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Ground- and Surface-Water Chemistry of Handcart Gulch, Park County, Colorado, 2003–2006

Open-File Report 2007–1020

Front cover: Photograph of Handcart Gulch showing the Continental Divide in the upper portion of the image, the rock glacier in the middle of the image, and the trunk stream in the lower right.

Ground- and Surface-Water Chemistry of Handcart Gulch, Park County, Colorado, 2003–2006

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Abstract

As part of a multidisciplinary project to determine the processes that control ground-water chemistry and flow in mineralized alpine environments, ground- and surface-water samples from Handcart Gulch, Colorado were collected for analysis of inorganic solutes and water and dissolved sulfate stable isotopes in selected samples. The primary aim of this study was to document variations in ground-water chemistry in Handcart Gulch and to identify changes in water chemistry along the receiving stream of Handcart Gulch.

Water analyses are reported for ground-water samples collected from 12 wells in Handcart Gulch, Colorado. Samples were collected between August 2003 and October 2005. Water analyses for surface-water samples are reported for 50 samples collected from Handcart Gulch and its inflows during a low-flow tracer injection on August 6, 2003. In addition, water analyses are reported for three other Handcart Gulch stream samples collected in September 2005 and March 2006. Reported analyses include field parameters (pH, specific conductance, temperature, dissolved oxygen, and Eh), major and trace constituents, oxygen and hydrogen isotopic composition of water and oxygen and sulfur isotopic composition of dissolved sulfate.

Ground-water samples from this study are Ca-SO_4 type and range in pH from 2.5 to 6.8. Most of the samples (75 percent) have pH values between 3.3 and 4.3. Surface water samples are also Ca-SO_4 type and have a narrower range in pH (2.7–4.0). Ground- and surface-water samples vary from relatively dilute (specific conductance of 68 μS/cm) to concentrated (specific conductance of 2,000 μS/cm).

Introduction

Handcart Gulch, an alpine watershed located along the Continental Divide in the southeastern portion of the Montezuma Mining District of the central Colorado Rocky Mountain Front Range, contains an unmined, porphyry-related molybdenite exploration target (fig. 1). Process-related studies by U.S. Geological Survey (USGS) scientists and collaborators were undertaken to determine the controls of ground-water chemistry and flow in this mineralized alpine environment (Caine and others, 2004; Manning and others, 2004; Verplanck and others, 2004; Kahn and others, 2005; Kahn, 2005; Caine and others, 2006). Understanding the natural variation of water chemistry in ground and surface water in mineralized alpine watersheds is important because it provides estimates of premining water quality in historically mined areas with similar geology and climate, as well as providing insight into the fundamental processes that liberate, transport, and deposit constituents that may degrade water quality. Also, chemical data can provide additional constraints when creating ground-water flow models.
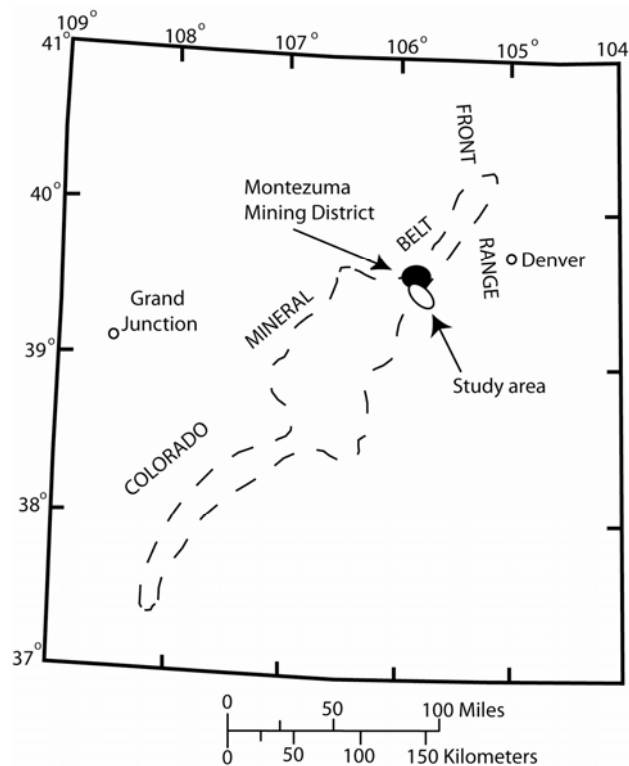
Figure 1. Map of central and western Colorado showing location of Colorado mineral belt and study area.

In the summers of 2001 and 2002, four wells in Handcart Gulch were drilled as mineral exploration boreholes by Mineral Systems, Inc. They were drilled in the upper portions of the watershed; one at Webster Pass on the Continental Divide at 3,688 m and range in depth from 365 to 1,065 m (fig. 2). In 2003 and 2004 Mineral Systems Inc. donated the boreholes to the U.S. Geological Survey, and the U.S. Geological Survey reconditioned three of the boreholes for use as scientific research monitoring wells. In the fall of 2003 the deep wells were supplemented by the drilling of nine new shallow wells (3–52 m deep) in the vicinity of the trunk stream of Handcart Gulch (fig. 2, table 1). Detailed descriptions of well construction, lithology, and water-level data and an overview of other research investigations were reported in Caine and others (2006). Water from three of the exploration boreholes and the nine shallower wells was sampled periodically between August 2003 and October 2005.

Base from U.S. Geological Survey Montezuma Quadrangle, 1:24,000 (1958)
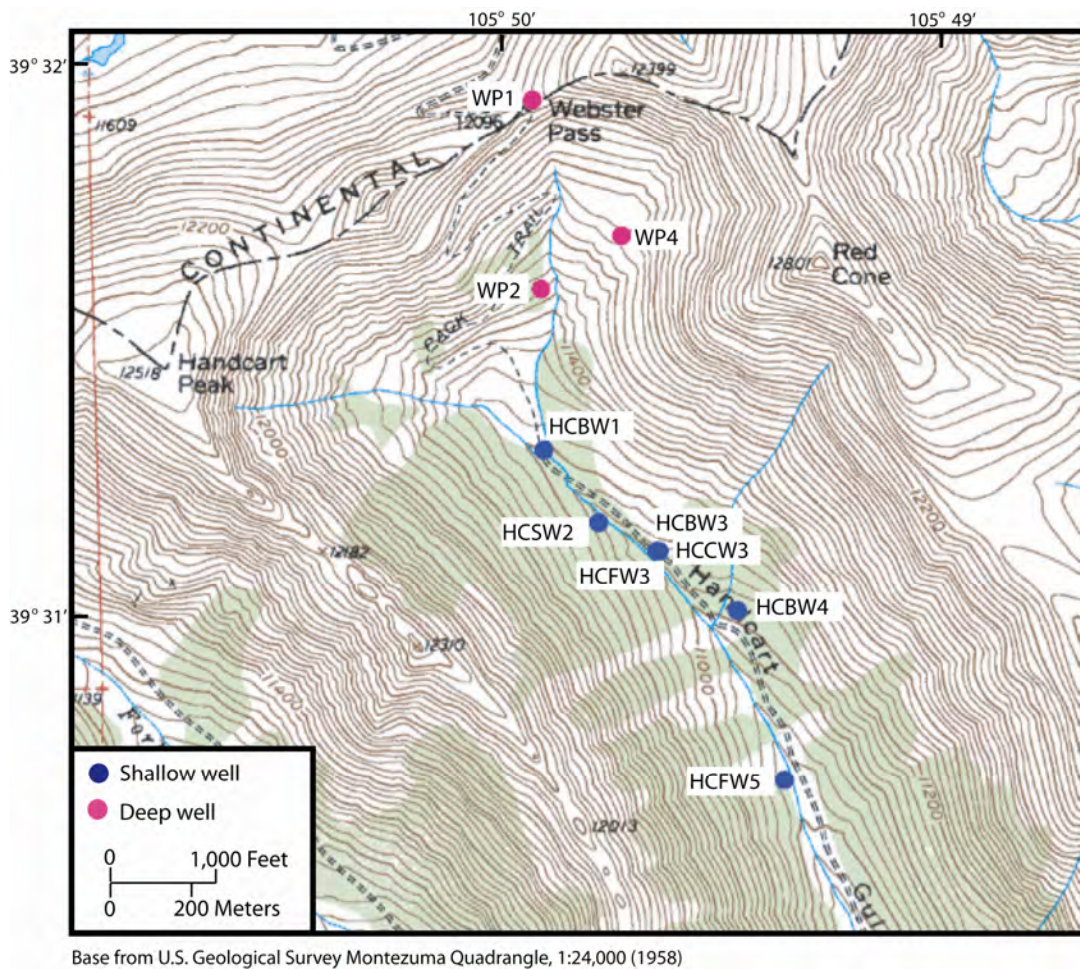
Figure 2. Map of Handcart Gulch showing well locations.

Table 1. Locations of well- and surface-water sampling sites.

[m, meters; HCG, Handcart Gulch; SW, southwest]

SAMPLE NUMBER	LATITUDE	LONGITUDE	LOCATION	ELEVATION[1] (m)
Wells				
WP1	39° 31' 51"	105° 49' 57"	Webster Pass	3687
WP2	39° 31' 34"	105° 49' 53"	Sub-basin SW of rock glacier	3507
WP4	39° 31' 40"	105° 49' 43"	On rock glacier	3570
HCBW1	39° 31' 18.3"	105° 49' 52.6"	See figure 2	3415
HCSW1	39° 31' 18.4"	105° 49' 52.8"	See figure 2	3415
HCBW2	39° 31' 11.2"	105° 49' 42.7"	See figure 2	3393
HCSW2	39° 31' 11.2"	105° 49' 42.7"	See figure 2	3393
HCBW3	39° 31' 08.4"	105° 49' 37.7"	See figure 2	3377
HCFW3	39° 31' 08.4"	105° 49' 37.7"	See figure 2	3377
HCCW3	39° 31' 08.4"	105° 49' 37.7"	See figure 2	3377
HCBW4	39° 31' 02.5"	105° 49' 27.6"	See figure 2	3360
HCFW5	39° 30' 45.7"	105° 49' 19.9"	See figure 2	3302
Surface Water				
HCG1	39° 31' 18.3"	105° 49' 52.6"	HCG adjacent to HCBW1	3415
HCG5	39° 30' 45.7"	105° 49' 19.9"	HCG adjacent to HCBW5	3302

[1] Land surface altitude

To evaluate the variation in flow and chemistry of the receiving stream of Handcart Gulch, a tracer injection and synoptic sampling study was undertaken in August 2003. Along the upper two kilometers of Handcart Gulch, 27 stream samples and 23 inflow samples were collected (fig. 3, table 2). Water chemistry and stream-flow data were used to calculate chemical loads from surface and subsurface flow (Kimball and others, 1999). In mountain streams a substantial amount of water can flow through the streambed or hyporheic zone, making it difficult to accurately measure streamflow with traditional velocity measurements within the stream channel. Tracer-injection methods are a reliable way to quantify total streamflow by using changes in concentration of a tracer (LiBr) injected at a constant rate and assuming conservation of mass (Kimball and others, 2002).

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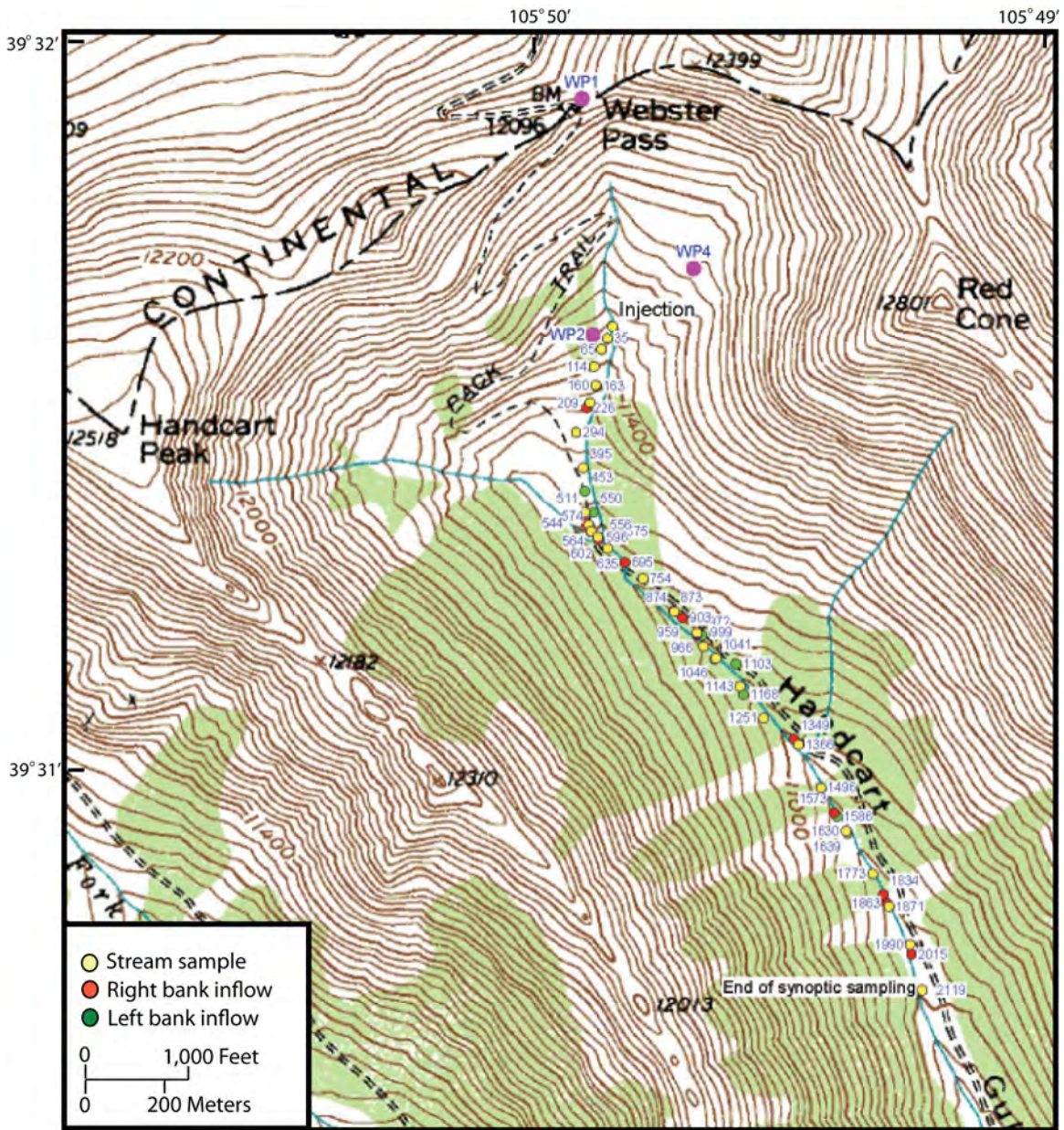
Figure 3. Map of Handcart Gulch showing tracer synoptic sampling locations.

Table 2. Locations of tracer synoptic sampling sites.

[ID, identification; HCG, Handcart Gulch; LBI, left bank inflow; RBI, right bank inflow; m, meters; T, transport]

Sample ID	Distance (m)	Site description	Latitude	Longitude
HC-0	0	T0 site - HCG upstream from injection, end of rock glacier	39° 31' 34.896"	105° 49' 51.132"
HC-35	35	HCG below injection	39° 31' 33.924"	105° 49' 51.672"
HC-65	65	HCG at top of cliff with waterfall	39° 31' 33.06"	105° 49' 52.248"
HC-144	114	HCG downstream from waterfall	39° 31' 31.692"	105° 49' 53.004"
HC-160	160	HCG upstream from LBI at toe of rock glacier	39° 31' 30.216"	105° 49' 52.824"
HC-163	163	LBI - toe of upper rock glacier	39° 31' 30.144"	105° 49' 52.752"
HC-209	209	HCG downstsream from rock glacier inflows	39° 31' 28.812"	105° 49' 53.4"
HC-226	226	RBI - pond on right bank	39° 31' 28.416"	105° 49' 53.724"
HC-294	294	HCG below inflows	39° 31' 26.436"	105° 49' 54.804"
HC-395	395	HCG stream site	39° 31' 23.628"	105° 49' 54.012"
HC-453	453	LBI - pond has stream water	39° 31' 21.756"	105° 49' 53.832"
HC-511	511	HCG upstream from iron bog area and inflows	39° 31' 20.064"	105° 49' 53.796"
HC-544	544	RBI - small inflow	39° 31' 19.2"	105° 49' 53.688"
HC-550	550	LBI - draining from bushes	39° 31' 20.064"	105° 49' 52.932"
HC-556	556	HCG downstream from iron-free inflows	39° 31' 19.056"	105° 49' 53.4"
HC-564	564	LBI - drains iron bog	39° 31' 18.84"	105° 49' 53.22"
HC-574	574	HCG pool on ferricrete at bottom of chute	39° 31' 18.552"	105° 49' 53.148"
HC-575	575	RBI - draining iron bog	39° 31' 18.516"	105° 49' 53.184"
HC-596	596	T1 site - HCG upstream from small inflow on right bank	39° 31' 18.12"	105° 49' 52.464"
HC-602	602	RBI - main tributary from Handcart Peak subbasin	39° 31' 17.904"	105° 49' 52.392"
HC-635	635	HCG downstream from RBI	39° 31' 17.22"	105° 49' 51.456"
HC-695	695	RBI - drains from rock face	39° 31' 16.104"	105° 49' 49.656"
HC-754	754	HCG downstream from chutes in ferricrete	39° 31' 14.844"	105° 49' 47.784"
HC-873	873	HCG upstream from LBI from ferricrete	39° 31' 12.252"	105° 49' 44.544"
HC-874	874	LBI - drains left bank rock glacier	39° 31' 12.288"	105° 49' 44.616"
HC-903	903	RBI - small hole in ferricrete	39° 31' 11.748"	105° 49' 43.68"
HC-959	959	HCG upstream from RBI	39° 31' 10.596"	105° 49' 42.204"
HC-966	966	RBI - drains bog across road	39° 31' 10.38"	105° 49' 42.168"
HC-972	972	LBI - drains toe of rock glacier, sample pit	39° 31' 10.38"	105° 49' 41.7"
HC-999	999	HCG along the rock glacier	39° 31' 9.516"	105° 49' 41.484"
HC-1041	1041	HCG upstream from LBI	39° 31' 8.58"	105° 49' 40.224"
HC-1046	1046	LBI - small inflow from rock glacier	39° 31' 8.508"	105° 49' 40.368"
HC-1103	1103	LBI - Pool near end of glacier that drains to stream	39° 31' 8.148"	105° 49' 38.136"
HC-1143	1143	HCG downstream from lower rock glacier inflows	39° 31' 6.348"	105° 49' 37.704"
HC-1168	1168	LBI - small inflow at base of boulder	39° 31' 5.7"	105° 49' 37.38"
HC-1251	1251	HCG at end of reach with little visible inflow	39° 31' 3.828"	105° 49' 35.256"
HC-1349	1349	RBI - draining along cascading reach	39° 31' 2.172"	105° 49' 32.124"
HC-1366	1366	HCG on ferricrete bed with chutes and cascades	39° 31' 1.74"	105° 49' 31.656"
HC-1496	1496	HCG downstream from small seeps	39° 30' 58.32"	105° 49' 29.316"
HC-1573	1573	RBI - from avalanche fan	39° 30' 56.34"	105° 49' 27.948"
HC-1586	1586	LBI - draining from bushes	39° 30' 56.052"	105° 49' 27.624"

Table 2. Locations of tracer synoptic sampling sites—Continued.

[ID, identification; HCG, Handcart Gulch; LBI, left bank inflow; RBI, right bank inflow; m, meters; T, transport]

Sample ID	Distance (m)	Site description	Latitude	Longitude
HC-1630	1630	HCG at narrow spot in ferricrete	39° 30' 54.9"	105° 49' 26.688"
HC-1639	1639	LBI - small stream inflow	39° 30' 54.684"	105° 49' 26.508"
HC-1773	1773	HCG downstream from bog area on right bank	39° 30' 51.48"	105° 49' 23.916"
HC-1834	1834	RBI - small inflow	39° 30' 49.824"	105° 49' 22.8"
HC-1863	1863	RBI - pond on right bank near iron bog	39° 30' 49.104"	105° 49' 22.404"
HC-1871	1871	T2 site - HCG at "log jam" on road	39° 30' 48.888"	105° 49' 22.224"
HC-1990	1990	HCG downstream of possible inflows	39° 30' 45.864"	105° 49' 20.028"
HC-2015	2015	RBI - drains ferricrete	39° 30' 45.108"	105° 49' 19.884"
HC-2119	2119	HCG end of study reach	39° 30' 42.264"	105° 49' 18.732"

Purpose and Scope

The purpose of this report is to present water-chemistry data from surface- and ground-water investigations conducted between 2003 and 2006 in Handcart Gulch, Colorado. Use of these data will aid in quantification and characterization of the processes that contribute to the natural conditions of low pH waters found in this and other unmined alpine watersheds. Data presented in this report include field measurements of pH, specific conductance, dissolved oxygen, Eh, and temperature, and laboratory determinations of the concentrations of major inorganic and selected trace element constituents. In addition, oxygen, hydrogen, and sulfur stable isotopic compositions of surface- and ground-water are reported.

Physical Description of the Study Area

Handcart Gulch drains approximately 7.9 km^2 of the Colorado Front Range, southeast of Montezuma, Colorado (fig. 1). This region is part of the Southern Rocky Mountain physiographic province. The study area within Handcart Gulch is located in the upper 2–3 km of the watershed, encompassing approximately 4.7 km^2 and ranging in elevation from 3,815 m at Handcart Peak to 3,300 m at the downstream end.

Geology

Handcart Gulch lies in the southeastern portion of the Montezuma Mining District (fig. 1). The bedrock geology consists of Precambrian gneisses, schists, amphibolites, and granites that have been intruded by a series of Tertiary-age stocks and veins. The largest and most well-studied stock in the district is the Montezuma stock, which is predominantly porphyritic quartz monzonite in composition but ranges to granite apalite (Neuerburg and others, 1974). Surface geology of Handcart Gulch was mapped by Lovering (1935) and primarily consists of quartz-biotite-sillimanite schists and gneisses, as well as hornblende gneisses. Small quartz monzonite porphyries crop out near Webster Pass and Red Cone. Along the valley floor much of the stream bed lies in ferricrete, iron-oxide cemented alluvial and colluvial deposits. Another important feature of Handcart Gulch is the presence of a rock glacier that lies below the Continental Divide (elevation 3,690 m) and above the trunk stream (elevation 3,375 m) on the norteast side of the upper watershed.

The Montezuma Mining District has a long mining history starting with the initial discovery of silver in 1864 (Lovering, 1935). Metals mined include silver, lead, zinc, and copper, and ore minerals include galena, sphalerite, and tennantite-tetrahedrite (Botinelly, 1979). Molybdenite is also associated with the Tertiary porphyry stocks. Because of the proximity to the Climax deposit near Leadville, this district has been explored for molybdenum mineralization. Within the upper portion of Handcart Gulch, no mining has occurred with the exception of one small adit with a waste-rock pile of approximately 10 m^3.

Climate and Vegetation

In this region surface water is fed by snowmelt, rainfall, and ground water. At higher elevations in the Southern Rocky Mountains most of the precipitation falls in the winter and spring forming the seasonal snowpack (Ingersoll, 2000). Although there is no meteorological station in Handcart Gulch, an adjacent watershed, Jackwacker Gulch, has a SNOwpack TELemetry (SNOTEL) station maintained by the U.S. Department of Agriculture - Natural Resources Conservation Service. Jackwhacker Gulch is located approximately 5 km northeast of Handcart Gulch and the station elevation is below timberline at 3,341 m. During the SNOTEL period of record from 1998 to 2006 the

maximum-recorded temperature was 26.7ºC on July 2, 2002 with a minimum temperature of -31ºC on March 3, 2002. The average high temperature was 16.2ºC, and average low temperature was -23.4ºC. Precipitation in Handcart Gulch averages 34.8 cm and primarily falls as snow (Kahn, 2005). Vegetation type is controlled primarily by climate, soil composition, and topography. The upper part of the study area lies above timberline within the tundra climate zones. The lower part of the study area lies within the subalpine climate zone.

Acknowledgments

Methods

Sampling Sites

During the field seasons of 2001 and 2002 four mineral exploration boreholes were drilled by Mineral Systems Inc. in the upper portion of Handcart Gulch (fig. 2). These boreholes were drilled to at least 455 m below the surface and were offered to the USGS for use in long-term research. Subsequently, three of these boreholes were logged, cased, and made assessable for ground-water sampling (Caine and others, 2006). During the field season of 2003, nine additional shallow wells (3–52 m) were drilled along the Handcart Gulch stream by the USGS (fig. 2).

Surface water samples collected during the August 6, 2003 tracer-injection study were located along a 2-km reach of the Handcart Gulch trunk stream (fig. 3). Two days prior to sample collection, a reconnaissance of the study reach was performed. Sample sites were selected and marked; their distance downstream of the most upstream water in Handcart Gulch, the outflow from the upper lobe of the rock glacier, were determined using a portable global positioning system (GPS, Garmin 12C, NAD27). Latitude and

longitude of the sampling sites were acquired at this time. Transport sites, labeled "T" (table 2), are where numerous samples are collected to determine transport characteristics of the stream. Sample sites were selected upstream and downstream from visible inflows and other features that could affect water quality. Twenty-three surface inflows (tributaries, springs, and seeps) were sampled.

Water-Chemistry Sampling

Between August 2003 and September 2005 water-chemistry samples were collected periodically from wells in Handcart Gulch. On August 6, 2003, 50 surface-water samples were collected during a stream-tracer study. In addition two surface-water samples were collected September 9, 2005 and one on March 17, 2006.

Before sampling of water in shallow wells, the static water level was measured, the wells were pumped for approximately twenty minutes, and pH, specific conductance, and temperature were monitored until they were stable. Deeper wells (WP1 and WP2) were sampled using a tripod and teflon bailer. On-site measurements of pH, specific conductance, temperature, and dissolved oxygen were obtained utilizing a flow-through cell, or were measured from an aliquot of sample water. At each site the pH electrode was calibrated using two buffers that bracketed the measured pH and thermally equilibrated with the water sample. At selected sites Eh was measured. Samples were filtered on site through either a disposable capsule filter having a nominal pore size of 0.45 μm or through a syringe filter having a pore size of 0.45 μm. In this report, constituent concentrations measured in filtered subsamples (FA) are called "dissolved," and constituent concentrations in unfiltered subsamples (RA) are called "total recoverable."

Several sample splits were collected for determination of concentrations of inorganic constituents, redox species, and dissolved organic carbon (DOC). Container preparation and stabilization of filtered samples are summarized in table 3. Samples for the determination of concentrations of cations and trace metals (As, Al, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Re, Sb, Se, SiO_2, Sm, Sr, Ta, Tb, Te, Th, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr), major anions (Br, Cl, F, NO_3, and SO_4), alkalinity, and DOC were filtered and stabilizing reagents were added when necessary. Sample bottles were pre-rinsed with filtered water prior to sample collection. Samples were collected for the determination of the isotopic composition of

dissolved sulfate-sulfur isotopes ($\delta^{34}S$ and $\delta^{18}O$) and water isotopes ($\delta^{2}H$ and $\delta^{18}O$) during selected samplings. Delta notation (δ) is used to describe the isotopic concentration of water and sulfate isotopes. In delta notation, the ratio of the heavy and light isotope is compared to that of a reference standard (Clark and Fritz, 1999).

Table 3. Sample container preparation and stabilization methods for samples.

[HCl, hydrochloric acid; HNO_3, nitric acid; N, normal; v/v, volume per volume; %, percent]

Sample type(s)	Storage container and preparation	Stabilization treatment
Cations and trace metals (Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Re, Sb, Se, SiO_2, Sm, Sr, Ta, Tb, Te, Th, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr)	Polyethylene bottles, soaked in 5% HNO_3 and rinsed 3 times with distilled water	1% (v/v) concentrated redistilled or Ultrex 7.7 N HNO_3 added
Iron redox species (Fe(T), Fe(II))	Opaque polyethylene bottles, soaked in 5% HCl and rinsed 3 times with distilled water	1% (v/v) redistilled 6 N or Omni 1:1 trace-metal grade HCl added
Alkalinity and major anions (Br, Cl, F, HCO_3, NO_3, and SO_4)	Polyethylene bottles filled with distilled water and allowed to stand for 24 hours, then rinsed 3 times with distilled water	None
Dissolved organic carbon (DOC)	Baked glass bottle	None
Oxygen and sulfur isotopes of dissolved sulfate (^{18}O and ^{34}S)	Polyethylene bottles filled with distilled water and allowed to stand for 24 hours, then rinsed 3 times with distilled water	None
Water isotopes (^{18}O and ^{2}H)	Glass bottle	None

On August 6, 2003 surface-water samples were collected during a LiBr tracer-injection study. Detailed description of tracer injection and synoptic sampling can be found in Kimball and others (1999). On August 5, 2003, a continuous injection of a concentrated LiBr solution was initiated at the upstream end of the study reach (fig. 3). The injection site was located in Handcart Gulch, 34 m downstream of the outflow from the southwest lobe of the rock glacier, the uppermost surface water in Handcart Gulch. All stream and inflow

samples were collected on August 6 in 1.8-liter HPDE bottles by submersing the neck of each bottle into the water near the thalweg or at the greatest flow of seeps and springs; sample bottles were triple rinsed with sample water prior to collection. Stream- and inflow-water temperature was measured in situ using an alcohol thermometer. Samples were transported to a central processing area where 125-ml aliquots were prepared for cation and anion analyses. Onsite processing included filtration, measurement of pH and specific conductance, and preservation of samples for iron speciation. Filtration was completed using tangential-flow units equipped with 0.45µm membranes (FA/FU) and a 10,000-Daltons filter membrane (UFA), equivalent to approximately 0.005 µm pore size (Alpers and others, 2000). Aliquots for iron speciation were placed in amber bottles and preserved with concentrated HCl to fix the ratio of ferrous to ferric iron in filtered samples (To and others, 1999). Aliquots for cation analysis were acidified to pH <2.0 with ultrapure nitric acid (HNO_3).

Laboratory Methods

All reagents were of a purity at least equal to the reagent-grade standards of the American Chemical Society. Double-distilled de-ionized water and re-distilled acids using a sub-boiling purification technique (Kuehner and others, 1972), were used in all preparations. The methods and detection limit for each analysis are summarized in table 4. USGS standard-reference water samples and blanks were included with each sample suite for inductively-coupled plasma atomic-emission spectroscopy (ICP-AES) and inductively-coupled plasma mass spectrometry (ICP-MS). Major cations (Ca, Mg, K, and Na), silica, and selected minor cations for total-recoverable and dissolved samples were determined using a Perkin Elmer Optima 3000™ ICP-AES (Briggs, 2002).
Minor and trace elements (As, Al, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Gd, Hf, Ho, La, Li, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Re, Sb, Se, Sm, Sr, Ta, Tb, Te, Th, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr) for total-recoverable and dissolved samples were analyzed with the ICP-MS using a method developed by the USGS (Meier and others, 1994; Lamothe and others, 2002). This method is used to directly determine the elements in the water samples without need for any pre-concentration or dilution. Elemental detection limits are in the sub-parts per billion range (table 4), and the working linear range is six or more orders of magnitude.

Table 4. Methods of analysis and detection limits.

[mg/L, milligram per liter; µg/L, microgram per liter; IC, ion chromatography; ICP-MS, inductively coupled plasma-mass spectrometry; ICP-AES, inductively coupled plasma-atomic emission spectroscopy]

Element	Detection limit	Method	Element	Detection limit	Method
Ag	3 µg/L	ICP-MS	Mn	0.2 µg/L	ICP-MS
Al	10 µg/L	ICP-AES	Mo	2 µg/L	ICP-MS
Al	2 µg/L	ICP-MS	Na	0.1 mg/L	ICP-AES
As	1 µg/L	ICP-MS	Nb	0.2 µg/L	ICP-MS
Ba	1 µg/L	ICP-AES	Nd	0.01 µg/L	ICP-MS
Ba	0.2 µg/L	ICP-MS	Ni	0.4 µg/L	ICP-MS
Be	0.05 µg/L	ICP-MS	NO_3	0.1 mg/l	IC
Bi	0.2 µg/L	ICP-MS	P	10 µg/L	ICP-MS
Br	0.03	IC	Pb	0.05 µg/L	ICP-MS
Ca	0.1 mg/L	ICP-AES	Pr	0.01 µg/L	ICP-MS
Cd	0.02 µg/L	ICP-MS	Rb	0.01 µg/L	ICP-MS
Ce	0.01 µg/L	ICP-MS	Sb	0.3 µg/L	ICP-MS
Cl	0.1 mg/l	IC	Sc	0.6 µg/L	ICP-MS
Co	0.02 µg/L	ICP-MS	Se	1 µg/L	ICP-MS
Cr	1 µg/L	ICP-MS	SiO_2	0.1 mg/L	ICP-AES
Cs	0.02 µg/L	ICP-MS	SO_4	0.05 mg/l	IC
Cu	0.5 µg/L	ICP-MS	Sm	0.01 µg/L	ICP-MS
Dy	0.005 µg/L	ICP-MS	Sr	1 µg/L	ICP-AES
Er	0.005 µg/L	ICP-MS	Sr	0.5 µg/L	ICP-MS
Eu	0.005 µg/L	ICP-MS	Ta	0.02 µg/L	ICP-MS
F	0.1 mg/l	IC	Tb	0.005 µg/L	ICP-MS
Fe	20 µg/L	ICP-AES	Te	0.1 µg/L	ICP-MS
Fe (T)	2 µg/L	FerroZine	Th	0.2 µg/L	ICP-MS
Fe (II)	2 µg/L	FerroZine	Ti	0.5 µg/L	ICP-MS
Ga	0.05 vg/L	ICP-MS	Tl	0.1 µg/L	ICP-MS
Gd	0.005 µg/L	ICP-MS	Tm	0.005 µg/L	ICP-MS
Ge	0.02 µg/L	ICP-MS	U	0.1 µg/L	ICP-MS
Ho	0.005 µg/L	ICP-MS	V	0.5 µg/L	ICP-MS
K	30 µg/L	ICP-MS	W	0.5 µg/L	ICP-MS
La	0.01 µg/L	ICP-MS	Y	0.01 µg/L	ICP-MS
Li	0.1 µg/L	ICP-MS	Yb	0.005 µg/L	ICP-MS
Lu	0.1 µg/L	ICP-MS	Zn	0.5 µg/L	ICP-MS
Mg	0.1 mg/L	ICP-AES	Zr	0.2 µg/L	ICP-MS
Mn	10 µg/L	ICP-AES			

Concentrations of major anions (Br, Cl, F, NO_3, and SO_4) were determined by ion chromatography (Brinton and others, 1995) using a Dionex 2010i™ ion chromatograph with 10-μL and 50-μL sample loops. Standards were prepared from compounds of the highest commercially-available purity. USGS standard reference water samples were used as independent quality control standards. Alkalinity (HCO_3^-) was determined using an Orion 960™ autotitrator and standardized H_2SO_4 (Barringer and Johnsson, 1989). Samples were diluted as necessary to bring the analyte concentration within the optimal range of the method. DOC concentrations (table 5) were determined by the wet persulfate-oxidation method (Aiken, 1992). Iron (II) redox species and total iron in filtered, HCl-acidified samples were determined using a modification of the FerroZine™ colorimetric method (Stookey, 1970; To and others, 1999) with a Hewlett Packard 8453™ diode array UV/VIS spectrophotometer.

Table 5. Dissolved organic carbon analyses.

[DOC, dissolved organic carbon; mg/L, milligram per liter]

WELL	DATE	DOC (mg/L)
HCBW1	9/8/2004	0.3
HCBW3	9/8/2004	0.4
HCFW3	9/8/2004	0.4
WP4	9/8/2004	0.2

Sulfur and oxygen isotopic determinations of dissolved sulfate ($\delta^{34}S$, $\delta^{18}O$) were performed by the USGS Crustal Imaging and Characterization Team Laboratory in Denver, Colo. The sulfate ion was removed from the samples by precipitation as barium sulfate ($BaSO_4$) following methods described by Carmody and others (1998). Sulfur-isotopic analyses were done by combustion using continuous-flow methods described by Giesemann and others (1994), with a Carlo Erba NC2500 elemental analyzer coupled to a Finnigan Delta Plus XP mass spectrometer. Values of $\delta^{34}S_{SO4}$ are relative to the standard Vienna Canyon Diablo Troilite (VCDT) with reproducibility of 0.2 per mil. Oxygen analyses of sulfate were done by pyrolysis with a Finnigan TC/EA coupled to a Finnigan Delta Plus XL mass spectrometer using continuous flow methods modified from Kornexl and others (1999). Values of $\delta^{18}O$ are relative to Vienna Standard Mean Ocean Water (VSMOW) with reproducibility of 0.4 per mil.

The oxygen and hydrogen isotopic compositions of water ($\delta^{18}O$, δ^2H) were also performed by the USGS Crustal Imaging Team Laboratory in Denver, Color. Oxygen isotopic compositions were determined using a Micromass Optima with an automated CO_2 equilibration technique adapted from Epstein and Mayeda (1953). Water samples were prepared for hydrogen-isotopic analyses using the Zn-reduction technique (Kendall and Coplen, 1985). The hydrogen analyses were preformed on a Finnigan MAT 252 mass spectrometer. Values of $\delta^{18}O$ and δ^2H were relative to VSMOW; they have reproducibility of approximately 0.2 and 1.0 per mil, respectively.

Quality Assurance and Quality Control

Quality control included replicate samples, field equipment blanks, analyses by alternative methods, and calculation of charge imbalance. Replicate samples were two samples considered to be essentially identical in composition and used to estimate variability in environmental data. These samples were collected immediately following the water-chemistry sample and were pumped from the same collection vessel. Each replicate sample was processed through all the steps of the routine water-chemistry sample using a new filter and clean equipment. Replicate samples were analyzed at the same time, using the same instruments as the other samples collected, during the same sampling trip. Analytical results of replicate samples are included in tables 6, 7, 8, and 9, and follow the corresponding water sample (labeled as duplicate). Most major, minor, and trace element replicate concentrations are within ±10 percent of the corresponding water-chemistry sample.

A field equipment blank is a sample prepared using blank (deionized) water that has passed through all the sampling and processing equipment. This type of sample is used to check for the potential contamination of the water-chemistry samples during collection, processing, handling, and analysis. Analytical results are included in tables 6, 7, 8, and 9. Most analytes were below analytical detection limits.

Concentrations of cations were determined by both ICP-AES and ICP-MS, and if concentrations of trace elements were at least three times the detection limit, good agreement between ICP-AES and ICP-MS results was observed (fig. 4). Barium, manganese, and strontium were chosen for this comparison because the range in concentrations of these elements was within the working range of both analytical techniques.
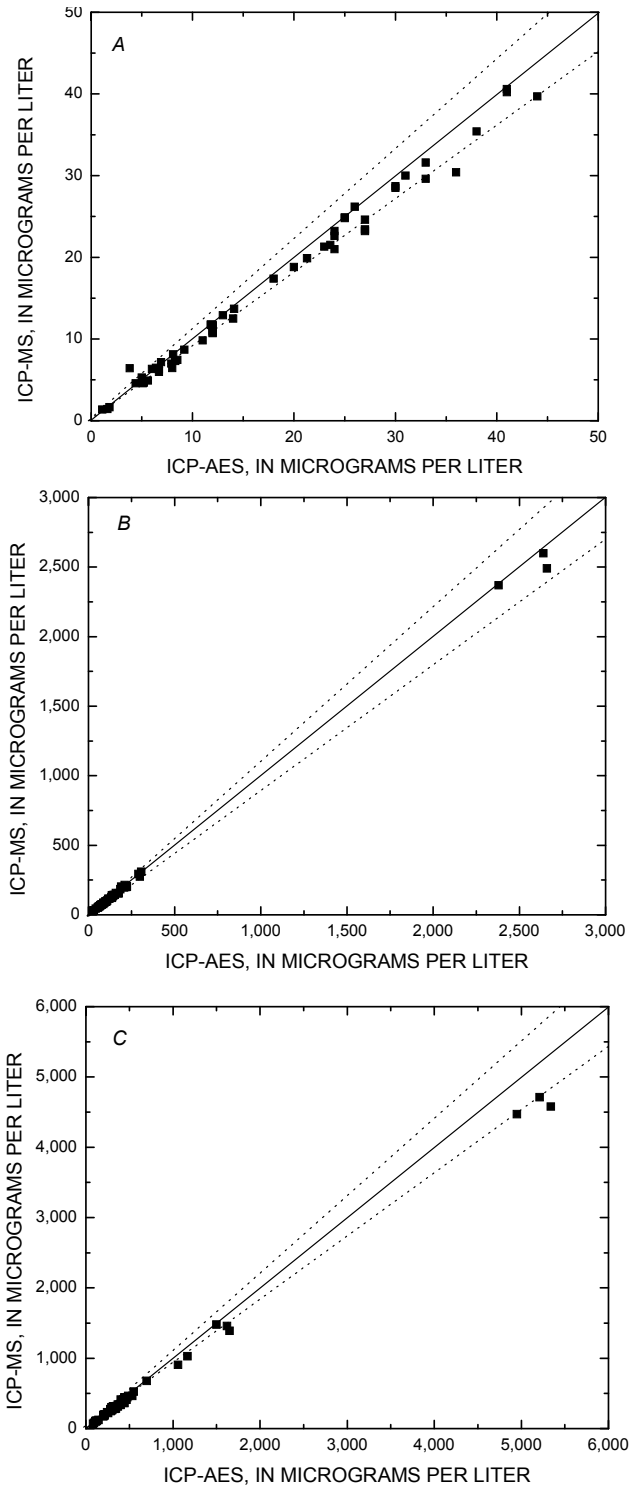
Figure 4. Comparison of analytical results by ICP-AES and ICP-MS with (*A*) barium concentration, (*B*) strontium concentration, and (*C*) manganese concentration. Diagonal line is 1:1 correspondence and dashed lines display 10 percent variation.

Data for all samples with complete analyses were checked using the computer program WATEQ4F (Ball and Nordstrom, 1991) for charge imbalance (C.I.), using the following calculation:

$$C.I.(percent) = \frac{100*(\text{sum cations} - \text{sum anions})}{(\text{sum cations} + \text{sum anions}) \div 2}$$

where sum cations is the sum of the cations in milliequivalents per liter and sum anions is the sum of the anions in milliequivalents per liter. Note that the results of this calculation are twice the value typically reported by an analytical laboratory because the denominator of the equation is the average of the cations and anions rather than the sum of the ions.

The percent C.I. reflects how well the major anions and cations balance and usually is an independent measure of the accuracy of the analytical techniques. The percent C.I. was low (<10 percent) for most samples (tables 6 and 8). Some dilute water samples had charge imbalances that were greater because of analytical imprecisions when determining concentrations at or near the detection limits.

Water Chemistry

The chemical data for samples collected from the shallow and deep wells are presented in tables 5, 6, and 7, and the chemical data for synoptic samples collected during tracer tests are presented in tables 8 and 9. Results of discharge calculations from the tracer study are presented in table 10. Water-isotopic data are presented in table 11 and dissolved sulfate-isotopic data in table 12.

Table 10. Tracer synoptic discharge results.

[m, meters; CFS, cubic feet per second; L/S, liters per second]

SITE	DISTANCE (m)	DISCHARGE, (CFS)	DISCHARGE, (L/S)
HC-114	114	0.016	0.44
HC-160	160	0.016	0.44
HC-209	209	0.072	2.05
HC-294	294	0.078	2.20
HC-395	395	0.089	2.53
HC-511	511	0.117	3.30
HC-556	556	0.139	3.93
HC-574	574	0.151	4.27
HC-596	596	0.176	4.98
HC-635	635	0.587	16.6
HC-754	754	0.626	17.7
HC-873	873	0.668	18.9
HC-959	959	0.737	20.9
HC-999	999	0.794	22.5
HC-1041	1041	0.810	22.9
HC-1143	1143	0.946	26.8
HC-1251	1251	0.961	27.2
HC-1366	1366	0.982	27.8
HC-1496	1496	0.982	27.8
HC-1630	1630	1.06	30.0
HC-1773	1773	1.09	30.8
HC-1871	1871	1.15	32.6
HC-1990	1990	1.17	33.2
HC-2119	2119	1.27	36.1

Table 11. Water isotopic analyses

[DUP, duplicate analysis; --, no data]

Site	Date collected	$\delta^{18}O$ (per mil)	$\delta^{2}H$ (per mil)
HCBW1A	9/7/2004	-18.1	-133.0
HCBW1B	9/7/2004	-18.3	-133.7
HCBW1C	9/7/2004	-17.5	-131.1
HCBW1	9/12/2005	-17.9	-132.3
HCBW2	9/7/2004	-18.1	-134.0
HCBW2	9/12/2005	-18.4	-136.0
HCBW2B	9/12/2005	-18.1	-135.0
HCSW2	9/12/2005	-17.6	-132.5
HCSW2 DUP	9/12/2005	--	-130.3
HCBW3	9/7/2004	-17.6	-133.0
HCBW3	9/12/2005	-18.1	-132.7
HCBW3 DUP	9/12/2005	-17.9	--
HCCW3	9/7/2004	-15.2	-112.4
HCCW3	9/12/2005	-16.3	-118.5
HCFW3	9/7/2004	-17.7	-131.8
HCFW3	9/12/2005	-17.8	-130.5
HCBW4	9/7/2004	-17.8	-134.7
HCBW4	9/12/2005	-18.4	-137.3
HCBW4 DUP	9/7/2004	-18.6	--
HCFW5	9/12/2005	-17.9	-136.2
HCBW5	9/12/2005	-18.3	-134.9
HCBW5 DUP	9/12/2005	--	-135.3
WP1	9/10/2004	-19.3	-144.9
WP1A	9/13/2005	-19.5	-142.9
WP1B	9/13/2005	-19.6	-144.7
WP1B DUP	9/13/2005	-19.6	--
WP2A	9/8/2004	-17.9	-136.0
WP2C	9/8/2004	-18.8	-141.0
WP2A	9/13/2005	-18.4	-136.8
WP2B	9/13/2005	-19.1	-141.2
WP4	9/8/2004	-18.5	-135.5
WP4	9/13/2005	-18.6	-134.3

Table 12. Dissolved sulfate isotopic analyses.

[DUP, duplicate analysis; --, no data]

Site	Date Collected	$\delta^{18}O$ (per mil)	$\delta^{34}S$ (per mil)
HCBW1A	9/7/2004	-8.1	-1.9
HCBW1B	9/7/2004	-8.0	-2.0
HCBW1C	9/7/2004	-7.6	-2.0
HCBW1	9/12/2005	-7.4	-1.8
HCBW2	9/7/2004	-7.5	-1.8
HCBW2	9/7/2004	-7.5	-1.7
HCBW2 DUP	9/12/2005	-7.4	-1.7
HCBW2 B	9/12/2005	-8.1	-1.6
HCSW2	9/12/2005	-7.2	-1.7
HCBW3	9/7/2004	-7.3	-1.9
HCBW3 DUP	9/7/2004	-7.3	-1.8
HCBW3	9/12/2005	-7.5	-1.7
HCCW3	9/7/2004	-7.1	-1.6
HCCW3 DUP	9/7/2004	-7.0	--
HCCW3	9/12/2005	-7.1	-1.5
HCCW3 DUP	9/12/2005	--	-1.5
HCFW3	9/7/2004	-7.1	-1.8
HCFW3	9/12/2005	-7.4	-1.6
HCBW4	9/7/2004	-8.0	-0.7
HCBW4	9/12/2005	-7.2	0.0
HCBW5 DUP	9/12/2005	-8.5	--
HCFW5	9/7/2004	-8.2	-1.1
HCFW5	9/12/2005	-7.9	-0.9
WP1	9/10/2004	-9.6	0.2
WP1A	9/13/2005	-10.1	-0.1
WP1B	9/13/2005	-10.0	-0.1
WP2A	9/8/2004	-11.5	-1.6
WP2B	9/8/2004	-11.2	-1.5
WP2B DUP	9/8/2004	-10.8	--
WP2C	9/8/2004	-9.6	-1.5
WP2A	9/13/2005	-11.8	-1.9
WP2A DUP	9/13/2005	-11.8	--
WP2B	9/13/2005	-11.6	-1.8
WP4	9/8/2004	-4.8	-0.8
WP4	9/13/2005	-5.8	-0.9
HCG1	9/12/2005	-6.6	-1.8
HCG5	9/12/2005	-7.6	-1.5

Ground-water samples are Ca-SO$_4$ dominated and range in pH from 2.51 to 6.77. Approximately, 75 percent of the samples have pH values between 3.3 and 4.3. Samples from well HCBW1 exclusively have pH values greater than 4.5. In general, with decreasing pH, dissolved sulfate concentration increases (fig. 5). Dissolved trace-metal concentrations are variable with dissolved copper ranging from <0.5 to 23,000 µg/L and dissolved zinc from 36 to 582 µg/L. A reconnaissance survey of dissolved organic carbon documented that it is quite low in these ground waters, 0.2–0.4 mg/L (table 5).
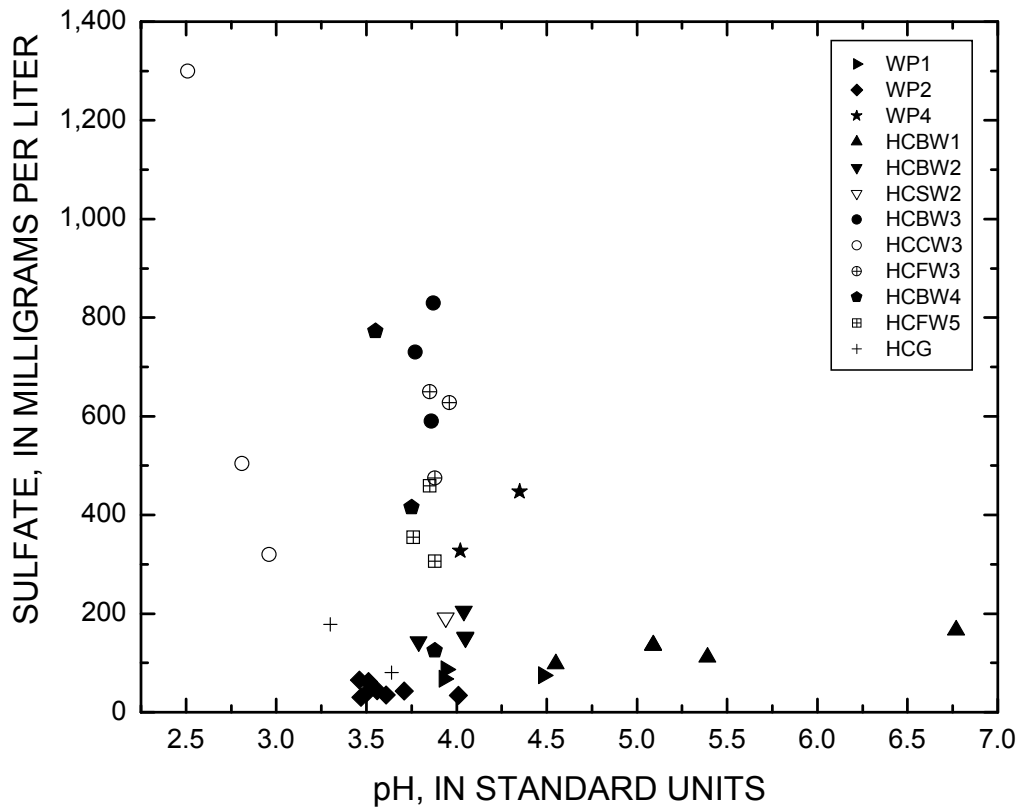
Figure 5. pH in relation to dissolved sulfate concentration for ground- and surface-water samples in Handcart Gulch.

Along the tracer-study reach, the pH of Handcart Gulch decreased from 3.98 to 3.24, and the pH of inflows to Handcart Gulch varied from 2.69 to 4.02 (fig. 6). The dissolved sulfate concentration increased by approximately a factor of 10, from 20.7 to 276 mg/L (fig. 7). The concentration of sulfate of the inflows was quite variable, 30.0–1,010 mg/L. Along the tracer-study reach, dissolved iron concentrations increased from 0.091 to 27.2 mg/L, with inflow concentrations varying from 0.110 to 124 mg/L (fig. 8). The total-recoverable iron concentration is greater than the dissolved-iron concentration for most of the stream samples in the downstream section of the study reach (fig 8), indicating that a fraction of the iron in the water column is colloidal. This is consistent with the observation of fresh-iron precipitates along the stream bed and the occurrence of ferricrete along much of the study reach.
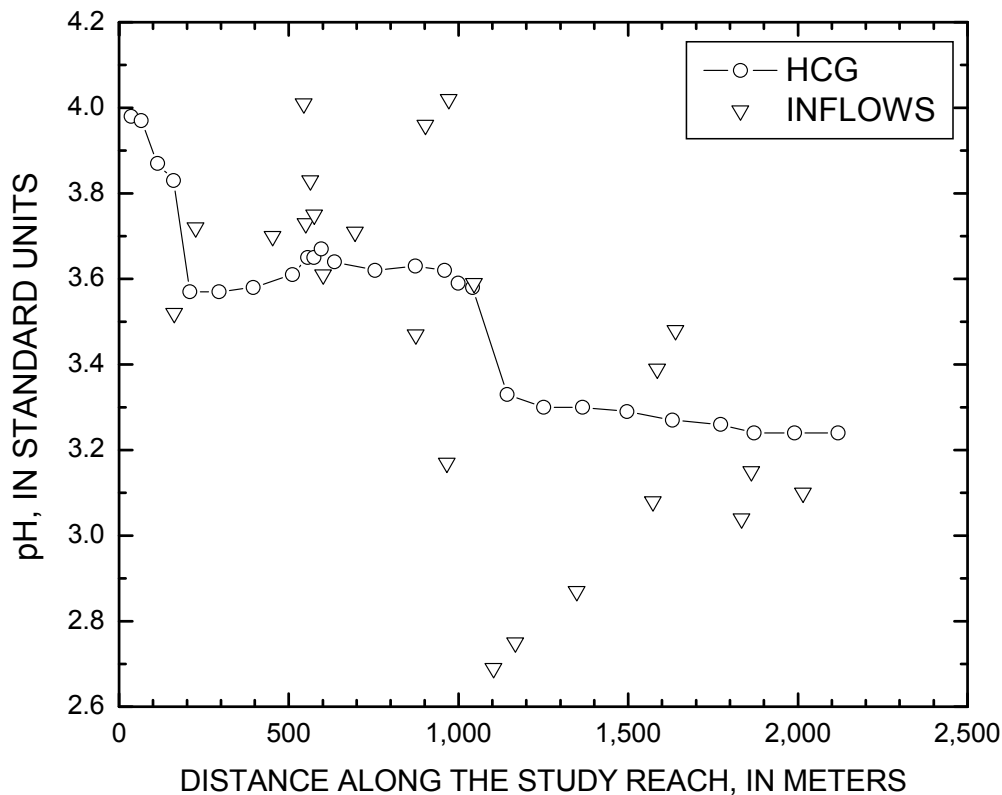
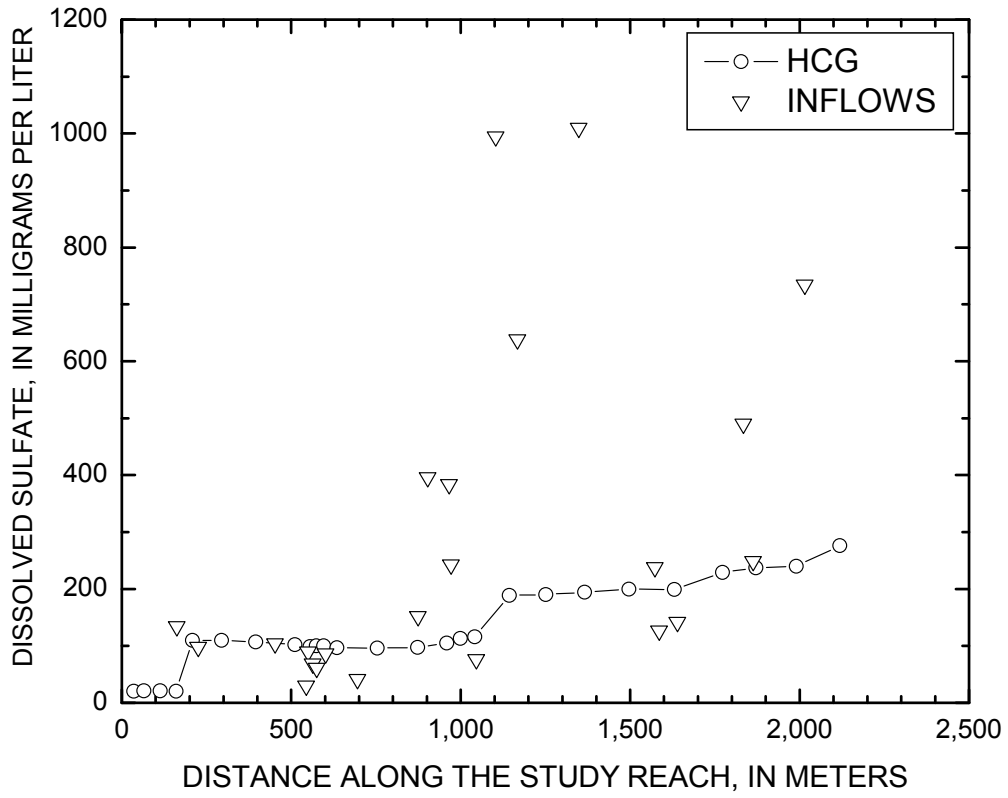**Figure 6.** pH as a function of downstream distance for Handcart Gulch.

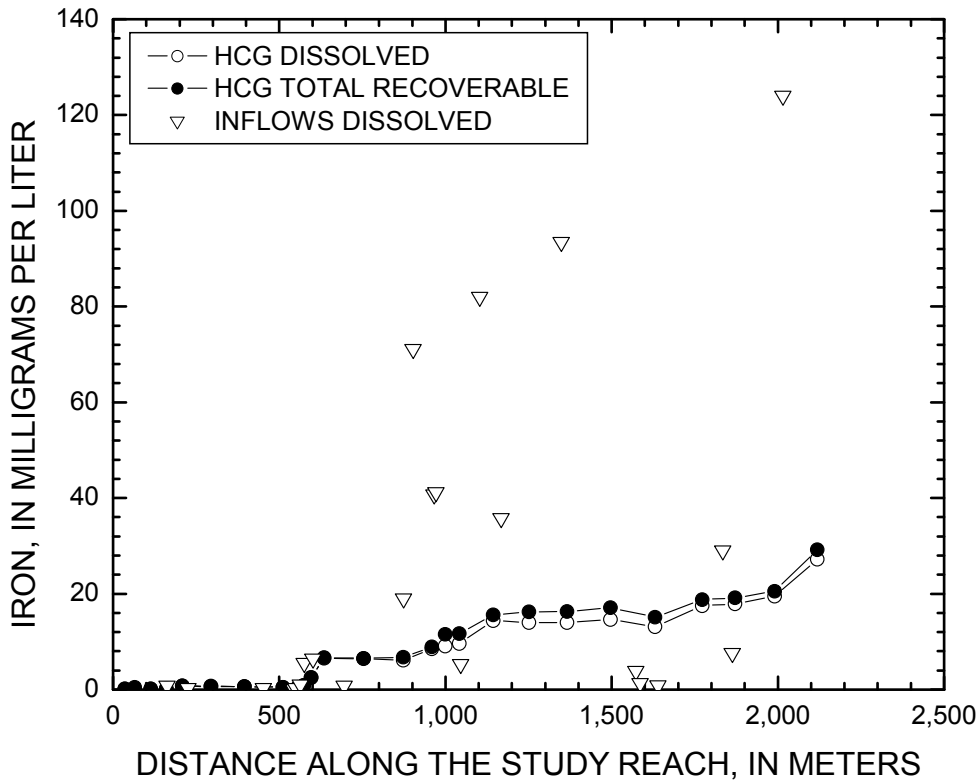**Figure 7.** Dissolved sulfate concentration as a function of downstream distance for Handcart Gulch.

Figure 8. Dissolved and total-recoverable iron concentration as a function of downstream distance for Handcart Gulch.

Dissolved copper concentration along the study reach increased from <0.010 to 0.216 mg/L, with a relatively steady increase in the lower 1,000 m (fig. 9). Little difference between the total-recoverable and dissolved fractions was observed, suggesting that most of the copper remained in solution. Dissolved copper concentrations of inflows in the upper 1,000 m of the study reach are low (<0.010–0.045 mg/L) compared to inflows in the lower 1,000 m (0.149–0.927 mg/L). Dissolved zinc concentrations along the study reach increased from <0.010 to 0.173 mg/L, but in contrast to the dissolved copper profile, the zinc profile (fig. 10) displayed a step-like increase at 635 m just downstream of the confluence of a major tributary entering from the northwest (fig. 3). Water entering Handcart Gulch in the reach between 596 m and 635 m tripled the discharge of the trunk stream (4.98–16.6 L/S; table 12 and fig. 11).
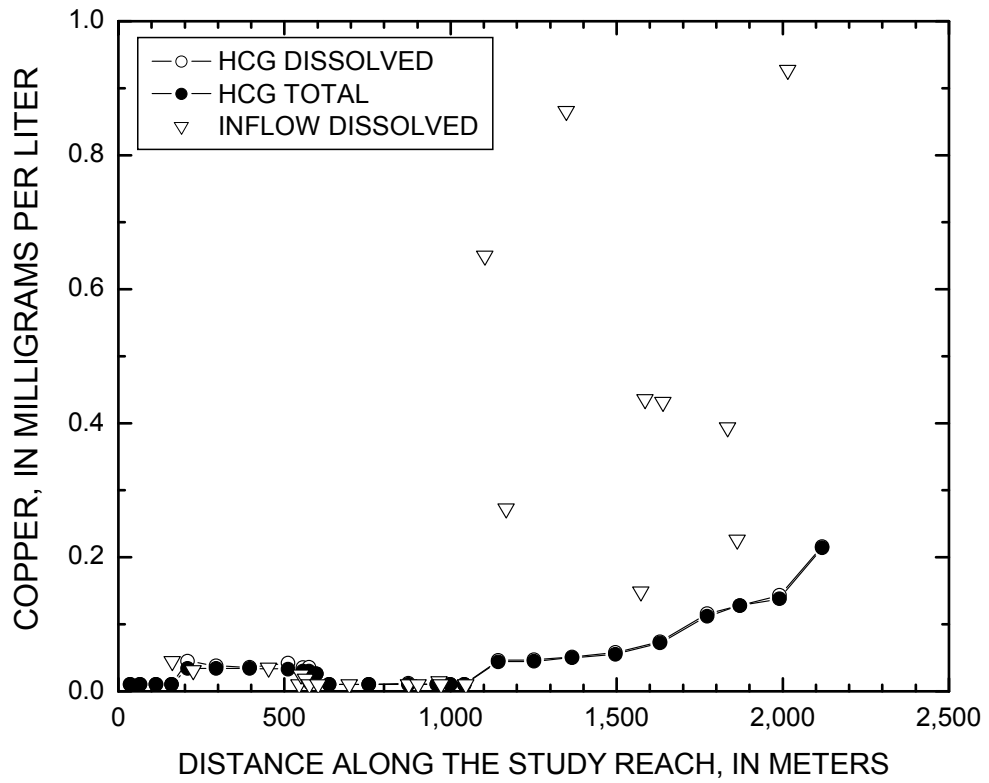
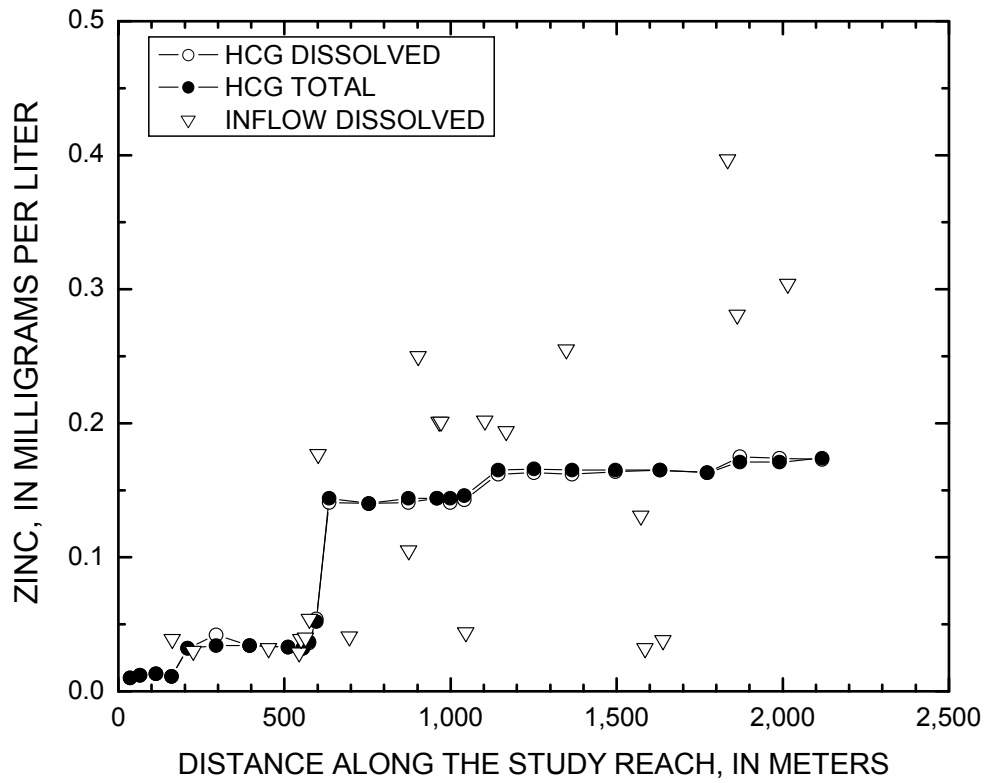**Figure 9.** Dissolved and total-recoverable copper concentration as a function of downstream distance for Handcart Gulch.

Figure 10. Dissolved and total-recoverable zinc concentration as a function of downstream distance for Handcart Gulch.
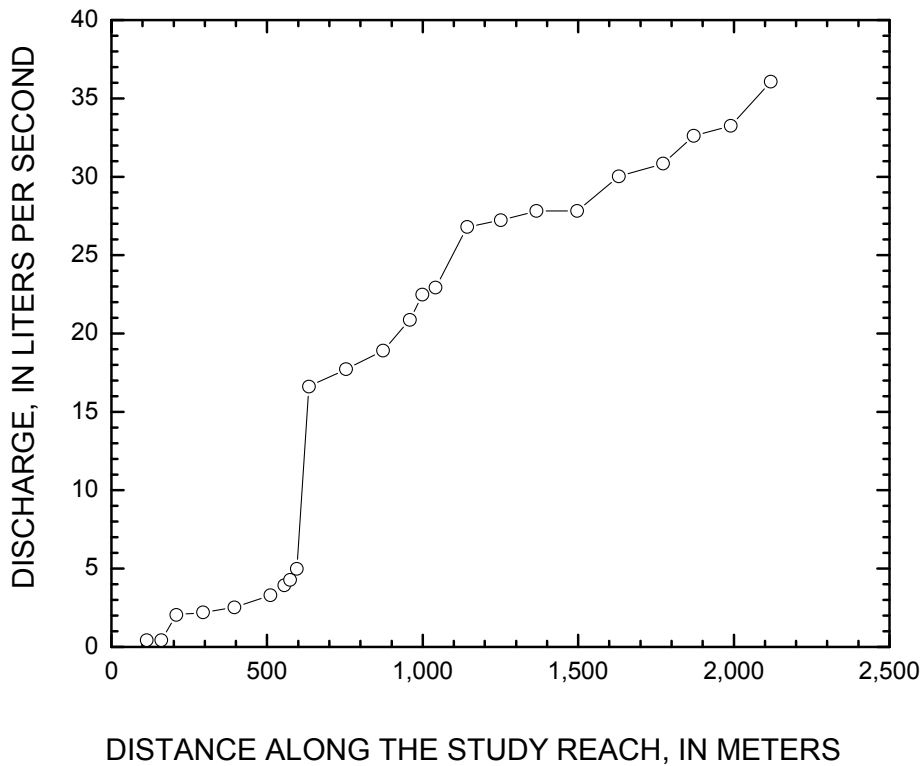
Figure 11. Discharge as a function of downstream distance for Handcart Gulch.

Discharge along the study reach increased from 0.44 to 36.1 L/S (table 12, fig. 11). Discharge data was combined with chemistry data to create loading profiles (figs. 12 *A–D*). Dissolved sulfate, iron, copper and zinc profiles displayed substantial downstream loading increases (fig. 12*A–D*).
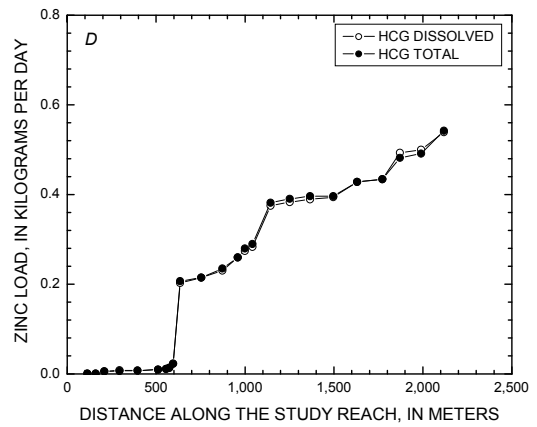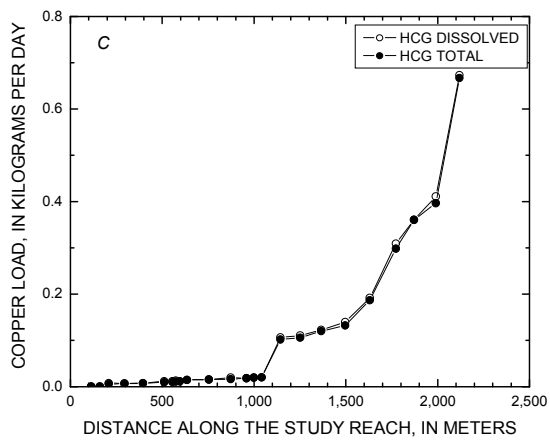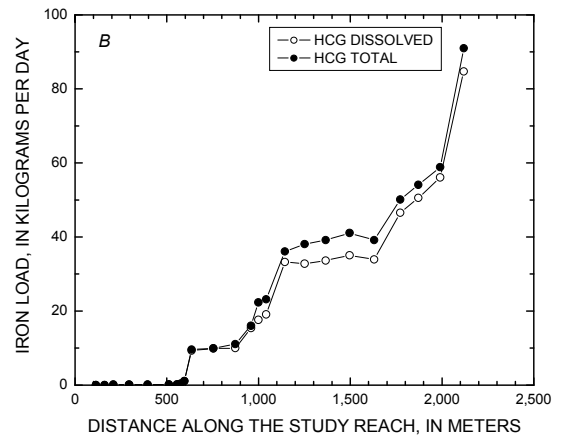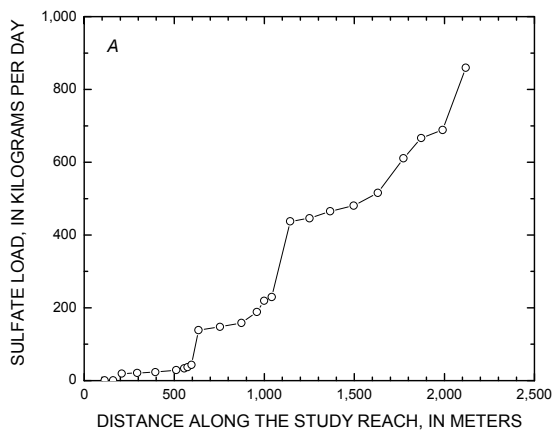
Figure 12. Constituent loads as a function of downstream distance for Handcart Gulch for (*A*) sulfate, (*B*) iron, (*C*) copper, and (*D*) zinc.

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