Characterization of Background Water Quality

By M. Alisa Mast, Philip L. Verplanck, Winfield G. Wright, and Dana J. Bove

Chapter E7 of

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

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Abstract

Water quality in historical mining districts is affected by metal-rich drainage from inactive mines and by weathering of mineralized bedrock in unmined areas. To characterize background water quality in the Animas River watershed study area, we sampled 146 streams and springs minimally affected by mining during low-flow conditions in 1997–99. Background springs and streams were dominantly calcium-bicarbonate-sulfate type water but displayed a wide range of chemical compositions for both major and trace-metal constituents. For example, pH values of background samples ranged from 2.58 to 8.49 and specific conductance ranged from 12 to 2,180 microsiemens per centimeter. Zinc was detected in more than one-half the background samples, and zinc concentrations exceeded acute aquatic-life standards in more than 30 percent of samples. The primary factor controlling the chemistry of background sites was the degree of bedrock alteration. Propylitically altered rock produced neutral surface water with low dissolved metal concentrations, whereas quartz-sericite-pyrite altered rock generated surface water with low pH and elevated dissolved metal concentrations. Drainage from 75 inactive mine sites and 95 mining-affected surface-water sites was sampled for comparison with background water quality. Mine-drainage chemistry was highly variable: pH values ranged from 2.35 to 7.77, and specific conductance ranged from 180 to 3,520 microsiemens per centimeter. Comparison of background samples with mine-drainage samples showed statistically significant differences in concentrations for all the major ions and many dissolved metals, including barium, copper, iron, manganese, strontium, and zinc. Higher concentrations of all metals except barium were at mine sites. Estimation of metal contributions from background sources on a watershed scale was complicated by a number of factors, including the large number of mining-related features, rugged topography, complex geology, and contributions of ground water from unknown sources. We explored several different approaches to estimate background water quality in the study area on different scales, including statistical descriptions, mass-balance calculations, isotopic applications, and rare-earth element geochemistry. The results demonstrate that metals released from weathering of altered rock from unmined areas are significant in some stream reaches and must be taken into account when water-quality standards and remediation goals are established for the Animas River watershed study area.

Introduction

One of the objectives of the Animas River watershed study is to characterize sources of metals to surface water that may have existed prior to mining activity. Although drainage from inactive mines can affect surface-water quality, background weathering of altered and mineralized bedrock is also an important source of metals and acidity in historical mining districts. Water-quality studies in highly mineralized yet unmined areas have demonstrated that background weathering processes can contribute substantial amounts of metals and acidity to streams (Bassett and others, 1992; Runnells and others, 1992; Miller and McHugh, 1994; Kirkham and others, 1995; Bove, 1996; Kelley and Taylor, 1997; Leybourne and others, 1998; Miller and others, 1999). For example, dozens of naturally occurring acidic springs are present in the headwaters of the Alamosa River in Colorado, which drains the Summitville acid-sulfate gold-silver-copper deposit (Kirkham and others, 1995). These springs had pH values as low as 1.4 and commonly had higher aluminum and iron concentrations than draining mines in the same area. In the Brooks Range of Alaska, streams draining undisturbed silver-lead-zinc massive sulfide deposits were reported to be acidic and contained elevated levels of cadmium, lead, and zinc that in some streams exceeded drinking-water and aquatic-life standards (Kelley and Taylor, 1997). Geologic data also provide evidence of natural acidic rock drainage (Helgen and Moore, 1996; Logsdon and others, 1996; Furniss and others, 1999; Church and others, 2000). In the New World mining district in Montana, radiocarbon dates revealed that ferricrete deposits were nearly 9,000 years old, suggesting that natural acidic rock drainage predated the earliest mining activity in the district (Furniss and others, 1999). The presence of Holocene ferricrete deposits and iron bogs directly associated with the distribution of hydrothermally altered rock (Bove and others, this volume, Chapter E3; Yager and Bove, this volume, Chapter E1 and pl. 2) in the San Juan Mountains provides strong evidence that acid rock drainage also was common in some parts of the Animas River watershed study area prior to mining (Logsdon and others, 1996; Nash, 1999; Verplanck and others, this volume, Chapter E15; Wirt and others, this volume, Chapter E17). This finding is further supported by geochemical studies in the Animas River which indicate that the weathering of exposed mineral deposits increased metal concentrations in streambed sediment prior to mining (Church and others, 2000; Church, Fey, and Unruh, this volume, Chapter E12).

Knowledge of background water quality in mining-affected areas can help establish cost-effective and technically feasible remediation goals for watersheds containing historical inactive mines. This concept is particularly important in areas where current water-quality standards may be lower than naturally occurring metal concentrations (Runnells and others, 1992). Several different approaches for estimating background metal contributions have recently been summarized by Alpers and Nordstrom (2000) and include statistical methods, examination of historical data, sediment sampling, geochemical modeling, comparison with analog areas, use of isotopic tracers, and mass-balance calculations. Because of the limitations and uncertainties associated with each of these approaches, Alpers and Nordstrom (2000) recommended that multiple approaches be used to help quantify premining conditions for a particular mining area. Determination of nonmining contributions of metals in historical mining areas can be a particularly challenging task because premining water-quality data from most mined areas are not available for comparison. In addition, most mineral deposits in relatively developed areas have been disturbed to some extent; thus, good analog sites for comparison with inactive mine sites are scarce (Maest, 1996).

Purpose and Scope

The purpose of this report is to identify and quantify dissolved constituent contributions from weathering of hydrothermally altered rock in unmined areas—herein referred to as background weathering—in the Animas River watershed study area. Water-quality samples were collected at more than 300 stream, spring, and mine sites in the study area during summer low-flow conditions in 1995 and 1997–99 and were analyzed for major inorganic and selected trace-element constituents. Field measurements at each site included streamflow, specific conductance, pH, water temperature, and dissolved oxygen. These data were used to:

- Characterize the water quality of background springs and streams and compare to water quality of mine drainage and mining-affected surface water

- Determine the relation between background water quality and the degree of bedrock alteration

- Evaluate different qualitative and quantitative methods for estimating contributions of metals from background weathering to surface water.

The results of this study should improve our understanding of how background weathering processes control surface-water chemistry in a mineralized area. They also provide information that will contribute toward establishing water-quality standards and cost-effective, technically feasible remediation goals in the Animas River watershed study area. Further, the results will help guide future investigations of background water quality in other geologically complex watersheds affected by historical mining activity.

Study Methods

Water-quality samples were collected at selected stream and spring sites throughout the watershed during summer low flow in 1995 and in 1997 through 1999. Because historical mining disturbance is so extensive throughout the study area (Church, Mast, and others, this volume, Chapter E5), determining whether a spring or stream has or has not been affected by mining is a challenge. Many of the water-quality sampling sites are obviously affected by historical mining activity, yet at other sites the extent to which mining activity has affected water quality is unclear. To address this issue, a ranking system was devised to evaluate the potential for the effects of mining on water quality (table 1). The ranking system consisted of four categories (I–IV), ranging from category I, having no evidence of mining activity, to category IV, having direct discharges from inactive mine sites. If a site appeared unaffected, but not unequivocally, the site was ranked category II. Conversely, sites that were not directly affected but had upgradient mining activity that likely affected the water quality were ranked as category III. Table 1 lists the many factors that were considered in the assignment of a category to each sampling site. An example of a category I site is a headwater stream or spring upgradient from any manmade disturbances. An example of a category II site is a spring along a valley side that has several dry prospect pits upgradient from it. An example of a category III site would be a stream or spring with an upgradient adit and mine-waste dump but no direct discharge or signs of direct discharge. Another example of a category III site is a spring in one subbasin that has a mine directly over the drainage divide that could influence the water quality of the spring. A category IV site would have obvious direct effects from mining upgradient or upstream from the site. The final assignment of category (whether I, II, III, or IV) was not a quantitative determination; however, the categories are considered to be the best assessment possible using the available information.

Table 1. Categories for ranking water-quality sampling sites and information used in their assignment.

Categories in ranking system
I—No manmade disturbances upgradient or upstream from the water-quality sampling site
II—Some potential manmade disturbances upgradient or upstream from the water-quality sampling site
III—Some manmade disturbances upgradient or upstream from the water-quality sampling site
IV—Definite manmade disturbances upgradient or upstream from the water-quality sampling site
Information used in assignment of categories
Number of mines visibly draining water upgradient from sampling site
Number of mines (draining/not draining) upgradient from sampling site
Number of mine-waste dumps upgradient from sampling site
Number of prospects upgradient from sampling site
Number of shafts upgradient from sampling site
Inventory of exploration drill holes, abandoned mill sites, buildings and machinery, logging, grazing, roads upgradient from sampling site
References used for determination of categories: • Direct observations • Topographic maps • Aerial photographs • Published mine maps • Written documentation • Oral communication

Of the 241 spring and stream sites sampled during the study, 108 sites were classified as category I, 38 sites as category II, 24 sites as category III, and 71 sites as category IV. Water-quality samples also were collected at 75 inactive mine sites for comparison with background water quality. Localities of streams, springs, and mine sites in the study area as well as the ranking information just discussed are in the study area database (Sole and others, this volume, Chapter G).

We collected samples for water-quality analyses by pumping water directly from the stream with polyvinyl tubing, through a 0.45-µm (micrometer) membrane filter, and into precleaned polyethylene bottles. A filtered aliquot for metal analyses was acidified to pH less than 2 using concentrated ultrapure nitric acid. A filtered, unpreserved aliquot was collected for sulfate analysis, and an unfiltered aliquot was collected for alkalinity. Field measurements at each site included discharge, specific conductance, pH, water temperature, and dissolved oxygen. Samples collected in 1995 were analyzed at the National Water Quality Laboratory according to methods in Fishman (1993), and results are published in the USGS National Water Information System (URL, http://waterdata.usgs.gov/nwis, accessed December 2002). For the 1997–99 samples, detailed descriptions of collection methods and analytical techniques and quality assurance data can be found in Mast, Evans, and others (2000). Major cation, silica, and dissolved metal concentrations were determined in the acidified samples by inductively coupled plasma–atomic emission spectrometry (ICP-AES). Alkalinity was determined by incremental titration within 5 hr of collection, and sulfate was determined by a turbidimetric method. Chemical results for all samples (including 1995) are in the relational database in Sole and others (this volume). Speciation calculations were made using the computer program PHREEQC (Parkhurst, 1995), and inverse geochemical models were solved with the NETPATH computer code (Plummer and others, 1994). Both computer programs were obtained from URL http://water.usgs.gov/software/geochemical.html (accessed January 2002).

Geology, Alteration, and Mineralization

Because water quality is strongly controlled by geology, a brief discussion of bedrock geology, alteration, and mineralization of the Animas River watershed study area is presented in this section to provide the reader with a geologic framework for interpretation of background water quality. More detailed descriptions of geology and alteration and mineralization of the study area can be found in Yager and Bove (this volume) and Bove and others (this volume). The study area lies within the San Juan volcanic field of Tertiary age. The most prominent volcanic features of the area are the San Juan, Uncompahgre, and Silverton calderas, which formed about 28 million years ago (Lipman and others, 1976; Bove and others, 2001). Thick volcanic sequences of lava flows, ash-flow tuffs, tuff breccias, conglomerates, and mudflow breccias make up most of the bedrock in the study area (Burbank and Luedke, 1969; Lipman and others, 1973; Ringrose, 1982). The unaltered lavas and tuffs generally are of intermediate composition and are composed of plagioclase, biotite, augite, quartz, and hornblende.

Subsequent to deposition and lithification, the volcanic bedrock in the study area was hydrothermally altered and mineralized to varying degrees (Burbank and Luedke, 1969) as shown by the distribution of major alteration assemblages in figure 1. The earliest hydrothermal event was related to resurgence of the San Juan and Silverton calderas and resulted

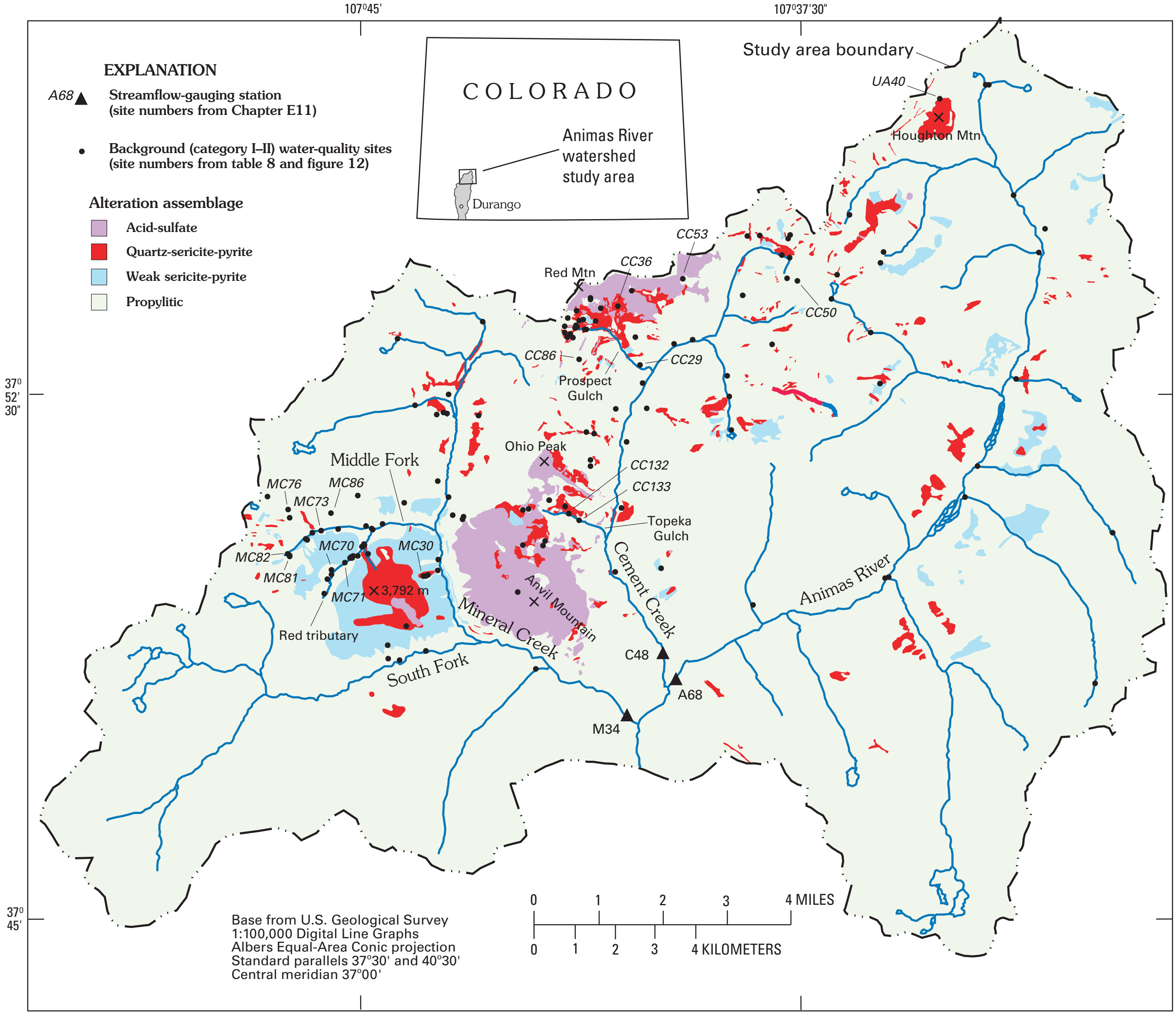

Figure 1. Animas River watershed study area, with distribution of major alteration assemblages.

in regional propylitic alteration of the bedrock (Burbank and Luedke, 1969). The propylitized bedrock underlies more than 90 percent of the study area; in outcrop it is characteristically green to gray in color (fig. 2*A*). The alteration assemblage comprises primarily epidote, chlorite, albite, illite, and calcite and includes finely disseminated pyrite (Burbank and Luedke, 1969).

The regional propylitic event was followed by three major episodes of magmatism, which were the source of most mineral deposition in the area (Casadevall and Ohmoto, 1977; Bove and others, this volume). Hydrothermal activity associated with these magmatic events superimposed more intense alteration assemblages (weak sericite-pyrite, quartz-sericite-pyrite, and acid-sulfate) upon the earlier propylitic assemblage (fig. 1). The earliest of these magmatic events was caused by monzonite intrusive activity and resulted in a subeconomic porphyry copper-molybdenum deposit (Ringrose, 1982), which is situated between Middle and South Forks Mineral Creek (fig. 1). The most intensely altered area of this early phase is centered on peak 3,792 m, south of Middle Fork Mineral Creek, which owes its distinct red color to quartz-sericite-pyrite altered bedrock at the center of the deposit (fig. 2*B*). The quartz-sericite-pyrite zone grades outward into a weak sericite-pyrite zone, which is characterized by metastable feldspars, sericite, pyrite, and occasional chlorite. Associated mineralized rock includes stockwork quartz-molybdenite-pyrite veinlets near the zone of most intense alteration, and polymetallic sulfide-bearing veins localized along fractures and faults on the periphery of the porphyry deposit (Ringrose, 1982). Minerals associated with the sulfide-bearing veins include sphalerite, tetrahedrite-tennantite, galena, and pyrite.

Later intrusions of dacite porphyry are related to a massive acid-sulfate hydrothermal system near Red Mountain and in the vicinity of Anvil Mountain and Ohio Peak (between Cement and Mineral Creeks). Much of the bedrock in this area is quartz-sericite-pyrite altered and contains as much as 20 percent pyrite; it commonly weathers to bright-red and orange fields of talus (fig. 2*C*). Extensive acid-sulfate alteration zones, which contain quartz, alunite, pyrophyllite, dickite, and diaspore with as much as 30 percent pyrite, are superimposed on the quartz-sericite-pyrite altered rock (Bove and others, 2000). Mineralization associated with the acid-sulfate alteration was localized along fault structures and hydrothermal breccia masses; dominant minerals are pyrite, sphalerite, galena, enargite, and tetrahedrite.

Later vein mineralization (post–20 Ma) was the cause of most economically important mineral deposits in the study area and appears to have been closely associated with intrusion of high-silica alkali rhyolite (Lipman and others, 1976). These veins are rich in pyrite and are mostly a polymetallic variety with variable proportions of chalcopyrite, galena, sphalerite, gold, and silver-bearing sulf-arsenide minerals (Nash, 1999). Manganese minerals including pyroxmangite and rhodochrosite are locally abundant in some veins. Adjacent to the vein, the wallrock is often altered to a quartz-sericite-pyrite assemblage. These envelopes of hydrothermally altered rock are narrow and typically are not more than twice the width of the vein (Bove and others, this volume).

Water-Quality Characteristics

We herein describe and compare water-quality characteristics of background and mining-affected surface water and drainage from selected mine sites in the Animas River watershed study area. For the purposes of this report, we combine the 108 category I and 38 category II sites into a group of 146 sites to represent background water quality in the study area. The rugged terrain of the watershed minimized mining-related features in the highest elevation areas; hence, many of the category I–II sites were located in headwater areas. Although some category III sites may be minimally affected by mining, category III and category IV sites were combined to represent mining-affected surface water in the watershed. In the assignment of category III and IV rankings, no consideration of distance from mine sites was made, despite the fact that metal concentrations can attenuate considerably downstream from mine contributions because of mixing and instream chemical reactions. Although more than 5,300 mining-related features have been mapped in the watershed (Church, Mast, and others, this volume), only about 170 mines have surface drainage (Peter Butler, Robert Owen, and William Simon, Unpublished report to Colorado Water Quality Control Commission, Animas River Stakeholders Group, 2001), of which 75 were sampled for water-quality analyses as part of this study (see Church, Mast, and others, this volume). Of these 75 sites, 20 are among a group of 32 mine sites that have been prioritized for remediation in the Animas River watershed by the Animas River Stakeholders Group (Unpub. report to Colorado Water Quality Control Commission, ARSG, 2001). These 32 sites represent the largest point sources of metals in the study area and account for nearly 80 percent of the annual metal loading to surface water from mining-related sources (Unpub. report to Colorado Water Quality Control Commission, ARSG, 2001).

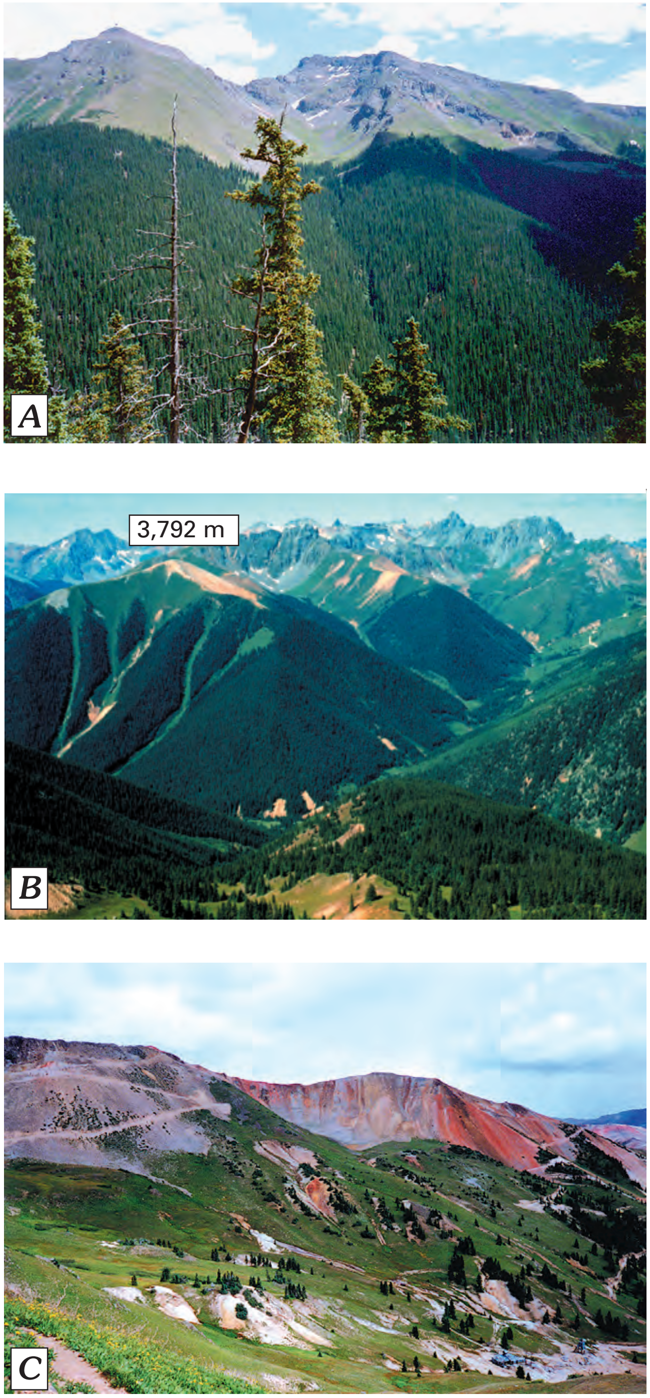

Figure 2. Areas of varied alteration. *A*, propylitized bedrock on east side of Cement Creek; *B*, subeconomic porphyry copper-molybdenum deposit centered on peak 3,792 m; *C*, acid-sulfate alteration in headwaters of Prospect Gulch.

Background Streams and Springs

Statistical summaries of dissolved constituent concentrations for background streams and springs (category I and II sites) are in table 2, and site locations are shown in figure 1. Of the 146 sites sampled, 90 were streams and 56 were springs. The background sites had a wide variation in chemical composition; pH ranged from 2.58 to 8.49, and specific conductance ranged from 12 to 2,180 µS/cm. All the sampled streams were well oxygenated (dissolved oxygen 6–9 mg/L), but many of the springs had low (<5 mg/L) dissolved oxygen concentrations. The low dissolved oxygen concentrations may indicate that many springs are fed by oxygen-depleted ground water discharging at the surface along faults or fractures. Springs and streams were dominantly calcium-sulfate type water. Sulfate concentrations ranged from 1 to 1,300 mg/L, and calcium concentrations ranged from 0.8 to 550 mg/L. Sites with high pH values (pH>6) typically had measurable concentrations of alkalinity (4–69 mg/L) and low aluminum and iron concentrations, whereas sites with low pH values (pH<6) had little measurable alkalinity and elevated concentrations of aluminum and iron (fig. 3). Other dissolved metals detected in most of the background samples include barium, copper, manganese, strontium, and zinc. Manganese was detected in 97 percent of samples, with concentrations ranging from less than 3 to 74,700 µg/L. Zinc and copper were detected in more than one-half the samples and reached concentrations as high as 14,400 µg/L and 372 µg/L, respectively. Other trace metals, including beryllium, chromium, cadmium, lead, lithium, nickel, and vanadium, were below detection in more than 90 percent of the background samples. Trace-metal concentrations showed patterns similar to those of aluminum and iron; the highest concentrations were at sites with lowest pH. For example, zinc was detected in more than 80 percent of samples with pH less than 4.5 but in only 30 percent of samples with pH greater than 4.5. Similarly, copper was detected in 69 percent of samples with pH less than 4.5 but in only 20 percent of samples with pH greater than 4.5. At the background sites, concentrations of several metals, including aluminum, copper, manganese, and zinc, were high enough to be potentially toxic to aquatic organisms (Colorado Water Quality Control Commission, 2001). Zinc and copper

Table 2. Summary statistics for dissolved constituent concentrations in background water-quality samples (category I–II) in the Animas River watershed study area.

[<, less than; ft^3/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25°C; mg/L, milligrams per liter; µg/L, micrograms per liter; $CaCO_3$, calcium carbonate; number of samples, 146]

Constituent	Minimum	25th percentile	Median	75th percentile	Maximum
Discharge, ft^3/s	0.001	0.020	0.069	0.50	7.46
Specific conductance, µS/cm	12	131	270	573	2,180
pH in standard units	2.58	3.60	4.89	6.83	8.49
Dissolved oxygen, mg/L	0.0	6.2	7.3	8.2	16.3
Alkalinity, mg/L as $CaCO_3$	<0.5	<0.5	<0.5	17.8	69.0
Sulfate, mg/L	1	41	90	230	1,300
Calcium, mg/L	0.8	14.1	27.6	47.3	550
Magnesium, mg/L	0.1	1.5	3.2	6.0	34.0
Sodium, mg/L	<0.1	0.8	1.5	3.7	13.0
Potassium, mg/L	0.1	0.3	0.5	0.8	2.8
Silica, mg/L	0.8	2.4	5.8	15.6	53.0
Aluminum, µg/L	<40	<40	359	4,130	71,400
Barium, µg/L	<2	12	22	34	101
Beryllium, µg/L	<1	<1	<1	<1	65
Cadmium, µg/L	<2	<2	<2	<2	84
Chromium, µg/L	<15	<15	<15	<15	50
Copper, µg/L	<4	<4	<4	14	372
Iron, µg/L	<30	<30	49	2,600	117,000
Lead, µg/L	<30	<30	<30	<30	141
Lithium, µg/L	<6	<6	<6	<6	43
Manganese, µg/L	<3	4	191	958	74,700
Molybdenum, µg/L	<10	<10	<10	<10	71
Nickel, µg/L	<20	<20	<20	<20	44
Strontium, µg/L	6	89	236	472	5,700
Vanadium, µg/L	<4	<4	<4	<4	11
Zinc, µg/L	<20	<20	28	194	14,400

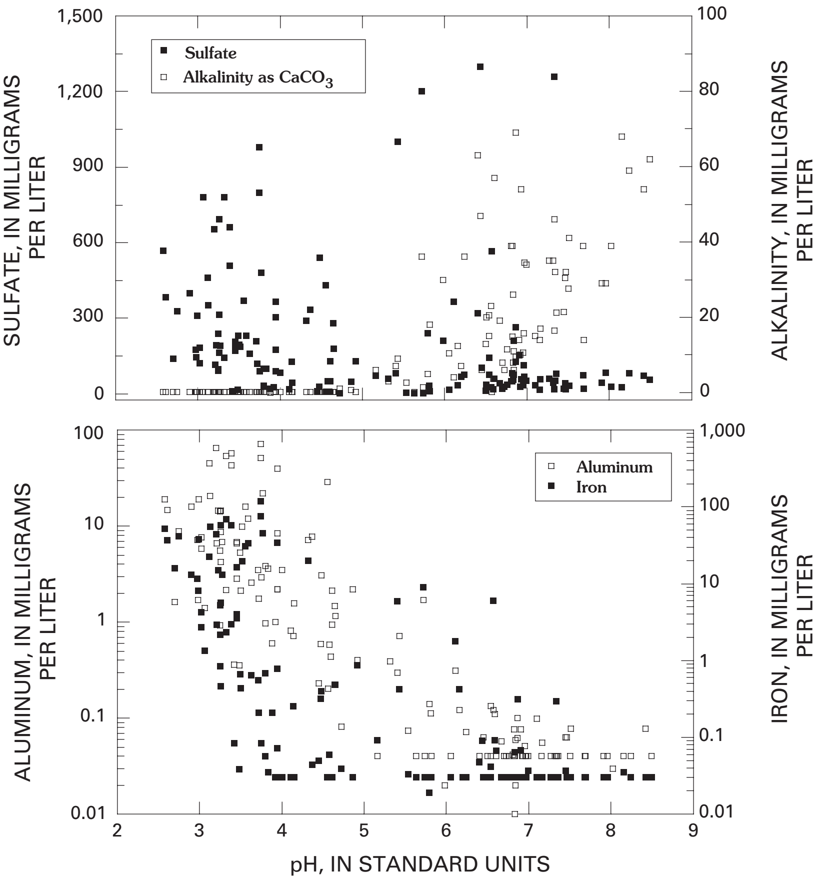

Figure 3. Dissolved sulfate, alkalinity, aluminum, and iron concentrations as a function of pH for background water-quality samples from Animas River watershed study area, 1997–99.

concentrations exceeded acute aquatic-life standards in 32 and 23 percent of samples, respectively, and chronic aquatic-life standards in 34 and 27 percent of samples, respectively. Manganese exceeded chronic aquatic-life standards in less than 10 percent of samples, whereas aluminum exceeded chronic aquatic-life standards in more than 50 percent of samples.

Statistical comparison of background stream and spring groupings using a Wilcoxon Signed-Ranks test indicated that spring samples were slightly more acidic and more concentrated than stream samples (p<0.01). The median pH of spring samples was 4.15, compared to a median pH of 6.11 for the stream samples. The median specific conductance of springs was 444 µS/cm compared to 230 µS/cm for the streams. Of the metals, only iron and manganese concentrations were statistically higher in the springs compared to the streams. The median concentrations of iron and manganese were 83 and 179 µg/L in the springs compared with 34 and 74 µg/L in the streams, respectively. These slight differences in chemistry probably reflect greater water-rock interaction and differing redox conditions in the spring environment compared to the stream channel, as well as less dilution by surface inflows.

A Spearman (nonparametric) correlation matrix was constructed to analyze relations among dissolved constituent concentrations in background streams and springs (table 3). Inspection of the correlation matrix indicated a high degree of collinearity within two dominant clusters of variables. In one cluster, strong positive correlations (r>0.550) were found among major cations and sulfate, with the exception of the correlation between calcium and potassium (r=0.453). Silica also was positively correlated with sulfate and major cations, with the exception of calcium (r=0.322). This cluster of related variables represents the most important dissolution products of mineral weathering. Pyrite and calcium sulfate minerals such as anhydrite and gypsum are the primary sources of sulfate, whereas major cations and silica primarily are derived from dissolution of carbonate and silicate minerals in the volcanic rock. The strong correlation between calcium and strontium (r=0.818) and weak correlation between calcium and silica (r=0.322) indicate that most calcium is probably derived from weathering of calcite and possibly gypsum rather than silicate minerals. In the second cluster of variables, strong positive correlations were found among sulfate, aluminum, iron, manganese, and zinc. Associations of metals with sulfate reflect the oxidation of pyrite and associated mineral deposits. Several metals also had strong negative correlations with pH (or positive correlations with hydrogen ion) because their solubility and adsorption characteristics are strongly controlled by pH.

Table 3. Spearman rank correlation coefficients (*r* values) showing the relation among dissolved constituent concentrations for background water-quality samples (category I–II) in the Animas River watershed study area.

[SO_4, sulfate; Ca, calcium; Mg, magnesium; Na, sodium; K, potassium; Si, silica; Al, aluminum; Ba, barium; Cu, copper; Fe, iron; Mn, manganese; Ni, nickel; Sr, strontium; Zn, zinc; *r* values greater than 0.550 shown in shaded cells]

	pH	SO_4	Ca	Mg	Na	K	Si	Al	Ba	Cu	Fe	Mn	Ni	Sr
SO_4	–.505													
Ca	.014	.766												
Mg	–.446	.923	.743											
Na	–.184	.618	.565	.620										
K	–.506	.684	.453	.715	.657									
Si	–.731	.695	.322	.638	.667	.731								
Al	–.838	.560	.092	.540	.264	.620	.753							
Ba	.130	–.346	–.297	–.254	–.324	–.150	–.282	–.210						
Cu	–.588	.384	.093	.346	.062	.382	.401	.558	–.074					
Fe	–.726	.596	.195	.539	.282	.521	.667	.730	–.198	.447				
Mn	–.731	.715	.326	.689	.361	.623	.699	.857	–.264	.541	.703			
Ni	–.216	.159	–.049	.115	–.170	.206	.067	.412	–.078	.299	.343	.302		
Sr	.177	.560	.818	.594	.408	.228	.061	–.056	–.065	–.087	.205	.153	.061	
Zn	–.564	.580	.299	.602	.234	.580	.486	.690	–.244	.545	.438	.706	.413	.109

Although sampling-site density was somewhat uneven across the watershed, some spatial patterns in water quality are apparent, as illustrated by the maps in figure 4. Among the three major basins (upper Animas River, Cement Creek, and Mineral Creek), streams and springs in the upper Animas River basin had distinctly higher pH values than those in the Cement and Mineral Creek basins. The median pH of background sites in the upper Animas River basin was 6.97, compared to the more acidic Cement and Mineral Creek basins, which had median pH values of 4.58 and 4.61, respectively. Although not shown in figure 4, the pattern for alkalinity was similar to that of pH. For example, the median alkalinity was 32 mg/L in the upper Animas River basin compared to less than 0.1 mg/L in the more acidic basins. The neutral water samples in the Animas River are attributed to the presence of carbonate minerals in the propylitically altered lavas that underlie most of this basin. Dissolved metals as illustrated by the spatial pattern in copper concentrations were typically lowest in the upper Animas River basin (fig. 4). This may be related to the higher pH of the surface water in that basin, or it may reflect fewer metal-rich sources compared with the other two basins. The exception to this pattern in dissolved metal concentrations was zinc, which tends to act more conservatively at high pH than other dissolved metals. Some of the most acidic and metal-rich background water was in the western part of the study area, particularly including streams and springs draining the mountains situated between Cement and Mineral Creeks and the area surrounding peak 3,792 m between South and Middle Forks Mineral Creek (fig. 1). Bedrock in both areas is extensively silicified and altered (Bove and others, this volume) and contains large amounts of disseminated pyrite (as much as 20 volume percent). Streams and springs draining these areas were generally characterized by low pH, high sulfate concentrations, and elevated levels of metals, particularly copper (fig. 4), manganese, and zinc (data not shown in fig. 4). Sodium (and silica) concentrations also were elevated in the vicinity of peak 3,792 m relative to other parts of the study area, perhaps because of weathering of the secondary albite that has replaced plagioclase during subsequent alteration events (Bove and others, this volume). Because the albite tends to be fine grained and is present throughout the groundmass, it may be more susceptible to weathering than the primary plagioclase grains.

To compare with other mineralized settings, water-quality data from background sites in the Animas River watershed study area are listed with water-quality data from mineralized but unmined areas in Colorado and Alaska (table 4). Water quality in the mineralized Summitville area in the eastern part of the San Juan Mountains was similar to the Animas River watershed study area for both major ion and dissolved metal concentrations. Both areas showed relatively high sulfate and calcium concentrations, and the dominant trace metals were manganese, zinc, and copper. This is not surprising, considering that the Summitville area is situated in the same volcanic field as the Animas River watershed study area and has undergone similar styles of alteration and mineralization (Miller and McHugh, 1994; Bove, 1996).

Geneva Basin in the Colorado Front Range is underlain by Precambrian gneiss and granite, which have been intruded by Tertiary dikes, sills, and stocks. Extensive pyritic alteration is associated with the Tertiary intrusions, and mineralization resulted mainly in small lead-zinc-silver veins (Bassett and others, 1992). Compared to the Animas River watershed study area, surface water in Geneva Basin had substantially lower calcium concentrations, yet higher concentrations of other major weathering products (not shown in table 4). This primarily reflects weathering of silicate minerals in the gneiss and granite that is accelerated by natural acidity produced by

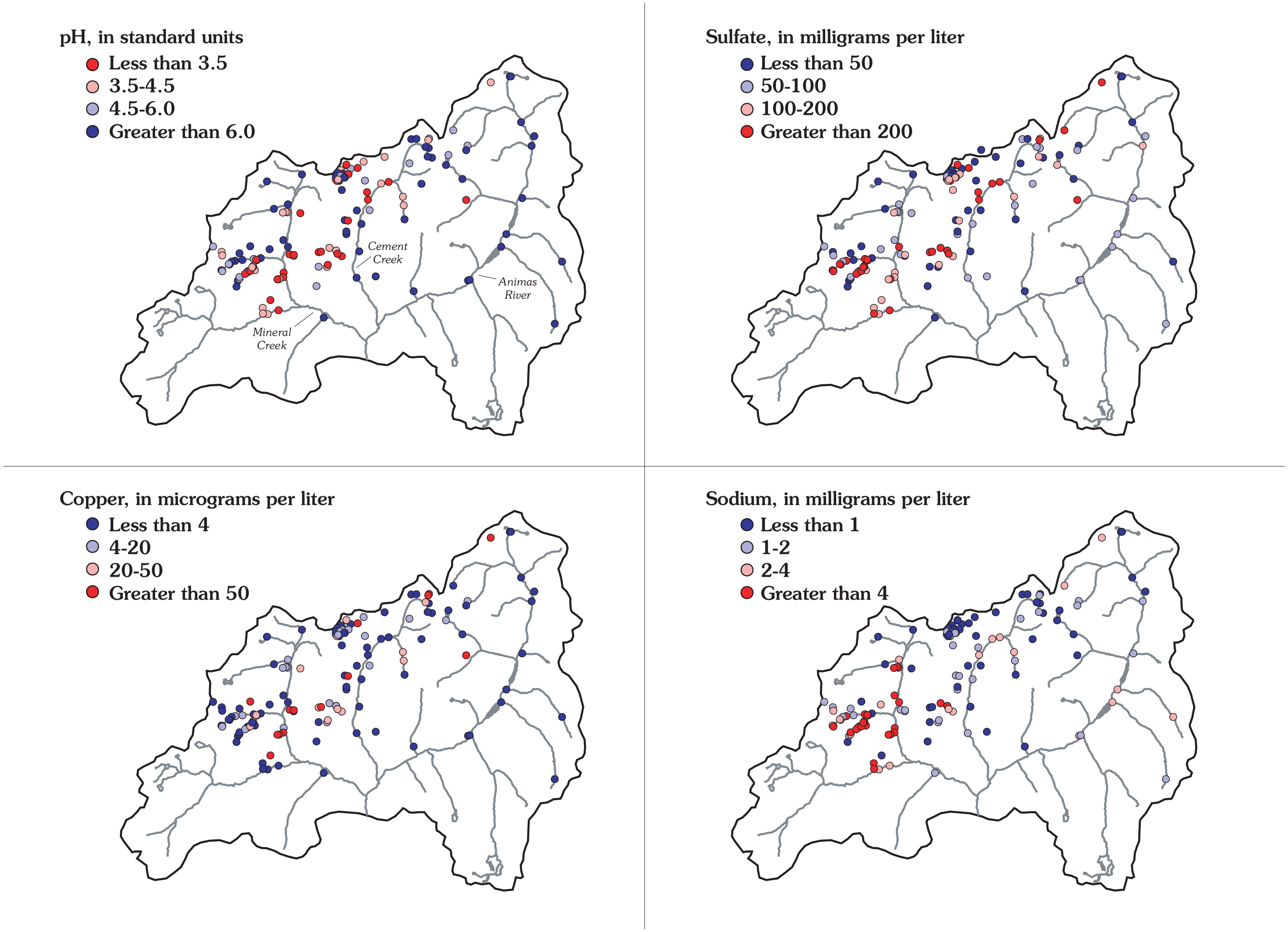

Figure 4. pH and dissolved concentrations of sulfate, copper, and sodium in background water-quality samples from Animas River watershed study area, 1997–99.

Table 4. Comparison of selected dissolved constituents in surface water draining selected mineralized but unmined areas in Colorado and Alaska.

[Spec. cond., specific conductance; µS/cm, microsiemens per centimeter at 25°C; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; --, not reported]

Unmined, mineralized areas	pH	Spec. cond. (µS/cm)	Sulfate (mg/L)	Calcium (mg/L)	Copper (µg/L)	Manganese (µg/L)	Lead (µg/L)	Zinc (µg/L)
Upper Animas River Basin, Colorado[a]	2.6–8.5	12–2,180	1–1,300	1–550	<4–372	<3–74,670	<30–141	<20–14,380
Summitville, Colorado[b]	2.5–8.5	50–2,400	6–1,250	6–170	<1–370	<10–15,000	<1–4	5–1,800
Geneva Basin, Colorado[c]	3.1–7.3	46–830	5.7–370	2–18	2–440	10–5,500	--	2–4,800
Drenchwater, Alaska[d]	2.8–7.0	38–2,150	12–1,180	5–23	<0.9–260	3–3,400	<0.3–10	4–2,600
Lik deposit, Alaska[d]	6.2–8.3	180–400	26–127	27–63	<10	<1–330	<10	<3–2,000
Weminuche Wilderness, unmineralized area, San Juan Mountains, Colorado[e]	5.2–8.7	4–22	0.7–5.5	0.4–3.3	0.2–0.4	1.8–7.2	0.1–1.5	0.5–1.2

[a] This study.

[b] Miller and others, 1999.

[c] McHugh and others, 1988.

[d] Kelley and Taylor, 1997.

[e] U.S. Geological Survey, unpublished data, 2000.

pyrite oxidation (Bassett and others, 1992). Dissolved metal concentrations were fairly similar between the Animas River watershed study area and Geneva Basin, perhaps reflecting similarities in the polymetallic vein deposits that occur in each area.

The Drenchwater and Lik deposits are shale-hosted silver-lead-zinc, massive sulfide deposits in the Brooks Range of northern Alaska. Despite different lithologies and deposit types than found in the Animas River watershed, this area was included in the comparison because it is one of only a few areas in the United States where water-quality studies were conducted prior to mining. Drenchwater deposit is acid producing and generates metal concentrations in surface water similar to those measured in the Animas River watershed study area (Kelley and Taylor, 1997). The only notable differences in water quality between the two areas were substantially lower concentrations of calcium and silica in the Drenchwater streams compared to the Animas River watershed study area. The Lik deposit yields nonacidic surface water with low dissolved metal concentrations, with the exception of zinc, compared to both the Drenchwater deposit area and the Animas River watershed study area. The water quality of the Lik deposit area is attributed to the presence of carbonate bedrock and abundant carbonate alteration minerals at Lik, which buffers the pH of the streams (Kelley and Taylor, 1997).

Lake chemistry in the Weminuche Wilderness in Colorado also was included in table 4 to provide comparable data for an unmineralized area with similar watershed characteristics to those of the study area, including topography, climate, and vegetation (Turk and others, 1993). The wilderness is located in the San Juan Mountains immediately south of the Animas River watershed study area but is outside the zone of extensive alteration/mineralization and drains metamorphic bedrock rather than volcanic bedrock. Surface water in the Weminuche Wilderness is dilute calcium-bicarbonate water containing very low concentrations of metals. Average sulfate concentrations in the study area were 300 times greater than in the adjacent wilderness, and average zinc concentrations, even in nonacidic surface water, were as much as 2,000 times greater in the study area than in the Weminuche Wilderness. These results illustrate striking differences in water quality between adjacent unmineralized and mineralized areas and clearly show that in mineralized areas, background metal concentrations in surface water can be substantially elevated because of background weathering of altered bedrock.

Mine Drainage and Mining-Affected Surface Water

Statistical summaries of dissolved constituent concentrations for drainage from 75 mines in the Animas River watershed study area that were sampled as part of this study are presented in table 5. As mentioned previously, although this group of mines represents less than one-half of the 170 draining mine sites in the study area, it includes 20 of the 32 draining adits with the largest metal loads (Unpub. report to Colorado Water Quality Control Commission, ARSG, 2001). Similar to background streams and springs, water quality at the sampled mine sites was quite variable; pH ranged from 2.35 to 7.77 and specific conductance ranged from 180 to 3,520 µS/cm. Mine drainage was dominantly calcium-sulfate water, in which sulfate ranged from 45 to 2,720 mg/L and calcium from 2 to 460 mg/L. Many samples contained elevated concentrations of aluminum (as much as 71,400 µg/L) and iron (as much as 686,000 µg/L). Nearly one-half the mines had low levels of dissolved oxygen (0–5.5 mg/L), indicating that flow from these adits may be derived from deep fracture systems in the bedrock or that pyrite oxidation was depleting the dissolved oxygen. Copper was detected in about one-half of the mine-water samples, but only 10 percent of samples had concentrations exceeding 1,000 µg/L. Although zinc was

Table 5. Summary statistics for dissolved constituent concentrations in mine-drainage samples from the Animas River watershed study area.

[<, less than; ft^3/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25°C; mg/L, milligrams per liter; µg/L, micrograms per liter; CaCO$_3$, calcium carbonate; number of samples, 75]

Constituent	Minimum	25th percentile	Median	75th percentile	Maximum
Discharge, ft^3/s	0.001	0.010	0.036	0.091	1.03
Specific conductance, µS/cm	180	474	741	1,090	3,520
pH in standard units	2.35	3.44	5.74	6.71	7.77
Dissolved oxygen, mg/L	0.0	1.6	5.5	8.2	11.6
Alkalinity, mg/L as CaCO$_3$	<0.5	<0.5	6.5	63.3	137
Sulfate, mg/L	45	169	309	509	2,720
Calcium, mg/L	2.0	36.8	79.6	164	460
Magnesium, mg/L	0.7	3.9	6.3	12.0	42.0
Sodium, mg/L	0.3	2.0	4.2	6.0	19.4
Potassium, mg/L	0.4	0.6	0.8	1.3	6.2
Silica, mg/L	2.0	5.5	10.0	16.0	30.0
Aluminum, µg/L	<40	42	616	4,700	71,400
Barium, µg/L	<2	6	10	15	62
Beryllium, µg/L	<1	<1	<1	<1	6
Cadmium, µg/L	<2	<2	<2	12	780
Chromium, µg/L	<15	<15	<15	<15	400
Copper, µg/L	<4	<4	6	89	98,600
Iron, µg/L	<30	225	4,650	17,800	686,000
Lead, µg/L	<30	<30	<30	<30	1,379
Lithium, µg/L	<6	<6	<6	18	56
Manganese, µg/L	<3	585	1,360	3,880	23,700
Molybdenum, µg/L	<10	<10	<10	<10	42
Nickel, µg/L	<20	<20	<20	<20	300
Strontium, µg/L	37	299	809	2,120	6,080
Vanadium, µg/L	<4	<4	<4	<4	5
Zinc, µg/L	<20	135	621	2,860	228,000

detected in more than 90 percent of adits, only 40 percent reached concentrations in excess of 1,000 µg/L. Other trace metals, including beryllium, cadmium, chromium, lead, lithium, nickel, and vanadium, were below detection in more than 50 percent of the sampled mine-drainage samples. On the basis of the mine-water classification scheme of Ficklin and others (1992), 40 percent of the mine-drainage samples would be classified as “near neutral, low metal” water types, and 20 percent as “acid, low metal” water types (fig. 5). Despite low base-metal concentrations in the “acid, low metal” group, many of these samples had elevated concentrations of dissolved iron, aluminum, and manganese. Approximately 15 percent of mine-drainage samples were classified as “near neutral, high metal” types. Many of these mines were associated with vein deposits located in areas where the surrounding bedrock had sufficient acid-neutralizing capacity to neutralize acidity produced by pyrite oxidation at the mine site. The elevated dissolved metal concentrations reflected the influence of other sulfide minerals such as sphalerite and chalcopyrite in the mineralized veins. The remaining 25 percent of mines were classified as “acid, high metal” and “high acid, high metal.” Many of the most acidic mine sites are in the intensely altered Red Mountain area, which is underlain by an extensive area of acid-sulfate hydrothermal alteration with associated polymetallic veins and breccia pipes (Bove and others, 2000). The high acidity of these mines reflects the low acid-neutralizing capacity of the acid-sulfate altered bedrock. Only one adit, the Koehler tunnel, fell in the range of the “high acid, extreme metal” water type. A more detailed discussion of mine-water chemistry and its relation to deposit type in the Animas River watershed study area can be found in Bove and others (this volume).

Although dissolved metal concentrations were elevated at some background sites in the study area, mine-drainage samples generally had higher dissolved metal concentrations than background sites. Results of a statistical comparison of background surface water (category I–II sites) with mine-drainage samples using the nonparametric Wilcoxon Signed-Ranks test are shown in table 6. This test was used rather than the parametric *t*-test due to the non-normal distribution of the chemical data sets. Results for comparison of background samples (category I–II sites) with mine-drainage samples show statistically significant differences (α=0.01) in concentrations for all the major ions (except potassium) and the

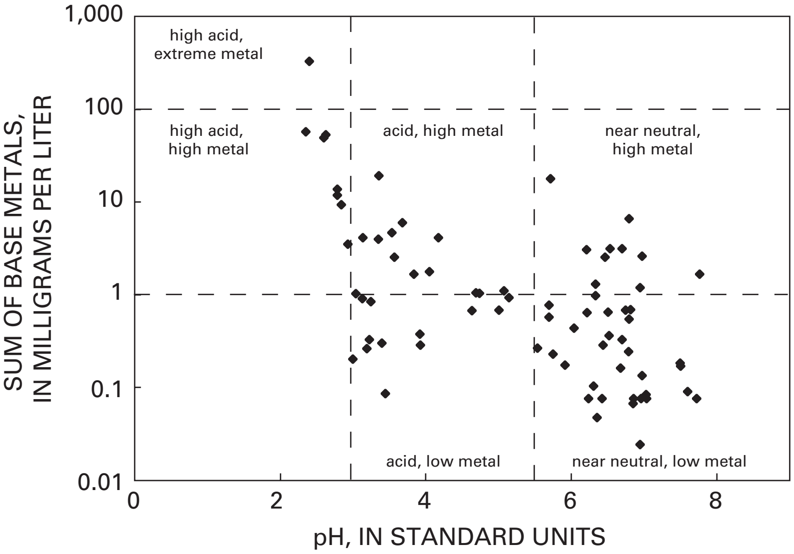

Figure 5. Sum of dissolved base-metal concentrations (zinc, copper, cadmium, lead, nickel) as a function of pH for mine-drainage samples from Animas River watershed study area, 1997–99.

dissolved metals barium, copper, iron, manganese, strontium, and zinc. For constituents with statistically significant differences, concentrations in the mine-drainage samples were higher than in the background samples with the exception of barium. Higher concentrations in the mine-drainage samples were not unexpected considering that chemical-weathering processes commonly are accelerated at mine sites because of greater oxygen availability and greater contact with freshly exposed mineral surfaces (Nordstrom and Alpers, 1999). Lower barium concentrations in mine drainage may reflect solubility controls on barium resulting from high concentrations of sulfate in the mine samples (Davis and others, 2000). Aluminum was not significantly different between the background and mine-drainage sample groups, perhaps because pH also was not significantly different between the two groups.

A statistical comparison of background surface water (category I–II sites) with mining-affected surface water (category III-IV sites) using the nonparametric Wilcoxon Signed-Ranks test also is shown in table 6. Results show statistically significant differences ($p>0.01$) in concentrations for copper, manganese, and zinc (table 6), which were generally higher in mining-affected sites than at background sites. No statistically significant differences in concentration were found for the remaining constituents except silica. The lack of distinction between the background and mining-affected streams may be due in part to attenuation of pH-dependent metals as mine drainage is mixed with dilute and higher pH surface water. By contrast, the elevated zinc and manganese concentrations in mining-affected water may reflect the tendency of these metals not to sorb or coprecipitate on particles at near-neutral pH values.

Box plots were constructed to compare the water quality of background sites with that of mine-drainage sites in each of the three major basins (fig. 6). Background sites include the 146 category I and II sites; mine-drainage sites included the 75 mine sites sampled as part of this study. Monthly samples collected at streamflow-gauging stations at the outlet of each basin (Animas River above Silverton, A68; Cement Creek, C48; and Mineral Creek, M34) were included for comparison (fig. 1, location of gauges). For more detailed information on sample-collection methods and analytical results at the streamflow-gauging stations, the reader is referred to Leib and others (this volume, Chapter E11). Results in figure 6 show substantial differences in water quality among the three basins. As noted previously, background samples in the upper Animas River basin had higher pH and lower sulfate, silica, and dissolved metal concentrations, except for zinc, compared with background samples in the Cement Creek and Mineral Creek basins. This most likely reflects the larger areal extent of propylitically altered rocks in the upper Animas River basin (Yager and Bove, this volume), which have a lower sulfide content and greater capacity to neutralize acidity than the more intensely altered mineral assemblages in other parts of the study area. Comparison of mine-drainage samples revealed that mine drainage in the Cement Creek and Mineral Creek basins was similar, with the exception of sodium, which was slightly higher in Mineral Creek, and sulfate and iron, which were higher in Cement Creek. In contrast, mines in the Animas River had substantially higher pH values and lower sulfate, magnesium, silica, aluminum, iron, and copper concentrations compared to mine drainage in the other two basins. Zinc was the only metal that was similar in concentration among the three basins. The differences in aluminum and iron concentrations are clearly related to pH, whereas variations in base-metal concentrations, particularly copper and manganese, may reflect differences in the chemical composition and mineralogy of mineral deposits within each basin. More aggressive weathering conditions in the acidic mines are probably

Table 6. Results from Wilcoxon Signed-Ranks test comparing dissolved constituent concentrations in background water-quality samples (category I–II) with mine-drainage samples and mining-affected surface water samples (category III–IV) in the Animas River watershed study area.

[*p*-values in bold indicate a statistically significant difference in concentration between the background and mining-affected sample groups at the 0.01 confidence level; <, less than]

Constituent	*p*-value for comparison with mine drainage	*p*-value for comparison with mining-affected surface water
pH	0.116	0.932
Specific conductance	**<.001**	.660
Sulfate	**<.001**	.706
Calcium	**<.001**	.376
Magnesium	**<.001**	.758
Sodium	**<.001**	.030
Potassium	**.006**	.907
Silica	.068	**<.001**
Aluminum	.954	.898
Barium	**<.001**	.733
Copper	**.019**	**<.001**
Iron	**<.001**	.424
Manganese	**<.001**	**.007**
Nickel	.107	.389
Strontium	**<.001**	.554
Zinc	**<.001**	**<.001**

the cause of higher silica and aluminum concentrations in the Cement Creek and Mineral Creek mines compared to mines in the upper Animas River basin (Nordstrom and Alpers, 1999).

Because stream water at the outlet of each basin is influenced by both background and mining-related sources of metals, concentrations measured at the gauging stations might be expected to fall between the range of concentrations measured at the background and mine-drainage sampling sites. This pattern is generally observed for the Animas River and Cement Creek basins but not always for Mineral Creek. In the Animas River, the ranges of concentrations at the gauging station and the background sites were similar except for manganese and zinc. These metals were higher at the gauging station and were more similar to concentrations measured in mine-drainage samples than to concentrations in the background samples. In Cement Creek, the ranges of concentrations at the gauging station were bracketed by the ranges of concentrations at the background and mine sites. In contrast, the range of concentrations measured at the Mineral Creek gauging station was not bracketed by the other two groups for pH, sodium, silica, and sulfate. These differences may be partly an artifact of sampling locations in this basin, which had the highest density of sites in the intensely altered area around peak 3,792 m. In addition, water quality at the Mineral Creek gauging station is influenced by the contribution of large volumes of dilute, high-pH water from South Fork Mineral Creek, which contributes more than 25 percent of the streamflow from this basin (Leib and others, 2003).

Relation Between Geology and Background Water Quality

To explore the relation between geology and water quality, background sites were grouped by the dominant alteration assemblage upstream from the sampling site on the basis of the major hydrothermal alteration assemblages mapped in the study area (fig. 1). Of the 146 samples, four water-quality sites were assigned to the acid-sulfate (AS) assemblage, 17 to weak sericite-pyrite (WSP), 33 to quartz-sericite-pyrite (QSP), and 69 to propylitic (PROP). Thirty-six of the PROP sites were further subdivided into a propylitic with vein-related alteration assemblage (PROP-V) because of the presence of large mineralized structures upgradient from the sites. Twenty-three sites were not assigned to an alteration assemblage because they drain areas underlain by a mixture of assemblages. For this study, the QSP group includes samples draining either QSP alteration and vein-related QSP alteration assemblages as mapped by Bove and others (this volume). Background springs and streams in the study area had a wide range of compositions that were spatially related to the degree of bedrock alteration (fig. 7). Streams and springs draining propylitically (PROP) altered rock had higher pH values (5.74–8.49) and relatively low dissolved metal concentrations (zinc, <20–237 µg/L; copper, <4–73 µg/L). Although not shown in figure 7, these sites also were characterized by measurable alkalinity (1.4–68 mg/L) and lower dissolved iron (30–310 µg/L) and aluminum (40–140 µg/L) concentrations. Propylitically (PROP) altered rock, which occurs throughout the study area, contains as much as 30 percent calcite (Bove and others, this volume), which dissolves to produce the neutral surface-water composition characteristic of this alteration assemblage. Despite the relatively high pH of these samples, most also had relatively high sulfate concentrations (>20 mg/L) relative to atmospheric deposition (<0.5 mg/L; Mast and others, 2001). These elevated sulfate concentrations indicate that disseminated pyrite in the propylitic bedrock also is an important source of solutes to surface water, although in this alteration assemblage calcite is sufficient to neutralize any acidity produced by the oxidizing pyrite. Some sulfate also may be derived from calcium sulfate minerals such as gypsum and anhydrite, which are common in some parts of the study area (Casadevall and Ohmoto, 1977; Bove and others, this volume).

In contrast to the propylitic assemblage, the QSP alteration assemblage generated acidic surface water (pH 2.70–6.16) with higher concentrations of iron (as much as 77 mg/L), reflecting an abundance of pyrite and a lack of acid-neutralizing minerals, particularly calcite. This acidic water also reacts readily with aluminosilicate minerals in the bedrock and can contain high concentrations of aluminum (as much as 66 mg/L) and silica (as much as 28 mg/L). The QSP samples also were enriched in zinc, copper, and manganese relative to the PROP samples because of the base-metal sulfide minerals associated with this alteration assemblage. Comparison of QSP samples from the subeconomic porphyry

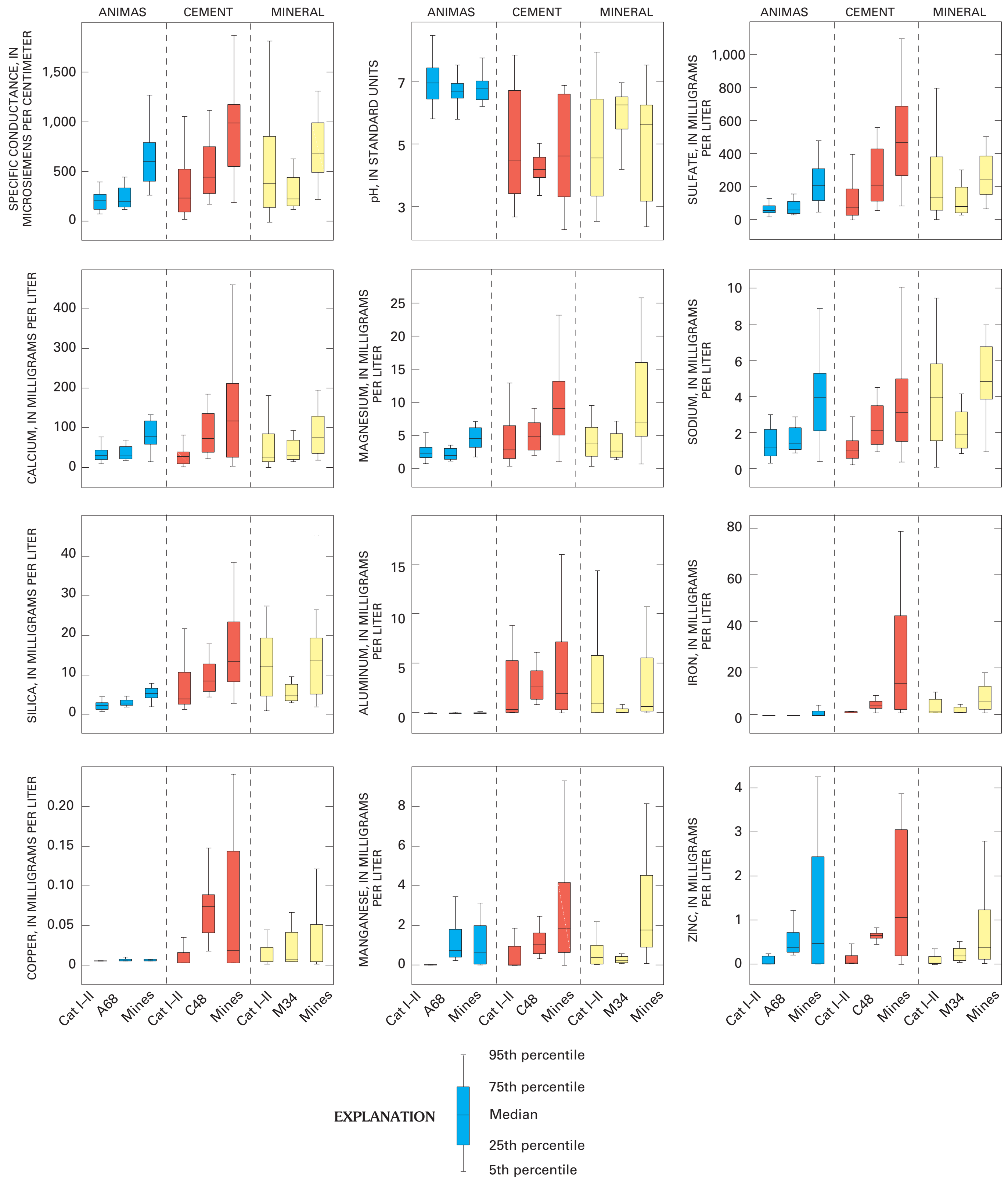

Figure 6. Comparison of dissolved constituent concentrations in background water-quality samples (category I–II), streamflow-gauging stations (A68, C48, M34), and mine-drainage samples (Mines) from the three major basins (upper Animas River, Cement Creek, Mineral Creek) of Animas River watershed study area, 1997–99.

copper-molybdenum deposit near peak 3,792 m with the acid-sulfate alteration near Red Mountain revealed no statistical differences in background water quality between these two deposit types. The AS assemblage was only represented by four samples; however, the AS samples showed a water-quality pattern distinctly different from that of the QSP alteration. Although the range of pH values was similar, sulfate concentrations were more than 10 times higher in the QSP samples than in the AS samples, and iron concentrations were more than 100 times higher. Median concentrations of copper and zinc were 31 and 201 µg/L, respectively, in the QSP samples, compared with detection-limit values in all but one AS sample. The AS sites may have lower concentrations because they may drain the surface of the acid-sulfate deposit, where post-mineralization oxidation has removed most of the sulfide minerals, leaving primarily silica (Plumlee and others, 1999). In contrast to this small group of AS samples, Bove and Knepper (2000) reported very high concentrations of metals at background sites draining an acid-sulfate assemblage in the headwaters of the Uncompahgre River north of Red Mountain. One explanation for the higher concentrations of metals in these samples compared to the four samples from the study area is that surface water in the area north of Red Mountain contacts the sulfide-rich core of the acid-sulfate altered zone rather than just the oxidized surface.

Samples from streams that drain WSP-altered rock are from localities primarily near the margins of the peak 3,792 m porphyry deposit; they generally were intermediate in composition between the QSP and PROP samples, perhaps reflecting a greater abundance of reactive minerals such as chlorite, feldspar, and calcite than occurs in the QSP assemblage. Although base-metal concentrations were elevated in only a few WSP samples, most had sulfate concentrations similar to that of the QSP samples. Some of the highest pH samples in this alteration assemblage had sulfate concentrations above 1,000 mg/L and relatively low zinc and copper concentrations. This water-quality signature may be a result of the dissolution of vein-filling gypsum or anhydrite (Bove and others, this volume), which could produce high concentrations of calcium and sulfate without the associated acidity and metals from sulfide oxidation. This explanation is supported by a sulfur isotope study (Wright and Nordstrom, 1999) in the vicinity of peak 3,792 m, which showed that many of the background sites with high sulfate and calcium concentrations had isotopic signatures more similar to that of gypsum than pyrite, indicating that dissolution of a calcium sulfate mineral was the dominant source of sulfate. The last alteration assemblage consists of samples that predominantly drain propylitically altered rock but are downstream from large mineralized structures or vein systems (PROP-V). Figure 7 shows that these samples have compositions ranging from PROP-like to QSP-like. The most acidic, metal-rich sites in this group were springs, many of which discharge along the middle reach of Cement Creek and may be related to large fault structures that run subparallel to the valley trend of Cement Creek (Luedke and

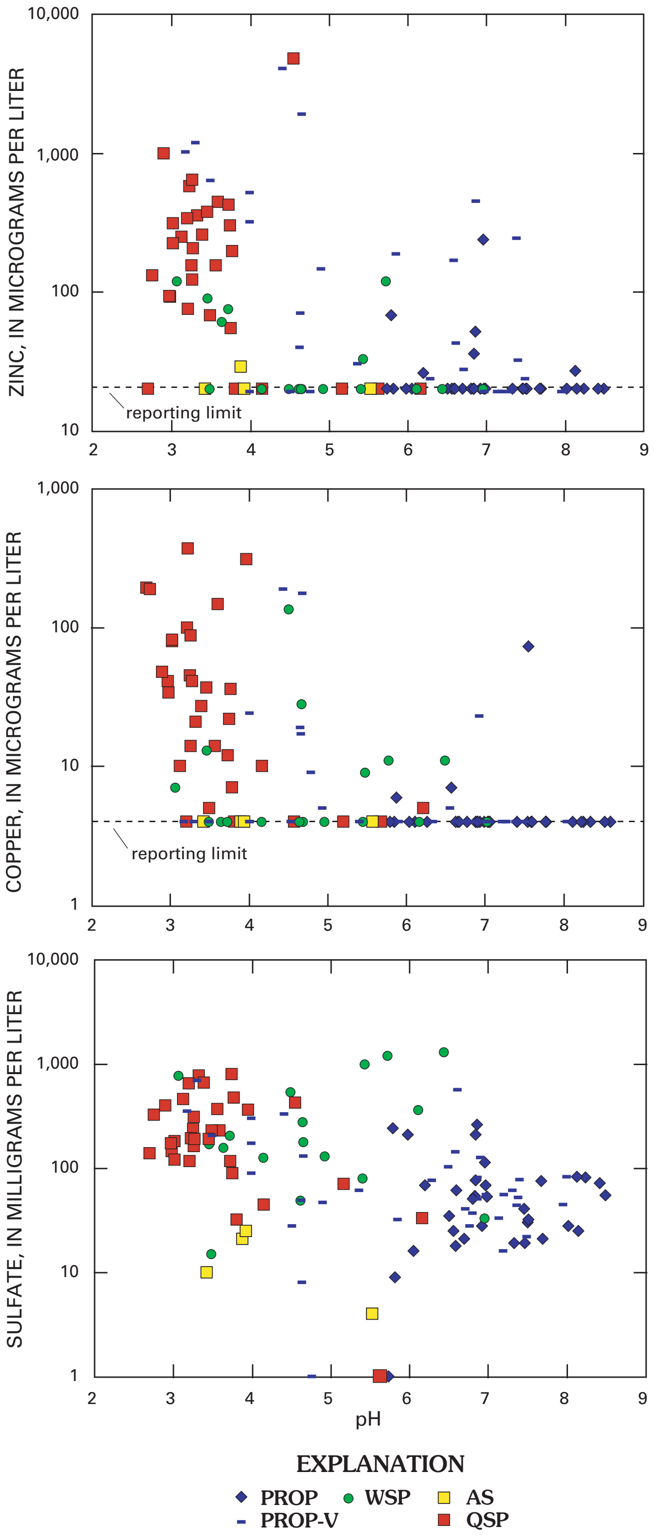

Figure 7. Dissolved zinc, copper, and sulfate concentrations as a function of pH for background water-quality samples from streams draining different bedrock alteration assemblages. Alteration assemblages are propylitic (PROP), propylitic with vein mineralization (PROP-V), weak sericite-pyrite (WSP), quartz-sericite-pyrite (QSP), and acid-sulfate (AS), 1997–99.

Burbank, 1996). An example of one of these springs is CC29 (fig. 1) near the mouth of Prospect Gulch, which discharges in a pool surrounded by terraces of actively forming ferricrete. Although the alteration assemblage upgradient from the site is predominantly PROP, the sample pH of 3.13 and zinc concentration of 1,070 µg/L were among the highest of the background samples. Bove and others (2000) suggested that the spring discharged at the base of a large fracture system that acted as a conduit transporting acidic water from QSP altered areas high above the site to the discharge point of the spring. The high zinc concentration in this sample may be the result of interaction of ground water with mineralized vein material along the fracture conduit. In contrast to the acidic springs in the PROP-V group, more than one-half of the samples in this group had neutral pH values and sulfate concentrations similar to the PROP group. Despite the similarities, most of these sites had higher zinc concentrations than the PROP samples, presumably reflecting the influence of mineral occurrences along the mineralized vein systems.

Although the sites previously discussed represent drainage from single alteration assemblages, many streams in the watershed flow across several different alteration assemblages, which can result in significant changes in water quality over a stream reach. An excellent example of this type of drainage regime is provided by a small tributary stream of Middle Fork Mineral Creek, referred to as Red tributary in Mast, Verplanck, and others (2000), that drains the northwest side of peak 3,792 m and is unaffected by mining (fig. 8). The tributary originates in an alpine cirque that is underlain by propylitically altered lavas of the San Juan Formation, then flows through progressively more altered rock related to the subeconomic porphyry copper-molybdenum deposit centered on peak 3,792 m. Water-quality samples were collected along the 2.1-km reach of the Red tributary during summer low flow to investigate downstream changes in stream chemistry in this unique area (table 7). At the head of the drainage (MC27, MC21) in the PROP area, stream water was a dilute calcium-sulfate-bicarbonate solution with a neutral pH and dissolved metal concentrations at or below analytical detection. Between MC21 and MC20, the alteration assemblage grades from PROP to WSP and the stream became acidic with substantial increases in dissolved aluminum, iron, manganese, and sulfate concentrations. The largest changes in solute concentrations occurred between MC19 and MC18, where the alteration transitions from WSP to QSP. This reach also is immediately downstream from a large debris fan that covers much of the northwest side of peak 3,792 m (fig. 8; Yager and Bove, this volume, pl. 1) and is composed of intensely altered rock from the center of the porphyry deposit (Yager and others, 2000). Concentrations of trace metals also had distinct patterns along the stream reach. Between the headwaters and mouth of Red tributary, manganese and zinc concentrations increased by nearly 1 to 3 orders of magnitude. By contrast, concentrations of most other trace metals, particularly copper and molybdenum, remained relatively low, even in the lower reach of the tributary where pH values were below 4.0. The relatively low concentrations of copper and molybdenum may indicate that most trace metals in this reach are derived from polymetallic veins along the margins rather than from deeper zones of copper and molybdenum enrichment in the core of the porphyry deposit.

Mass-loading profiles for the Red tributary were calculated to help determine sources and sinks of dissolved metals along the stream reach (Kimball, 1997). Discharge was multiplied by concentration to obtain the solute loads at each sampling point along the stream reach (fig. 8). Sites MC44 and MC43 were the major contributors of surface-water inflow along the reach. These two sources, combined with a number of small springs, accounted for less than 20 percent of the measured flow at MC22. This indicates that ground-water discharge along the channel is the dominant source of flow to the stream during low flow. The loading profiles in figure 9 show substantial increases in solute loadings along the reach, particularly between MC19 and MC17. For example, along this 384-m reach, sulfate loads increased by 4 times, aluminum by 43 times, iron by 184 times, and zinc by 12 times. Because the increase in discharge was only 20 percent, the results suggest that ground-water discharge along the tributary was rich in dissolved metals and sulfate. The average concentration of solutes in the ground water can in fact be estimated on the basis of the difference in loads between MC19, MC17, and MC43 (Kimball, 1997). The calculation yields concentrations of 3,880 mg/L for sulfate, 315,000 µg/L for aluminum, 530,000 µg/L for iron, and 18,000 µg/L for zinc. These concentrations were five times higher than those measured in any of the sampled springs in the Red tributary subbasin, indicating that a different source of ground water was contributing metals to the Red tributary. Yager and others (2000) suggested that the source of this metal-rich ground water is a large debris fan on the northwest side of peak 3,792 m composed predominantly of quartz-sericite-pyrite altered rock (fig. 8). Figure 9 also shows that iron loads decreased slightly downstream from MC17. This pattern probably is the result of precipitation of iron oxyhydroxide minerals, as evidenced by the thick, reddish-orange precipitates that coat the streambed downstream from MC18. Formation of iron oxyhydroxide also is consistent with speciation calculations using PHREEQC (Parkhurst, 1995), which indicated that stream water in the lower reach was in equilibrium with ferrihydrite. Although loss of other constituents was not apparent from the loading profiles, hydroxysulfate minerals such as jarosite (potassium-iron hydroxysulfate), schwertmannite (iron hydroxysulfate), or jurbanite (aluminum hydroxysulfate) (Nordstrom and Alpers, 1999) also might have been forming in the stream channel. Speciation calculations indicated that stream water was saturated with respect to jarosite and jurbanite at MC18, MC17, and MC22. Although the streambed precipitate was not analyzed, schwertmannite and jarosite were identified in soil samples collected at the toe of the large debris fan upgradient from the lower stream reach, indicating that hydroxysulfate minerals may be actively forming in this highly acidic weathering environment (Yager and others, 2000).

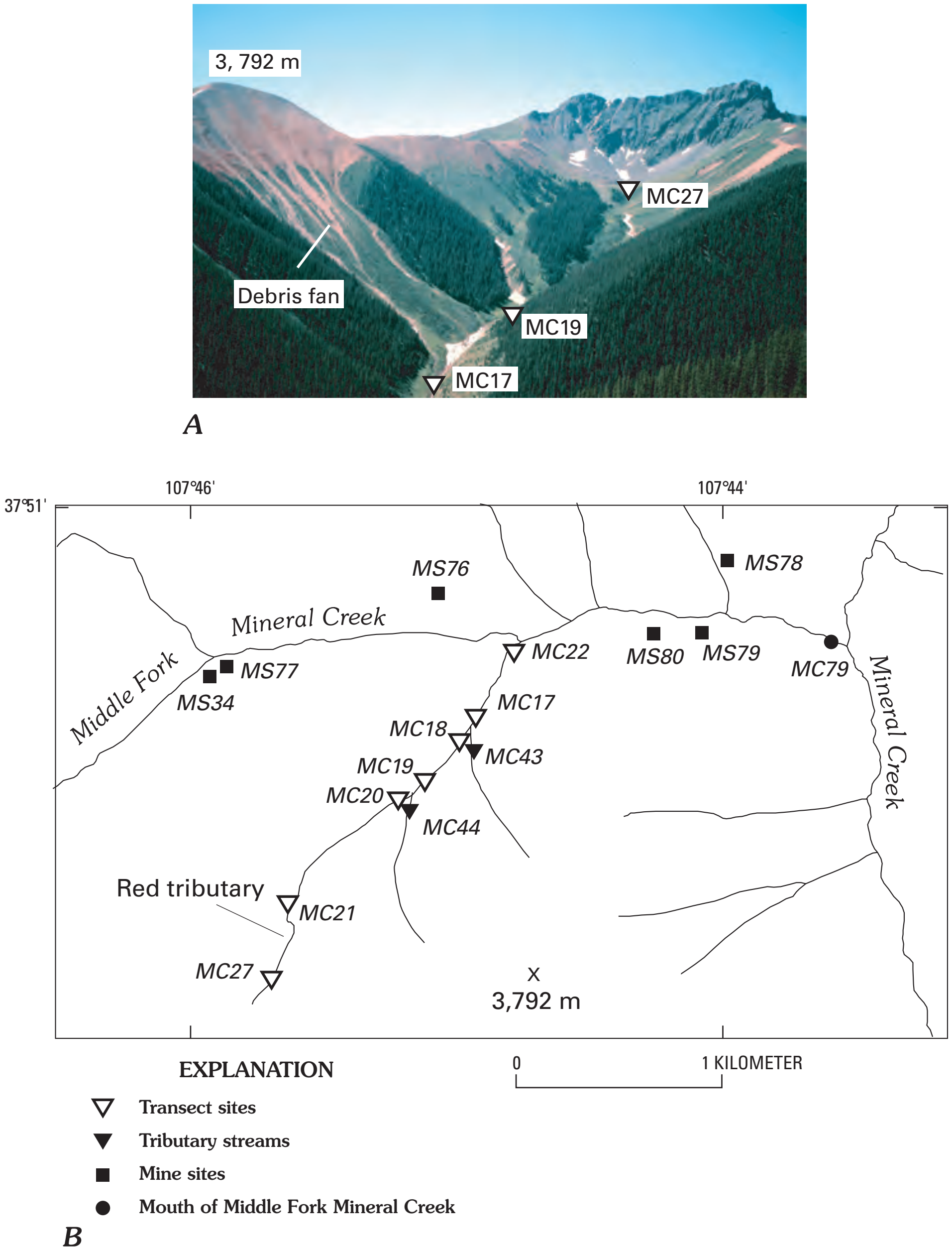

Figure 8. Red tributary and peak 3,792 m area. *A*, photograph of Red tributary and peak 3,792 m looking toward the south; *B*, map showing the Red tributary drainage with stream transect sampling sites.

Inverse Geochemical Modeling of Selected Background Springs

To constrain the likely weathering reactions controlling background water quality in the Animas River watershed study area, inverse geochemical models were developed for background water draining different alteration assemblages in the watershed. Inverse modeling uses mass-balance calculations based on water-quality and mineralogic data to infer water-rock interactions along a known flow path (Alpers and Nordstrom, 1999). For this study, the calculations were made using the computer code NETPATH (Plummer and others, 1994). To avoid the complications of mixing and instream chemical reactions, only spring-water samples were used in the modeling exercise. The chemistry of meteoric water was estimated from snowpack samples from Red Mountain Pass (Mast and others, 2001), and mineral assemblages and compositions were obtained from Bove and others (2000) and Yager and others (2000). Model results for nine samples are presented in table 8, which represent the different bedrock alteration assemblages in the watershed. Positive values in table 8 indicate mineral dissolution and negative values

Table 7. Dissolved constituent concentrations at stream transect sites along the Red tributary of Middle Fork Mineral Creek, October 2, 1999.

[Site numbers in figure 8; Alter., bedrock alteration assemblage; QSP, quartz-sericite-pyrite; WSP, weak sericite-pyrite; PROP, propylitic; Dist., distance downstream from headwater site in meters; Q, discharge in cubic feet per second; SC, specific conductance in microsiemens per centimeter at 25°C; Alk, alkalinity in milligrams per liter as $CaCO_3$; concentrations of calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), sulfate (SO_4), silica (Si), aluminum (Al), and iron (Fe) in units of milligrams per liter; concentrations of copper (Cu), manganese (Mn), and zinc (Zn) in micrograms per liter; <, less than]

Site	Alter.	Dist.	Q	SC	pH	Ca	Mg	Na	K	Alk	SO_4	Si	Al	Fe	Cu	Mn	Zn
MC27	PROP	0	<0.01	58	6.50	8.8	0.6	0.4	0.2	13	17	0.77	0.040	0.012	<4	<3	<20
MC21	PROP	408	.201	109	6.95	14	1.2	1.7	0.3	11	34	4.4	.051	.001	<4	19	<20
MC20	WSP	1,188	.487	419	4.65	61	4.3	4.6	0.5	<0.5	185	11.8	1.17	.510	4	494	25
MC19	WSP	1,284	.708	586	4.64	86	5.2	4.9	0.6	<0.5	276	12.1	1.47	.555	28	625	34
MC18	QSP	1,596	(1)	1,780	3.74	113	34	6.8	1.1	<0.5	1,090	16.2	71.4	130.4	20	2,150	353
MC17	QSP	1,668	.863	1,370	3.74	109	27	6.1	0.9	<0.5	846	15.6	51.5	83.8	22	1,770	325
MC22	QSP	2,136	1.01	1,410	3.32	112	28	7.0	1.0	<0.5	859	17.8	54.0	71.9	21	1,840	354

[1] Not measured.

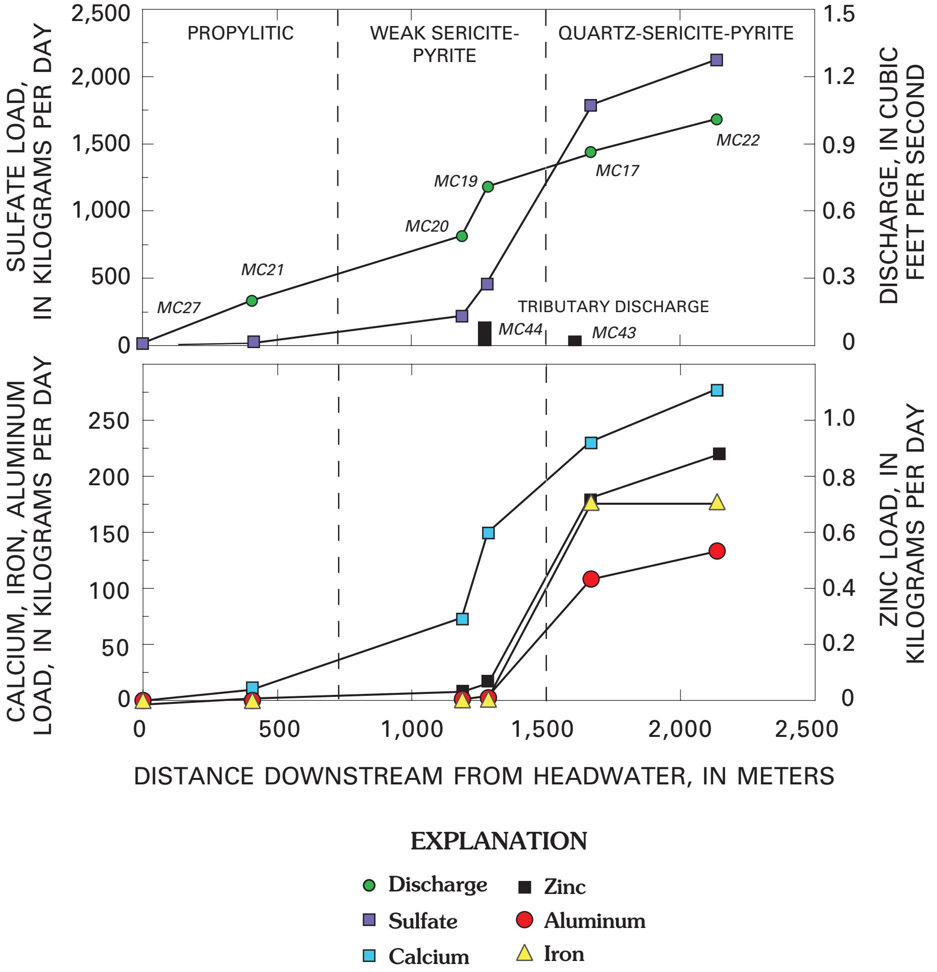

Figure 9. Discharge and mass loading profiles for dissolved sulfate, calcium, aluminum, iron, and zinc along the Red tributary of Middle Fork Mineral Creek, October 2, 1998. Sampling sites and numbers in figure 8.

Table 8. Results of mass-balance modeling of background springs draining different alteration assemblages in the Animas River watershed study area.

[Positive values indicate mineral dissolution, and negative values indicate mineral precipitation in units of millimoles of mineral per liter of water; site numbers (in parentheses) in figure 1; diss., dissolved; precip., precipitate; PROP, propylitic; WSP, weak sericite-pyrite; QSP, quartz-sericite-pyrite; AS, acid-sulfate; PROP-V, propylitic with vein mineralization; WSP-*cal*, modeled with calcite only; WSP-*gyp*, modeled with gypsum only; zinc from pyrite expressed as percentage of measured concentration; --, not included in model; <, less than; %, percent]

Mineral phase (diss. or precip.)	PROP (CC50)	WSP (MC70)	QSP (MC30)	QSP (CC36)	QSP (UA40)	AS (CC53)	PROP-V (CC86)	PROP-V (CC29)	WSP-*cal* (MC82)	WSP-*gyp* (MC82)
Pyrite	0.143	0.414	0.944	1.236	1.89	0.127	0.741	1.82	6.25	1.01
Calcite	.312	.517	.537	.869	.555	.028	1.09	.793	10.49	--
Chlorite	.005	.021	.037	.081	.032	.002	.067	.069	.163	.163
Sericite	.020	.029	.020	.020	.056	.003	.020	.020	.029	.029
Albite	.016	.280	.221	.011	.106	.001	.043	.046	.337	.337
Pyroxmangite	<.001	.008	.014	.027	.117	<.001	.010	.014	.047	.047
Kaolinite	–.036	–.132	--	.152	.586	--	–.158	.266	–.111	–.111
Ferrihydrite	–.142	–.307	–.868	–1.142	–1.89	–.127	–.741	–.837	–6.09	–6.09
Gibbsite	--	–.114	–.059	--	--	.016	--	--	–.444	–.444
Silica	–.013	--	--	–.421	–1.63	.171	--	--	--	--
Gypsum	--	--	--	--	--	--	--	--	--	10.49
Sphalerite	--	--	.0048	.0024	.220	--	.0027	.016	.0018	.0018
(zinc from pyrite)			(15%)	(41%)	(<1%)		(22%)	(9%)	(269%)	(43%)

indicate mineral precipitation. Although the results may not be the only reasonable models that account for the observed spring-water chemistry, they appear to be consistent with the mineralogy of the different alteration assemblages. Additional mineralogical data, particularly for soil minerals, would help to further constrain the weathering reactions.

The PROP spring (CC50 in fig. 1) is located in the headwaters of Cement Creek (fig. 1) and discharges from the base of a large talus slope composed of dense, dark-green, propylitically altered rock. The chemistry of CC50 was controlled primarily by dissolution of calcite and some pyrite; this result is consistent with the presence of calcite and disseminated pyrite associated with the propylitic alteration. Dissolution of small amounts of chlorite and albite was needed to account for other cations. The major secondary phases formed were ferrihydrite, which is required to remove the iron released by pyrite dissolution, and kaolinite, required to remove silica and aluminum. Precipitation of a small amount of silica also was required for CC50. Although the sample was close to saturation with respect to amorphous silica, the result might also be an artifact of the model due to differences in the composition of secondary minerals actually forming in the soil and the kaolinite used in the model.

The WSP spring (MC70) is located in the Red tributary subbasin and has a thick mound of ferricrete at its discharge point. The chemistry of MC70 also was dominated by calcite and pyrite dissolution; however, considerably more pyrite oxidation was needed at MC70 to account for the lower pH and higher sulfate concentration at this site, as compared with CC50. Another notable difference between these two springs was the increased importance of albite weathering in the WSP zone, which was necessary to account for the higher sodium and silica concentrations in this sample. This difference may reflect the additional acidity produced by pyrite oxidation, which might increase the dissolution rate of silicate minerals in the WSP alteration relative to the PROP alteration. Precipitation of ferrihydrite, kaolinite, and a small amount of aluminum hydroxide was necessary to remove iron, silica, and aluminum from solution. This result is consistent with speciation calculations that show the spring to be close to saturation with respect to ferrihydrite, kaolinite, and amorphous aluminum hydroxide.

Three springs (MC30, CC36, and UA40) were modeled to represent QSP or vein-related QSP alteration associated with different deposit types in the Animas River watershed study area. MC30 is on the east flank of peak 3,792 m and drains the center of the subeconomic porphyry copper-molybdenum deposit; CC36 is near Red Mountain within the acid-sulfate deposit; and UA40 discharges at the base of Houghton Mountain, which is an area hydrothermally altered by adjacent rhyolite intrusions. The model results for all three springs showed a predominance of pyrite weathering to account for the low pH values and high sulfate concentrations characteristic of these samples. Substantial amounts of calcite were necessary to account for the calcium, which was somewhat unexpected due to the paucity of calcium-bearing minerals in the QSP assemblage. One possibility is that calcium weathers from calcite contained in pods of less altered rock surrounded by QSP altered rock. Alternatively, calcium may be derived from vein-filling anhydrite or gypsum, which is present in some mineralized areas of the watershed (Casadevall and Ohmoto, 1977; McCusker, 1982). The highly acidic water in the QSP zone appears to promote the dissolution of an aluminosilicate mineral such as kaolinite in CC36 and UA40, which is a common component of the QSP assemblage. This result is consistent with speciation calculations, which indicate that the samples were undersaturated with respect to kaolinite. There also was substantially more albite dissolution in MC30 compared to CC36, perhaps because of differences in the mineralogy of the different deposit types. CC36 and UA40 also were close to saturation with respect to amorphous silica; however, the substantial amounts of silica precipitation required by the models may be an artifact of choosing kaolinite in the model rather than a more aluminum-rich phase such as andalusite or gibbsite. Substantial amounts of ferrihydrite precipitation were required to remove iron released by pyrite oxidation. MC30 and CC36 also were close to saturation with respect to jarosite, indicating that some iron also could be removed by formation of iron-sulfate minerals. Although the pH was similar between the QSP and AS samples, the model results for the AS spring were quite different, reflecting the dilute character of this water sample.

Two additional samples (CC86 and CC29) were modeled as examples of springs draining the PROP-V alteration assemblage. Spring CC29 discharges near the mouth of Prospect Gulch (discussed in previous section) and was acidic, whereas spring CC86, which is in the headwaters of Georgia Gulch, had measurable alkalinity. The results for the two springs indicate that more pyrite dissolution was required for CC29, because of higher sulfate concentrations, and more calcite dissolution was required for CC86, because of higher calcium and alkalinity. In contrast, dissolution of chlorite, sericite, albite, and pyroxmangite was nearly identical between the two samples. The only other difference was that CC86 required precipitation of kaolinite and CC29 required dissolution, which is consistent with the difference in pH of these two samples.

Spring MC82 (table 8) is in the Middle Fork Mineral Creek subbasin; it is categorized as WSP but has anomalously high concentrations of calcium, sulfate, and strontium. As discussed in the previous section, this water-quality signature may be a result of dissolution of some vein-filling gypsum or anhydrite, which could produce high concentrations of calcium and sulfate without the associated acidity and metals from pyrite oxidation. Results in table 8 are shown for two models (WSP-*cal* and WSP-*gyp*), one with calcite and one with gypsum. The first model requires 10.5 millimoles per liter (mmol/L) of calcite dissolution and 6 mmol/L of pyrite oxidation, which is considerably higher than pyrite oxidation amounts for even the most acidic QSP springs. In contrast, the model with gypsum resulted in 1 mmol/L of pyrite oxidation, with the remainder of sulfate coming from gypsum. This result appears to be more consistent with pyrite oxidation amounts modeled for the other springs and is consistent with speciation calculations, indicating that MC82 was close to saturation with respect to gypsum. Although the results for the gypsum-only model seem reasonable, it is not possible to distinguish between the two calcium sources (calcite versus gypsum) based on concentration data alone. The relative importance of gypsum dissolution can be better constrained using stable sulfur isotope data, which are discussed in detail by Nordstrom and others (this volume, Chapter E8).

Zinc concentrations in the background springs were modeled with the mineral sphalerite. Results are shown at the bottom of table 8 and indicate similar amounts of sphalerite dissolution for the QSP springs MC30 and CC36, the PROP-V spring CC86, and the WSP spring MC82. Substantially larger amounts of sphalerite were modeled at CC29 and particularly UA40 because of the high zinc concentrations at these two sites. Model results for sphalerite are not presented for the PROP spring CC50, the WSP spring MC70, and the AS spring CC53 because dissolved zinc concentrations were below the detection limit of 20 µg/L. In addition to sphalerite, trace metals in pyrite could also be a source of zinc to surface water (Bove and others, 2000). To compare the relative importance of zinc from sphalerite and pyrite, the amount of zinc liberated by pyrite oxidation was calculated based on the number of moles of pyrite dissolved in each model and the zinc concentration of disseminated pyrite from the Animas River watershed study area, which averages 435 parts per million (D.J. Bove, unpub. data, 2000). Results of these calculations for the modeled springs are presented at the bottom of table 8 in parentheses and are expressed as the percentage of the dissolved zinc derived from pyrite oxidation, with 100 percent indicating that all the dissolved zinc can be accounted for by pyrite oxidation. These values range from less than 1 percent in UA40 to just over 40 percent for CC36 and MC82 (gypsum model only), indicating that most zinc in the background springs was derived from zinc-rich ore minerals rather than pyrite oxidation. The low percentage at UA40 may indicate that flow in the spring is localized along a highly mineralized structure with significant zinc-bearing minerals. Zinc concentrations estimated from pyrite oxidation at CC50 (8 µg/L), MC70 (22 µg/L), and CC53 (7 µg/L) were consistent with the analytical results for these samples (all were <20 µg/L), indicating that contributions of zinc from deposit-related minerals were minimal at these sites. For MC82, the zinc concentration estimated from oxidation of pyrite in the calcite-only model was nearly three times the measured concentration in the sample. By contrast, the estimated zinc concentration for the gypsum-only model was only 40 percent of the measured concentration, further supporting the hypothesis that dissolution of calcium sulfate minerals is an important control on the water quality of this spring site.

Approaches for Describing Background Water Quality

Describing background sources of metals to surface water is an important aspect of reclamation in watersheds affected by inactive, historical mining, which needs to be addressed in order to establish realistic remediation goals for mining-affected surface water (Runnells and others, 1992; Alpers and Nordstrom, 2000). This need is particularly important in extensively mineralized areas such as the Animas River watershed study area, where naturally occurring dissolved metal concentrations in some springs and streams have been shown to exceed existing State and national water-quality standards (Wright and Janik, 1995). Differentiating between nonmining and mining-affected dissolved constituents is often a challenging task, particularly in historical mining districts, because water-quality data that predate historical mining activities generally are not available (Alpers and Nordstrom, 2000). Determination of background in these areas also may be complicated by a lack of information on the extent of underground workings of inactive mines and their effect on ground-water hydrology and chemistry. Many methods for describing background water quality in mining-affected areas have been published in the literature and are summarized by Alpers and Nordstrom (2000). One of the most frequently used approaches is the use of remote and proximal analogs. For remote analogs, water-quality data from a mining-affected area can be compared with water-quality data from an unmined, mineralized area that is distant from the mine site (Runnells and others, 1992; Kelley and Taylor, 1997). For proximal analogs, water-quality data from a mining-affected area can be compared with water-quality data from a nearby area (Miller and others, 1995; Will, 1998). Stable isotopes of water also have proved useful as tracers of mining-related contamination particularly in ground-water environments (Alpers and others, 1999). Geochemical modeling using both inverse and forward techniques is another approach that has been cited in the literature. Inverse modeling uses field data to interpret water-rock interactions, whereas forward modeling is used to predict or simulate geochemical reactions (Alpers and Nordstrom, 1999). Statistical methods also have been used to determine background metal concentrations—for example, the use of probability distribution diagrams as described by Runnells and others (1998). As pointed out by Alpers and Nordstrom (2000), each of these approaches has its limitations, and the success of a particular approach may differ from site to site depending on factors such as geology, hydrology, topography, climate, and mine-site geography. To overcome some of these limitations, it may be necessary to use several approaches to document uncertainties and establish a reasonable range of values for the mine site of interest (Alpers and Nordstrom, 2000).

Analysis of water-quality data collected in the Animas River watershed has shown that background weathering of hydrothermally altered bedrock is a significant source of metals and acidity to streams in some parts of the study area (Wright and Janik, 1995; Wright and Nordstrom, 1999; Bove and others, 2000; Mast, Verplanck, and others, 2000; Yager and others, 2000). However, quantification of background water quality, particularly on the watershed scale, has proved to be a difficult task, because of a number of complicating factors. One of the difficulties in describing background in the Animas River watershed is that of quantifying inputs of acidity and metals from mines and mine-related sites to streams. Church, Mast, and others (this volume) identified more than 5,300 mine-related sites scattered throughout the study area, of which 373 were determined to have the potential for significant environmental effect to streams. Although the water quality of most flowing adits in the study area has been characterized (Unpub. report to Colorado Water Quality Control Commission, ARSG, 2001), metal loads to streams can be difficult to quantify because of the mixing and chemical reactions that occur between the mine site and the stream (Plumlee and others, 1999). Mines also may affect ground-water chemistry, but because of the complexity of subsurface flow paths and geochemical reactions, it is very difficult to quantify the effect of ground-water contamination on streams. Metal loadings from nondraining mines and waste-rock piles also are poorly constrained in the study area. In addition to the inventoried sites, an estimated 8.6 million tons of tailings from milling operations were flushed into streams (Jones, this volume, chapter C), some of which were deposited as fluvial sediment (Church, Fey, and Unruh, this volume). This mining-affected sediment also may contribute metals to surface water; however, the magnitude of this contribution is difficult to quantify separately. Other human-related features and activities that may affect water quality include the extensive network of 4-wheel drive roads and the large numbers of sheep that are grazed at high elevations throughout the study area during summer.

Hydrologic factors also can complicate estimation of background water quality in the Animas River watershed study area. The accumulation of a deep seasonal snowpack causes large seasonal fluctuations to occur in streamflow, and the proportions of nonmining and mining-affected dissolved constituents may vary significantly through the annual hydrologic cycle (Leib and others, 2003; Leib and others, this volume, Chapter E11; Sullivan and Drever, 2001). Further, once metals enter the surface-water system, processes including precipitation, sorption, and sedimentation can change dissolved metal concentrations in streams, making it difficult to trace the metals from source to stream. Another complicating factor is the lack of knowledge of ground-water chemistry and flow paths in the study area. Few direct measurements of ground water in the basin have been made, but the highly fractured nature of the bedrock would suggest that subsurface flow would be an important component of the hydrologic system (Yager and Bove, this volume). The example of the Red tributary illustrated that ground water accounted for most of the discharge and metal load in stream water draining that highly altered area of the watershed. Results from tracer-injection studies on the lower reach of Cement Creek indicated that diffuse subsurface flow accounted for about 25 percent of the flow in the stream during low flow and a significant fraction of the instream chemical load (Kimball and others, 2002; Kimball and others, this volume, Chapter E9).

Perhaps the factor that most complicates the estimation of background water quality in the study area is the complex geology. Metal-source determination presents a challenge because of the temporal and spatial overlap of magmatism, mineralization, hydrothermal alteration, and fracturing within the San Juan and Silverton calderas, where historical mining activities were centered (Yager and Bove, this volume). Multiple episodes of mineralization created deposits with a range in metal concentrations that in some parts of the study area overlap each other (Burbank and Luedke, 1969; Bove and others, this volume; Nash and Fey, this volume, Chapter E6; Yager and Bove, this volume). As demonstrated here and by Bove and others (this volume), the type of mineral deposit and degree of hydrothermal alteration have a strong influence on water chemistry; therefore, a detailed understanding of geology is critical in defining background sources of metals to surface water.

In light of the complicating factors discussed herein, the use of a single method is unlikely to provide an adequate estimate of background water quality, in a large, complex watershed such as the Animas River watershed study area. In some situations, evaluation of background sources in smaller and more geologically similar subbasins of the study area may be more feasible. In the following sections, several different approaches are presented for describing or estimating background water quality on different scales within the study area, including (1) statistical descriptions of water quality, (2) mass balance calculations, (3) isotopic applications including use of strontium isotopes and stable isotopes of sulfate, and (4) rare-earth elements as tracers in surface water. None of these approaches has proven to be completely successful in the Animas River watershed because of the complexities and difficulties described previously. The approaches presented here are techniques that may be applied in other areas where complexities may be minimized, possibly through investigations on smaller scales.

Statistical Descriptions

Statistical methods to describe geochemical background in the literature range from simple approaches such as statistical summaries and probability distribution diagrams to complex techniques such as multivariate analysis and pattern recognition (Runnells and others, 1998). Because of the relatively large number of water-quality samples collected in the Animas River watershed study area, simple statistical summaries may provide useful information regarding ranges of dissolved metal concentrations in background surface water, which can then be compared to dissolved metal concentrations measured at mine sites. One means of presenting these statistical summaries is with box plots, which provide a concise graphical means of comparing the central values, spread, and symmetry of the data among different groups of samples (Helsel and Hirsch, 1992). For the standard box plot, the lower and upper ends of the box define the 25th and 75th percentiles, respectively, and the center line is the median. The whiskers generally extend to the 5th and 95th percentiles. In the study area, water quality was found to be strongly controlled by the degree of bedrock alteration, so background water-quality samples were grouped by the major mapped alteration assemblages shown in figure 1—propylitic (PROP), weak sericite-pyrite (WSP), and quartz-sericite-pyrite (QSP)—for the box plots (fig. 10). The one exception was the AS group, which was combined with the QSP group because of the small number of samples (*n*=4). The concentration ranges in mine adit discharge from 75 sites also were included for comparison, although the mines were not subdivided by alteration or deposit type. For many of the background samples in the PROP group, most of the dissolved metal concentrations, particularly copper and zinc, were below the analytical reporting limits. Rather than substitution of a single value for the "less than" values, as is more commonly done, we estimated summary statistics using the maximum likelihood method described by Helsel and Hirsch (1992). The resulting box plots comparing background water and mine discharge are presented in figure 10 for pH and dissolved calcium, sulfate, copper, manganese, and zinc concentrations. Copper, manganese, and zinc were chosen because they are dissolved constituents that are potentially most toxic to aquatic organisms in the study area (Unpub. report to Colorado Water Quality Control Commission, ARSG, 2001). Sulfate concentrations and pH are indicators of the extent of pyrite oxidation, and calcium concentrations are a general indicator of weathering.

The box plots of pH show the expected trend with the highest values in the least altered (PROP) rock and the lowest values in the most intensely altered (QSP) rock (fig. 10). The mine-drainage samples fall within the range of values defined by all three background groups. Calcium shows a slightly different pattern with higher concentrations in the WSP group compared to both the PROP and QSP sample groups. The high calcium in the WSP group probably reflects the influence of gypsum dissolution, particularly for samples collected in the vicinity of the porphyry deposit at peak 3,792 m. The range of calcium concentrations in the mine samples is similar to the WSP group, indicating that gypsum may be a common accessory mineral in mineral deposits throughout the study area. Sulfate concentrations were elevated in the WSP and QSP groups relative to the PROP group, reflecting the influence of large amounts of pyrite associated with the more intensely altered rock and mineral deposits and to a lesser extent the presence of secondary sulfate minerals such as gypsum along veins and fractures. The patterns among metals (copper, zinc, and manganese) were similar and showed increasing concentrations with increasing alteration intensity; the highest concentrations were in the mine-drainage samples. In contrast to sulfate, which is derived from ubiquitous pyrite, these metals are derived from deposit-related sulfides and accessory minerals, which tend to be localized along mineralized veins and structures and are common at inactive mine sites and in waste dumps. A similar observation was made by Wirt and others (2001) in Prospect Gulch, where surface water draining inactive mine sites had elevated base-metal concentrations relative to naturally acidic surface water produced by regional weathering of the intensely altered bedrock.

Although figure 10 shows some pronounced differences between background and mining-affected water samples, the application of these statistical summaries to

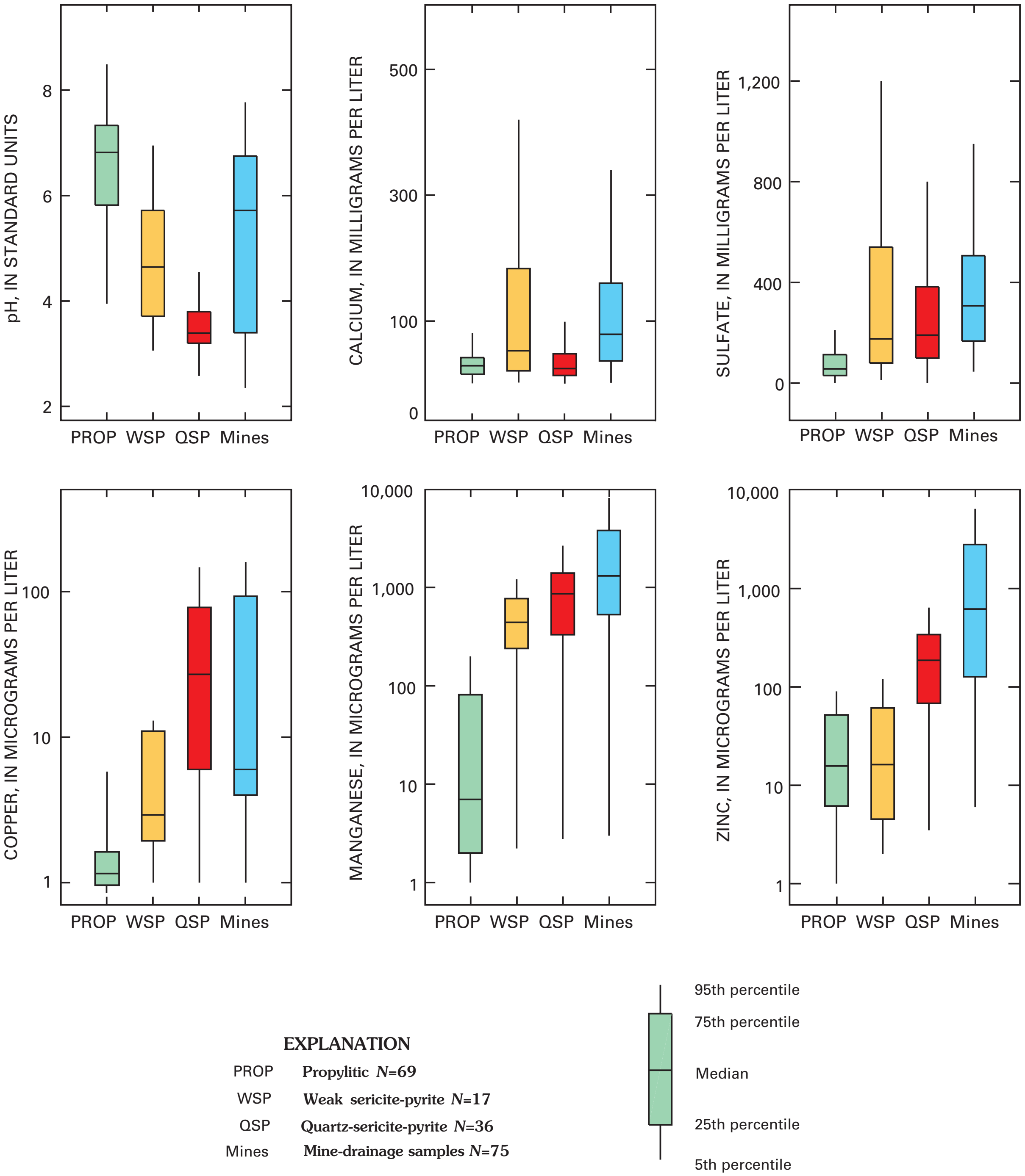

Figure 10. Comparison of dissolved constituent concentrations in mine-discharge samples and in background water-quality samples draining different alteration assemblages.

estimate background has several limitations. First, many of the category I–II sites are located in headwater areas of the watershed and may not accurately represent the chemistry of higher order streams because of mixing and instream chemical reactions, as well as differences in hydrologic residence times. Second, the chemistry of category I–II sites may not be representative of deeper ground water that is perhaps a more important component of flow in higher order streams and that may be the source of discharge at many mine sites. Finally, because the distribution of alteration assemblages is variable within the study area (fig. 1), mine sites need to be evaluated individually to determine which alteration assemblage and corresponding background water-quality type are most representative at the mine site of interest.

In addition to the simple box plot approach, background water quality in the study area also was evaluated using principal component analysis (PCA), a more complex statistical analysis tool useful for evaluating similarities and differences between multivariable data. Kimball and others (this volume) provide a good description of the use of PCA in evaluating water-quality data. In summary, principal components represent a set of new, transformed reference axes that are linear combinations of the original variables. The first principal component (PC1) is oriented along the direction of the greatest variance in the data, and the second principal component (PC2) is orthogonal to PC1 and is oriented to show the next greatest amount of variance in the data. Depending on how strongly correlated the variables are, more principal components can be generated, and each is orthogonal to the previous. In general, three principal components will explain a large percentage of the variance for the type of data presented here. The data analysis presented herein includes water-quality results for all the category I–II spring and stream samples in addition to mine-drainage samples. All analytical results were converted to millimoles per liter and log transformed. The principal component score is the projection of each sample onto the principal component axis and is a useful tool in comparison of samples.

Figure 11*A* displays the principal component scores for the first two principal components (PC1 and PC2) with samples coded by alteration type for the category I–II samples and the mine-drainage samples. The inset plot displays the eigenvectors that represent the projection of the original variables in PC1 and PC2 space. Trace metals cadmium, copper, nickel, lead, and zinc, which are contained primarily in sulfide minerals, plot in the lower right quadrant of the inset plot along with hydrogen ion. The upper right quadrant contains constituents that are primarily derived from the weathering of rock-forming minerals, such as calcium, magnesium, sodium, and silica. Although aluminum is primarily derived from the weathering of rock-forming minerals, its aqueous chemical properties are strongly controlled by pH; thus, it plots in the lower right quadrant. In the inset plot, the sulfate eigenvector lies between calcium and iron because pyrite and calcium sulfate minerals such as gypsum and anhydrite are the two dominant sources of stream-water sulfate. The only constituent that plots in the upper left quadrant is alkalinity, which increases with decreasing acidity. The lower left quadrant of the inset plot does not contain any eigenvectors and represents a field for samples that have low concentrations of dissolved constituents. In the biplot of principal components (fig. 11*A*), samples from AS, PROP, and QSP alteration assemblages plot in separate fields, although samples from PROP-V and WSP alteration assemblages, and mine-drainage samples overlap these fields. As expected from the box plots (fig. 10) and geochemical modeling, most of the QSP and some of the mine-drainage samples plot in the lower right quadrant, but many of the mine samples plot in the upper portion of the plot as well. The PROP samples plot on the left side of the biplot in a field consisting of higher alkalinity and pH and lower solute concentrations. The spring and stream samples classified as PROP-V primarily plot within the field defined by PROP samples, but some of the PROP-V samples plot in the metal-rich field.

To further investigate patterns in the data set, the PCA scores were grouped using a clustering analysis routine to see if mine-drainage samples are statistically distinct from category I–II samples (fig. 11*B*). The clustering analysis utilizes all the principal component scores, not just PC1 and PC2; thus on the two-dimensional plot in figure 11*B* some groups overlap. Group 1 represents sites with dilute, circumneutral water chemistry and contains samples from all the alteration assemblages (table 9). Water collected at these sampling sites probably has short flow paths and minimal water-rock interaction. Group 2 primarily consists of PROP and mine-drainage samples that are within areas of extensive propylitic alteration. These samples have relatively high pH and high alkalinity, calcium, and strontium concentrations. The category I– II samples in this group are typically at lower elevations than the group 1 samples and probably have longer hydrologic residence times. Group 3 samples plot between groups 1 and 2, and the group primarily contains PROP and PROP-V samples with low metal concentrations. Eighteen of the twenty group 4 samples are from locations in the Middle Fork Mineral Creek subbasin. Groups 5 and 6 samples are acidic; these two groups contain both category I–II samples and mine-drainage samples. Group 6 samples generally have higher solute concentrations than group 5 samples. Of the 33 samples in group 7, thirty-one are from mines that produced ore. Group 8 also consists almost entirely of mine-drainage samples, but differs from group 7 in that these samples are all acidic and have extremely high dissolved metal concentrations. The eight groupings provide some insights into controls on water quality in the study area. First, the classification of sampling sites by alteration assemblage appears to provide a reasonable predictor of water quality, although samples for a given alteration type can exhibit a wide range in water composition. This range in composition is likely a result of differences in hydrologic residence times as well as variations in mineralogy within each alteration assemblage. Overall, the groups that are primarily composed of category I and II samples have low trace-metal concentrations. Mine-drainage samples primarily fall in groups with elevated metal concentrations (groups 7 and 8); however, some samples cluster in groups that are dominantly composed of category I–II samples. Many of these low-metal mine-drainage samples were collected from prospects and small adits that never produced ore and hence produce minimal acid-mine drainage.

Overall, the PCA and the clustering analysis of this data set demonstrate that alteration assemblage is the dominant control on background water quality, and this results in a wide range in water quality across the study area. Similarly, mine-drainage samples also exhibit a wide range in water quality, which is largely controlled by the alteration type of the surrounding bedrock. Differences in mineral deposit type also control water quality at mines, particularly for trace-metal concentrations (Bove and others, this volume). In addition, many of the sites classified as mining related were prospects or small mines that do not produce significant acid-mine drainage.

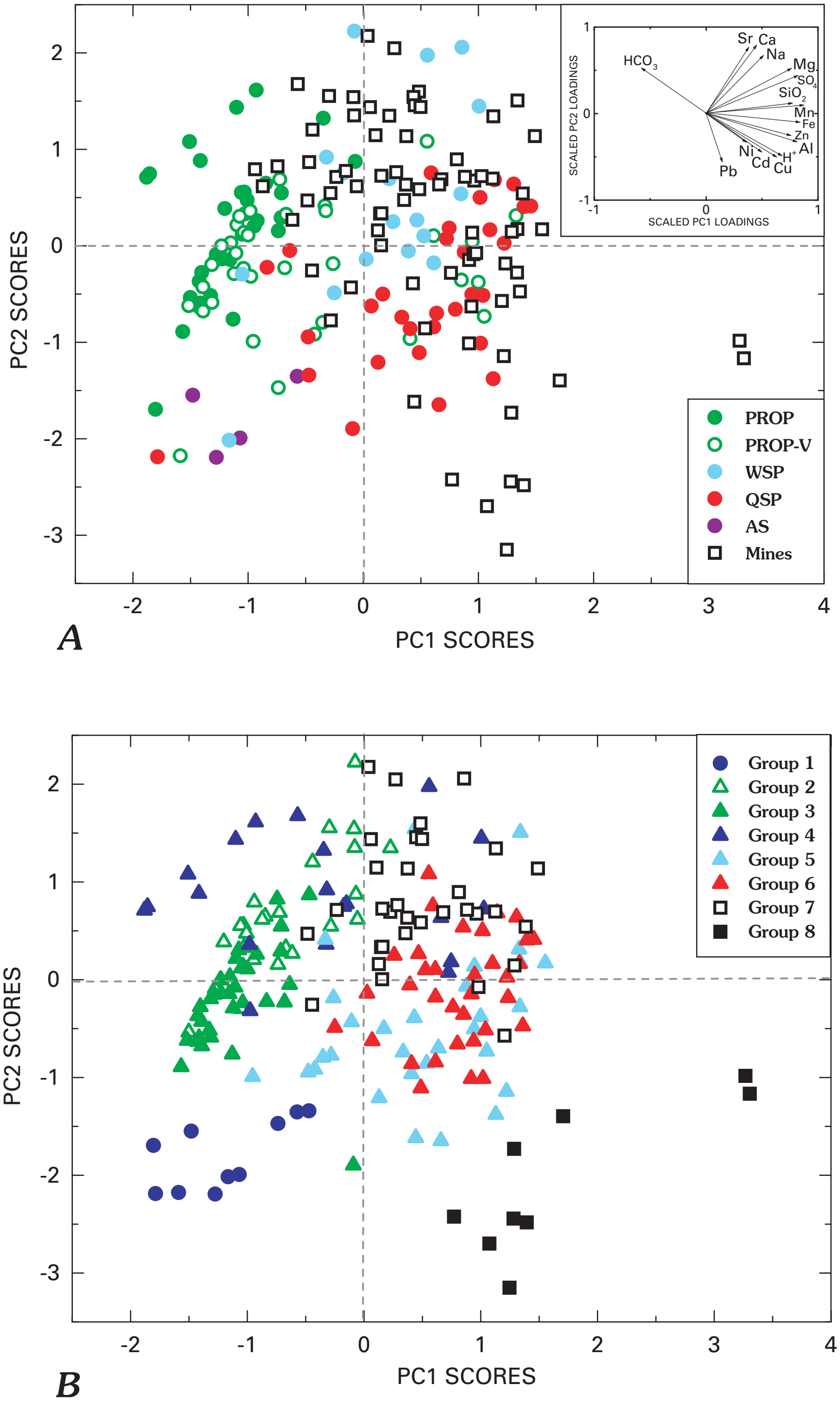

Figure 11. Principal component scores for background streams and springs (category I–II) and mine drainage by primary alteration type (*A*) and groupings by cluster analysis (*B*). PROP, propylitic; PROP-V, propylitic with vein mineralization; WSP, weak sericite-pyrite; QSP, quartz-sericite-pyrite; AS, acid-sulfate mineralization. Inset in *A* displays principal component loadings for water-quality constituents.

Table 9. Median water-quality composition for groups defined by cluster analysis of principal component scores, and number of mines and background samples (by alteration assemblage) in each group, 1997–99.

[Spec. cond., specific conductance; µS/cm, microsiemens per centimeter at 25°C; mg/L, milligrams per liter; --, below detection; N, number of samples; PROP, propylitic; PROP-V, propylitic with vein mineralization; WSP, weak sericite-pyrite; QSP, quartz-sericite-pyrite; AS, acid-sulfate]

Constituent	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
Spec. cond. µS/cm	56	260	162	375	609	576	770	1,090
Field pH	4.26	7.04	6.96	5.42	3.78	3.49	6.34	2.63
Alkalinity, mg/L	0.1	50	19	6	0.1	0.1	20	0.1
Sulfate, mg/L	9.0	77	44	160	200	230	360	370
Calcium, mg/L	1.83	43.7	22.5	34.5	36.0	48.0	129	17.2
Magnesium, mg/L	0.37	3.19	1.64	3.85	6.83	5.90	7.72	1.87
Sodium, mg/L	0.35	3.16	0.80	3.30	1.09	4.86	4.63	0.67
Silica, mg/L	12.5	9.46	3.72	19.0	10.5	45.5	22.0	24.7
Aluminum, mg/L	0.359	--	--	0.345	2.21	6.87	0.232	9.17
Barium, mg/L	0.046	0.023	0.023	0.019	0.017	0.016	0.011	0.010
Cadmium, mg/L	--	--	--	--	--	--	0.003	0.18
Copper, mg/L	--	--	--	--	0.018	0.024	--	3.00
Iron, mg/L	0.036	--	--	0.448	0.721	6.07	4.75	60.3
Manganese, mg/L	0.018	--	--	0.329	1.18	0.970	2.27	3.80
Nickel, mg/L	--	--	--	--	--	--	--	0.032
Lead, mg/L	--	--	--	--	--	--	--	0.47
Strontium, mg/L	0.012	0.620	0.236	0.285	0.258	0.295	1.00	0.069
Zinc, mg/L	--	--	--	0.033	0.687	0.224	0.620	44.7
All samples (N)	10	25	35	20	30	35	33	9
PROP (N)	1	11	14	7	0	0	0	0
PROP-V(N)	2	2	16	3	9	4	0	0
WSP (N)	1	2	0	4	0	8	2	0
QSP (N)	2	0	3	2	9	16	0	0
AS (N)	4	0	0	0	0	0	0	0
Mine (N)	0	10	2	4	12	7	31	9

Mass-Balance Approach

The mass-balance approach is simply a budget used to show the sources of the dissolved constituents in water (Drever, 1988). In this application, synoptic water-quality data and discharge measurements were used to estimate metal loads from weathering sources in unmined areas (background) of Middle Fork Mineral Creek, a 25-km^2 subbasin of the Animas River watershed study area (Mast, Verplanck, and others, 2000). The total load from mining sources was calculated by multiplying the measured discharge at each mine site by the concentration and then summing the loads of all the mines. Assuming that the major mining-related sources are accounted for and that contributions of mining-affected ground water are minimal, contributions from background weathering can be estimated from the difference between the load of Middle Fork Mineral Creek and the total load from the mines. The concentrations and loads of selected dissolved constituents for the six major mines in the subbasin (MS34, MS76, MS77, MS78, MS79, and MS80; fig. 8) and at the mouth of Middle Fork Mineral Creek (MC79) are listed in table 10. All samples were collected in late September and thus represent an estimate of background weathering only for low-flow conditions.

The results of the calculations indicate that contributions from springs, streams, and ground water in unmined areas accounted for about 80 percent of the discharge of Middle Fork Mineral Creek as well as a substantial fraction of the solute and metal loads in the study basin. For the major cations and sulfate, between 65 and 75 percent of the stream load was derived from background weathering of altered rock. Contributions of dissolved metals from background weathering varied over a slightly wider range—56 percent for manganese, 66 percent for iron, 76 percent for zinc, 81 percent for copper, and 90 percent for aluminum. The background contribution of zinc (76 percent), which should be fairly conservative in the stream channel (Kimball, 1997), was similar to the contribution of sulfate (72 percent), which also should be conservative. Nearly all aluminum from background weathering was derived from the Red tributary, which discharges acidic and aluminum-rich water into the lower reach of Middle Fork Mineral Creek (fig. 8). Red tributary, which drains the intensely altered area around peak 3,792 m, also contributed a substantial portion of the base-metal load in Middle Fork Mineral Creek, similar in magnitude to contributions from mining-related sources in the subbasin. For example, 20 percent of the zinc and 24 percent of the copper in Middle Fork

Table 10. Concentrations and loads of dissolved constituents at the mouth of Middle Fork Mineral Creek and at major mines in the subbasin, and estimated contributions (percent) from background weathering.

[MC79, mouth of Middle Fork Mineral Creek; MS34 and MS76–80, major mine sites in study area; sampling localities in figure 8; discharge in cubic feet per second; <, less than]

Constituent	Concentrations, in milligrams per liter							Loads in kilograms per day		Percent
	MC79	MS34	MS76	MS77	MS78	MS79	MS80	MC79	Mines	Background
Discharge	7.95	0.009	1.03	0.60	0.025	0.030	0.040	7.95	1.73	78
Calcium	130	359	110	400	20	91	64	2,530	883	65
Magnesium	11	42	3.9	33	5.4	6.3	5.9	214	60	72
Sodium	4.6	8.0	3.6	7.8	4.4	6.0	6.8	89	22	75
Potassium	0.5	0.9	0.5	0.8	0.5	0.5	0.1	9.7	2.6	73
Sulfate	430	1,300	200	1,200	83	360	263	8,360	2,340	72
Silica	23	29	17	29	35	49	45	447	96	79
Aluminum	7.20	21.2	<0.001	8.60	0.16	7.39	4.14	140	14	90
Copper	0.011	<0.004	0.003	0.013	0.002	0.097	0.051	0.21	0.04	81
Iron	15.6	73.0	0.47	67.0	9.35	4.10	11.4	303	102	66
Manganese	1.10	5.92	0.53	5.10	1.80	2.95	1.09	21.4	9.3	56
Zinc	0.23	0.62	0.039	0.53	0.26	2.33	0.22	4.5	1.1	76

Mineral Creek were derived from the Red tributary, compared with 24 percent of the zinc and 19 percent of the copper from mining-related sources.

Although this example demonstrates that background weathering is a significant source of metals to Middle Fork Mineral Creek, the limitations and assumptions of this technique need to be considered in evaluation of results of mass-balance calculations. For example, because many metals such as iron and aluminum are not conservative in the stream channel (Kimball, 1997), these calculations might actually underestimate metal contributions from background sources, if metals from mine discharge are attenuated along the stream channel. Additionally, if some of the mine-adit discharge is fed by metal-rich springs that existed prior to mining (Nash, 1999), contributions from background also would tend to be underestimated. Finally and most importantly, if the assumption that all mining-related sources are accounted for is not met, particularly concerning contributions of mining-affected ground water, background weathering could be significantly overestimated by this technique.

Isotopic Applications

A wide variety of stable isotopes has been used in hydrologic studies to trace sources of water and dissolved constituents in natural and contaminated environments (Clark and Fritz, 1997; Krouse and Grinenko, 1991). In mining-affected areas, the most common application has been the use of stable isotopes of water to delineate mining-affected ground-water plumes (Alpers and others, 1994; Finley and others, 1997; Davis and others, 2000). It also may be possible to distinguish background weathering from mining-related solute sources if mineral deposits have isotopically distinct signatures or if isotopic fractionation processes or geochemical reactions in the mine setting differ from those in the natural environment (Taylor and others, 1984; Wright and Nordstrom, 1999). In this study, strontium isotopes and stable isotopes of sulfate were evaluated as possible tracers to distinguish background from mining-related solute sources in the Animas River watershed study area. Strontium was not found to be a useful isotopic tracer because mineral deposits did not have an isotopic composition distinctly different from that of the host bedrock (Verplanck and others, 2001). Stable sulfur and oxygen isotopes of sulfate were found to be strongly controlled by geologic sources and in some situations were useful for separating mining from background at individual mine sites. In pyrite-dominated environments, the oxygen isotopes of sulfate in background water appeared to be different from those in mining-affected water; however, the usefulness of this technique as a tracer of background has not been clearly established. For a more detailed discussion of sulfur isotope studies in the study area, see Nordstrom and others (this volume, Chapter E8).

Strontium Isotopes

The usefulness of strontium isotopes to discriminate between background and mining-affected surface water was tested on a smaller scale by sampling a suite of water and rock samples from the Middle Fork Mineral Creek subbasin. Results include strontium isotopic compositions ($^{87}Sr/^{86}Sr$) of water and rock samples and isotopic and elemental data from leaching experiments. Leaching experiments with dilute sulfuric acid were undertaken to determine the composition of the easily extractable fraction. Verplanck and others (2001) described sampling sites and chemical results in detail. Six rock samples that span the range in lithology and alteration intensity were collected. During low flow in 1995, eight water samples were collected from background streams and springs and two were collected from mine discharge.

The concentration of strontium in ground water is generally 5–20 mg/L; at these low concentrations the isotopic composition can be easily affected by interaction with bedrock along the flow path (Wadleigh and others, 1985). The strontium isotopic composition of volcanic and plutonic bedrock, the primary units within the Middle Fork Mineral Creek subbasin, is a function of the initial isotopic composition and the amount of radioactive decay of ^{87}Rb to ^{87}Sr, which has a half-life of 48.8×10^9 years. Because individual minerals within a rock can have very different rubidium:strontium ratios, the strontium isotopic ratios of water interacting with bedrock may not reflect the whole-rock ^{87}Sr/^{86}Sr but more likely would reflect the ^{87}Sr/^{86}Sr of the more easily weathered components (Kendall and others, 1995).

The measured whole-rock ^{87}Sr/^{86}Sr ratios of six rock samples range from 0.70638 to 0.71261 (Verplanck and others, 2001). The two samples of the quartz monzonite porphyry had the lowest ^{87}Sr/^{86}Sr ratios, less than 0.70674, and samples of the San Juan Formation had distinctly higher ^{87}Sr/^{86}Sr ratios, 0.70702 to 0.71261. For a given lithology, the propylitically altered samples had lower ^{87}Sr/^{86}Sr ratios than the more intensely altered samples (fig. 12*A*). The propylitically altered samples had consistently higher calcium and strontium concentrations, as well as lower potassium and rubidium concentrations, than the more intensely altered samples. Similar to the whole-rock samples, the leachates of quartz monzonite samples had lower ^{87}Sr/^{86}Sr ratios, less than 0.70704, than the leachates from the San Juan Formation samples, 0.70704 to 0.70863 (Verplanck and others, 2001). For a given lithology, the leachates from the propylitically altered samples also had lower ^{87}Sr/^{86}Sr ratios and higher strontium concentrations than the more intensely altered rock types.

The water samples had strontium concentrations that ranged from 0.028 to 5.7 mg/L and ^{87}Sr/^{86}Sr ratios from 0.70654 to 0.70899 (Verplanck and others, 2001). Variation in the ^{87}Sr/^{86}Sr ratios of the water samples was not correlated with strontium concentration but was correlated with pH (fig. 12*B*). Samples with lower ^{87}Sr/^{86}Sr ratios were the more acidic, and samples with higher ^{87}Sr/^{86}Sr ratios were generally less acidic. Water interacting with QSP altered rock leads to much different water quality than water interacting with propylitically altered units (Mast, Verplanck, and others, 2000). Spatially, the samples with the lowest ^{87}Sr/^{86}Sr ratios (MC71, MC43, MS79) were taken along the flanks of peak 3,792 m within or downgradient from the zone of altered quartz monzonite. The two samples with the lowest ^{87}Sr/^{86}Sr (MS79 and MC43) were from within or adjacent to the most intensely altered quartz monzonite porphyry. The ^{87}Sr/^{86}Sr of these samples (0.70654 and 0.70700) was similar to the weak, sericitically altered quartz monzonite sample (0.70674 whole-rock and 0.70704 leachate). Sample MS79 was from a seep below the largest mine in the study area, and sample MC43 was from a small stream upgradient of any mining activity. The pH values, strontium concentrations, and ^{87}Sr/^{86}Sr ratio were quite similar, demonstrating that in this environment the ^{87}Sr/^{86}Sr cannot be used as a tool for separating mining-affected water from naturally acidic drainage.

Water samples collected in more intensely altered San Juan Formation had distinctly higher ^{87}Sr/^{86}Sr (>0.7080) than samples from either propylitically altered San Juan Formation or all quartz monzonite regions. Sample MS77, from an adit within the weak sericite-pyrite zone, had a pH of 5.7 and ^{87}Sr/^{86}Sr ratio of 0.70853, which is within the range of nearby springs (pH of 5.7–6.8 and ^{87}Sr/^{86}Sr of 0.70816–0.70899). Similar to the other mine-water sample, this sample did not have a distinct strontium isotopic signature compared with background springs in the same lithology.

In the Middle Fork Mineral Creek subbasin, the strontium isotopic signature of spring, stream, and mine water was controlled by variations in the bedrock geology and intensity of hydrothermal alteration. Mine-water discharge did not have a unique ^{87}Sr/^{86}Sr ratio because the mineral deposits did not have an isotopic composition distinctly different from that of their host rock. The mining activity focused on base-metal-rich quartz veins, which did not appear to have unique ^{87}Sr/^{86}Sr ratios.

Sulfur and Oxygen Isotopes of Sulfate

Stable isotopes of sulfur have been extensively used in environmental studies to fingerprint different sulfate sources, because sulfur is widely distributed in terrestrial materials and commonly has a large separation in isotopic values (Krouse and Grinenko, 1991). In the Animas River watershed study area, the major sources of sulfur in dissolved sulfate are pyrite, calcium sulfate minerals, including gypsum and anhydrite, and atmospheric deposition. Upon oxidation or dissolution of minerals, little or no fractionation of sulfur isotopes occurs, so the resulting isotopic signature of surface water should be representative of the geologic source. Once dissolved in surface water, the sulfur in sulfate can be fractionated by sulfate-reducing bacteria (Krouse and Grinenko, 1991); however, the importance of this process in the study area is poorly understood. Stable sulfur isotopic ratios of minerals in the study area are presented by Bove and others (this volume). The sulfur isotopic composition of pyrite ranges from –6.9 to +2.5 per mil, with an average of –2.4 per mil. Calcium sulfate minerals are considerably heavier; values range from +14.6 to +18.0 per mil, with an average of +16.5 per mil. The sulfur isotopic composition of atmospheric deposition ranges from +4.0 to +4.4 per mil (Mast and others, 2001); however, extremely low sulfate concentrations in precipitation render the isotopic influence of this source negligible. Because pyrite and gypsum are widespread throughout the watershed, sulfur isotopic data alone likely would not be useful for discriminating background from mining-related sources of sulfate except perhaps on smaller scales, where individual vein deposits might be isotopically distinct from the surrounding host rock.

Oxygen isotopes of dissolved sulfate have been utilized in a few studies to trace sulfur cycling in watershed studies (Mayer and others, 1995) and to examine mechanisms of

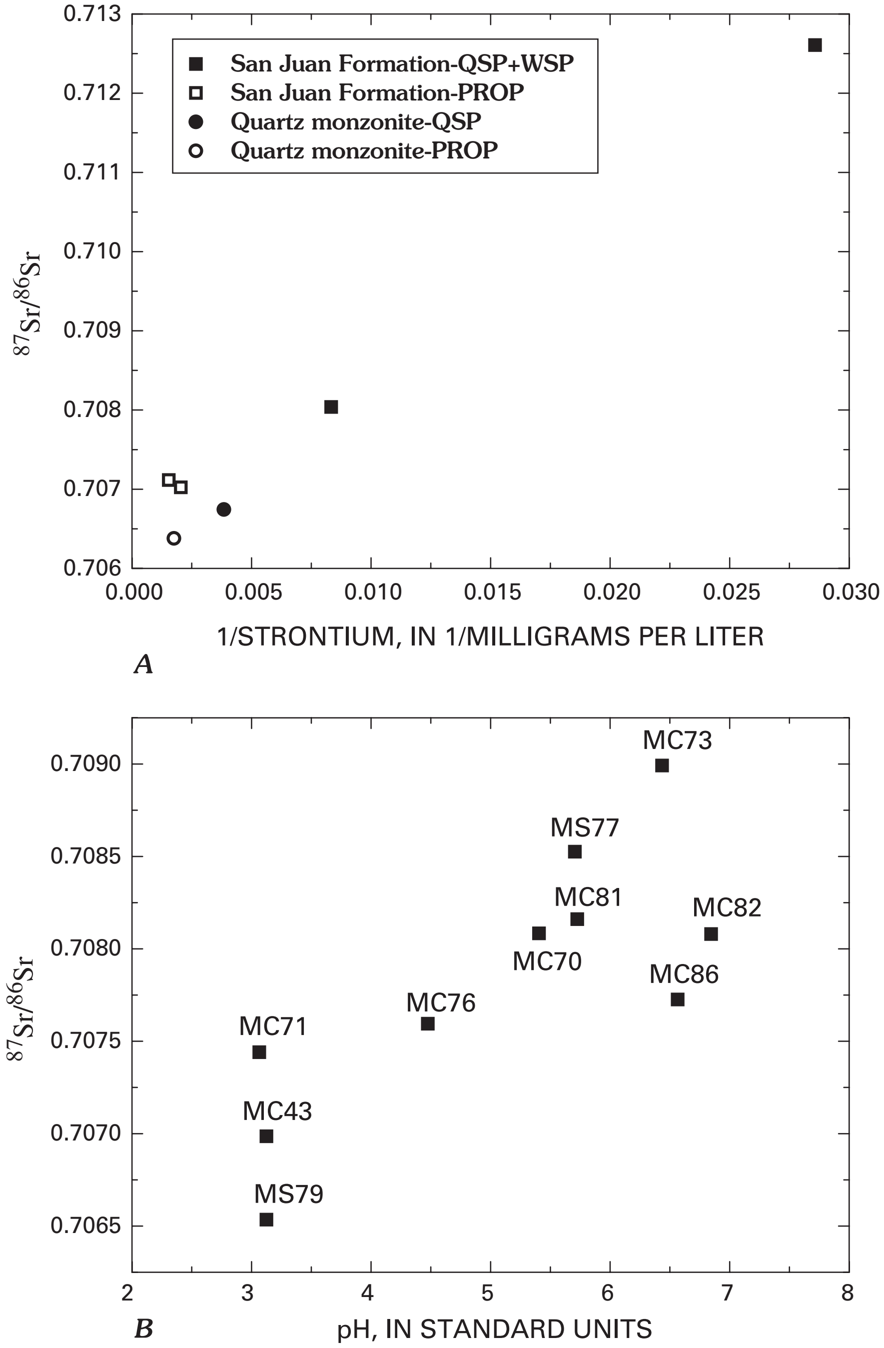

Figure 12. Relation between *A*, $^{87}Sr/^{86}Sr$ and 1/strontium for whole-rock samples, and *B*, $^{87}Sr/^{86}Sr$ and pH for water samples from Middle Fork Mineral Creek subbasin. QSP, quartz-sericite-pyrite; WSP, weak sericite-pyrite; PROP, propylitic. Surface-water sites in figure 1 and figure 8.

pyrite oxidation in the laboratory (Taylor and others, 1984; Van Stempvoort and Krouse, 1994). During oxidation of pyrite, the sulfur in the resulting sulfate acquires the isotopic signature of pyrite; however, the oxygen can be derived from either water molecules (–50 to +10 per mil depending on distance from ocean, and on elevation, latitude, and temperature) or atmospheric oxygen (+23.5 per mil) dissolved in the water (Nordstrom and others, this volume). The relative amounts of oxygen from water and aqueous dissolved oxygen incorporated into the sulfate molecule may be affected by microbiota that play a role in sulfide oxidation and by the rate at which the sulfide minerals are oxidized (Wright and Nordstrom, 1999). Incorporation of dissolved oxygen ($O_{2(aq)}$) in the sulfate anions is thought to result from sulfide oxidation reactions at neutral pH where the oxidant is atmospheric oxygen. Oxygen from the water molecule (H_2O) is thought to predominate in more acidic conditions where aqueous ferric iron is the primary oxidant (Taylor and others, 1984). Wright and Nordstrom (1999) proposed that the relative importance of these two oxidation pathways may reflect the weathering environment, which might be useful for distinguishing background from mining-affected sources of sulfate in pyrite-dominated systems. In some mineralized areas, including the Animas River watershed study area, primary calcium sulfate minerals such as gypsum and anhydrite are associated with the mineral deposits. Weathering of these minerals will produce sulfate with an oxygen isotopic composition of the dissolving mineral phases, which can greatly complicate the interpretation of oxygen isotopes in terms of mechanisms of pyrite oxidation (Nordstrom and others, this volume).

Sulfur and oxygen isotopes of dissolved sulfate were measured at a variety of stream, spring, and mine sites in the Animas River watershed study area to determine if sulfate isotopes were useful for separating background from mining sources of sulfate. For a complete discussion of this study, see Chapter E8 of this volume (Nordstrom and others). Sulfur and oxygen isotopes of dissolved sulfate are presented in figure 13 with the range of isotopic values for pyrite (sulfur only) and gypsum/anhydrite samples collected in the study area (Bove and others, this volume). The water samples show a strong linear correlation (r^2=0.64) between sulfur and oxygen isotopic values. This trend represents a mixing line between sulfate derived from anhydrite/gypsum dissolution (heavier isotopic values) and sulfate derived from pyrite oxidation (lighter isotopic values). Simple mixing calculations based on the average sulfur isotopic composition of the minerals indicate that dissolution of calcium sulfate minerals accounts for more than 20 percent of the dissolved sulfate in nearly half of the samples. Figure 13 also differentiates between background samples and mining-affected samples. Although the oxygen isotopic values appear to undergo a shift between these two sample groups, the importance of gypsum/anhydrite dissolution greatly complicates the interpretation of this pattern. Nordstrom and others (this volume) determined that spatial variation in the sulfur isotopic composition of mineral phases probably accounts for much of the difference

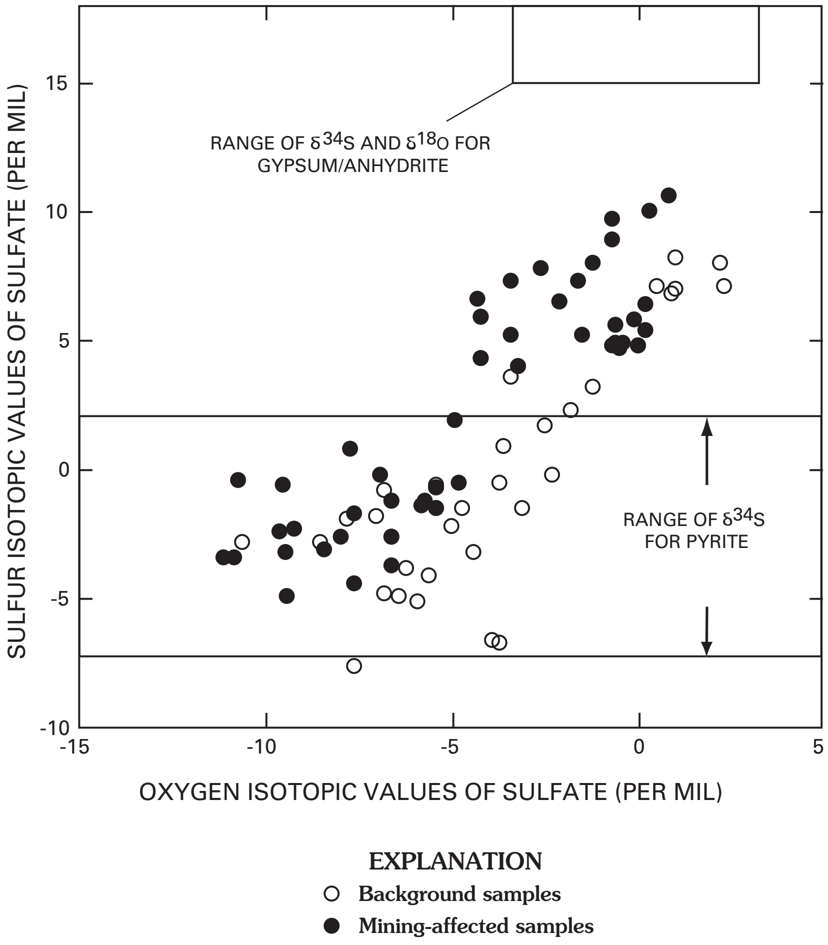

Figure 13. Stable sulfur and oxygen isotopes of dissolved sulfate in background and mining-affected water-quality samples, and range of isotopic values for selected minerals from the Animas River watershed study area.

and concluded that no recognizable differences could be noted in the stable isotopes of dissolved sulfate derived from background and from mining sources.

The results presented here and in Nordstrom and others (this volume) for the Animas River watershed study area suggest that stable isotopes of dissolved sulfate likely would not be useful for distinguishing mining from background sources of sulfate, at least on a watershed scale. At smaller scales, however, cases may exist in which discharge from a single mine has an isotopically distinct signature from background surface water because of local differences in mineralogy. In such situations, oxygen or sulfur isotopes of dissolved sulfate may be useful in mass-balance calculations to determine the proportion of stream-water sulfate derived from the mine. The following example describes the application of stable isotopes of dissolved sulfate to determine the proportion of sulfate from mine drainage in Topeka Gulch, a small tributary on the west side of Cement Creek where mine discharge is isotopically distinct from surface water draining the surrounding host rock (fig. 1). To determine the percentage of the dissolved sulfate that comes from the mine, the isotope-dilution equation can be used where

$$\text{Percent sulfate from mining} = \frac{(\delta^{18}O_{background} - \delta^{18}O_{mining\text{-}affected})}{(\delta^{18}O_{background} - \delta^{18}O_{mine})} \times 100$$

In this example, background surface water is represented by Topeka Gulch at CC132, which had an oxygen isotopic value of –6.8 per mil; and mining-affected surface water is represented by Topeka Gulch at CC133, which had a value of +0.3 per mil (fig. 1). The mine site, located downstream from CC132 but upstream from CC133, had an isotopic value of +0.83 per mil. Using these values, the isotope-dilution equation calculates that 93 percent of the dissolved sulfate in Topeka Gulch came from the draining mine adit. The same calculation can be made using stable sulfur isotopes, which yields a similar value with 96 percent of the sulfate coming from the mine adit discharge. Although mass balances also can be calculated using concentration data, for these calculations stream and mine discharges would be required. Discharge measurements in steep mountainous streams can be difficult to measure accurately, and large errors in the mass-balance accounting of dissolved constituents can result. When the isotope-dilution equation is used, discharges are not needed, eliminating that source of error. This method also is useful if mine water is discharging diffusely from fractures in bedrock and it is not possible to sample at the adit; the isotopic signature of the mine water likely still will be present in the stream downgradient from the mine site, assuming that the mine site was adequately bracketed. Therefore, the calculation of the percentage of mine water in the stream using the isotope dilution equation fully accounts for the effects of the entire mine site on the environment.

Rare-Earth Elements in Surface Water

Rare-earth element geochemistry is a powerful tool for constraining geochemical processes in many petrologic studies (Smedley, 1991) but is just beginning to be applied to aqueous systems. One limitation to using rare-earth elements as hydrologic tracers is their limited solubility in nonacidic water (Davis and others, 2000). The rare-earth elements are a suite of 14 metals from atomic number 57 (lanthanum) to 71 (lutetium) that have similar chemical and physical properties because they generally form stable $^{+}3$ ions of similar size. Small differences arise in that with increasing atomic number there occurs a systematic decrease in ionic radius. The rare-earth elements are trivalent, with the exception of cerium (also $^{+}4$) and europium (also $^{+}2$). The behavior of cerium and europium relative to the other rare- earth elements potentially can be used as a probe of redox potential and pH of an environmental system (Loveland, 1989).

Two subbasins, Prospect Gulch and Middle Fork Mineral Creek, were used for investigation of techniques for identifying source-water signatures with rare-earth elements. These two subbasins were chosen for their differing geologic characteristics, particularly bedrock composition and types of alteration. Detailed discussions of the bedrock geology, alteration assemblages, and mining history for Prospect Gulch are found in Burbank and Luedke (1969), Fisher and Leedy (1973), and Bove and others (2001), and, for the Middle Fork Mineral Creek subbasin, Ringrose (1982) and Yager and others (2000).

In Prospect Gulch, five mine-drainage samples (pH 2.4–3.6) and four acidic springs (pH 3.3–5.7) were sampled during low flow in 1997. Rare-earth element concentrations for the spring and mine-discharge samples from Prospect Gulch, normalized to North American Shale Composite (NASC), display enrichment in the middle (Sm-Dy) rare-earth elements (fig. 14*A*). The spring and mine samples had similar overall patterns except that one spring exhibited a negative cerium anomaly.

During low flow in 1995, five mine-drainage samples (pH 3.1–5.7) and five background springs (pH 3.1–6.8) were sampled in the Middle Fork Mineral Creek subbasin. The rare-earth element patterns of these samples display a greater range in shape than the patterns in samples from Prospect Gulch. The mine-drainage samples have two types of patterns (fig. 14*B*): two samples display a more sinusoidal pattern and three display an enrichment of middle rare-earth elements. The two samples with the sinusoidal pattern are from the north side of the subbasin, which is underlain predominantly by propylitically altered volcanic rock. The three middle rare-earth element-enriched mine-drainage samples are from the south side of the subbasin, within or near the quartz monzonite porphyries. The rare-earth element patterns of the background spring samples display enrichment of middle rare-earth elements; however, four of the five samples also have a negative cerium anomaly. The presence of the cerium anomaly reflects

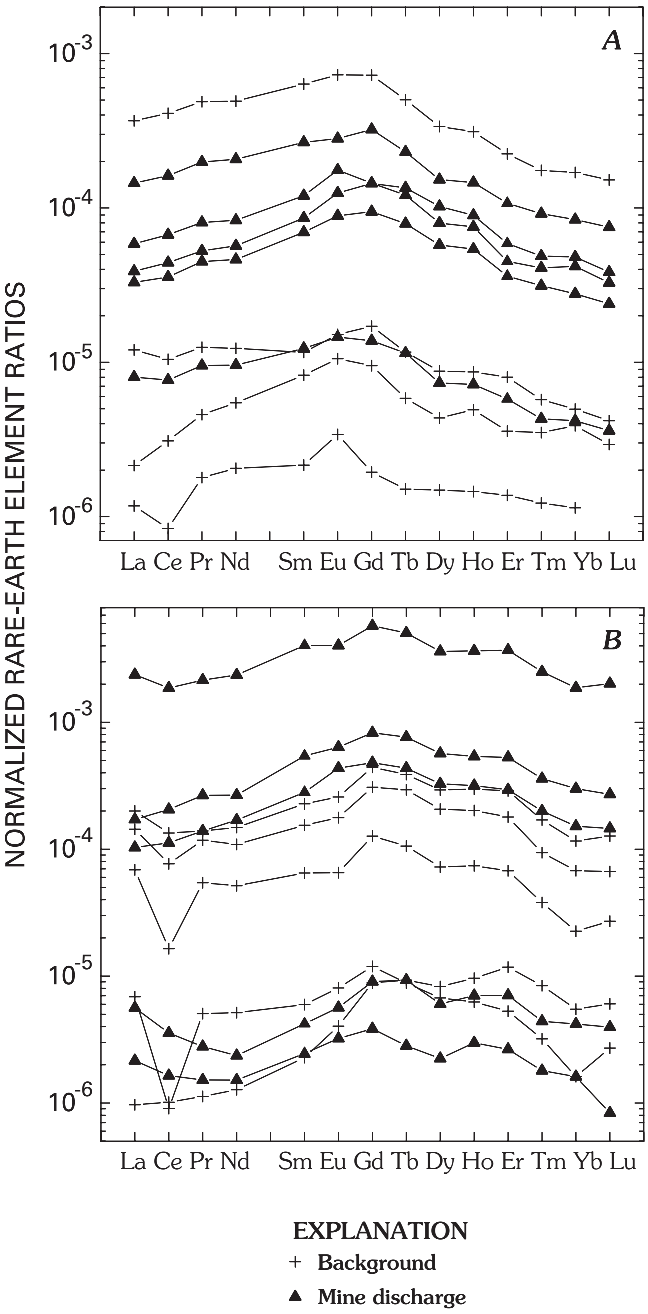

Figure 14. Rare-earth element ratios (normalized to the North American Shale Composite) of background water-quality and mine-discharge samples from *A*, Prospect Gulch, and *B*, Middle Fork Mineral Creek.

differing redox conditions in some of the spring environments as compared with the mine setting, but because this feature is not observed in all the springs, it is not a viable signature.

To discriminate between water derived from springs and mine drainage using rare-earth elements, a fundamental difference between the two settings, such as host-rock mineralogy, mineral composition, mineral grain size, redox conditions, or residence time, must occur. In these subbasins, the mine and background samples do not appear to have unique rare-earth element signatures.

Summary

This investigation was conducted as part of the Abandoned Mine Lands Initiative to characterize background water quality in the Animas River watershed study area. Although there remains little doubt that the water quality and aquatic resources of the Animas River watershed study area have been adversely affected by drainage from historical mine sites, background weathering of mineralized bedrock also may contribute substantial amounts of metals and acidity to surface water. The results of this study will improve understanding of the weathering processes controlling surface-water chemistry in a mineralized watershed, which should aid resource managers in establishing cost-effective and technically feasible remediation goals for the Animas River watershed study area.

During summer low flow in 1997–99, we sampled 241 streams and springs in the watershed, more than one-half of which were determined to be minimally affected by mining and thus representative of background water quality. The chemistry of background streams and springs varied over a considerable range; pH ranged from 2.58 to 8.49 and specific conductance from 12 to 2,180 µS/cm. Sites with neutral pH values were of the calcium-bicarbonate-sulfate water type, whereas low-pH samples were dominated by dissolved aluminum, iron, and sulfate. Other metals detected in background water were barium, copper, manganese, strontium, and zinc. Several trace metals, including zinc, copper, and manganese, were present at concentrations that exceeded aquatic-life standards at many of the background sites. Zinc, the metal most toxic to fish in the Animas River watershed study area, reached concentrations as high as 14,400 µg/L and was detected in more than one-half of background samples.

Water quality was measured at 75 inactive mine sites that were observed to be discharging directly into surface water during low-flow conditions in late summer and fall. The chemical composition of mine drainage was highly variable; pH ranged from 2.35 to 7.77 and specific conductance from 180 to 3,520 µS/cm. Mine drainage chemistry was dominated by sulfate (45–2,720 mg/L) and calcium (2–460 mg/L) concentrations, and many samples contained elevated concentrations of aluminum (as much as 71 mg/L) and iron (as much as 686 mg/L). Comparison of background samples with mine-drainage samples showed statistically significant differences in concentrations for all the major ions and many dissolved metals, including barium, copper, iron, manganese, strontium, and zinc, with higher concentrations at mine sites with the exception of barium.

The chemistry of springs and streams minimally affected by mining was strongly controlled by the degree of bedrock alteration. Chemical characteristics of surface water draining five major alteration assemblages differed as a function of bedrock mineralogy. Calcium-bicarbonate-sulfate water was characteristic of propylitically altered rock, whereas the QSP-altered rock generated acidic, metal-rich surface water.

Among the five alteration assemblages, dissolved metal concentrations varied the most widely in samples categorized as propylitically altered with associated vein mineralization.

To further constrain the possible weathering reactions controlling background water quality in the Animas River watershed study area, inverse geochemical models based on water quality and mineralogic data were constructed. The composition of springs draining the alteration assemblages could be reproduced by modeling weathering of variable amounts of pyrite, calcite, and aluminosilicate minerals, with pyrite and aluminosilicate dissolution becoming more substantial in the intensely altered rock types. A few sites had anomalously high concentrations of calcium and sulfate associated with high pH and low metal concentrations. Inverse modeling results indicated that this water-quality signature was derived from dissolution of vein-filling gypsum or anhydrite. Modeling of base-metal sources revealed that zinc was derived primarily from weathering of sphalerite but that oxidation of disseminated pyrite also was an important zinc source in some areas. These results suggest that the chemistry of background surface water minimally affected by mining in the Animas River watershed study area should be somewhat predictable if information is available on patterns of bedrock alteration and the associated mineral assemblages.

Estimation of metal contributions from background sources on a watershed scale was complicated by several factors, including large number of mine sites in the study area, limited characterization of mining-related sites, complex geology, and unknown contributions of ground water. Several approaches for estimating background in the watershed were explored, including statistical descriptions, mass-balance calculations, isotopic applications, and rare-earth element geochemistry. The two statistical techniques used to describe geochemical background in the study area ranged from simple statistical summaries using box plots to a more complex approach using principal component analysis (PCA) and cluster analysis. The box plots revealed that pH and major dissolved constituents at background and mine-discharge sites exhibited similar ranges in concentrations but that some metals, particularly zinc, were elevated in mine drainage relative to background. The PCA of this data set confirmed that background samples had a wide range in water quality, which is primarily controlled by the degree of bedrock alteration. The cluster analysis showed that most of the mine-discharge samples fell in water-quality groups with high dissolved metal concentrations; however, they did not cluster in one group consisting solely of mining-affected water. The mass-balance approach was applied in the Middle Fork Mineral Creek subbasin to determine the magnitude of metal loading to surface water from the highly altered bedrock of the subeconomic porphyry copper-molybdenum deposit at peak 3,792 m. The results showed that background sources accounted for 56–90 percent of the metal load, which was primarily derived from the highly altered rock types associated with the porphyry copper-molybdenum deposit. This approach can be problematic because of the nonconservative nature of many dissolved metals and the difficulties with identifying and sampling all mining-affected water, particularly ground water; therefore, the results of this approach should be interpreted with care. The range of stable sulfur and oxygen isotopic values of dissolved sulfate was found to be controlled primarily by the relative importance of pyrite and gypsum/anhydrite dissolution. Although oxygen isotopes of sulfate were found to differ among the pyrite-dominated samples, the usefulness of this technique as a tool for distinguishing background weathering from mining sources is still under investigation. Stable isotopes of sulfur were successfully used at a smaller scale to determine the percent of stream-water sulfate in the Topeka Gulch subbasin that came from mining-related sources. To discriminate between water derived from springs and mine drainage using strontium isotopes and rare-earth elements, a fundamental difference between the two settings, such as host-rock mineralogy, mineral composition, mineral grain size, redox conditions, or residence time, must be recognized. In the Animas River watershed study area, the mine and background water samples do not appear to have unique strontium isotopic or rare-earth element signatures; thus, these tracers are not useful for discriminating metal sources to surface water.

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