Characterization of Metals in Water and Bed Sediment in Two Watersheds Affected by Historical Mining in Montana and Colorado

By David A. Nimick, Stanley E. Church, Tom E. Cleasby, David L. Fey, Briant A. Kimball, Kenneth J. Leib, M. Alisa Mast, and Winfield G. Wright

ABSTRACT

Characterization of metals in water and bed sediment is essential for planning effective and cost-efficient remediation in watersheds affected by historical mining. To aid cleanup efforts on Federal land, pilot investigations that are part of the USGS Abandoned Mine Lands Initiative are being conducted in two watersheds in Colorado and Montana. Assessment of ore-related metals and other trace elements in water and sediment in these watersheds provides information to delineate stream reaches having elevated metal concentrations, determine sources of contaminated material, understand the transport of dissolved and particulate metals, and evaluate the potential for metal toxicity to biota.

INTRODUCTION

Metals from mineralized areas and abandoned mine lands affect water quality and biota in many watersheds of the United States. As part of a cooperative effort with Federal land-management agencies, the USGS implemented an Abandoned Mine Lands Initiative in 1997. The goal of the initiative is to develop a strategy for gathering and communicating the scientific information needed to formulate effective and cost-efficient characterization and remediation of the effects of historical mining using a watershed approach (Buxton and others, 1997). The overall scientific strategy is based on understanding the fundamental geologic, hydrologic, geochemical, and biologic processes that cause the environmental degradation often observed downstream from historical mining districts. The watershed approach is intended to identify and characterize those contaminated sites that have the most profound effect on water and ecosystem quality within the watershed. Land-management agencies then can utilize the scientific information to prioritize and develop effective remediation plans. The pilot studies are being conducted in two watersheds: the Boulder River watershed near Helena, Montana (fig. 1), and the upper Animas River watershed upstream from Silverton, Colorado (fig. 2).

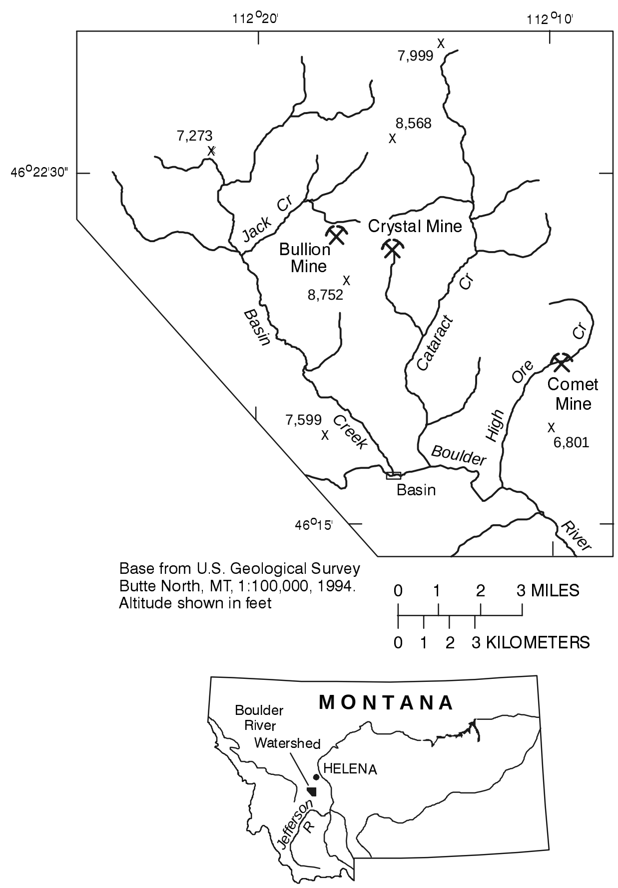

Figure 1. Location of the Boulder River watershed, southwestern Montana.

In characterizing the occurrence of metals in a watershed, key objectives include determining the

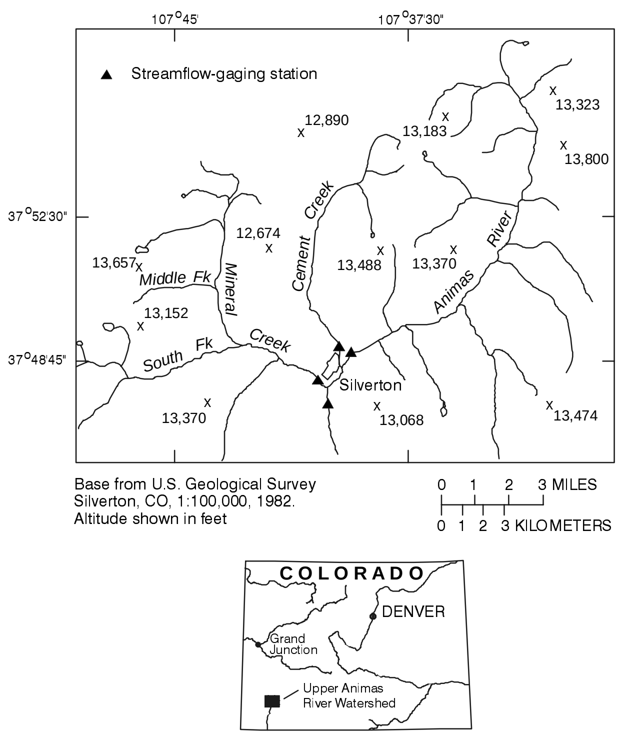

Figure 2. Location of the upper Animas River watershed, southwestern Colorado.

seasonal and spatial distribution of ore-related metal concentrations in water and bed sediment throughout the watershed, and then identifying the significant natural and mining-related source(s) of those contaminants. Sources of these metals can be determined from downstream changes in ore-related metal concentrations in water and bed sediment and from metal-loading studies using tracer-injection techniques. Natural and mining-related sources of metals in mineralized watersheds can be distinguished by comparing water-quality and isotope data in relation to the location of mined areas and geologic units.

DESCRIPTION OF STUDY AREAS

Historical metal-mining activity began in the late 1870s in the Boulder River and upper Animas River watersheds. Principal metals produced include silver, gold, lead, zinc, and copper. Ore bodies are sulfidic, and acidic drainage occurs in both areas. The mining districts in the Boulder River watershed are located primarily in three tributaries to the river (fig. 1), whereas the mining districts in the upper Animas River watershed are located in the headwaters (fig. 2). There are about 120 inactive mines and prospects in the Boulder River watershed and over 1,000 in the upper Animas River watershed. Mineralization in the Boulder River watershed occurs in quartz veins, and hydrothermal alteration is confined to narrow halos around the mineral deposits. In the upper Animas River watershed, mineralization is in vein and breccia-pipe deposits, but alteration occurs on a regional scale. The primary environmental effect of mining in both watersheds is degraded water quality and aquatic habitat, both of which adversely affect aquatic and fishery resources. Some streams are devoid of fish and others have impaired fisheries. Inactive mines can affect streams through direct discharge of acid drainage from adits, seepage from waste rock and tailings piles, and erosion of mining waste and tailings by storm or snowmelt runoff.

METALS IN WATER

Degradation of water quality can be one of the most negative effects of historical mining activity on aquatic biota. Water quality was characterized by systematic sampling of streams throughout the watersheds, comparing metal concentrations to aquatic-life standards, and estimating annual loading of metals to the main streams in the watershed. Water-quality measurements also were made in reference streams draining unmineralized subbasins underlain by the same or similar lithologic units.

Boulder River Watershed

In streams of the Boulder River watershed, pH values are near-neutral to slightly alkaline except in isolated circumstances where acid discharge from inactive mines affects small streams with limited dilution or acid-neutralization capacity. In comparison to five reference streams, ore-related metal concentrations in many stream reaches draining mined areas are elevated. For example, cadmium, copper, lead, and zinc concentrations commonly exceed chronic aquatic-life criteria (U.S. Environmental Protection Agency, 1986). Downstream concentration profiles in streams of the Boulder River watershed indicate that the primary sources of ore-related metals are three large inactive mines: the Comet Mine in High Ore Creek, the Bullion Mine in a tributary to Jack Creek, and the Crystal Mine in a tributary to Cataract Creek. Downstream from these three mines, chronic aquatic-life criteria for at least one ore-related metal were exceeded at all sampling sites, including sites in the Boulder River between Basin Creek and the Jefferson River. Arsenic is pervasive in both mined and unmined areas; concentrations are elevated throughout the watershed, but are typically much lower than the chronic aquatic-life criterion [190 micrograms per liter (µg/L)].

During snowmelt runoff, cadmium (fig. 3) and zinc concentrations decrease, whereas lead (fig. 3) concentrations increase. Cadmium and zinc are predominantly dissolved [using 0.001-micrometer (µm) filtration] and presumably are diluted during high flow. Lead is primarily in the particulate phase (>0.45 µm in size), and its concentration increases as higher flows transport more sediment. Copper is partitioned more equally into both the dissolved and particulate phases. Partitioning and seasonality are important factors affecting the severity and timing of aquatic toxicity.

The occurrence of cadmium and zinc in the dissolved phase indicates that ore-related metals are introduced to streams by inflow of surface and ground water rather than by entrainment of tailings by runoff. At the Bullion and Crystal Mines, adit discharge is likely the primary source of metals. At the Comet Mine, leachate from tailings appears to be the primary source.

The annual loads of ore-related metals from Basin, Cataract, and High Ore Creeks, and at two sites on the Boulder River upstream and downstream of these tributary streams, were estimated by applying metal-transport regression relations developed from water-quality data for 12 sample sets to daily mean flow estimates derived from the continuous streamflow record for a nearby stream gage on the Boulder River. Although the three tributaries combined contributed only 33 percent of the annual streamflow at the downstream sampling site on the Boulder River, they contributed 41 to 89 percent of the cadmium, copper, lead, and zinc loads. Cataract Creek contributed the largest metals loads to the Boulder River.

Upper Animas River Watershed

During low flow in the upper Animas River watershed (fig. 2), Cement Creek has the lowest pH (3.9) and transports most of its metal load in the

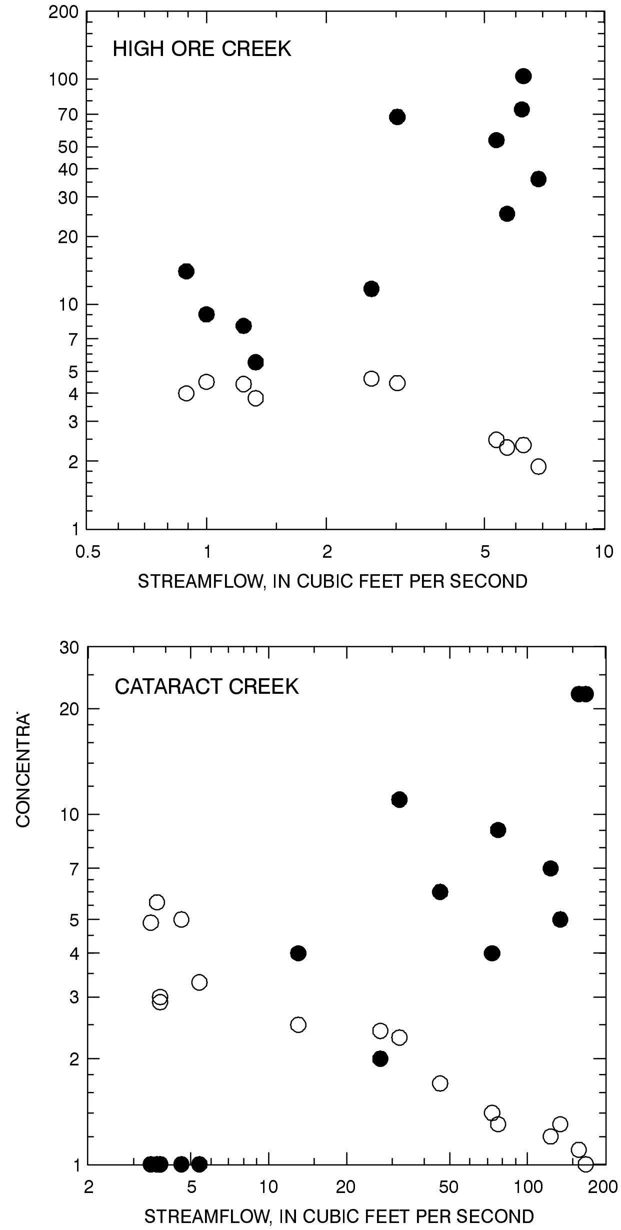

Figure 3. Relation of streamflow to concentrations of dissolved cadmium (open circles) and total-recoverable lead (solid circles) in water from High Ore and Cataract Creeks, Boulder River watershed, Montana, 1996-98.

dissolved (0.001-µm filtration) phase. Mineral Creek has a pH of 4.5 to 6.5 at low flow and transports most of its metal load in the colloidal phase (>0.45 µm). Similarly, most of the metal load in the Animas River upstream of Cement Creek is colloidal. Downstream from Cement Creek, the dissolved metal load from Cement Creek is largely partitioned to the colloidal phase in the higher-pH water of the Animas River (Church and others, 1997). After forming, colloids aggregate, settle, and become an integral component of the bed sediment, where they are stored until subsequent high flow transports the metal-rich sediment downstream. Zinc and aluminum concentrations commonly exceed aquatic-life criteria in the upper Animas River watershed; copper may also impact aquatic health (Besser and others, 1998; Nimmo and others, 1998).

Preliminary data suggest that during low flow Mineral Creek and Cement Creek contribute 80 to 90 percent of the dissolved (using 0.45-µm filtration) sulfate, iron, and copper loads to the upper Animas River watershed. During high flow, the contribution of sulfate, iron, and copper from Cement and Mineral Creeks decreases to about 50 to 60 percent because of the increases in metal loading from mainstem sources upstream of the tributaries. Contributions of dissolved zinc from the two tributaries are approximately the same (30 percent) during high flow and low flow.

METALS IN BED SEDIMENT

Ore-related metals derived from mine wastes and acidic drainage typically accumulate in the bed sediment of streams downstream from inactive, historical mines. Concentration profiles for bed sediment can be used to delineate stream reaches having elevated ore-related metal concentrations, help locate sources of contaminated material, and help define the transport of dissolved and particulate metals. In addition, biologists can use concentration data to evaluate the potential metal toxicity of bed sediment to biota.

Total and leachable metal concentrations were determined in bed sediment from both watersheds. Most of the total metal content in the sediment occurred in the operationally-defined leachable, or colloidal, fraction, which is reasonable because ore-related metals typically are associated with iron oxyhydroxide (for example, ferrihydrite) and oxyhydroxysulfate (for example, schwertmannite) mineral coatings. The total extraction used a mixture of strong acids, whereas the leachable extraction used warm (50^{o} C) 2M HCl-1%H_2O_2 (Church and others, 1993). Downstream profiles of total zinc concentrations in bed sediment (figs. 4 and 5) are shown as examples of the downstream trends in metal concentrations in both watersheds.

Boulder River Watershed

Profiles of ore-related metal concentrations in bed sediment in the Boulder River watershed

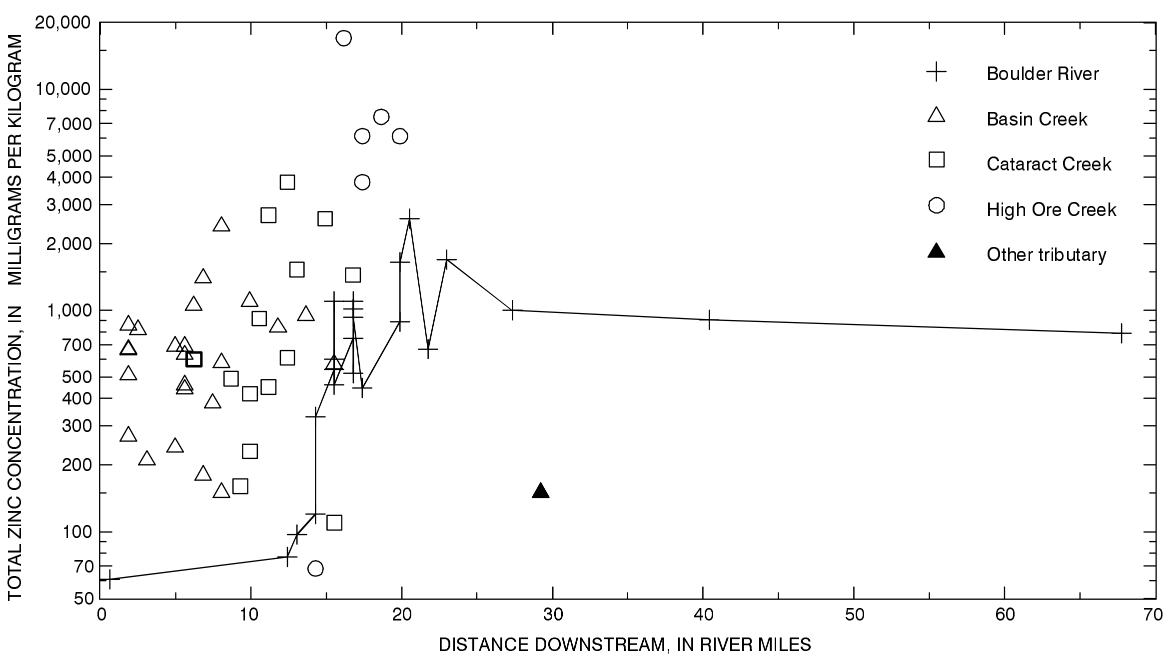

Figure 4. Total zinc concentration in bed sediment from the Boulder River and its tributaries. Boulder River data are plotted by distance downstream from an arbitrary starting point upstream of Basin Creek. Data for tributaries are plotted in river miles along the tributary; the confluences with the Boulder River are at 15.5 miles for Basin Creek, 17 miles for Cataract Creek, and 20 miles for High Ore Creek.

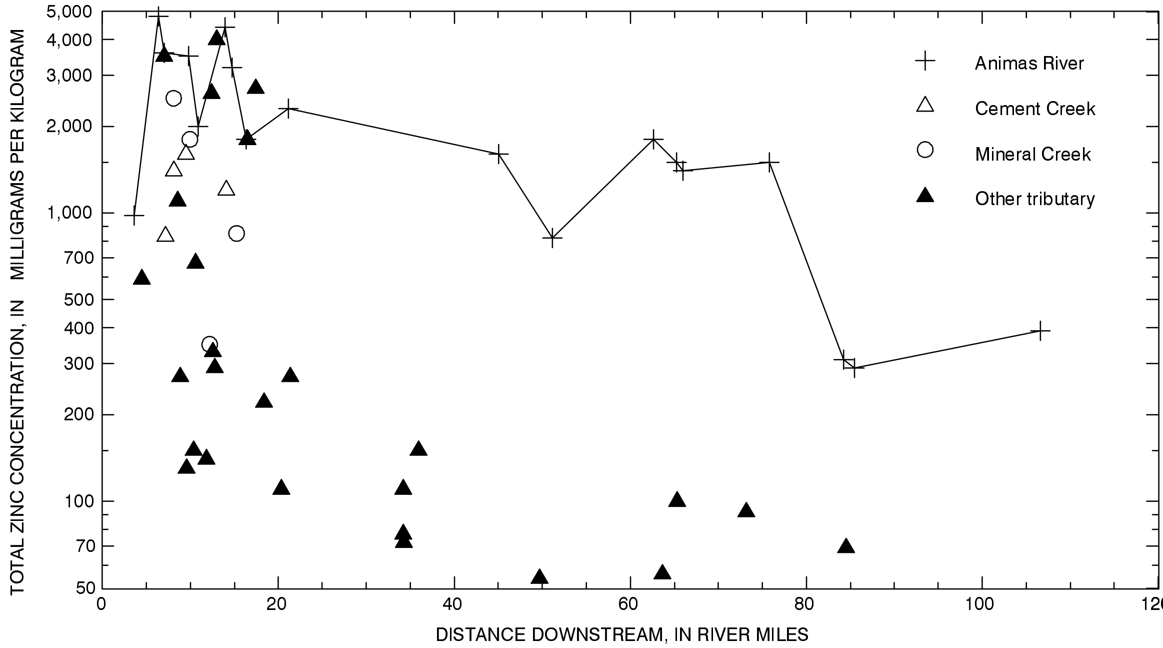

Figure 5. Total zinc concentrations in bed sediment from the Animas River and its tributaries. Animas River data are plotted by distance downstream from an arbitrary starting point. Data for Cement Creek and Mineral Creek are in river miles along the tributary; the confluences with the Animas River are at 15 miles for Cement Creek and 16 miles for Mineral Creek. Data for tributaries of Cement Creek, Mineral Creek, and the Animas River are for samples taken at the mouth of each tributary.

were similar to the concentration profiles observed for water. The highest concentrations of leachable and total ore-related metals in bed sediment occur immediately downstream from the three large mines cited previously; however, concentrations of these metals in unmineralized subbasins are near average concentrations in the Earth's crust. Arsenic, antimony, copper, lead, and zinc are concentrated in the leachable phase, indicating sorption to the bed sediment. Concentrations of trace elements not associated with the mineral deposits (for example, barium, cobalt, strontium, and titanium) are similar in mineralized and unmineralized subbasins.

The downstream concentration profile for each element is determined by the rate at which the dissolved element sorbs to colloids and the rate of downstream transport of the colloidal phase of the bed sediment. Total and leachable concentrations of arsenic, copper, lead, and zinc (fig. 4) in bed sediment of the Boulder River are elevated above crustal values for more than 60 miles downstream of the study area. Downstream concentration profiles indicate that arsenic and lead are removed from solution within a short distance from their sources. Copper and zinc are transported farther downstream and sorbed to colloids as the pH of the stream increases downstream from the source of acidity.

Upper Animas River Watershed

Downstream profiles of metal concentrations in bed sediment in the upper Animas River watershed are similar to the patterns observed in the Boulder River watershed. Copper, lead, arsenic, and zinc are concentrated in the colloidal (leachable) phase of the sediment, with the highest concentrations occurring immediately downstream from historical mining areas. Arsenic and copper concentrations in bed sediment of the Animas River approach crustal values about 60 miles downstream, whereas lead and zinc (fig. 5) concentrations do not approach crustal values for more than 100 miles downstream. Unlike the Boulder River watershed, there were numerous mill sites in the upper Animas River watershed. Prior to

1935, tailings at these mill sites were impounded behind earthen dams. Many of these dams eventually failed, and large masses of tailings were transported downstream and deposited on the flood plains of the Animas River and its tributaries. These deposits now provide a large, diffuse source of mining-related metals to the watershed. In addition, weathering of the extensively altered rocks in the watershed provides a substantial natural load of ore-related metals and other trace elements to the streams.

SOURCES OF METALS

Characterizing sources of metals to streams in mined watersheds involves not only identifying and quantifying point and nonpoint sources along stream reaches but also distinguishing between sources that are related to mining and those that are not. Refining methods to address these issues has been an important part of the pilot watershed investigations.

Quantification of Metal Sources to Streams

Detailed metal-loading studies (or tracer-injection studies) have been an important tool for identifying and quantifying individual surface and subsurface sources of metal loading to specific stream reaches from both mining-related and natural geologic sources. These studies utilize tracer-injections to accurately determine streamflow in coarse-substrate stream channels and synoptic water-quality sampling to determine metal concentrations (Kimball, 1997).

Three studies have been conducted in the Boulder River watershed. One study helped characterize metal loading from the many mines along an 8-mile reach of Cataract Creek in 1997 (Cleasby and others, 1998). Two tracer studies conducted in 1998 were designed to characterize metal sources at specific mine sites scheduled for remediation. These two studies were conducted along 1- to 2-mile reaches of the small streams directly affected by surface and subsurface inflow from the Bullion and Crystal Mines.

Seven tracer studies have been conducted in the upper Animas River watershed. Four of these were used to characterize loading to Cement Creek and the Animas River from mining-related and natural geologic sources. Two studies focused on loading in smaller subbasins, and one specifically examined geochemical reactions in the mixing zone below the confluence of an acidic and a neutral-pH stream.

In analyzing results of tracer studies, four calculations integrate all the metal sources and processes of the watershed: (1) the instream load is calculated for each stream site as the product of sample concentration and discharge, (2) the cumulative total load to the stream is calculated by summing all positive changes of instream load between stream sites, (3) the cumulative load from visible surface inflows is calculated by summing the products of inflow sample concentrations and the flows as estimated by the change in discharge between stream sites bracketing the inflow, and (4) the load derived from nonpoint sources is estimated by subtracting surface inflow loads from total instream load.

Comparison of the load calculations for a tracer-injection study in Cement Creek indicates that 65 percent of the dissolved zinc load at low flow was from nonpoint sources in contrast to point sources such as adit discharge. Presumably, these nonpoint sources include, but are not limited to, the ground-water metals load derived from the weathering of altered rock within the watershed and from diffuse flow of subsurface waters through alluvial fans beneath the inflowing tributary streams. Sixty-nine percent of the zinc load in Cement Creek was transported to the Animas River as dissolved (<0.001 µm filtration) zinc; the other 31 percent of the zinc load was transferred to colloidal iron and was either transported as colloidal load or settled and was temporarily stored in the streambed. Most of the colloidal bed-sediment load is flushed annually by snowmelt or rainfall runoff and contributes to large zinc loads in the Animas River during high flow.

Distinguishing Natural Geologic and Mining Related Sources of Metals

Watersheds that experienced historical mining activity also contain undisturbed mineralized rocks that may weather and contribute acidity and metals to streams. Differentiating between metals loads derived from undisturbed natural geologic sources and mining-related sources is essential to put the anthropogenic contribution in perspective. Information on the relative contributions of metals from natural geologic sources and mining-related sources in a watershed is useful for prioritizing subbasins for remediation and for establishing post-mining water-quality goals.

In the Boulder River watershed, natural sources of metals appear to be minimal because metal concentrations in water and sediment upstream of mining activities are not elevated. This conclusion is reasonable because the mineralized veins only crop out in small areas and hydrothermal alteration is not extensive.

Both natural and mining-related sources contribute acid and metals to the upper Animas River watershed. Metal loads from these two sources were distinguished by areal water-quality sampling, by comparing water-quality data to the geology of specific stream reaches, and by examining isotopes of oxygen in sulfate extracted from these waters.

More than 70 streams, springs, and adits were sampled during summer 1997 in the Cement Creek basin. Although prospect pits, historical mines, and abandoned mill sites are scattered throughout this area, much of the watershed, particularly at higher elevations, is relatively undisturbed. Water from springs draining altered volcanic rock upstream of any past mining activity can have pH values as low as 3 or as high as 8, depending upon the degree of alteration and the mineralogy of the alteration suite within the area of the subbasin sampled (Bove and others, 1998). Mining-affected and unmined areas produce acidic to neutral surface waters; however, concentrations of major ions and dissolved trace elements generally are higher at the affected sites than at unmined sites. The median pH of water samples collected at the mining-affected sites was 4.3 (range of 2.8 to 7.3) compared to the median value of 6.6 (range of 3.0 to 8.0) at the unmined sites. Sulfate concentrations at all sites ranged from 1 to 450 µg/L and were generally higher at the mining-affected sites (median of 138 µg/L) than at the unmined sites (median of 56 µg/L). Dissolved zinc concentrations were highly variable among the sample sites, ranging from <10 to 14,600 µg/L. Results from springs and streams in unmined areas revealed a geographic pattern in surface-water chemistry that appears to be related to the degree of bedrock alteration. The eastern part of the Cement Creek basin is underlain primarily by propylitically altered lavas, which produce neutral surface water (pH values of 6.4 to 8.0) with relatively low concentrations of dissolved metals except zinc (as high as 230 µg/L). The western part of the Cement Creek basin is more intensely altered than the eastern part and includes pervasive argillic alteration in the northwest quadrant and quartz-sericite-pyrite alteration localized along structures (Luedke and Burbank, 1996). Water draining from this part of the Cement Creek basin is generally more acidic (pH ranging from 3.2 to 4.6) and has elevated concentrations of dissolved metals.

The oxygen isotopes of dissolved sulfate are a useful diagnostic tool for distinguishing natural and mining-related sources of dissolved constituents. The kinetics of sulfide-oxidation reactions differ in natural and mining-related geochemical systems; hence, oxygen-isotope ratios are larger in natural springs draining unmined areas and smaller in mine-drainage water. Dissolved-constituent concentrations also are higher in mine drainage. Given these differences, the proportion of dissolved constituents derived from natural and mining-related sources can be determined using the isotope and concentration data in mass-balance calculations. This method has been applied in two subbasins using data collected during low flow. In the Middle Fork Mineral Creek subbasin, 71 percent of the dissolved sulfate is estimated to originate from natural sources. In the Cement Creek subbasin, 75 percent of the dissolved zinc comes from natural sources.

CONCLUSIONS

The watershed approach is designed to identify the contaminant sources that have the most profound effect on water quality. In the Boulder River watershed, a few large mines appear to be the most important sources of ore-related metals, and loading from natural geologic sources is minimal. In contrast, ore-related metals in the upper Animas River watershed are derived from both mining-related and natural sources. In some drainages, the proportion of metals derived from undisturbed natural geologic sources may be so large that complete cleanup of mining-related sources may not decrease metal concentrations in streams to a level that is suitable for aquatic organisms. In addition, no single mine can be considered the primary source of metals. Instead, significant loads are contributed by small subbasins where the combined load from numerous mines and natural sources constitute a large source to one of the major streams in the watershed. Consequently, remediation planning in the Boulder River watershed targets individual mines whereas entire subbasins may be targeted in the upper Animas River watershed.

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AUTHOR INFORMATION

David Nimick and Tom Cleasby, U.S. Geological Survey, Helena, Montana

David Fey, Alisa Mast, and Stan Church, U.S. Geological Survey, Denver, Colorado

Ken Leib and Winfield Wright, U.S. Geological Survey, Durango, Colorado

Briant Kimball, U.S. Geological Survey, Salt Lake City, Utah

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