Trace Elements in Water in Streams Affected by Historical Mining

By David A. Nimick and Thomas E. Cleasby

Chapter D5 of
Integrated Investigations of Environmental Effects of Historical Mining in the Basin and Boulder Mining Districts, Boulder River Watershed, Jefferson County, Montana

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Abstract

Investigation of trace elements in water of the Boulder River watershed provided information to (1) delineate stream reaches having elevated concentrations of trace elements, (2) determine sources of the trace elements, (3) understand the transport of dissolved and particulate forms of trace elements, (4) evaluate the potential for trace-element toxicity to biota, and (5) establish a long-term water-quality monitoring plan. Water-quality data collected in and near the watershed during 1996–2000, as well as historical data, were used for the assessment.

Concentrations of trace elements associated with ore deposits in the watershed varied greatly, with the highest concentrations occurring in small streams downstream from a few inactive mines. Cadmium, copper, lead, and zinc concentrations in streams affected by historical mining commonly were higher than aquatic-life standards. Concentrations exceeded acute aquatic-life standards by as much as 200-fold. Few stream reaches had acidic pH (less than 6.5). Of all of the inactive mines in the watershed, the Bullion, Crystal, and Comet mine sites produced most of the trace-element load to the watershed and had the largest effect on trace-element concentrations in streams. Cataract Creek, which drains the Crystal mine, contributed larger dissolved trace-element loads to the Boulder River than either Basin or High Ore Creeks, which drain the Bullion and Comet mines, respectively.

Introduction

More than 140 inactive mines and 15 mills are scattered throughout the Basin, Cataract, and High Ore Creek basins in the Boulder River watershed study area (fig. 1), but knowledge about the individual or cumulative effects of these sites on streams in the watershed is limited. Water is the main transport mechanism for trace elements derived from historical hard-rock mining areas and serves as the habitat for aquatic organisms that may be exposed to potentially toxic concentrations. Therefore, assessing the distribution, magnitude, and sources of trace elements in water is an integral component of any study of the environmental effects on aquatic ecosystems in watersheds that contain inactive mines. Understanding the distribution and magnitude of trace elements in streams throughout an affected watershed is important for prioritizing remediation activities and establishing restoration goals. Characterization of trace-element sources and pathways is essential for planning effective and cost-efficient remediation. Integrating water-quality data with streambed-sediment data and biological measures of aquatic health then allows assessment of the vulnerability of aquatic ecosystems to the effects of historical mining in the study area.

Purpose and Scope

This report assesses the concentrations, sources, and loads of mining-related trace elements in streams draining historical mining areas in the Boulder River watershed near the town of Basin in southwestern Montana. Trace elements of particular interest were those which are associated with the ore deposits in the watershed and which can pose a toxic risk to aquatic life. Trace-element concentrations and associated physical and chemical data were determined for water samples from 64 sites during 1996–2000. These data are presented in the database (Rich and others, this volume, Chapter G and accompanying CD-ROM). In addition, we utilized water-quality data presented by Kimball and others (this volume, Chapter D6) and historical water-quality data (Nimick and Cleasby, 2000, table 4).

To help us characterize environmental conditions in streams of the Boulder River watershed, we set goals of determining the seasonal and spatial distribution of trace-element concentrations in surface water throughout the watershed, and then identifying the significant mining- and nonmining-related source(s) of those trace elements. Source areas were determined from concentration gradients showing downstream changes in trace-element concentrations in water and from trace-element loads revealing areas where major increases occurred in the mass of elements transported. We distinguished mining- and nonmining-related sources of trace
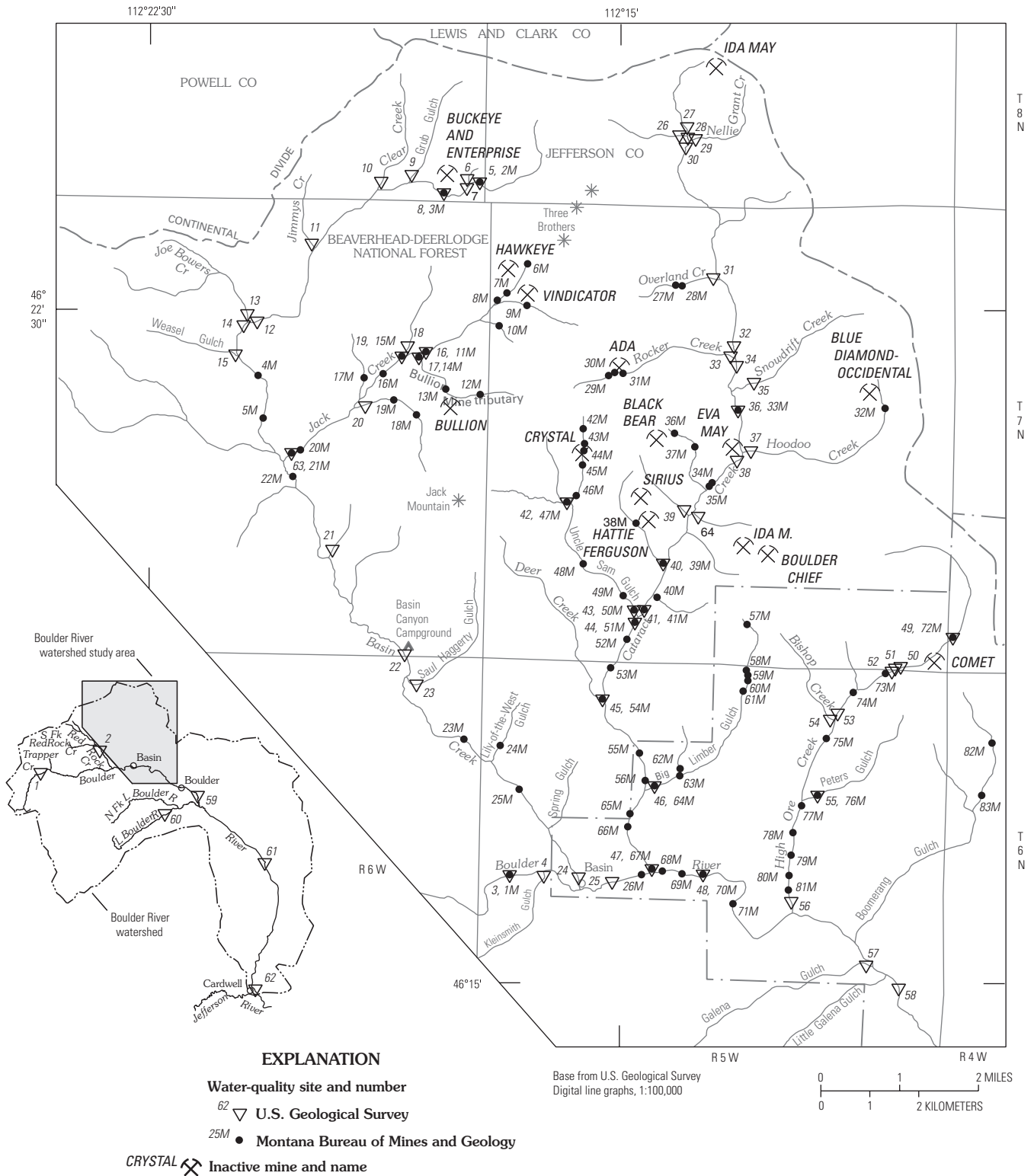
Figure 1.   Water-quality sites and selected inactive mines in Boulder River watershed study area, Montana.

elements in mineralized watersheds by comparing water-quality data to the location of mined areas and geologic units.

The water-sampling program conducted during this study had four objectives. The first objective was to determine what mining-related trace elements occurred at concentrations that were potentially toxic to aquatic organisms. To accomplish this objective, we analyzed samples from selected sites during the early part of the study for a large suite of trace elements. The second objective was to characterize the range of concentrations of the potentially toxic trace elements throughout the watershed both spatially and seasonally. To accomplish this objective, samples were collected once during high-flow conditions and once during low-flow conditions at many sites throughout the watershed. To efficiently evaluate many sites in the watershed, samples from some sites were analyzed only for total-recoverable zinc, because zinc is associated with the watershed's ore deposits and occurs more frequently in detectable concentrations in surface water than the other deposit-related trace elements. The third objective was to characterize trace-element loads at five key sites in the watershed during a complete hydrologic cycle. For this objective, samples were collected 13 times during 1996–97 over a wide range of flow conditions. The fourth objective was to establish a water-quality monitoring program to determine long-term seasonal and annual variations near areas where remediation activities had been planned by State and Federal agencies. This last part of the water-sampling program was initiated in 1997 before any remediation started, so that pre-remediation conditions could be documented. Sampling at five key sites in the watershed continued during 1998–2000 but at a lower frequency than in 1997. Long-term monitoring sites also were established downstream from the Bullion, Crystal, Comet, and Buckeye mines as well as the reach of Cataract Creek between Uncle Sam Gulch and Hoodoo Creek. Results for this fourth objective are reported in this chapter for the five key sites as well as for the Comet mine by Gelinas and Tupling (this volume, Chapter E2) and for the Buckeye and Enterprise mines by Cannon and others (this volume, Chapter E1).

Trace elements of particular concern for this study were those typically associated with polymetallic veins (Becraft and others, 1963; Ruppel, 1963), which were the primary rocks mined in the watershed. These trace elements include antimony, arsenic, cadmium, copper, gold, iron, lead, silver, and zinc. In contrast, trace elements that are not associated with polymetallic vein systems are called rock-forming trace elements and include chromium, strontium, vanadium, and the rare-earth elements.

Previous Investigations

The first systematic assessment of the effects of historical mining on water quality in the Boulder River watershed took place in the 1970s (summarized by Ken Knudson, consulting biologist, Helena, Mont., written commun., 1984). Results showed that trace-element concentrations were higher in High

Ore Creek than in Basin or Cataract Creeks. No streamflow data were collected and therefore loads could not be calculated. In 1985, Phillips and Hill (1986) sampled 14 sites during spring runoff. Results indicated that, although concentrations were high in High Ore Creek (as noted by Knudson, written commun., 1984), the load of trace elements contributed by Cataract Creek to the Boulder River was greater than the load from High Ore Creek because of the much larger streamflow in Cataract Creek. The Montana Bureau of Mines and Geology collected water-quality samples from numerous sites throughout the watershed as part of the inventories of inactive mines completed in the mid-1990s for the USDA Forest Service (Metesh and others, 1994, 1995, 1996) and Bureau of Land Management (Marvin and others, 1997). Data from these mine-inventory reports were useful for characterizing the range and distribution of trace-element concentrations throughout the watershed because many sites were sampled.

Data Collection

Water-quality samples for this study were collected from 64 sites (fig. 1) between October 1996 and October 2000. Water-quality sites were located throughout the study area on both small and large streams and at locations upstream and downstream from selected inactive mines. We also collected samples at three sites on the Boulder River (sites 59, 61, and 62) downstream from the study area to determine the extent of trace-element enrichment from the Basin and Boulder mining districts.

Reference sites were selected in drainages that had a geologic setting similar to that of the study area except without mineralized rocks. We sampled these sites to establish a reference for water-quality comparison with mineralized areas. No sites were available in unmined, mineralized zones to indicate natural background conditions in the study area. Reference sites (fig. 1) included the Boulder River upstream from the Boulder River watershed study area (site 1), Red Rock Creek (site 2), and the Little Boulder River (site 60).

The area upstream from site 1 is underlain by Late Cretaceous plutonic rocks of the Boulder batholith as well as the Late Cretaceous Elkhorn Mountains Volcanics and Eocene Lowland Creek Volcanics (Wallace, 1987). Little historical mining took place in this area of the Boulder River watershed (Elliott and others, 1992). The areas upstream from site 2 (Red Rock Creek) and site 60 (Little Boulder River) are underlain by Late Cretaceous plutonic rocks of the Boulder batholith and the Elkhorn Mountains Volcanics (Wallace, 1987). Elliott and others (1992) did not indicate any historical mines or prospects in these two areas, but small producing historical mines did exist in the Little Boulder River basin upstream from the sampling site. However, with the exception of one placer mine, these mines and prospects are not close to the Little Boulder River.

Methods of data collection and analysis, as well as quality-assurance data, are in Nimick and Cleasby (2000).

The types of data collected included streamflow, field measurements of physical and chemical properties, suspended-sediment concentration, and analytical results for major ions, nutrients, and dissolved and total-recoverable trace elements. Streamflow was measured according to methods described by Rantz and others (1982). Water samples typically were collected from multiple verticals across the stream using depth- and width-integration methods. These methods provide a vertically and laterally discharge-weighted sample that is representative of the entire flow through the cross section of a stream. Grab samples were collected when streamflow was too low to allow use of a depth-integrating sampler. Sampling equipment consisted of standard USGS depth-integrating suspended-sediment samplers (models DH-81, DH-48, and D-74TM), which are either constructed of plastic or coated with a nonmetallic epoxy paint; both types are equipped with interchangeable nylon nozzles for sampling a wide range of stream depths and velocities.

General Water Chemistry

Without elevated trace-element concentrations, the water in almost all streams in the Boulder River watershed study area generally is not toxic to aquatic organisms and water quality would be considered good. Concentrations of dissolved solids were low (generally less than 120 mg/L), presumably because the granitic and volcanic rocks in the watershed weather relatively slowly, producing few solutes, and because ground water has a relatively short residence time in the local flow paths in the bedrock (McDougal and others, this volume, Chapter D9). Dissolved solids concentrations were higher, ranging as high as 273 mg/L, in streams such as Bullion Mine tributary, Uncle Sam Gulch, and High Ore Creek where mine-drainage effects were most pronounced.

The major-ion chemistry of streams varied depending on the geology of their drainage basins and the relative amount of mine drainage they received. The Boulder River above Kleinsmith Gulch (site 3) and the Little Boulder River (site 60) had a calcium-sodium bicarbonate type water. Basin Creek had a similar water type during high flow, but during low-flow conditions, the water was a calcium-magnesium bicarbonate-sulfate type, with the addition of sulfate indicating the effects of mine drainage. Streams that are upstream from most mining and drain the interior of the study area, such as Jack Creek above the Bullion Mine tributary, High Ore Creek above the Comet mine, and Cataract Creek above Uncle Sam Gulch, had a calcium bicarbonate type water. Cataract Creek downstream from Uncle Sam Gulch also had calcium bicarbonate type water, although the proportion of sulfate was greater than it was upstream. High Ore Creek at the mouth had calcium sulfate-bicarbonate water, showing the effects of mine drainage.

Hardness is an important property of water because the toxicity of some trace elements increases as hardness decreases. Hardness values were relatively low (12–87 mg/L) year-round in most streams throughout the study area.

Values in High Ore Creek downstream from the Comet mine and Galena Gulch were higher, ranging from 44 to 180 mg/L. Hardness values typically were lowest during high flow, such as during spring runoff, owing to dilution; they were highest during low flow.

We measured the concentration of suspended sediment routinely in samples collected for this study during 1996–2000 because transport of trace elements in the particulate fraction can be important, particularly during high flow (fig. 2). Suspended-sediment concentrations typically were low (generally less than 7 mg/L) during low flow in streams both upstream and downstream of mined areas. Concentrations of suspended sediment were slightly higher in streams such as the Bullion Mine tributary (site 17), Uncle Sam Gulch (site 43), and High Ore Creek (site 56) that were most affected by mining. Low-flow suspended-sediment concentrations were as high as 15 mg/L in these streams, likely resulting from the presence of colloidal material produced during neutralization of acidic mine drainage. Suspended-sediment concentrations during high-flow conditions were higher, ranging as high as

Figure 2. Flood-plain tailings eroding at Jack Creek during snowmelt runoff upstream from site 19, May 1997.

76 mg/L in the Boulder River above Kleinsmith Gulch (site 3) and lower Basin and Cataract Creeks (sites 24 and 47). In High Ore Creek, the maximum concentration (86 mg/L) was similar except for a March 1999 sample (308 mg/L) that likely was affected by remediation activities. High-flow suspended-sediment concentrations generally were higher in the Bullion Mine tributary (site 17), Jack Creek (site 19), Uncle Sam Gulch (site 43), and the Boulder River below Little Galena Gulch (site 58), where maximum values ranged from 99 to 174 mg/L.

Water-Quality Standards

One of the most important reasons for characterizing water quality in streams affected by historical mining is to determine whether trace elements occur at concentrations that may be toxic to aquatic organisms. The relative magnitude of trace-element concentrations in water in various stream reaches can be evaluated by comparing measured concentrations with State and Federal aquatic-life standards. Except for aluminum, standards issued by the State of Montana (Montana Department of Environmental Quality, 1999) are applicable

to the total-recoverable concentration of each trace element, whereas Federal standards (U.S. Environmental Protection Agency, 1999) are applicable to the dissolved concentration. Dissolved concentrations are defined by the regulatory agencies as the concentration in a 0.45-μm filtrate. For aluminum, the Montana standards are applicable to the dissolved concentration and the U.S. Environmental Protection Agency (EPA) standards are applicable to the total-recoverable (unfiltered) concentration. Aquatic-life standards for some metals (such as cadmium, copper, lead, and zinc) that are found regularly in the Boulder River watershed are dependent on hardness. Table 1 shows the range of hardness values measured in different streams in the watershed and the corresponding range of hardness-adjusted values for the State and Federal acute and chronic aquatic-life standards. In general, the lower values of the aquatic-life standards applied when streamflow was high because hardness values in the Boulder River watershed were lowest during these high-flow periods. Metals generally are more toxic to aquatic organisms than to humans. Human-health standards (Montana Department of Environmental Quality, 1999) for cadmium (5 μg/L), copper (1,300 μg/L), lead (15 μg/L), and zinc (2,100 μg/L) typically are higher than the hardness-adjusted aquatic-life standards for the watershed.

Table 1. Aquatic-life standards for selected trace elements in the Boulder River watershed.

[Abbreviations: μg/L, micrograms per liter; μm, micrometer; mg/L, milligrams per liter]

Constituent	Boulder River, Basin Creek, and Cataract Creek		High Ore Creek[1]	
	Minimum	Maximum	Minimum	Maximum
Hardness (mg/L)	12	87	44	180
Acute aquatic-life standard (μg/L)[2]				
Aluminum[3,4]	750	750	750	750
Arsenic[3]	340	340	340	340
Cadmium	1.0/0.5	3.9/3.7	1.8/1.8	8.8/8.1
Copper	3.8/1.8	12/12	6.5/6.2	24/23
Lead	14/6.0	68/55	29/26	173/122
Zinc	37/19	106/104	60/58	197/193
Chronic aquatic-life standard (μg/L)[2]				
Aluminum[3]	87	87	87	87
Arsenic[3]	150	150	150	150
Cadmium	0.8/0.4	2.2/2.0	1.3/1.2	3.9/3.5
Copper	2.9/1.5	8.3/8.0	4.6/4.4	15/15
Lead	0.5/0.2	2.7/2.2	1.1/1.0	6.7/4.7
Zinc	37/20	106/105	60/59	197/194

[1]Includes Galena Gulch, in which the geology is similar to High Ore Creek.

[2]The first number is the Montana aquatic-life standard (Montana Department of Environmental Quality, 1999). The second number is the EPA standard (U.S. Environmental Protection Agency, 1999). Except for aluminum, Montana aquatic-life standards refer to total-recoverable concentrations, whereas EPA aquatic-life standards refer to dissolved (0.45-μm filtration) concentrations. For aluminum, the Montana standards refer to dissolved (0.45-μm filtration) concentrations and EPA standards refer to total-recoverable concentrations. When hardness is less than 25 mg/L, the Montana standard computed for a hardness of 25 mg/L applies.

[3]Aquatic-life standards for aluminum and arsenic are not dependent on hardness. Only one value is listed because the Montana and EPA standards are the same.

[4]Montana and EPA standards for aluminum apply when pH values are between 6.5 and 9.0.

Arsenic is not as toxic to aquatic organisms as the other trace elements at similar concentrations, and human-health standards for arsenic are lower than aquatic-life standards. The Montana human-health standard of 18 µg/L (Montana Department of Environmental Quality, 1999), the EPA maximum contaminant level of 50 µg/L (U.S. Environmental Protection Agency, 1999), and the proposed maximum contaminant level of 10 µg/L are much lower than the acute and chronic aquatic-life standards for arsenic (340 and 150 µg/L, respectively).

Trace Elements in Water

We characterized the magnitude and extent of trace elements in surface water in the Boulder River watershed by systematic sampling of streams throughout the study area during a wide range of hydrologic conditions, comparing metal concentrations to aquatic-life standards, estimating annual loading of trace elements to the main streams in the watershed, and analyzing concentration data for temporal trends. We also made water-quality measurements in reference streams draining subbasins underlain by unmineralized rock of the same or similar lithologic units as those in the Boulder River watershed study area.

Water samples initially were analyzed for a broad suite of trace elements. Concentrations of some elements, such as beryllium, chromium, mercury, nickel, and silver, consistently were near or less than the minimum reporting level of the analytical laboratory or less than the applicable aquatic-life standard; routine analysis for these trace elements therefore was discontinued early in the study. Other elements, particularly the metals cadmium, copper, lead, and zinc, had concentrations greater than the applicable aquatic-life standards at many sites downstream from inactive mines. Therefore, this report focuses on these metals, as well as arsenic, which is pervasive throughout the watershed. Historical water-quality data collected during 1991–97 from inventories of inactive mines (Metesh and others, 1994, 1995, 1996; Marvin and others, 1997; summarized in Nimick and Cleasby, 2000, table 4) and other investigations also were used to characterize study-area streams.

The data described herein were collected either as part of a periodic sampling program (most of the 1996–2000 data) or as part of a one-time sampling event (most of the historical data). These types of sampling programs are designed to provide a broad overview of water-quality conditions in a watershed or a record of water quality at one or more sites over a long time period. Other water-quality sampling programs with different purposes also were conducted during this investigation of the Boulder River watershed. Although an integral part of the watershed study, results of these programs are reported elsewhere in this volume. These other sampling programs included synoptic-sampling studies of closely spaced sites along specific stream reaches where more detailed information

on trace-element loading was needed (Cannon and others, this volume, Chapter E1; Kimball and others, this volume, Chapter D6) and hourly sampling during 1- to 2-day periods at selected sites to document effects of diel (24-hour) cycles or storm runoff on trace-element concentrations (Lambing and others, this volume, Chapter D7).

Ribbon Maps

Ribbon maps are used in this chapter to display the large amount of trace-element data collected and compiled during this study for water-quality sites throughout the watershed. These maps use colors to indicate the approximate range in concentration of a specific constituent in different stream reaches and different hydrologic conditions. The maps also are useful for assessing exceedances of water-quality criteria throughout the watershed (table 1). A common assessment method in some studies is to compare each trace-element concentration in a water-quality sample to a specific standard. Summarizing this type of information for many samples from multiple sites would be tedious, especially when some criteria, such as aquatic-life standards for metals, vary depending on hardness. Ribbon maps, on the other hand, provide a way to summarize and display this information if the concentration ranges used in the maps bracket values for water-quality criteria. Although the ribbon maps are less specific and less precise than tabulated data, they may be more useful for evaluating exceedances on a watershed scale. A ribbon map can be used to display the range of all the data for the constituent, only data for a specific period, or only data for specific hydrologic conditions.

Ribbon maps were constructed for arsenic, cadmium, copper, lead, and zinc concentrations in water. The color coding for each map is similar. The concentration ranges represented by each color are the same for the dissolved (0.45-µm filtration) and total-recoverable concentration maps for an individual trace element but differ among the trace elements. The only exception is for cadmium, where the concentration ranges represented by blue and green are not the same on the dissolved and total-recoverable maps because the lower minimum reporting level for the analytical method for dissolved cadmium provided more definition relative to the aquatic-life standards.

The concentration ranges depicted by color coding on the ribbon maps are considered approximate because the data were limited, most sites were sampled only once or a few times, and samples were collected over a 10-year period (1991–2000) and at different streamflow conditions. Therefore, the data likely did not represent the full range of concentrations. Similarly, concentrations at some sampling sites extended over more than one concentration range. At these sites, the median concentration value for the available data was used to designate the appropriate concentration range for the site. Minimum reporting levels for historical data were higher than for the 1996–2000 data. At sites where only historical

data less than the minimum reporting level were available, the assumption was made that concentrations at the site were in the lowest (blue) concentration range. Owing to the limited number of sampling sites, the exact location where a trace-element concentration changed from one concentration range to the next was roughly estimated based on likely dilution effects from tributary inflows; therefore, the location of these color changes is considered approximate. Despite these limitations, ribbon maps have the benefit of summarizing data from many water samples and thereby provide an overall picture of trace-element concentrations in various stream reaches of the watershed.

Separate ribbon maps were constructed for dissolved and total-recoverable trace-element concentrations because the importance of these two fractions is different during different streamflow conditions. Dissolved concentrations of some trace elements tended to be higher during low flow than during high flow because the effect of dilution is minimal during low flow. In contrast, total-recoverable concentrations tended to be higher during high flow (particularly for arsenic, copper, and lead) because trace-element-enriched streambed sediment is entrained during high flow. In addition, during low flow, little particulate or colloidal material was transported by most streams in the study area, and total-recoverable concentrations were approximately equal to the dissolved concentrations. Therefore, ribbon maps show either dissolved concentrations during low flow or total-recoverable concentrations during high flow. Because streamflow data were not available for some of the concentration data and because of the difficulty in determining whether flow was high or low for any given site in a particular year, we defined high flow as occurring during April–June and low flow during July–March. On the basis of the 58-year streamflow record for the Boulder River near Boulder (USGS streamflow-gauging station number 06033000, site 59), spring runoff (streamflow greater than 150 ft^3/s at this site) generally occurs between mid-April and June. Runoff periods during 1996–2000 are shown in Church, Nimick, and others (this volume, Chapter B, fig. 3).

For all ribbon maps, concentrations increase as the color changes from blue through green and yellow to orange and red. Reaches colored blue had concentrations either less than most water-quality criteria or less than the laboratory minimum reporting level applicable to most of the water-quality samples collected during 1996–2000. Concentration ranges represented by green and yellow were chosen to broadly represent applicable water-quality criteria. For arsenic, the applicable criteria were the Montana human-health standard (18 μg/L) and the EPA maximum contaminant level (50 μg/L). For metals, the freshwater acute and chronic aquatic-life standards (table 1) were used to define concentration ranges. Aquatic-life standards (table 1) are dependent on hardness, which generally is dependent on streamflow. Standards based on the measured hardness in the Boulder River and Basin and Cataract Creeks were used because these basins constitute most of the study area. Hardness values in High Ore Creek tended to be higher than in the other study area streams

(table 1); therefore, the aquatic-life standards were somewhat higher than the color-coded values. Green reaches had concentrations within or near the range of the Montana and EPA chronic aquatic-life standards. Concentrations in the yellow reaches were higher and ranged from about the maximum of the chronic standards up to about the maximum values of the acute standards. For arsenic, green reaches had detectable concentrations less than the Montana human-health standard, and yellow reaches had concentrations between the Montana human-health standard and the EPA maximum contaminant level. For zinc, acute and chronic aquatic-life standards were nearly equal (table 1); consequently, green color-coding was not used. Orange reaches had trace-element concentrations that almost always exceeded the maximum value of the acute standard (maximum contaminant level for arsenic) and ranged up to 10 times the maximum value of this standard. Red reaches had concentrations that exceeded this standard by more than 10 times. Data used to construct the ribbon maps consisted of data for 1996–2000 collected for this study (Rich and others, this volume, Chapter G and accompanying CD-ROM) and data for 1991–97 compiled from the Ground Water Information Center database at the Montana Bureau of Mines and Geology (Nimick and Cleasby, 2000, table 4).

pH

In many mining-affected watersheds, streams have low pH values owing to acidic mine drainage. However, few stream reaches in the Boulder River watershed were acidic (fig. 3), and pH values were near-neutral to slightly alkaline everywhere except in isolated circumstances, where acid discharge from inactive mines affected small streams. The primary acidic (pH values less than 6.5) reaches were in Uncle Sam Gulch downstream from the Crystal mine and the Bullion Mine tributary (fig. 4) downstream from the Bullion mine. Rocker Creek downstream from the Ada mine also was somewhat acidic (pH of 5.8). Although other inactive mine sites had acidic drainage, the paucity of acidic stream reaches in the watershed likely results from acid-neutralizing capacity provided by mafic minerals and secondary calcite in the granitic rocks of the Boulder batholith (Desborough and Fey, 1997; Desborough, Briggs, and Mazza, 1998; Desborough and others, 1998; Desborough and Driscoll, 1998).

Trace-Element Partitioning

Trace elements transported in a stream are either dissolved or in a particulate form. This partitioning is important for studies of streams affected by mine drainage because toxicity depends greatly on the chemical form of each trace element, with the dissolved form typically being more toxic than particulate forms (Brown and others, 1974; Erickson and others, 1996). Dissolved species of trace elements are analyzed in filtered water samples whereas concentrations of particulate forms are determined by the difference between
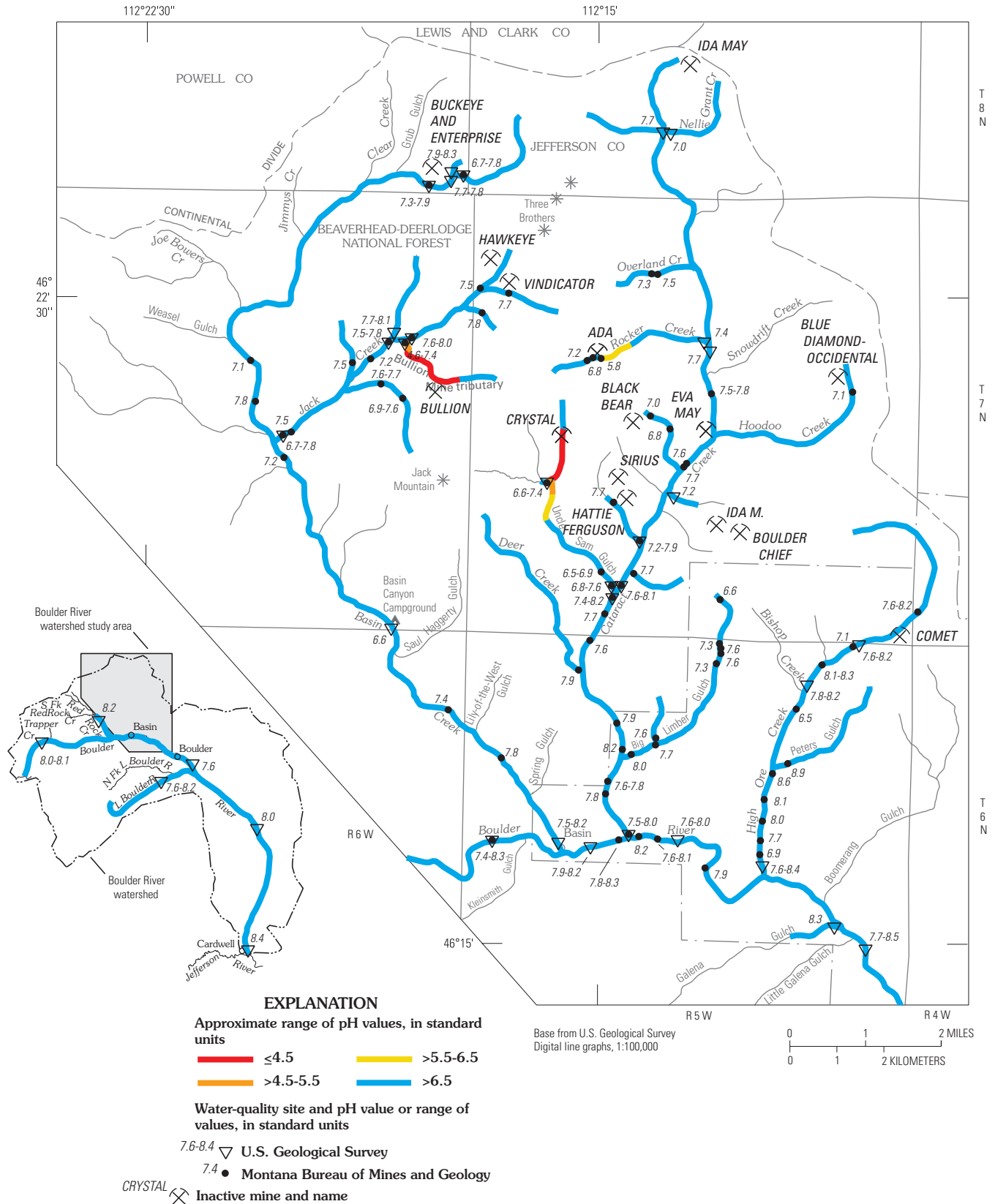
Figure 3.   Approximate values of pH during low-streamflow conditions (July–March), 1991–2000. Site locations and numbers are shown in figure 1. Values of pH for Bullion Mine tributary and Uncle Sam Gulch were defined by data from Kimball and others (this volume) and are not shown.

Figure 4.   Acidic water in Bullion Mine tributary, August 1998. Bullion mine is on bare hillslope (top center of photograph).

total-recoverable (unfiltered) and filtered concentrations. Dissolved species include ionic forms (for example, Zn^{2+}) and aqueous ion pairs (for example, $ZnHCO_3^+$). These forms are not retained by normal filtration, which typically uses a 0.45-µm pore-size filter, or by ultrafiltration, which typically uses a 10,000-Dalton nominal (about 0.001-µm) pore-size filter. Particulate forms include colloidal material and coarser particles that can settle to the streambed. Colloidal material is too fine to settle unless it aggregates and often is defined operationally as particles ranging in size from 0.001 to 1 µm (Rees and Ranville, 1990). Large quantities of colloidal material, typically oxyhydroxides of aluminum, iron, and manganese, form as acidic inflows are neutralized in the receiving stream (Chapman and others, 1983; Kimball and others, 1995; Schemel and others, 2000). The colloidal material aggregates, settles to the streambed, and coats the streambed material, which subsequently can be entrained and transported downstream during high flow (Church and others, 1997). Although 0.45-µm filtration is commonly used to separate the dissolved and particulate fractions in water-quality studies, trace-element concentrations in a 0.45-µm filtrate may be higher than the actual dissolved fraction because some colloids can pass through the filter (Kimball and others, 1995). Ultrafiltration can be used to determine concentrations of actual dissolved trace elements (Kimball and others, 1995). In this study, aliquots of selected water samples collected in 1996–98 were filtered through 0.45-µm and 10,000-Dalton pore-size filters to determine the possible presence and role of the colloidal fraction in transporting trace elements (D.A. Nimick, unpub. data).

The general pattern of trace-element partitioning among unfiltered samples (total-recoverable concentrations) and 10,000-Dalton and 0.45-µm filtrates from the Boulder River watershed depended primarily on the trace element and, to a lesser extent, on the proximity of the sampling site to principal source areas. Limited data indicate that aluminum and iron were almost entirely associated with colloidal or particulate material in streams both upstream and downstream from historical mining areas in the study area. Many total-recoverable aluminum and several total-recoverable iron concentrations were at least 100 µg/L or higher, whereas concentrations of aluminum and iron in ultrafiltrates typically were much lower. Limited data also indicate that cadmium and zinc partitioned mostly to the dissolved (ultrafiltrate) phase, particularly during low flow. In contrast, lead partitioned almost exclusively to the colloidal or particulate fraction during most flow conditions. Large amounts of arsenic and copper also partitioned to the solid phase but, unlike lead, arsenic and copper also were present in substantial proportions in the dissolved phase. During high flow, the partitioning of many trace elements shifted with increased proportions of each trace element in the particulate or colloidal phase because of entrainment of streambed sediment.

Differences in concentrations between 0.45-µm filtrates and ultrafiltrates varied between trace elements. Iron concentrations typically were two- to three-fold (or more) higher in 0.45-µm filtrates than in ultrafiltrates, indicating a substantial portion of colloidal iron in most streams. In contrast, concentrations of arsenic, cadmium, and zinc in 0.45-µm filtrates typically were similar or only 10–20 percent higher than in ultrafiltrates, indicating that only small amounts of these trace elements were present as colloidal material even though colloidal iron was present. Thus, concentration data for 0.45-µm filtrates generally can be assumed to be representative of dissolved arsenic, cadmium, and zinc concentrations.

Partitioning of copper in 0.45-µm filtrates and ultrafiltrates is not known because of copper contamination introduced during the 0.001-µm filtration. Partitioning of lead also is not known because concentrations in one or both filtrates typically were less than the minimum reporting level. On the basis of these evaluations, data for 0.45-µm filtrates are used in this report to define dissolved concentrations of trace elements.

Relation of Streamflow and Concentration

Streamflow is an important factor in controlling trace-element concentrations as well as the proportion of dissolved and colloidal or particulate trace elements being transported (fig. 5). In many streams, dissolved (filtered) concentrations typically decrease as streamflow increases owing to dilution. Total-recoverable concentrations typically increase during high flow because colloidal and particulate material is entrained from the streambed or eroded from streambanks. However, these general relations are not universal. Therefore, the streamflow-concentration relations need to be determined for each trace element.

The relation between streamflow and dissolved (0.45-µm filtration) trace-element concentrations is shown in figure 6 for five sites in the Boulder River watershed. At one site (site 56, High Ore Creek), data are segregated into a pre- and a post-remediation period to illustrate remediation effects on water quality. At Boulder River below Little Galena Gulch (site 58), Cataract Creek (site 47), and High Ore Creek (site 56, pre-remediation), dissolved cadmium and zinc concentrations decreased as streamflow increased during snowmelt runoff. This relation is expected because cadmium and zinc are likely to exist in the dissolved phase (Smith, 1999). For High Ore Creek (site 56) this generalization applies to the period before September 1997, when remediation activities began at the Comet mine (Gelinas and Tupling, this volume). The decrease in dissolved cadmium and zinc concentrations with increased streamflow at these three sites suggests that the sources of these metals were relatively constant, for example from ground-water or adit discharge, as opposed to leaching of mine wastes or tailings either in piles or in fluvial deposits, where loading would be expected to increase during snowmelt or storm runoff. This relation did not hold for Boulder River above Kleinsmith Gulch (site 3) or for Basin Creek (site 24). At these sites, cadmium and zinc concentrations did not change appreciably with increased streamflow, perhaps because upstream loading of these metals was relatively insignificant and concentrations were controlled more by desorption from streambed sediment. Dissolved arsenic concentrations generally did not vary with streamflow at most sites, probably because concentrations were low and, as shown in a later section, because arsenic is derived from the entire watershed and not primarily from the mined areas. In High Ore Creek, post-remediation dissolved arsenic concentrations during low flow are higher than pre-remediation concentrations and decrease with increased streamflow. Dissolved

Figure 5. Cataract Creek at Basin (site 47) during high-streamflow conditions, June 1997 (top), and low-streamflow conditions, October 1996 (bottom).

copper concentrations increased at all five sites as streamflow increased. This pattern, which is the reverse of the pattern for cadmium and zinc at sites 58, 47, and 56 (pre-remediation), likely is an artifact of filter pore size. Copper is more likely to exist in the particulate or colloidal phase than in the dissolved phase (Smith, 1999). Colloidal material is more readily
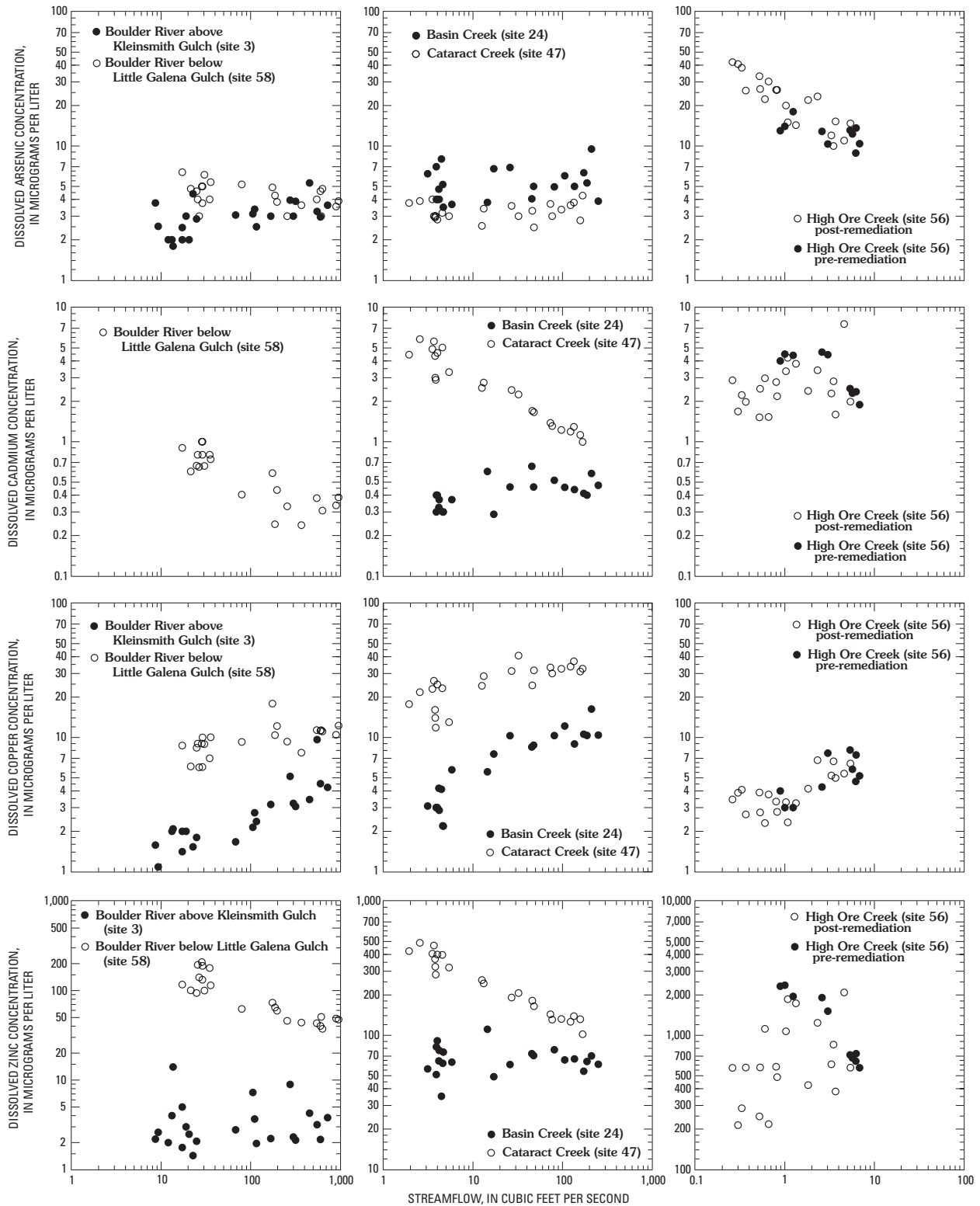
Figure 6. Relation of streamflow to dissolved (0.45-μm filtration) trace-element concentrations at five sites, 1996–2000. Dissolved cadmium concentrations for the Boulder River above Kleinsmith Gulch (site 3) were less than the minimum reporting levels and are not shown.

entrained from the streambed during high flows than during low flows and, thus, more colloids would move in suspension in the water column during high flow. Because some colloidal material can pass through the 0.45-μm filter used in this study, copper concentrations in 0.45-μm filtrates would be expected to increase as streamflow increases.

The relation between streamflow and dissolved and total-recoverable concentrations is not the same for each trace element during low-flow and high-flow conditions. Figure 7 shows the relation between streamflow and dissolved and total-recoverable trace-element concentrations for Cataract Creek (site 47). These relations are typical for other watershed streams with elevated trace-element concentrations. Total-recoverable and dissolved concentrations of aluminum and iron increased greatly with streamflow. Copper and manganese total-recoverable concentrations increased moderately with increasing flow. Although dissolved copper increased as total recoverable copper increased, dissolved manganese remained relatively constant as flows changed and total-recoverable manganese increased. The patterns for arsenic and lead are somewhat similar to that of manganese. Dissolved arsenic concentrations were consistently low (2–5 μg/L) during all flow conditions, but total-recoverable arsenic concentrations increased about 10-fold during high flow. Similarly, dissolved lead concentrations were consistently low (<1–1 μg/L), but total-recoverable concentrations increased as much as 20-fold during high flow. These increases in total-recoverable arsenic and lead concentrations indicate that arsenic and lead may be associated with the hydrous metal oxide coatings on streambed sediment and transported when colloids are resuspended during high flow (Church, Unruh, and others, this volume, Chapter D8). Total-recoverable concentrations of cadmium and zinc were only slightly higher than dissolved concentrations, indicating that, although suspended sediment was enriched in cadmium and zinc (Church, Unruh, and others, this volume, fig. 12), the amount of particulate cadmium and zinc in the water column was small relative to the dissolved fraction. This relation demonstrates that these metals strongly partition to the dissolved phase.

Seasonal differences in streamflow are an important factor affecting the severity and timing of aquatic toxicity. The importance of understanding these factors is demonstrated in figure 7 using aluminum, cadmium, copper, lead, and zinc data for Cataract Creek (site 47). These graphs show the EPA hardness-adjusted aquatic-life standards for each water sample. Total-recoverable copper concentrations increased from 13 to 90 μg/L and total-recoverable lead concentrations increased from less than 1 to 22 μg/L as streamflow increased from 1.9 to 168 ft^3/s. In contrast, hardness (not shown) and the aquatic-life standards for copper and lead decreased as streamflow increased. Similar to copper and lead, total-recoverable aluminum concentrations also increased with streamflow from 12 to 952 μg/L and exceeded the acute aquatic-life standard during high flow. The implication of these trends is that the toxicity of copper and lead is much greater during

high flow. For cadmium and zinc, concentrations decreased about three- to four-fold as streamflow increased. The aquatic-life standards for cadmium and zinc also decreased as streamflow increased, but the decreases in these standards were somewhat less than for concentration. Therefore, the degree of aquatic toxicity for cadmium and zinc was slightly greater during low flow, although the difference between high-flow and low-flow toxicity for cadmium and zinc was not nearly as great as it was for copper and lead. Part of the convergence of the aquatic-life standards and concentrations of cadmium and zinc at high-flow results from the regulatory restriction that hardness-adjusted aquatic standards do not continue to decrease as hardness decreases to values less than 25 mg/L, which happened every spring during snowmelt runoff in Cataract Creek.

Trace-Element Concentrations

Trace-element concentrations in streams of the Boulder River watershed varied greatly, with the highest concentrations occurring in small streams downstream from just a few of the inactive mines in the watershed. The lowest concentrations generally were in stream reaches upstream from areas of historical mining or in headwater streams where small inactive mines had little effect. Cadmium, copper, lead, and zinc concentrations commonly exceeded chronic aquatic-life standards. The highest concentrations were in streams downstream from three large inactive mines: the Crystal mine (fig. 8) in a tributary to Cataract Creek, the Bullion mine (fig. 9) in a tributary to Jack Creek, and the Comet mine in High Ore Creek (Gelinas and Tupling, this volume, fig. 3). Downstream from these three mines, the chronic aquatic-life standard for at least one metal associated with the watershed's ore deposits was exceeded at all sampling sites, including sites in the Boulder River between Basin Creek and the Jefferson River.

The magnitude and distribution of trace elements in water are shown by ribbon maps for zinc, cadmium, copper, lead, and arsenic. Of these, zinc probably provides the best overall indicator for several reasons. First, concentration data for dissolved and total-recoverable zinc are available for more sites than for other trace elements. Second, zinc is a mobile metal that occurs at many sites in concentrations well above the minimum reporting level; however, concentrations of zinc are relatively low in areas unaffected by mining. Finally, exceedances of aquatic-life standards typically are larger for zinc than for other trace elements. Therefore, zinc is very useful for assessing the effects of mine drainage in the watershed. For some sites, only total-recoverable zinc concentration data were available; these data also were used to construct the dissolved zinc ribbon map because zinc occurs primarily in the dissolved phase and the total-recoverable concentrations provide an upper limit on the dissolved zinc concentrations at the sites with limited or no dissolved zinc data.
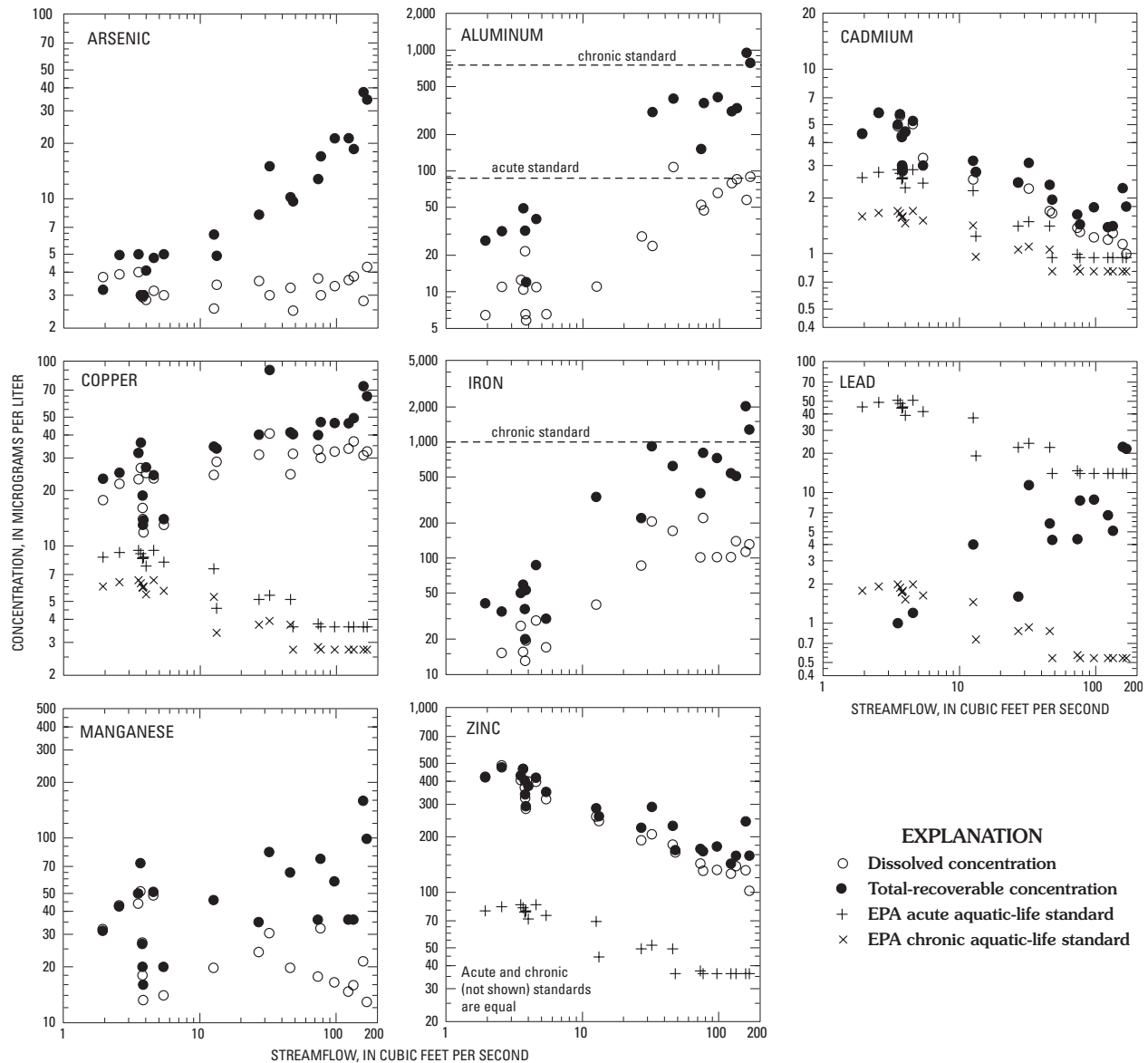
Figure 7. Relation of streamflow to dissolved (0.45-μm filtration) and total-recoverable trace-element concentrations in Cataract Creek (site 47), 1996–2000. Dissolved lead data are not shown because concentrations were equal to or less than minimum reporting level of 1 μg/L. U.S. Environmental Protection Agency (EPA) aquatic-life standards vary with hardness for cadmium, copper, lead, and zinc; standards for manganese have not been established. Standards for arsenic are not shown because they are much higher than measured concentrations.

Zinc

Dissolved zinc concentrations during low flow (fig. 10) ranged from <1 μg/L at some sites to 21,000 μg/L in Uncle Sam Gulch below the Crystal mine (site 44M). At sites in areas upstream from historical mining and in many headwater areas that were mined, dissolved zinc concentrations generally were <50 μg/L, and at most sites, the concentrations were <10 μg/L.

Three inactive mines (Crystal, Bullion, and Comet) had a profound effect on zinc concentrations in the watershed. Downstream from these mines, zinc concentrations were as high as 50–200 times the acute aquatic-life standard (19–197 μg/L, table 1). Discharge from the adit at the Crystal mine increased dissolved zinc concentrations in Uncle Sam Gulch from 12 μg/L upstream from the mine to 58,600 μg/L downstream from the mine (Kimball and others, this volume). Zinc concentrations were elevated throughout Uncle Sam Gulch, although dilution from tributaries decreased dissolved concentrations during low flow to 1,750–5,730 μg/L at the mouth (site 43). The Bullion Mine tributary (site 17) had dissolved zinc concentrations ranging from 2,130 to 5,820 μg/L, which elevated concentrations in Jack Creek to 205–405 μg/L at the mouth. The Comet mine site had a similar effect

Figure 8. Crystal mine, June 1997. Acidic discharge drains from adit (out of view near lower right of photograph) to Uncle Sam Gulch on far left.

Figure 9. Bullion mine, June 1997. Primary adits are on hillslope denuded by mine wastes above Bullion Mine tributary, which flows from right to left at edge of trees at center right of photograph. Acid discharge from one adit flows downslope in lower right corner.

on High Ore Creek. Upstream from the Comet mine (site 49), zinc concentrations were low, ranging from <1 to 54 µg/L. However, at all sites on High Ore Creek downstream from the mine, dissolved zinc concentrations were much higher, ranging from 388 to 5,214 µg/L prior to the start of remediation activities (Gelinas and Tupling, this volume).

The effect of drainage from each of these three mines extended far downstream (fig. 10). For example, the zinc loading from Uncle Sam Gulch affected concentrations in Cataract Creek downstream to its mouth. Dissolved zinc concentrations during low flow, from 191 to 634 µg/L at the mouth, were always higher than the acute aquatic-life standard (19–104 µg/L, table 1) in this lower reach of Cataract Creek. Zinc loading from Bullion Mine tributary increased dissolved zinc concentrations in Jack Creek from 12.3–33 µg/L (site 16) to between 205 and 1,280 µg/L

Figure 10. Approximate concentrations of dissolved zinc during low-streamflow conditions (July–March), 1991–2000. Site locations and numbers are shown in figure 1. Values in red are supplemental total-recoverable zinc concentrations for sites where dissolved zinc data are limited or do not exist. Concentration data from Kimball and others (this volume), although not shown, were used to define color coding for Bullion Mine tributary and Uncle Sam Gulch.

(sites 19 and 63) and, farther downstream, to 35–91 µg/L at the mouth of Basin Creek (site 24). Fluvial tailings along Jack Creek (Church, Unruh, and others, this volume) upstream and downstream from site 19 might be an additional source of zinc and other trace elements at downstream sampling sites.

The effect of drainage from these three mines continued downstream into the Boulder River, where dissolved zinc concentrations during low flow increased incrementally downstream from Basin, Cataract, and High Ore Creeks. Upstream from Basin Creek, concentrations in the Boulder River were 1–6 µg/L, whereas concentrations ranged from 25 to 70 µg/L between Basin and Cataract Creeks. Between Cataract and High Ore Creeks, concentrations were higher, ranging from 55 to 159 µg/L. Finally, downstream from High Ore Creek, concentrations in the Boulder River ranged from 73 to 208 µg/L. On the basis of one sampling episode during low flow, dissolved zinc concentrations exceeded the acute aquatic-life standard downstream from the Basin and Boulder mining districts almost to the Jefferson River (fig. 10).

Other inactive mines contributed dissolved zinc to streams in the Boulder River watershed during low flow but not to the same degree as in those reaches affected by the Crystal, Bullion, and Comet mines. In the Cataract Creek basin upstream from Uncle Sam Gulch, dissolved zinc concentrations were 100 µg/L or higher in four unnamed tributaries between Uncle Sam Gulch and Hoodoo Creek, in Rocker Creek downstream from the Ada mine, and in the headwater portion of Cataract Creek downstream from the Ida May mine. In upper Basin Creek, the Buckeye and Enterprise mines were a source of trace elements (Cannon and others, this volume). Dissolved zinc concentrations in upper Basin Creek downstream from these mines (site 8) generally were less than about 40 µg/L. Similarly, mines in upper Big Limber Gulch and Hoodoo Creek in the Cataract Creek basin appear to be the cause of slightly elevated dissolved zinc concentrations during low flow (fig. 10).

Total-recoverable zinc concentrations during high flow (fig. 11) tended to be lower than dissolved concentrations during low flow, particularly in reaches where zinc concentrations were elevated. Concentrations in Basin Creek downstream from the Buckeye and Enterprise mines were an exception to this generalization. In this reach, loading of zinc and other trace elements was substantial during spring runoff, resulting in higher concentrations during high flow (Cannon and others, this volume). In reaches relatively unaffected by historical mining, such as Cataract Creek upstream from Hoodoo Creek, total-recoverable zinc concentrations were low during high flow (generally less than 50 µg/L) but slightly higher than low-flow dissolved concentrations.

Cadmium

The spatial distribution of dissolved cadmium concentrations during low flow (fig. 12) was similar to the distribution of dissolved zinc concentrations, indicating that sources of cadmium and zinc were similar. Cadmium concentrations

exceeded the acute aquatic-life standard (0.4–3.9 µg/L, table 1) in many of the same reaches where zinc exceeded this standard, particularly in headwater areas near inactive mines. However, in comparison to zinc, dissolved cadmium concentrations were not as elevated above the acute aquatic-life standard. This is shown by the lesser extent of yellow-, orange-, and red-colored reaches on the dissolved cadmium ribbon map (fig. 12) compared to the zinc map (fig. 10). Uncle Sam Gulch and the Bullion Mine tributary are the only red reaches on the cadmium ribbon map, whereas other stream reaches are red on the zinc map. Because the relative degree of exceedance of the aquatic-life standard was smaller for cadmium concentrations than zinc concentrations, exceedances of the cadmium standards did not extend as far downstream below major sources as did exceedances of the zinc standard. For instance, dissolved cadmium concentrations at the mouth of Basin Creek barely exceeded 0.4 µg/L (fig. 12). Although cadmium concentrations in the Boulder River increased incrementally downstream through the study area, aquatic-life standards were only exceeded downstream from Cataract Creek. Similar to zinc, total-recoverable cadmium concentrations during high flow (fig. 13) generally were lower than dissolved concentrations during low flow except in Basin Creek downstream from the Buckeye and Enterprise mines.

Copper

Dissolved copper concentrations during low flow (fig. 14) exceeded the acute aquatic-life standard (1.8–12 µg/L, table 1) by more than 10 times (red color) downstream from the Bullion and Crystal mines in the Bullion Mine tributary and Uncle Sam Gulch, respectively. In contrast, concentrations in High Ore Creek downstream from the Comet mine were much lower (2–8 µg/L). Although High Ore Creek is colored green on the dissolved copper ribbon map, indicating exceedance of the chronic criteria for other parts of the watershed where hardness values are lower, none of the low-flow concentrations actually exceeded the hardness-adjusted standard. The small amount of copper relative to zinc and cadmium that leaches from the Comet mine area probably results from the different ore body at this site compared to the polymetallic veins that compose ore bodies near the Crystal and Bullion mines (O'Neill and others, this volume, Chapter D1). The copper loading from the Bullion Mine tributary increased copper concentrations in Jack Creek and, farther downstream, in Basin Creek. Similarly, the copper loading from Uncle Sam Gulch affected Cataract Creek downstream to its mouth. Similar to cadmium and zinc, dissolved copper concentrations in the Boulder River were enriched downstream from Basin Creek; concentrations generally ranged between the acute and chronic aquatic-life standards. Dissolved copper concentrations in the Boulder River were highest in the reach between Cataract and High Ore Creeks and decreased downstream from High Ore Creek. Total-recoverable copper concentrations during high flow (fig. 15) typically were higher than dissolved copper concentrations during low flow, most

Figure 11. Approximate concentrations of total-recoverable zinc during high-streamflow conditions (April–June), 1996–2000. Site locations and numbers are shown in figure 1.
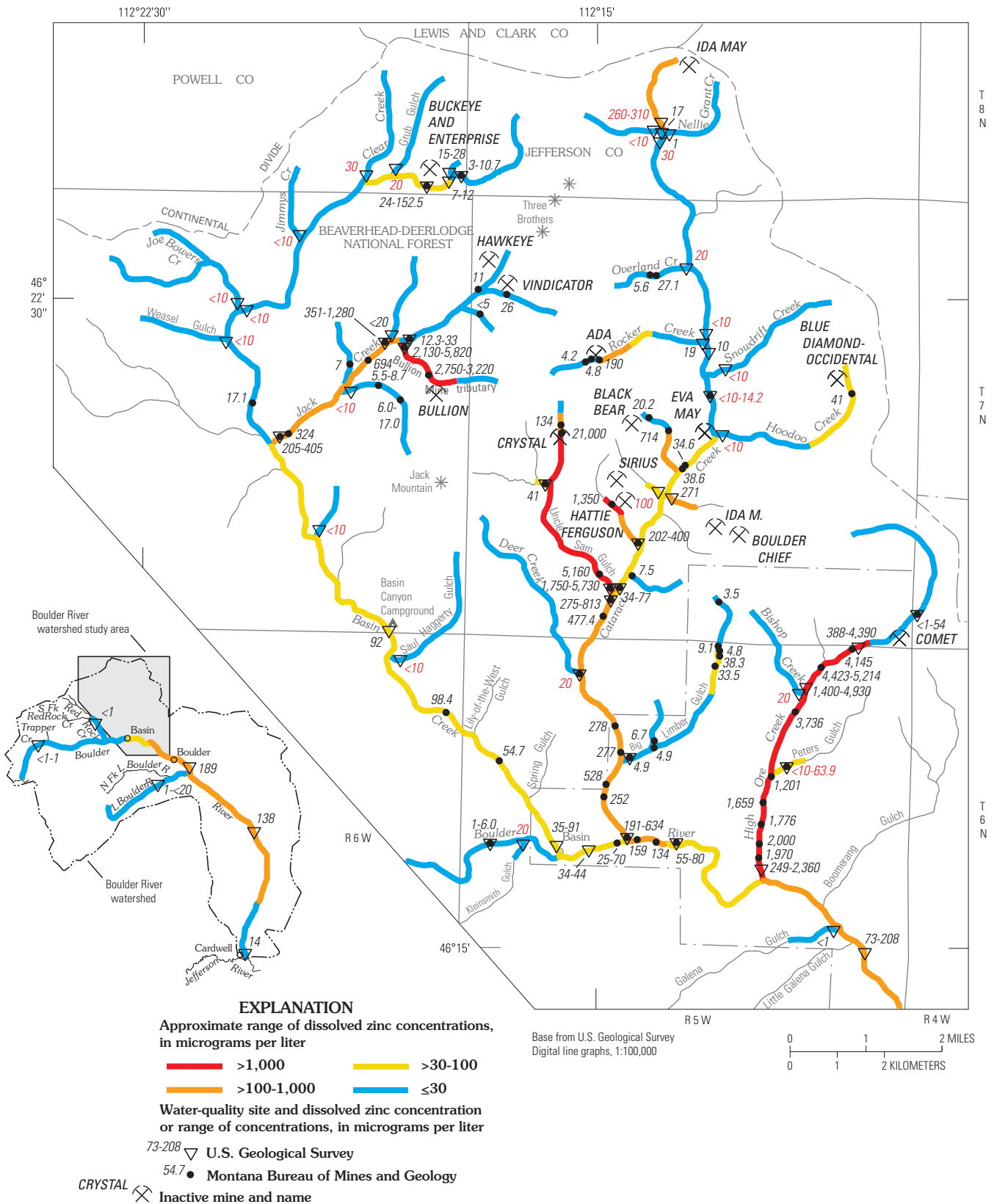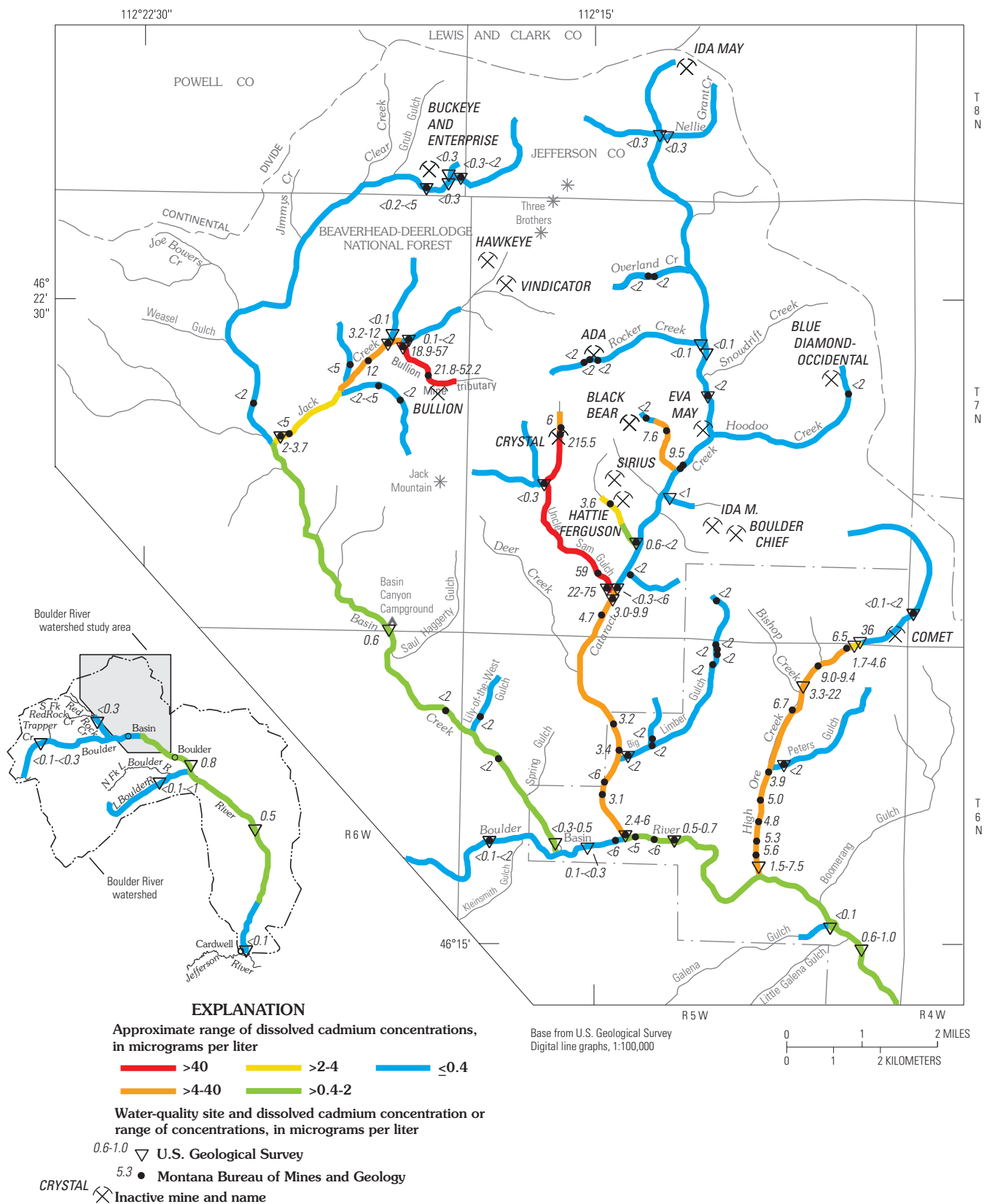
Figure 12. Approximate concentrations of dissolved cadmium during low-streamflow conditions (July–March), 1991–2000. Site locations and numbers are shown in figure 1.

Figure 13. Approximate concentrations of total-recoverable cadmium during high-streamflow conditions (April–June), 1996–2000. Site locations and numbers are shown in figure 1.

Figure 14. Approximate concentrations of dissolved copper during low-streamflow conditions (July–March), 1991–2000. Site locations and numbers are shown in figure 1. Concentration data from Kimball and others (this volume), although not shown, were used to define color coding for Bullion Mine tributary and Uncle Sam Gulch.
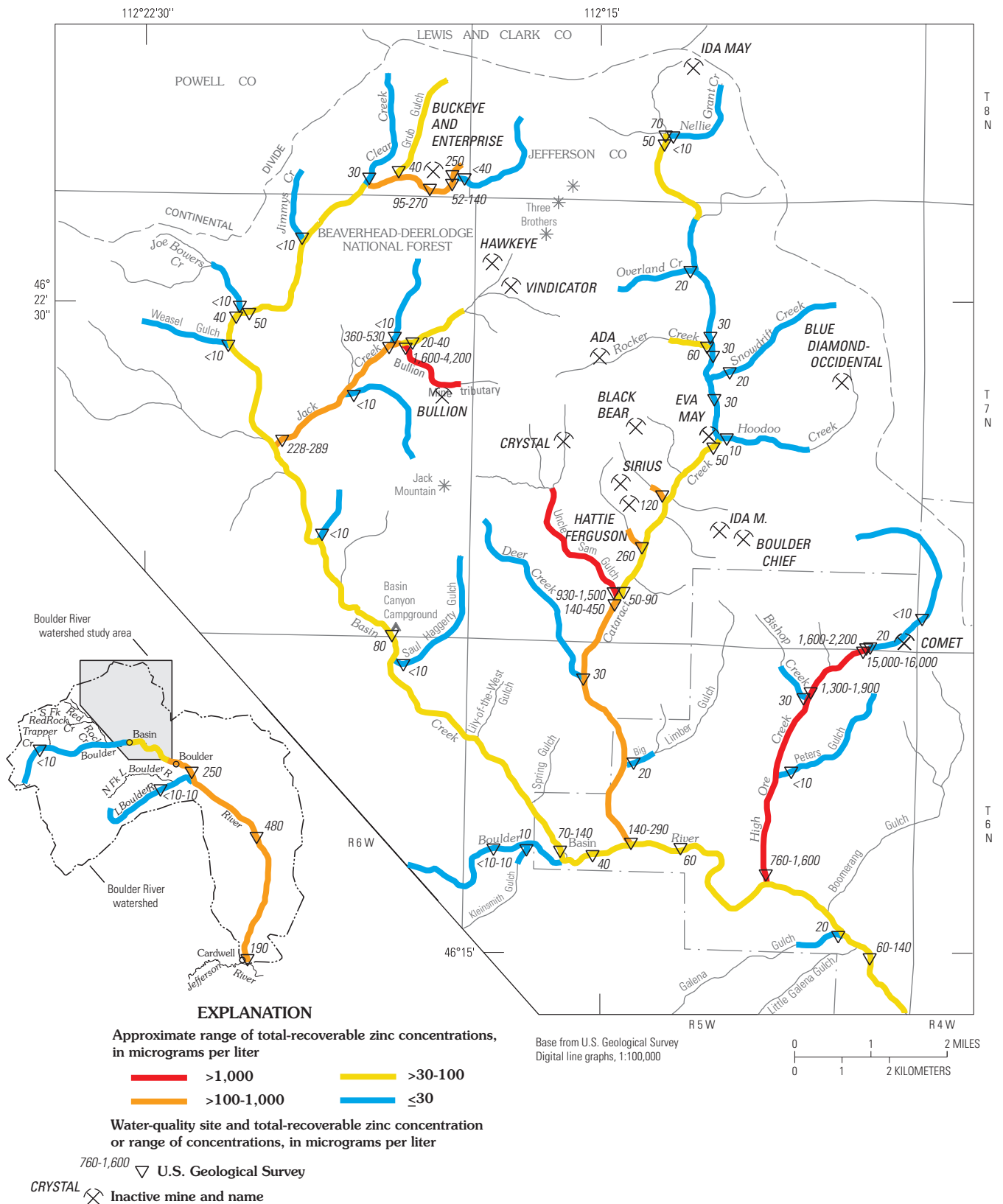
Figure 15.   Approximate concentrations of total-recoverable copper during high-streamflow conditions (April–June), 1996–2000. Site locations and numbers are shown in figure 1.

likely because copper partitions more strongly than zinc or cadmium to the particulate phase, thus enriching stream sediment, which is transported during high flow.

Lead

Dissolved lead concentrations in almost all parts of the study area were less than the minimum reporting level and are not shown on a ribbon map. The only sites where dissolved lead concentrations were typically higher than the minimum reporting level during low flow were the Bullion Mine tributary (site 17), where concentrations ranged from <1 to 8.7 µg/L, and Uncle Sam Gulch just downstream from the Crystal mine (site 44M), where the concentration was 78.6 µg/L. Both sites had acidic pH values (fig. 3).

Similar to copper, total-recoverable lead concentrations during high flow (fig. 16) were higher than during low flow because lead partitions strongly to the colloidal or particulate phase. Total-recoverable lead concentrations generally ranged between the chronic and acute aquatic-life standards (yellow color) throughout most of the watershed downstream from not only the Bullion, Crystal, and Comet mines, but also the Buckeye and Enterprise mines on upper Basin Creek and the Eva May mine on upper Cataract Creek.

Arsenic

Dissolved arsenic was present at low concentrations in both mined and unmined parts of the study area and in reference streams in other parts of the watershed. Concentrations during low flow (fig. 17) were not substantially elevated in any stream. Dissolved concentrations were much lower than the chronic aquatic-life standard (150 µg/L) throughout the watershed and exceeded the Montana human-health standard (18 µg/L) only locally. Dissolved arsenic concentrations generally ranged from 1 to 5 µg/L at almost all sampling sites in the study area, as well as in areas upstream from historical mining (sites 1, 2, 49, and 60, fig. 1). Few sites had concentrations less than the minimum reporting level (1 µg/L). Concentrations in lower Basin Creek as well as in the Boulder River downstream from the study area were slightly higher, ranging as high as 9 µg/L. These higher concentrations in Basin Creek appear to come from mining- and nonmining-related sources near the Buckeye and Enterprise mines (Cannon and others, this volume) as well as in Jack Creek, and possibly other tributaries. The higher dissolved arsenic concentrations in the Boulder River downstream from the study area appear to result from sources near or downstream from Boulder. Three stream reaches had concentrations higher than the Montana human-health standard of 18 µg/L: Basin Creek downstream from the Buckeye and Enterprise mines (site 8), an unnamed and unmined tributary to Uncle Sam Gulch (site 42), and High Ore Creek downstream from the Comet mine (sites 52, 53, and 56). Mine wastes, mill tailings, and fluvial deposits appear

to be the source of arsenic in High Ore Creek (Gelinas and Tupling, this volume). However, arsenic in Basin Creek near the Buckeye and Enterprise mines appears to be derived not only from mined areas, where the median arsenic concentration in mine wastes exceeds 1 weight percent (Church, Unruh, and others, this volume, table 2), but also from unmined areas (Cannon and others, this volume). The unnamed tributary to Uncle Sam Gulch drains an unmined area; therefore, the arsenic, which presumably is leaching naturally from arsenic-rich geologic sources, in this drainage is nonmining related.

The spatial pattern of total-recoverable arsenic concentrations during high flow (fig. 18) was much different from the pattern for low-flow dissolved concentrations. The high-flow total-recoverable concentrations were higher than low-flow dissolved concentrations (fig. 17) at almost all sites having data for both flow conditions. No other trace element, with the exception of lead, had such a large difference between the low-flow dissolved and high-flow total-recoverable concentrations. The maximum dissolved arsenic concentration in the watershed during low flow was 44 µg/L, whereas the maximum total-recoverable concentration during high flow was 760 µg/L. The chronic aquatic-life standard (150 µg/L) was equaled or exceeded at one or more sites downstream from the Buckeye, Bullion, Crystal, or Comet mines. Whereas the effect of historical mining areas is not readily apparent in the dissolved arsenic map (fig. 17), the effect is very apparent in the total-recoverable map (fig. 18). Because arsenic in mine drainage adsorbs to streambed sediment quickly (Smith, 1999), dissolved concentrations during low flow are low. However, during high flow, arsenic-rich sediment is entrained within the water column and produces the high total-recoverable concentrations observed during this study. This same process also is the cause of the high concentrations of total-recoverable lead during high-flow conditions in the watershed.

Aluminum

Aluminum is not discussed in detail and ribbon maps are not presented because aluminum concentrations, unlike concentrations of other trace elements, do not appear to be overly toxic in the watershed. The toxicity of aluminum in neutral to alkaline surface water is not well understood (U.S. Environmental Protection Agency, 1999, p. 19), and therefore the established aquatic-life standards may be conservative. Typically, the primary concern regarding aluminum toxicity is not in reaches with neutral to slightly alkaline pH but rather in reaches that are mixing zones where acidic water rich in dissolved aluminum is neutralized, resulting in the formation of aluminum hydroxide colloids. These colloids can then coat the streambed and the gills of aquatic organisms.

Dissolved aluminum concentrations during low flow were consistently low in almost all streams. Concentrations only exceeded the chronic aquatic-life standard of 87 µg/L in the Bullion Mine tributary and the upper and middle reaches

Figure 16. Approximate concentrations of total-recoverable lead during high-streamflow conditions (April–June), 1996–2000. Site locations and numbers are shown in figure 1.

Figure 17. Approximate concentrations of dissolved arsenic during low-streamflow conditions (July–March), 1996–2000. Site locations and numbers are shown in figure 1.
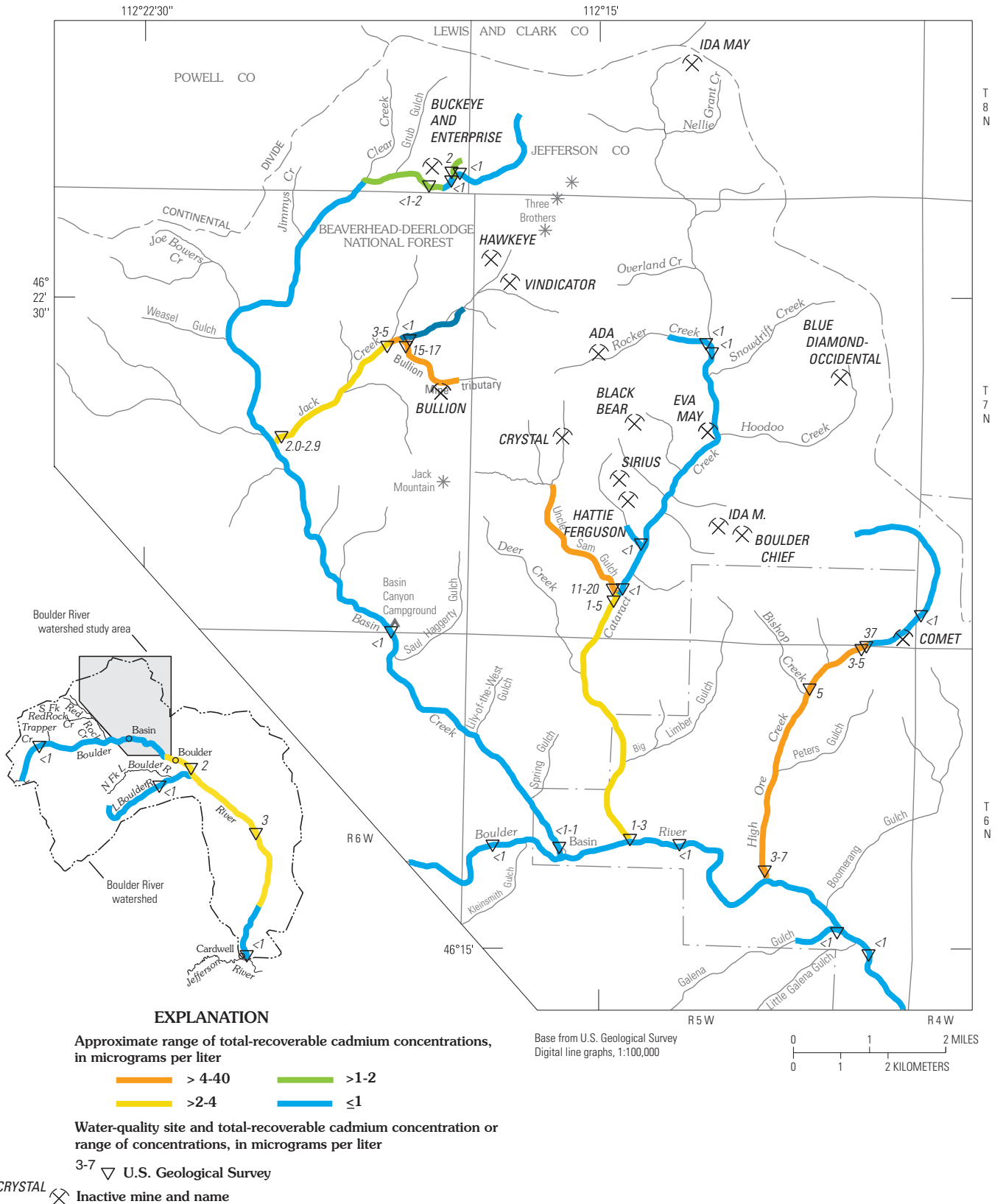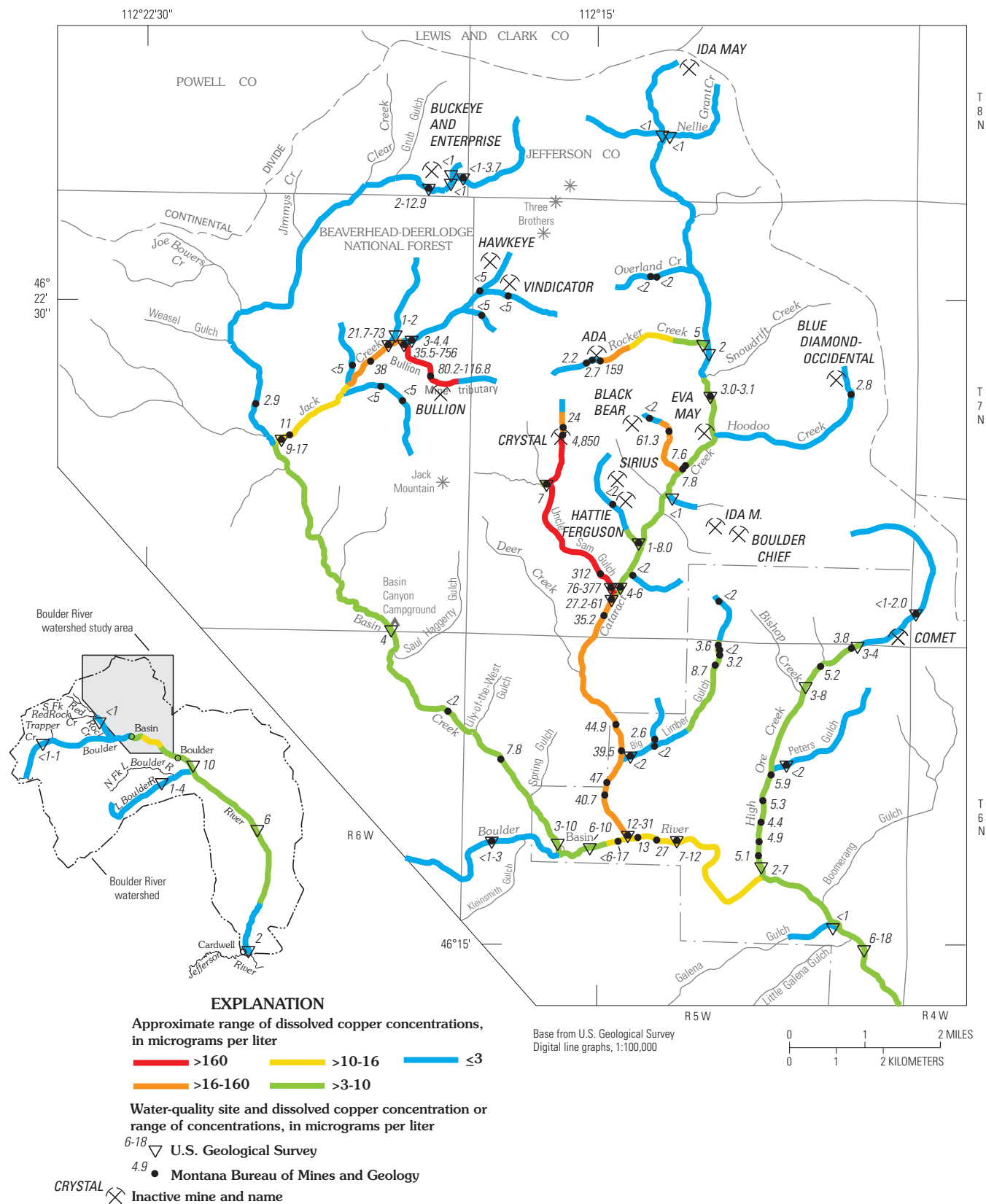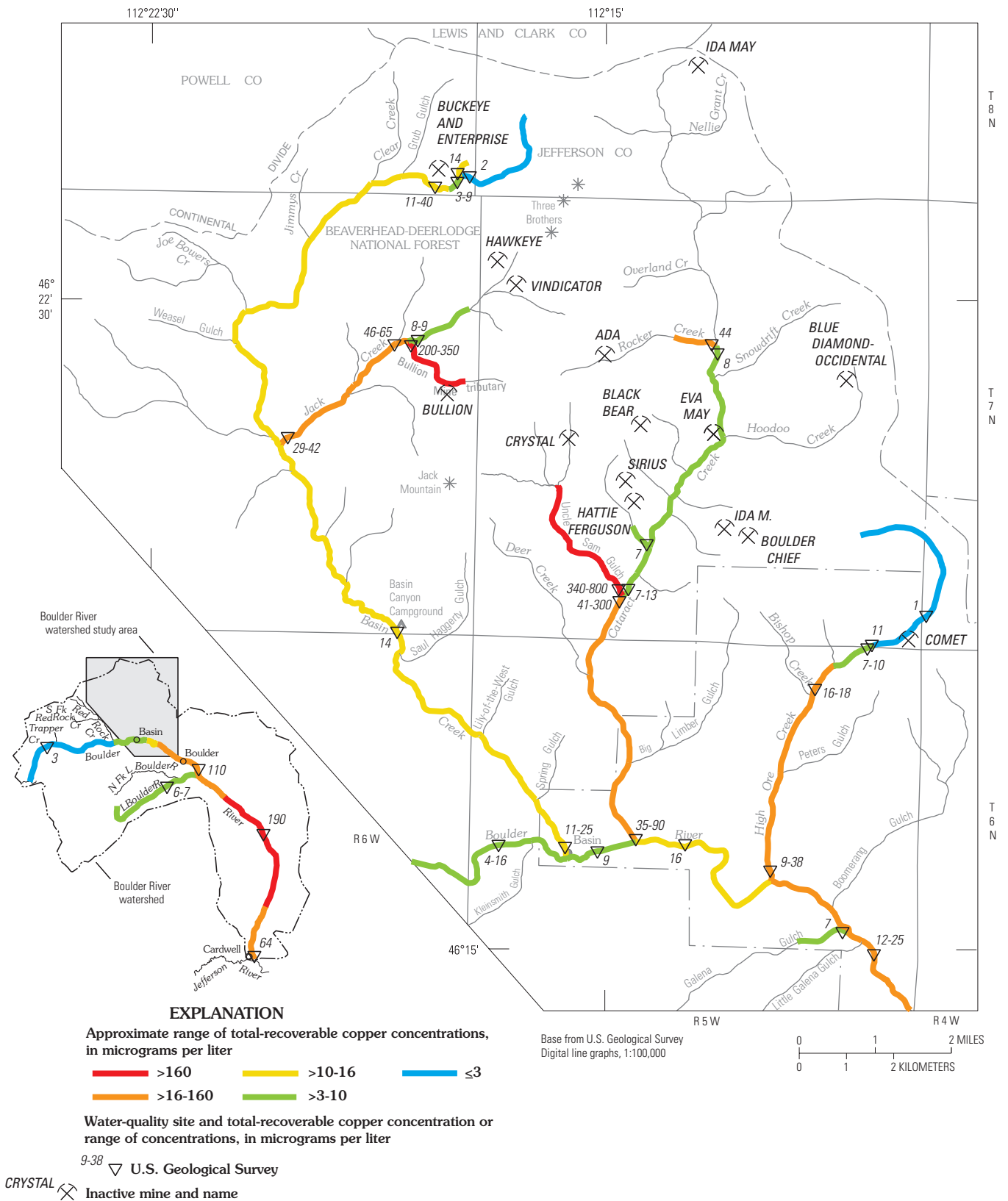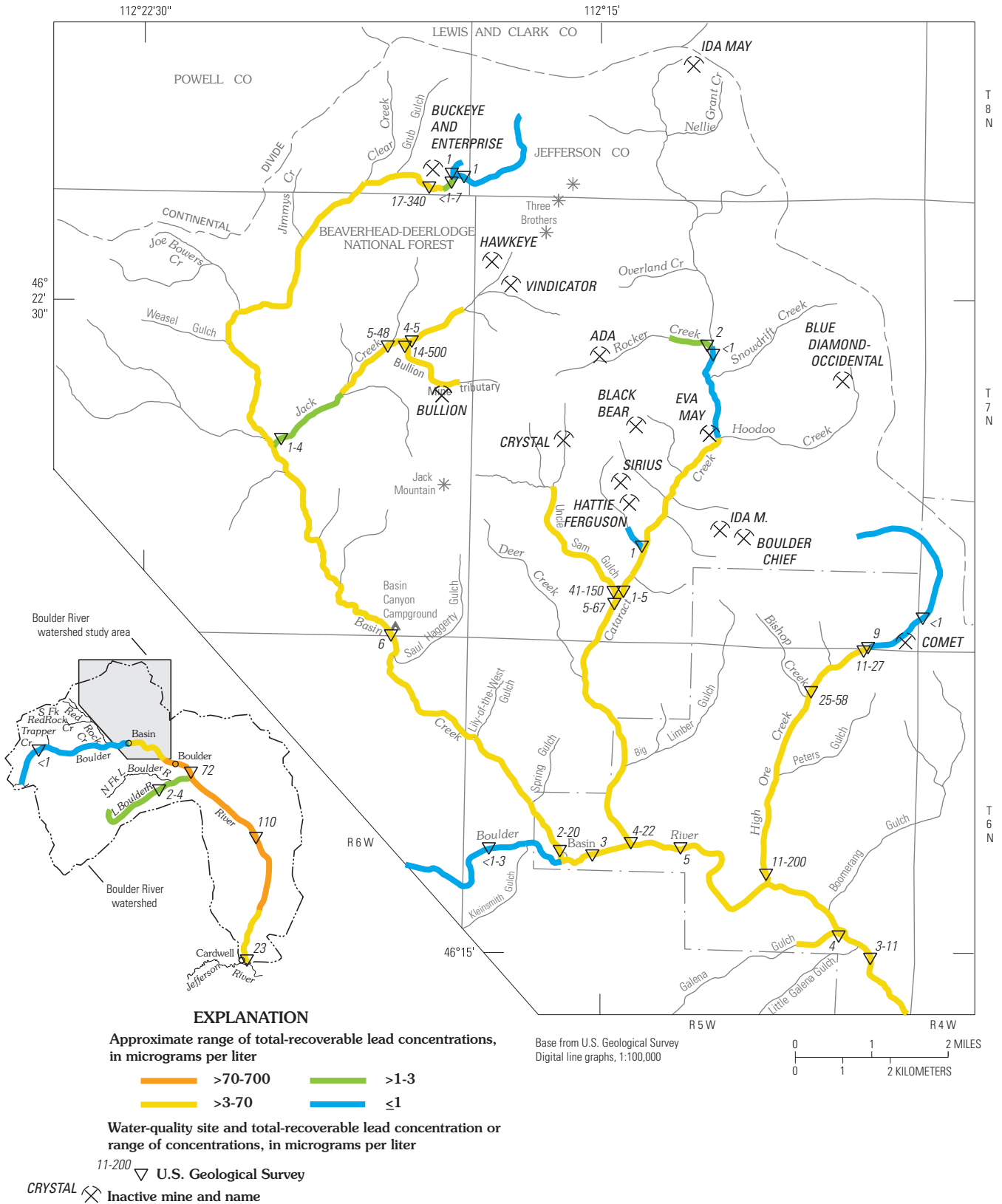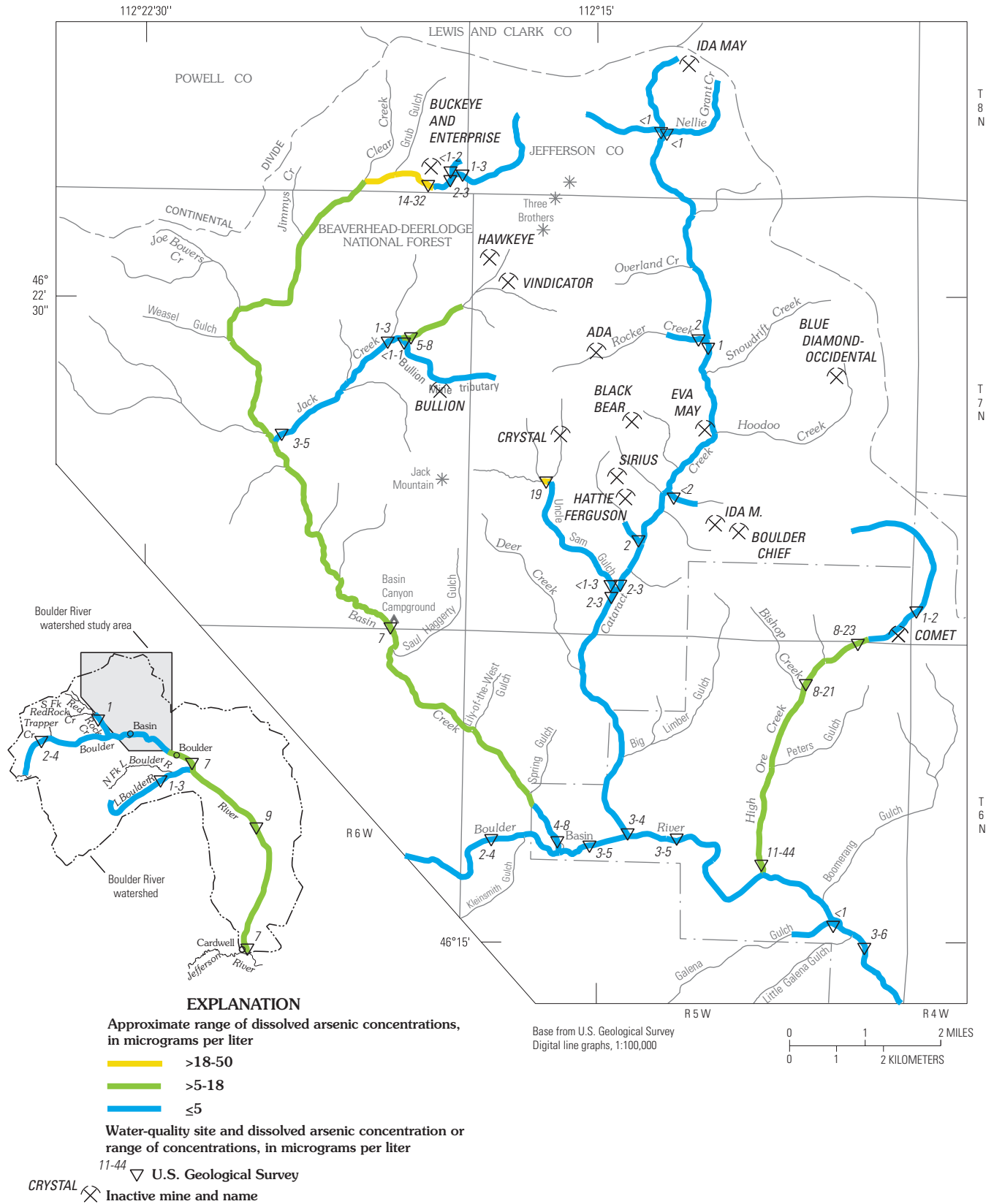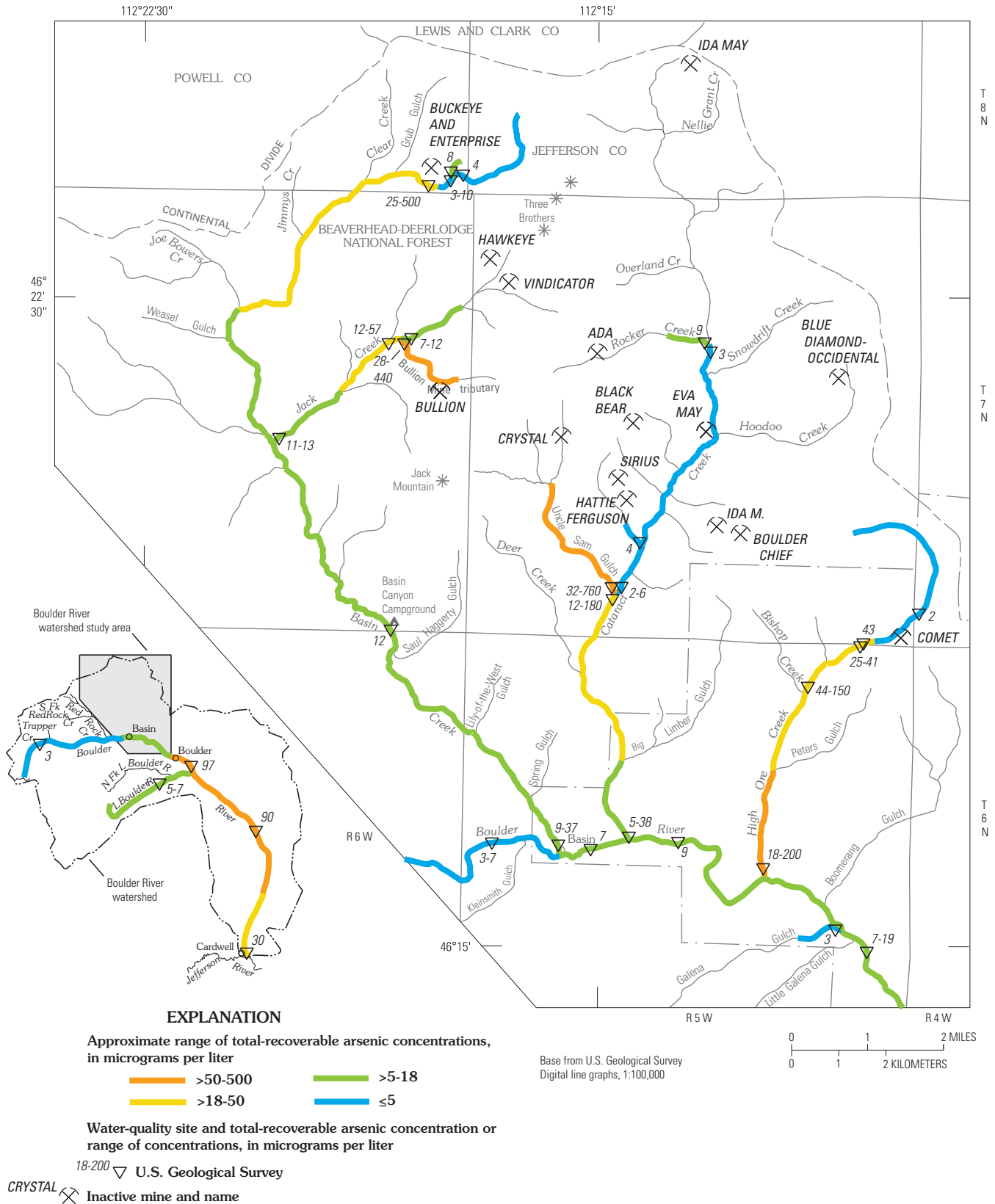
Figure 18. Approximate concentrations of total-recoverable arsenic during high-streamflow conditions (April–June), 1996–2000. Site locations and numbers are shown in figure 1.

of Uncle Sam Gulch on the basis of data collected by Kimball and others (this volume) and data for sites 17 and 43 (Rich and others, this volume). These reaches generally were acidic, and therefore dissolved concentrations of aluminum and other metals would be expected to be elevated. Total-recoverable aluminum concentrations during low flow typically were somewhat higher than dissolved concentrations, and exceeded the chronic aquatic-life standard at sites in Basin Creek (site 8), Jack Creek (site 19), Uncle Sam Gulch and Cataract Creek (sites 43 and 44), and High Ore Creek (site 56) downstream from the Buckeye, Bullion, Crystal, and Comet mines, respectively. The maximum total-recoverable low-flow concentration at these sites was 570 µg/L, which did not exceed the acute aquatic-life standard of 750 µg/L.

Total-recoverable aluminum concentrations typically were highest during high flow, exceeding the acute aquatic-life standard (750 µg/L) in some samples from many sites, including some sites in streams upstream from mining activities. For example, the median total-recoverable aluminum concentration during high-flow conditions in the Boulder River was the same (560 µg/L) upstream (site 3) and downstream (site 58) from the study area. This value also was higher than the median high-flow total-recoverable concentrations (370–445 µg/L) at the mouths of Basin, Cataract, and High Ore Creeks. These data indicate that the primary source of aluminum was not related to historical mining. In addition, although total-recoverable aluminum concentrations exceeded the acute and chronic aquatic-life standards in many parts of the watershed during high flow, the distribution of total-recoverable aluminum does not correlate well with stream reaches where aquatic health is thought to be impaired (Farag and others, this volume, Chapter D10).

Concentration Trends During 1996–2000

Temporal trends in trace-element concentrations can be caused by changes in hydrologic conditions over multi-year periods (for example, several dry years followed by several wet years) or by changes in loading resulting from remediation activities in mined areas. Changes due to varying hydrologic conditions do not necessarily imply that contaminant supply has changed, but rather just indicates fluctuating delivery and transport rates. Actual trends caused by a physical change in either contaminant supply or delivery process are more readily detected by statistically accounting for the effect of flow variation. Trace-element concentration data collected during 1996–2000 for this study at five key sites in the study area were analyzed statistically for trends. Generally, a 4-year period is too short to demonstrate systematic trends. However, some preliminary trends are discernible in the concentration data.

Temporal profiles of dissolved zinc concentrations during 1996–2000 are depicted in figure 19 for five sites in the watershed. These graphs show the full range of concentration variation over the sampling period, seasonal patterns related to streamflow, and year-to-year patterns over the 4-year period. Trend tests were performed on these data sets to estimate the probability that the data exhibit a temporal trend. Because apparent trends are sometimes indicated by the seasonal change in concentration caused by streamflow variations, concentration data frequently are adjusted prior to the trend test to account for the variation due to streamflow. In this case, streamflow adjustment was incorporated into the trend test by using a linear regression of streamflow and concentration. The residuals from this regression were then evaluated for temporal trends (table 2) using the non-parametric Kendall's tau correlation (Helsel and Hirsch, 1992).

Variations in dissolved zinc concentrations in the Boulder River above Kleinsmith Gulch during 1996–2000 indicated no statistical trend. As a result, the magnitude of zinc load for a given flow did not vary appreciably during the study period. Presumably, loading of other trace elements from similar areas underlain by unmineralized rock upstream from the study area may also have shown little change. Similarly, dissolved zinc data for Basin and Cataract Creeks appear to have had no trend during 1996–2000. The absence of zinc concentration trends is consistent with the lack of remediation activity in the Basin and Cataract Creek basins. In contrast, dissolved zinc concentrations for High Ore Creek and the Boulder River below Little Galena Gulch exhibited a decreasing trend during 1996–2000. These trends and the related remediation activities conducted in 1997–2000 in the High Ore Creek valley are discussed in a subsequent chapter (Gelinas and Tupling, this volume).

Sources of Trace Elements

Mining-Related Sources

Although the Boulder River watershed has more than 140 inactive mines and 15 mills (Martin, this volume, Chapter D3), only a few are significant sources of trace elements to streams. The downstream concentration profiles depicted in the ribbon maps (figs. 10–18) clearly show the influence of the Comet, Crystal, and Bullion mines (and, to a lesser extent, the Buckeye and Enterprise mines) on trace-element concentrations in the watershed. Ribbon maps depicting trace-element concentrations in streambed sediment also show the influence of these mines (Church, Unruh, and others, this volume). Waste rock was present at each of these mines, and mill tailings were present at three of these mines. Runoff from and erosion of these mine wastes likely contributed to the trace-element load discharged from these sites. Analysis of metal leaching from selected waste piles demonstrated that mine-waste materials at the Bullion and Buckeye mines had a high potential to impact streamwater quality (Fey and
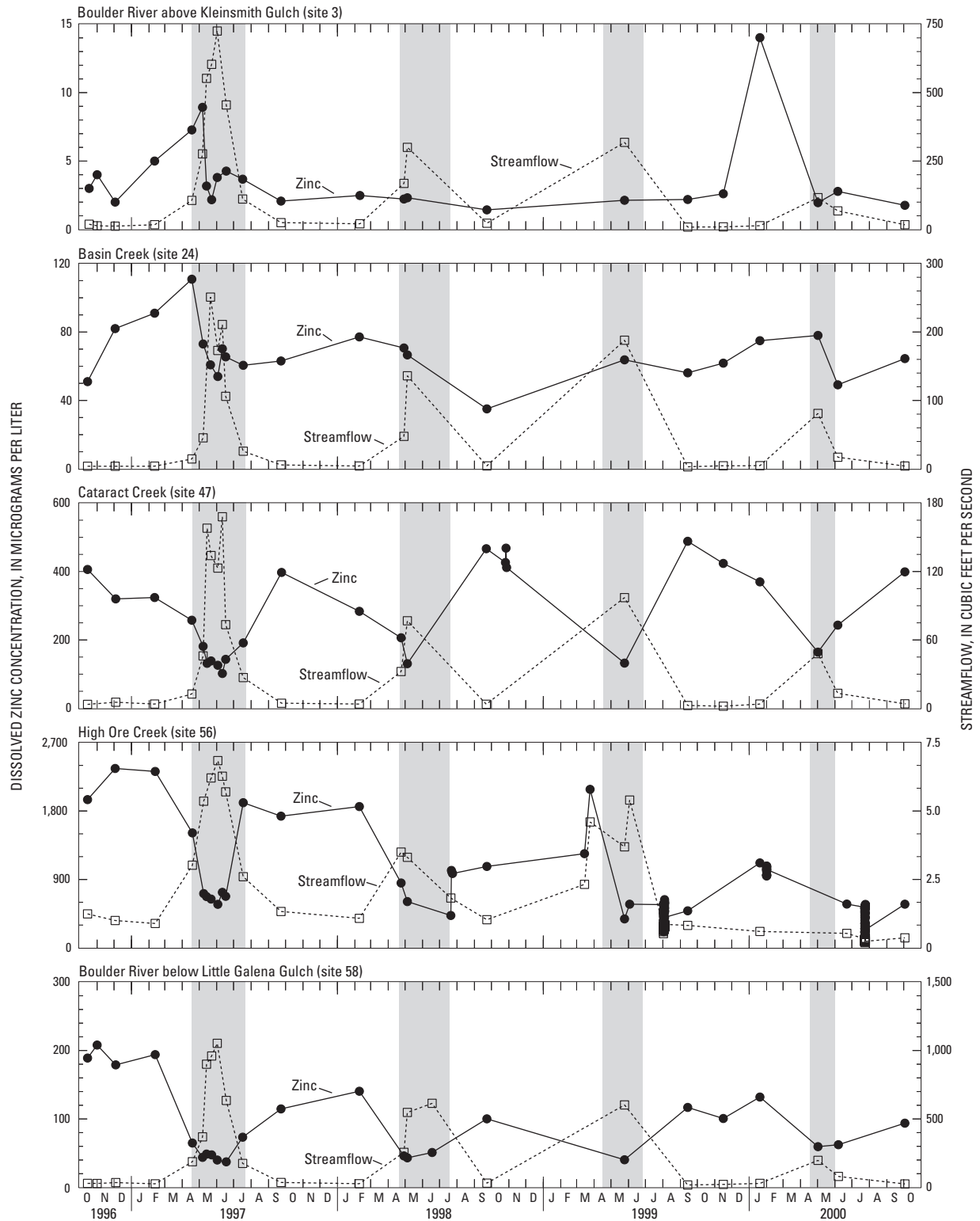
Figure 19.   Temporal profiles of dissolved zinc concentration and streamflow at five sites, 1996–2000. Shaded areas indicate periods of high streamflow during spring runoff. Lines connecting the data points are for visual generalization of temporal patterns and do not imply actual knowledge of concentrations or streamflow between sampling dates.

Table 2. Results of linear regression and Kendall's correlation for trend tests of dissolved zinc concentration for five sites in the Boulder River watershed.

Site number (fig. 1)	Station name	Linear regression of dissolved zinc concentration and streamflow		Kendall's correlation, residuals and time data pairs[1]		Conclusion[2]
		Slope	R²	τ	p value	
3	Boulder River above Kleinsmith Gulch	0.207	0.006	−0.059	0.692	No trend.
24	Basin Creek	200	.001	−.039	.780	No trend.
47	Cataract Creek	−3.04	.952	−.028	.853	No trend.
56	High Ore Creek	.134	.007	−.362	.0081	Decreasing trend.
58	Boulder River below Little Galena Gulch.	−2.32	.803	−.536	.0002	Decreasing trend.

[1]The p value indicates the probability of obtaining the computed τ value if no temporal trend in the data exists. Thus, small p values (generally less than about 0.05) indicate temporal trends, whereas large p values indicate no temporal trends. Decreasing trends are associated with negative values of τ.

[2]Trend tests are based on a short-term (4-year) dataset; consequently, conclusions regarding trend are considered preliminary.

Desborough, this volume). At the Crystal mine, adit discharge was sufficient to make this mine the most significant source of trace elements in the watershed. Detailed investigations of trace-element sources are reported for the Crystal and Bullion mines (Kimball and others, this volume) and the Buckeye and Enterprise mines (Cannon and others, this volume). Remediation activities started in late 1997 in the Comet mine area in the High Ore Creek basin; consequently, a detailed investigation of trace-element sources was not conducted there for this study.

The ribbon maps (figs. 10–18) show that effects from historical mining exist in stream reaches other than those affected by the Comet, Crystal, Bullion, Buckeye, and Enterprise mines. In particular, inactive mines along Cataract Creek and in tributaries to Cataract Creek contribute sufficient copper, zinc, and, in some cases, cadmium to increase concentrations in these reaches to levels near aquatic-life standards.

Premining Background Sources

Watersheds that experienced historical mining activity also contain undisturbed mineralized rocks that might weather and contribute acid and trace elements to streams. These mineralized rocks can be either mineral deposits or surrounding rock affected by hydrothermal alteration. Differentiating between trace-element loads derived from undisturbed geologic sources and mining-affected sources is essential for the mining-related contribution to be put in perspective. In addition, land managers can use information on the relative contributions of trace elements from undisturbed geologic sources and mining-related sources in a watershed for prioritizing subbasins for remediation and for establishing post-remediation water-quality goals.

In the Boulder River watershed, sources of cadmium, copper, lead, and zinc in undisturbed areas appear to be small because concentrations of these metals in water are not elevated at reference sites upstream from mining activities or even in some headwater drainages with inactive mines. This

conclusion is reasonable for two reasons. First, mineralized veins and surrounding zones affected by hydrothermal alteration, which contain pyrite and other sulfide minerals that are the source of trace elements associated with ore deposits, have limited areal extent in the watershed. Second, the acid-neutralizing capacity provided by mafic minerals and secondary calcite in the Boulder batholith limits the migration of acidic, metal-rich water produced by oxidation of the veins and altered rock (Desborough, Briggs, Mazza, and Driscoll, 1998; Desborough, Briggs, and Mazza, 1998). However, premining water-quality data do not exist for stream reaches downstream from mined areas; hence, the reasons stated are somewhat speculative. Arsenic, on the other hand, appears to have small but pervasive sources throughout the undisturbed parts of the watershed.

Trace-Element Loading to the Boulder River

Early biological studies in the watershed (Vincent, 1975; Nelson, 1976) postulated that trace-element loads from Basin, Cataract, and High Ore Creeks affected fisheries in the Boulder River. We determined the relative importance of each of the three major tributaries as contributors of dissolved trace elements to the Boulder River by estimating the annual streamflow and loads of dissolved trace elements during water year 1997 (October 1996 through September 1997). This loading analysis used only data for water year 1997 (fig. 20) because data were collected less frequently in subsequent years and because remediation activities began at the Comet mine along High Ore Creek in late 1997, which affected trace-element loads from this stream to the Boulder River (Gelinas and Tupling, this volume).

The annual loads of dissolved trace elements from Basin Creek (site 24), Cataract Creek (site 47), and High Ore Creek (site 56), and at sites on the Boulder River upstream (site 3) and downstream (site 58) of these tributary streams, were estimated in a multi-step process utilizing water-quality data for 13 sample sets collected between October 1996 and September
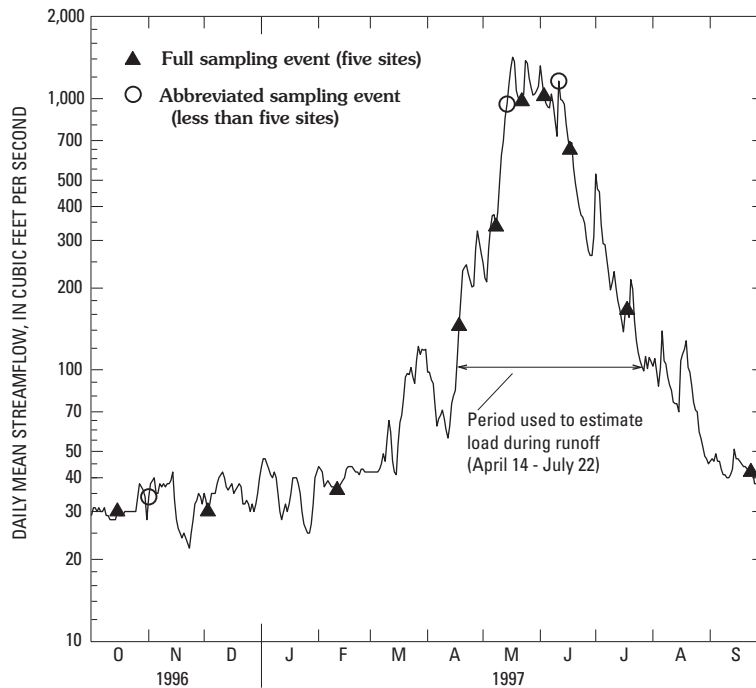
Figure 20. Hydrograph for Boulder River at Boulder (site 59) and sampling dates for water-quality data used for analysis of trace-element loading at five sites, water year 1997.

1997 and the daily mean streamflow record for a nearby site on the Boulder River (site 59, USGS streamflow-gauging station 06033000; Shields and others, 1998). First, a regression model relating daily mean streamflow at the gauging station to instantaneous streamflow measured at the time of sampling was developed for each sampling site. Second, the flow relation for each site was applied to the daily mean flows at the gauging station to construct a daily flow record for water year 1997 for each site. Third, a set of regression models relating instantaneous streamflow at the time of sampling to the concentration of each trace element was developed. Fourth, these regression models were used with the estimated daily streamflow values for each site to estimate daily trace-element concentrations. Fifth, daily loads for each trace element were estimated by multiplying estimated daily streamflow and concentration. Finally, daily loads were summed for the year to estimate the annual loads for water year 1997 at each site (table 3).

Basin, Cataract, and High Ore Creeks together contributed 33 percent of the annual streamflow in the Boulder River (site 58) at the downstream end of the study area (fig. 21), roughly in proportion to their total drainage area compared to the drainage area upstream from the Boulder River below Little Galena Gulch. The dissolved arsenic load contributed by the three tributaries was 38 percent of the load at site 58, about the same proportion as streamflow, indicating that the mineralized rocks in the study area contribute little if any excess dissolved arsenic. In contrast, the three tributaries contribute nearly all the dissolved cadmium load (89 percent) and zinc load (83 percent) and more than half of the dissolved copper load (56 percent). On an annual basis, Cataract Creek contributes more cadmium, copper, and zinc to the Boulder River than Basin and High Ore Creeks. The contribution of cadmium and copper from Cataract Creek was more than twice as large as the load from Basin Creek, and from 6 to almost 40 times greater than the load from High Ore Creek. The load of dissolved zinc from Cataract Creek was almost 1.5 to 2 times as large as the loads from Basin and High Ore Creeks. High Ore Creek contributed little dissolved copper, accounting for only 1 percent of the load at site 58. Most of the dissolved trace-element load in Basin and Cataract Creeks was transported during runoff. In contrast, the High Ore Creek basin, which has lower mountains and therefore less snowmelt runoff from its headwaters, contributed almost half of its streamflow and trace-element load outside of the snowmelt runoff period.

Figure 21.   Boulder River below Little Galena Gulch (site 58) during spring runoff, June 1997.

Table 3.   Estimated annual streamflow and annual loads of dissolved trace elements for five sites in the Boulder River watershed, water year 1997.

[Numbers in parentheses are negative. Period used to estimate load during runoff for 1997 was April 14 to July 22.   >, greater than; <, less than; --, not applicable]

Station name	Site number (see fig. 1)	Streamflow			Dissolved arsenic		
		Annual stream-flow (acre-feet)	Percent of streamflow at site 58	Percent of streamflow during runoff period	Annual load, in tons	Percent of load at site 58	Percent of load during runoff period
Boulder River above Klein-smith Gulch.	3	31.7×10^6	67	83	0.422	57	87
Basin Creek	24	8.32×10^6	18	86	.173	23	88
Cataract Creek	47	6.40×10^6	14	84	.082	11	83
High Ore Creek	56	0.596×10^6	1	55	.029	4	51
Unaccounted for[1]	--	0.0456×10^6	(<1)	--	.033	4	--
Boulder River below Little Galena Gulch.	58	47.0×10^6	100	82	.739	100	80

Site number (fig. 1)	Dissolved cadmium			Dissolved copper			Dissolved zinc		
	Annual load, in tons	Percent of load at site 58	Percent of load during runoff period	Annual load, in tons	Percent of load at site 58	Percent of load during runoff period	Annual load, in tons	Percent of load at site 58	Percent of load during runoff period
3	<0.012	<17	81	0.521	27	87	0.47	4	85
24	.015	21	88	.334	18	94	2.05	19	84
47	.041	58	65	.710	37	88	4.13	38	63
56	.007	10	5	.011	1	67	2.96	27	36
--	>.004	>6	--	.324	17	--	1.37	12	--
58	.071	100	70	1.90	100	84	11.0	100	60

[1]Unaccounted for streamflow and loads were calculated by subtracting the sum of the values for sites 3, 24, 47, and 56 from the value for site 58. The resulting value could represent unsampled inflows or be an artifact of the analysis. Percents may not total to exactly 100 due to rounding.

Summary

Concentrations, sources, and loads of trace elements in streams affected by historical mining in the Boulder River watershed near Basin in southwestern Montana were investigated during this study. Study results are essential for land managers to plan effective and cost-efficient remediation, prioritize remediation activities, and establish restoration goals. Specific objectives were to determine which trace elements associated with ore deposits in the watershed occurred at levels that potentially could be toxic to aquatic organisms, characterize trace-element concentrations throughout the watershed, identify primary source areas by quantifying trace-element loads at key sites in the watershed, and establish a water-quality monitoring program to determine long-term seasonal and annual variations near areas where remediation activities were likely. The study focused on those trace elements associated with the polymetallic veins exploited by historical mining.

The magnitude and extent of trace elements in the Boulder River watershed were assessed by systematic sampling of streams throughout the area during a wide range of hydrologic conditions, comparison of trace-element concentrations to aquatic-life standards, estimation of annual loading of trace elements to the main streams in the watershed, and analysis of concentration data for temporal trends. Water-quality measurements also were made in reference streams draining unmineralized subbasins underlain by the same or similar lithologic units. Almost all streams in the Boulder River watershed had near-neutral to alkaline pH and, except for elevated trace-element concentrations, generally good water quality.

Trace-element concentrations in streams of the Boulder River watershed varied greatly; the highest concentrations occur in small streams downstream from a few of the inactive mines in the watershed, and the lowest concentrations are generally in stream reaches upstream from areas of historical mining or in headwater streams where small inactive mines had little effect. Cadmium, copper, lead, and zinc concentrations commonly exceeded chronic aquatic-life standards. Zinc exceeded these standards to a greater degree than did the other metals. The highest concentrations were in streams downstream from three large inactive mines: the Crystal mine in Uncle Sam Gulch, the Comet mine in High Ore Creek, and the Bullion mine in a tributary to Jack Creek. Downstream from these three mines, the chronic aquatic-life standard for at least one trace element associated with the metal ore deposits in the watershed was exceeded at all sampling sites, including sites in the Boulder River between Basin Creek and the Jefferson River. Because hardness decreases while concentrations increase, the toxicity of copper and lead was much higher during high flow compared to low flow. Toxicity of cadmium and zinc also was slightly higher during high flow compared to low flow.

In the Boulder River watershed, sources of cadmium, copper, lead, and zinc in undisturbed areas appear to be small; however, arsenic is pervasive at low concentrations throughout the watershed. Basin, Cataract, and High Ore Creeks together contributed 33 and 38 percent of the annual streamflow and dissolved arsenic, respectively, at the downstream Boulder River site, roughly in proportion to their percentage of the total drainage area. In contrast, the three tributaries contributed nearly all the dissolved cadmium (89 percent) and zinc (83 percent) as well as more than half of the dissolved copper (56 percent). On an annual basis, Cataract Creek contributed more cadmium, copper, and zinc than either Basin Creek or High Ore Creek.

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