

Effects of the May Day Mine Site on Stream-Water Quality in the Cement Creek Basin, August 2000

By Winfield G. Wright, Briant A. Kimball, and Robert L. Runkel

Chapter E23 of

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

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Contents

Abstract.....	947
Introduction.....	947
Study Area Description.....	949
Purpose and Scope	949
Acknowledgments.....	949
Methods of Study.....	952
Stream Tracer-Injection Study.....	952
Quantification of Constituent Concentrations and Loads	953
Evaluation of Sources	954
Effects of the May Day Mine Site on Stream-Water Quality.....	954
pH and Constituent Concentrations.....	956
Constituent Loads	957
Constituent Attenuation	961
Evaluation of Water Sources	964
Mineral Saturation.....	968
Summary and Conclusions.....	970
References Cited.....	970

Figures

1. Map showing location of May Day mine site in Cement Creek basin of Animas River watershed.....	948
2. Map showing location of study reach, sample sites, and reach distances referenced to study of Kimball and others (2002).....	950
3. Sketch map showing study reach affected by May Day mine site	951
4–17. Graphs showing:	
4. Bromide concentrations at fixed sites illustrating plateau conditions.....	952
5. Longitudinal stream profile of discharges in the study reach	953
6. Longitudinal stream profile of pH in Cement Creek through study reach and pH values of inflows and tributaries	956
7. Longitudinal stream profiles of dissolved and total constituent concentrations in study reach, for aluminum, copper, and iron.....	958
8. Longitudinal stream profiles of dissolved and total constituent concentrations in study reach, for manganese, sulfate, and zinc	959
9. Longitudinal stream profiles of constituent loads in study reach, for aluminum, copper, and iron	960
10. Longitudinal stream profiles of constituent loads in study reach for manganese, sulfate, and zinc	962
11. Longitudinal stream profiles of change in dissolved and total iron loads in study reach.....	963

12. Longitudinal stream profile of change in dissolved sulfate loads in study reach.....	964
13. Longitudinal stream profiles of change in dissolved and total zinc loads in study reach.....	965
14. Oxygen and hydrogen isotopes of water samples collected from study reach and from selected springs, streams, and inactive mines as part of other studies in Animas River watershed study area.....	966
15. Oxygen and hydrogen isotopes of water and dissolved zinc concentrations for sites affecting May Day reach.....	967
16. Principal components analysis, including dissolved constituents and isotopes, showing groups of inflows and stream sites in study reach affected by May Day mine.....	968
17. Longitudinal stream profile of saturation index for selected mineral species in water samples from study reach.....	969

Table

1. Sites where water-quality samples were collected in the tracer study reach, August 17, 2000.....	955
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Conversion Factors, Abbreviations, and Acronyms

Multiply	By	To obtain
meter (m)	3.281	foot (ft)
liter per second (L/s)	0.03532	cubic foot per second (ft ³ /s)
cubic meter per second (m ³ /s)	35.3	cubic foot per second (ft ³ /s)
kilometer (km)	0.6214	mile (mi)
milligram per second (mg/s)	0.1904	pound per day (lb/d)

The following terms and abbreviations also are used in this report:

micrograms per liter (µg/L)

milligrams per liter (mg/L)

parts per thousand relative to the Vienna Standard Mean Ocean Water (per mil VSMOW)

Principal Components Analysis (PCA)

Saturation Index (SI)

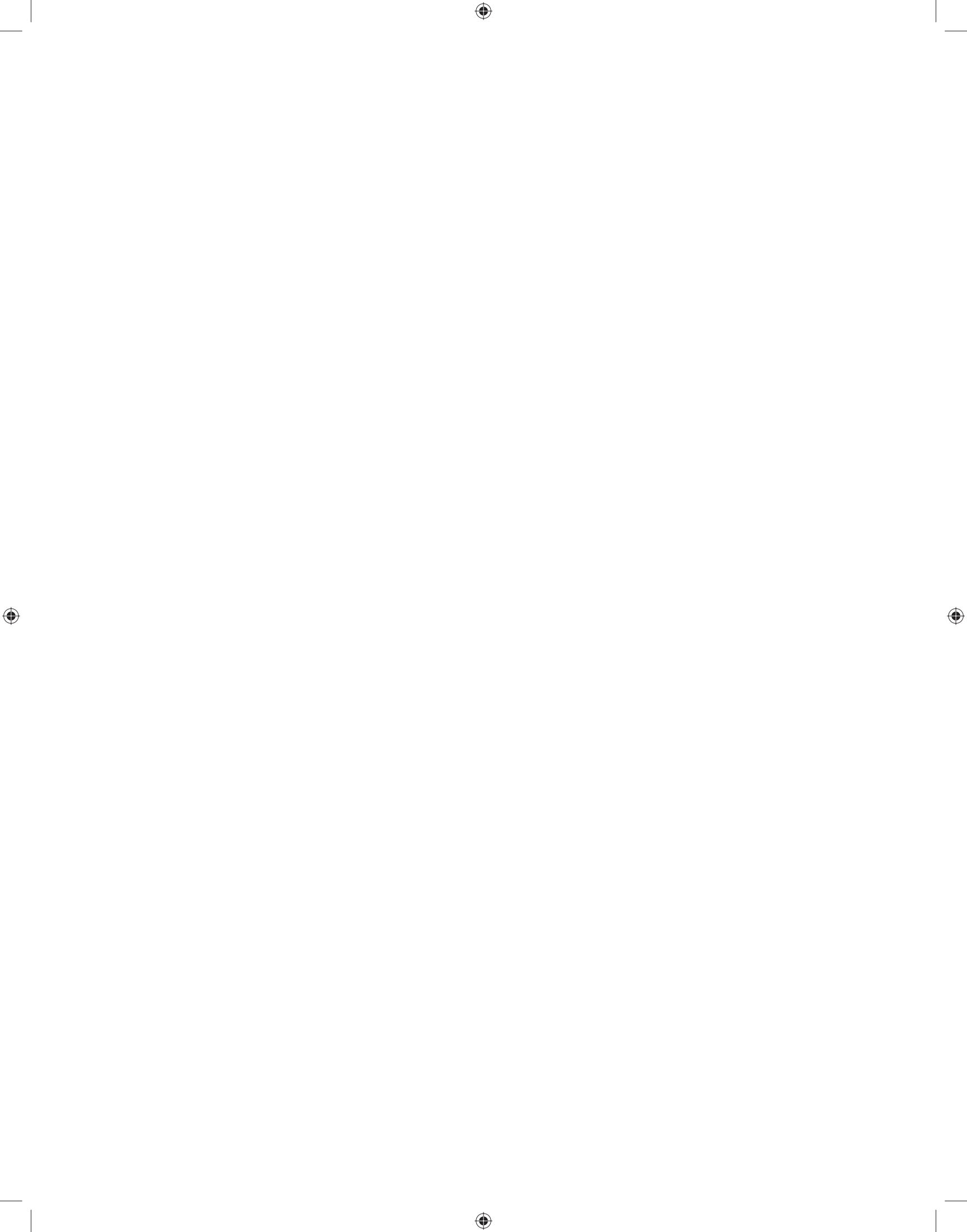
millimoles per liter (mmol/L)

milliliters per minute (mL/min)

milligram per second (mg/s)

Conversion of constituent-loading units:

Milligrams per second (mg/s) × 0.0864 = kilograms per day (kg/d)



Chapter E23

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Abstract

A tracer-injection study was done in the reach of Cement Creek that included Illinois Gulch and the May Day mine site. A lithium bromide tracer was used for the study; however, the tracer was not well mixed in certain sections of the study reach because of the large inflow at Illinois Gulch. Because of the uncertainty of tracer-dilution calculations downstream from Illinois Gulch, streamflow discharges were calculated from the dilution of lithium at certain control points, and streamflows between the control points were determined by linear interpolation. Water-quality samples were collected from stream sites, tributaries, springs, and seeps that affected the study reach. The May Day mine does not have any obvious mine drainage discharging from the adit; therefore, well points were installed downgradient from the May Day mine to further characterize contaminant flow paths from the site. The inflow from Illinois Gulch had higher pH values than did Cement Creek, and the mixing of the pH 7.39 water with the pH 3.8 stream caused precipitation of dissolved iron. The inflows in the reach affected by the May Day mine site had low pH values but low discharges; hence, the pH of the stream was not greatly affected. Dissolved constituent concentrations fluctuated throughout the study reach, but the dissolved concentrations decreased most noticeably downstream from Illinois Gulch due to dilution by the large inflow. Total constituent concentrations increased in the reach affected by the May Day mine. Cumulative instream loads were greater than the total loads, indicating that nonconservative behavior and removal of some metals occurred in the study reach. Cumulative inflow loads were less than cumulative instream loads, indicating that diffuse ground-water sources were contributing loads to the study reach. The use of light stable isotopes of water and the technique of principal components analysis helped in the inventory of sources of water to the study reach. Mineral saturation calculations indicated supersaturation of iron and sulfate phases downstream from Illinois Gulch.

Introduction

Quantifying the effects of an inactive mine site on the environment is a difficult task, especially in mountainous terrain such as the Animas River watershed study area (fig. 1), and particularly at mine sites where no obvious mine drainage is discharging from an adit or portal. Several methods can be used for characterization of sites of inactive mines. For example, monitoring wells can be drilled around a mine site, but water samples collected from wells may only describe the contaminant concentrations in the immediate vicinity of the well, and the effects of the site on a larger scale may be difficult to describe from discrete well data. Leach tests can be performed on waste-rock samples, which might simulate the effects of rainfall or snowmelt passing through the waste-rock material (Smith, Ramsey, and Hageman, 2000; Hageman and Briggs, 2000); however, laboratory or field leach tests may not adequately represent actual field conditions. Surface geophysics can be used around a mine site to map the extent of the waste-rock pile, high conductivity zones within the waste-rock pile, and high conductivity zones of ground water discharging from the site (Campbell and Fitterman, 2000; Smith, McCafferty, and McDougal, 2000). These methods, however, do not provide conclusive evidence of the effects of the overall mine site on the environment.

A useful method for describing the effects of mine sites on stream-water quality is the application of tracer-injection studies (Kimball, 1997), and the tracer-injection data are particularly useful for reactive transport modeling (Runkel and Kimball, 2002). The value of a tracer-injection study is the ability to collect numerous synoptic samples in a short period of time without the need to make streamflow and inflow discharge measurements. Inflows can be direct (from a tributary or a draining adit) or diffuse (seepage from underground mine workings, seepage from waste-rock piles, or local and regional ground-water discharge). Diffuse inflow sources are the more difficult to quantify. For detailed descriptions of tracer-injection studies, see Kimball and others (this volume, Chapter E9).

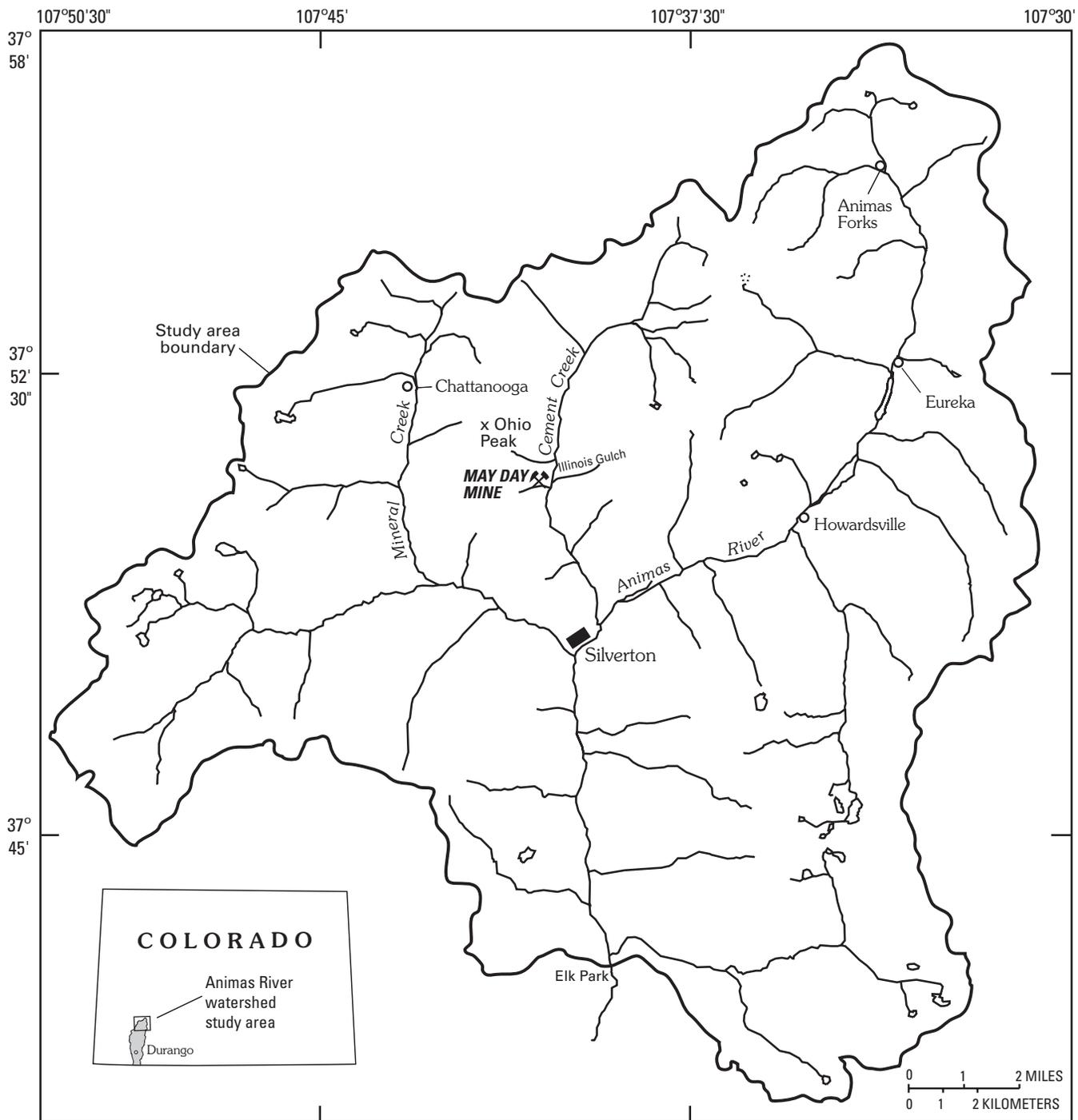


Figure 1. Location of May Day mine site in Cement Creek basin of Animas River watershed.

Previous studies of the entire reach of Cement Creek (Kimball and others, 2002; Walton-Day and others, 2000) indicated that the reach affected by the May Day mine (AMLI site # 181, fig. 1) contributed constituent loads to Cement Creek; however, the Illinois Gulch inflow (fig. 1) caused constituent mixing and possible attenuation difficult to interpret using the few sampling sites in the reach. Other studies of the May Day mine site and waste-rock pile (Smith and others, 2001; Wright and others, 1998) indicated high concentrations of metals

present in the waste-rock pile; however, the dissolved constituent loads from the site could not be adequately explained by hydrogeochemical and mass-balance studies.

The May Day mine site is located on land administered by the Bureau of Land Management. To better quantify constituent sources from the May Day mine to Cement Creek, a detailed tracer-injection study was done to demonstrate the effects of Illinois Gulch, the Yukon tunnel (AMLI site # 186), and the May Day mine on stream-water quality.

The tracer study reach was referenced to the original distances of Kimball and others (2002) (fig. 2). Additions to the tracer study included water-quality samples collected from drips and pools inside the mine. Springs, seeps, and inflows were mapped near the mine site, and well points were installed along the streambanks to characterize contaminant flow paths and sample diffuse ground-water inflows (fig. 3). This report describes the results of the tracer-injection study.

Study Area Description

The May Day mine site is located near San Juan County Road 110 approximately 45 m west of Cement Creek (fig. 3). Coordinates of the May Day mine are lat 37°50'49" N., long 107°40'43" W., at an elevation of 3,018 m above sea level. The May Day mine (about 1,000 m of tunnels) was excavated through propylitically altered andesitic lavas (Burns Member of the Oligocene Silverton Volcanics; Yager and Bove, this volume, Chapter E1) to access north-south-trending vein structures subparallel to the Cement Creek valley. Production and mining records from the May Day mine are generally lacking, but mining probably occurred from about 1910 to 1950. Minerals extracted from the mine included sulfide minerals galena (PbS), sphalerite (ZnS), pyrite (FeS₂), and chalcopyrite (CuFeS₂); gangue minerals included quartz and feldspars, and the wall rock consists of andesitic lavas. The May Day mine entrance has no perennial mine drainage, but pools of water form near the entrance from snowmelt runoff during April–June of each year, and pools are present in the back of the mine during wet years. The volume of the mine waste-rock pile is about 5,000 m³ (Hein and Fitterman, 1998).

The May Day mine site is a difficult site to characterize because mine drainage does not discharge directly from the adit, and the area has complex hydrogeology. Airborne conductivity mapping (Smith and others, 2001) has shown a linear feature (indicating a possible linear zone of fractured rock) near the May Day mine site. The linear feature originates in the Ohio Peak area northwest of the mine site (fig. 1) and projects into the lower segment of Cement Creek near Topeka Gulch and the May Day mine (Smith and others, this volume, Chapter E4). This linear feature may act as a conduit for discharge of ground water from mineralized areas near Ohio Peak into Cement Creek.

The tracer study includes the reach affected by the Yukon tunnel (fig. 2), which was a much larger underground mine than the May Day mine. The Yukon tunnel operated from about 1900 to the 1980s (Colorado State Archives, <http://www.archives.state.co.us/hmrfi/g.htm>, accessed December 31, 2002), and the primary target was tungsten from the mineral huebnerite (MnWO₄). The waste-rock pile of the Yukon tunnel contains abundant pyrite and other sulfide minerals, and it is at least three times larger than the May Day mine waste-rock pile. A small mill operated at the site during the 1970s. Mine drainage from the main, northern Yukon adit (fig. 2) is routed through a pipe into Illinois Gulch, about 50 m upstream from the confluence with Cement Creek. Discharge of water from the

adit was about 0.03 m³/s (Jim Herron, Bruce Stover, and Paul Krabacher, Unpublished Cement Creek reclamation feasibility report, Upper Animas River Basin, Colorado Division of Minerals and Geology, 1998). Concentrations of dissolved constituents in water from the Yukon adit were not high (pH=6.9, Al=<40 µg/L (micrograms per liter), Cu= <4 µg/L, Fe=200 µg/L, Mn=660 µg/L, SO₄=530 mg/L, and Zn=80 µg/L; Mast and others, 2000). Diffuse ground water seeps into and saturates the waste-rock pile and discharges into a constructed wetland before entering Cement Creek. Concentrations of dissolved constituents in the seeps below the Yukon waste-rock pile were extremely high (pH=2.5, Al=208 mg/L (milligrams per liter), Cu=14 mg/L, Fe=1,200 mg/L, Mn=56 mg/L, SO₄=2,700 mg/L, and Zn=46 mg/L; Mast and others, 2000). A small amount of water also discharges from the southern Yukon adit (fig. 2). It is difficult to sort out the contribution of Yukon adit drainage to the study reach because the drainage is included with the flow from Illinois Gulch; however, dissolved trace metals were below the detection limit in water from Illinois Gulch upstream from the Yukon adit (Mast and others, 2000). Most of the constituent loading in the Yukon reach should, therefore, come from seepage below the Yukon waste-rock pile.

Purpose and Scope

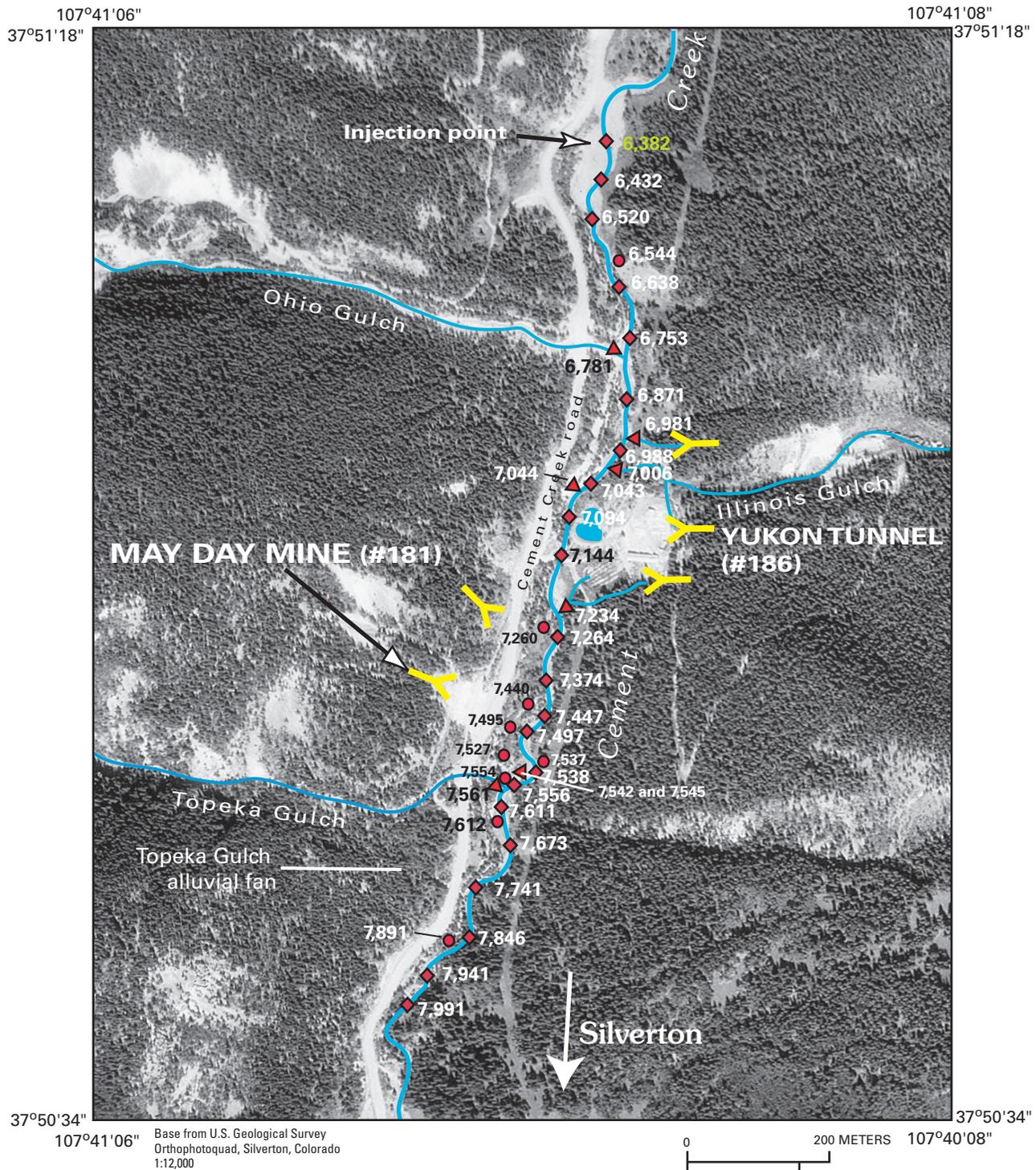
The objectives of this study were to:

- Quantify the sources of constituent loading from the May Day mine site to Cement Creek
- Describe the effects of the Illinois Gulch mixing zone on constituent transport in Cement Creek.

During August 15–17, 2000, the tracer-injection study was conducted in a 1,609-m reach of Cement Creek. Earlier tracer-injection studies in Cement Creek (Walton-Day and others, 2000; Kimball and others, 2002) measured the reach distances beginning from the headwaters of Cement Creek. To be consistent with the previous studies, the reach distances in this chapter are referenced to the headwaters distances. Therefore, the injection point for this tracer-injection study (local reach distance of 0 m) was assigned a reach distance of 6,382 m; the end of the reach for this study (local reach distance of 1,609 m) was assigned a reach distance of 7,991 m.

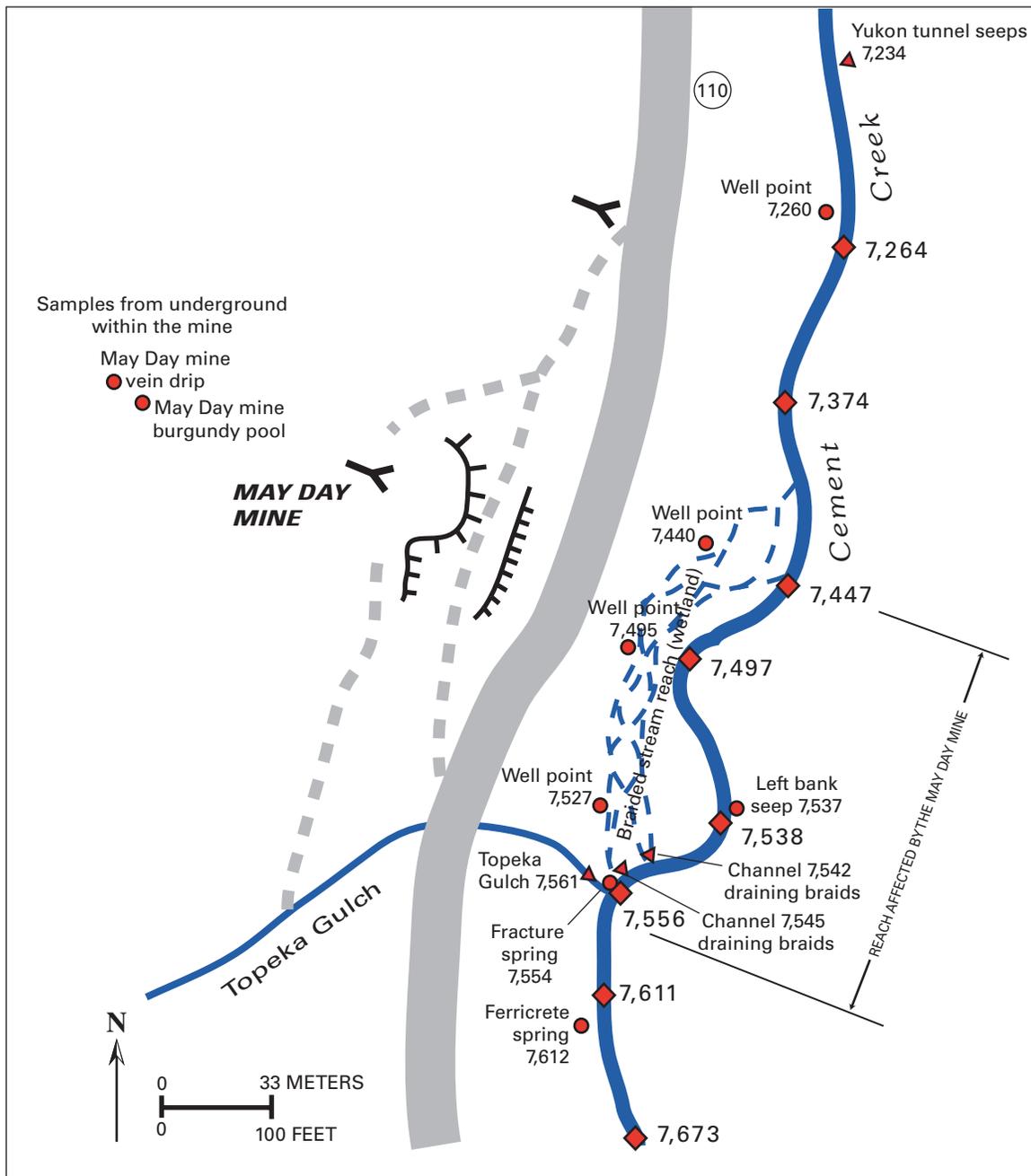
Acknowledgments

Tracer-injection studies require an intensive period of data collection by many technical specialists. The authors acknowledge the assistance of Katherine Walton-Day, Robert E. Broshears, Jonathan B. Evans, Kenneth J. Leib, Tracy J. Yager, Philip L. Verplanck, Adam Kimball, Stephanie Odell, Bruce Stover, Aaron Packman, Katherine Zillich, Andrew Gleason, and Loren Wickstrom. This work was partially funded by the Bureau of Land Management. The Bureau of Reclamation installed ground-water monitoring wells at the May Day mine site.



- EXPLANATION**
-  Adit
 -  6,520 Stream sample and distance, in meters, relative to headwaters reference point
 -  Inflow or tributary sample
 -  Spring or well-point sample

Figure 2. Location of study reach, sample sites, and reach distances referenced to previous study of Kimball and others (2002).



EXPLANATION

- ◆ 7,497 Stream sampling cross section and distance, in meters, relative to headwaters reference point
- 7,527 Well point, seep, or spring sample and number
- ▲ 7,234 Inflow (tributary) sample and number
- Y Adit
- Waste piles—Hachures on downslope side
- Abandoned road

Figure 3. Study reach affected by May Day mine site.

Methods of Study

Stream Tracer-Injection Study

An important part of the tracer-injection study is the measurement of the stream length, location of all visible inflows, and collection of numerous instream and inflow samples. On August 15, 2000, a cloth tape was used to measure the tracer-injection reach; instantaneous discharge measurements were made to estimate the necessary tracer concentration and injection rate; and inflows and tributaries were marked. Calculations were done to estimate the necessary concentration of tracer solution so that dilution of the tracer by inflows could be observed. Beginning on August 16, 2000, a solution of concentrated lithium bromide (18,045 mg/L as lithium) was pumped into Cement Creek at an injection rate of 198 mL/min upstream from Ohio Gulch at reach distance 6,382 m (fig. 2). In order to conduct a synoptic sampling event, and to use the tracer concentrations to calculate streamflow discharges, tracer concentrations must be steady throughout the reach (called the plateau condition). Automatic samplers were placed at fixed locations in the study reach; when steady tracer concentrations were obtained at these fixed sites, plateau conditions were achieved. The injection pump shut down overnight, but the pump was restarted 7 hours before the synoptic. Plateau conditions were achieved almost immediately after injection began on August 16, and plateau conditions were again quickly achieved after the pump was restarted on August 17 (fig. 4). The synoptic sampling effort—or snapshot in time—was done on August 17, 2000 (fig. 4).

Tracer concentrations in the stream were used to compute the streamflow discharges in the study reach, and the streamflow discharge profile was constructed from the discharge data. Dissolved lithium was used in this study for the tracer concentrations. Construction of the streamflow discharge profile in the study reach was difficult, owing to poor mixing of the tracer in certain segments, such as downstream from Illinois Gulch. Therefore, discharges were computed at selected control points in the stream where confidence in the lithium data was better (sites 6,638, 6,988, 7,043, 7,094, 7,538, and 7,941; fig. 2). Discharge was computed via the equation:

$$Q_{stream} = Q_{injection} * C_{injection} / (C_{stream} - C_{background}) \quad (1)$$

where

- Q_{stream} was the calculated discharge at the control point in the stream,
 - $Q_{injection}$ was the flow rate of the injection pump (0.033 L/s),
 - $C_{injection}$ was the lithium concentration of the injectate (18,045 mg/L),
 - C_{stream} was the lithium concentration in the stream at the control point (from analytical data),
- and
- $C_{background}$ was the background lithium concentration (0.02 mg/L).

Discharge at the remaining sites was estimated by linear interpolation between the control points (fig. 5). The streamflow discharges were verified by instantaneous discharge measurements (using a flow anemometer) done on the day of

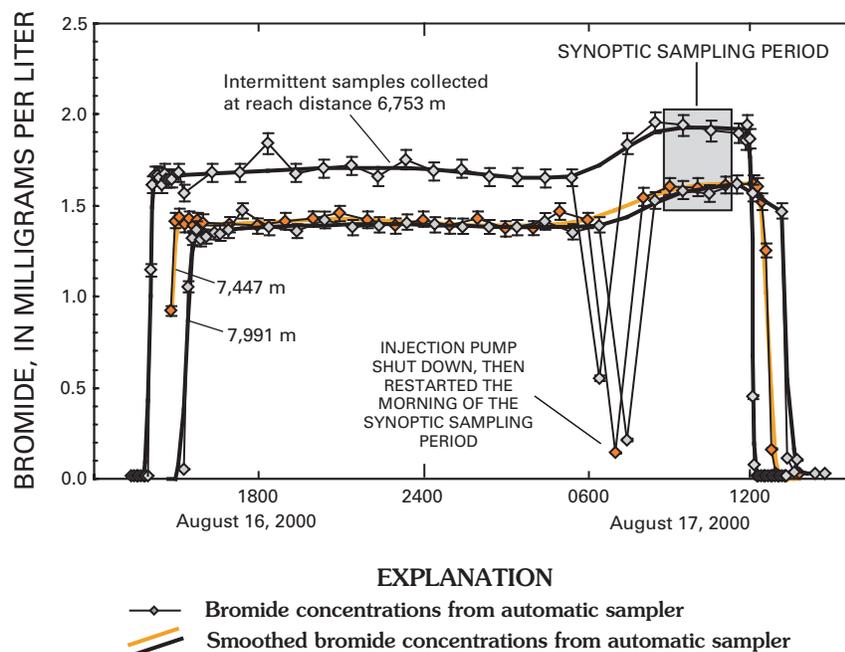


Figure 4. Bromide concentrations at fixed sites illustrating plateau conditions. Error bars show plus-or-minus standard deviation of laboratory analyses.

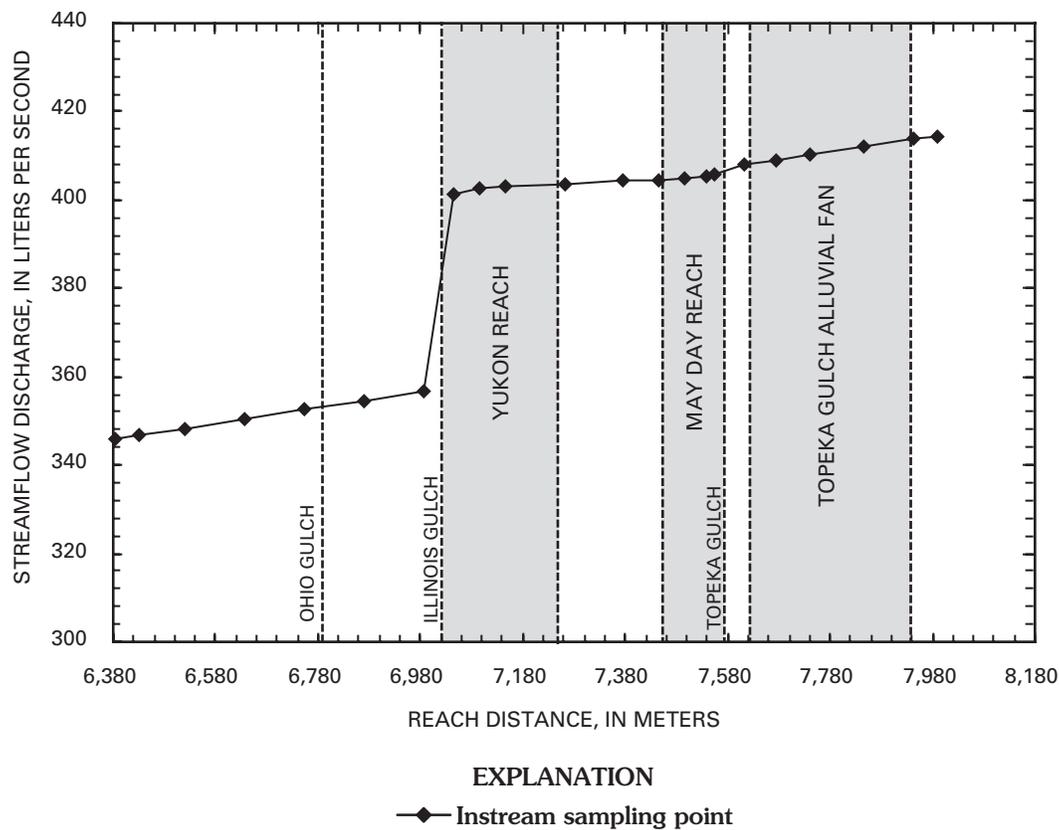


Figure 5. Longitudinal stream profile of discharges in the study reach.

the synoptic. For example, from equation 1, the discharge at site 7,941 was 413.6 L/s, and the instantaneous discharge measurement at the next site downstream (7,991) was 414.5 L/s on August 17, 2000, at 1300 hours. Inflow discharges were estimated by the difference of discharge between streamflow discharge at upstream and downstream sites.

On the day of the synoptic, water samples were collected from 41 sites throughout the study reach (table 1; fig. 2). This collection included 22 stream samples, 12 inflow samples, 4 samples from well points, 1 seep site, and 2 samples from inside the mine. Stream samples were collected via depth- and width-integrated sampling techniques (Edwards and Glysson, 1988), and inflow samples were collected via grab methods. Samples were placed in 2-L pre-cleaned polyethylene containers and transported in dark plastic bags (to prevent the effects of sunlight on water samples) to a central location near the study reach. Field measurements for pH and other properties were done within 1 hour of sample collection. Stream samples were filtered through a laboratory-scale, tangential-flow, ultra-filtration apparatus with 10,000-Dalton molecular weight filters, and they were filtered at the central location near the study reach within 2 hours of sample collection. Samples were decanted for analysis of total (unfiltered) constituent concentrations. Inflows were sampled for total (unfiltered) analyses. Details of sample collection, filtration methods, and laboratory analyses for tracer-injection studies are described in Kimball and others (2002).

Quantification of Constituent Concentrations and Loads

Longitudinal stream profiles of pH values, constituent concentrations, and constituent loads are used in this chapter to illustrate the effects of tributaries, mine sites, springs, and diffuse sources on the fate and transport of contaminants in the stream. The synoptic sampling effort collects the numerous samples to characterize the study reach, and laboratory analyses of the samples provide data to construct the longitudinal profiles of constituent concentrations. Loads are computed by multiplication of the streamflow discharge by constituent concentrations (Kimball and others, 2000; Kimball and others, this volume). To describe the stream-water quality of the study reach, different characteristics of the data are presented:

1. Total instream concentrations and loads from unfiltered analyses. These data represent what the fish and aquatic life actually are exposed to in the stream.
2. Dissolved instream concentrations and loads from samples filtered through the ultrafiltration apparatus. These data represent what actually is in the dissolved phase, and indicate the constituents that result from mineral dissolution.
3. Colloidal instream load—total load (1) minus the dissolved load (2). This represents the solid phases that are being transported as suspended particulates in the stream.

Colloidal load is part of the suspended load; however, this is quite different from the typical definition of suspended sediment transport, where silt- and sand-sized particles are transported by saltation (Graf, 1971). Colloids result from the chemical precipitation of dissolved constituents that are supersaturated with respect to a mineral phase. Colloids frequently are composed of amorphous (unidentifiable or noncrystalline) solids. In waters affected by acid-rock drainage, these solids consist of amorphous iron oxyhydroxide, iron sulfate, aluminum hydroxide, and aluminum sulfate phases (Schemel and others, 2000).

4. Cumulative instream load—sum of positive total load changes in a downstream direction. Because the total (unfiltered) load is the combination of all constituent phases—dissolved and colloidal—being transported by the stream, it becomes useful to sum the positive changes of instream load between stream sites in a cumulative downstream direction. This sum gives the best estimate of the total loading along the study reach. The cumulative instream load also indicates the total load in the stream if attenuation or colloid precipitation was not taking place.
5. Cumulative inflow loads—sum of inflow loads in a downstream direction. Inflows are the obvious tributaries, primarily consisting of visible streams and springs, and these obvious inflows are sampled during the synoptic. Inflow constituent loads are computed by multiplication of the inflow discharge by the inflow total (unfiltered) concentrations (Kimball and others, 2000). The inflow loads are summed in a downstream direction and compared to the cumulative instream loads, which also are total (unfiltered) loads. If the cumulative inflow loads do not equal the cumulative instream loads, there was probably a diffuse ground-water inflow that was not sampled. In addition to the diffuse nature of some lateral inflows, ground water can be moving down valley in the subsurface and can be forced to the surface by geologic structures or fractures, discharging to the stream as diffuse ground water (Wyrick and Borchers, 1981).

Evaluation of Sources

There are few methods to distinguish sources of constituents that enter a stream reach; for example, do they come from bedrock or mining-related sources? These sources may be evaluated using the light stable isotopes of water (Muir and Coplen, 1981; Hoefs, 1987). Oxygen and hydrogen stable isotopes can be affected by the source of the water (different weather patterns, altitude of precipitation, or connate water deposited in rock formations), and the isotopes are fractionated by evaporation, plant transpiration (Hoefs, 1987), and water-rock interaction (Plumlee and others, 1999). Hence, light stable

isotope values can help to identify different sources of water. During the tracer-injection study, isotope samples were collected from selected well points, springs and seeps, and pools inside the mine (fig. 3).

Patterns in the chemistry and pH of stream and inflow samples were evaluated by use of Principal Components Analysis (PCA), a multivariate analysis technique (Daultrey, 1976; Joreskog and others, 1976; Grundy and Miesch, 1987). Principal components represent a set of new, transformed reference axes that are linear combinations of the original variables; PCA is a transformation of data, not a statistical treatment. A principal components transformation orients the data points so that the first of the new axes, principal component 1 (PC1), is oriented along the direction of the greatest variance in the data. The second principal component (PC2) is orthogonal to PC1, and is oriented to show the next greatest amount of variance in the data. This is easy to picture in two dimensions. One can imagine drawing a line that would go through the two most distant points in a bivariate plot of data; that would be the direction of PC1. It would be at some angle to the original *x* and *y* axes, but any point along the line could be described by a linear equation. PC2 would be drawn perpendicular to PC1, and it would have its own linear equation. In multidimensional space, each subsequent principal component is orthogonal to the first two and represents a decreasing amount of the total variance.

Typically, the first two or three principal components show enough of the variance in the data set to enable the recognition of groups among samples; this is the advantage of using the method for multivariate data. Synoptic samples are plotted by their PCA scores, which are the coordinates of the original data points on the new principal component axes. Adding vectors representing the correlations of original variables with the new principal component axes to the plot of scores creates a biplot. The vectors help identify variations in chemistry among the groups of samples. For the analysis, chemical concentrations, including pH, were converted to millimoles per liter and used in the biplots after logarithmic transformation.

Effects of the May Day Mine Site on Stream-Water Quality

The mixing zone downstream from Illinois Gulch and the reach affected by the May Day mine were of primary interest, and a considerable stream length was required to adequately mix the tracer solution; therefore, the injection point was located upstream from Ohio Gulch (fig. 2). Longitudinal stream profiles of pH values, constituent concentrations, and constituent loads illustrate the effects of inflows and mine sites on stream-water quality.

Table 1. Sites where water-quality samples were collected in the tracer study reach, August 17, 2000.

[--, not applicable]

Site description	Distance from headwaters of Cement Creek (meters)	Sample from stream, east bank, or west bank (fig. 2)	Features described in figures and graphs
Mainstem sites			
Upstream from injection	6,382	stream	
First site downstream from injection	6,432	stream	
Downstream 129 meters from injection	6,520	stream	
Downstream from diffuse inflows	6,638	stream	
Upstream from Ohio Gulch, autosampler	6,753	stream	
Downstream 90 meters from Ohio Gulch	6,871	stream	
Upstream from Illinois Gulch	6,988	stream	
Downstream 37 meters from Illinois Gulch	7,043	stream	Yukon tunnel reach
Downstream 88 meters from Illinois Gulch	7,094	stream	
At Bridge to Yukon tunnel	7,144	stream	
Downstream from Yukon tunnel seeps	7,264	stream	
Downstream from seepage along banks	7,374	stream	
Near beginning of braided reach, autosampler	7,447	stream	May Day mine reach
Adjacent to braided reach	7,497	stream	
Upstream from May Day inflows	7,538	stream	
Upstream from Topeka Gulch	7,556	stream	
Downstream from Topeka Gulch	7,611	stream	Topeka Gulch alluvial fan
Downstream from Topeka Gulch alluvial fan	7,673	stream	
Near end of Topeka Gulch alluvial fan	7,741	stream	
Downstream from cascading reach	7,846	stream	
Downstream from large spring	7,941	stream	
End of study reach, autosampler	7,991	stream	
Tributary, well point, and spring sites			
Spring discharging from hill	6,544	east	
Ohio Gulch at mouth	6,781	west	
Unnamed adit upstream from Illinois Gulch	6,981	east	
Illinois Gulch	7,006	east	Yukon tunnel reach
Draining small gully on right bank	7,044	west	
Yukon tunnel seep 7,234	7,234	east	
Well point 7,260	7,260	west	
Well point 7,440	7,440	west	May Day mine reach
Well point 7,495	7,495	west	
Well point 7,527	7,527	west	
Left bank seep 7,537	7,537	east	
First channel draining braided reach	7,542	west	
Channel draining braided reach	7,545	west	
Fracture spring 7,554	7,554	west	
Topeka Gulch at mouth	7,561	west	
Large ferricrete spring 7,612	7,612	west	Topeka Gulch alluvial fan
Spring in Topeka Gulch alluvial fan	7,891	west	
Sites inside the May Day mine			
North mineralized vein within mine	--	--	Mine sample
Burgundy pool in mine	--	--	Mine sample

pH and Constituent Concentrations

The longitudinal profile of pH and constituent concentrations in the study reach was affected by several factors: (1) inflows with low or high pH (direct and diffuse sources), (2) inflows with low or high constituent concentrations (direct and diffuse sources), (3) dilution from inflows, (4) analytical error in laboratory measurement of constituent concentrations, and (5) measurement error in collection of adequate width-integrated samples across the stream cross section. The analytical error was addressed by showing the analytical precision of each measurement on the concentration profiles; the error bars show the plus-or-minus precision estimates for each analytical determination. If the lower error limit of a downstream concentration was greater than the upper error limit of an upstream concentration, there was probably a significant increase in a constituent concentration entering the stream between those two points (Kimball and others, 2002). The errors associated with loads can be cumulative because of the analytical concentration error and the possible error in

discharge computation. These errors are discussed in Kimball and others (this volume), but the method was not applied to loading data presented in this chapter.

The most apparent feature of the pH profile in the study reach was the increase in stream pH due to streamflow from Illinois Gulch (fig. 6). In general, the west side (right bank) of the Cement Creek basin contains metal-rich rocks and very low pH water, and the east side contains propylitically altered rocks with higher pH water (Mast and others, 1998). This reflects the distribution of hydrothermally altered rocks in the watershed (Bove and others, this volume, Chapter E3). From previous studies, the mainstem of Cement Creek has a pH of less than 4 for most of its 11.6 km length (Kimball and others, 2002; Walton-Day and others, 2000); however, in the lower reaches several tributaries that drain rocks from the east side of Cement Creek have circumneutral pH; these include Illinois Gulch. The pH of Cement Creek at the injection point was about 3.65 on the day of the synoptic sampling (fig. 6). Downstream from the confluence with Illinois Gulch, which had a pH of 7.39, the pH of Cement Creek increased to 4.16

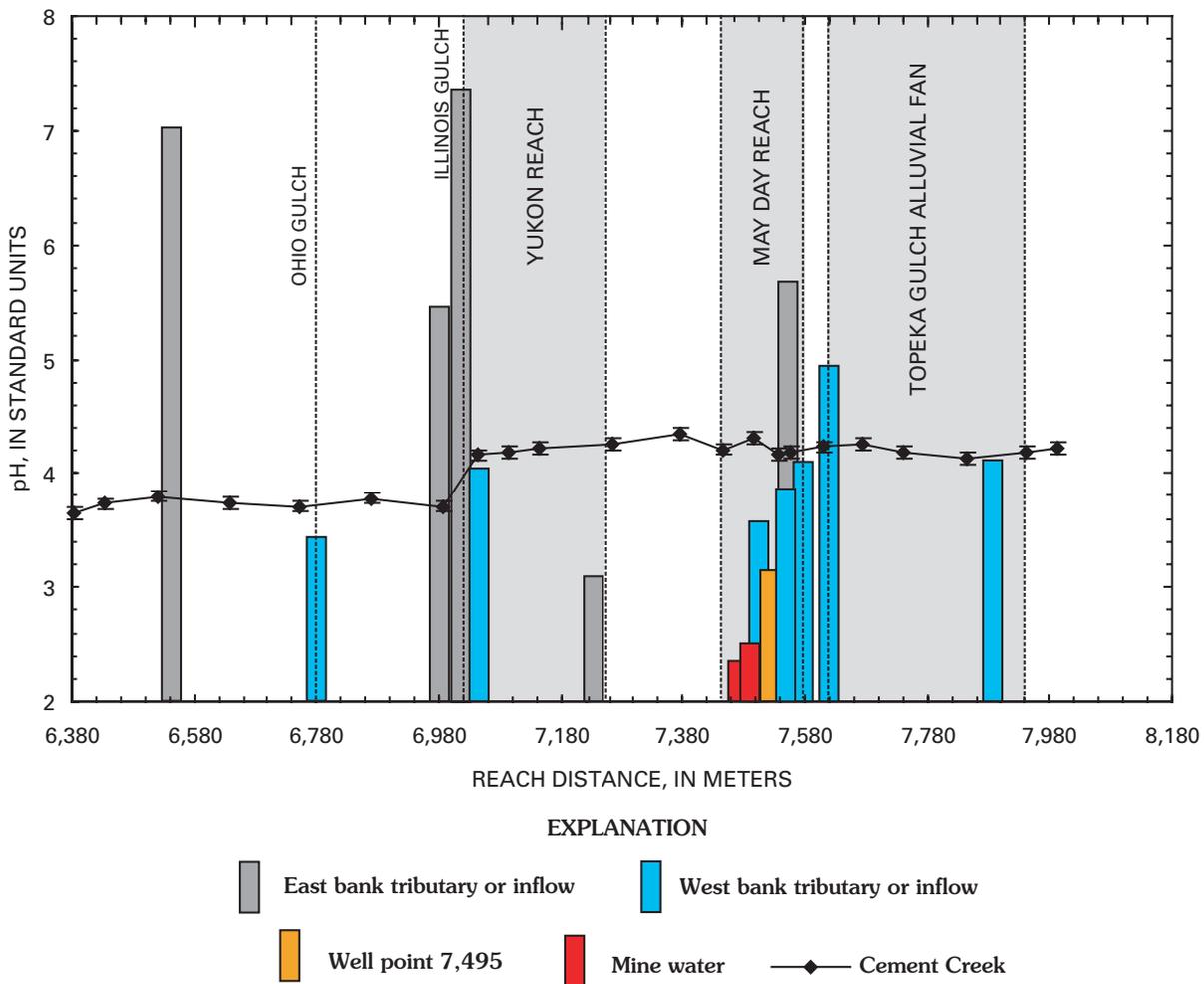


Figure 6. Longitudinal stream profile of pH in Cement Creek through study reach and pH values of inflows and tributaries. Error bars represent ±0.05 pH units.

and continued to increase to 4.35 even though the seeps from the Yukon site had a pH of 3.09. The stream pH decreased to 4.21 at reach distance 7,447 m. The pH fluctuated between 4.31 and 4.17 through the reach affected by the May Day mine site (fig. 6). Even though the water from the pools inside the May Day mine had a pH of 2.49, the pH in Cement Creek was only slightly affected by inflows from the mine site because of small inflow discharges.

Increases and decreases of dissolved and total aluminum concentrations alternated between sites throughout the study reach (fig. 7A). The dissolved and total aluminum concentrations were mostly the same at each site because of the low stream pH (fig. 7A). Aluminum precipitation from the dissolved phase occurs between pH 4.4 and 5.4, and aluminum does not completely precipitate from solution until pH exceeds 5.4 (Nordstrom and Ball, 1986). Hence, with the stream pH of 3.65 to 4.19, a substantial amount (between 5.3 and 6.4 mg/L) of dissolved aluminum was present in the stream. Downstream from Illinois Gulch, dissolved and total aluminum concentrations showed a decrease that was probably caused by dilution. Total aluminum concentrations increased in the May Day reach, possibly due to increased concentrations of aluminum particulates.

Total copper concentrations showed alternating increases and decreases throughout the study reach (fig. 7B). There may have been contamination of the water-quality samples for the dissolved copper analyses due to a malfunction of the ultrafiltration apparatus; therefore, dissolved copper results are not presented. Samples for analysis of total copper did not contact the filtration apparatus; therefore, total copper results are presented. Total copper concentrations increased at 6,988 m, just downstream from the inflow of the adit at 6,981 m (fig. 2). Downstream from Illinois Gulch, the total copper decreased, possibly due to dilution. Generally, total copper increased slightly in Cement Creek as it flowed past the Yukon site, and total copper increased in the May Day reach. Total copper increased at 7,846 m, downstream from the Topeka Gulch alluvial fan (fig. 2), and then decreased to the end of the study reach.

In contrast to the aluminum profile, dissolved iron concentrations in the study reach were consistently less than total iron concentrations (fig. 7C), a condition caused by the pH values of the stream being greater than that for iron solubility. Theoretical iron solubility occurs at about pH 1.7 (Garrels and Christ, 1965), but other factors affecting iron solubility, such as photoreduction (McKnight and others, 1988), contribute to the presence of dissolved iron in water measuring above this pH. Dissolved iron concentrations decreased downstream from Illinois Gulch (from 5.25 to 4.18 mg/L). The slight increase of total iron downstream from Illinois Gulch shows inflows from the Yukon tunnel. Dissolved iron concentrations were not significantly affected by the May Day reach; however, total iron concentrations increased at the May Day reach (fig. 7C). Total iron concentrations increased steadily from 7,741 m to 7,941 m, in the reach affected by the Topeka Gulch alluvial fan.

Dissolved and total manganese concentrations showed alternating increases and decreases throughout the study reach (fig. 8A). However, because both the dissolved and the total concentrations were within the analytical error limits along most of the study reach, they essentially were equal. That total manganese concentrations decreased downstream from Illinois Gulch indicated dilution by the inflow. Total manganese increased substantially in the May Day reach (fig. 8A). Total manganese decreased downstream from Topeka Gulch, then increased at the lower end of the study reach.

Dissolved sulfate concentrations alternately increased and decreased throughout the study reach (fig. 8B); analyses for total sulfate concentrations were not done for this study, and are not shown on the graph. Downstream from the injection point, dissolved sulfate concentrations began a strong decrease just upstream from Illinois Gulch.

Dissolved and total zinc concentrations showed alternating increases and decreases throughout the study reach (fig. 8C). The dissolved concentration was greater than the total concentration at a few sites due to analytical error; the differences were less than 10 percent. Dissolved zinc concentrations decreased from the Ohio Gulch inflow to the May Day reach, followed by alternating increases and decreases from the May Day reach to the end of the study reach (fig. 8C). Total zinc concentrations decreased downstream from Illinois Gulch, increased in the May Day reach, and fluctuated downstream from Topeka Gulch (fig. 8C). Patterns of manganese and zinc concentrations were similar, possibly due to similar geologic sources of manganese and zinc minerals (Bove and others, this volume).

Constituent Loads

Increase in a constituent load reflects an input of constituent mass to the stream; decrease in constituent load reflects instream geochemical, biological, or physical processes by which mass is being removed. Longitudinal loading profiles were constructed for the study reach and show the loads for the different load fractions: (1) total load, (2) dissolved load, (3) colloidal load, (4) cumulative instream load, and (5) cumulative inflow load.

The longitudinal profile for aluminum loads showed that the dissolved and total fractions were about the same and the colloidal loads were small: the low pH values in the stream contributed to aluminum's remaining in the dissolved phase (fig. 9A). The dissolved aluminum load ranged from 2,047 to 2,268 mg/s in the study reach. In contrast, the colloidal aluminum load ranged from 0 to 342 mg/s; because of the graph scale, the colloidal aluminum load is not shown (fig. 9A). Aluminum loads were relatively constant throughout the study reach, except for an increase of total load upstream from Illinois Gulch (unnamed mine site 6,981—fig. 2; table 1), in the May Day reach, and through the Topeka Gulch alluvial fan (fig. 9A). Total aluminum loads decreased in the Yukon

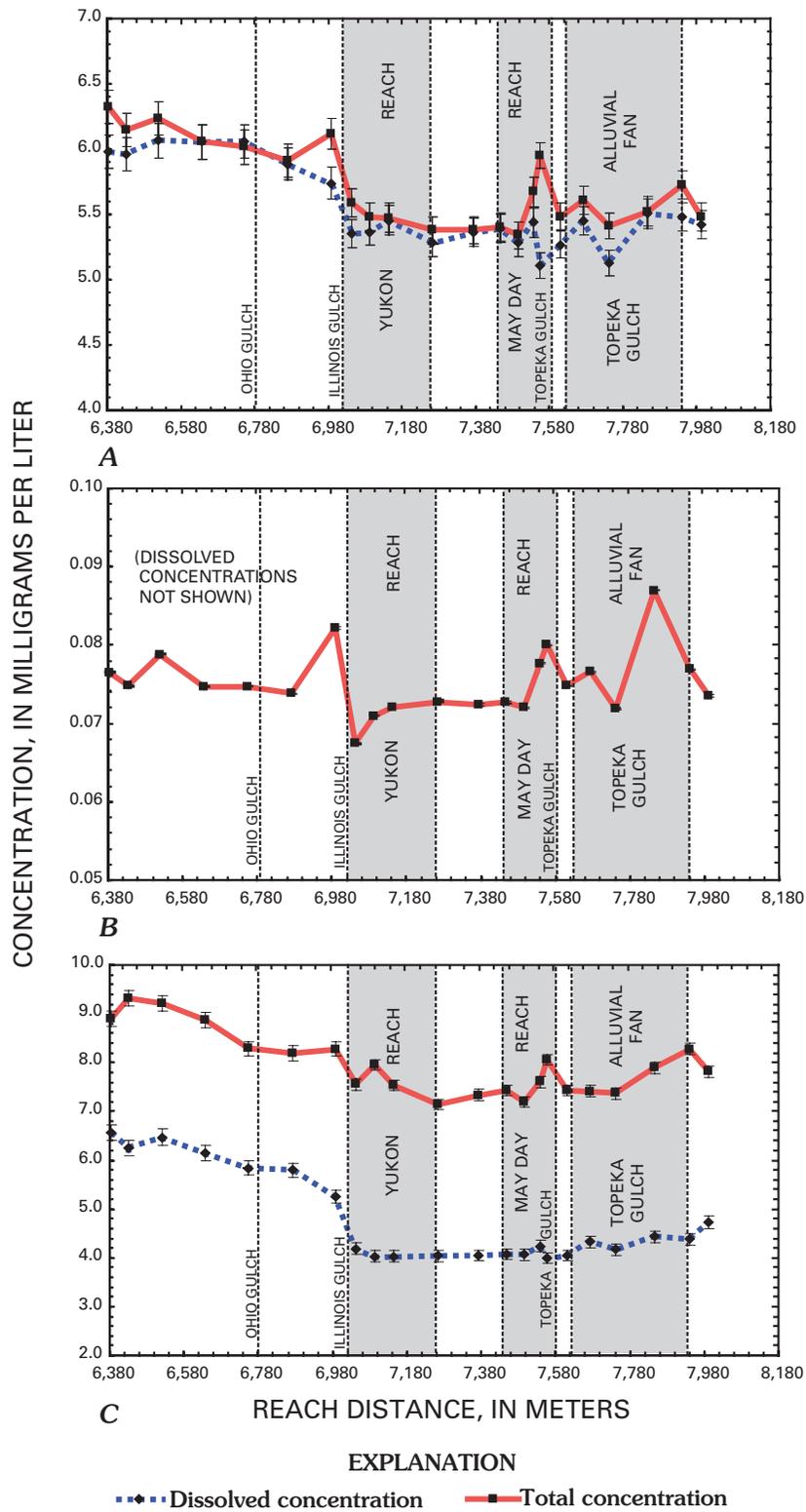


Figure 7. Longitudinal stream profiles of dissolved and total constituent concentrations in study reach. *A*, aluminum; *B*, copper; *C*, iron. Error bars show plus-and-minus analytical precision for each concentration.

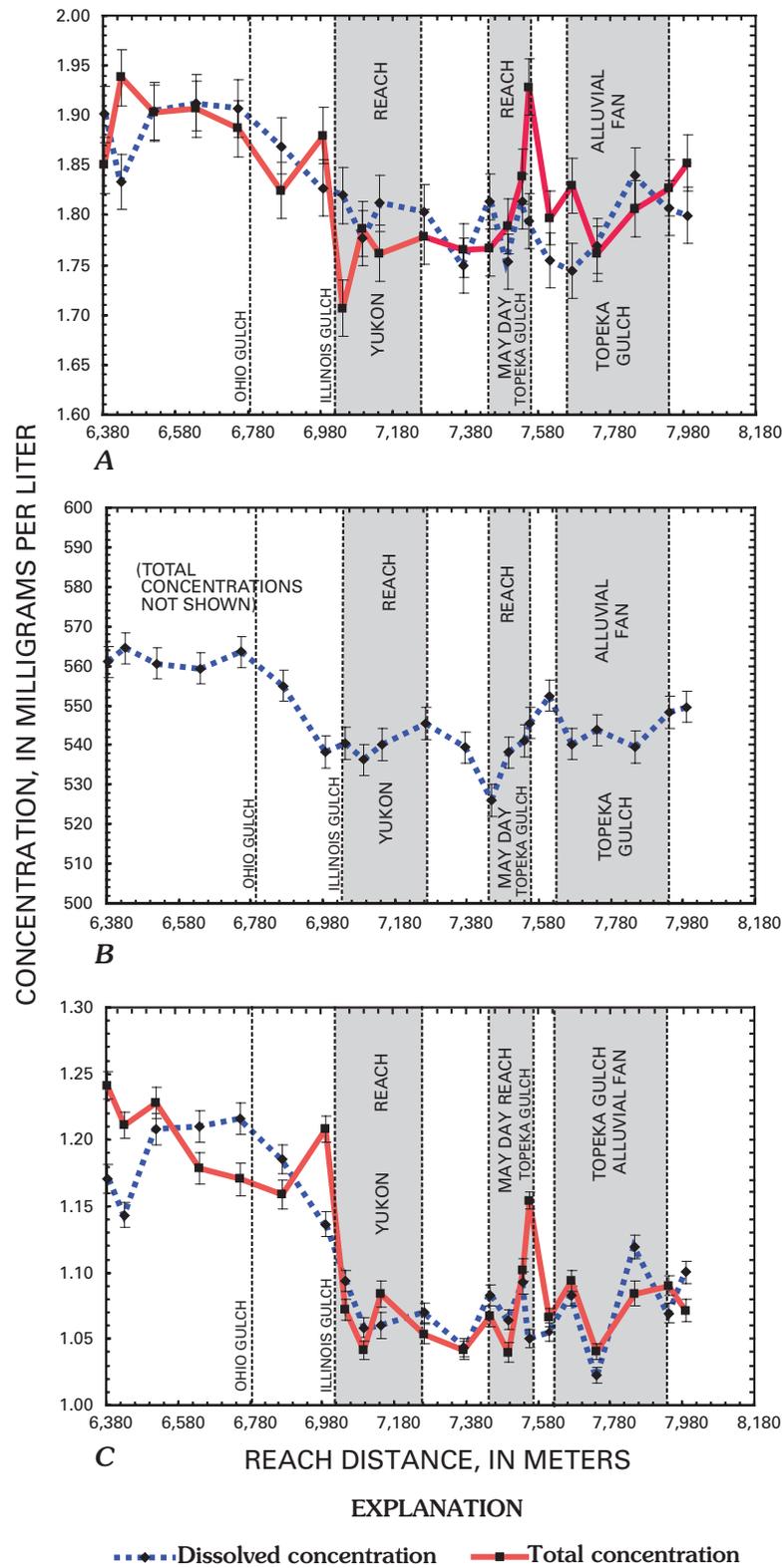


Figure 8. Longitudinal stream profiles of dissolved and total constituent concentrations in study reach. *A*, manganese; *B*, sulfate; *C*, zinc. Error bars show plus-and-minus analytical precision for each concentration.

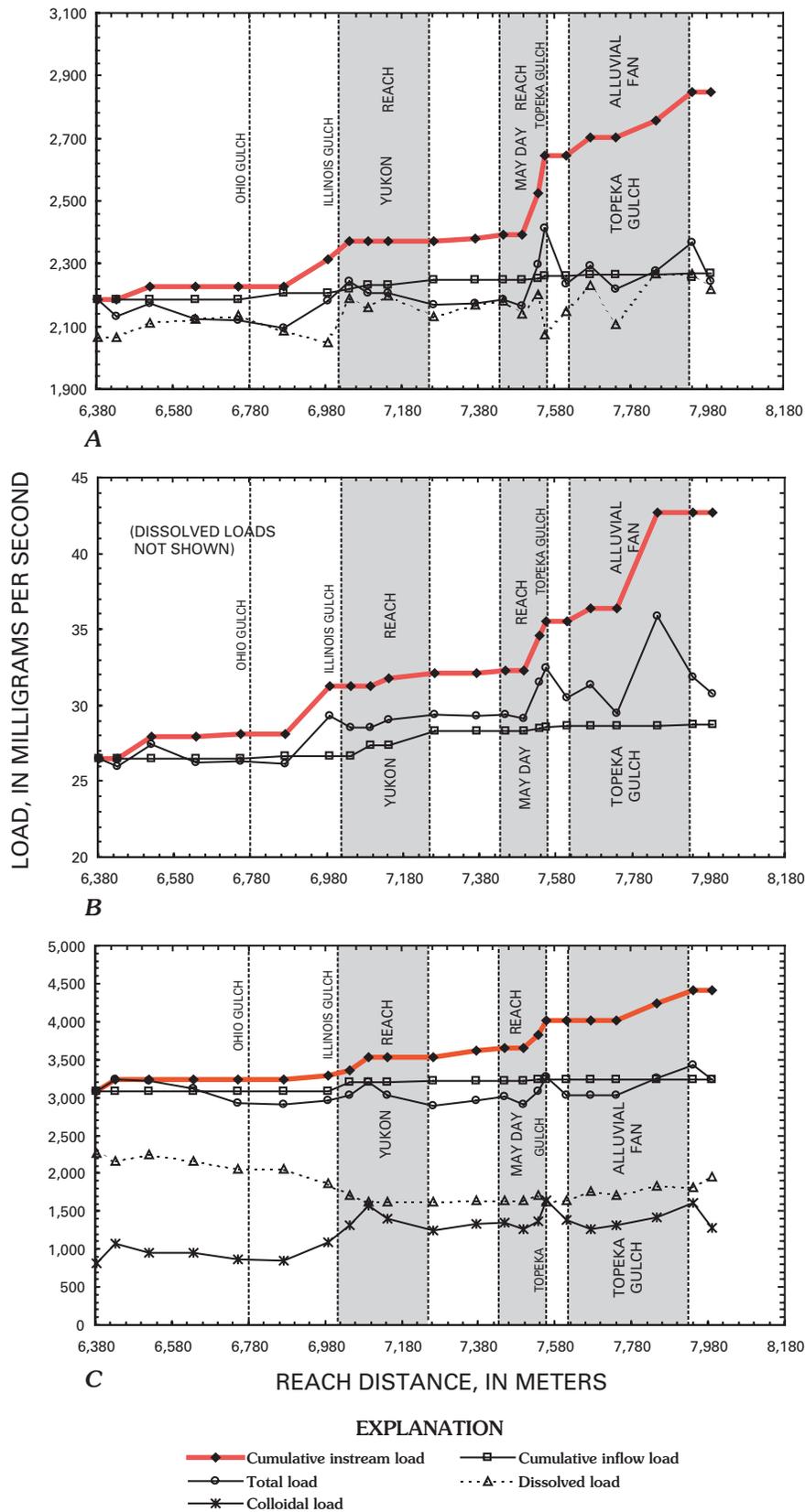


Figure 9. Longitudinal stream profiles of constituent loads in study reach. A, aluminum; B, copper; C, iron.

reach. In the May Day reach, total aluminum load increased from 2,163 to 2,415 mg/s for a gain of 252 mg/s. Cumulative instream loads were greater than the total loads throughout the study reach, indicating that nonconservative behavior and removal of aluminum took place. Some divergence of cumulative instream and total load occurred at Illinois Gulch, but most of the divergence occurred downstream from the May Day reach. Cumulative inflow loads were less than the cumulative instream loads, indicating the presence of unsampled or diffuse sources of aluminum loading in the study reach.

The longitudinal profile of total copper loads showed increases and decreases in the study reach (fig. 9B). Dissolved and colloidal copper loads are not presented, owing to copper contamination from the filtration equipment. Total copper loads increased upstream from Illinois Gulch, through the May Day reach, and in the lower end of the study reach affected by the Topeka Gulch alluvial fan (fig. 2; table 1). Gains in total copper loads were small in the Yukon reach. In the May Day reach, total copper load increased from 29.4 to 32.4 mg/s for a gain of 3.0 mg/s. Cumulative instream loads were greater than the total loads, indicating nonconservative behavior and removal of copper in the study reach. Cumulative inflow loads were less than cumulative instream loads, indicating diffuse sources of copper loading in the study reach.

The longitudinal profiles for iron loads showed that the dissolved and total fractions were quite different (fig. 9C), and colloidal loads were substantial compared to the other constituents. In the Yukon reach (affected by the mixing of Illinois Gulch and Cement Creek water), total iron load increased, dissolved load decreased, and colloidal load increased indicating precipitation of iron colloids (fig. 9C). Colloidal loads increased in the May Day reach, but the dissolved load remained essentially the same (fig. 9C). In the May Day reach, total iron loads increased from 3,006 to 3,267 mg/s for a gain of 261 mg/s. Cumulative instream loads were greater than the total loads, indicating nonconservative behavior and removal of iron in the study reach. Some divergence of cumulative instream and total load occurred between Illinois Gulch and the May Day reach, but most of the divergence occurred downstream from the May Day reach. Cumulative inflow loads were much less than the cumulative instream loads, indicating diffuse sources of iron loading in the study reach.

The longitudinal profile for manganese loads showed that the dissolved and total fractions were nearly the same, except in the May Day reach (fig. 10A). Colloidal loads were small compared to the total and dissolved loads; because of the graph scale, colloidal loads are not shown. Manganese loads increased upstream from Illinois Gulch, at Illinois Gulch, through the May Day reach, and downstream from Topeka Gulch. In the May Day reach, total manganese loads increased from 714 to 782 mg/s for a gain of 68 mg/s. Cumulative instream loads were greater than the total loads, indicating nonconservative behavior and removal of manganese in the study reach. Cumulative inflow loads were much less than the cumulative instream loads, indicating diffuse sources of manganese loading in the study reach.

The longitudinal profile for dissolved sulfate loads showed alternating decreases and increases (fig. 10B). Total sulfate was not analyzed; therefore, cumulative dissolved instream loads are shown rather than cumulative instream loads. The dissolved sulfate load increased at Illinois Gulch, the Yukon reach, the May Day reach, and downstream from Topeka Gulch. In the May Day reach, dissolved sulfate loads increased 8,000 mg/s. The large sulfate increase in the Yukon reach may be caused by the presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the Yukon tunnel. Cumulative dissolved loads were greater than the dissolved loads, indicating nonconservative behavior and removal of sulfate in the study reach. Cumulative inflow loads were less than the cumulative dissolved loads, indicating diffuse sources of sulfate loading in the study reach.

The longitudinal profile for zinc loads showed that the dissolved and total loads were nearly the same (fig. 10C), but the colloidal loads were small; because of the graph scale, colloidal loads are not shown. The cumulative instream zinc loads increased upstream from Illinois Gulch, in the Yukon reach, in the May Day reach, and downstream from Topeka Gulch (fig. 10C). In the May Day reach, zinc load increased 37.0 mg/s. Cumulative instream loads were greater than the total loads, indicating nonconservative behavior and removal of zinc in the study reach. Cumulative inflow loads were less than the cumulative instream loads, indicating diffuse sources of zinc loading in the study reach.

Constituent Attenuation

Constituent attenuation results from processes in the environment that act to reduce the mass of contaminants or constituents (Webster and others, 1994). The processes causing constituent attenuation may include adsorption, colloid precipitation, coprecipitation of metals with colloid formation, reaction with organic matter, losses to biofilm, and settling of colloids from the stream onto the streambed. Loss of the total load best reflects attenuation because the total mass (which includes dissolved and colloidal fractions) is removed from the system. Loss of dissolved load may result from colloid formation or other chemical and biological processes. Longitudinal profiles of changes in load between sampling points are shown to describe attenuation in the study reach.

The longitudinal profile of dissolved iron load showed alternating increases and decreases throughout the study reach; however, small changes may be due to analytical error. The dissolved iron load shows general patterns of load decrease in the upper portions of the study reach (fig. 11A), indicating iron precipitation and colloid formation. The dissolved iron load generally increased in the lower end of the study reach (fig. 11A), indicating gains of dissolved iron mass from inflows or the dissolution of iron colloids by low-pH inflows. The longitudinal profile of total iron load showed alternating increases and decreases throughout the study reach (fig. 11B). Decreases reflect a loss of iron mass from the system.

The longitudinal profile of dissolved sulfate load showed alternating increases and decreases throughout the study reach (fig. 12). A large increase of dissolved sulfate load came from

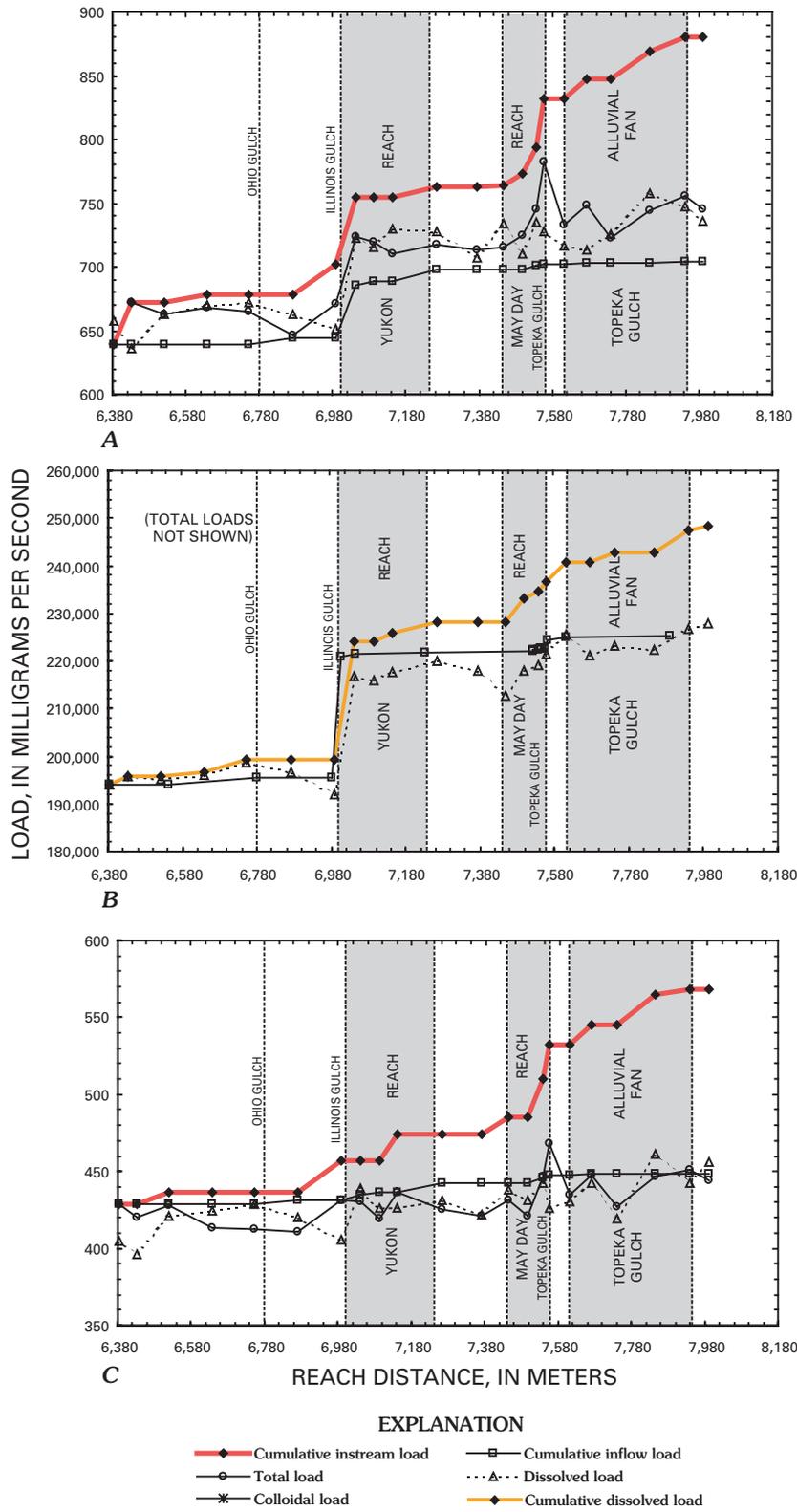


Figure 10. Longitudinal stream profiles of constituent loads in study reach. A, manganese; B, sulfate; C, zinc.

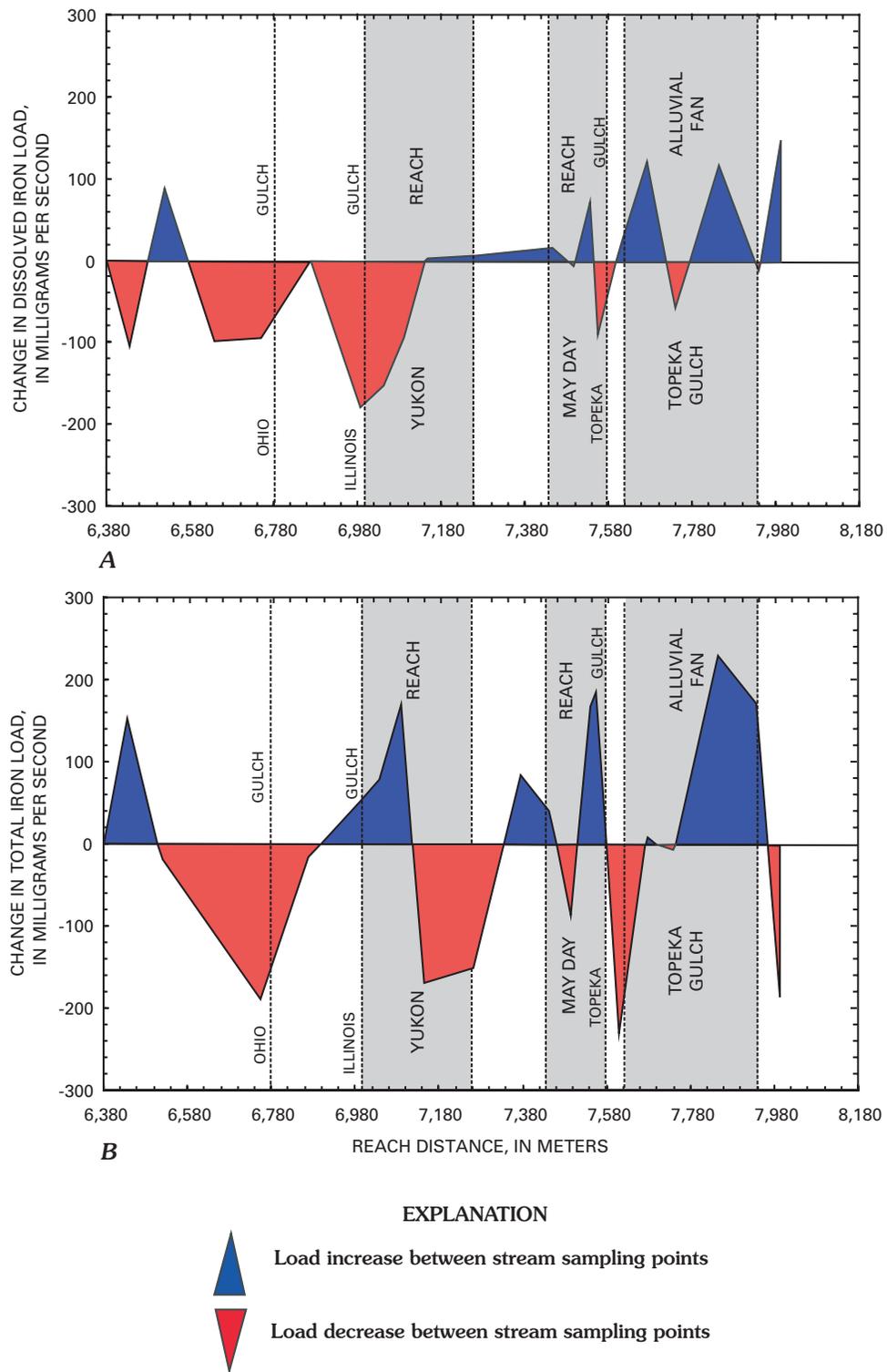


Figure 11. Longitudinal stream profiles of change in *A*, dissolved iron, and *B*, total iron loads in study reach.

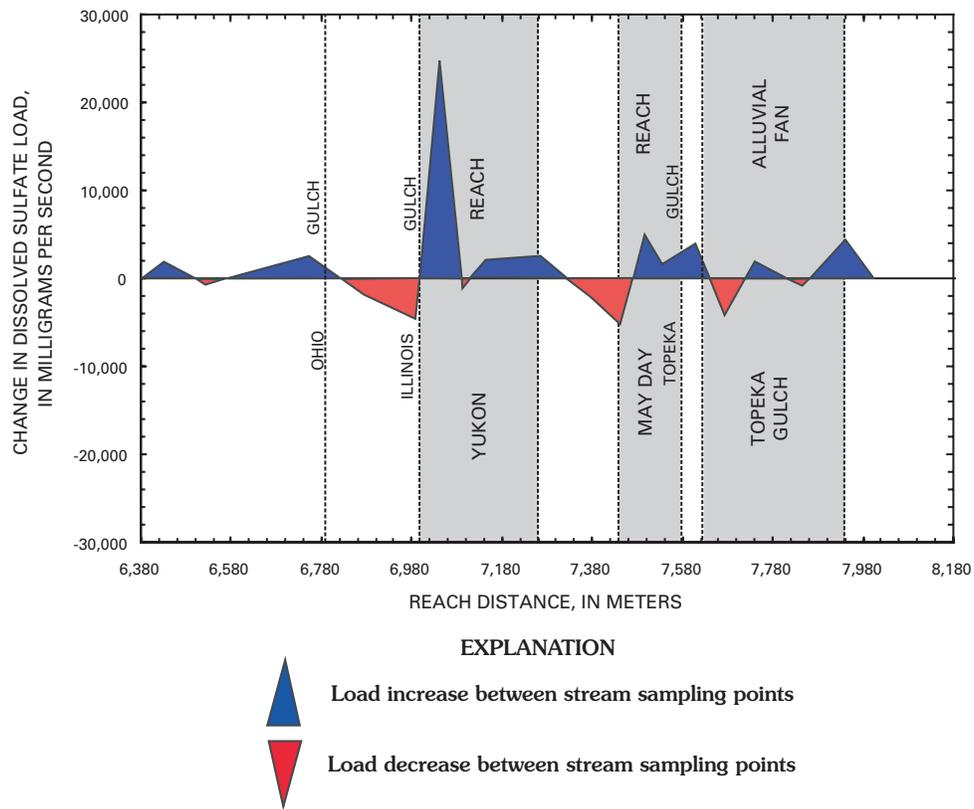


Figure 12. Longitudinal stream profile of change in dissolved sulfate loads in study reach.

Illinois Gulch (fig. 12) possibly due to the presence of gypsum and sulfate minerals in the Yukon tunnel and discharge of sulfate-rich mine drainage into Illinois Gulch from the Yukon adit. In several segments in the study reach, dissolved sulfate showed a decrease in load; however, the loss was only about 2 percent, which may be due to error. If dissolved sulfate losses did occur in the study reach, they could be due to precipitation of sulfate-containing colloids such as schwertmanite (Desborough and others, 2000).

The longitudinal profile of dissolved zinc loads showed alternating increases and decreases throughout the study reach (fig. 13A). An increase in zinc load reflects a gain of dissolved zinc mass from inflows and dissolution of colloids by low-pH inflows. Decreases may reflect a loss of dissolved zinc mass due to coprecipitation or adsorption of zinc along with the formation of iron sulfate colloids. These gains and losses were relatively small compared to the total zinc mass being transported by the stream (fig. 10C). Dissolved zinc loads decreased downstream from Ohio Gulch and the Yukon reach, with slight losses in the May Day reach and downstream from Topeka Gulch. Dissolved zinc loads increased just downstream from the injection point, at Illinois Gulch, at the Yukon tunnel settling ponds, and downstream from Topeka Gulch (fig. 13A). Total zinc loads increased at the inflow of the unnamed mine, in the Yukon reach, in the May Day reach, and through the Topeka Gulch alluvial fan (fig. 13B).

Evaluation of Water Sources

Water in the study reach came from three sources: (1) inflows or obvious tributaries, (2) obvious springs or seeps, and (3) diffuse ground-water inflows. The May Day mine site has no perennial discharge, and contaminant flow paths from the mine to the stream might occur as diffuse inflows; therefore, an evaluation of whether water from the May Day mine site discharges to Cement Creek was important. Two approaches were taken: (1) the use of light stable isotopes as a hydrologic tracer, and (2) principal components analysis (PCA).

Samples were collected in the May Day reach for analysis of the oxygen and hydrogen light stable isotopes of water. The ratio of the ¹⁸O and ¹⁶O isotopes and the ²H and ¹H isotopes is referenced to an international standard (The Vienna Standard Mean Ocean Water, or VSMOW), expressed in the delta notation:

$$\delta^{18}\text{O} = \left(\frac{^{18}\text{O}/^{16}\text{O}_{(\text{sample})}}{^{18}\text{O}/^{16}\text{O}_{(\text{standard})}} - 1 \right) \times 1,000 \quad (2)$$

where the units are in parts per thousand referenced to the standard, or per mil VSMOW. A similar expression is developed for the $\delta^2\text{H}$ isotopes. Craig (1961) plotted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope values from around the world and developed a global

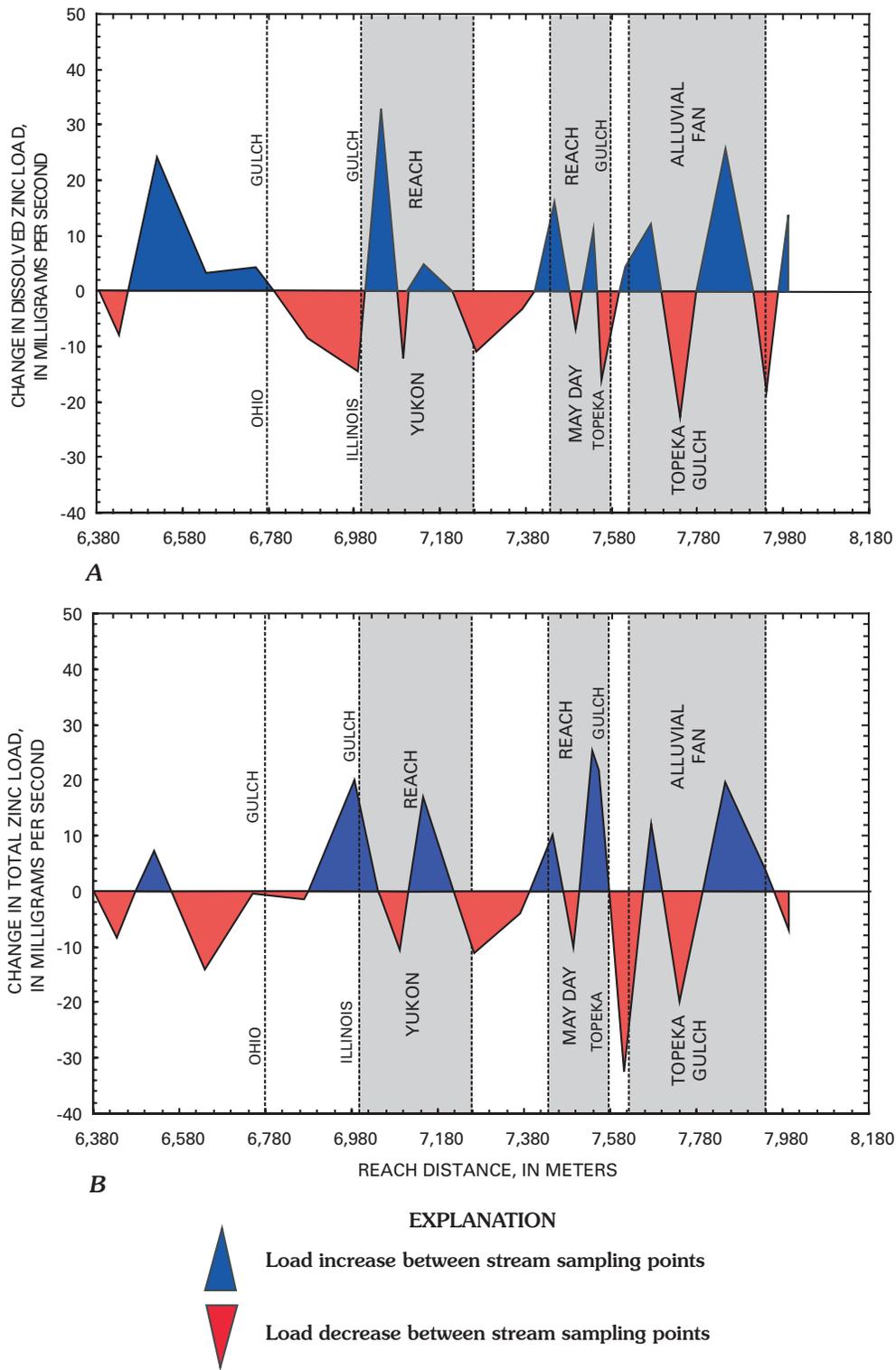


Figure 13. Longitudinal stream profiles of change in *A*, dissolved zinc, and *B*, total zinc loads in study reach.

meteoric water line (GMWL), and an equation for the slope of the GMWL with the expression $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$. Most $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope values should fall on or near the GMWL unless the isotopes have been fractionated by evaporation, plant transpiration, or water-rock interaction.

As part of previous studies in the Animas River watershed during 1995, isotope data were collected from springs, streams, and mines in Middle Fork Mineral Creek (Sole and others, this volume, Chapter G). An equation for the slope of these data has the expression $\delta^2\text{H} = 8.3 \delta^{18}\text{O} + 17$ (fig. 14), which differs only slightly from the GMWL. For the purposes of this discussion, this is called the “Animas meteoric water line” (AMWL). Samples collected from Cement Creek during the May Day reach tracer study plotted on the AMWL (fig. 14). May Day mine pool and drip samples plotted below the AMWL (fig. 14). May Day reach well-point data also plotted below and to the right of the AMWL (fig. 14), and the

slope of the line through the May Day data is significantly different ($p < 0.03$). The samples from fracture spring 7,554 and ferricrete spring 7,612 plot between the May Day mine and the well-point data (fig. 14). These data suggest several different sources of water in the May Day reach: (1) May Day mine waters, (2) well-point waters, or (3) a mixture of May Day mine and well-point waters. The source of the well-point waters is uncertain; however, the water could have traveled far distances along fractures, experiencing isotopic fractionation along the ground-water flow path. These water samples were distinctly different ($p < 0.01$) from the water in Cement Creek.

Dissolved zinc concentrations combined with the isotope data may help to clarify the sources of water in the May Day reach. Dissolved zinc concentrations of water samples from inside the mine were extremely high (19,000 and 181,000 $\mu\text{g/L}$); therefore, the dissolved zinc concentrations were superimposed on the light stable isotope graph to

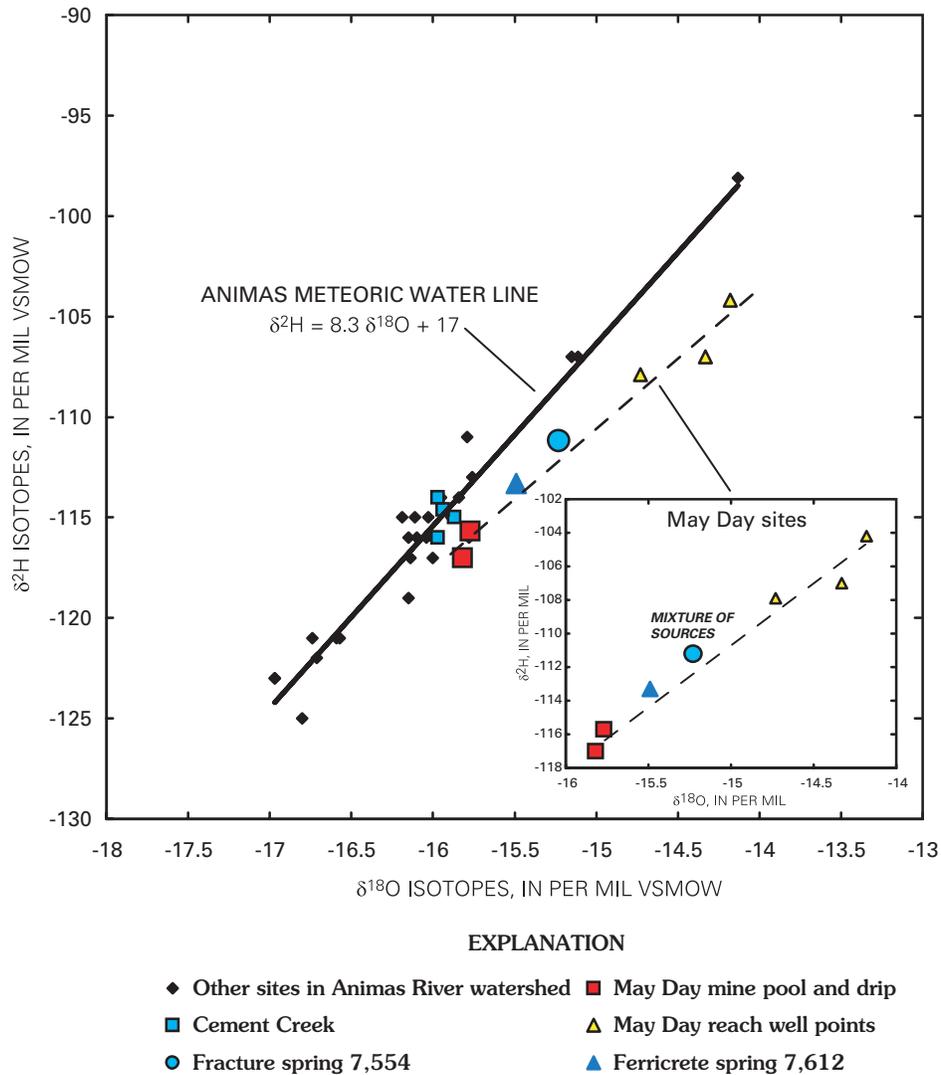


Figure 14. Oxygen and hydrogen isotopes of water samples collected from study reach and from selected springs, streams, and inactive mines as part of other studies in Animas River watershed study area. VSMOW, Vienna Standard Mean Ocean Water.

determine whether the different isotope values might have been affected by the mine water (fig. 15). The dissolved zinc concentrations were elevated in water from fracture spring 7,554 and the May Day reach well points; therefore, water from these sites might have been affected by the May Day mine site. This is further evidence that water from fracture spring 7,554 is a mixture of water from the May Day mine and the well points.

To further describe sources of water in the May Day reach and determine whether water from the May Day mine discharges to Cement Creek, principal components analysis was done on the water samples. Although the processes contributing to patterns might not be described through PCA, different groups (or sources) can be identified. Patterns were displayed using scaled principal component loadings. In a

loading plot each point corresponds to a sample, and the coordinates are given by the scaled principal component loading of the samples. The plot indicates the similarities and correlations between samples (Varmuza, 2001). PCA analysis of samples in the reach affected by the May Day mine reveals a mixture of sources (fig. 16): (1) Cement Creek and other streams, (2) ground water such as fracture spring 7,554, (3) ground water from the Topeka Gulch alluvial fan and ferricrete spring, (4) ground water from the well points, and (5) May Day mine water. Water from fracture spring 7,554 plots in the middle of the groups (fig. 16) and might be a mixture of waters from the different sources. In addition, because of the high zinc concentrations (fig. 15), fracture spring 7,554 might be affected by water from the May Day mine.

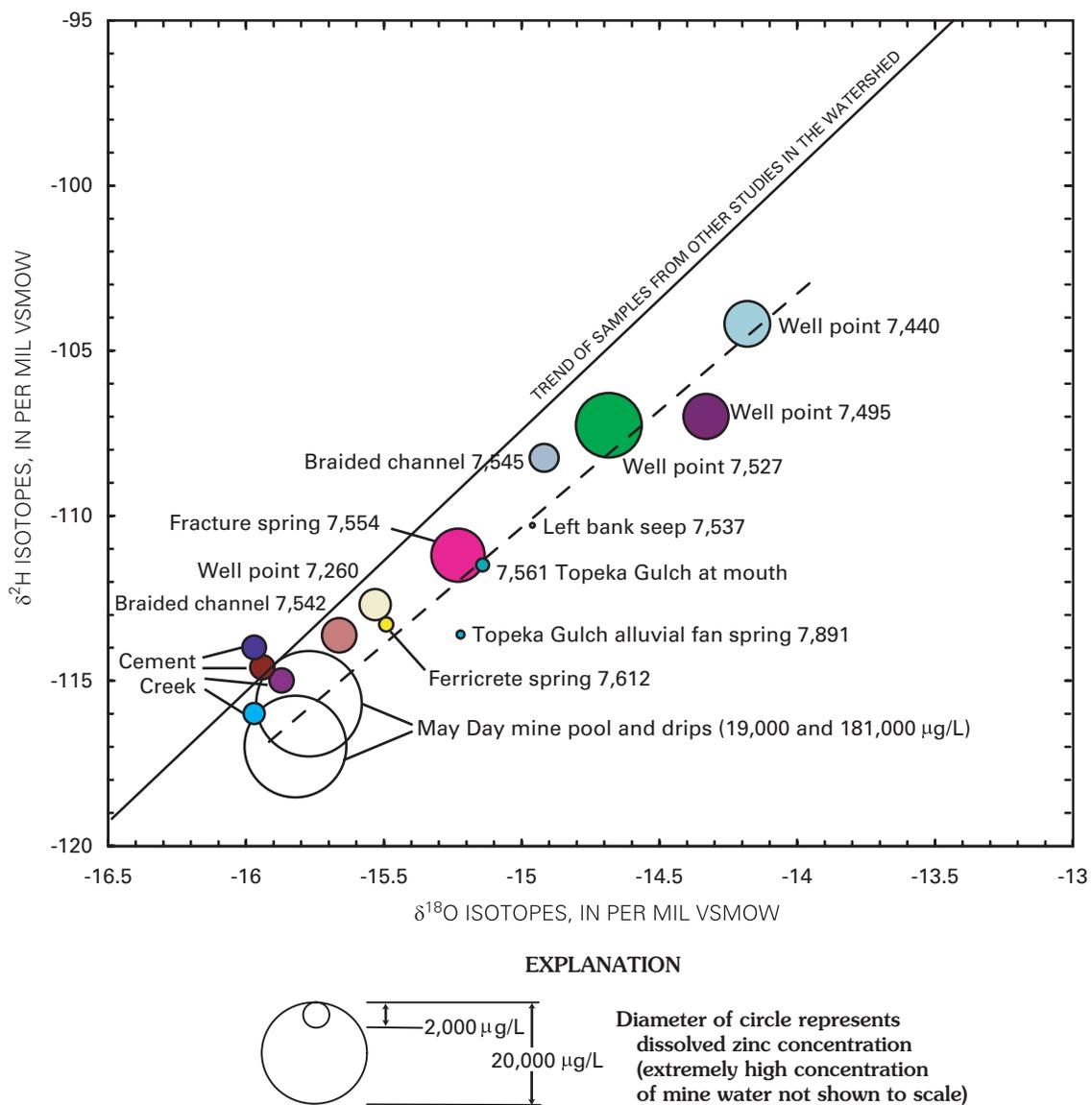


Figure 15. Oxygen and hydrogen isotopes of water and dissolved zinc concentrations for sites affecting May Day reach. VSMOW, Vienna Standard Mean Ocean Water; $\mu\text{g/L}$, micrograms per liter. Dashed line, linear regression of samples collected in the May Day reach.

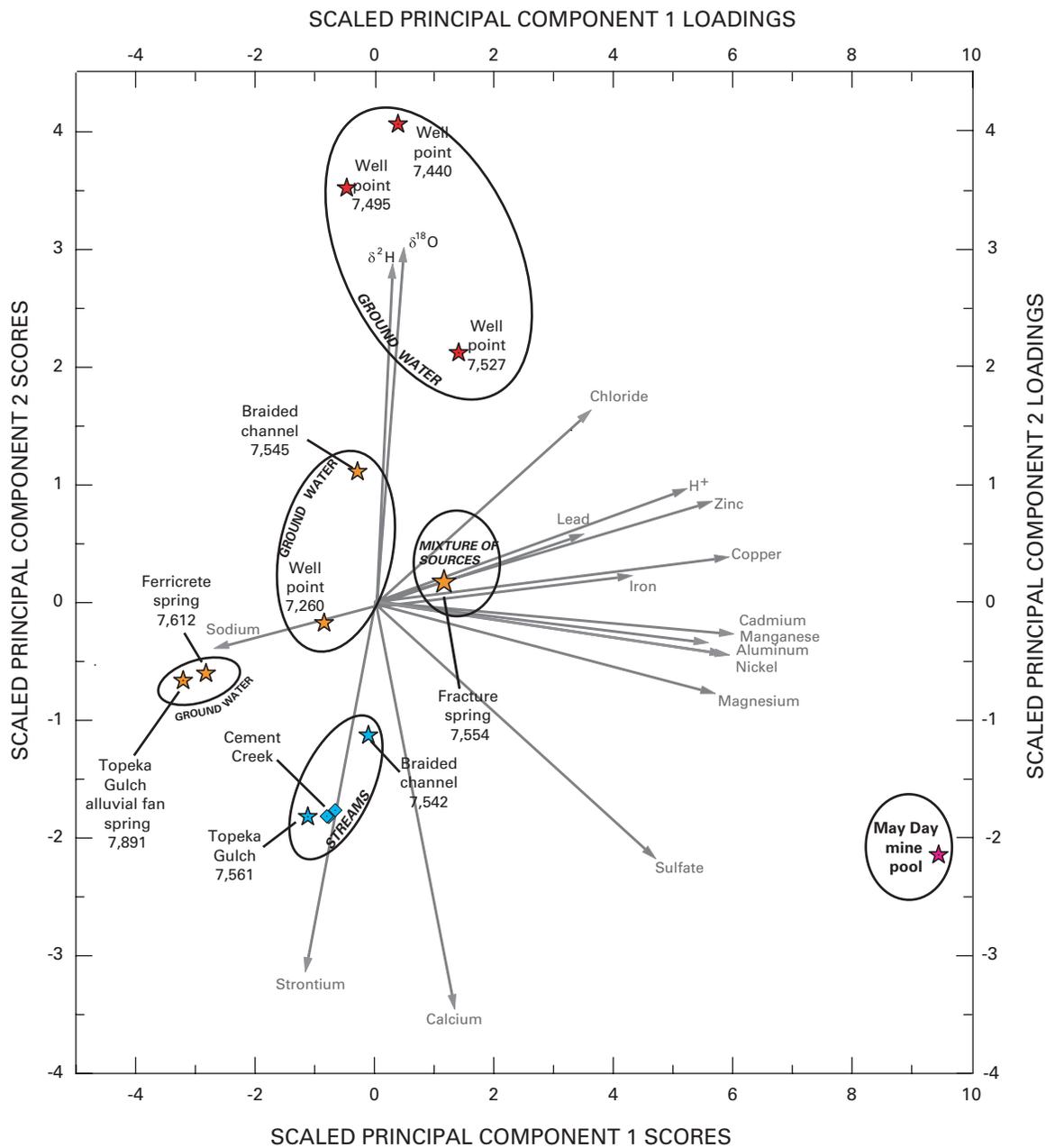


Figure 16. Principal components analysis, including dissolved constituents and isotopes, showing groups of inflows and stream sites in study reach affected by May Day mine.

Mineral Saturation

Alternating increases and decreases of constituent mass were evident in the study reach. Increases were explained by inflows or sources. Decreases, however, were more difficult to explain, and might have been caused by loss of constituent mass through physical, chemical (mineral saturation), or biological processes (Broshears and others, 1996). To describe mineral saturation, equilibrium geochemical modeling was done for each stream sample in the study reach using WATEQ4F (Ball and Nordstrom, 1991) and PHREEQC (Parkhurst and Appelo, 1999).

The saturation index (SI) is the log of the ion-activity product divided by the mineral solubility. Negative SI represents undersaturation of the mineral species, where the species would remain in the dissolved phase, and positive SI represents supersaturation of the mineral species, where the species would precipitate from the dissolved phase into the solid or colloidal phase. Iron and sulfate species were examined because of the predominance of these constituents in waters of the study area. Aluminum species also were examined because of the mixing of Cement Creek (pH \approx 4) with circumneutral Illinois Gulch water in the tracer study reach. Regarding iron sulfate minerals, schwertmannite ($\text{Fe}^{3+}_{16}\text{O}_{16}(\text{OH})_{12}(\text{SO}_4)_2$) has

been found in bed sediment from Cement Creek (Desborough and others, 2000); however, the schwertmannite mineral species is not in the WATEQ4F database; therefore, a modified PHREEQC database was used to model schwertmannite. A log activity of -18.0 for schwertmannite as determined by Bigham and others (1996) was added to the WATEQ4F thermodynamic database (Ball and Nordstrom, 1991) used with PHREEQC. Geochemical modeling results indicated that the SI of schwertmannite was positive throughout the entire length of the study reach (fig. 17). The SI of schwertmannite decreases between reach distance 6,638 and 6,740, which may be caused by inflow of low-pH water. Similarly, the SI of schwertmannite fluctuates in the reach affected by the May Day inflows and the May Day alluvial fan. Ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 0.5(\text{H}_2\text{O})$), aluminum sulfate ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), and aluminum silicate ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$) became supersaturated in the mixing zone of Cement Creek and Illinois Gulch (fig. 17). The large dissolved sulfate load (fig. 10B) and high-pH water (fig. 6) entering Cement Creek from Illinois Gulch caused supersaturation of these minerals. Mineral saturation fluctuated in the May Day reach, owing to inflow of low-pH water (fig. 17).

Alternating increases and decreases of dissolved constituent loads (figs. 11–13) may have resulted from adsorption and coprecipitation of dissolved constituents in the presence of actively forming colloids. Desborough and others (2000) identified schwertmannite in sediment from the Cement Creek streambed, which included a sample collected downstream from the Yukon tunnel. Total digestion of the solid-phase sample showed copper, lead, and zinc concentrations of 45, 450, and 140 parts per million, respectively. These

data indicate that iron-sulfate precipitates adsorb or coprecipitate metals. These processes are reflected by a decrease of dissolved constituent loads in stream reaches of actively forming colloids. When low-pH water enters the study reach, these colloids may dissolve, thereby releasing the metals into solution and increasing the dissolved constituent load.

Saturation of ferrihydrite, aluminum sulfate, and aluminum silicate minerals is probably present in ground water beneath the May Day mine site. A linear feature—or zone of fractured rock—originates in the Ohio Peak area northwest of the May Day mine site, and the linear feature passes beneath the mine site, continuing along the lower reach of Cement Creek (Smith and others, 2001). This linear feature acts as a conduit for transport of ground water beneath the May Day mine. Ground water from the Ohio Peak area mixes with the acidic and constituent-rich water from inside the mine. Using PHREEQC (Parkhurst and Appelo, 1999), geochemical modeling was done mixing upgradient water from Topeka Gulch (Wright and Janik, 1995) with water from inside the May Day mine to produce the chemical composition of water that discharges at fracture spring 7,554 in the tracer study reach. The modeling indicated that about 25–45 percent of the dissolved constituents at fracture spring 7,554 resulted from upgradient sources. Minerals that were supersaturated with respect to the solution included ferrihydrite, gibbsite, goethite, jarosite, illite, and aluminum silicate. If these solid-phase minerals were, in fact, precipitating colloids in the subsurface before discharging to fracture spring 7,554, this may have contributed to the increases of total constituent concentrations and loads in the reach affected by the May Day mine (figs. 7–10).

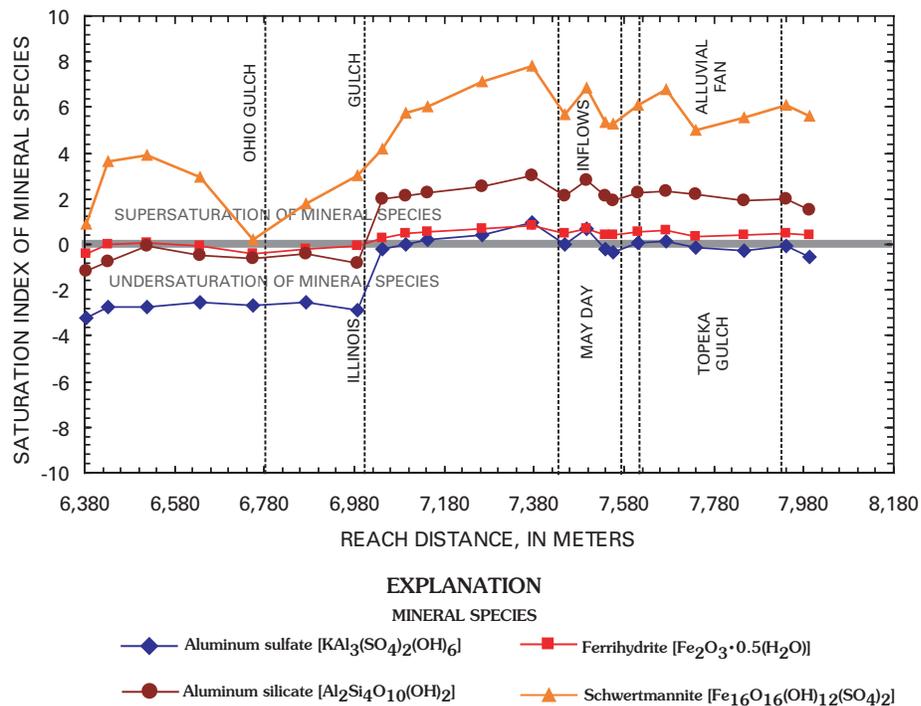


Figure 17. Longitudinal stream profile of saturation index for selected mineral species in water samples from study reach.

Summary and Conclusions

The tracer-injection study in a reach of Cement Creek showed sources of dissolved constituents to the study reach. These sources included inflows from an unnamed mine upstream from Illinois Gulch, Illinois Gulch, the Yukon tunnel, the May Day mine, and diffuse ground water. The increase in discharge was the greatest where Illinois Gulch enters Cement Creek. Only a slight discharge increase was evident in the reach affected by the May Day mine. The changes in pH were most noticeable downstream from Illinois Gulch owing to the large inflow of circumneutral pH water. Plotting the data on longitudinal stream profiles indicated alternating increases and decreases of dissolved constituent concentrations in the study reach. Concentration increases generally indicated inflows of constituent-rich water from mine sites or ground water, and concentration decreases generally indicated dilution by large inflows or adsorption onto iron precipitates. Total constituent (or unfiltered) concentrations increased and decreased through the reach, and the total constituent concentrations most noticeably increased at the May Day mine inflows, possibly indicating inflows of constituent-rich water in the reach affected by the May Day mine.

Alternating increases and decreases of dissolved and total constituent loads were noted in the study reach. Plotting longitudinal profiles of the cumulative instream loads in the study reach allowed for observation of the loads that might result if no attenuation took place in the stream. Large differences observed between the cumulative instream load and the total load for iron and sulfate indicated that geochemical reactions were taking place in the study reach. Decreases of dissolved constituent loads indicated precipitation of colloids. Total constituent loads increased in the May Day reach, indicating inflow of iron and aluminum supersaturated ground water from the linear feature beneath the May Day mine site. Even though the Yukon tunnel is a much larger mine, the loads from the May Day reach were sometimes larger than loads from the Yukon reach, possibly due to the linear feature that transports ground water beneath the May Day site. At the end of the study reach, cumulative inflow loads were much less than the cumulative instream loads, indicating the effect of diffuse ground-water sources in the study reach ("unsampled load" in Kimball and others, this volume). The change in dissolved and total loads through the course of the longitudinal stream profiles indicated the gains and losses of mass in the study reach. Some of the losses were the result of nonconservative behavior of constituents.

Study of oxygen and hydrogen light stable isotopes of water samples indicated different sources of water in the May Day reach compared to that of other samples collected in the Animas River watershed study area. The reason for isotopic fractionation of the May Day inflow water is uncertain; however, the fractionation might be related to water-rock interaction or to ground-water flow paths from different source areas discharging into Cement Creek through fractures. Because of the extremely high dissolved zinc concentrations

in water from the May Day mine (as high as 181,000 $\mu\text{g/L}$), the dissolved zinc concentrations combined with light stable isotope data indicated that the well-point and seep samples in the May Day reach were probably affected by the mine. Grouping of samples by principal component analysis of the dissolved constituent data also indicated that these samples are distinct chemically and isotopically, and water from fracture spring 7,554 may be a mixture of both sources.

In conclusion, water from the inactive May Day mine and its waste-rock pile appears to contribute to Cement Creek. Even though the May Day mine has no perennial discharge, and the water inside the mine may only be ephemeral, the data indicate that the mine affects the streamflow despite no obvious contaminant flow path from the mine to the stream. Compared to the constituent loads present in Cement Creek at the upstream end of the study reach, the May Day reach only contributes a small percentage of loading. In addition, loads also entered the study reach from the Topeka Gulch alluvial fan downstream from the May Day site. The mass-loading study helped quantify these loading contributions.

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