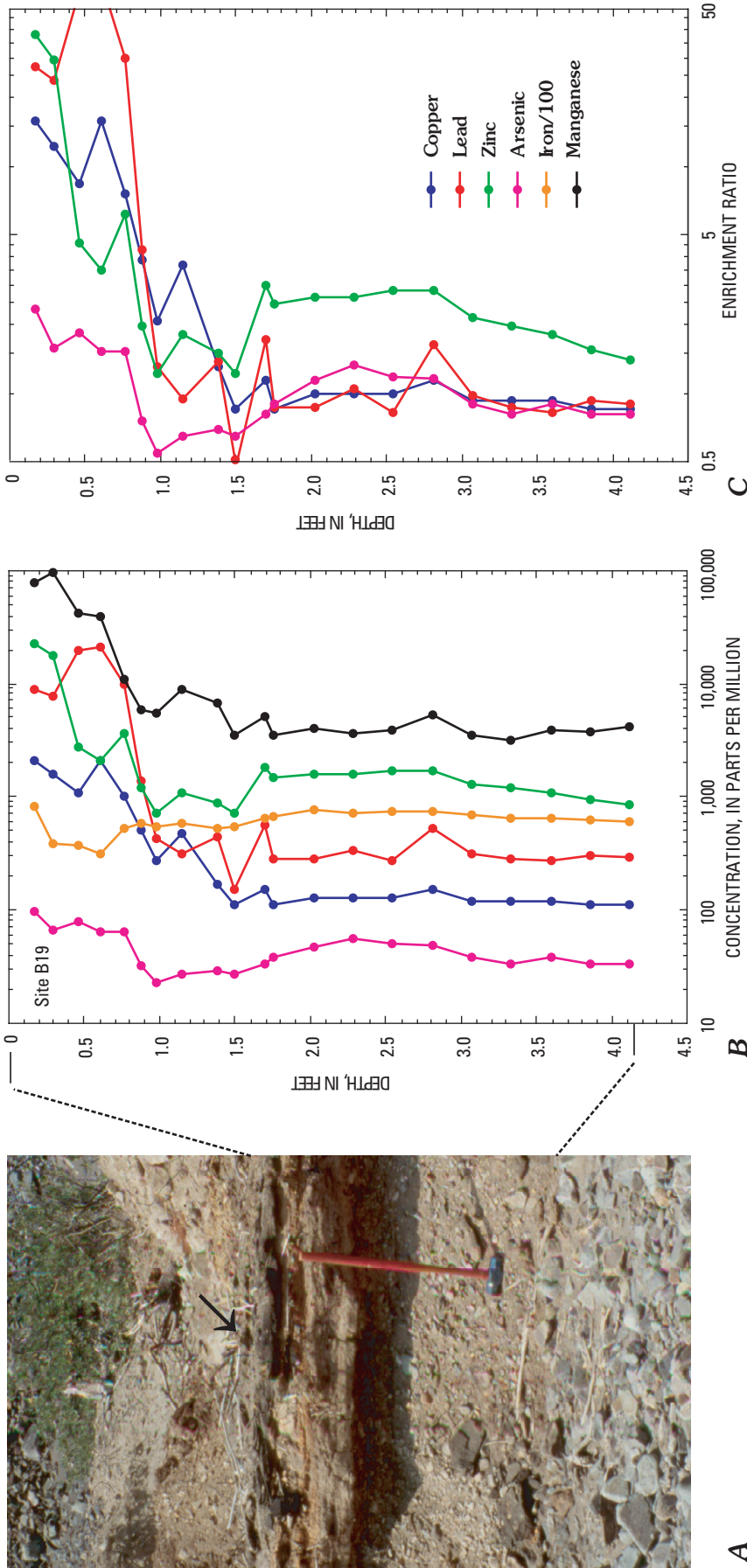


Figure 14. Site B19, flotation mill tailings downstream from Eureka. A, View of site on west bank of Animas River (site has been remediated by Sunnyside Gold, Inc.). B, Stratigraphic profile of geochemical data for copper, lead, zinc, arsenic, iron, and manganese. C, Enrichment ratios of copper, lead, zinc, and arsenic plotted against depth below surface of terrace. Note the presence of fluvial tailings in core site above 1 ft in depth and effect of downward mobilization of copper, manganese, and zinc down to a depth of 1.7 ft. Mill tailings are from the settling ponds directly downstream from the Sunnyside Eureka Mill on the Animas River. Note dead willow buried in the mill tailings (marked by arrow on A). Values for most intervals below 2 ft depth are very consistent and have been used to determine the premining geochemical baseline (table 2) except for lead and manganese at 2.8 ft depth. Dashed lines (A to B) indicate thickness of analyzed section in B and C.

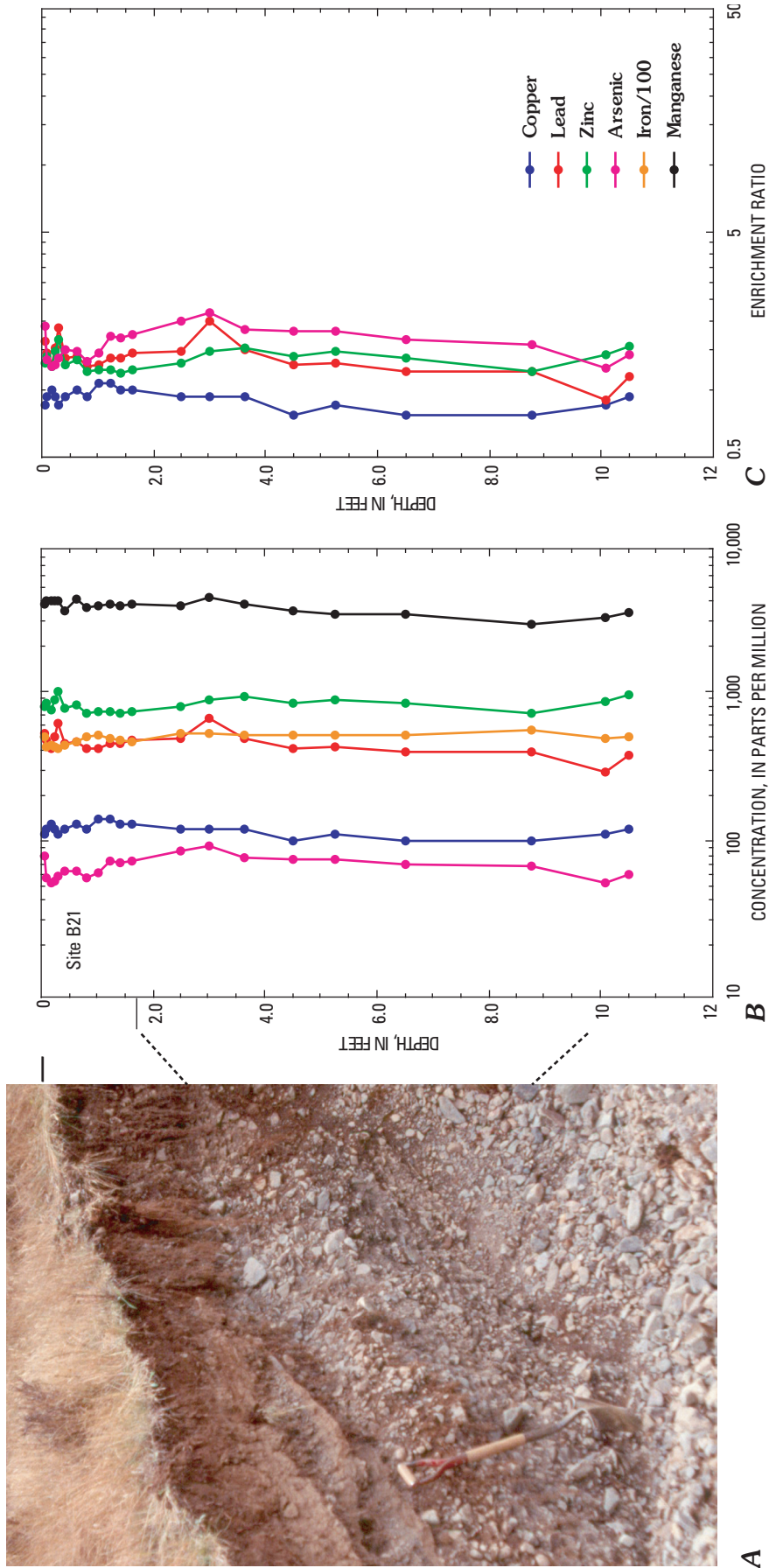
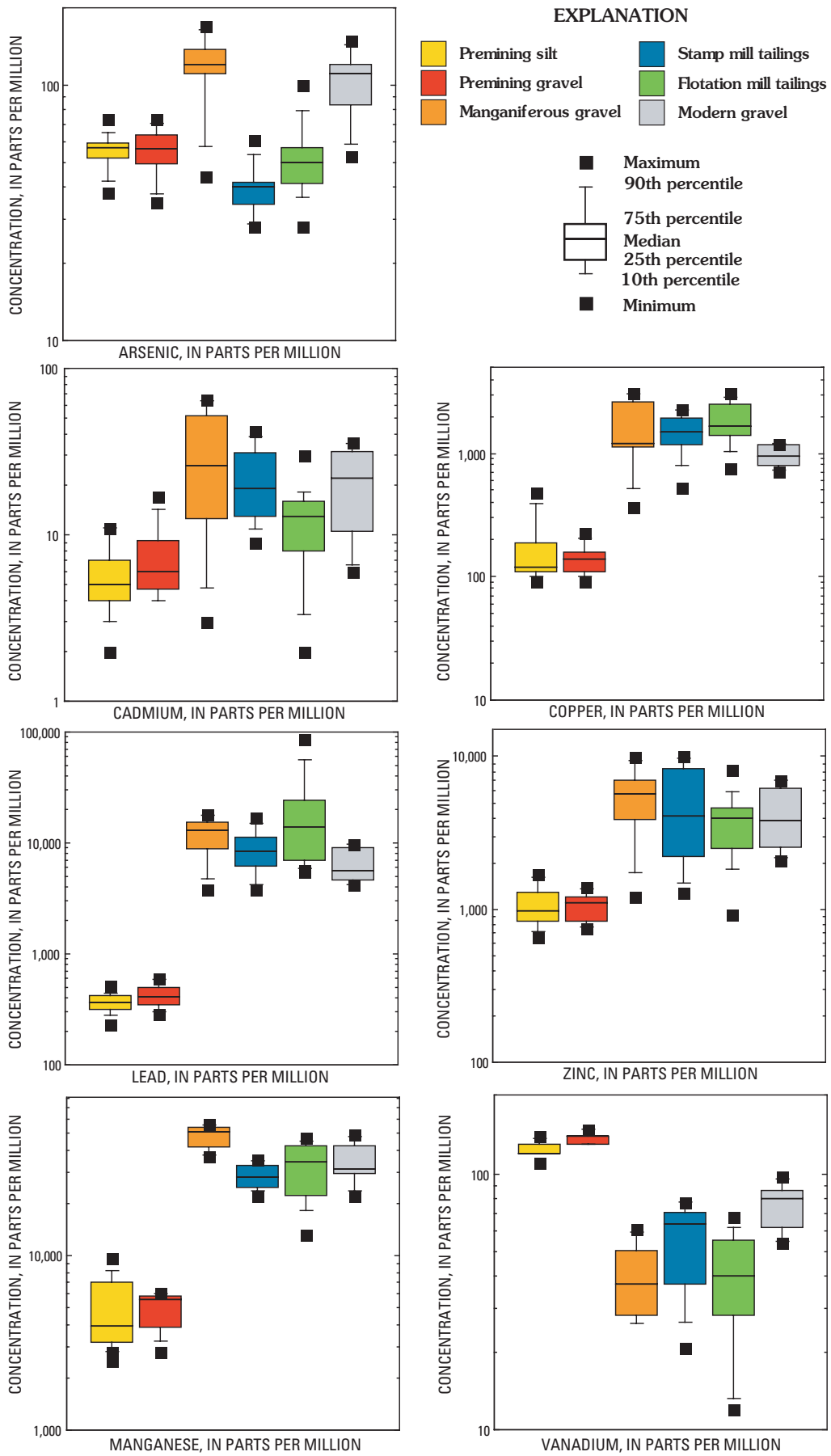


Figure 15. Site B21, which is inside the railroad turnaround loop at Eureka on the east side of the Animas River valley (Sloan and Skowronski, 1975). *A*, View of south pit wall; east pit wall where shovel is sitting is sloped for access; pit access provided by Sunnyside Gold, Inc. *B*, Stratigraphic profile of geochemical data, plotted against depth below surface of the terrace, for copper, lead, zinc, iron, and manganese; scaled to photograph. *C*, Enrichment ratios of copper, lead, zinc, and arsenic, indicating a very consistent geochemical composition of the fine sand and silt fraction of the stream gravel. Fine silt and sand dominate the upper 1.5 ft of the stratigraphic section, whereas rest of section is gravel; boundary marked on view *A*. Geochemical baseline is for about 1885.



The methodology for the determination of premining geochemical background was greatly strengthened by the work of Vincent and Elliott (this volume), who mapped and described the premining and mining era sedimentation in the braided reach of the Animas River valley downstream from Eureka. They document the aggradation of sediment in the braided channel reach downstream caused by the operation of the Sunnyside mills at Eureka between 1899 and 1931. They determined the rate of aggradation prior to and after milling, using dendrochronology, buried human artifacts, and the historical record to provide a chronology of sedimentation events. They document about 3 ft of sediment that accumulated in the reach immediately downstream from the mill because of the increased bed load. The geochemical data from the premining and postmining deposits are an internally consistent documentation of these two periods of sedimentary deposition in the reach downstream from the Sunnyside mills at Eureka.

Site *B23* (fig. 4) is in the Forest Queen (mine # 195) bio-reactor pit discussed in Stanton, Fey, and others (this volume, Chapter E25) and does not provide geochemical background data for stream sediment. Concentrations of deposit-related trace elements in sediment at this site are low relative to what we obtained from other sites within this stream reach (table 2).

At site *B24* (fig. 4), we took a core from the Animas River through a deposit of fluvial tailings into uncontaminated sand and gravel. Determination of premining geochemical baseline at this site is tenuous. Concentration data from sample intervals show a great deal of variation down core (fig. 17A), and enrichment of zinc below a depth of 2 ft indicates that zinc is mobile. In addition, values for manganese are high, greater than 16,000 ppm. Only three samples from 1.3 to 2 ft in depth were averaged to give the data in table 2.

Site *B25* (fig. 4) is on a 2.5-ft high terrace deposit on Cunningham Creek. The data from all four samples are generally consistent, and enrichment factors are 1.5 or less—except that manganese, lead, and cadmium are somewhat elevated in the second sample from the top of the section in interval 2. Dendrochronological data from this site indicate that a live tree has been growing on this terrace since 1936.

At site *B26* (fig. 4), we collected a single sample from the top 2 ft of an 8-ft high gravel terrace on the Animas River downstream from the alluvial fan extending from Brendel

Gulch. Values from this sample may not be fully representative of the entire basin because of undue influence from gravel of the Brendel Gulch alluvial fan (Blair and others, 2002), but with the exception of manganese (1,800 ppm), they are in generally good agreement with other values from the basin.

Site *B27* (fig. 4) is on an island in the Animas River in the narrow part of the valley downstream from Cunningham Creek. Fluvial tailings deposits from the Sunnyside Eureka Mill (site # 164) cover the island. Pruess (1996) recognized that these tailings were deposited during the 1911 Gladstone flood, on the basis of hydrologic analysis of the flood deposits. Geochemical data (table 1 and figure 12) and the lead isotopic data from the mill tailings at site *B27* (table 1) strongly support his hypothesis. We dug through these fluvial tailings into the gravel on the bar. The minimum value obtained from the fifth depth interval at the bottom of this pit in the bar is our best estimate of premining geochemical baseline. The last sample listed at site *B27* is from the side of the gravel bar and shows evidence of contamination by stream water that has infiltrated the gravel deposit. The concentration of lead in the upper three intervals averages 3,200 ppm, and the lead isotopic composition (site *B27*, table 1) is very close to that of the early stamp mill tailings from the Sunnyside Mill # 2 at Eureka (site # 165, fig. 4).

Site *B28* (fig. 4) is in a perched beaver pond on the west side of the Animas River, west of the railroad tracks, downstream from the confluence with Mineral Creek. Data from this site provide evidence of windblown contaminants within the basin, but not the premining streambed-sediment geochemical baseline.

Site *B29* (fig. 4) is on a terrace deposit on the west bank of the Animas River downstream from the confluence with Mineral Creek. A thick ledge of ferricrete protects this site from erosion by the river. The Denver and Rio Grande Railroad tracks were built on this terrace in 1882 (Jones, this volume, table 4; Sloan and Skowronski, 1975) and are alongside the outcrop. Evidence of windblown contamination by lead and copper appears in the top two intervals (fig. 18A); variable amounts of contamination by manganese and zinc appear in both the top and bottom intervals. Enrichment values for most of the deposit-related trace elements are less than 1.5 throughout the intervals sampled (fig. 18B). Although several elements show evidence of contamination at either the top or the bottom of the core, the premining geochemical baseline values are fairly consistent throughout the sampled interval.

Site *B30* (fig. 4) is 5 mi downstream from Silverton, directly downstream from a narrow canyon section of the Animas River at Elk Park. Where the Animas River valley widens again and along an abandoned section of river channel, flood deposits from the 1911 Gladstone flood amount to 1.5 ft of flood debris on top of earlier overbank deposits. These deposits (site *B30*) are largely tailings from the early stamp mills upstream. The data from the sampled intervals in the cores are shown graphically in figure 19

Figure 16 (facing page). Box plots of geochemical data from six stratigraphic units from the trench at site *B22* (Vincent and Elliott, this volume). Note that the premining sediment, which makes up the material in which the willow thickets that lined the Animas River banks prior to mining were rooted, and the premining gravel have very consistent geochemical compositions. Data from four intervals associated with the mining era are shown for comparison. The data from the stamp mill tailings and the flotation mill tailings are in table 1 and figure 12.

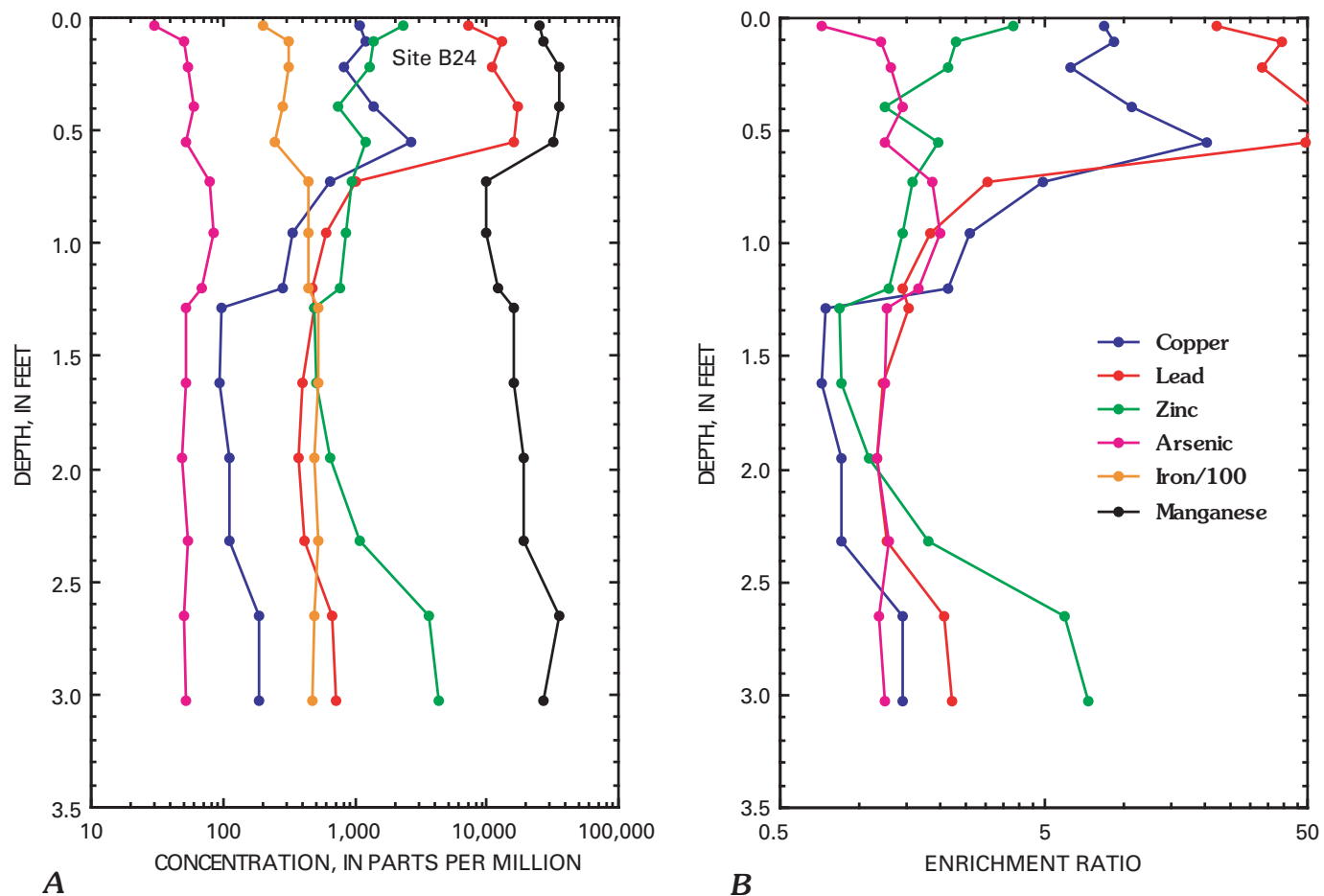


Figure 17. Graphs of data from site B24. A, Stratigraphic profile of geochemical data for copper, lead, zinc, arsenic, iron, and manganese. B, Enrichment ratios for copper, lead, zinc, and arsenic plotted against depth below surface of terrace. Note fluvial tailings at site B24 and their impact on deposit-related trace element distribution above 1.3 ft depth. Values for premining geochemical baseline (table 2) were used from the interval from 1.3 to 2.0 ft. Manganese, zinc, and copper all show evidence of infiltration below this depth.

(fig. 19A and table 1), and photographs of the site are in figure 20. In figure 20A, the fluvial tailings deposit contains a barrel slat like those found at the Sunnyside Mill # 2 site (Vincent and Elliott, this volume) and a nearly complete intact bottle labeled “Prepared by Dr. Peter Fahrney & Sons, Chicago Illinois.” According to the Web site by Dr. Richard Cannon (2004, <http://glswrk-auction.com/061.htm>), “Dr. Peter Fahrney, 1840–1905, grandson of the early Dr. Peter Fahrney, carried on the proprietary medicine business from Chicago.***During the 1890s, Dr. Fahrney’s sons ran the business and set up an elaborate manufacturing plant in Chicago.” The bottle was machine made, indicating that the bottle was manufactured after 1900, but was sealed with a cork. This was an alcoholic cough syrup that we presume was used by workers in the mill. This artifact was manufactured during the same period of time that the Sunnyside Mill # 2 was processing ore from the Sunnyside mine at Eureka (1899–1915).

Figure 20B shows a site downstream where we channeled the overbank section to determine the geochemical stratigraphy. The upper 1.5 ft of core 96ABS126 shows the geochemical data from the fluvial tailings at the top of the core; the large concentration of manganese implicates the tailings from the Eureka graben-type mineralization (Bove and others, this volume). The copper, manganese, and zinc variations in the data indicate that these elements have been mobilized to contaminate the cored intervals below the fluvial tailings in core 96ABS126 (table 1). The data from figure 12 indicate that the tailings have been mixed with uncontaminated sediment and with tailings from other deposits in the watershed. The Colorado blue spruce rooted in the tailings at the site is 27 years old (top left, fig. 20B). ^{14}C dating of a charcoal layer 1.5 ft below the 1911 tailings deposit gives an age of $2,930 \pm 130$ years (Verplanck and others, this volume), which suggests that the 1911 Gladstone flood was at least a 1,000-year flood event. The cored interval

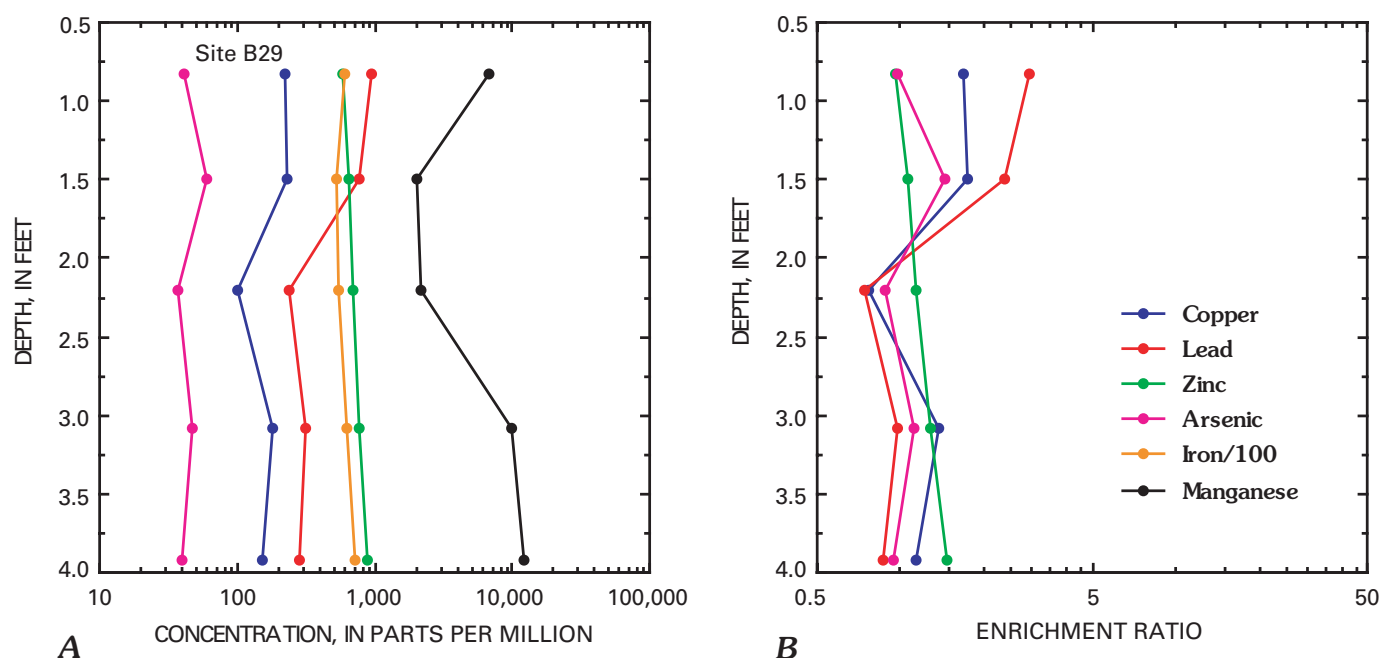


Figure 18. Graphs of data from site *B29*. *A*, Stratigraphic profile of geochemical data for copper, lead, zinc, arsenic, iron, and manganese. *B*, Enrichment ratios of copper, lead, zinc, and arsenic plotted against depth below surface of terrace. Values for premining geochemical baseline (table 2) were used from the interval from 2.3 to 3.9 ft. Manganese, zinc, and copper show evidence of infiltration below 3.1 ft depth.

at 96ABS127 (fig. 19B) is only about 50 ft away, but at a lower elevation. Premining geochemical background values are similar between the two cores and comparable with a third core from several hundred feet away (98ABB225, fig. 19C) that is only about 3–4 ft above low-flow water level. In contrast, soil background values from Elk Park have lower concentrations of deposit-related trace elements (except copper, table 2).

In summary, we obtained premining geochemical baseline data from 10 sites in the upper Animas River basin upstream from the confluence with Mineral Creek (table 2). Mean values for these sites are arsenic, 43 ± 16 ppm; copper, 128 ± 29 ppm; lead, 324 ± 80 ppm; zinc, 703 ± 322 ppm, cadmium, 2.5 ± 1 ppm; silver was below the limit of detection (< 2 ppm). In contrast, the mean values for barium (754 ± 71 ppm), strontium (193 ± 27 ppm) and vanadium (132 ± 17 ppm) showed much lower variability among sites. For the suite of deposit-related trace elements, the within-site variability is smaller than the among-site variability, indicating that the exposed mineral deposits had a local effect on the streambed-sediment geochemistry.

Cement Creek Basin

Although five premining geochemical background sites are located on Cement Creek (*B13* to *B17*, fig. 4), three are single-sample sites. Only two sites are defined on the basis of

multiple samples from different stratigraphic intervals (sites *B13* and *B16*). Site *B11* is from an iron bog on Prospect Gulch and is discussed by Stanton, Yager, and others (this volume, Chapter E14). Site *B12* is from a peat bog and is discussed in Vincent and others (this volume).

Site *B13* (fig. 4) is in an active iron bog on the east side of Cement Creek which is discussed in detail by Stanton, Fey, and others (this volume). The upper stratigraphic interval in the core (fig. 21, above 0.65 ft) is a mixed interval containing both organic and iron oxyhydroxide formed by emergence of ground water from the east side of Cement Creek. The layer at 0.65 ft is largely organic, probably grasses that grew on a former streambed-sediment deposit.

This core contains premining sediment deposited in a previously active channel that was cut off by construction of the Silverton, Gladstone, & Northerly Railroad in 1899 (Sloan and Skowronski, 1975). The railroad went into foreclosure in 1915 and disrepair during World War I. The tracks were closed in 1923 and abandoned in 1926. Clastic sediment from Cement Creek was once again deposited in this channel.

Ground water has been draining this slope for thousands of years. A road cut in the hillside immediately downstream from site *B13* and about 30 ft above low-flow water level exposed a colluvial ferricrete deposit containing a goethite-replaced log that was dated at $7,680 \pm 200$ years B.P. by ^{14}C (Verplanck and others, this volume, table 2; Yager and Bove, this volume, pl. 2). Live trees surrounding the bog have ages

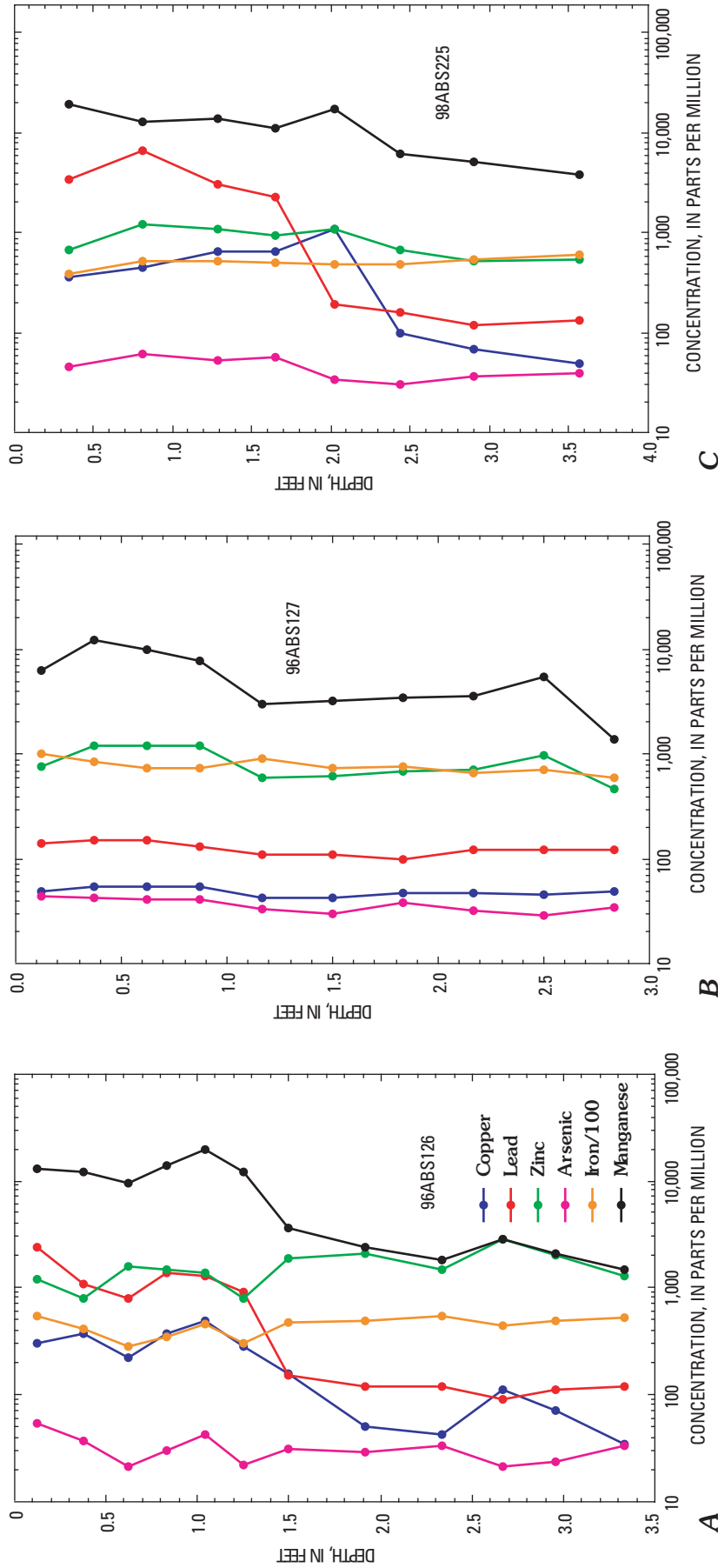


Figure 19. Stratigraphic profile of geochemical data, plotted against depth below surface, for copper, lead, zinc, arsenic, iron, and manganese from cores from bank of abandoned Animas River channel at Elk Park (site B30). Background values were determined from samples below 1.5 ft depth in cores 96ABS126 (A) and 96ABS127 (B) and below 2.5 ft depth in core 98ABS225 (C).



A

B

Figure 20. Site *B30*, Elk Park. *A*, Fluvial stamp mill tailings deposited by the Gladstone flood of 1911; deposit is about 50 in. thick. Deposit contains barrel slat (arrow) and nearly complete and intact cough syrup bottle labeled "Prepared by Dr. Fahrney & Sons, Chicago Illinois." Note crossbedding and jumbled logs, indicative of high-energy depositional environment of a flood deposit. *B*, Site of core 96ABS126, site *B30*. Colorado blue spruce (at top left, arrow), rooted in tailings, is 27 years old (rooted in 1973). ^{14}C date from charcoal at depth of 18 in. below tailings deposited by 1911 Gladstone flood (arrow) is $2,930 \pm 130$ years. Downward movement of copper, manganese, and zinc is also evident in this core. Dark marks on rule are at 6-in. spacing; exposure is about 42 in.

ranging from 66 to 132 years whereas three dead trees in the bog have ages of 19, 73, and 270 years (Jeff Dean, Univ. of Arizona, written commun., 1999; Vincent and others, this volume). Data from the interval from 0.8 to 1.7 ft were used to calculate premining geochemical background at this site (fig. 21*B*). Concentrations of the deposit-related trace elements were fairly consistent throughout this interval. The increase in copper, zinc, and manganese concentrations below 1.7 ft suggests that the interval below 1.7 feet has been contaminated by trace elements transported recently by ground water. Enrichment values for copper, zinc, and manganese exceed 2 below a depth of 1.7 ft (fig. 21*C*). Several lines of evidence, particularly the evidence from the tracer study (Kimball and others, this volume), indicate that ground water enters Cement Creek at this site.

Site *B14* (fig. 4) is located in a 5-ft high cutbank along Cement Creek. Sample 00ABFC209A is from about 2 ft above low-flow water level at an interval sampled for ^{14}C dating. Wood from the unconsolidated sand stratigraphically above this sample gave a ^{14}C age of 230 ± 60 years B.P. (Vincent and others, this volume). The sample is premining streambed sediment from Cement Creek. Concentrations in this sample are low with respect to the other premining streambed-sediment samples obtained from Cement Creek (table 2).

Data from site *B15* (fig. 4) are from a single sand sample collected about 8 ft above low-flow water level from a 25-ft cutbank gravel deposit along Cement Creek. We have no independent age control on this streambed-sediment sample.

Site *B16* (fig. 4) is from a well-exposed cutbank (fig. 22*A*) upstream from Ohio Gulch that is diagramed in figure 4 in Vincent and others (this volume). All the concentration data

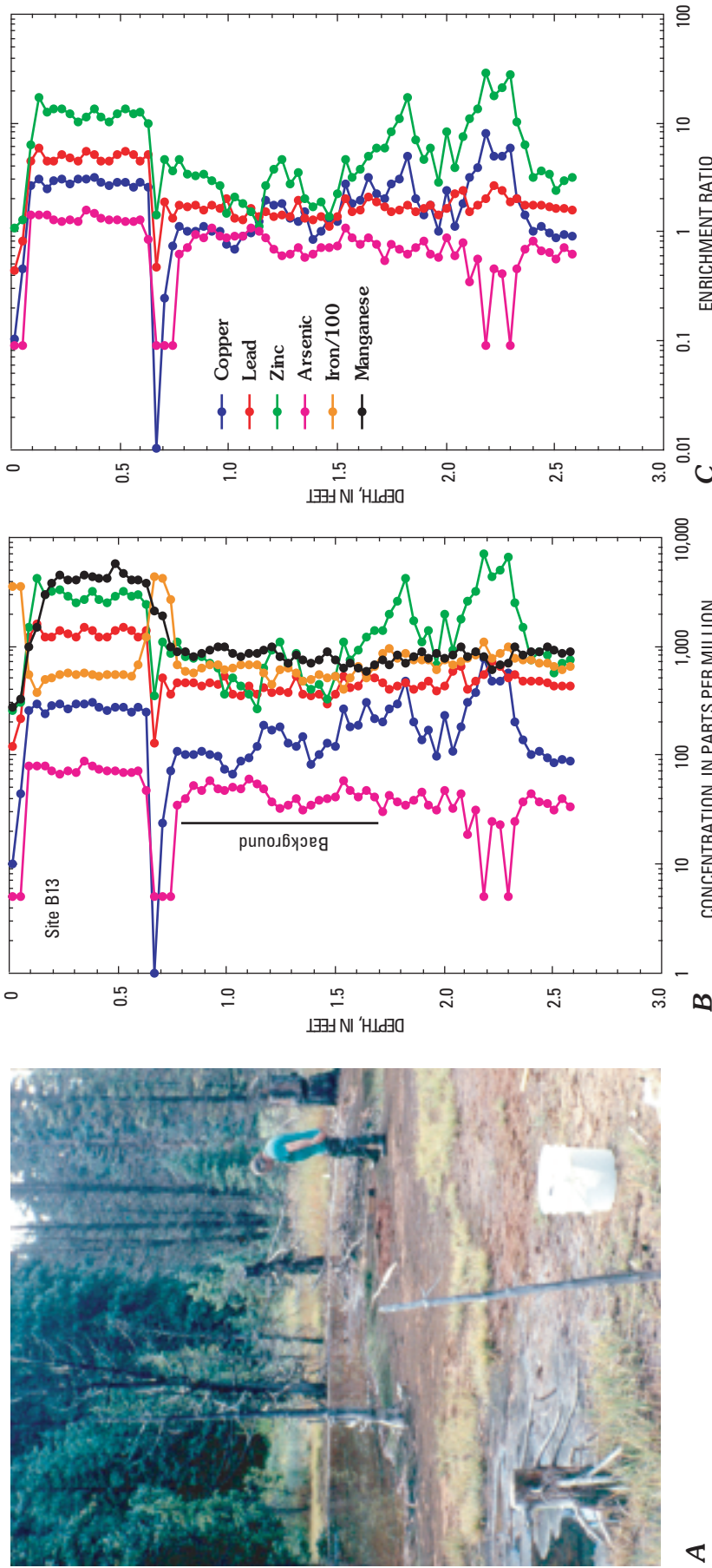


Figure 21. Site B13, a large bog on the east bank of Cement Creek. A, View of site looking southeast. B, Stratigraphic profile of geochemical data for copper, lead, zinc, arsenic, iron, and manganese. C, Enrichment ratios for copper, lead, zinc, and arsenic plotted against depth below surface of bog. Enrichment ratios calculated relative to the average value for background determined from Cement Creek basin. Bog chemistry is discussed in Stanton, Yager, and others (this volume). Interval used for premining geochemical background (table 2) is indicated. Upper interval is contaminated by historical mining. Lower intervals show influence of metals in ground water following establishment of bog. In photograph, large dead tree stump behind geologist (Mark Stanton) was 273 years old (Vincent and others, this volume). Live trees surrounding this bog range in age from 66 to 132 years.

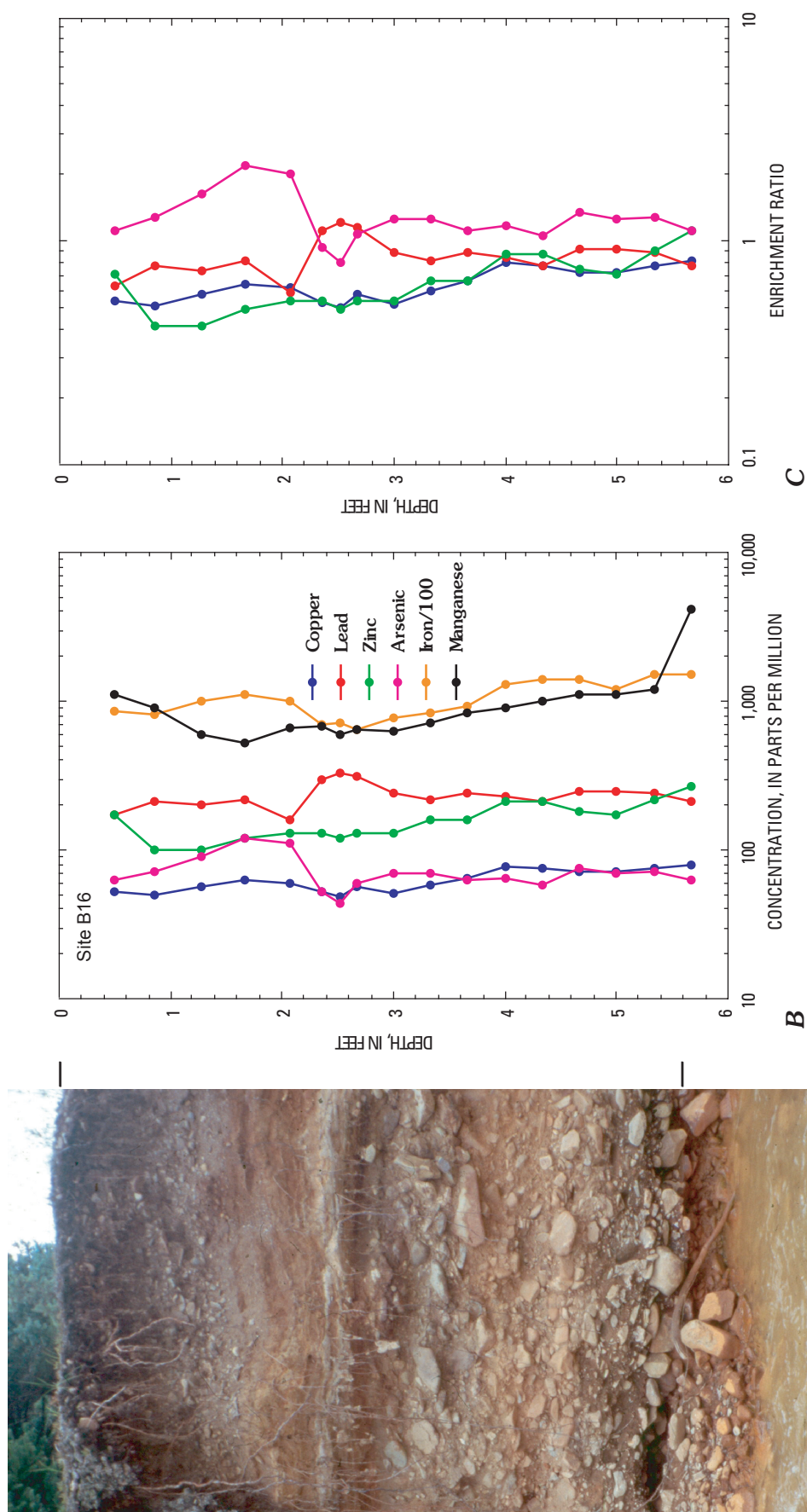


Figure 22. Site B16. A, View of site on east bank, Cement Creek. B, Stratigraphic profile of geochemical data for copper, lead, zinc, arsenic, iron, and manganese; scaled to photograph. C, Enrichment ratios of copper, lead, zinc, and arsenic plotted against depth below surface of terrace. Geomorphologic history of this site and ^{14}C ages obtained are described in detail in Vincent and others (this volume). A ^{14}C age determined from near the top of the gravel section was 725 ± 120 years B.P. A large Engelmann spruce on top of the bank is 143 years old and provides a minimum date of 1858 for the top of this terrace. All data except for that from bottom interval, which shows infiltration by stream water, were used to calculate premining geochemical baseline (table 2).

(fig. 22B), with the exception of manganese in the lowest sample (5.7 ft), are very consistent throughout the exposed gravel and sand section. Iron is enriched in the fine sediment in the upper 2.5-ft section. A ^{14}C age from wood in the stratigraphic section places the age of this gravel-to-sand interface at about 725 ± 120 years B.P. The gravel section could be as old as 2,500 years B.P., but probably is not as old as the stump exposed in growth position beneath a peat deposit just 100 ft upstream (Vincent and others, this volume), which was dated at $2,840 \pm 80$ years B.P. The large Engelmann spruce on top of the terrace (fig. 22A) is 143 years old and began to grow in 1858, a date that is 15 years before the signing of the Brunot Treaty with the Ute Tribe in 1873, which allowed exploration for mineral deposits within the Animas River watershed. Data from all the intervals were used except the lowest one, which shows elevated manganese concentrations caused by the infiltration of contaminated stream water (fig. 22B). All the age control data indicate that this site provides a good estimate of the premining geochemical baseline. Note that the fine sediment at about 2 ft depth does show an increase in concentrations of arsenic and iron, and that lead is enriched at the top of the gravel section at about 2.5 ft depth.

Site *B17* (fig. 4) is from the bottom few inches of a 1-ft deep pit dug into the terrace on which the Silverton, Gladstone, and Northerly Railroad grade was built in 1899 (Sloan and Skowronski, 1975). Since the canyon is narrow here, we presumed that the terrace was created before mining. The upper level in this pit contained largely sand. Elevated trace-element concentrations in the upper sample suggested that it had been contaminated. The lower sample was from an interval that contained fairly large cobbles, sand, and silt. The geochemical data from the lower of the two samples were used to estimate premining baseline. The data from this interval are reasonably consistent with those from other sites along Cement Creek, and lead isotopic data are more radiogenic than the ore lead from the deposits in the Cement Creek basin (table 2).

In summary, we obtained premining geochemical baseline data from five sites in the Cement Creek basin (table 2). Mean values for these sites are arsenic, 48 ± 20 ppm; copper, 82 ± 55 ppm; lead, 297 ± 88 ppm; zinc, 192 ± 124 ppm; cadmium and silver were at or below the limit of detection (< 2 ppm). In contrast, the mean values for barium (779 ± 105 ppm), strontium (288 ± 64 ppm), and vanadium (174 ± 28 ppm) had much lower variability among sites. For the suite of deposit-related trace elements, the within-site variability is smaller than among-site variability, indicating that the exposed mineral deposits had a local effect on the streambed-sediment geochemistry. The premining geochemical background values determined from site *B14* had much lower concentrations than did the other sites in the Cement Creek basin.

We did not find any mill tailings deposits in the Cement Creek basin to sample during the course of our studies. We did, however, sample the material that was

flushed from the American tunnel at Gladstone (mine # 96, fig. 3) near site *B14* when Lake Emma collapsed in 1978 (table 1), flooding the Sunnyside mine (Bird, 1999; Jones, this volume).

Mineral Creek Basin

Samples from stream terraces were collected at six sites in the Mineral Creek basin in an attempt to determine the premining geochemical baseline levels of the deposit-related trace elements in this basin (*B1*, *B2*, *B4*, *B5*, *B6*, and *B8*; fig. 4). Samples from four additional sites (*B3*, *B7*, *B9*, and *B10*) were collected from perched beaver ponds and iron bogs in order to evaluate the windblown dust component of the sediment. Geochemical profiles of five sites are in figure 23, and photographs of sites *B2* and *B6* are in figure 24.

Site *B1* (figs. 4 and 23A) is in the upper reaches of Mineral Creek just south of Chattanooga on U.S. Highway 550. The sample is from a terrace about 1.5 ft above low-flow water level. The site is protected from stream erosion by a large rock outcrop and is mantled with willow. Data from the upper five intervals show good reproducibility for all deposit-related trace elements, and all seven sample intervals have good reproducibility with the exception of manganese, zinc, and cadmium (not shown), whose concentrations are in italics in table 2. The enrichment ratio for most intervals for all the deposit-related trace elements is less than 2.5. We interpret the data from the lowermost two or three intervals of the core from site *B1* to show that these intervals were affected by infiltration of contaminated stream water, which raised the concentrations of manganese, cadmium, and zinc.

Site *B2* (figs. 4 and 23B) proved to be a young terrace. The top of the terrace was barren of vegetation (fig. 24A). All the intervals sampled are contaminated; enrichment factors for most intervals were generally greater than 3 to 5. This site contained no useful premining geochemical baseline data. It does provide data for contaminants from breccia-pipe deposits from the upper reaches of Mineral Creek basin (table 1).

Site *B3* (fig. 4) is located in a beaver pond fed by iron-rich ground water. Whereas it is a geochemical baseline site for windblown contaminants, it does not provide any useful data for the streambed-sediment geochemical baseline and will not be discussed further here.

Site *B4* (fig. 4) is on a terrace near the confluence with Middle Fork Mineral Creek. We do not include a diagram of the data; they are fairly consistent throughout the terrace, and enrichment ratios generally do not exceed 1.0 with a maximum value of 1.3. The minimum calendar date of this surface is 1915 on the basis of dendrochronological dates on live trees, but the geochemical data indicate that all intervals sampled are premining in age.

Site *B5* (figs. 4 and 23C) is on a terrace along the lower portion of Middle Fork Mineral Creek. All four sampled intervals give very consistent data for all of the deposit-related trace elements. Normal weathering processes elevated the manganese concentration in the top interval (fig. 23C). Enrichment ratios are near 1 or less.

Site *B6* (figs. 4, 23D, and 24B) is on a low terrace in the lower reaches of Mineral Creek just upstream from the confluence with South Fork Mineral Creek. The site is dug in the terrace below a large stump that gave a minimum calendar date of 1876, almost before the onset of mining (Jones, this volume). Six live trees from this terrace gave dendrochronological ages ranging from 150 to 250 years (Jeff Dean, University of Arizona, written commun., 1999). The two uppermost layers are contaminated, most likely by deposition of younger overbank sediment or by wind-blown material. Likewise, interval 4 from a depth of 1.8 ft is contaminated, possibly by material from above falling into the interval during sampling. Data from intervals 3, 5, and 6 were averaged from this site (table 2). As one can see (fig. 23D), there is a great deal of variation in the geochemical data from this site.

Site *B8* (fig. 4) is on a terrace deposit on South Fork Mineral Creek. It is about 30 ft above low-flow water level and is part of the old terrace deposits mapped by Blair and others (2002). Data from this site are very consistent and are not shown in figure 23. Enrichment factors are generally less than 0.4 and do not exceed 1. The data reflect the fact that South Fork Mineral Creek drains an area outside the caldera margin that has not been extensively mineralized.

Sites *B7* and *B9* (fig. 4) are in perched iron bogs located on the north side of South Fork Mineral Creek. They are well above the high-flow water level in Mineral Creek and contain a record of windblown contamination that has been dated using ^{210}Pb and ^{137}Cs radiometric methods (Marci Marot, unpub. data, 1999). The effect of windblown contamination is also shown in the core from site *B10*.

Site *B10* (figs. 4 and 23E) is in a large perched beaver pond on the south side of Mineral Creek south of the confluence with South Fork Mineral Creek. The upper 0.6 ft interval contains a record of windblown contamination that has accumulated since circa 1950. The data from below 0.65 ft down to 1.25 ft provide an estimate of the windblown sediment background values for the deposit-related trace elements prior to mining. Below 1.25 ft in the core, ^{210}Pb and ^{137}Cs activity indicates that some metals have been transported into the core by ground water (Marci Marot, unpub. data, 1999). As shown in figure 23E, the data are remarkably consistent throughout the interval; they have enrichment patterns that vary from 0.2 to 1. The background data from this site reflect windblown materials and may not be directly relevant to the streambed-sediment geochemical baseline. However, the premining geochemical baseline values from site *B10* are very similar to those determined from South Fork Mineral Creek at site *B8*.

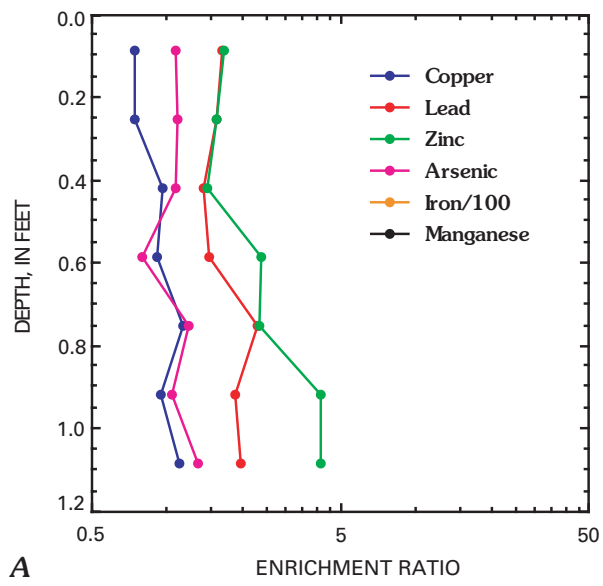
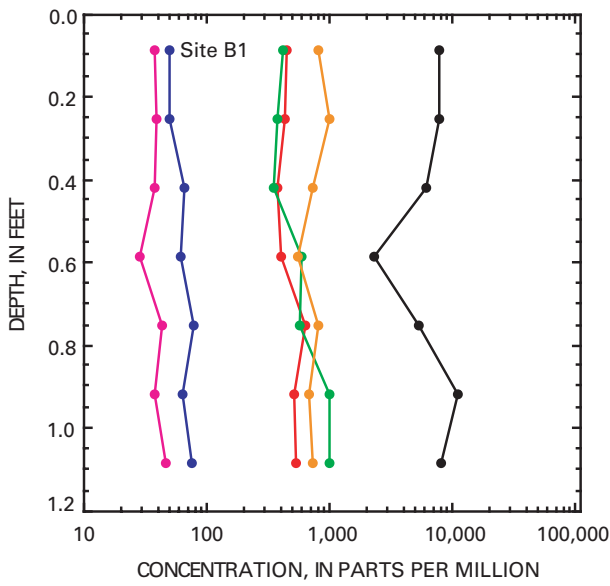
In summary, we obtained premining geochemical baseline data from five sites in the Mineral Creek basin (table 2). Mean values for these sites are arsenic, 33 ± 5.7 ppm; copper, 54 ± 20 ppm; lead, 189 ± 160 ppm; zinc, 214 ± 114 ppm; cadmium and silver were at or below the limit of detection (<2 ppm). In contrast, the mean values for barium (747 ± 47 ppm), strontium (238 ± 39 ppm), and vanadium (111 ± 12 ppm) had much lower variability among sites. For the suite of deposit-related trace elements, within-site variability is smaller than among-site variability, indicating that the exposed mineral deposits had a local effect on the streambed-sediment geochemistry. The premining geochemical background values determined from the perched beaver pond (site *B10*) generally had lower concentrations of the deposit-related trace elements than did the other sites in the Mineral Creek basin.

Effect of Historical Mining and Milling on Streambed Sediment

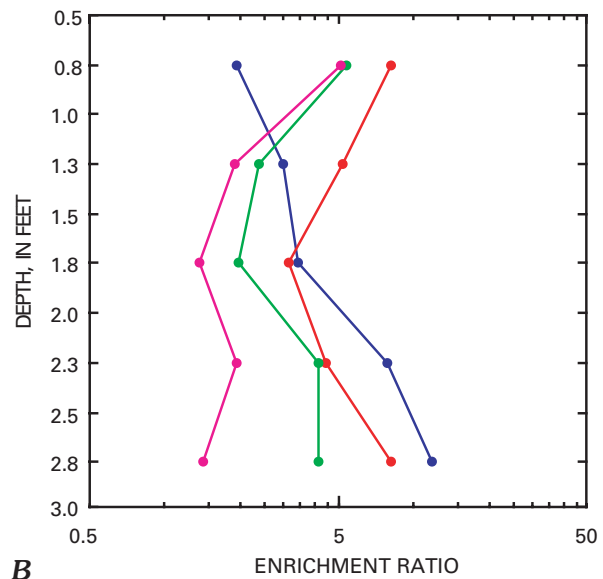
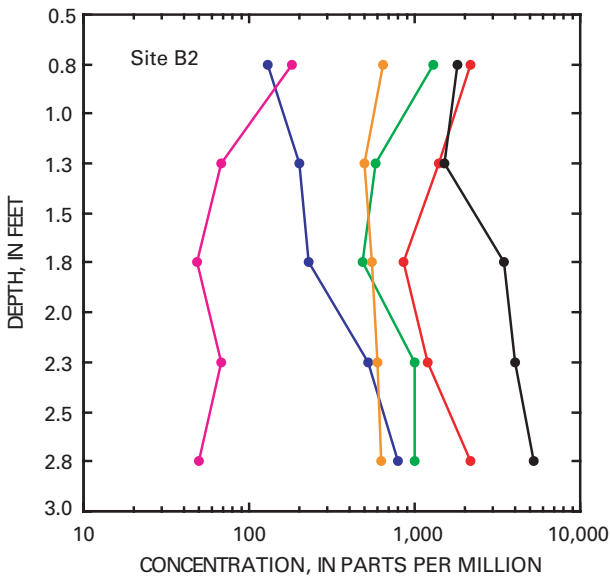
To demonstrate the effect of historical mining on the stream reaches in the watershed, we compared concentrations determined in premining sediment from terrace deposits (table 2) with those in modern streambed sediment. Both the total-digestion data from this study and the NURE data have been used to define current geochemical baseline conditions (figs. 25–31).

Arsenic

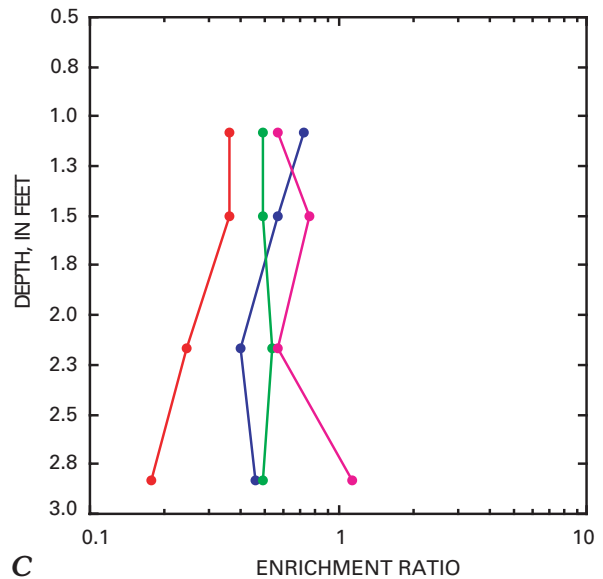
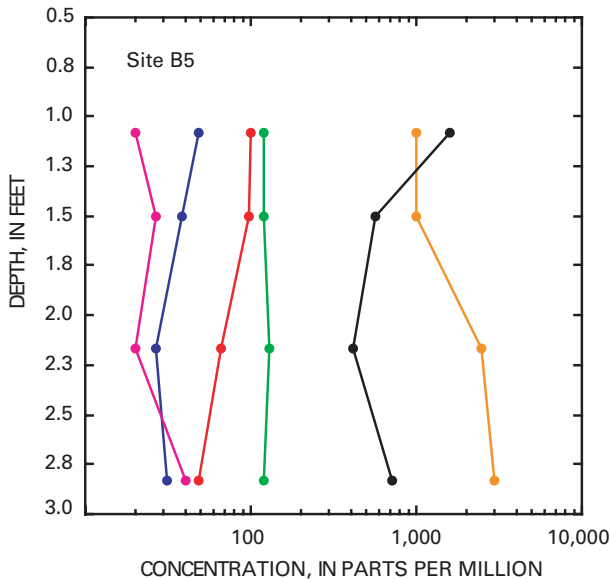
The concentration of arsenic in premining streambed sediment throughout the Animas River watershed study area was elevated by a factor of 10–20 above crustal abundance. Concentrations range between 20 and 40 ppm throughout much of the watershed study area and are between 40 and 60 ppm in the upper Animas River basin upstream from Eureka and throughout the Cement Creek basin (fig. 25A, table 2). Arsenic in modern streambed sediment (fig. 25B) is elevated above premining geochemical baseline concentrations in the braided reach downstream from Minnie Gulch. Arsenic concentrations are also elevated above premining geochemical baseline concentrations in upper Mineral Creek and reflect mining and milling of the arsenic-rich breccia-pipe deposits exploited between 1882 and 1900 upstream from Chattanooga. Elevated concentrations of arsenic in modern streambed sediment also occur upstream from Animas Forks. The effect of historical mining on the concentrations of arsenic is also evident in the streambed sediment of the Animas River downstream to Elk Park. Arsenic concentrations in streambed sediment from tributary streams downstream of the Silverton caldera have values near crustal abundance.



A



B



C

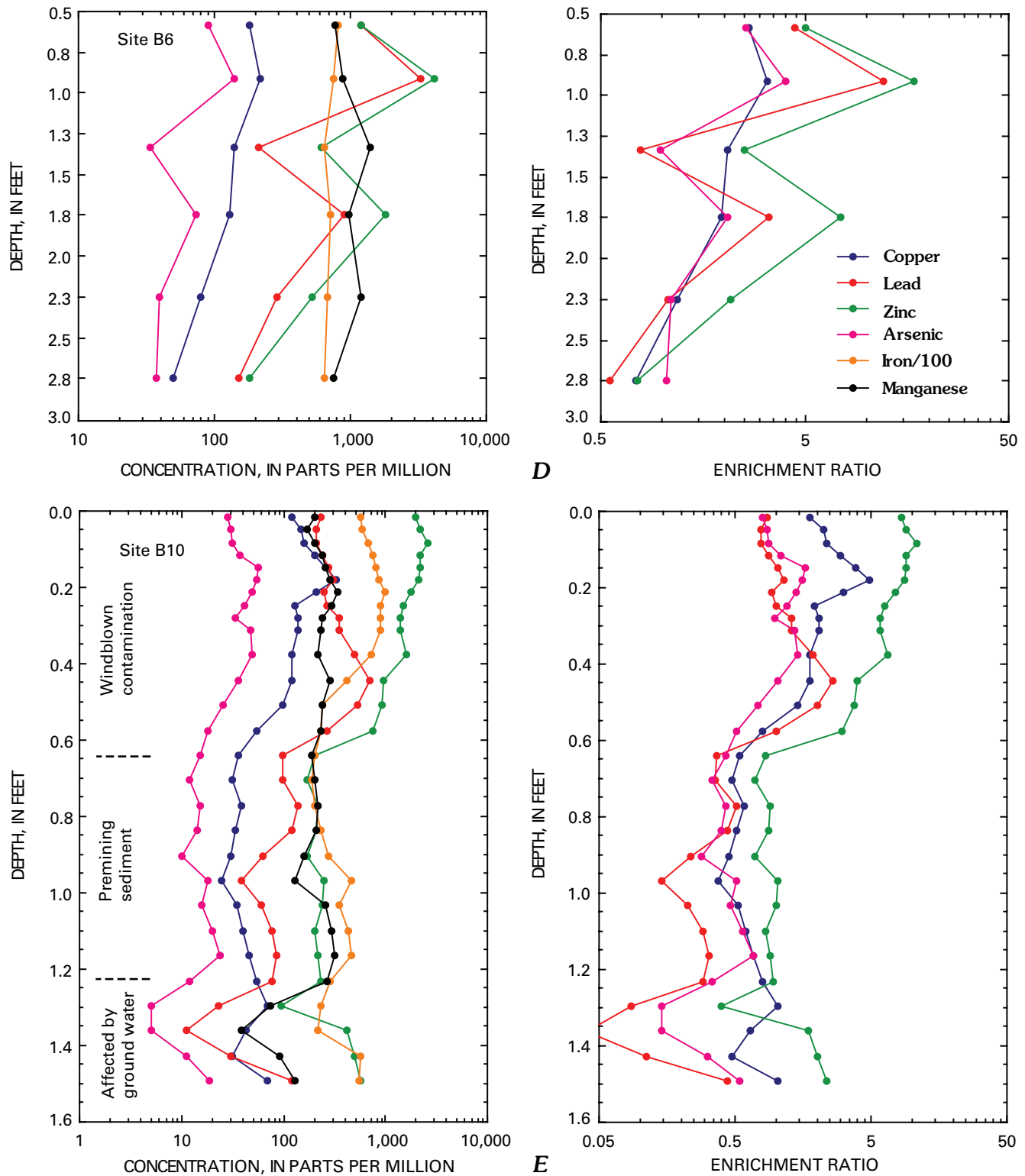


Figure 23 (above and facing page). Geochemical data from terrace deposits at sites *A, B1; B, B2; C, B5; D, B6; and E, B10* (locations, fig. 4), Mineral Creek basin, used to evaluate premining geochemical background (table 2). Geochemical data and enrichment ratios are plotted against depth below surface of terrace. Enrichment ratios calculated relative to average value for background determined from Mineral Creek basin (table 2). Enrichment ratios exceeding ≈ 2 are considered contaminated by historical mining activity.



A



B

Figure 24. Sites *B2* and *B6* on terraces, Mineral Creek basin. *A*, Site *B2*, showing lack of soil profile and established plants on terrace; terrace is about 3 ft high; view is of west bank, Mineral Creek. Light-colored area is the top of the terrace; cutbank is darker colored section. All gravel samples from this site were contaminated. *B*, Site *B6*; view is of east bank, Mineral Creek. Stump growing on top of low terrace gave a minimum date for formation of terrace of 1876. Live trees on this terrace were large, as much as 2 ft in diameter, and gave dendrochronological ages of 150–250 years. Shovel handle is 20 in. long.

Copper

The premining concentration of copper in streambed sediment in the Mineral Creek basin (table 2) was near the crustal abundance value of 68 ppm. Copper concentrations in the Cement Creek and Animas River basins are elevated by as much as a factor of two above crustal abundance (fig. 26A; table 2). Copper concentrations in modern streambed sediment (fig. 26B) are substantially elevated above premining geochemical baseline concentrations in Mineral Creek, again reflecting the production of “gray copper ore” from the breccia-pipe deposits in the upper reaches of Mineral Creek basin. Besser and others (2001) and Kimball and others (this volume) have identified this reach as the largest

contributor of dissolved copper in the Animas River watershed study area. Copper concentrations have been elevated above premining geochemical baseline concentrations in streambed sediment of the upper Animas River by a factor of 3–6 in the reach extending downstream from Eureka to the confluence with Mineral Creek. Elevated concentrations of copper in modern streambed sediment also occur upstream from Animas Forks. Although we have not measured premining sediment concentrations in Arrastra Creek, the high concentrations in modern streambed sediment probably also reflect copper introduced by historical mining. Copper concentrations in streambed sediment from tributary streams downstream of the Silverton caldera have values near crustal abundance.

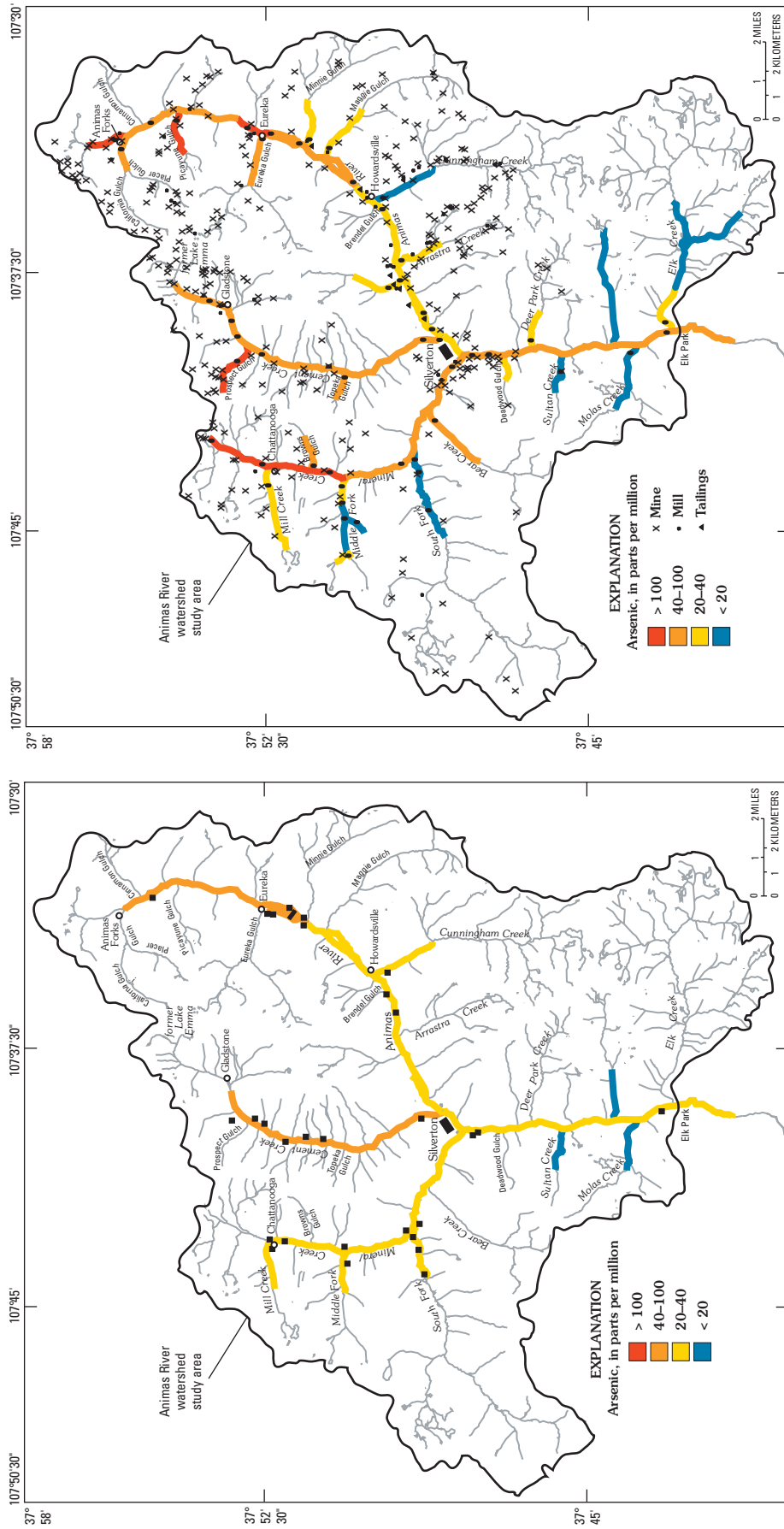
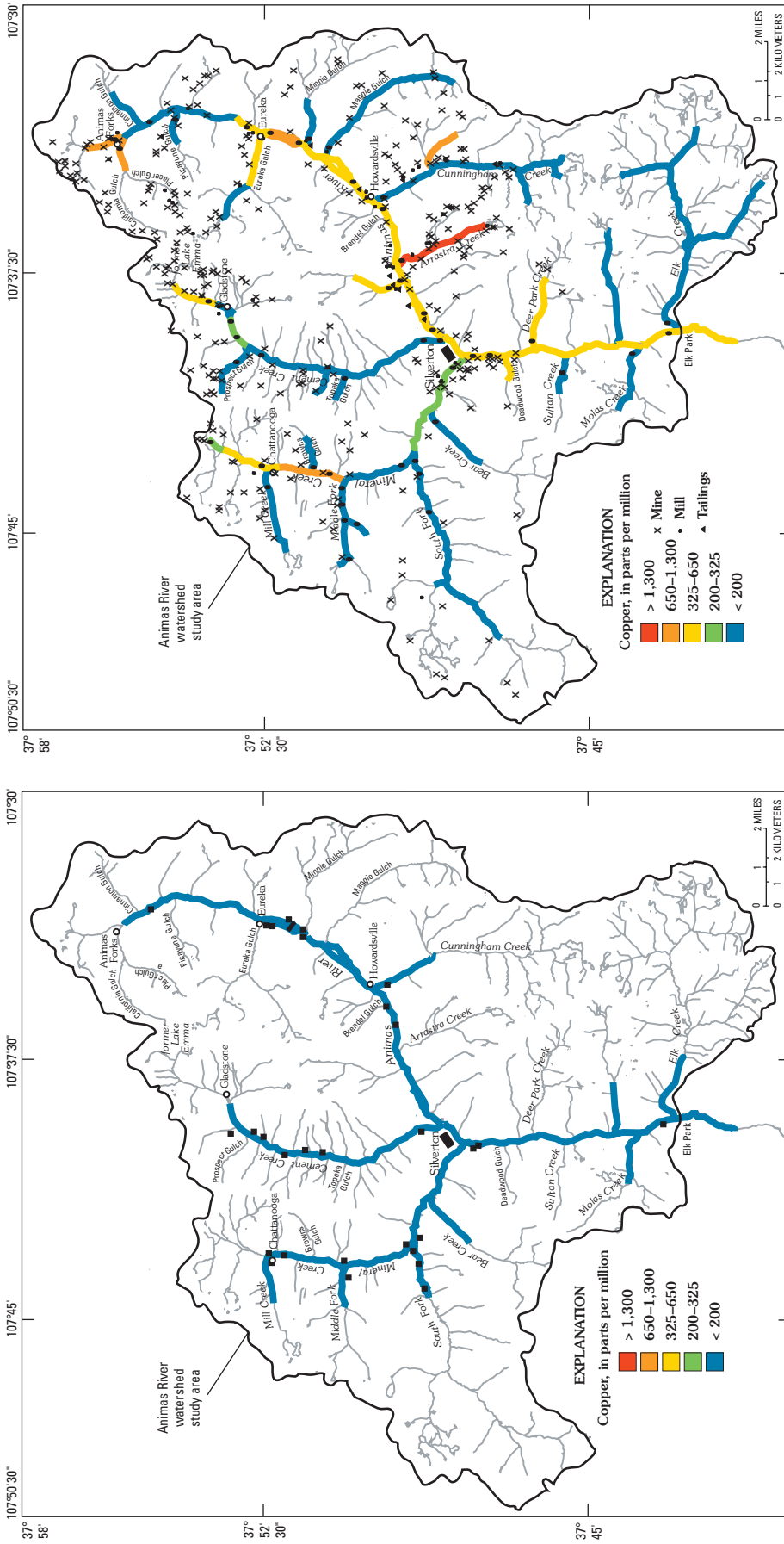


Figure 25. Concentration of arsenic from total-digestion data from A, sediment from premining terrace deposits (dot, sample locality), and B, modern streambed sediment. (Solid oval dot on stream segment, sample locality.) Premining geochemical baseline data from table 2. Note that although the breccia-pipe deposits in upper reach of Mineral Creek basin contain the high concentrations of arsenic, premining geochemical baseline concentrations in that basin are not elevated as they are in modern streambed sediment in Mineral Creek and Prospect Gulch.



A

B

Figure 26. Concentration of copper from total-digestion data from A, sediment from premining terrace deposits (dot, sample locality), and B, modern streambed sediment. Premining geochemical baseline data from table 2. Copper concentrations are elevated in modern streambed sediment where pH is high enough that copper is sorbed onto iron colloids or, in the case of upper Cement and Mineral Creeks, directly downstream of major sources of contaminants.

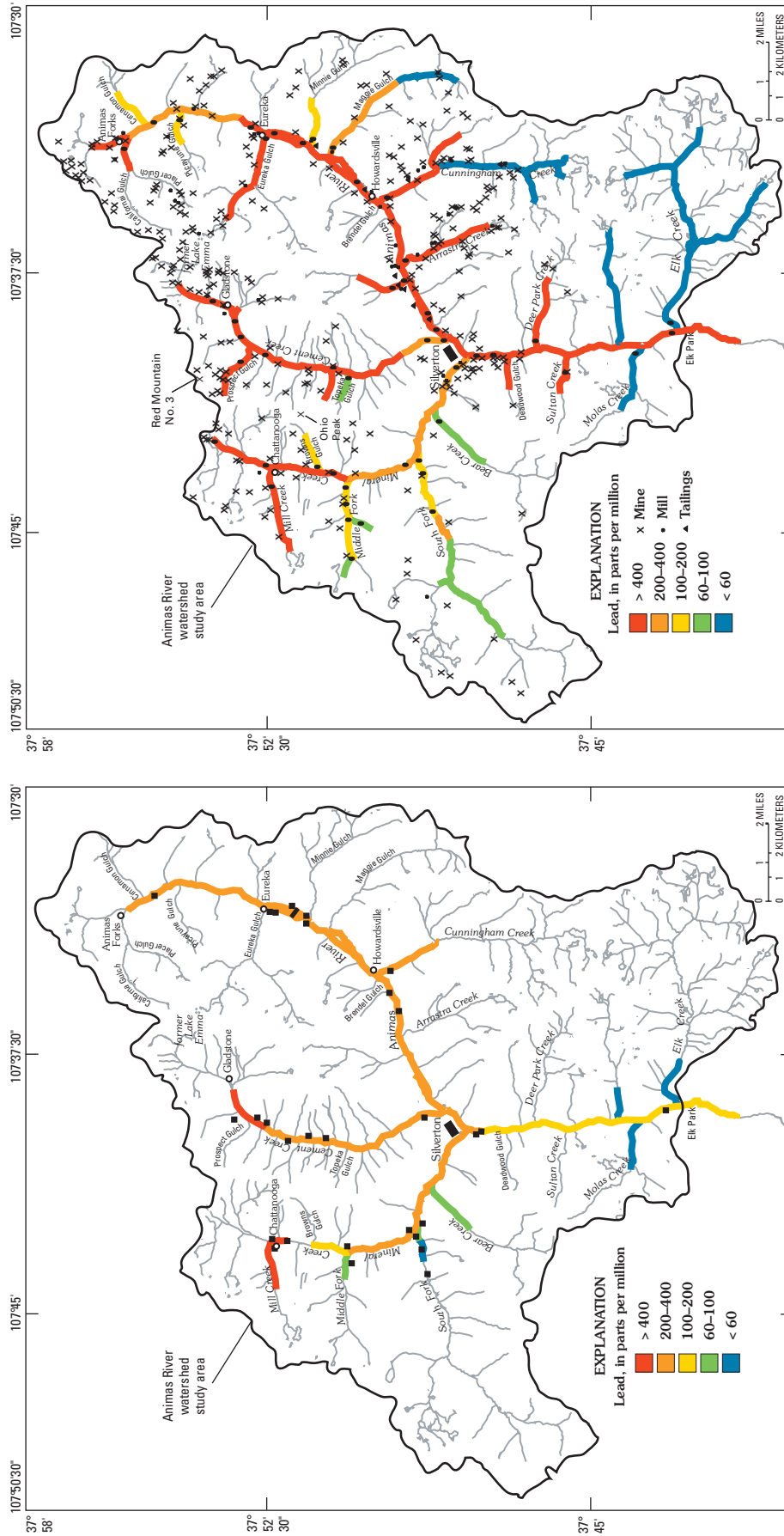
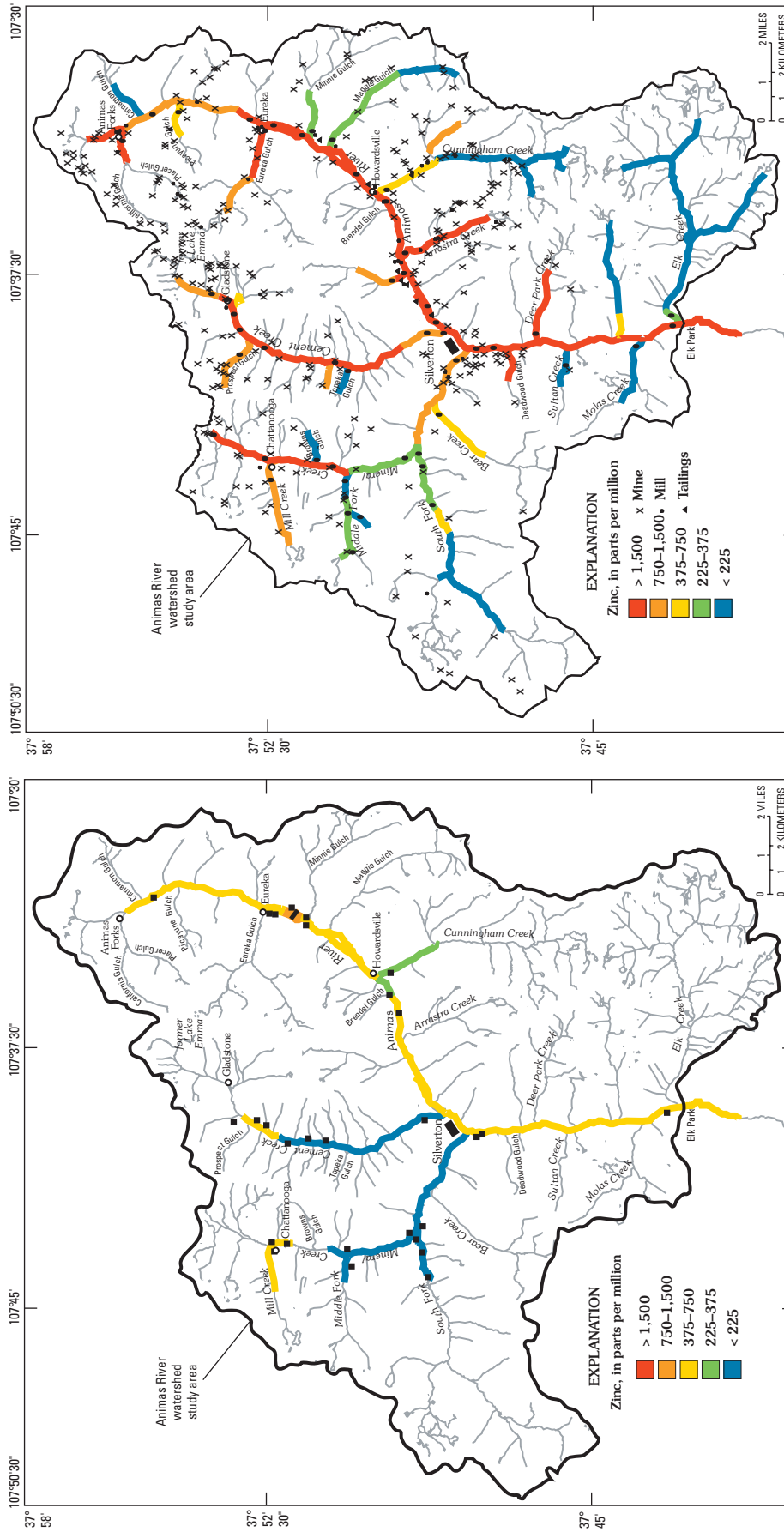


Figure 27. Concentration of lead from total-digestion data from A, sediment from premining terrace deposits (dot, sample locality), and B, modern streambed sediment. Premining geochemical baseline data from table 2. Lead concentrations were elevated in the premining geochemical baseline, but do not have the lead isotopic signature of the ores. Lead enrichment in modern streambed sediment is substantial, often approaching 1,000 ppm. Every stream reach affected by historical mining is contaminated by lead. This contamination can be traced downstream from Silverton for more than 100 mi (Church and others, 1997).



A

B

Figure 28. Concentration of zinc from total-digestion data from A, sediment from premining terrace deposits (dot, sample locality), and B, modern streambed sediment. Premining geochemical baseline data from table 2. Zinc concentrations in premining sediment approach 1,000 ppm in the vicinity of Eureka. These elevated zinc concentrations indicate that the mineral deposits were exposed at the surface when found by early miners (for example, Bird, 1999). Modern streambed sediment in the Animas River downstream from Eureka was affected. Historical mining and milling has had a major effect on zinc concentrations in modern streambed sediment throughout the Animas River watershed study area.

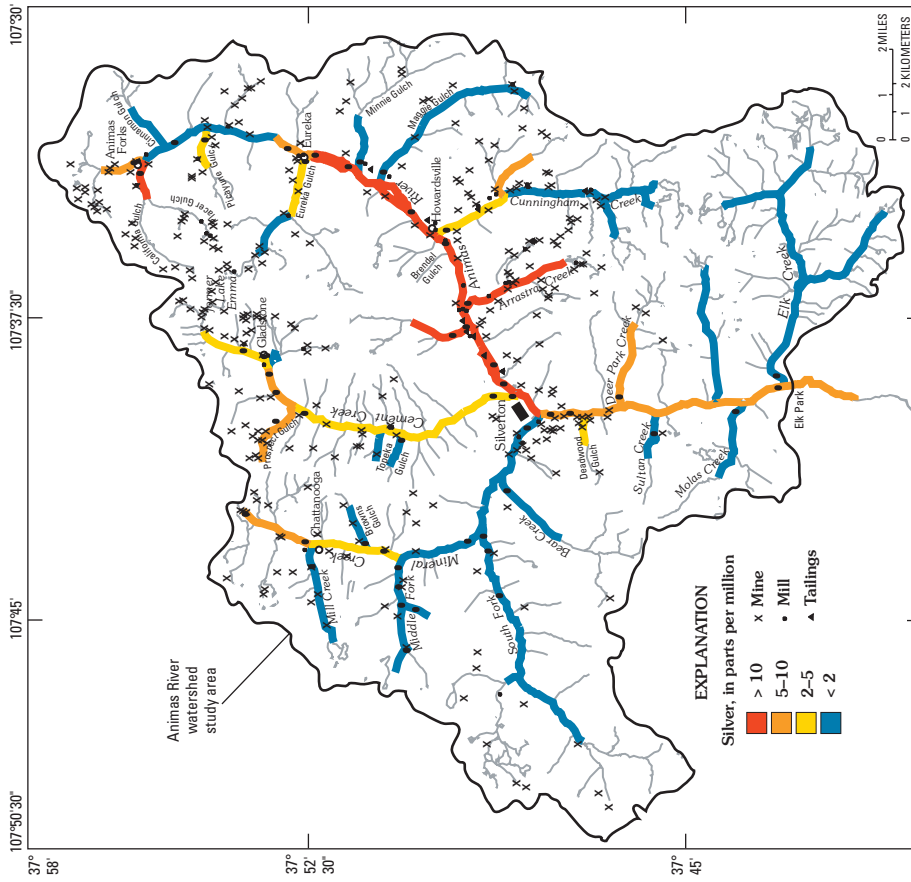


Figure 30. Concentration of silver from total-digestion data from modern streambed sediment. Premining geochemical baseline data from table 2 indicate that silver concentrations would probably have been less than 2 ppm throughout the watershed study area. Pattern of contamination from historical mining mimics that of lead (fig. 27B).

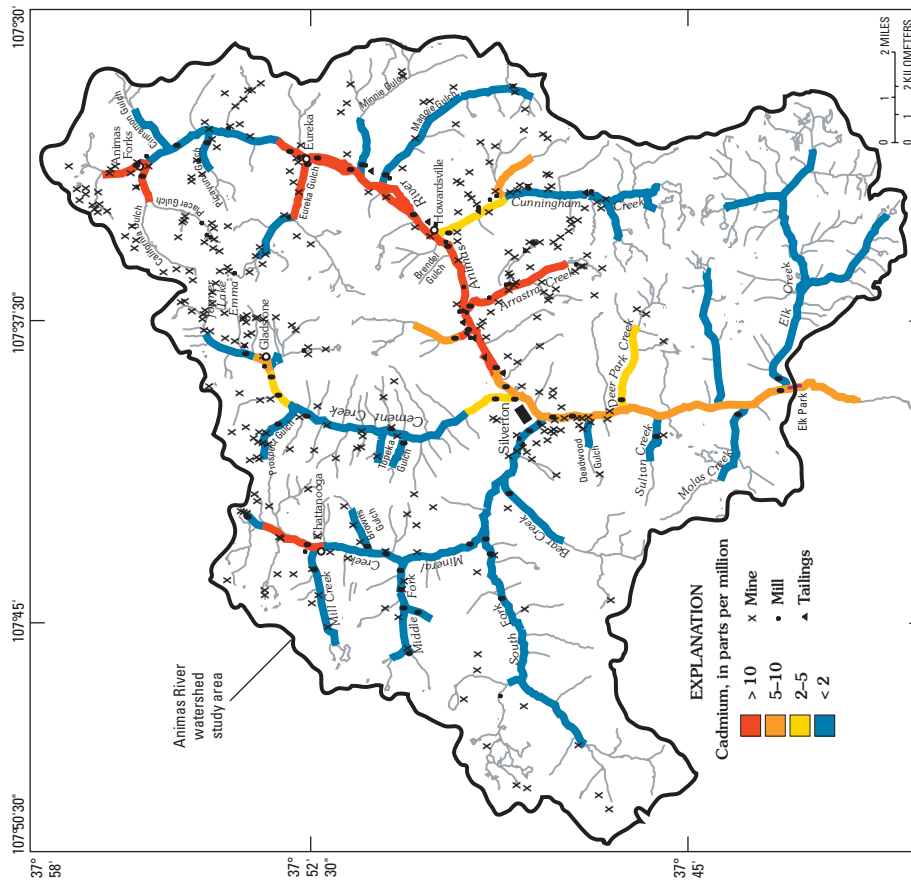


Figure 29. Concentration of cadmium from total-digestion data from modern streambed sediment. Premining geochemical baseline data from table 2 indicate that cadmium concentrations would probably have been less than 2 ppm throughout the watershed. Pattern of contamination from historical mining mimics that of zinc (fig. 28B).

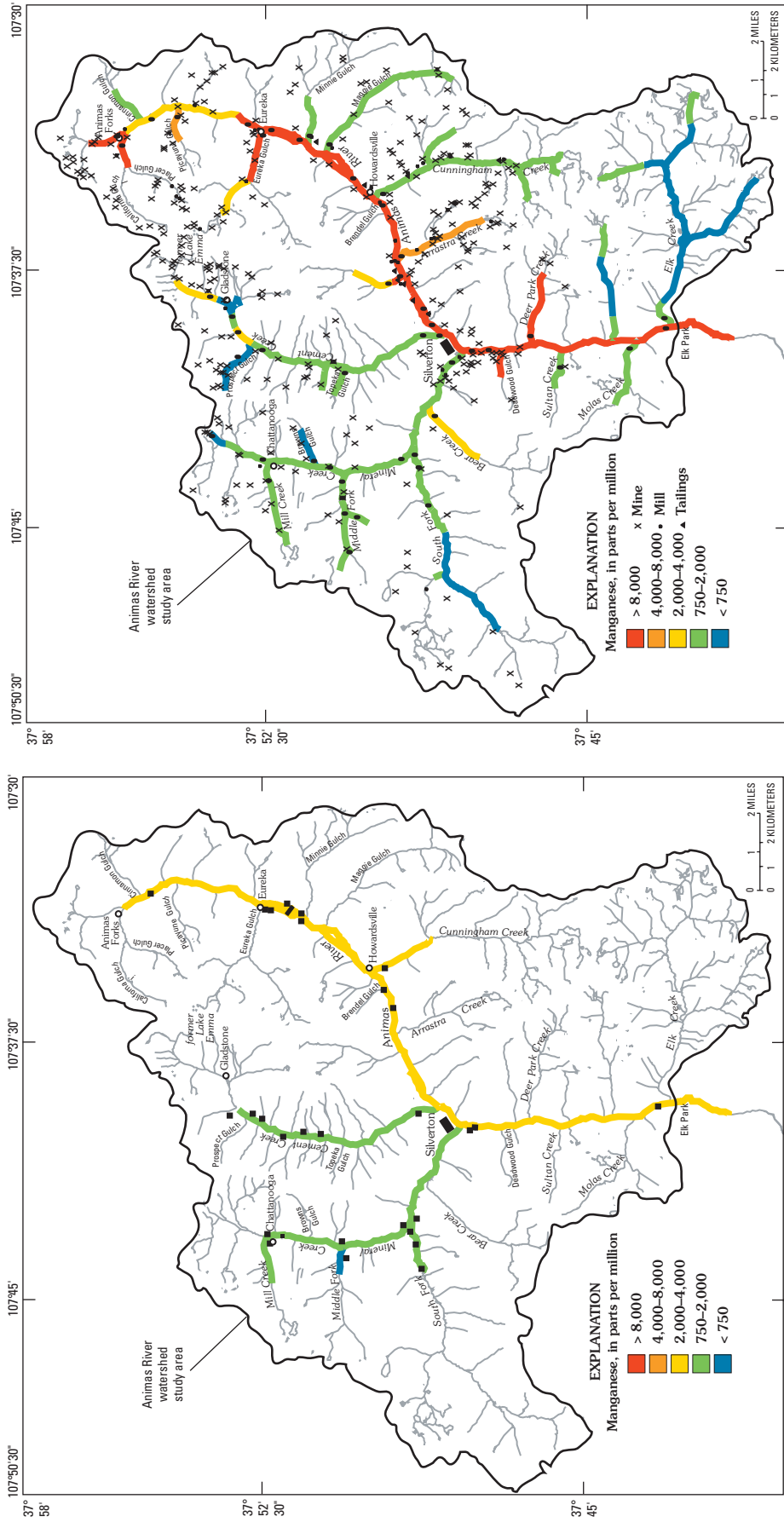


Figure 31. Concentration of manganese from total-digestion data from A, sediment from premining terrace deposits (dot, sample locality), and B, modern streambed sediment. Premining geochemical baseline data from table 2. Because of the mobility of manganese, premining geochemical baseline determinations are often tentative (data are in italics, table 2). Ribbon intervals, however, are selected broadly enough to smooth the data and show that manganese concentrations were elevated in streambed sediment of the upper Animas River basin prior to mining. Concentrations determined in modern streambed sediment downstream from Eureka implicate the milling and disposal of tailings by the Sunnyside Eureka Mill as a major source of contaminants in the Animas River.

Lead

The premining concentration of lead in streambed sediment (table 2; fig. 27A) was high prior to mining, generally 200 ppm or more in Mineral Creek (more than 15 times crustal abundance), about 240 ppm in Cement Creek (more than 18 times crustal abundance), and more than 400 ppm in the Animas River downstream from Eureka (table 2 or more than 30 times crustal abundance). These data reflect the fact that many of the veins exploited in the watershed were exposed at the surface. Lead contamination from historical mining, however, is widespread throughout the study area both in the form of windblown dust and in streambed sediment (fig. 27B). Because of its high silver content, galena (PbS) has been an ore mineral produced in all the mining districts from their inception. Galena is a very heavy mineral (specific gravity of 7.6); as a result, it is transported slowly in the fluvial environment. Enrichment of lead above these elevated geochemical baseline concentrations in streambed sediment shows that lead has been elevated above premining geochemical baseline concentrations by factors of 2–5 in the upper Animas River, factors of 1–3 in Cement Creek, and factors of 2–3 in Mineral Creek (fig. 27B). Elevated concentrations of lead in modern streambed sediment also occur upstream from Animas Forks. Downstream of Silverton, lead is elevated above premining geochemical baseline concentrations in the streambed sediment of the Animas River about 15-fold over the premining geochemical baseline concentration. Lead concentrations in streambed sediment from tributary streams downstream of the Silverton caldera have values that range between 1 and 2 times crustal abundance.

Zinc

The premining concentration of zinc in streambed sediment was also high (table 2; fig. 28A), generally less than 200 ppm in the Mineral and Cement Creek basins but perhaps as high as 400 ppm in the upper reaches of Mineral and Cement Creeks (table 2, that is, from about 3 to 5 times crustal abundance). However, at the confluence with Eureka Gulch, premining values for zinc exceed 1,000 ppm in the streambed sediment of the Animas River immediately downstream from Eureka (more than 13 times crustal abundance). Zinc contamination from historical mining was extensive (fig. 28B). Zinc did not become a commodity produced at the Sunnyside Mill # 2 at Eureka (site # 165, fig. 4) until about 1912, and most of the sphalerite (ZnS) was not recovered in the milling process. At the beginning of the 20th century, sphalerite was hand sorted and discarded at the mines, because miners were assessed a penalty by the mills if bulk ore contained more than 10 percent sphalerite (Ransome, 1901). The mills discharged sphalerite directly into the rivers along with the other mill waste. Jones (this volume, table 1) indicates that sphalerite was recovered as a product in the Animas River watershed as early as 1904. Modern streambed sediment

in Mineral Creek is elevated above premining geochemical baseline concentrations in zinc by factors of 3–5, in Cement Creek by factors of 3–6, and in the Animas River downstream from the Sunnyside mills at Eureka by factors of 3–5 (table 2). Elevated concentrations of zinc also occur in modern streambed sediment upstream of Animas Forks. Downstream of Silverton, zinc is elevated above premining geochemical baseline concentrations in the streambed sediment of the Animas River about 6–8-fold over the premining value. Zinc concentrations in streambed sediment from tributary streams downstream of the Silverton caldera have values between 1 and 2 times crustal abundance.

Cadmium

Cadmium behaves very similar to zinc and occurs in the primary zinc mineral sphalerite. The distribution of cadmium in modern streambed sediment (fig. 29) closely resembles that of zinc. Premining geochemical baseline concentrations of cadmium were less than 2 ppm (the limit of detection) to 4 ppm with one exception (table 2). Crustal abundance of cadmium is only 0.16 ppm (Fortescue, 1992). A map of the premining geochemical baseline values for cadmium would show stream reaches in blue and yellow, indicating low concentrations of cadmium in premining streambed sediment. The higher premining geochemical baseline concentrations of cadmium follow the enrichment of zinc as shown in figure 28A. Much of the zinc contamination from historical mining in the Animas River can be traced to the Sunnyside mills at Eureka (fig. 28B). Enrichment factors of 2–5 for cadmium in modern streambed sediment in the Animas River downstream from Eureka can also be attributed to discharges from the Sunnyside mills. Elevated cadmium concentrations in the upper reach of Mineral Creek correlate well with elevated zinc concentrations (fig. 28B). Furthermore, elevated concentrations of cadmium occur in modern streambed sediment upstream of Animas Forks and can be traced downstream from Silverton in streambed sediment of the Animas River.

Silver

Silver was the primary metal targeted in the early production in the study area, although free gold was also commercially very important (Jones, this volume, table 1). Silver was recovered from the galena concentrate, but data from the mill tailings also indicate that substantial silver was discarded in the mill waste, incorporated either in galena or sphalerite. Silver concentration in modern streambed sediment in numerous places exceeds 10 ppm (parts per million); in mill tailings at sites B20 and B22 (table 1; fig. 4), it exceeds 100 ppm. Almost all the silver concentrations measured at the premining geochemical baseline sites were less than the limit of detection (2 ppm). Crustal abundance for silver is only 0.08 ppm (Fortescue, 1992). Silver contamination from historical mining in modern streambed sediment is evident downstream from

the Silver Ledge Mill (site # 138, fig. 4) at Chattanooga in the upper reaches of Mineral Creek; downstream from the early Gold King and Mogul Mills (sites # 94 and # 93 respectively, fig. 4) near Gladstone in the Cement Creek basin; and especially downstream from the Sunnyside mills at Eureka (sites # 164 and # 165, fig. 4 and fig. 30). Elevated concentrations of silver also occur in streambed sediment upstream of Animas Forks (possibly from the Bagley Mill, site # 20, or the Hanson or Mastodon Mills, sites # 51 and # 52, fig. 4) and can be traced downstream from Silverton in streambed sediment of the Animas River (fig. 30).

Manganese

Manganese is strongly enriched above premining geochemical baseline concentrations in the gangue minerals associated with ore in the Eureka graben. Manganese enrichment is clearly evident in premining geochemical baseline data (table 2) as well as in water from mines and springs in the Eureka graben area (Mast and others, this volume; Bove and others, this volume). Premining geochemical baseline values for manganese in streambed sediment (fig. 31A) were elevated by factors of 2–4 above crustal abundance values (table 2, CA_{Mn} is 1,060 ppm; Fortescue, 1992). Elevated manganese concentrations in modern streambed sediment (fig. 31B), exceeding 30,000 ppm (more than 28 times crustal abundance), are also readily apparent in the mill tailings from the Animas River reach downstream from Eureka (table 1). Manganese provides an excellent geochemical tracer of contamination from the Eureka district in general and the Sunnyside mills at Eureka in particular. Fluvial tailings containing elevated manganese concentrations are present in the 1911 flood deposits at Elk Park (fig. 12) and in an abandoned oxbow of the Animas River immediately upstream from Durango. Contamination from the Sunnyside Eureka Mill (site # 164, fig. 4) at Eureka is evident from the map showing the distribution of manganese in modern streambed sediment from the Animas River watershed study area (fig. 31B).

Summary of the Effects of Historical Mining and Milling Practices

Historical mining and large-scale milling, in particular during the period from 1917 until 1935 when the mining industry was restricted from dumping mill tailings into the Nation's surface streams, have had a dramatic effect on the current streambed-sediment geochemistry in the Animas River downstream from the Sunnyside Eureka Mill (site # 164). This effect is manifest in modern streambed sediment as elevated concentrations of all the deposit-related trace elements, particularly copper, lead, zinc, cadmium, and silver. Concentration of manganese, which is strongly elevated in the Eureka graben deposits, is also prevalent in the mill waste. Figures 25–31 demonstrate that concentrations of many of these elements

were elevated in streambed sediment by factors of 2–5 above crustal abundance values prior to mining. However, historical milling practices and associated dumping of mill waste into the Animas River have impacted the Animas River for many miles downstream (Church and others, 1997).

Lead Isotopic Results

Lead isotopic data provide an independent tracer of the contamination process. As all of the mineral deposits in the watershed were mined for the silver content in galena (PbS), it follows that concentration of lead in the mineral deposits had to be very high. It is thus impossible to “contaminate” the lead from one deposit unless it is mixed with lead from another mineral deposit. Lead isotopic data for modern stream-sediment, contaminant, and premining-geochemical-baseline samples are summarized on conventional $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams in figure 32. Not shown in figure 32 are data from Molas and Elk Creeks, the two southernmost tributaries (fig. 27B). Streambed sediment from these two tributaries is characterized by more radiogenic lead ($^{206}\text{Pb}/^{204}\text{Pb} > 20$), and these data were omitted from figure 32 to expand the scale of the graphs where most of the data plot. Data are from Church and others (1997), Church and others (2000), and Fey and others (2000). All the analytical results are in the database (Sole and others, this volume).

The lead isotopic data form well-correlated linear trends on both diagrams (fig. 32). Consequently, the lead isotopic signature of any given sample may be represented by a single lead isotopic ratio. For the remainder of this discussion, $^{206}\text{Pb}/^{204}\text{Pb}$ value will be used to denote the isotopic signatures of the samples. The least radiogenic lead is found among the ore leads, or contaminants ($^{206}\text{Pb}/^{204}\text{Pb} < 18.4$), whereas the most radiogenic lead ($^{206}\text{Pb}/^{204}\text{Pb} > 18.8$) is found among sediment samples from the Mineral Creek basin, some premining geochemical baseline samples, and some sediment samples from tributaries to the upper Animas River, which indicate that little ore lead is present in modern streambed sediment from these areas. Much more radiogenic lead characterizes the streambed sediment from the Precambrian rock south of the Silverton caldera (Molas and Elk Creeks, fig. 27). Streambed sediment from sites on the upper Animas River in the study area shows a range in $^{206}\text{Pb}/^{204}\text{Pb}$ of 18.35–18.76, although only one of the modern streambed-sediment samples analyzed has $^{206}\text{Pb}/^{204}\text{Pb} > 18.6$. Premining geochemical baseline samples show a much larger range of lead isotopic compositions, and are somewhat more radiogenic than modern streambed sediment of the Animas River.

The different mineral deposit types in the Animas River watershed study area have different lead isotopic signatures, so differences of as little as 0.05 in the $^{206}\text{Pb}/^{204}\text{Pb}$ value in different samples can be significant. However, the interpretation of the data must be made in a geologic and, in the case of evaluating sources of metal contamination in

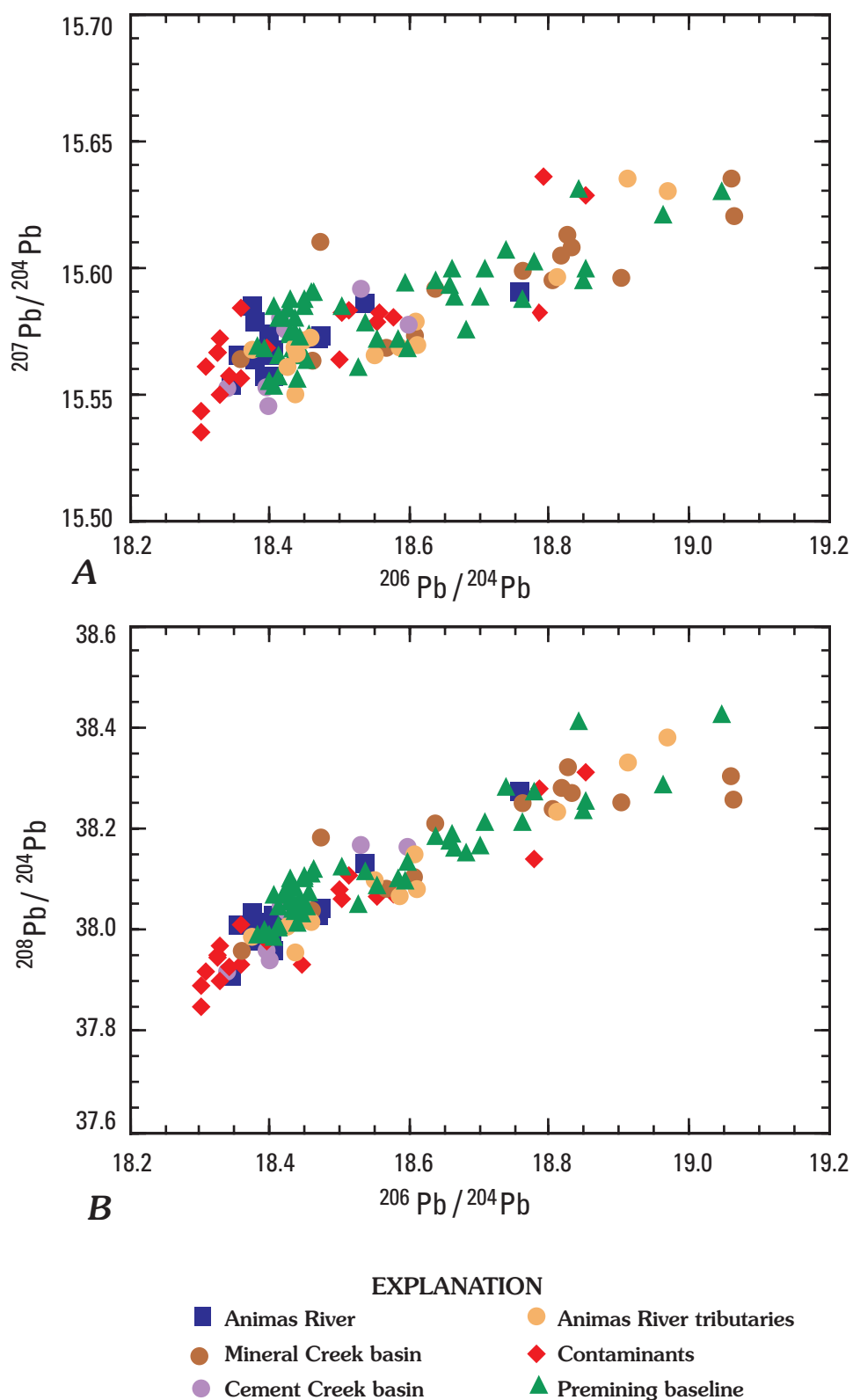


Figure 32. Lead isotopic compositions in Animas River watershed study area. *A*, $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$; *B*, $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ for modern stream sediment, geochemical baseline samples, and contaminants. Samples from Molas Creek and Elk Creek tributaries ($^{206}\text{Pb}/^{204}\text{Pb} > 20$) have been omitted to expand the scale where most of the data plot. Lead isotopic data from the different materials sampled form a single array in conventional lead isotopic diagrams.

modern streambed sediment from historical mining, a topographic context. As shown by the analyses of contaminants identified, the lead isotopic signature of the mineral deposits processed in the upper reaches of Mineral Creek near Chattanooga had a $^{206}\text{Pb}/^{204}\text{Pb}$ value of 18.52 (site *B2*, table 1, fig. 4); the $^{206}\text{Pb}/^{204}\text{Pb}$ value from the Koehler tunnel is 18.50 (mine # 75, fig. 3; Church and others, 1997). Lead from the Bonner mine adit (site # 172, fig. 3) and the Paradise portal (mine # 168, fig. 3), both on Middle Fork Mineral Creek, has $^{206}\text{Pb}/^{204}\text{Pb}$ values of 18.45 and 18.78, respectively (Church and others, 1997; Church and others, 2000). Lead from the Lake Emma sediment deposit from the American tunnel (mine # 96) has a $^{206}\text{Pb}/^{204}\text{Pb}$ value of 18.33 (site *S20*, fig. 3, table 1). Ore treated at the Sunnyside Eureka Mill (site # 164) also has a $^{206}\text{Pb}/^{204}\text{Pb}$ value of about 18.33 (table 1, site *B19*). Tailings from the Kittimack Mill (site # 194, just upstream from site *S36* on the Animas River, fig. 3) gave a $^{206}\text{Pb}/^{204}\text{Pb}$ value of 18.79 (Church and others, 1997) and from the Silver Lake Mill # 2 (site # 219, fig. 4, table 1) gave a $^{206}\text{Pb}/^{204}\text{Pb}$ value of 18.78. These data, although by no means exhaustive, are in good agreement with published lead isotopic results for galena from a few mines in the study area (Doe and others, 1979; Church and others, 1997), although some of the early ore stages in the Sunnyside mine (mine # 116, fig. 3) may have a slightly lower $^{206}\text{Pb}/^{204}\text{Pb}$ value (Doe and others, 1979). An evaluation of the relative importance of contamination from each of the various ore types is theoretically possible if all the end members could be identified and their sources located on the ground. However, the contamination from the Eureka graben ores, most likely from the Sunnyside Eureka Mill (site # 164, fig. 4), dominates the lead isotopic signature in modern streambed sediment in the Animas River.

Upper Animas River Basin

Lead isotopic and abundance data from streambed sediment from the upper Animas River and its tributaries are in figure 33. The $^{206}\text{Pb}/^{204}\text{Pb}$ value in modern streambed sediment from the West Fork Animas River (mi 2.3, fig. 33A) differs from that in the North Fork Animas River upstream from the confluence at Animas Forks. The mineral deposits in West Fork Animas River have a lead isotopic signature similar to those in Eureka Gulch (mi 6.6), which are typical for the Eureka graben ores as a whole (sites *B19–B24*, fig. 4, table 1). Sediment lead from the North Fork Animas River is more radiogenic.

The $^{206}\text{Pb}/^{204}\text{Pb}$ data from modern streambed sediment from Minnie and Maggie Gulches (mi 8.0 and 8.6, respectively), and from Cunningham and Arrastra Creeks (mi 10.6 and 12.0, respectively) all have $^{206}\text{Pb}/^{204}\text{Pb}$ values that are similar to that found in the North Fork Animas River, but are significantly higher than the rest of the $^{206}\text{Pb}/^{204}\text{Pb}$ postmining data from streambed sediment from the upper Animas River basin. The lead isotopic signature of modern streambed

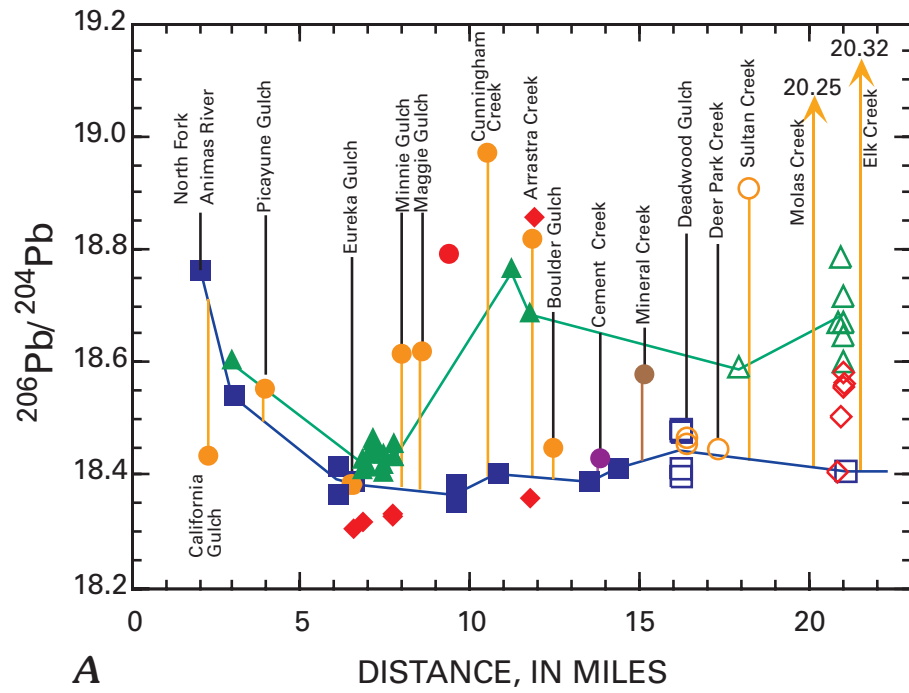
sediment in Boulder Gulch (mi 12.5) is similar to that of the Eureka graben ores. This signature is probably from wind-blown material from the open Mayflower Mill tailings repository (site # 510, fig. 4) immediately downstream.

The results clearly indicate that two general isotopically distinct sources of lead are present in the upper Animas River basin. A radiogenic lead signature ($^{206}\text{Pb}/^{204}\text{Pb} > 18.6$) predominates in the Silverton caldera margin and mineral deposits to the east and north, just outside the caldera. This source is present in the extreme northern portion of the upper Animas River basin (site *S26*, fig. 3) and in tributaries entering the upper Animas River from the east and southeast. The second source, characterized by $^{206}\text{Pb}/^{204}\text{Pb} < 18.4$, represents the mineral deposits from within the Silverton caldera. This lead isotopic signature is found in the streambed sediment of the Animas River downstream from Eureka and in tributaries entering the upper Animas River from the west and northwest. The streambed-sediment sample collected from Cement Creek just upstream from the confluence with the Animas River (site *S25*, mi 14, fig. 33A) also bears the lead isotopic signature of mineral deposits within the caldera.

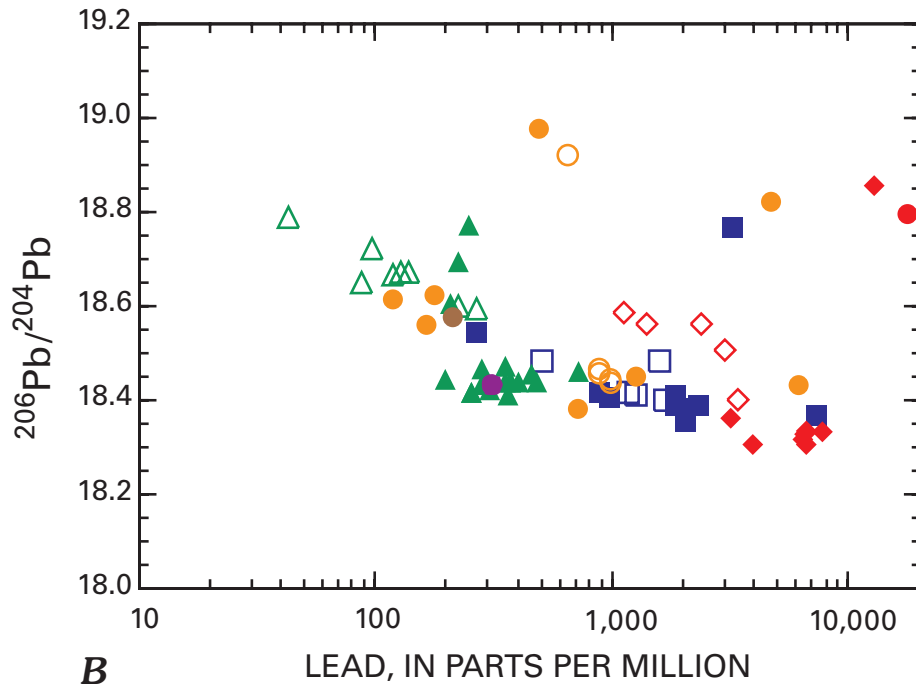
The two apparent sources of lead do not simply represent mineralized versus unmineralized rock. Contaminants and contaminated streambed sediment with both lead isotopic signatures are found in the upper Animas River basin (fig. 33B). However, in the Animas River downstream from Eureka (mi 6.6), the nonradiogenic or Eureka graben signature clearly dominates the lead isotopic signature in modern streambed sediment (fig. 33A). The primary source of lead with this signature in the upper Animas River basin is the mill tailings from the Sunnyside Eureka Mill (site # 164, fig. 4).

Lead isotopic data from the premining geochemical baseline samples are very similar to those in the Animas River upstream from Eureka. The elevated lead concentrations in the premining sediment at Eureka (sites *B20–B22*, mi 7.0–7.5, fig. 33A) indicate that the mineralized veins were exposed prior to their discovery, as Bird (1999) described the discovery outcrop of the Sunnyside vein at Lake Emma (mine # 116, fig. 3). Casadevall and Ohmoto (1977) and Bove and others (this volume) have described extensive outcrops of the Eureka graben vein system at the surface in this region.

Figure 33 (facing page). $^{206}\text{Pb}/^{204}\text{Pb}$ versus *A*, distance, and *B*, leachable lead concentrations for modern stream sediment, geochemical baseline samples, and contaminants from the upper Animas River basin. All drainages are labeled; tie lines indicate confluence of tributary with mainstem. Leachable lead concentrations are those leached from a sample with a warm 2M HCl-H₂O₂ digestion. Note the stark contrast in compositions of lead from premining geochemical baseline samples (table 2) and those from modern streambed sediment. Mill tailings from downstream of the flotation mill, Sunnyside Eureka Mill (site # 164, fig. 4), have a dominant effect on the composition of lead in modern streambed sediment. Also shown are contaminant data from Kittimack tailings site (site # 192, fig. 4; Church and others, 1997).



A



B

EXPLANATION

- | | |
|--|--|
| ■ Animas River upstream from Silverton | ● Kittimack Mill site |
| □ Animas River downstream from Silverton | ◆ Contaminants upstream from Silverton |
| ● Mineral Creek | ◇ Contaminants downstream from Silverton |
| ● Cement Creek | ▲ Premining baseline samples upstream from Silverton |
| ● Other tributaries upstream from Silverton | △ Premining baseline samples downstream from Silverton |
| ○ Animas tributaries downstream from Silverton | |

Downstream from Eureka, the lead isotopic signature from premining geochemical baseline samples indicates that streambed sediment in the Animas River prior to mining had a consistently higher $^{206}\text{Pb}/^{204}\text{Pb}$ value than that in modern streambed sediment in the Animas River. Although the lead isotopic signature of the premining geochemical baseline samples at Eureka is very similar to that of the contaminants and Animas River sediment at this site, lead concentrations are much lower than in modern streambed sediment (fig. 33B). During the premining era, the influx of more radiogenic lead from downstream tributaries had a pronounced effect on the lead isotopic signature of the Animas River sediment. In contrast, the influx of streambed sediment from these same sources today with their radiogenic lead isotopic signature has virtually no effect on modern Animas River sediment because of its much higher present lead concentrations (fig. 33B).

Cement Creek Basin

Lead isotopic data from modern streambed sediment from Cement Creek have a narrow range of values and are similar to those of the upper Animas River basin (fig. 34A) and the Eureka graben ore-lead signature ($^{206}\text{Pb}/^{204}\text{Pb}=18.3\text{--}18.4$). The lead isotopic data from the ferricrete deposit (site *S18*) in the upper reach of Cement Creek basin, upstream from the confluence at Gladstone (fig. 3), downhill from the Red and Bonita mine (mine # 99), also reflect the Eureka graben deposit $^{206}\text{Pb}/^{204}\text{Pb}$ value at 18.35 (Church and others, 1997). The contaminated section of core at site *B13* (figs. 4 and 34A, mi 8.7) and sediment from former Lake Emma also bear this lead isotopic signature. Although the lead isotopic signatures are similar, modern streambed sediment in Cement Creek is characterized by much lower lead concentrations than in the Animas River (figs. 34B and 7). The lead isotopic signature of modern streambed sediment from Cement Creek is consistent with mixing between Lake Emma sediment and premining geochemical baseline sediment (fig. 34B).

The lead isotopic value from modern streambed sediment in Prospect Gulch (fig. 34A) closely approximates that from the Koehler tunnel (mine # 75) at the head of Mineral Creek (site *S1*, fig. 3). Deposits in Prospect Gulch (fig. 27B), for example the Henrietta (level #7, mine # 85) and the Lark (mine # 86), and the Koehler tunnel (mine # 75) are all associated with the breccia-pipe deposits at Red Mountain # 3 near Chattanooga (fig. 3). The lead isotopic signature from these two deposits is intermediate between those of the Eureka graben ores and the more radiogenic-lead deposits in the headwaters of the upper Animas River and southeast of the Animas River near Silverton. The data from modern streambed sediment from Topeka Gulch (*S25*, figs. 3 and 34A) have a slightly higher $^{206}\text{Pb}/^{204}\text{Pb}$ value of 18.60. No significant mineralized rock has been exploited in Topeka Gulch. This signature represents premining geochemical baseline of the hydrothermally altered area around Ohio Peak (Bove and others, this volume;

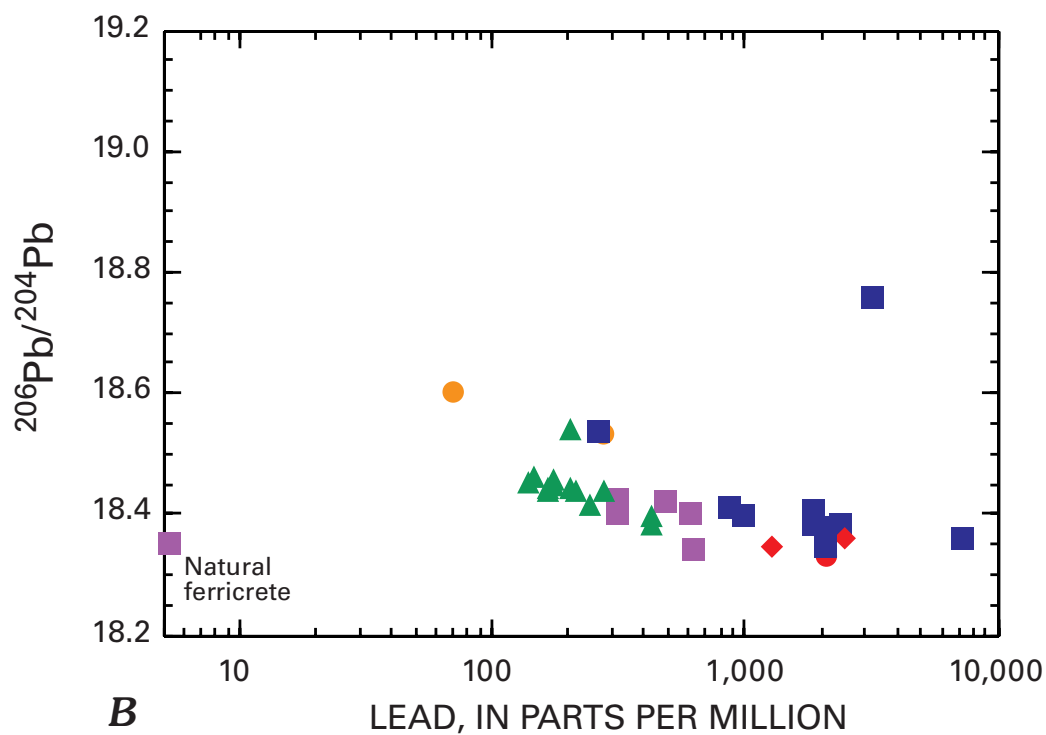
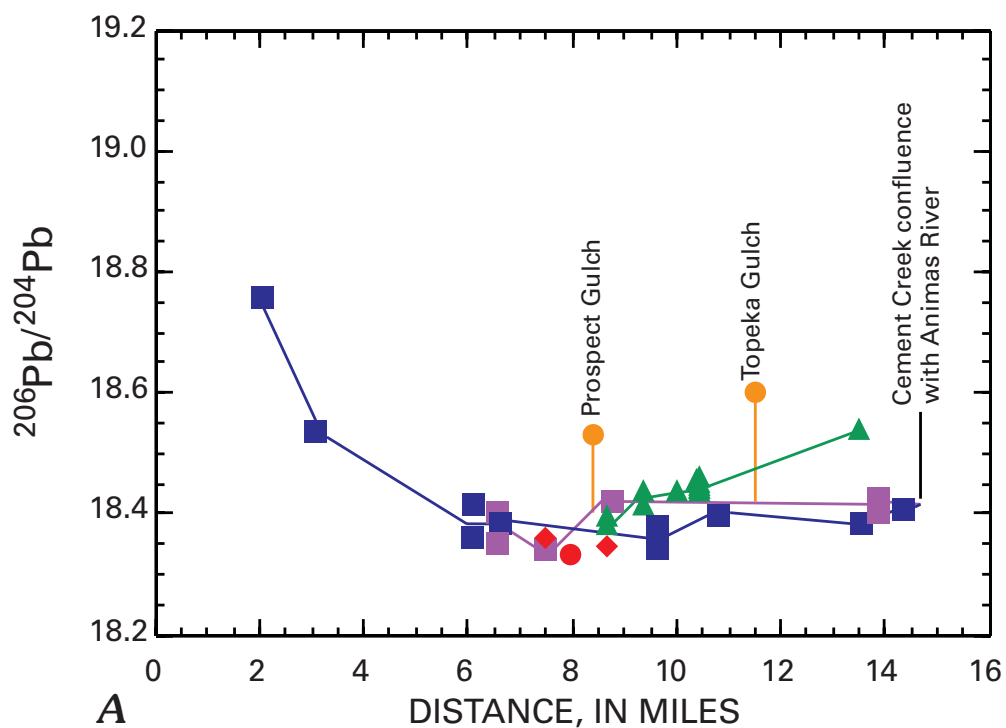
fig. 4) if one assumes that windblown dust has had a minor influence on the streambed sediment in the Topeka Gulch subbasin.

Lead isotopic data from the premining geochemical baseline samples in upper Cement Creek are very similar to those in modern streambed sediment of Cement Creek and reflect the signature of the Eureka graben deposits. The $^{206}\text{Pb}/^{204}\text{Pb}$ values from the premining geochemical baseline terrace deposits progressively increase downstream (fig. 34A). Near the mouth of Cement Creek, the lead isotopic composition of the premining terrace sample (site *B17*, fig. 4) is similar to that of the tributary streams. The results indicate that prior to mining in this area, streambed sediment in upper Cement Creek had a Eureka graben signature that was attenuated downstream by the influx of more radiogenic sediment from unmineralized tributaries such as Topeka Gulch. The lack of attenuation in modern streambed sediment is a consequence of the higher lead concentrations in upper Cement Creek, which resulted from historical mining (fig. 27A).

Mineral Creek Basin

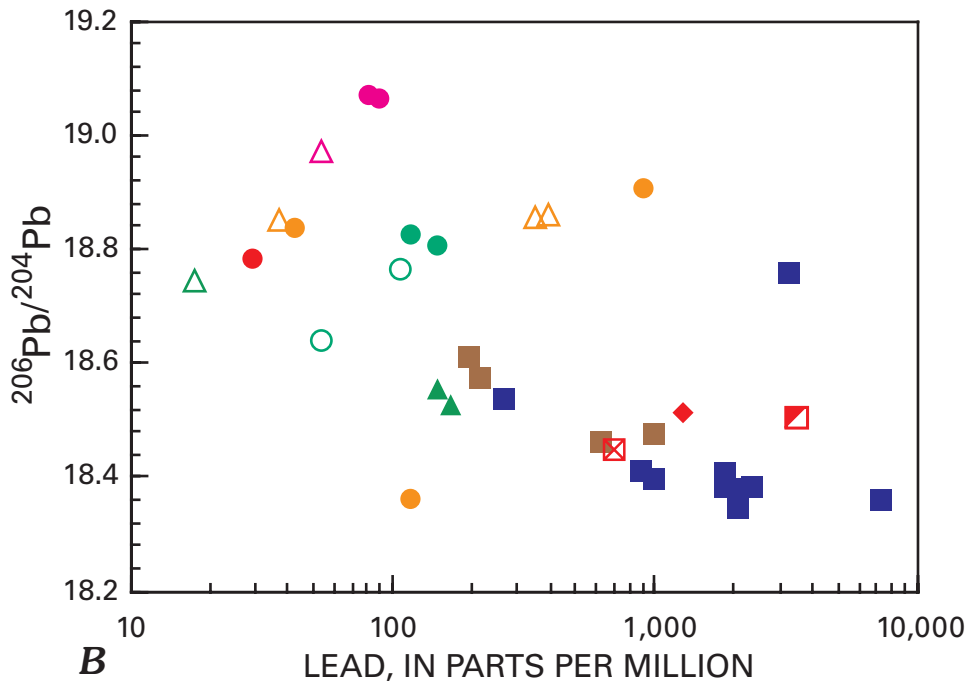
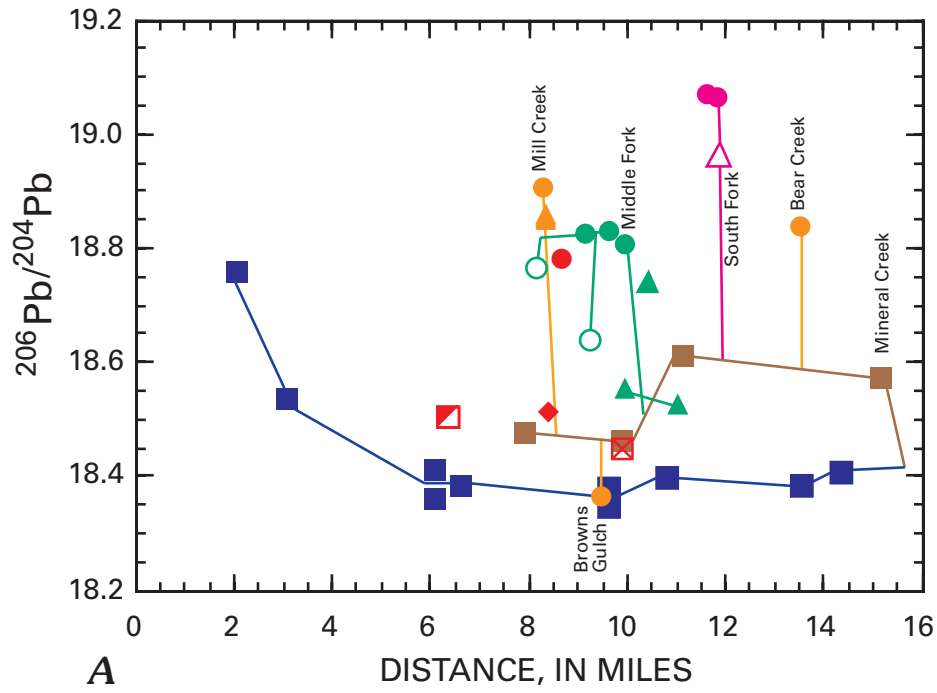
Lead isotopic data from modern streambed sediment from the Mineral Creek basin have a wide range in $^{206}\text{Pb}/^{204}\text{Pb}$ values (fig. 35). Mineral Creek is characterized by streambed sediment with $^{206}\text{Pb}/^{204}\text{Pb}$ between 18.46 and 18.61. The $^{206}\text{Pb}/^{204}\text{Pb}$ values from South Fork Mineral Creek basin are approximately 19.0, and the $^{206}\text{Pb}/^{204}\text{Pb}$ values from Middle Fork Mineral Creek are about 18.80. Other tributaries entering Mineral Creek from the southwest (Bear Creek) and west (Mill Creek) are also characterized by radiogenic lead ($^{206}\text{Pb}/^{204}\text{Pb}=18.8\text{--}18.9$). In contrast, modern streambed sediment from Browns Gulch, which enters Mineral Creek from the east (site *S4*, fig. 3), has a Eureka graben lead isotopic signature. This is analogous to that observed for the upper Animas River basin discussed previously. Drainages from outside the Silverton caldera are characterized by lead that is more radiogenic than the lead that is found in streams that drain the volcanic rock in the Silverton caldera.

Figure 34 (facing page). $^{206}\text{Pb}/^{204}\text{Pb}$ versus *A*, distance, and *B*, leachable lead concentrations for modern stream sediment, geochemical baseline samples, and contaminants from Cement Creek basin. All drainages are labeled; tie lines indicate confluence of tributary with mainstem. Leachable lead concentrations are those leached from a sample with a warm $2\text{M}\text{HCl}\text{-H}_2\text{O}_2$ digestion. The sample of Lake Emma sediment represents a blowout deposit created during the collapse of Lake Emma into the Sunnyside workings. Although Lake Emma would plot at mi 4.5 (fig. 3), the sample was actually collected at site *S20* (mi 8). Note contrast in lead isotopic composition between premining geochemical baseline samples (table 2) and that in modern streambed sediment of Cement Creek. Data from modern streambed sediment from Animas River are shown for reference.



EXPLANATION

- Upper Animas River
- Cement Creek
- Cement Creek tributaries
- ◆ Cement Creek contaminants
- Lake Emma blowout sediment
- ▲ Cement Creek baseline samples



EXPLANATION

- Upper Animas River
- Mineral Creek
- Middle Fork Mineral Creek
- South Fork Mineral Creek
- Other Mineral Creek tributaries
- Middle Fork tributaries
- ▲ Mineral Creek premining baseline sample
- ▲ Mill Creek premining baseline samples
- ▲ Middle Fork premining baseline sample
- ▲ South Fork premining baseline sample
- ⊠ Koehler tunnel
- ⊠ Bonner mine adit
- Paradise portal
- ◆ Other Mineral Creek contaminants

Lead isotopic compositions in four contaminated sites within the Mineral Creek basin have been measured. The $^{206}\text{Pb}/^{204}\text{Pb}$ value measured from sediment in the settling pond at the Koehler tunnel (mine site # 75, site *S1*, fig. 3) is 18.50, in good agreement with the value in contaminated fluvial sediment at Chattanooga (18.52, site *B2*; fig. 4 and table 1). The lead in outflow from the Bonner mine adit (mine # 172) on Middle Fork Mineral Creek (site *S10*, fig. 3) is only slightly less radiogenic ($^{206}\text{Pb}/^{204}\text{Pb}=18.45$). In contrast, lead in the white precipitate from the Paradise portal (mine # 168, fig. 3), also on Middle Fork Mineral Creek, is characterized by $^{206}\text{Pb}/^{204}\text{Pb}$ of 18.78 (Church and others, 1997). Three of these sites contribute to the deposit-related trace-element suite in modern streambed sediment. Paradise portal is largely a source of dissolved and colloidal aluminum (Wright, Simon, and others, this volume) derived from altered rock, as shown by studies of the alteration suite present at peak 3,792 m (in Mount Moly alteration area in Bove and others, this volume; Yager and others, 2000) and strontium isotopes of the alteration facies (Verplanck and others, 2001).

Mineral Creek upstream from the confluence with Middle Fork Mineral Creek is characterized by lead in modern streambed sediment with $^{206}\text{Pb}/^{204}\text{Pb}$ of 18.46–18.48, similar to that observed in the Koehler tunnel (mine # 75, fig. 3) at the head of Mineral Creek (a “breccia-pipe” deposit lead isotope signature, fig. 35A). Downstream from the confluence with Middle Fork Mineral Creek, lead concentrations in modern streambed sediment from Mineral Creek decrease (fig. 10 and fig. 35B), and $^{206}\text{Pb}/^{204}\text{Pb}$ increases to about 18.6 as a result of dilution with more radiogenic lead from Middle Fork Mineral Creek and of erosion from Ohio Peak (fig. 27B), which has a composition like that from Topeka Gulch on Cement Creek (fig. 34A). Downstream from site *S12* (fig. 3 and fig. 35, mi 11.1), $^{206}\text{Pb}/^{204}\text{Pb}$ in the modern streambed sediment of Mineral Creek decreases slightly to 18.57 at site *S17* (figs. 3 and 35A), just upstream from the confluence with the Animas

River. The influence of radiogenic lead contributed by South Fork Mineral Creek and Bear Creek is not observed in the modern streambed sediment of Mineral Creek (fig. 35A) because of the overwhelming amount of ore lead in modern streambed sediment.

Lead isotopic data from the two premining geochemical baseline samples from Mineral Creek (fig. 35B, sites *B4* and *B6*, fig. 4) are similar to those in modern streambed sediment from Mineral Creek downstream from the confluence with Middle Fork Mineral Creek. Three additional sites (*B1*, *B5*, and *B8*, fig. 4) provided reasonable premining geochemical baseline values for Mill Creek, Middle Fork, and South Fork tributaries, respectively, and the iron bog on South Fork Mineral Creek (*B7*, fig. 4) also gave premining radiogenic lead isotopic values ($^{206}\text{Pb}/^{204}\text{Pb}=18.9$ – 19.1). The premining geochemical baseline sample from South Fork Mineral Creek (*B8*, fig. 4) had a slightly lower lead concentration and lower $^{206}\text{Pb}/^{204}\text{Pb}$ value (18.966) than that in modern streambed sediment. Premining geochemical baseline samples from Mill Creek (site *B1*, fig. 4) consisted of both sieved intervals and cores, and although the samples had a uniform lead isotopic signature ($^{206}\text{Pb}/^{204}\text{Pb}=18.85$), lead concentrations varied by an order of magnitude (fig. 35B). The premining geochemical baseline sample from Middle Fork Mineral Creek had $^{206}\text{Pb}/^{204}\text{Pb}$ only slightly lower than in the modern streambed sediment, but a much lower lead concentration. This geochemical baseline value is comparable with the data from the tributaries of Middle Fork Mineral Creek and Paradise portal (mine # 168), which drains a large hydrothermally altered zone on the west side of peak 3,792 m (Yager and others, 2000; Bove and others, this volume). Paradise portal drains a large area of hydrothermally altered rock that contributes a large load of aluminum to the stream, but only a small amount of the other deposit-related trace elements (Wright, Simon, and others, this volume).

Gladstone Flood Deposits at Elk Park

The lead isotopic data from the 1911 Gladstone flood deposits at Elk Park (site *B30*, fig. 4) represent multiple sources. Thick stamp mill tailings deposits (sample 02ABB-EP2, $^{206}\text{Pb}/^{204}\text{Pb} = 18.34$, table 1; fig. 20A) have a mean lead isotopic signature that matches that of the Sunnyside ore (early stamp mill tailings, site *B22*, table 1). However, the finer silts (fig. 20B) have a more radiogenic signature and probably represent mixtures of tailings material from the Sunnyside Mill # 2 (mine # 165, $^{206}\text{Pb}/^{204}\text{Pb} = 18.33$, table 1, site *B22*) and the Silver Lake Mill # 2 (mine # 219; $^{206}\text{Pb}/^{204}\text{Pb} = 18.78$). The elevated manganese concentrations typical of the deposits from the Eureka graben clearly are present in the 1911 deposits (fig. 12). Clearly, the flood deposits at Elk Park (site *B30*, fig. 4) are mixtures of stamp mill tailings from streams scoured by this flood event. The deposits are not elevated in either copper or arsenic, so they do not contain a large component of mill tailings from the breccia-pipe deposits

Figure 35 (facing page). $^{206}\text{Pb}/^{204}\text{Pb}$ versus *A*, distance, and *B*, leachable lead concentrations for modern stream sediment, geochemical baseline samples, and contaminants from Mineral Creek basin. All drainages are labeled; tie lines indicate confluence of tributary with mainstem. Leachable lead concentrations are defined as the lead leached from a sample with warm 2M HCl-H₂O₂ digestion. Also shown are contaminant data from the Koehler tunnel (mine # 75, fig. 3) at the head of Mineral Creek, and the Bonner adit (mine # 172, fig. 3) and Paradise portal (mine # 168, fig. 3), Middle Fork Mineral Creek (Church and others, 1997). Lead isotopic data from tributaries flowing in from the west, outside the Silverton caldera, have more radiogenic values of lead. Note that premining geochemical baseline lead isotopic values are not very different from that in modern streambed sediment of Mineral Creek downstream from confluence with Middle Fork Mineral Creek. Data from modern streambed sediment from Animas River are shown for reference.

from the upper reach of Mineral Creek. There are other fine-grained overbank deposits at Elk Park that do give a signature like that currently found in the Animas River ($^{206}\text{Pb}/^{204}\text{Pb}$ value of 18.40). Also, deposits of fluvial tailings in an abandoned meander of the Animas River near Durango can be matched both chemically and isotopically with the mill tailings from the Sunnyside mills at Eureka; we interpret these deposits in the abandoned meander to represent annual deposition during the period the Sunnyside Mill # 2 (site # 165, fig. 4) was in operation.

Summary of Lead Isotopic Data

The isotopic composition of lead in premining sediment indicates that the mineral deposits were exposed in the Eureka Gulch subbasin prior to mining (fig. 36A). Both the isotopic composition of lead and the elevated deposit-related trace-element concentrations in premining geochemical baseline samples indicate the presence of the mineral deposits and their effect on the Animas River downstream from Eureka. Near Eureka and in the upper Cement Creek subbasin, the Eureka graben lead isotopic signature dominates the lead isotopic data in both premining and modern streambed sediment (fig. 36B). However, the $^{206}\text{Pb}/^{204}\text{Pb}$ values in premining sediment increase and concentrations of deposit-related trace elements decrease downstream from those reaches (figs. 27A, 33, and 36).

Away from the area affected by the exposed mineral deposits in the Eureka graben, the isotopic signatures measured in modern stream sediment stand in marked contrast to those observed in premining baseline samples (fig. 36A and B). However, that effect was small relative to the large impact caused by historical mining and milling practices in the early part of the 20th century. Areas within the watershed where high lead concentrations in premining sediment have low values of $^{206}\text{Pb}/^{204}\text{Pb}$ indicate that the exposed mineral deposits had a local effect on the premining geochemical baseline. The lead isotopic data in modern streambed-sediment samples provide independent and unequivocal evidence of the effect of historical mining on the three major streams of the Animas River watershed study area. The lead isotopic signatures, in combination with lead concentration data in modern streambed sediment, clearly reflect both the type of mineral deposit and the specific source of lead identified in this study (fig. 36).

The Animas River downstream from Eureka to the southern margin of the study area is dominated by the Eureka graben lead isotopic signature ($^{206}\text{Pb}/^{204}\text{Pb}=18.3\text{--}18.4$) even though radiogenic lead ($^{206}\text{Pb}/^{204}\text{Pb}>18.7$) is being contributed by tributaries to the Animas River. The Eureka graben signature is also found throughout the Cement Creek drainage, and in tributaries that drain west into Mineral Creek, such as Browns Gulch.

Modern streambed sediment in Mineral Creek upstream from the confluence with Middle Fork Mineral Creek is characterized by slightly more radiogenic lead than that found in the upper Animas River and Cement Creek and reflects

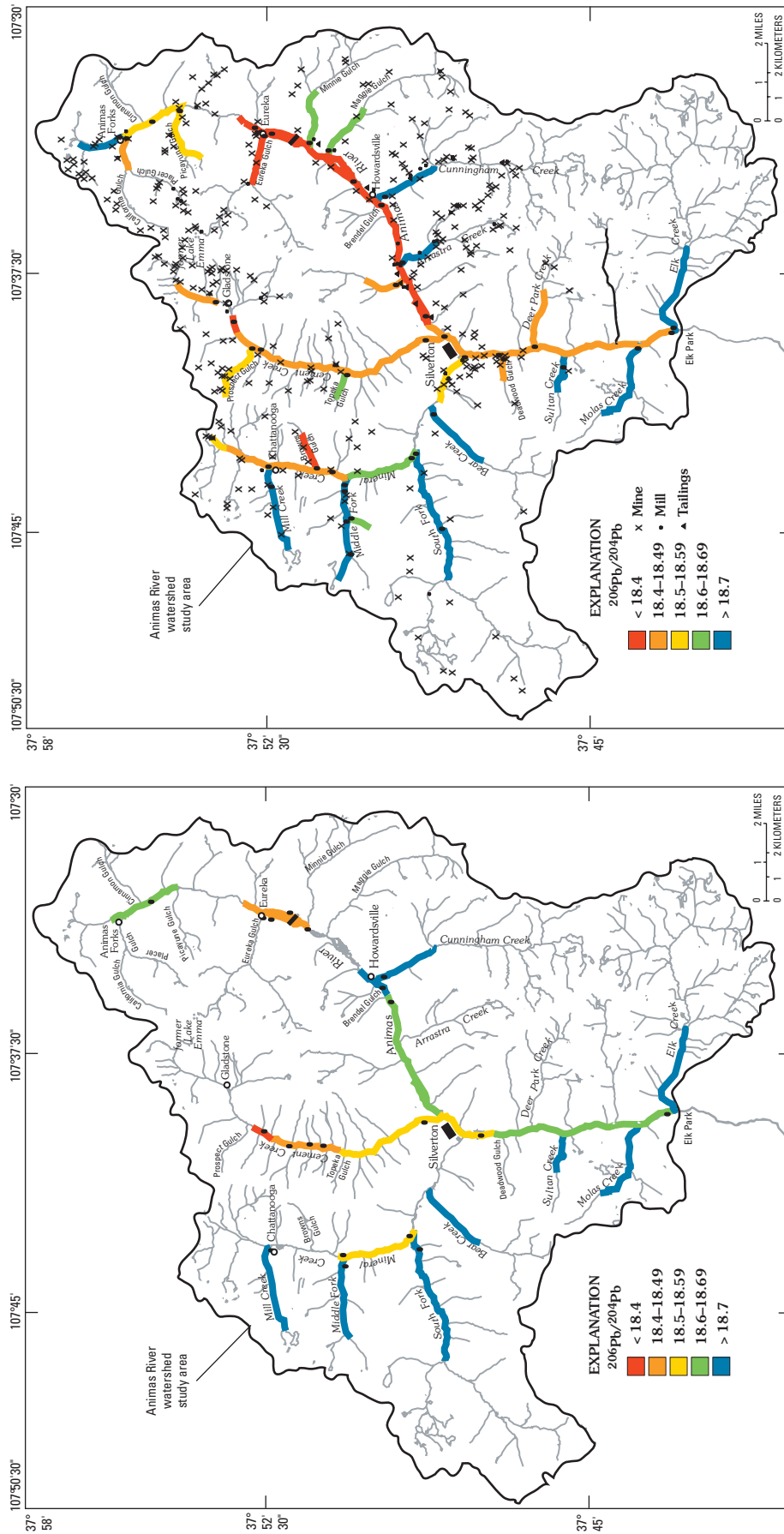
the lead isotopic signature of the breccia-pipe deposits found in the headwaters of the Mineral Creek basin. Downstream from the confluence with Middle Fork Mineral Creek, modern streambed sediment has a more radiogenic lead signature and represents a mixture between lead from upper Mineral Creek and radiogenic lead contributed by the lower tributaries, predominantly Middle Fork Mineral Creek.

Lead in modern streambed sediment from lower Cement Creek is isotopically indistinguishable from that in the Animas River immediately upstream from the confluence with Cement Creek. Contributions of sediment from Mineral Creek have little to no effect on the lead isotopic composition of streambed sediment downstream from the confluence. Deposit-related trace-element concentration data (figs. 25–31) indicate that the principal contributor to the present-day bed load is the large amount of mill tailings, in excess of 2.5 millions tons, released by the Sunnyside Eureka Mill (mine # 164, fig. 4).

Comparison of Streambed Sediment Data from the Animas River Watershed Study Area with Sediment-Quality Guidelines

Sediment-quality criteria to evaluate toxicity of metals to aquatic biota have only recently been defined and are not currently regulated. Sediment-quality guidelines for trace-element concentrations in streambed sediment (table 3) are summarized from Jones and others (1997) and from MacDonald and others (2000). Different definitions are used to define the effect of sediment-borne contaminants on aquatic life (see the footnotes, table 3). For the purposes of this discussion, we adopt the terminology used in MacDonald and others (2000). The Threshold Effect Concentration (TEC) is defined as the “contaminant concentration below which harmful effects on sediment-dwelling organisms were not expected,” whereas the Probable Effect Concentration (PEC) is defined as the “contaminant concentration above which harmful effects on sediment-dwelling organisms were expected to occur frequently” (MacDonald and others, 2000). No TEC or PEC values have been determined for silver and iron. We primarily rely on the Screening Level Concentration (SLC) value for these two elements (table 3), which is defined as “the highest concentration that can be tolerated by approximately 95 percent of the benthic fauna” (U.S. EPA, 1996) to assess effects on biota.

Concentrations of the deposit-related trace elements in modern streambed sediment exceed the consensus TEC (or SLC) and PEC concentrations values in Cement and Mineral Creeks and the Animas River throughout much of the watershed study area (table 4). Concentrations of toxic metals are elevated in the iron colloidal component of the streambed sediment. Iron concentrations in excess of 40,000 ppm in streambed sediment are toxic to most aquatic life (table 3). Leachable



B

A

Figure 36. $^{206}\text{Pb}/^{204}\text{Pb}$ values in streambed sediment for A, premining geochemical baseline (dot, sample locality), and B, modern streams, Animas River watershed study area. Major stream reaches all show effects of historical mining and have lower values of $^{206}\text{Pb}/^{204}\text{Pb}$.

Table 3. Summary of screening level concentrations proposed for streambed sediment.

[Concentrations in parts per million, ppm; leaders (-), no value recommended; bold values are recommended consensus values]

	ARCS ¹		Ontario MOE ⁴		EPA-IV SLC ⁵	OSWER SLC ⁶	Range of SLC ⁷	Range of AET ⁸	Consensus TEC ⁹	Consensus PEC ¹⁰
	TEC ²	PEC ³	Low	Severe						
Arsenic	12.1	57	6	33	7.24	8.2	7-12	33-57	9.79	33.0
Cadmium	0.592	11.7	0.6	10	1	1.2	0.6-1.0	10-12	0.99	4.98
Copper	28	77.7	16	110	18.7	34	16-34	78-110	31.6	149
Iron	--	--	20,000	40,000	--	--	20,000	40,000	--	--
Lead	34.2	396	31	250	30.2	47	30-47	250-400	35.8	128
Mercury	0.174	0.486	0.2	2.0	--	--	--	--	0.18	1.06
Silver	--	--	--	--	2	--	2	--	--	--
Zinc	159	1,532	120	820	124	150	120-160	820-1,532	121	459

¹ARCS—Assessment and Remediation of Contaminated Sediments Project, EPA Region IV, Great Lakes Program (U.S. EPA, 1996).²TEC—Threshold Effect Concentration, the contaminant concentration below which harmful effects on sediment-dwelling organisms were not expected.³PEC—Probable Effect Concentration, the contaminant concentration above which harmful effects on sediment-dwelling organisms were expected to occur frequently.⁴Ontario MOE—Low, the lowest effect level of screening level concentration (5th percentile); Severe, the severe effect level of screening level concentration (95th percentile; Persuad and others, 1993).⁵EPA-IV—Ecological screening values for sediments (U.S. EPA, 1995), screening level concentrations.⁶OSWER—Office of Solid Waste and Emergency Response (U.S. EPA, 1996) screening level concentrations.⁷SLC—Screening Level Concentration, the highest concentration of a contaminant that can be tolerated by approximately 95 percent of the benthic fauna.⁸AET—Apparent Effects Threshold, that concentration above which statistically significant biologic effects always occur.⁹Consensus-based TEC from MacDonald and others (2000); predicted TEC shown accurately predicts no toxic effect more than 80 percent of the time ($n=347$) for all trace elements in table except for arsenic, where the TEC shown accurately predicts no toxic effect 74 percent of the time ($n=150$). The EPA-IV SLC value of 2 ppm was used as the TEC for Ag.¹⁰Consensus-based PEC from MacDonald and others (2000); predicted PEC shown accurately predicts a toxic effect 90 percent or more of the time ($n=347$) for all trace elements in table except for arsenic, where the PEC shown accurately predicts a toxic effect 76.9 percent of the time ($n=150$). Values >4 ppm were used for the PEC for Ag.

Table 4. Sites where concentrations of deposit-related trace elements in streambed sediment exceed sediment-quality guidelines, Animas River watershed study area.

[Data are from total digestions of sediment; trace-element concentrations expressed in parts per million, ppm; data from Church and others (2000); data are in database (Sole and others, this volume); bold, shaded values exceed consensus PEC sediment quality concentrations, table 3; values in italics exceeded consensus TEC sediment quality concentrations, table 3]

Site No.	Arsenic ppm	Copper ppm	Cadmium ppm	Zinc ppm	Lead ppm	Silver ppm	Mercury ppm
Mineral Creek basin							
S2	38	<i>81</i>	<2	1,100	940	<2	0.05
S3	265	365	12	3,350	985	7	<i>0.56</i>
S4	47	<i>50</i>	<2	<i>130</i>	170	<2	0.06
S5	130	880	<2	1,800	660	3	<i>0.39</i>
S11	35	<i>30</i>	<2	<i>190</i>	200	<2	--
S12	79	<i>145</i>	<2	<i>270</i>	255	<2	--
S13	<i>15</i>	180	<2	600	320	25	--
S14	<10	<i>36</i>	<2	<i>276</i>	166	<2	--
S16	41	<i>60</i>	<2	480	<i>91</i>	<2	--
S17	49	245	<2	935	255	<2	0.13
Cement Creek basin							
S18	52	410	<2	830	790	2	0.05
S19	42	180	5	1,550	680	3	0.10
S20	44	270	3	1,800	1,000	6	--
S21	180	180	<2	920	500	5	--
S22	78	170	<2	1,600	610	3	0.11
S23	46	<i>80</i>	<2	<i>140</i>	<i>96</i>	<2	0.05
S24	57	<i>123</i>	3	1,300	383	3	0.15
Upper Animas River basin							
S26	110	830	110	8,200	4,000	9	--
S27	90	1,200	34	5,000	6,600	20	--
S28	56	<i>120</i>	<2	980	300	<2	0.09
S29	110	<i>70</i>	<2	590	190	2	0.03
S30	110	600	19	3,900	900	7	--
S31	45	430	10	3,500	820	3	0.07
S32	51	550	11	3,600	1,900	5	<i>0.89</i>
S33	69	790	20	4,100	3,900	26	--
S34	<i>30</i>	<i>76</i>	<2	<i>270</i>	160	<2	--
S35	<i>16</i>	<i>68</i>	<2	<i>270</i>	210	<2	0.05
S36	42	500	10	3,500	2,100	12	0.14
S37	<i>16</i>	110	<2	670	520	<2	0.02
S38	38	520	14	3,450	2,000	11	0.08
S39	<i>26</i>	2,200	10	2,600	4,700	35	<i>0.43</i>
S40	<i>30</i>	490	6	1,500	1,300	6	--
S42	38	510	16	3,400	2,200	16	--
S43	35	470	8	3,200	1,900	12	0.09
S44	51	425	8	2,250	1,300	8	0.09
S45	<i>32</i>	340	<2	1,800	990	2	0.10
S46	33	390	4	2,700	1,200	5	0.10
S47	<i>15</i>	<i>36</i>	<2	<i>220</i>	690	<2	0.10
S48	<i>11</i>	<i>11</i>	<2	<i>110</i>	32	<2	0.03
S49	40	370	8	2,300	1,000	6	--
S50	<i>17</i>	<i>34</i>	<2	<i>270</i>	18	<2	0.07

concentrations of iron, as determined using the HCl-peroxide leach of streambed sediment (fig. 37), exceed the 40,000 ppm (table 3, Severe or PEC threshold) concentrations in modern streambed sediment in Cement Creek and in Mineral Creek upstream from the confluence with South Fork Mineral Creek. Leachable concentrations of iron exceed 20,000 ppm (table 3, Low or SLC threshold) in the Animas River downstream from Eureka to Elk Park, the lower reaches of South Fork Mineral Creek south of peak 3,792 m, and Mineral Creek downstream from the confluence with South Fork Mineral Creek.

Concentrations of leachable aluminum (fig. 38) are also extremely high. There are no consensus-based standards for aluminum, but freshly precipitated aluminum colloids are considered toxic to fish (Besser and others, this volume). High concentrations of aluminum colloids in the Animas River watershed study area occur downstream of mixing zones where the pH of the stream water exceeds 5–5.5 (Schemel and others, 2000; Kimball and others, this volume; Wright, Simon, and others, this volume). This phenomenon is well demonstrated by the aluminum concentration data in streambed sediment of Cement Creek, where the pH is in the range of 3.5–3.7, the mixing zone in Mineral Creek downstream from the confluence with South Fork Mineral Creek (fig. 11), and the upper Animas River at its headwaters as well as downstream from the confluence with Cement Creek. These iron and aluminum colloids are the residence sites of the toxic deposit-related trace elements listed in table 4. High concentrations of the deposit-related trace elements in modern streambed sediment occur wherever there are elevated concentrations of iron in the streambed sediment. Elevated iron or aluminum concentrations alone, however, are not a good proxy for elevated concentrations of toxic metals in streambed sediment.

Concentrations of arsenic in modern streambed sediment (table 4; fig. 25B) and premining sediment concentrations (table 5; fig. 25A) exceed the consensus PEC values throughout much of the Animas River watershed study area. Where streambed-sediment concentrations do not exceed the PEC value of 33 ppm, they exceed the consensus TEC concentration of 9.8 ppm (figs. 6, 8, and 10). Very high concentrations of arsenic in modern streambed sediment in the Boulder River watershed study area, Montana, did not seem to affect aquatic life in that drainage system (Finger and others, 2004).

Concentrations of copper in modern streambed sediment (table 4; figs. 6, 8, 10, and 26B) exceed the consensus PEC in Mineral Creek upstream from the confluence with the Animas River and at site *S13* on South Fork Mineral Creek. At all other sites, the concentration of copper in streambed sediment exceeds the consensus TEC value (table 4). In contrast, copper concentrations in premining streambed sediment from Mineral Creek exceed the consensus TEC value, but do not exceed the consensus PEC value (table 5; fig. 26A). Reduction of the amount of copper from historical mining sources in the Mineral Creek basin has been identified as a restoration objective for improvement of the aquatic habitat (U.S. Geological Survey, 2000) and is supported by this study.

Concentrations of copper in modern streambed sediment in Cement Creek generally exceed the consensus PEC value (table 4; fig. 26B) whereas in the premining streambed sediment, concentrations generally exceed the consensus TEC value (table 5; fig. 26A).

Concentrations of copper in modern streambed sediment exceed the consensus PEC value in the headwaters of the upper Animas River, in the reach immediately downstream from the Sunnyside Eureka Mill (site # 164, fig. 4) all the way down to Elk Park. Eureka Gulch and Arrastra Creek contain modern streambed sediment with copper concentrations that exceed the consensus PEC concentration (149 ppm, table 3), and in all but one of the other tributaries sampled, copper concentrations exceed the consensus TEC concentration (31.6 ppm, table 3). Copper in modern streambed sediment from Boulder Gulch (*S40*, fig. 3) exceeds the consensus PEC value, and from Bear Creek (*S16*, fig. 3) exceeds the consensus TEC value. Premining sediment had concentrations of copper that generally exceed the consensus TEC value for the upper Animas River basin (table 5; fig. 26A).

Concentrations of zinc in modern streambed sediment in Mineral Creek (table 4; figs. 6, 8, and 10) generally exceed the consensus PEC value of 459 ppm (table 3). All the Mineral Creek tributaries have values that exceed either the consensus PEC or the TEC value (121 ppm, table 3). In the premining streambed sediment, concentrations of zinc from Mineral Creek and its tributaries generally exceed the consensus TEC value, but not the PEC concentration (table 5; fig. 28A). Cadmium exceeds the consensus PEC value at *S3* (table 4; figs. 3 and 29) immediately downstream from the mining activity that occurred in the upper reaches of Mineral Creek basin where the breccia-pipe deposits were exploited, but otherwise cadmium was not detected. This is expected because, under the acidic conditions found in Mineral Creek, much of the zinc and all the cadmium should be dissolved in the stream (Kimball and others, this volume). The consensus TEC value for cadmium is below the limit of detection (2 ppm) used for analysis of streambed sediment in this study, so no conclusions can be drawn except that the zinc concentration is elevated above crustal abundance (CA) by factors of 3 to 5. Because cadmium is isochemical with zinc, we would expect that cadmium concentrations would also be elevated by a similar amount, suggesting that premining streambed sediment concentration would be in the range of 0.5–0.8 ppm (CA_{Cd} is 0.16 ppm, Fortescue, 1992). Following this logic, we suggest that the cadmium concentrations in premining sediment should be less than the PEC value. The cadmium data in table 5 are in the 3–5 ppm range where detected and may reflect the high degree of mobility of cadmium in the near-surface environment.

Concentrations of zinc in modern streambed sediment from Cement Creek exceed the consensus PEC, whereas concentrations of cadmium are generally below detection. The value of 5 ppm cadmium at site *S19* (fig. 3; table 4) may be

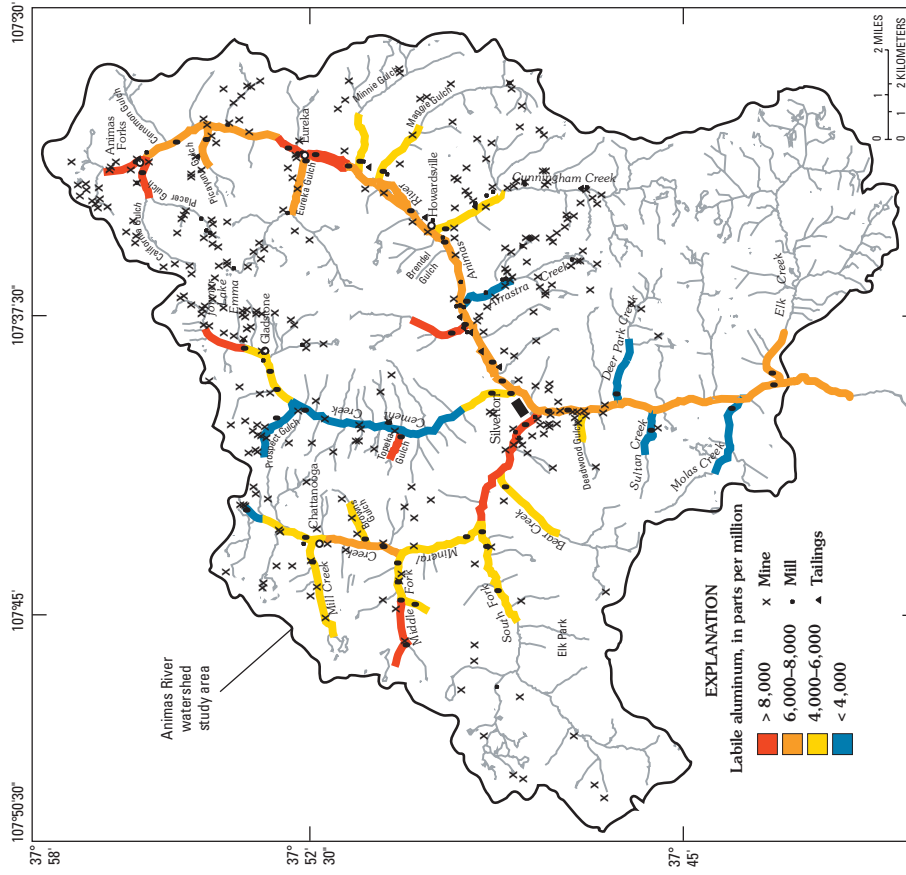


Figure 38. Concentration of aluminum in modern streambed sediment. Ribbon intervals are arbitrary and have been selected to show variations in data. High concentrations of aluminum generally occur downstream from confluences where low-pH water and high-pH water mix (fig. 11) and in stream reaches where tributaries drain altered areas.

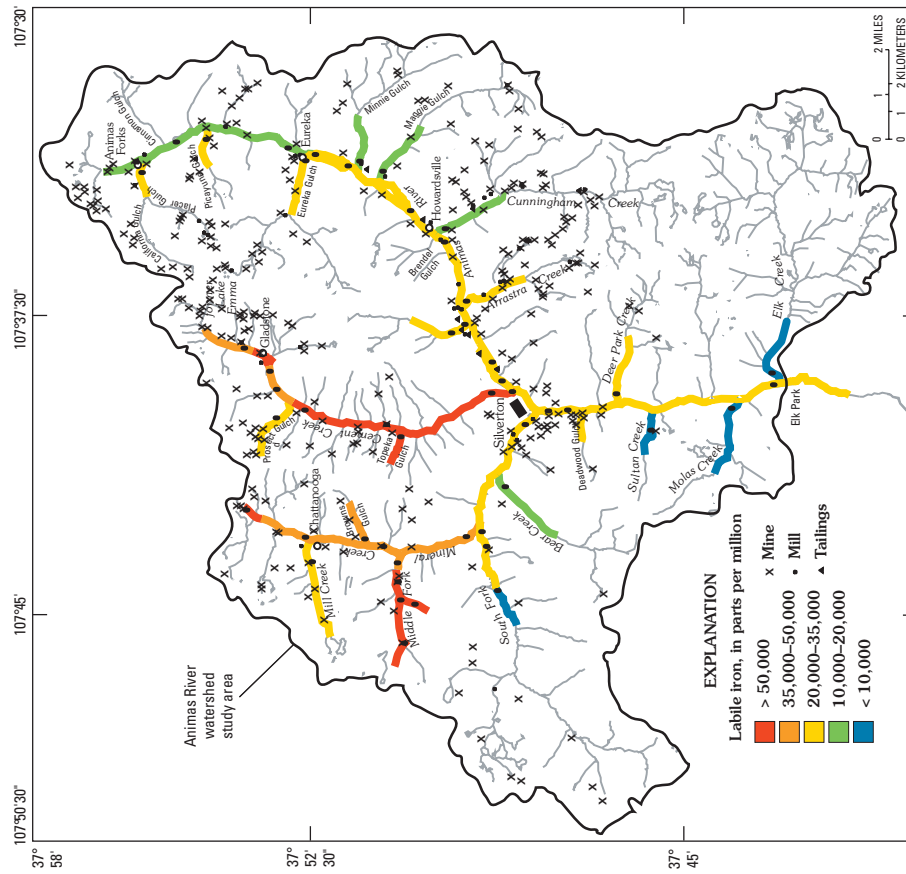


Figure 37. Concentrations of leachable iron in modern streambed sediment. Ribbon intervals are arbitrary and have been selected to show variations in data.

Table 5. Sites where concentrations of deposit-related trace elements in premining geochemical baseline streambed sediment exceed sediment-quality guidelines, Animas River watershed study area.

[Data are from total digestions of sediment; trace-element data expressed in parts per million (ppm); data are from Church and others (2000); data are in database (Sole and others, this volume); bold, shaded values exceed consensus PEC sediment quality concentrations, table 3; values in italics exceeded consensus TEC sediment quality concentrations, table 3]

Site No.	Sample No.	<i>n</i>	Arsenic ppm	Copper ppm	Cadmium ppm	Zinc ppm	Lead ppm	Silver ppm
Mineral Creek basin								
B1	97ABS312	7	38	<i>63</i>	<2	<i>410</i>	450	<2
B4	98ABB236	4	35	<i>60</i>	<2	<i>200</i>	150	<2
B5	98ABB233	4	<i>24</i>	<i>35</i>	3	<i>120</i>	<i>75</i>	<2
B6	98ABB221	3	37	<i>80</i>	4	<i>180</i>	210	<2
B8	98ABB230	3	<i>31</i>	<i>32</i>	2	<i>160</i>	<i>58</i>	<2
B10	999292	10	<i>15</i>	<i>35</i>	<2	<i>210</i>	<i>78</i>	<2
Cement Creek basin								
B13	97ABS324A	24	45	<i>130</i>	2	<i>400</i>	420	2
B14	00ABFC-209	1	<i>18</i>	<i>21</i>	2	<i>80</i>	240	<2
B15	99-ABB-127	1	43	<i>47</i>	2	<i>120</i>	360	<2
B16	96ABS121 & 122	17	69	<i>62</i>	<2	<i>160</i>	235	<2
B17	98ABB241	1	65	150	<2	<i>200</i>	230	<2
Upper Animas River basin								
B18	98ABB237	5	60	<i>100</i>	4	610	210	3
B19	96ABS140	10	40	<i>120</i>	3	1,350	300	<2
B20	96ABS001B	6	35	160	4	590	320	<2
B21	96ABS131 & 132	19	68	<i>120</i>	2	820	450	<2
B22	Premining silt	19	55	<i>120</i>	2	1,000	360	<2
B22	Premining gravels	10	55	<i>140</i>	3	1,050	410	<2
B24	96ABS118 & 119	3	51	<i>100</i>	5	540	425	3
B25	98ABB232	3	<i>26</i>	<i>110</i>	3	<i>300</i>	310	<2
B26	97ABS313	1	<i>21</i>	<i>100</i>	<2	<i>340</i>	290	<2
B27	98ABB234	1	<i>24</i>	190	3	470	210	<2
B29	98ABB240	3	40	<i>145</i>	2	665	280	<2
B30	96ABS126	6	<i>30</i>	<i>40</i>	<2	800	<i>120</i>	<2
B30	96ABS127	6	33	<i>46</i>	<2	670	<i>110</i>	<2
B30	98ABB225	4	35	<i>48</i>	--	530	150	<2

affected by the water treatment by Sunnyside mine at the American tunnel at Gladstone (mine # 96, fig. 3) during the period of sampling. Premining concentrations of zinc exceed the consensus TEC value at site *B13* (fig. 4), but the data from this core below a depth of 1.7 ft show how mobile zinc is in the near-surface environment (fig. 21). Likewise, the cadmium data from the premining sediment (table 5) exceed the consensus PEC value, but may not have exceeded the TEC prior to mining.

Concentrations of zinc in modern streambed sediment in the Animas River (table 4) are elevated above the consensus PEC value, in some places by more than an order of magnitude. Zinc concentrations from the tributary streams are lower, but many exceed the consensus TEC value. Cadmium concentrations likewise reflect the elevated concentration of zinc and, in one place, it exceeds the consensus PEC concentration. Many zinc and some cadmium concentrations in premining streambed sediment exceed the consensus TEC value. Whereas these

elevated concentrations are real, the data from sites *B19* and *B22* are tentative owing to the high mobility of zinc and cadmium in the near-surface environment (table 2). Reduction of the sources of zinc directly related to historical mining activity in the Animas River watershed has been recommended as a remediation objective (U.S. Geological Survey, 2000). Elevated concentrations of zinc and cadmium in Boulder Gulch and Bear Creek are probably the result of windblown transport of dust, as discussed previously for copper.

Concentrations of lead in modern streambed sediment are elevated in all three of the major basins in the Animas River watershed study area (table 4; figs. 6, 8, 10, and 27B) and exceed the consensus PEC concentration (128 ppm, table 3) throughout much of the study area. Silver concentrations likewise are in some places elevated (fig. 30), although no consensus values exist for silver in streambed sediment (table 3). Unlike zinc and cadmium, silver and lead are not easily mobilized in the near-surface environment.

Concentrations of total mercury were determined in modern streambed sediment (table 4). Only a minor amount of gold was recovered early in the mining history of the Animas River watershed study area. Mercury was used in the mills to recover free gold (Bird, 1999; Jones, this volume). Mercury concentrations measured in modern streambed sediment generally exceed crustal abundance (CA_{Hg} is 0.086 ppm; Fortescue, 1992) by a factor of 2 at most sites. At sites S3 and S5 in the upper reach of Mineral Creek (table 4), two values exceed the consensus TEC value for mercury (0.18 ppm, table 3) and none exceed the consensus PEC value (1.06 ppm, table 3). On the upper Animas River at site S32 (fig. 3) immediately downstream from the Sunnyside Eureka Mill (site # 164, fig. 4), we measured 0.89 ppm mercury, the highest value detected (table 4), and at site S39 (fig. 3) on Arrastra Creek we measured a value of 0.43 ppm mercury. At both sites the measured concentration of total mercury exceeds the consensus TEC value. Both these localities are downstream from mills where mercury was used to amalgamate gold (Jones, this volume, table 2). Further investigations of mercury in modern streambed sediment may be warranted.

Summary

The primary goal of this study was to characterize the current condition of streambed sediment throughout the Animas River watershed study area. We achieved this goal by mapping the changes in both leachable and total concentrations of deposit-related trace elements in the upper Animas River, Cement Creek and Mineral Creek, and their major tributaries. Concentrations of copper, lead, zinc, arsenic, cadmium, silver, and manganese have been shown to exceed Probable Effect Level Concentrations (PEC) at many localities throughout the area. Although sediment-quality guidelines have not been adopted by the regulatory community, these values have been shown to cause toxic effects in aquatic organisms (table 3). Streambed sediment in Mineral and Cement Creeks and the Animas River upstream from Silverton exceeds the PEC for copper, lead, and zinc. Cadmium and silver exceed the PEC in streambed sediment from the Animas River downstream from Eureka, where the Sunnyside Eureka Mill operated from 1917 to 1930.

A second goal of this study was to identify, in modern streambed sediment, the major sources of contaminants within the watershed. Studies of streambed-sediment geochemistry and lead isotopic signatures indicate that the Sunnyside Eureka Mill (site # 164) was by far the dominant source of contaminants. Mill tailings totaling more than 2.5 million tons were dumped into the Animas River at Eureka before the Depression caused the mill to close (Jones, this volume). Historical mining practices and the Gladstone flood in 1911 appear to have removed much of the early stamp mill tailings produced near the beginning of the 20th century. These early mill tailings are now dispersed in the flood plain of the Animas River. Reprocessing of existing mill and mine waste from the

early periods of production and milling during World War II resulted in removal of much of those early mill tailings and mine waste remaining at that time (Jones, this volume).

A third objective was to determine the premining geochemical baseline. We have approached this goal by sampling old terrace deposits described in the geomorphological studies of Blair and others (2002). Detailed geochronology of wood preserved in the fluvial sediment in these terraces and studies of the dendrochronology of trees growing on the terraces established age constraints at most sites. Migration of deposit-related trace elements, particularly when associated with elevated concentrations of manganese, resulted in spurious results that were not used in the compilations. Premining geochemical baseline values were established at 5 localities in the Mineral Creek basin, 5 localities in Cement Creek, and 10 localities in the upper Animas River basin upstream from the confluence with Mineral Creek. The premining geochemical baseline values varied between basins and showed local geochemical anomalies immediately downstream from major mineral deposits.

A fourth objective was to quantify the present contributions to the streams from specific sites. This objective has been only partially achieved in that the results from sites within the upper Animas River basin are totally overwhelmed by the very large effect of the Sunnyside Eureka Mill (site # 164). Contributions from the mines and mills in Cement and Mineral Creeks are discernible, but small. The effect of streambed sediment at the confluences of these two creeks mixing with sediment from the Animas River is also overwhelmed by the dominant contribution from the Sunnyside Eureka Mill. Both Cement and Mineral Creeks have a large component of dissolved and colloidal loads (Kimball and others, this volume) that can be attributed to weathering of altered rock that is exposed in these two basins (Bove and others, this volume). Downstream from the confluence with Mineral Creek, the contribution to the lead, copper, and zinc loads in the Animas River south to Aztec, N. Mex., has been documented by Church and others (1997).

References Cited

- Atwood, W.W., and Mather, K.F., 1932, Physiography and Quaternary geology of the San Juan Mountains, Colorado: U.S. Geological Survey Professional Paper 166, 176 p.
- Besser, J.M., Brumbaugh, W.G., May, T.W., Church, S.E., and Kimball, B.A., 2001, Bioavailability of metals in stream food webs and hazards to brook trout (*Salvelinus fontinalis*) in the upper Animas River Watershed, Colorado: Archives of Environmental Contamination and Toxicology, v. 40, p. 48–59.
- Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., and Wolf, M., 1996, Schwertmannite and the chemical modeling of iron in acid sulfate waters: *Geochimica et Cosmochimica Acta*, v. 60, p. 2111–2121.

- Bird, A.G., 1999, Silverton gold (revised edition): Lakewood, Colo., privately published, 223 p.
- Blair, R.W., Jr., Yager, D.B., and Church, S.E., 2002, Surficial geologic maps along the riparian zone of the Animas River and its headwater tributaries, Silverton to Durango, Colorado, with upper Animas River watershed gradient profiles: U.S. Geological Survey Digital Data Series DDS-71.
- Briggs, P.H., 1996, Forty elements by inductively coupled-plasma-atomic emission spectrometry, *in* Arbogast, B.F., ed., Analytical methods manual for the Mineral Resources Program: U.S. Geological Survey Open-File Report 96-525, p. 77-94.
- Burbank, W.S., and Luedke, R.G., 1968, Geology and ore deposits of the San Juan Mountains, Colorado, *in* Ridge, J.D., ed., Ore deposits of the United States, 1933-1967, the Graton-Sales Volume, Volume 1: American Institute of Mining, Metallurgical, and Petroleum Engineers, p. 714-733.
- Burbank, W.S., and Luedke, R.G., 1969, Geology and ore deposits of the Eureka and adjoining districts, San Juan Mountains, Colorado: U.S. Geological Survey Professional Paper 535, 73 p.
- Casadevall, Thomas, and Ohmoto, Hiroshi, 1977, Sunnyside mine, Eureka mining district, San Juan County, Colorado—Geochemistry of gold and base metal ore deposition in a volcanic environment: *Economic Geology*, v. 92, p. 1285-1320.
- Church, S.E., 1981, Multielement analysis of fifty-four geochemical reference samples using inductively coupled plasma-atomic emission spectrometry: *Geostandards Newsletter*, v. 5, p. 133-160.
- Church, S.E., Fey, D.L., and Blair, Robert, 2000, Pre-mining bed sediment geochemical baseline in the Animas River watershed, southwestern Colorado, *in* ICARD 2000; Proceedings of the Fifth International Conference on Acid Rock Drainage, Volume 1: Society for Mining, Metallurgy, and Exploration, Inc., p. 499-512.
- Church, S.E., Fey, D.L., Unruh, D.M., Vaughn, R.B., and Taggart, J.E., Jr., 2000, Geochemical and isotopic data from streambed sediment, Animas River watershed, Colorado, 1995-1999: U.S. Geological Survey Open-File Report 00-244, 16 p.
- Church, S.E., Holmes, C.W., Briggs, P.H., Vaughn, R.B., Cathcart, James, and Marot, Marci, 1993, Geochemical and lead-isotope data from stream and lake sediments, and cores from the upper Arkansas River drainage—Effects of mining at Leadville, Colorado, on heavy-metal concentrations in the Arkansas River: U.S. Geological Survey Open-File Report 93-534, 61 p.
- Church, S.E., Kimball, B.A., Fey, D.L., Ferderer, D.A., Yager, T.J., and Vaughn, R.B., 1997, Source, transport and partitioning of metals between water, colloids, and bed sediments of the Animas River, Colorado: U.S. Geological Survey Open-File Report 97-151, 136 p.
- Desborough, G.A., Leinz, Reinhard, Sutley, Stephen, Briggs, P.H., Swayze, G.A., Smith, K.S., and Breit, George, 2000, Leaching studies of schwertmannite-rich precipitates from the Animas River headwaters, Colorado and Boulder River headwaters, Montana: U.S. Geological Survey Open-File Report 00-004, 16 p.
- Doe, B.R., Steven, T.A., Delevaux, M.H., Stacey, J.S., Lipman, P.W., and Fisher, F.S., 1979, Genesis of ore deposits in the San Juan volcanic field, southwestern Colorado—Lead isotopic evidence: *Economic Geology*, v. 74, p. 1-26.
- Durango Democrat, 1902, Nov. 15 edition, Durango, Colo.
- Durango Evening Herald, 1911, Oct. 5-11 editions, Durango, Colo.
- Fey, D.L., Church, S.E., and Unruh, D.M., 2000, Geochemical and lead isotopic data from sediment cores, fluvial tailings, iron bogs, and pre-mining terrace deposits, Animas River watershed, Colorado, 1995-1999: U.S. Geological Survey Open-File Report 00-465, 91 p.
- Fey, D.L., Unruh, D.M., and Church, S.E., 1999, Chemical data and lead isotopic compositions in stream-sediment samples from the Boulder River watershed, Jefferson County, Montana: U.S. Geological Survey Open-File Report 99-575, 147 p.
- Finger, S.E., Farag, A.M., Nimick, D.A., Church, S.E., and Sole, T.C., 2004, Synthesis of water, sediment, and biological data using hazard quotients to assess ecosystem health, Chapter C *in* Nimick, D.A., Church, S.E., and Finger, S.E., eds., Integrated investigations of environmental effects of historical mining in the Basin and Boulder mining districts, Boulder River watershed, Jefferson County, Montana: U.S. Geological Survey Professional Paper 1652, p. 29-48.
- Fortescue, J.A.C., 1992, Landscape geochemistry—Retrospect and prospect—1990: *Applied Geochemistry*, v. 7, p. 1-54.
- Furrer, Gerhard, Phillips, B.L., Ulrich, K-U., Pöthig, Rosemarie, and Casey, W.H., 2002, The origin of aluminum flocs in polluted streams: *Science*, v. 297, p. 2245-2247.
- Gillam, M.L., 1998, Late Cenozoic geology and soils of the lower Animas River Valley, Colorado and New Mexico: Boulder, Colo., University of Colorado Ph. D. dissertation, 477 p.

- Hoffman, J.D., and Buttleman, Kim, 1994, National Geochemical Data Base; National Uranium Resource Evaluation data for the conterminous United States, *with* MAPPER display software by R.A. Ambroziak and MAPPER documentation by C.A. Cook: U.S. Geological Survey Digital Data Series DDS-0018-A, CD-ROM.
- Jones, D.S., Suter, G.W., II, and Hull, R.N., 1997, Toxicological benchmarks for screening contaminants of potential concern for effects on sediment-associated biota; 1997 revision: U.S. Department of Energy Report ES/ER/TM-95/R4, 30 p., unpaginated appendices.
- Kimball, B.A., Callender, Edward, and Axtmann, E.V., 1995, Effects of colloids on metal transport in a river receiving acid mine drainage, upper Arkansas River, Colorado, U.S.A.: *Applied Geochemistry*, v. 10, p. 285-306.
- Kimball, B.A., Runkel, R.L., Walton-Day, Katherine, and Bencala, K.E., 2002, Assessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling; Cement Creek, Colorado, U.S.A.: *Applied Geochemistry*, v. 17, p. 1183-1207.
- Lipman, P.W., Fisher, F.S., Mehnert, H.N., Naeser, C.W., Luedke, R.G., and Steven, T.A., 1976, Multiple ages of mid-Tertiary mineralization and alteration in the western San Juan Mountains, Colorado: *Economic Geology*, v. 71, p. 571-588.
- MacDonald, D.D., Ingersoll, C.G., and Berger, T.A., 2000, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems: *Archives of Environmental Contamination and Toxicology*, v. 39, p. 20-31.
- Milhous, R.T., 1999, Aquatic physical habitat and hydrology in abandoned mine land studies, *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxics Hydrology Program—Proceedings of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999, Volume 1, Contamination from hardrock mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A, p. 47-54.
- National Institute of Standards and Technology (NIST), 1993a, Certificate of Analysis Standard Reference material 2704, Buffalo River Sediment.
- National Institute of Standards and Technology (NIST), 1993b, Certificate of Analysis Standard Reference material 2709, San Joaquin Soil.
- National Institute of Standards and Technology (NIST), 1993c, Certificate of Analysis Standard Reference material 2711, Montana Soil.
- OSWER (Office of Solid Waste and Emergency Response, Environmental Protection Agency), 1996, Ecotox thresholds: ECO Update, v. 3, p. 1-12.
- Osterwald, D.B., 1995, Cinders and smoke: Lakewood, Colo., Western Guideways Ltd., 168 p.
- Persuad, D., Jaaugmagi, R., and Hayton, A., 1993, Guidelines for the protection and management of aquatic sediment quality in Ontario: Ontario Ministry of the Environment and Energy, 30 p.
- Pruess, J.W., 1996, Paleoflood reconstructions within the Animas River Basin upstream from Durango, Colorado: Fort Collins, Colo., Colorado State University M.S. thesis, 192 p.
- Ransome, F.L., 1901, A report on the economic geology of the Silverton quadrangle, Colorado: U.S. Geological Survey Bulletin 182, 265 p.
- Ringrose, C.F., 1982, Geology, geochemistry, and stable isotope studies of a porphyry-style hydrothermal system, west Silverton district, San Juan Mountains, Colorado: Aberdeen, Scotland, University of Aberdeen Ph. D. dissertation, 257 p.
- Schemel, L.E., Kimball, B.A., and Bencala, K.E., 2000, Colloid formation and transport of aluminum and iron in the Animas River near Silverton, Colorado: *Applied Geochemistry*, v. 15, p. 1003-1018.
- Shannon, S.S., Jr., 1980, Uranium hydrogeochemical and stream sediment reconnaissance of the Durango NTMS quadrangle, Colorado, including concentrations of 42 additional elements: Los Alamos Scientific Laboratory informal report LA-7345-MS Supplement, Los Alamos, N. Mex., U.S. Department of Energy, Grand Junction, Colo., GJBX-138(80), 121 p.
- Sloan, R.E., and Skowronski, C.A., 1975, The Rainbow Route, An illustrated history of the Silverton Railroad, the Northern Silverton Railroad, and the Silverton, Gladstone, & Northerly Railroad: Denver, Colo., Sundance Publications Limited, 416 p.
- Smith, K.S., 1999, Metal sorption on mineral surfaces—An overview with examples relating to mineral deposits, *in* Plumlee, G.S., and Logsdon, M.J., eds., The environmental geochemistry of mineral deposits—Part A, Processes, techniques, and health issues: Society of Economic Geologists, *Reviews in Economic Geology*, Volume 6, p. 161-182.

- Unruh, D.M., Fey, D.L., and Church, S.E., 2000, Chemical data and lead isotopic compositions of geochemical baseline samples from streambed sediments and smelter slag, lead isotopic compositions in fluvial tailings, and dendrochronology results from the Boulder River watershed, Jefferson County, Montana: U.S. Geological Survey Open-File Report 00–38, 75 p.
- U.S. Environmental Protection Agency, 1995, National sediment inventory; Documentation of derivation of freshwater sediment quality: Washington, D.C., Office of Water, EPA Report.
- U.S. Environmental Protection Agency, 1996, Calculation and evaluation of sediment effect concentrations for the amphipod *Hyalella azteca* and the midge *Chironomus riparius*: Chicago, Ill., Great Lakes National Program Office, EPA Report 905–R96–008.
- U.S. Geological Survey, 2000, Interim report on the scientific investigations in the Animas River watershed, Colorado to facilitate remediation decisions by the U.S. Bureau of Land Management and the U.S. Forest Service, March 29, 2000 meeting, Denver, Colo.: U.S. Geological Survey Open-File Report 00–245, 34 p.
- Verplanck, P.L., Unruh, D.M., and Fey, D.L., 2001, Evaluation of strontium isotopes as a geochemical tracer in the Middle Fork Mineral Creek basin, southwestern Colorado: U.S. Geological Survey Water-Resources Investigations Report 00–4290, 20 p.
- Warren, R.G., Gallimore, D.L., Martell, C.J., Sandoval, W.F., Garcia, S.R., Minor, M.M., and McInteer, Carlotta, 1981, Data release for intermediate-density hydrogeochemical and stream sediment sampling in the Vallecito Creek Special Study Area, Colorado, including concentrations of uranium and forty-six additional elements: Los Alamos Scientific Laboratory informal report LA–8483–MS, Los Alamos, N. Mex., U.S. Department of Energy, Grand Junction, Colo., GJBX–217(81), 101 p.
- Wirt, Laurie, Leib, K.J., Bove, D.J., Mast, M.A., Evans, J.B., and Meeker, G.P., 1999, Determination of chemical-constituent loads during base-flow and storm-runoff conditions near historical mines in Prospect Gulch, upper Animas River watershed, southwestern Colorado: U.S. Geological Survey Open-File Report 99–159, 43 p.
- Wirt, Laurie, Leib, K.J., Melick, Roger, and Bove, D.J., 2001, Metal loading assessment of a small mountainous sub-basin characterized by acid drainage—Prospect Gulch, upper Animas River watershed, Colorado: U.S. Geological Survey Open-File Report 01–258, 36 p.
- Yager, D.B., Mast, M.A., Verplanck, P.L., Bove, D.J., Wright, W.G., and Hageman, P.L., 2000, Natural versus mining-related water quality degradation to tributaries draining Mount Moly, Silverton, Colorado, in ICARD 2000; Proceedings of the Fifth International Conference on Acid Rock Drainage, Volume 1: Society for Mining, Metallurgy, and Exploration, Inc., p. 535–547.