

Mass Loading of Selected Major and Trace Elements in Lake Fork Creek near Leadville, Colorado, September–October 2001

By Katherine Walton-Day, Jennifer L. Flynn, Briant A. Kimball, and Robert L. Runkel

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Conversion Factors

Multiply	By	To obtain
centimeter (cm)	0.3937	inch (in)
gram (g)	0.002205	pound (lb)
gram per day (g/d)	0.002205	pound per day (lb/d)
kilometer (km)	0.6214	mile (mi)
kilogram per day (kg/d)	2.205	pound per day (lb/d)
liter (l)	0.2642	gallon (gal)
liter per second (L/s)	0.0353	cubic foot per second (ft ³ /s)
meter (m)	3.281	foot (ft)
micrometer (µm)	0.00003937	inch (in)
milliliter (mL)	0.03381	ounce (oz)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$$

Horizontal coordinate information is referenced to North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum which is the National Vertical Geodetic Datum of 1929 (NGVD29).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

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

inductively coupled plasma-mass spectrometry (ICP-MS)

micrograms per liter (µg/L)

micromoles per day per meter (µmol/d/m)

microsiemens per centimeter at 25 degrees Celsius (µS/cm)

milligrams per liter (mg/L)

milligrams per second (mg/s)

milliliters per minute (mL/min)

Mountain Daylight Time (MDT)

U.S. Geological Survey (USGS)

Mass Loading of Selected Major and Trace Elements in Lake Fork Creek near Leadville, Colorado, September–October 2001

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Abstract

A mass-loading study of Lake Fork Creek of the Arkansas River between Sugarloaf Dam and the mouth was completed in September–October 2001 to help ascertain the following: (1) variation of pH and aqueous constituent concentrations (calcium, sulfate, alkalinity, aluminum, cadmium, copper, iron, manganese, lead, and zinc) and their relation to toxicity standards along the study reach; (2) location and magnitude of sources of metal loading to Lake Fork Creek; (3) amount and locations of metal attenuation; (4) the effect of streamside wetlands on metal transport from contributing mine tunnels; and (5) the effect of organic-rich inflow from the Leadville National Fish Hatchery on water quality in Lake Fork Creek. The study was done in cooperation with the Bureau of Land Management, U.S. Department of Agriculture Forest Service, and U.S. Fish and Wildlife Service.

Constituent concentrations and pH showed variable patterns over the study reach. Hardness-based acute and chronic toxicity standards were exceeded for some inflows and some constituents. However, stream concentrations did not exceed standards except for zinc starting in the upper parts of the study reach and extending to just downstream from the inflow from the Leadville National Fish Hatchery. Dilution from that inflow lowered stream zinc concentrations to less than acute and chronic toxicity standards. The uppermost 800 meters of the study reach that contained inflow from the Bartlett, Dinero, and Nelson mine tunnels and the Dinero wetland was the greatest source of loading for manganese and zinc. A middle section of the study reach that extended approximately 2 kilometers upstream from the National Fish Hatchery inflow to just downstream from that inflow was the largest source of aluminum, copper, iron, and lead loading. The loading was partially from the National Fish Hatchery inflow but also from unknown sources upstream from that inflow, possibly ground water. The largest sources for calcium and sulfate load to the stream were the parts of the study reach containing inflow from the tributaries Halfmoon Creek (calcium) and Willow Creek (sulfate).

The Arkansas River and its tributaries upstream from Lake Fork Creek were the source of most of the calcium (70 percent), sulfate (82 percent), manganese (77 percent), lead (78 percent), and zinc (95 percent) loads in the Arkansas River downstream from the Lake Fork confluence. In contrast, Lake Fork Creek was the major source of aluminum (68 percent), copper (65 percent), and iron (87 percent) loads to the Arkansas River downstream from the confluence.

Attenuation was not important for calcium, sulfate, or iron. However, other metals loads were reduced up to 81 percent over the study reach (aluminum, 25 percent; copper, 20 percent; manganese, 81 percent; lead, 30 percent; zinc, 72 percent). Metal attenuation in the stream occurred primarily in three locations (1) the irrigation diversion ditch; (2) the beaver pond complex extending from upstream from the Colorado Gulch inflow to just downstream from that inflow; and (3) the stream reach that included the inflow from Willow Creek. The most likely attenuation mechanism is precipitation of metal oxides and hydroxides (primarily manganese), and sorption or coprecipitation of trace elements with the precipitating phase.

A mass-balance calculation indicated that the wetland between the Dinero Tunnel and Lake Fork Creek removed iron, had little effect on zinc mass load, and was a source for, or was releasing, aluminum and manganese. In contrast, the wetland that occurred between the Siwatch Tunnel and Lake Fork Creek removed aluminum, iron, manganese, and zinc from the tunnel drainage before it entered the creek.

Inflow from the National Fish Hatchery increased dissolved organic carbon concentrations in Lake Fork Creek and slightly changed the composition of the dissolved organic carbon. However, dissolved organic carbon loads increased in the stream reach downstream from the fish hatchery where some metal loads decreased, indicating that precipitation of metal organic complexes probably is not promoting metal removal in that reach. The greatest effect of the inflow from the National Fish Hatchery seems to be that it diluted Lake Fork Creek and lowered stream zinc concentrations below hardness-based acute and chronic toxicity standards.

Introduction

Planning remedial actions in streams affected by acid mine drainage is a complex process. One must first understand the location and magnitude of sources of metal loading to the stream. Sources can then be ranked by the severity of their effect on stream-water quality. Generally, those sources having the greatest effect will be chosen for remediation. However, if a stream receives acid and metal loading from many diffuse sources, or sources that cannot be readily remediated (such as ground-water inflow to the stream), then it may be fiscally prohibitive to remediate enough sites to significantly improve stream-water quality. In the context of multiple sources of water-quality degradation to a stream and limited financial resources available for remediation, tools are needed that contribute to an understanding of the relative importance of all sources to the stream. Mass loading studies are such a tool.

Lake Fork Creek is a tributary to the Arkansas River about 8 km west of Leadville, Colo., in the Rocky Mountains (fig. 1). Mine drainage from a local mining district degrades water quality of the creek (Nelson and Roline, 2003). Mining, primarily of silver and some gold, zinc, and lead, began in the 1880s, with production peaking before the drop in the price of silver in 1893. Some mining activity continued until the 1920s (Singewald, 1955). Many abandoned mines possibly contribute drainage to the creek, and tailings piles are evident in several locations. Some site-specific remediation has already occurred. Relocation of tailings piles near the Nelson Tunnel (fig. 2) was completed in 2001. Relocation of tailings piles in the Dinero wetland (fig. 2) was completed in 2003. Information about possible diffuse sources of mine drainage still is needed. A mass-loading study was done by the U.S. Geological Survey (USGS) in cooperation with the Bureau of Land Management, U.S. Department of Agriculture Forest Service, and U.S. Fish and Wildlife Service. The study was done to help determine the location and magnitude of sources of trace elements to Lake Fork Creek. Sampling for this study was completed during relocation of the tailings piles near the Nelson Tunnel in 2001 but before relocation of the tailings piles in the Dinero wetland.

The mass-loading study at Lake Fork Creek consisted of injection of a conservative tracer and synoptic water-quality sampling. Tracer injection provides estimates of streamflow that are used to quantify the amount of water entering the stream through tributaries and ground-water inflow. Synoptic sampling of main-stem and inflow chemistry provides a spatially detailed “snapshot” of stream-water quality. When used together, these techniques provide a description of the watershed that includes both streamflow and concentration. Streamflow and concentration data can be used to construct mass-loading curves that identify and quantify the greatest sources of mass loading to a stream (for example in Cleasby and others, 2000; Kimball and others, 2002; Nimick and Cleasby, 2001). Sources representing the greatest contributions in terms of mass loading may subsequently be targeted for remedial actions.

Purpose and Scope

The purpose of this report is to describe mass loading of selected major and trace elements to identify and quantify sources of metal loads to Lake Fork Creek during September 11–13, 2001. Mass loads were estimated by using streamflow and water-quality data collected at 24 stream sites, 29 inflow sites, and 1 outflow site (streamflow data only) (figs. 2 and 3). In addition, the data were used to:

- describe variation of pH and constituent concentration along the creek (calcium, sulfate, alkalinity, aluminum, cadmium, copper, iron, manganese, lead, and zinc) and their relation to toxicity standards;
- locate and quantify zones of natural attenuation along the creek;
- assess the effect of nearstream wetlands on metal transport; and
- quantify the effect of organic-rich inflow from the Leadville Fish Hatchery on water quality.

The study included the segment of Lake Fork Creek from Sugarloaf Dam at Turquoise Lake to just downstream from the confluence of Lake Fork Creek and the Arkansas River, for a total study reach of approximately 9,725 m.

Metal loads were quantified from metal concentrations and streamflow. Synoptic samples were analyzed to provide metal concentrations. Streamflow was determined by tracer injection and by velocity-meter measurements, volumetric measurements, and visual estimates at selected sites. Concentration and load profiles were constructed for selected aqueous chemical constituents for the stream and inflows. Mass balances were constructed for two wetlands adjacent to the stream to determine the effects of the wetlands on trace-element transport.

Description of Study Area

Lake Fork Creek begins at an elevation of 3,520 m and runs through Turquoise Lake and the Sugarloaf mining district to the Arkansas River 8 km west of Leadville, Colo. (fig. 1). This report focuses on the 9,725-m reach of Lake Fork Creek running from Sugarloaf Dam at Turquoise Lake (elevation of 2,975 m) to the confluence with the Arkansas River (elevation of 2,875 m) (figs. 2 and 3). Lake Fork Creek downstream from Sugarloaf Dam flows between forested mountains to the west and an open valley of marsh, grass, and shrubbery to the east. Beginning just downstream from the confluence with Colorado Gulch, the creek flows through an open valley to the confluence with the Arkansas River (figs. 2 and 3). Quaternary gravels and glacial drift overlie Tertiary sandstone and Precambrian granitic rocks in the area (Tweto and others, 1978). Many abandoned mine tunnels including the Bartlett, Dinero, Nelson, and Siwatch Tunnels contribute flowing water to the drainage. Additional mine drainage possibly occurs from the many

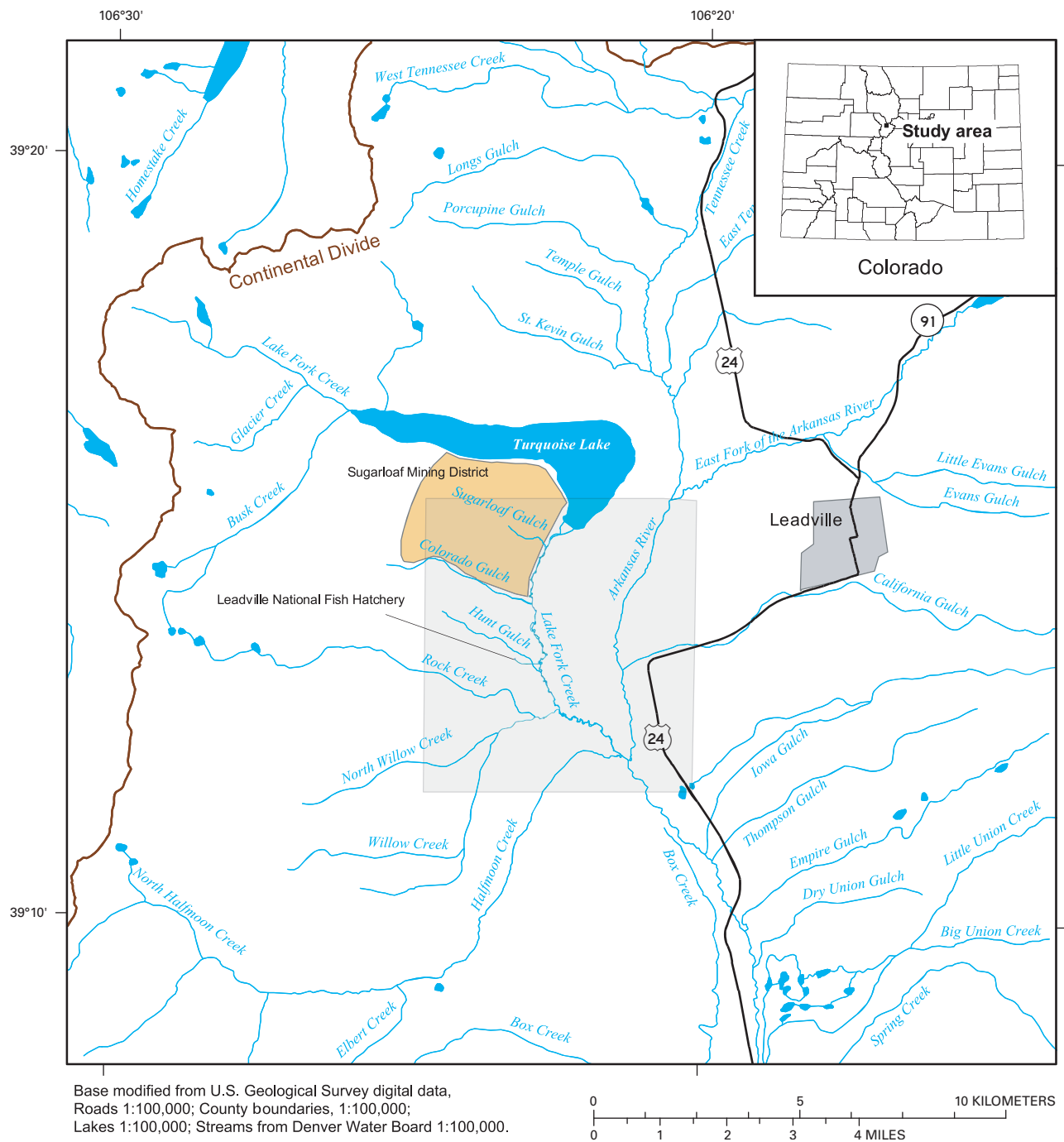


Figure 1. Location of the study area within Colorado and the upper Arkansas River Basin.

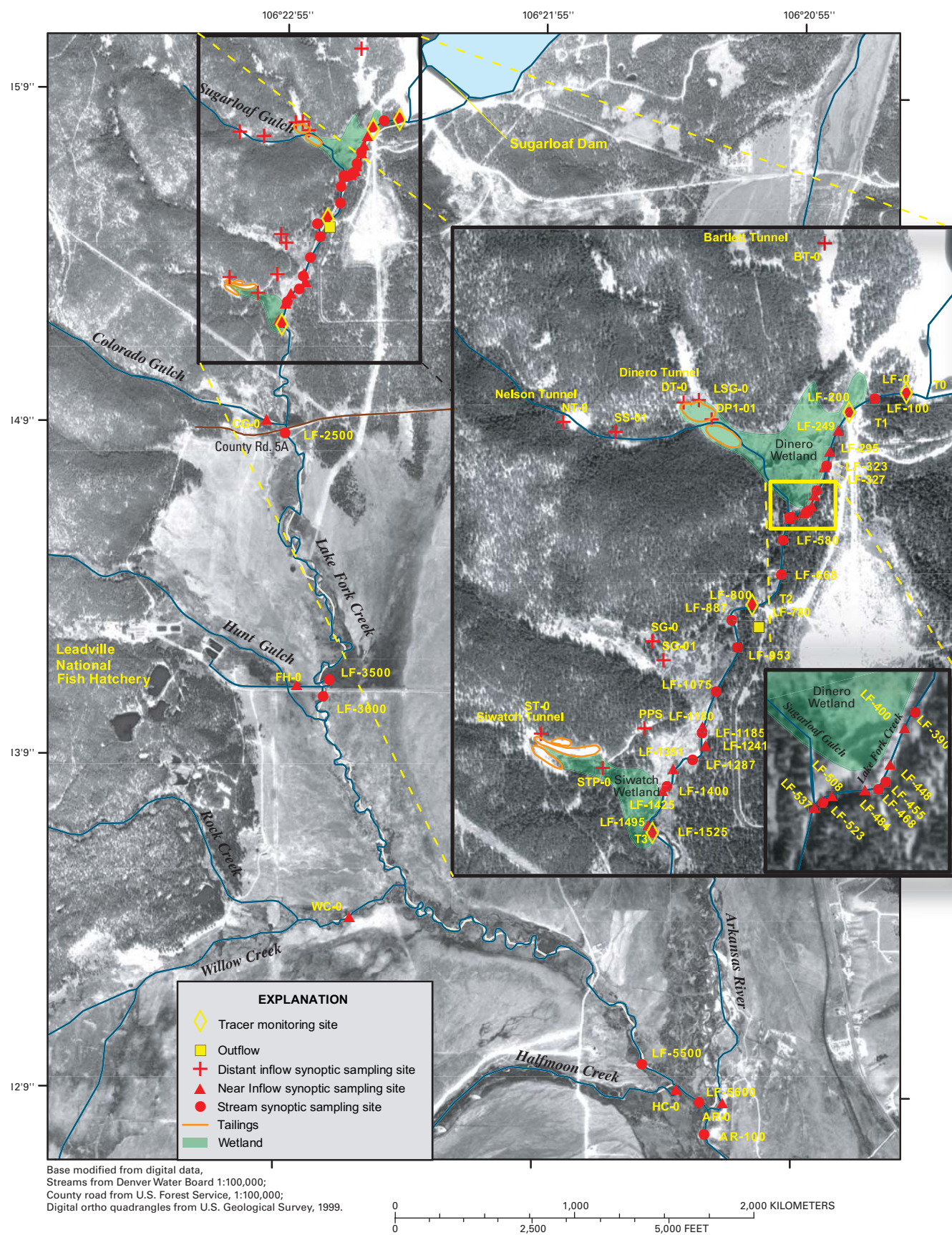


Figure 2. Aerial photograph of study area showing sampling-site locations.

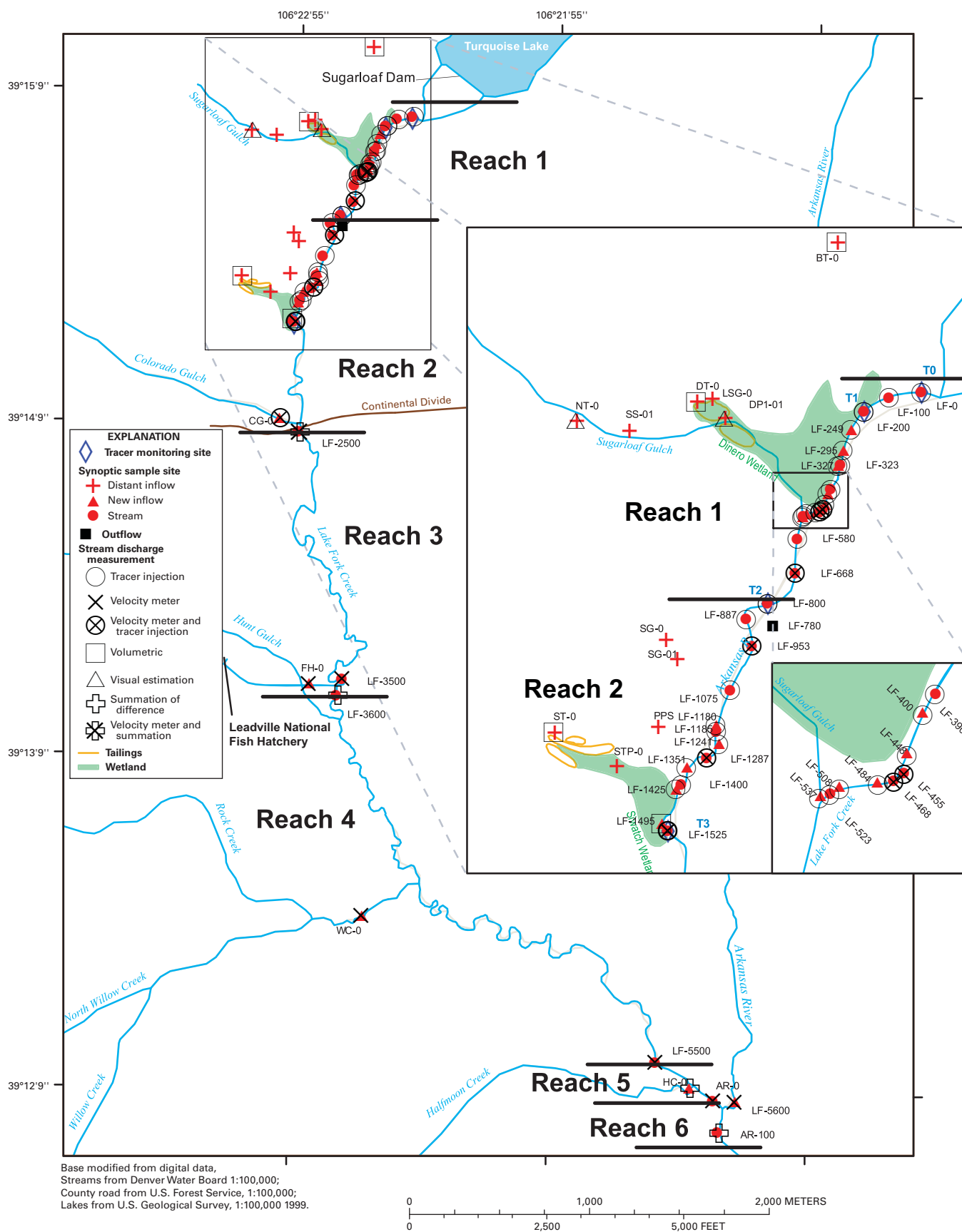


Figure 3. Study area showing sampling-site locations, streamflow measurement sites, and numbered reaches.

prospects in the area, particularly in Colorado Gulch. Tailings and mine-waste piles are evident in several locations in the study area, including at the mouths of the Bartlett, Dinero, and Siwatch Tunnels. Flowing surface-water tributaries to Lake Fork Creek include Sugarloaf Gulch, Colorado Gulch, Hunt Gulch, Willow Creek, and Halfmoon Creek. Part of the flow from Rock Creek was diverted for use in the Leadville National Fish Hatchery and discharged directly into Lake Fork Creek approximately 300 m upstream from the natural confluence between Hunt Gulch and Lake Fork Creek (FH-0, figs. 2 and 3). Surface runoff and subsurface flow also contribute inflow to Lake Fork Creek. Wetlands and active beaver ponds are adjacent to the creek in much of the study reach. Most of the annual precipitation falls as snow in the winter, with summer afternoon thunderstorms contributing some substantial rainfall. This area averages 43 cm precipitation per year, the average annual maximum daily temperature is 9.2 degrees Celsius, and the average annual minimum daily temperature is –6.9 degrees Celsius (Sugarloaf Reservoir climate station; Western Regional Climate Center, <http://www.wrcc.dri.edu>, accessed June 2005).

Previous Work

Several water-quality investigations have been done in the area. A study of the upper Arkansas River that included the study area showed that Sugarloaf Gulch contributes metals including zinc and manganese to Lake Fork Creek and that acidic drainage in Sugarloaf Gulch is not from Nelson Tunnel but from other diffuse sources (S.M. Nelson, U.S. Bureau of Reclamation, written commun., 1992).

Investigation of manganese speciation processes in the stream showed that manganese contributed to the stream by acid mine drainage was removed from the stream at a rate of $64 \pm 17 \mu\text{mol/d/m}$ through biogeochemical processes including surface-catalyzed oxidation and photoreduction (Scott and others, 2002). A study of wetland processes at nearby St. Kevin Gulch (Walton-Day, 1996) indicated that the natural wetland removed iron but not zinc from acid mine drainage that flowed through the wetland. A study of the Dinero wetland in the study area demonstrated that the natural wetland acted as a sink for iron, zinc, and manganese in summer months and as a source of manganese and zinc in the winter months (August and others, 2002). During summer months, the mass flow reduction by the wetland was more than 90 percent for iron, 65 percent for zinc, and 25 percent for manganese.

Previous studies concerning macroinvertebrates noted that taxa richness and abundance was lower directly downstream from Sugarloaf Dam compared to a site upstream from the dam and that the effects were similar to others attributed to dams (Nelson and Roline, 1996). Additional decreases in taxa abundance and richness were noted at a site downstream from the Dinero wetland and were attributed to the direct effects of metal toxicity and indirect effects of metals on habitat. Some recovery in taxa richness and abundance was noted at a site downstream from Colorado Gulch (Nelson and Roline, 1996). A later study noted additional recovery in macroinvertebrate taxa richness and abundance just downstream from the confluence between Lake Fork Creek and inflow from the Leadville National Fish Hatchery (Nelson and Roline, 2003). A survey of water quality and macroinvertebrate distribution noted low abundances of

macroinvertebrates at the confluence between Lake Fork Creek and Sugarloaf Gulch, and a lack of macroinvertebrates within Colorado Gulch, a tributary to Lake Fork Creek (Barrack, 2001).

Loading studies have been completed and published for Colorado Gulch, a tributary to Lake Fork Creek (Colorado Mountain College/Natural Resources Management Institute, 2003). High- and low-flow loading studies along Lake Fork Creek were completed between 2002 and 2004, but the results were not published at the time of completion of this report (2005) (Karmen King, Grayling Environmental, oral commun., June 2005). Although these studies have contributed to the understanding of metal sources in Lake Fork Creek, there has been no published, comprehensive, synoptic study of the relative importance of different sources of metal loads from Sugarloaf Dam to the mouth of the Lake Fork. The study described in this report provides that information.

Acknowledgments

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Methods of Study

Tracer-Injection Experiments

Application of metal-loading studies to identify loading sources on inactive mine lands has been demonstrated by Bencala and McKnight (1987), Cleasby and others (2000), Kimball and others (1994; 2002; 2004), and Nimick and Cleasby (2001). The approach includes tracer injections to quantify streamflow by tracer dilution (Kilpatrick and Cobb, 1985) and synoptic sampling to provide spatially dense profiles of pH and constituent concentrations.

Using the tracer-dilution method (Kilpatrick and Cobb, 1985), a tracer that is geochemically nonreactive is continuously injected into the stream at a constant rate and concentration. Given sufficient time, all portions of the stream including side pools and the hyporheic zone will become saturated with the tracer, and stream concentrations will reach a plateau (Kimball and others, 2002). Decreases in plateau concentration with stream length indicate dilution of the tracer by additional water entering the channel from surface- and ground-water inflows. Consideration of this dilution allows for the calculation

of streamflow at each stream site. Streamflow and concentration can be combined to construct load profiles as in Kimball and others (2002) and as described in a subsequent section of this report, "Mass-Loading Analysis."

Sampling Sites and Stream Reaches

Stream- and inflow-sampling sites were chosen during field reconnaissance conducted before the tracer injection and synoptic sampling experiment. In the upper 1,525 m of the study reach (from LF-0 to LF-1525), sampling sites were closely spaced to help identify potential sources of contamination from the Sugarloaf mining district (figs. 2 and 3). From LF-1525 downstream to the confluence, sampling sites were more widely spaced and were designed to bracket the contributions from the major tributaries (figs. 2 and 3). Sampling sites are identified with alphanumeric identifiers; the alpha characters designate an abbreviated site name (for example, AR, Arkansas River; BT, Bartlett Tunnel; CG, Colorado Gulch; DP, Dinero tailings pile; DT, Dinero Tunnel; FH, Fish Hatchery; HC, Halfmoon Creek; LF, Lake Fork; LSG, Little Sugarloaf Gulch; NT, Nelson Tunnel; PPS, Periscope Pipe Spring; SG, Strawberry Gulch; SS, side seep; ST, Siwatch Tunnel; STP, Siwatch Tunnel pond; WC, Willow Creek) and numeric characters represent an incremental site number for the site name or distance downstream (in meters) from LF-0 (for all Lake Fork Creek sites from LF-0 downstream through LF-1525).

Division of the study area into six stream reaches facilitates data presentation and discussion (fig. 3). Reach 1 was the uppermost and extended from the outfall of Turquoise Lake at the Sugarloaf Dam to the irrigation diversion structure just upstream from LF-800 (fig. 3). Reach 1 contained inflow from the Bartlett, Dinero, and Nelson Mine Tunnels, from the seeps that occurred at the downstream toes (eastern edges) of the two Dinero tailings piles, and from several small seeps that flowed from the Dinero wetland directly into Lake Fork Creek. Reach 2 extended from LF-800 to the sampling site downstream from Colorado Gulch (LF-2500 at 2,310 m downstream distance) and contained inflow from the Siwatch Tunnel, Colorado Gulch, and several small seeps. Reach 3 contained the Rock Creek portion of flow contributed by the Leadville National Fish Hatchery effluent (hereinafter termed "Fish Hatchery effluent") and ran from 2,310 m (site LF-2500) to 4,655 m distance (site LF-3600). Reach 4 extended from 4,655 m (site LF-3600) to 9,115 m (site LF-5500), the sampling site upstream from Halfmoon Creek, and contained the inflows from Hunt Gulch (not sampled) and Willow Creek (site WC-0 at 6,295 m). Reach 5 extended from 9,115 m (site LF-5500) to 9,515 m (site LF-5600) and bracketed the inflow from Halfmoon Creek (site HC-0 at 9,365 m). The confluence of Lake Fork Creek and the Arkansas River was in Reach 6.

Streamflow

Streamflow for the upper part of the study area (from 0 to 1,525 m) was determined using the tracer injection method

(Bencala and others, 1990; Kilpatrick and Cobb, 1985; Kimball and others, 2002). A continuous tracer injection was conducted from 0 to 1,525 m starting at 1130 hours September 11, 2001, and continuing through 1530 hours September 12, 2001. A solution containing 250,500 mg/L sodium bromide (NaBr) was injected at an average rate of 228 mL/min.

Calculation of streamflow from the tracer-injection data relies on assuming conservation of mass of the tracer during stream transport. The calculation is based on a simple mass balance that considers the concentration and injection rate of the added tracer, and the assumption that the concentration of the added tracer is much greater than the naturally occurring concentration. Concentrations of bromide in mountain stream environments typically are low, with background concentrations at or near the detection limit (0.1 mg/L). Spatial variability in background concentrations also is low, such that background concentrations are nominally uniform. Given the assumption of uniform background concentrations, stream discharge at any location downstream from the injection is given by:

$$Q_S = \frac{(Q_{INJ} C_{INJ})}{C_S - C_{bg}} \quad (1)$$

where

- Q_S is stream discharge, in liters per second;
- Q_{INJ} is the injection rate, in liters per second;
- C_{INJ} is the injectate concentration, in milligrams per liter;
- C_S is the tracer concentration at plateau, in milligrams per liter; and
- C_{bg} is the naturally occurring background concentration, in milligrams per liter.

For this study, Q_S for stream sites in Reach 1 was determined using a mass flow of tracer ($Q_{INJ} C_{INJ}$) of 952 mg/s. The loss of tracer-mass flow to the irrigation diversion at the beginning of Reach 2 decreased the mass flow of tracer to 604 mg/s for streamflow calculations from 800 to 1,525 m.

The discharge of an inflow is assigned the difference in discharge between the downstream and upstream stream sites:

$$Q_i = (Q_b - Q_a) \quad (2)$$

where

- Q_i is inflow discharge, in liters per second;
- Q_b is the downstream discharge, in liters per second; and
- Q_a is the upstream discharge, in liters per second.

Streamflow in the lower part of Reach 2 and through all downstream study reaches (Reaches 2–6) was measured using the velocity-meter method (Rantz and others, 1982). At each confluence (except the Willow Creek confluence), streamflow was measured at two of the three possible sites: (1) main stem upstream from confluence, (2) tributary upstream from confluence, and (3) main stem downstream from confluence; the streamflow at the third site was determined by difference or summation, as appropriate. These sites are the "summation of difference" sites in figure 3. Velocity-meter measurements also

were collected at six sites (LF-455, LF-468, LF-668, LF-953, LF-1287, and LF-1525) along the tracer-injection reach to compare with the tracer-calculated flow measurements, and at one site (LF-780) to quantify the flow loss to the diversion ditch. Replicate velocity-meter measurements made at two sites (LF-1525 and LF-2500) between September 10 and September 13 indicated less than 1 percent difference in the measurements. Most of the velocity-meter measurements were rated fair (less than 8 percent error) except for the measurement at Colorado Gulch (CG-0) that was rated poor (error greater than 8 percent) and the measurement at the diversion ditch (LF-780) that was rated good (error less than 5 percent; K.J. Leib, U.S. Geological Survey, written commun., September 2003).

Streamflow at several inflow sites in the tracer-injection study reach was measured using volumetric methods, using a 10.16 cm (4-inch) cut-throat flume, or was estimated based on visual observation, where the width, depth, and water velocity were observed and estimated using best professional judgment. These inflow sites included the Bartlett (BT-0), Dinero (DT-0), and Siwatch (ST-0) mine tunnels (cut-throat flume); site LF-1495 (volumetric measurement); and the Nelson Tunnel (NT-0) and the toe seep from the north Dinero tailings pile (DP1-01). Inflow at all other sites in the tracer-injection reach was determined from the difference in streamflow between stream sites upstream and downstream from the inflow.

Collection of Water-Quality Samples

Twenty-four stream sites and 29 inflow sites were sampled along Lake Fork Creek and Arkansas River from the outfall of Sugarloaf Dam downstream to approximately 100 m downstream from the confluence of Lake Fork Creek and the Arkansas River. Data from the 24 stream sites and 18 of the inflow sites were used to construct the mass-loading profiles. Data from the other inflow sites were used to construct the mass balances for the near-stream wetlands and to provide additional information on the composition of water in the study reach. Two types of inflow sites were termed “near-inflow” and “distant-inflow” sites (figs. 2 and 3). Near-inflow sites flowed directly into the stream and were designated “near-inflow” sites in figures 2 and 3. Inflows located at some distance from the stream that did not necessarily reach the stream as a discrete, visible surface inflow were referred to as “distant-inflow” sites in figures 2 and 3. The Bartlett (BT-0), Dinero (DT-0), Nelson (NT-0), and Siwatch (ST-0) Tunnels, seeps at the toe of the northern Dinero tailings pile (DP1-01), an acidic seep between the Nelson Tunnel and the Dinero wetland (SS-01), a neutral seep slightly east of the Dinero Tunnel (LSG-0), Periscope Pipe Spring (PPS), two seeps in Strawberry Gulch (SG-0 and SG-01), and flow exiting a pond near the Siwatch Tunnel (STP-0) were the distant inflows. All other inflows were near-stream inflows. Samples from stream sites and larger inflow sites were collected using the DH-81 sampler to collect a composite sample across the width and depth of the channel—an

equal-width-increment (EWI) sample (Wilde and others, 1999). Grab samples were collected at smaller inflow sites.

New 2-L polyethylene jugs were triple-rinsed with sample water, filled with composited sample, and then transported to a central location in the study area for filtering and analysis of field properties. Three large-volume (approximately 20 L) bulk samples were collected at the fish hatchery effluent (FH-0) and at the stream sites immediately upstream and downstream (LF-3500 and LF-3600). These samples were immediately chilled and transported on ice to USGS laboratories in Boulder, Colo., for isolation of organic matter. At three sites termed “transport sites” (T1 at 200 m, T2 at 800 m, and T3 at 1,525 m; figs. 2 and 3), samples were collected between 0900 and 1500 continuously throughout the tracer-injection using autosamplers. Samples in the tracer-injection study reach downstream to LF-2500 (2,310 m) were collected between 0900 and 1500 and processed September 12, 2001. On September 13, 2001, site LF-2500 was resampled, and samples at all downstream sites to AR-100 (9,725 m) were collected and processed. A few additional samples were collected at some inflow sites in Reach 1 on October 3, 2001 (tables 1–3). Comparison of unfiltered samples collected at the Dinero Tunnel (DT-0) on September 12 and October 3 (tables 1–3) indicated minimal variation in water quality and supported including the October 3 samples in the mass-loading analysis.

Composited synoptic samples were split into as many as five aliquots for analysis. A 125-mL unfiltered aliquot of sample was dispensed into a clean, deionized-water (DI) rinsed bottle for immediate analysis of pH and specific conductance. An additional 125-mL unfiltered aliquot was collected into an acid and DI-rinsed bottle for analysis of unfiltered “total-recoverable” (or “total”) trace-element content. The remaining composite sample was filtered through a 0.45- μ m filter using tangential flow filtration. One 125-mL aliquot was filtered into a clean, DI-rinsed bottle for analysis of anions by ion chromatography and alkalinity by acidometric titration. A second 125-mL aliquot was filtered into an acid and DI-rinsed bottle for analysis of major cation and trace-element content. All sample bottles were rinsed with unfiltered or filtered sample water as appropriate before sample collection. For sites LF-2500 and all downstream samples collected on September 13, a third 125-mL aliquot was pressure filtered through a 0.45- μ m Supor filter directly into a baked, amber glass bottle with no sample rinse for analysis of dissolved organic carbon (DOC). Unfiltered and filtered samples for major cation and trace-element analysis were acidified the day of sample collection using 1 mL of ultrapure nitric acid per 125-mL sample.

In this study, the dissolved portion of samples was operationally defined as sample that passed through a 0.45 μ m filter. Colloid concentrations were estimated for aluminum and iron as the difference between analyte concentrations in “total” and “dissolved” samples. Because colloids can extend to sizes well less than 0.45 μ m, the dissolved fraction defined herein contained some colloidal particles, and the colloid fraction was underestimated.

Table 1. Results for field properties and major ion analyses in water samples from Lake Fork Creek, September–October 2001.

[Dissolved, concentration measured in a sample filtered through a membrane having a pore size of 0.45 micrometer; L/s, liters per second; mg/L, milligrams per liter; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; CaCO_3 , calcium carbonate; <, less than; NS, no sample; NA, not applicable; NM, not measured; A, B, and C in site name, indicate replicate samples for a site; FBLNK, field blank]

Site (figs. 2 and 3)	Source ¹ (meters)	Distance (meters)	Date	Dis- charge (L/s)	Tem- perature (degrees Celsius)	Specific conduc- tance (μS/cm at 25 degrees Celsius)	pH (standard units)	Hardness (mg/L)	Chloride ² (mg/L)	Bromide ² (mg/L)	Sulfate ³ (mg/L)	Alkalinity Dissolved				
												(mg/L as CaCO ₃)	calcium (mg/L)	magnesium (mg/L)	sodium (mg/L)	potassium (mg/L)
Method detection limit	NA	NA	NA	NA	NA	0.50	NA		0.20	0.10	1.00	0.063	0.007	0.179	0.046	
LF-0	Stream	0	09/12/01	238.5	8	23	6.99	9.27	<0.20	<0.10	2.04	2.82	0.537	0.523	0.201	
LF-100	Stream	100	09/12/01	238.5	8	29	7.01	9.40	<0.20	3.65	2.04	2.86	0.540	1.51	0.253	
LF-200A	Stream	200	09/12/01	238.5	8	29	7.29	8.53	0.2	3.64	2.05	2.59	0.495	1.51	0.227	
LF-200B	Stream	200	09/12/01	238.5	8	29	7.22	8.53	<0.20	3.71	2.05	2.61	0.485	1.43	0.227	
BT-0	Distant inflow	220	09/12/01	1.68	6	217	5.98	70.5	0.38	<0.10	76.3	17.7	6.35	3.21	1.13	
LF-249	Near inflow	249	10/03/01	0.1	8	149	6.26	89.1	NS	NS	NS	21.8	8.37	3.15	0.914	
LF-295	Near inflow	295	10/03/01	0.1	6	167	6.45	101	NS	NS	NS	24.0	9.85	3.53	0.920	
LSG-0	Distant inflow	305	09/12/01	0.01	9	44	6.19	13.3	<0.20	<0.10	0.97	3.63	1.01	2.16	0.206	
LF-323	Stream	323	09/12/01	238.7	9	30	7.33	9.44	<0.20	3.76	2.29	2.85	0.558	1.50	0.194	
DT-0	Distant inflow	325	09/12/01	2.59	10	806	6.37	263	0.51	<0.10	385	72.4	19.8	6.83	1.93	
DT-0	Distant inflow	325	10/03/01	2.59	10	763	6.35	263	NS	NS	NS	NS	NS	NS	NS	
LF-327 ⁴	Near inflow	327	09/12/01	0.2	12	664	5.24	262	<0.20	<0.10	338	71.8	20.0	5.71	0.826	
DPI-01	Distant inflow	335	10/03/01	⁵ 0.008– 0.067	10	963	3.56	250	NS	NS	NS	67.4	19.8	5.81	1.57	
LF-390	Stream	390	09/12/01	238.9	9	30	7.19	9.91	<0.20	3.8	2.44	3.02	0.571	1.54	0.141	
LF-400 ⁴	Near inflow	400	09/12/01	0.1	14	733	4.11	246	0.62	<0.10	349	66.3	19.4	6.31	1.92	
LF-448 ⁴	Near inflow	448	09/12/01	0.1	12	741	3.98	249	0.67	<0.10	346	67.4	19.6	6.33	2.32	
LF-455A	Stream	455	09/12/01	239.1	10	32	7.26	10.6	<0.20	3.88	2.88	2.84	0.579	1.61	0.286	
LF-455B	Stream	455	09/12/01	239.1	10	33	7.29	10.6	<0.20	3.9	3.67	3.16	0.635	1.52	0.220	
LF-455C	Stream	455	09/12/01	239.1	10	40	7.26	10.6	<0.20	3.89	6.54	3.46	0.750	1.59	0.299	
LF-468	Stream	468	09/12/01	239.1	9	37	7.29	10.8	<0.20	3.97	5.29	3.19	0.670	1.56	0.273	
LF-484 ⁴	Near inflow	484	09/12/01	0.3	12	729	3.97	260	0.61	<0.10	378	70.1	20.7	6.43	2.16	

Table 1. Results for field properties and major ion analyses in water samples from Lake Fork Creek, September–October 2001.—Continued.

[Dissolved, concentration measured in a sample filtered through a membrane having a pore size of 0.45 micrometer; L/s, liters per second; mg/L, milligrams per liter; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; CaCO_3 , calcium carbonate; <, less than; NS, no sample; NA, not applicable; NM, not measured; A, B, and C in site name, indicate replicate samples for a site; FBLNK, field blank]

Site (figs. 2 and 3)	Source ¹	Distance (meters)	Date	Dis- charge (L/s)	Specific conduc- tance			pH (standard units)	Hardness (mg/L)	Chloride ² (mg/L)	Bromide ² (mg/L)	Sulfate ³ (mg/L)	Alkalinity Dissolved				Dissolved sodium (mg/L)	Dissolved potassium (mg/L)								
					Tem- perature (degrees Celsius)	at 25 degrees Celsius)	(μS/cm						NS	NS	NS	NS			NS	NS	NS	NS	NS	NS	NS	NS
SS-01	Distant inflow	495	10/03/01	NM	13	210	4.07	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS						
NT-0	Distant inflow	500	09/12/01	0.6	9	204	6.65	68.3	0.27	<0.10	<0.10	64.6	19.3	17.1	6.16	3.75		0.842								
LF-508 ⁴	Near inflow	508	09/12/01	0.4	8	770	3.72	235	0.6	<0.10	<0.10	370	<0.20	63.0	18.8	5.89	2.21									
LF-523	Stream	523	09/12/01	239.8	8	45	7.13	13.4	<0.20	3.97	3.97	8.46	6.85	3.90	0.885	1.66	0.267									
LF-537 ⁴	Near inflow	537	09/12/01	5.6	8	746	3.68	229	0.56	<0.10	<0.10	356	<0.20	61.7	18.0	6.33	2.10									
LF-580	Stream	580	09/12/01	245.4	8	48	6.98	14.0	<0.20	3.87	3.87	10.3	7.30	4.06	0.938	1.64	0.297									
LF-668	Stream	668	09/12/01	246.8	8	48	7.07	14.6	<0.20	3.83	3.83	10.4	7.55	4.22	0.972	1.66	0.259									
LF-800	Stream	800	09/12/01	156.5	8	48	7.14	13.9	<0.20	3.81	3.81	10.4	7.15	4.03	0.927	1.57	0.254									
LF-887	Stream	887	09/12/01	157.9	8	49	7.02	14.6	<0.20	3.84	3.84	10.3	7.05	4.22	0.986	1.68	0.187									
LF-953	Stream	953	09/12/01	158	8	48	7.18	13.7	0.21	3.82	3.82	10.2	7.30	3.98	0.917	1.66	0.290									
SG-01	Distant inflow	1,000	09/12/01	NM	8	67	6.39	23.8	<0.20	<0.10	<0.10	2.43	27.6	6.23	1.98	2.58	0.494									
SG-0	Distant inflow	1,000	09/12/01	NM	14	78	6.02	29.4	<0.20	<0.10	<0.10	1.89	29.7	7.69	2.48	2.70	0.614									
LF-1075	Stream	1,075	09/12/01	163.4	8	48	7.01	13.5	0.2	3.7	3.7	9.74	6.85	3.92	0.889	1.64	0.314									
LF-1180	Near inflow	1,180	09/12/01	0.3	9	62	6.31	17.0	1.37	0.39	0.39	10.4	14.2	4.68	1.27	2.82	0.694									
LF-1185	Stream	1,185	09/12/01	163.7	7	46	7.09	15.2	0.23	3.84	3.84	10.0	7.15	4.42	1.01	1.78	0.265									
LF-1241	Near inflow	1,241	09/12/01	0.5	6	33	5.85	11.6	<0.20	<0.10	<0.10	7.77	5.85	3.41	0.738	0.717	0.199									
LF-1287	Stream	1,287	09/12/01	164.2	6	47	7.08	13.8	0.22	3.68	3.68	9.56	6.80	3.95	0.946	1.97	0.247									
PPS	Distant inflow	1,300	09/12/01	NM		3,930	6.47	666	1,080	1.17	1.17	59.6	1,370	157	65.0	623	60.8									
LF-1351	Near inflow	1,351	09/12/01	1.7	5	1,870	7.18	358	281	0.67	0.67	32.8	471	92.7	30.2	247	8.90									
LF-1400	Stream	1,400	09/12/01	165.9	6	47	7.15	14.1	0.23	3.64	3.64	9.54	6.80	4.08	0.934	1.63	0.211									
LF-1425	Near inflow	1,425	09/12/01	0.1	6	1,040	7.03	205	97.1	0.22	0.22	93.8	299	52.0	17.9	113	11.2									
ST-0	Distant inflow	1,490	09/12/01	1.91	10	426	6.39	166	0.27	<0.10	<0.10	169	24.3	41.8	15.0	4.48	1.24									
STP-0	Distant inflow	1,490	09/12/01	1.91	8	382	6.11	154	0.39	<0.10	<0.10	170	3.12	37.9	14.3	4.44	1.20									

Table 1. Results for field properties and major ion analyses in water samples from Lake Fork Creek, September–October 2001.—Continued.

[Dissolved, concentration measured in a sample filtered through a membrane having a pore size of 0.45 micrometer; L/s, liters per second; mg/L, milligrams per liter; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; CaCO_3 , calcium carbonate; <, less than; NS, no sample; NA, not applicable; NM, not measured; A, B, and C in site name, indicate replicate samples for a site; FBLNK, field blank]

Site (figs. 2 and 3)	Source ¹	Distance (meters)	Date	Dis- charge (L/s)	Specific conductance			pH (standard units)	Hardness (mg/L)	Chloride ² (mg/L)	Bromide (mg/L)	Alkalinity Dissolved			Dissolved sodium (mg/L)	Dissolved potassium (mg/L)
					Tem- perature (degrees Celsius)	at 25 degrees Celsius)	($\mu\text{S}/\text{cm}$)					mg/L as CaCO_3	calcium (mg/L)	magnesium (mg/L)		
LF-1495	Near inflow	1,495	09/12/01	2.4	8	373	6.5	158	0.54	<0.10	164	15.3	38.7	14.8	4.33	1.26
LF-1525	Stream	1,525	09/12/01	168.4	6	54	6.91	16.1	0.34	3.65	12.1	8.05	4.57	1.13	1.79	0.312
CG-0	Near inflow	2,255	09/12/01	12.6	12	245	7.15	40.2	28.6	<0.10	16.8	50.9	9.39	4.02	28.1	2.77
LF-2500	Stream	2,310	09/12/01	181	11	61	6.95	18.6	0.97	2.38	12.5	10.7	5.19	1.36	2.27	0.294
LF-2500	Stream	2,310	09/13/01	181	8	64	7.05	18.6	<0.20	<0.10	12.4	9.50	5.20	1.37	2.70	0.460
LF-3500	Stream	4,535	09/13/01	282	10	93	6.96	22.9	3.99	1.27	11.9	19.2	6.33	1.71	6.79	0.894
FH-0	Near inflow	4,585	09/13/01	217.8	9	38	7.43	13.8	0.4	<0.10	2.57	14.1	4.27	0.744	1.21	0.278
LF-3600	Stream	4,655	09/13/01	499.8	9	69	7.16	18.8	2.23	0.71	7.66	17.4	5.39	1.29	4.24	0.650
WC-0	Near inflow	6,295	09/13/01	153.2	12	61	7.52	23.6	0.32	<0.10	1.97	27.2	6.33	1.89	2.49	0.629
LF-5500	Stream	9,115	09/13/01	906.1	10	93	7.8	32.6	1.41	1.15	10.3	28.8	8.56	2.72	3.57	0.745
HC-0	Near inflow	9,365	09/13/01	495.9	10	89	7.9	39.1	<0.20	<0.10	5.51	36.3	9.71	3.59	1.27	0.555
LF-5600A	Stream	9,515	09/13/01	1,402	10	94	7.62	36.5	1.17	0.85	9.37	31.7	9.52	3.17	3.77	0.640
LF-5600B	Stream	9,515	09/13/01	1,402	10	94	7.72	36.5	<0.20	<0.10	9.24	31.6	9.33	3.10	3.03	0.585
AR-0	Near inflow	9,575	09/13/01	928	10	271	8.19	113	1.68	<0.10	61.3	65.9	28.3	10.2	3.38	0.950
AR-100	Stream	9,725	09/13/01	2,330	10	174	8.03	74.1	1.65	0.46	31.2	45.3	19.1	6.41	3.19	0.661
LF-BLNKA	FBLNK	NA	09/12/01	NA	NA	1	NA	NA	<0.20	<0.10	<1.0	NM	<0.063	<0.007	<0.179	<0.046
LF-BLNKB	FBLNK	NA	09/13/01	NA	NA	1	NA	NA	<0.20	<0.10	<1.0	NM	<0.063	0.011	<0.179	<0.046

¹Near inflow sites flowed directly into the stream. Distant inflow sites were located at some distance from the stream and did not necessarily reach the stream as discrete, visible surface inflow.

²Chloride concentrations below 1 mg/L are estimated (Appendix 1).

³Sulfate concentrations below 10 mg/L are estimated (Appendix 1).

⁴Charge balance error for these six samples ranged from 10 to 17 percent.

⁵Range of estimates for flow of Dinero north pile toe seep used in wetland mass-balance calculations.

Table 2. Analytical results for aluminum, silica, manganese, iron, zinc, lead, copper, cadmium, and silver in water samples from Lake Fork Creek, September–October 2001

[Total, concentration measured in an unfiltered sample; dissolved, concentration measured in a sample filtered through a membrane having a pore size of 0.45 micrometer; L/s, liters per second; mg/L, milligrams per liter; <, less than; µg/L, micrograms per liter; NM, not measured; NS, no sample; NA, not applicable; A, B, and C in site name, indicate replicate samples for a site; FBLNK, field blank]

Site (figs. 2 and 3)	Source ¹	Date	Dis- tance (meters)	Dis- charge (L/s)	Dis- solved alum- inum ² (µg/L)	Total alum- inum ² (µg/L)	Dis- solved silica (mg/L)	Total silica (mg/L)	Dis- solved manga- nese (mg/L)	Total manga- nese (mg/L)	Dis- solved iron (mg/L)	Total iron (mg/L)	Dis- solved zinc (mg/L)	Total zinc (mg/L)	Dis- solved lead (µg/L)	Total lead (µg/L)	Dis- solved copper ³ (µg/L)	Total copper (µg/L)	Dis- solved cad- mium (µg/L)	Total cad- mium (µg/L)	Dis- solved silver (µg/L)	Total silver (µg/L)
Detection limit	NA	NA	NA	NA	4	4	0.068	0.068	0.004	0.004	0.004	0.004	0.004	0.004	0.06	0.06	0.30	0.30	0.26	0.26	0.21	0.21
LF-0	Stream	0	09/12/01	238.5	57	52	1.86	1.37	<0.004	0.009	0.081	0.120	<0.004	<0.004	0.17	0.26	1.26	0.98	<0.26	<0.26	<0.21	<0.21
LF-100	Stream	100	09/12/01	238.5	55	51	1.85	1.46	0.005	0.007	0.081	0.114	0.004	<0.004	0.15	0.26	1.03	0.84	<0.26	<0.26	<0.21	<0.21
LF-200A	Stream	200	09/12/01	238.5	47	56	1.67	1.74	<0.004	0.007	0.074	0.127	<0.004	<0.004	0.14	0.23	1.24	0.98	<0.26	<0.26	<0.21	<0.21
LF-200B	Stream	200	09/12/01	238.5	52	51	1.69	1.37	0.011	0.007	0.076	0.111	0.004	0.004	0.13	0.25	1.08	0.94	<0.26	<0.26	<0.21	<0.21
BT-0	Distant inflow	220	09/12/01	1.68	172	203	7.30	8.23	2.09	1.99	<0.004	2.05	0.587	0.612	0.09	4.78	8.16	11.3	4.0	4.1	<0.21	0.32
LF-249	Near inflow	249	10/03/01	0.1	12	216	6.45	6.97	0.324	0.359	1.92	3.91	0.026	0.037	0.14	1.07	0.36	0.62	<0.26	<0.26	<0.21	<0.21
LF-295	Near inflow	295	10/03/01	0.1	<4	17	6.92	6.82	0.004	0.400	0.009	0.661	0.014	0.006	0.06	0.22	0.46	<0.30	<0.26	<0.21	<0.21	<0.21
LSG-0	Distant inflow	305	09/12/01	0.01	102	1,280	3.72	5.62	0.657	0.778	0.639	2.47	0.114	0.147	0.31	2.75	2.99	3.73	0.69	1.1	<0.21	<0.21
LF-323	Stream	323	09/12/01	238.7	57	72	1.82	1.92	0.005	0.006	0.081	0.133	0.007	<0.004	0.24	0.22	2.36	0.95	<0.26	<0.26	<0.21	<0.21
DT-0	Distant inflow	325	09/12/01	2.59	53	76	13.2	14.7	36.2	37.4	29.7	30.5	10.6	11.0	<0.06	0.92	0.41	0.87	3.4	4.2	<0.21	<0.21
DT-0	Distant inflow	325	10/03/01	2.59	NS	49	NS	14.3	NS	36.6	NS	32.1	NS	10.6	NS	0.97	NS	<0.30	NS	3.9	NS	<0.21
LF-327 ⁴	Near inflow	327	09/12/01	0.2	269	1,030	7.96	10.0	20.2	21.3	0.852	1.93	4.51	4.79	0.28	1.22	1.10	1.30	1.8	1.9	<0.21	<0.21
DPI-01	Distant inflow	335	10/03/01	50,008– 0.067	2,050	2,180	13.0	13.7	51.7	55.4	2.21	2.45	19.2	20.1	4.3	3.71	101	95.5	69	68	3.3	3.3
LF-390	Stream	390	09/12/01	238.9	57	71	1.85	1.94	0.017	0.017	0.082	0.123	0.007	0.004	0.22	0.25	1.53	0.89	<0.26	<0.26	<0.21	<0.21
LF-400 ⁴	Near inflow	400	09/12/01	0.1	672	772	10.7	11.3	35.2	37.6	0.635	0.639	5.02	5.00	3.24	2.83	8.25	7.33	6.5	6.6	<0.21	<0.21
LF-448 ⁴	Near inflow	448	09/12/01	0.1	791	788	10.6	12.1	36.3	38.8	0.165	0.182	5.45	5.80	1.04	0.98	10.9	9.78	7.6	7.4	<0.21	<0.21
LF-455A	Stream	455	09/12/01	239.1	57	57	1.84	1.70	0.057	0.050	0.082	0.121	0.012	0.010	0.15	0.25	1.16	0.87	<0.26	<0.26	<0.21	<0.21
LF-455B	Stream	455	09/12/01	239.1	57	61	1.88	1.85	0.141	0.134	0.082	0.133	0.022	0.022	0.17	0.26	1.43	0.94	<0.26	<0.26	<0.21	<0.21
LF-455C	Stream	455	09/12/01	239.1	60	83	1.84	1.99	0.398	0.405	0.083	0.126	0.062	0.061	0.20	0.25	1.81	1.00	<0.26	<0.26	<0.21	<0.21
LF-468	Stream	468	09/12/01	239.1	53	69	1.77	1.97	0.287	0.301	0.079	0.119	0.046	0.042	0.21	0.25	1.56	1.03	<0.26	<0.26	<0.21	<0.21
LF-484 ⁴	Near inflow	484	09/12/01	0.3	753	803	11.2	10.7	41.2	39.1	0.292	0.343	5.53	5.53	2.60	2.43	9.33	9.57	7.1	7.7	<0.21	<0.21
SS-01	Distant inflow	495	10/03/01	NM	NS	1,620	NS	12.7	NS	3.17	NS	0.552	NS	2.09	NS	40.4	NS	NS	NS	4.6	NS	2.11
NT-0	Distant inflow	500	09/12/01	0.631	17	24	10.7	11.6	2.99	2.95	2.11	3.43	0.177	0.191	<0.06	0.11	0.39	<0.30	<0.26	<0.26	<0.21	<0.21
LF-508 ⁴	Near inflow	508	09/12/01	0.4	670	568	11.1	10.6	36.6	34.7	0.529	0.609	6.71	6.21	5.75	5.81	11.9	11.1	9.9	11	<0.21	<0.21

Table 3. Analytical results for lithium, vanadium, chromium, cobalt, nickel, strontium, molybdenum, barium, and arsenic in water samples from Lake Fork Creek, September–October 2001

[Total, concentration measured in an unfiltered sample; dissolved, concentration measured in a sample filtered through a membrane having a pore size of 0.45 micrometer; L/s, liters per second; <, less than; µg/L, micrograms per liter; NM, not measured; NS, no sample; NA, not applicable; A, B, and C in site name, indicate replicate samples for a site; FBLNK, field blank]

Site (figs. 2 and 3)	Source ¹	Distance (meters)	Date	Dis- charge (L/s)	Dis- solved lithium (µg/L)	Total lithium (µg/L)	Dis- solved vana- dium (µg/L)	Total vana- dium (µg/L)	Dis- solved chrom- ium (µg/L)	Total chrom- ium (µg/L)	Dis- solved cobalt (µg/L)	Total cobalt (µg/L)	Dis- solved nickel ² (µg/L)	Total nickel (µg/L)	Dis- solved stron- tium (µg/L)	Total stron- tium (µg/L)	Dis- solved molyb- denum (µg/L)	Total molyb- denum (µg/L)	Dis- solved barium (µg/L)	Total barium (µg/L)	Dis- solved arsenic (µg/L)	Total arsenic (µg/L)
Detection limit	NA	NA	NA	NA	1.50	1.50	0.06	0.06	0.04	0.04	0.02	0.02	0.69	0.69	0.40	0.40	0.10	0.10	0.08	0.08	0.16	0.16
LF-0	Stream	0	09/12/01	238.5	<1.50	<1.50	<0.06	0.10	0.07	0.10	0.02	0.03	<0.69	<0.69	17.1	17.5	0.31	0.27	4.68	6.13	<0.16	<0.16
LF-100	Stream	100	09/12/01	238.5	<1.50	<1.50	<0.06	0.09	0.07	0.10	<0.02	0.02	<0.69	<0.69	16.5	15.4	0.30	0.26	4.77	5.46	<0.16	<0.16
LF-200A	Stream	200	09/12/01	238.5	2.37	1.52	<0.06	0.09	0.07	0.10	<0.02	0.02	0.85	<0.69	15.7	18.0	0.26	0.28	4.45	6.06	<0.16	<0.16
LF-200B	Stream	200	09/12/01	238.5	1.59	1.55	<0.06	0.08	0.08	0.10	<0.02	0.02	<0.69	<0.69	16.0	17.6	0.27	0.28	4.58	6.00	<0.16	<0.16
BT-0	Distant inflow	220	09/12/01	1.68	2.40	2.25	<0.06	<0.06	<0.04	<0.04	4.0	4.6	7.4	7.2	98.0	108	<0.10	0.24	27.3	27.0	0.46	4.4
LF-249	Near inflow	249	10/03/01	0.1	1.54	<1.50	0.24	0.96	<0.04	0.24	1.3	1.5	2.8	1.5	112	121	0.38	0.50	49.5	54.9	0.86	1.3
LF-295	Near inflow	295	10/03/01	0.1	<1.50	<1.50	<0.06	0.11	<0.04	<0.04	<0.02	0.20	1.8	<0.69	103	121	0.10	0.17	37.9	49.9	<0.16	0.26
LSG-0	Distant inflow	305	09/12/01	0.01	<1.50	<1.50	0.37	1.9	0.27	0.88	0.45	0.63	3.3	3.4	20.1	22.8	0.45	0.53	9.88	20.7	0.62	0.95
LF-323	Stream	323	09/12/01	238.7	NM	1.56	<0.06	0.09	0.10	0.08	0.02	0.03	<0.69	<0.69	17.7	17.3	0.24	0.29	5.08	5.86	<0.16	<0.16
DT-0	Distant inflow	325	09/12/01	2.59	7.23	NM	<0.06	<0.06	<0.04	<0.04	19	21	37	36	284	265	0.52	0.57	18.8	18.1	8.2	9.0
DT-0	Distant inflow	325	10/03/01	2.59	NS	6.92	NS	<0.06	NS	<0.04	NS	17	NS	29	NS	293	NS	0.65	NS	21.3	NS	7.3
LF-327 ³	Near inflow	327	09/12/01	0.2	5.42	5.57	<0.06	0.64	0.05	0.39	1.9	2.0	20	22	278	290	<0.10	<0.10	44.6	48.4	0.17	0.52
DP1-01	Distant inflow	335	10/03/01	0.008- 0.067 ⁴	8.52	7.20	<0.06	<0.06	0.63	0.60	21	19	36	36	220	203	<0.10	<0.10	3.12	2.96	0.42	0.23
LF-390	Stream	390	09/12/01	238.9	NM	<1.50	0.06	0.09	0.10	0.09	0.02	0.03	<0.69	<0.69	17.0	16.7	0.21	0.30	4.53	5.64	<0.16	<0.16
LF-400 ³	Near inflow	400	09/12/01	0.1	7.09	6.47	<0.06	0.06	0.07	0.06	10	11	25	25	243	277	<0.10	<0.10	30.8	30.6	<0.16	0.16
LF-448 ³	Near inflow	448	09/12/01	0.1	8.07	6.86	<0.06	<0.06	0.07	0.06	9.9	8.8	26	23	253	257	<0.10	0.14	34.2	36.0	<0.16	<0.16
LF-455A	Stream	455	09/12/01	239.1	1.90	<1.50	<0.06	0.08	0.07	0.10	0.03	0.04	1.4	<0.69	17.1	15.8	0.31	0.27	4.71	5.51	<0.16	<0.16
LF-455B	Stream	455	09/12/01	239.1	<1.50	<1.50	<0.06	0.09	0.08	0.10	0.06	0.06	<0.69	<0.69	18.3	16.6	0.28	0.27	4.86	5.68	<0.16	<0.16
LF-455C	Stream	455	09/12/01	239.1	NM	1.57	<0.06	0.09	0.06	0.07	0.15	0.15	0.72	<0.69	20.4	20.5	0.29	0.30	4.70	6.29	<0.16	<0.16
LF-468	Stream	468	09/12/01	239.1	<1.50	1.68	<0.06	0.10	0.07	0.10	0.08	0.11	<0.69	<0.69	16.8	19.3	0.26	0.32	4.78	6.81	<0.16	<0.16
LF-484 ³	Near inflow	484	09/12/01	0.3	6.70	6.98	<0.06	<0.06	0.06	0.07	10	11	25	25	266	283	<0.10	<0.10	32.9	32.2	<0.16	<0.16
SS-01	Distant inflow	495	10/03/01	NM	NS	6.09	NS	0.06	NS	0.11	NS	4.7	NS	5.1	NS	39.7	NS	<0.10	NS	39.5	NS	0.63
NT-0	Distant inflow	500	09/12/01	0.631	2.46	2.58	<0.06	<0.06	1.06	<0.04	1.3	1.5	1.6	2.2	62.2	68.8	0.44	0.51	25.8	28.2	10	19

Table 3. Analytical results for lithium, vanadium, chromium, cobalt, nickel, strontium, molybdenum, barium, and arsenic in water samples from Lake Fork Creek, September–October 2001—Continued.

[Total, concentration measured in an unfiltered sample; dissolved, concentration measured in a sample filtered through a membrane having a pore size of 0.45 micrometer; L/s, liters per second; <, less than; µg/L, micrograms per liter; NM, not measured; NS, no sample; NA, not applicable; A, B, and C in site name, indicate replicate samples for a site; FBLNK, field blank]

Site (figs. 2 and 3)	Source ¹	Distance (meters)	Date	Dis- charge (L/s)	Dis- solved lithium (µg/L)	Total lithium (µg/L)	Dis- solved vana- dium (µg/L)	Total vana- dium (µg/L)	Dis- solved chrom- ium (µg/L)	Total chrom- ium (µg/L)	Dis- solved cobalt (µg/L)	Total cobalt (µg/L)	Dis- solved nickel ² (µg/L)	Total nickel (µg/L)	Dis- solved stron- tium (µg/L)	Total stron- tium (µg/L)	Dis- solved molyb- denum (µg/L)	Total molyb- denum (µg/L)	Dis- solved barium (µg/L)	Total barium (µg/L)	Dis- solved arsenic (µg/L)	Total arsenic (µg/L)
LF-508 ³	Near inflow	508	09/12/01	0.4	8.95	7.08	<0.06	<0.06	0.08	0.06	13	12	28	24	259	260	<0.10	<0.10	19.1	20.3	<0.16	<0.16
LF-523	Stream	523	09/12/01	239.8	<1.50	1.61	<0.06	0.09	0.07	0.10	0.16	0.19	1.0	<0.69	18.7	20.5	0.25	0.27	5.03	6.12	<0.16	<0.16
LF-537 ³	Near inflow	537	09/12/01	5.6	7.19	6.61	<0.06	<0.06	0.12	0.13	12	11	25	20	246	238	<0.10	<0.10	19.9	21.3	<0.16	<0.16
LF-580	Stream	580	09/12/01	245.4	1.73	1.58	<0.06	0.09	0.08	0.10	0.20	0.25	<0.69	<0.69	21.4	22.6	0.27	0.27	5.14	6.55	<0.16	<0.16
LF-668	Stream	668	09/12/01	246.8	<1.50	<1.50	<0.06	0.08	0.06	0.10	0.22	0.23	1.4	<0.69	18.3	22.9	0.23	0.25	4.53	6.49	<0.16	<0.16
LF-800	Stream	800	09/12/01	156.5	1.61	1.62	<0.06	0.09	0.08	0.09	0.20	0.22	<0.69	<0.69	20.7	23.0	0.25	0.26	5.05	6.45	<0.16	<0.16
LF-887	Stream	887	09/12/01	157.9	2.15	2.09	<0.06	0.09	0.08	0.10	0.20	0.22	<0.69	<0.69	21.1	23.3	0.24	0.27	5.15	6.56	<0.16	0.16
LF-953	Stream	953	09/12/01	158	2.13	2.33	<0.06	0.08	0.07	0.10	0.20	0.22	2.2	<0.69	22.2	23.6	0.22	0.27	5.11	6.48	<0.16	<0.16
SG-01	Distant inflow	1,000	09/12/01	NM	<1.50	<1.50	0.07	0.24	0.19	0.08	0.14	0.40	0.86	0.85	45.2	47.0	0.44	0.57	16.7	23.0	1.1	2.6
SG-0	Distant inflow	1,000	09/12/01	NM	NM	1.44	<0.06	0.53	0.04	0.16	1.1	1.4	0.73	0.80	40.2	40.9	0.19	0.48	28.3	48.0	1.9	15
LF-1075	Stream	1,075	09/12/01	163.4	2.26	2.57	<0.06	0.09	0.07	0.10	0.18	0.20	1.0	<0.69	20.6	23.0	0.23	0.30	4.84	6.14	<0.16	<0.16
LF-1180	Near inflow	1,180	09/12/01	0.3	16.2	15.8	<0.06	0.08	0.06	0.08	0.21	0.64	<0.69	<0.69	45.8	45.3	0.11	0.12	11.0	19.5	0.31	0.57
LF-1185	Stream	1,185	09/12/01	163.7	2.48	2.73	<0.06	0.10	0.09	0.12	0.20	0.21	1.1	0.74	23.9	24.0	0.26	0.29	4.93	5.97	<0.16	<0.16
LF-1241	Near inflow	1,241	09/12/01	0.5	<1.50	<1.50	<0.06	<0.06	0.06	0.08	<0.02	<0.02	<0.69	<0.69	20.0	19.3	<0.10	<0.10	3.44	3.67	0.16	<0.16
LF-1287	Stream	1,287	09/12/01	164.2	2.45	2.45	<0.06	0.08	0.06	0.10	0.16	0.18	1.2	<0.69	20.3	22.1	0.22	0.24	5.10	5.70	<0.16	<0.16
PPS	Distant inflow	1,300	09/12/01	NM	3,640	3,750	0.37	1.0	0.05	0.18	1.3	1.4	0.81	<0.69	4,240	4,410	2.7	2.7	94.4	87.9	5.8	43
LF-1351	Near inflow	1,351	09/12/01	1.7	873	879	0.07	0.20	0.05	0.04	3.6	3.3	2.3	1.6	1,170	1,160	2.6	2.4	309	335	1.0	1.6
LF-1400	Stream	1,400	09/12/01	165.9	2.34	2.54	<0.06	0.09	0.07	0.10	0.15	0.19	1.7	<0.69	20.2	22.8	0.22	0.26	4.87	6.21	<0.16	<0.16
LF-1425	Near inflow	1,425	09/12/01	0.1	693	703	0.20	0.52	0.10	0.14	0.62	0.47	0.88	<0.69	924	908	1.2	1.0	69.1	81.5	0.46	0.83
ST-0	Distant inflow	1,490	09/12/01	1.91	7.17	7.19	<0.06	<0.06	0.04	<0.04	7.6	7.9	12	12	103	107	1.2	1.4	27.7	29.3	0.79	1.8
STP-0	Distant inflow	1,490	09/12/01	1.91	6.93	6.43	<0.06	<0.06	<0.04	0.05	0.25	0.22	2.7	2.5	96.2	84.9	<0.10	<0.10	1.55	1.46	<0.16	<0.16
LF-1495	Near inflow	1,495	09/12/01	2.4	6.31	5.44	<0.06	0.06	<0.04	0.04	0.25	0.26	2.6	1.3	96.9	99.8	<0.10	<0.10	15.0	14.5	<0.16	<0.16
LF-1525	Stream	1,525	09/12/01	168.4	4.50	2.98	<0.06	0.11	0.07	0.13	0.14	0.21	1.3	<0.69	24.0	23.8	0.23	0.23	5.07	6.06	<0.16	<0.16
CG-0	Near inflow	2,255	09/12/01	12.6	139	132	<0.06	0.07	0.12	<0.04	0.69	0.73	2.2	1.4	152	154	0.24	0.32	19.1	19.2	3.7	6.9
LF-2500	Stream	2,310	09/12/01	181	6.47	7.46	<0.06	0.08	0.06	0.09	0.11	0.11	0.88	<0.69	30.9	32.1	0.20	0.21	4.20	4.97	0.26	0.34
LF-2500	Stream	2,310	09/13/01	181	10.6	10.4	<0.06	0.07	0.05	0.08	0.12	0.13	0.96	<0.69	33.8	36.6	0.21	0.20	5.05	5.38	0.32	0.37
LF-3500	Stream	4,535	09/13/01	282	NM	NM	0.06	0.14	<0.04	0.04	0.23	0.27	<0.69	<0.69	58.8	60.9	0.13	0.17	9.20	10.0	0.34	0.45
FH-0	Near inflow	4,585	09/13/01	217.8	2.00	2.44	0.15	0.31	0.05	0.15	0.03	0.06	<0.69	<0.69	28.0	32.1	0.29	0.34	6.33	6.75	0.40	<0.16

Table 3. Analytical results for lithium, vanadium, chromium, cobalt, nickel, strontium, molybdenum, barium, and arsenic in water samples from Lake Fork Creek, September–October 2001—Continued.

[Total, concentration measured in an unfiltered sample; dissolved, concentration measured in a sample filtered through a membrane having a pore size of 0.45 micrometer; L/s, liters per second; <, less than; µg/L, micrograms per liter; NM, not measured; NS, no sample; NA, not applicable; A, B, and C in site name, indicate replicate samples for a site; FBLNK, field blank]

Site (figs. 2 and 3)	Source ¹	Distance (meters)	Date	Dis- charge (L/s)	Dis-			Dis-			Dis-			Dis-			Dis-			Dis-		
					Dis- solved lithium (µg/L)	Total lithium (µg/L)	vana- dium (µg/L)	Total vana- dium (µg/L)	Dis- solved chromium (µg/L)	Total chromium (µg/L)	Dis- solved cobalt (µg/L)	Total cobalt (µg/L)	Dis- solved nickel ² (µg/L)	Total nickel (µg/L)	Dis- solved stron- tium (µg/L)	Total stron- tium (µg/L)	Dis- solved molyb- denum (µg/L)	Total molyb- denum (µg/L)	Dis- solved barium (µg/L)	Total barium (µg/L)	Dis- solved arsenic (µg/L)	Total arsenic (µg/L)
LF-3600	Stream	4,655	09/13/01	499.8	17.1	15.8	0.11	0.25	0.05	0.13	0.14	0.18	1.1	<0.69	46.5	48.6	0.23	0.24	9.31	9.23	0.20	0.38
WC-0	Near inflow	6,295	09/13/01	153.2	1.80	1.71	0.54	0.89	0.23	0.39	0.09	0.17	<0.69	<0.69	54.3	47.3	0.21	0.21	12.5	13.8	0.26	0.30
LF-5500	Stream	9,115	09/13/01	906.1	NM	11.8	0.20	0.33	0.09	0.15	0.03	0.07	<0.69	<0.69	53.8	54.1	0.34	0.47	19.9	19.8	0.21	0.34
HC-0	Near inflow	9,365	09/13/01	495.9	<1.50	<1.50	<0.06	0.08	0.10	0.08	0.02	0.03	<0.69	<0.69	76.1	80.7	0.38	0.37	22.2	22.9	<0.16	<0.16
LF-5600A	Stream	9,515	09/13/01	1,402	NM	9.02	0.15	0.27	0.07	0.18	0.03	0.10	<0.69	<0.69	59.9	62.9	0.33	0.49	21.5	24.0	0.21	0.28
LF-5600B	Stream	9,515	09/13/01	1,402	NM	8.14	0.17	0.27	0.08	0.13	0.04	0.07	<0.69	<0.69	59.5	60.0	0.31	0.37	19.0	20.9	0.25	0.25
AR-0	Near inflow	9,575	09/13/01	928	1.95	2.04	0.08	0.14	0.11	0.06	0.23	0.26	<0.69	<0.69	86.7	91.8	3.0	2.9	68.7	69.0	0.21	0.37
AR-100	Stream	9,725	09/13/01	2,330	5.66	5.68	0.14	0.19	0.06	0.08	0.12	0.14	<0.69	<0.69	71.7	74.7	1.5	1.5	39.3	40.8	0.22	0.27
LF-BLNKA	FBLNK	NA	09/12/01	NA	<1.50	<1.50	<0.06	<0.06	<0.04	<0.04	<0.02	<0.02	<0.69	<0.69	<0.40	<0.40	<0.10	<0.10	<0.08	0.08	<0.16	<0.16
LF-BLNKB	FBLNK	NA	09/13/01	NA	<1.50	<1.50	<0.06	<0.06	<0.04	<0.04	<0.02	<0.02	0.82	<0.69	<0.40	<0.40	<0.10	<0.10	<0.08	<0.08	<0.16	<0.16

¹Near inflow sites flowed directly into the stream. Distant inflow sites were located at some distance from the stream and did not necessarily reach the stream as discrete, visible surface inflow.

²Dissolved nickel concentrations are affected by contamination (Appendix 1).

³Charge balance error for these six samples ranged from 10 to 17 percent.

⁴Range of estimates for flow of Dinero north pile toe seep used in wetland mass-balance calculations.

In this study, the dissolved portion of samples was operationally defined as sample that passed through a 0.45 μm filter. Colloid concentrations were estimated for aluminum and iron as the difference between analyte concentrations in “total” and “dissolved” samples. Because colloids can extend to sizes well less than 0.45 μm , the dissolved fraction defined herein contained some colloidal particles, and the colloid fraction was underestimated.

Samples from the autosamplers at the transport sites were collected and filtered each day of the tracer-injection study using 0.45- μm capsule filters. These samples were analyzed for anions only to help monitor tracer concentration in the stream and to verify continuous operation of the tracer-injection pump.

Several analytical laboratories were used to generate data for this study. A quality assessment of all laboratories used in this study is included in Appendix 1, and a summary of methods is included in the rest of this subsection of the report. Analysis for major and trace-element content was by ICP–MS. The method used was a modification of EPA method 200.8 (U.S. Environmental Protection Agency, 1994) and is on file with the USGS Branch of Quality Services (BQS) (Alan Shiller, University of Southern Mississippi, written commun., 2003). Analysis of anions was by ion chromatography using the method described by Kimball and others (1999). Alkalinity was measured by acidometric titration in two different laboratories. Samples having specific conductance greater than 67 $\mu\text{S}/\text{cm}$ were analyzed at USGS laboratories in Salt Lake City, Utah, using titration with a fixed endpoint ($\text{pH} = 4.5$) with EPA method 310.1 (U.S. Environmental Protection Agency, 1983). Samples having specific conductance less than 67 $\mu\text{S}/\text{cm}$ were measured by titration and gran plot (U.S. Environmental Protection Agency, 1987) at USGS laboratories in Lakewood, Colo. Two field blank samples and five replicate samples were included to assess data quality. These samples are discussed in Appendix 1.

Dissolved organic carbon concentration and ultraviolet absorbance were measured on filtered stream samples and organic matter isolates according to methods described in Weishaar and others (2003). Organic carbon fractionation was conducted on the three bulk samples collected at sites FH-0, LF-3500, and LF-3600 by using macroporous resins as described by Aiken and others (1992).

The isolation of organic matter by using porous resins (Aiken and others, 1992) uses two macroporous amberlite resins, XAD-8, and XAD-4, that are set up in columns in series. The bulk sample is acidified to pH less than 2 and then run through the columns. Each column retains different types of organic matter based primarily on the ionic character of the organic matter. The XAD-8 column retains hydrophobic organic acids (HPOA), which are primarily fulvic acids and hydrophobic organic neutral compounds (HPON). The HPOA are eluted from the column by using concentrated sodium hydroxide. The HPON are eluted from the column by using methanol but are quantified by difference. The XAD-4 resin retains hydrophilic acids and some less hydrophilic organic compounds termed transphylic organic acids (TPIA) and neu-

tral compounds (TPON). The TPIA are eluted from the XAD-4 column by using concentrated sodium hydroxide, and the TPON are eluted by using methanol. Low-molecular-weight hydrophilic acids (LMW) are transported through both columns and recovered at the exit of the column setup. (Aiken and others, 1992; G.R. Aiken, U.S. Geological Survey, oral commun., 2003).

The specific ultraviolet absorbance of a sample (SUVA) is defined as the ultraviolet absorbance measured at 254 nanometers divided by the concentration of dissolved organic carbon in the sample. Greater values of SUVA indicate a greater aromatic character of the dissolved organic matter present, but not necessarily greater reactivity of the organic matter (Weishaar and others, 2003).

Mass-Loading Analysis

Mass load is calculated for each stream site along the study reach as:

$$M_a = C_a Q_a (0.0864) \quad (3)$$

where

M_a is the constituent load at location a , in kilograms per day (or grams per day);

C_a is the concentration of the selected constituent at location a , in milligrams per liter (or micrograms per liter);

Q_a is the discharge at location a , in liters per second; and

0.0864 is the conversion factor to obtain load in kilograms per day (where concentration is in milligrams per liter) or in grams per day (where concentration is in micrograms per liter).

Sampled stream load was calculated from the total-recoverable concentration for trace elements, and from the dissolved concentrations for calcium and sulfate. The longitudinal profile of sampled stream load constitutes the basic data from the mass-loading study.

For each stream segment, the change in load between a pair of stream sites accounts for the gain or loss of constituent load. The change in load for the segment starting at location a and ending at location b is:

$$\Delta M_s = (C_b Q_b - C_a Q_a) (0.0864) \quad (4)$$

where

ΔM_s is the change in sampled stream load for the segment from a to b , in kilograms per day (or grams per day);

C_b is the concentration of the selected constituent at location b , in milligrams per liter (or micrograms per liter);

Q_b is the discharge at location b , in liters per second; and

C_a , Q_a and 0.0864 were defined previously.

Gains in constituent load (ΔM_s is greater than zero) imply that there is a source that contributes to the stream between the two stream sites. Stream load also can decrease within a stream segment (ΔM_s is less than zero), meaning that a net loss of the

constituent occurred as a result of physical, chemical, or biological processes. Summing only the increases in load between stream sites along the study reach (positive values of ΔM_s) leads to the cumulative instream load. At the end of the study reach, the cumulative instream load is the best estimate of the total load added to the stream but is likely a minimum estimate; it only measures the net loading between sites and does not include the gain in load that occurs when a negative ΔM_s in a stream segment results from a small increase in mass loading that is offset by a larger decrease in mass load. The cumulative instream load will be greater than the sampled stream load at the end of the study reach if there has been any loss of a constituent over the study reach.

For those segments that include a sampled inflow, it is possible to calculate a second value for load that is based upon the change in discharge between stream sites. This change, multiplied by constituent concentration in an inflow sample, produces an estimate of the inflow load for a stream segment. If stream sites a and b surround an inflow sample, location i :

$$\Delta M_i = C_i(Q_b - Q_a)(0.0864) \quad (5)$$

where

ΔM_i is the change in sampled inflow load from location a to b , in kilograms per day (or grams per day);

C_i is the concentration of the selected constituent at inflow location i , in milligrams per liter (or micrograms per liter); and Q_a , Q_b , and 0.0864 were defined previously.

Alternately, if discharge from the inflow is measured directly:

$$\Delta M_i = C_i Q_i (0.0864) \quad (6)$$

where

Q_i is the measured discharge of the inflow site, and ΔM_i , C_i , and 0.0864 were defined previously.

Summing the inflow loads along the study reach produces a longitudinal profile of the cumulative inflow load. This sum can be compared to the cumulative instream load to indicate how well the sampled inflows account for the load measured in the stream. For a nonreactive (conservative) constituent, the cumulative instream and cumulative inflow load profiles would be equal if the sampled inflows were perfectly representative of the constituent concentration for all the water entering the stream, but that is rarely the case. It is common in streams affected by mine drainage for the cumulative instream load to be greater than cumulative inflow load. This result can indicate important areas of unsampled load, which is defined as:

$$\text{Unsampled load} = \Delta M_s - \Delta M_i \quad (7)$$

This quantity can be calculated for individual stream segments or for the entire study reach. Unsampled load in a stream

segment indicates that there is an inflow source in the segment in addition to what was collected during the synoptic sampling. This source may be dispersed, subsurface inflow (ground water) that can have higher concentrations of metals than the surface-water inflows in the same stream segment. The source also may be subsurface inflow occurring in stream segments having no sampled inflow.

In considering estimates of stream discharge and metal concentration at each stream site, it is possible to predict the error for the change in load along a stream segment. The error is determined by the precision of both discharge and chemical measurements (Taylor, 1997), according to an equation from McKinnon (2002):

$$\text{Load Error} = (\sqrt{Q_a^2 \Delta C_a^2 + C_a^2 \Delta Q_a^2})(0.0864) \quad (8)$$

where

C_a is the concentration error at the upstream site, in milligrams per liter (or micrograms per liter);

Q_a is the discharge error at the upstream site, in liters per second; and Q_a , C_a , and 0.0864 were defined previously.

Values of C_a are the product of constituent concentration and laboratory precision values derived from replicate analysis of standard reference samples. Values of Q_a are 10 percent of the streamflow discharge for velocity-meter measurements and between 5.1 and 5.6 percent (values based on the laboratory precision of the bromide analyses plus a factor of safety) of the streamflow discharge for streamflow estimated using tracer concentration. Load error is calculated for each stream site and compared to the change in load from that site to the next site downstream, ΔM_s . If ΔM_s is greater than the calculated load error, then there has been a significant change in load. The profile of cumulative instream load only increments when changes of stream load are greater than the load error; stream reaches where the cumulative instream load profile is flat contained no significant increases in load.

Proportions of load were used to help estimate the relative importance of sources in each reach along Lake Fork Creek and the relative importance of Lake Fork Creek compared to the Arkansas River at the confluence. Proportions of load along Reaches 1 through 5 were estimated by comparing the cumulative instream load at the end of each reach to the cumulative instream load at the mouth of Lake Fork Creek (LF-5600). In contrast, sampled stream loads were used when comparing the proportions of load in Lake Fork Creek at the mouth to those in the Arkansas River downstream from the confluence. For this latter comparison, cumulative instream load would overestimate the amount of load attributed to Lake Fork Creek because cumulative instream load includes load that has been removed by attenuation along the creek.

Bromide Concentration

The calculation of streamflow from the tracer data was complicated by problems with the tracer data. These problems included increasing concentrations of bromide in the upper part of Reach 1 and in some stream segments, and inadequate mixing downstream from one inflow. These problems and their solutions are detailed in Appendix 2. These problems were accounted for by incorporating a factor of safety into the bromide error calculation (eq. 8 and associated text).

The concentrations of bromide at the three transport sites (fig. 4) indicated relatively stable plateau concentrations. The profiles indicated steady flow during the injection and a steady pump rate. The plateau concentrations are slightly different from those measured in synoptic samples at all three sites for reasons detailed in Appendix 2.

Streamflow

Tracer-calculated streamflow generally compares well to streamflow measured by velocity meter in the upper 1,525 m of

the study (table 4). Tracer-calculated streamflow measurements were within 10 percent of the velocity-meter measurements except at LF-1287 and LF-1525, where the velocity-meter measurements were as much as 20 percent less than the tracer-calculated streamflow (table 4). At sites LF-1287 and LF-1525, the valley had widened into a wetland area, where there was likely a greater component of hyporheic flow (bank and sub-stream flow) than in upstream reaches. This morphology would cause lower streamflow in a velocity-meter measurement relative to a tracer measurement because the velocity meter only measured water traveling in the active channel, whereas the tracer was contained in all of the water, even water that temporarily exited the stream channel (Zellweger and others, 1989; Kimball, 1997; Harvey and Wagner, 2000). The velocity-meter measurement at LF-2500 was not large enough to account for the addition of flow from Colorado Gulch between LF-1525 and LF-2500. Therefore, the streamflow at LF-2500 was the sum of those at LF-1525 and CG-0. This number is within the range of error of the velocity-meter measurement.

The tracer-calculated and velocity-meter measurements indicate that Lake Fork Creek is a gaining stream, and streamflow increased from about 239 L/s at the reservoir outfall to

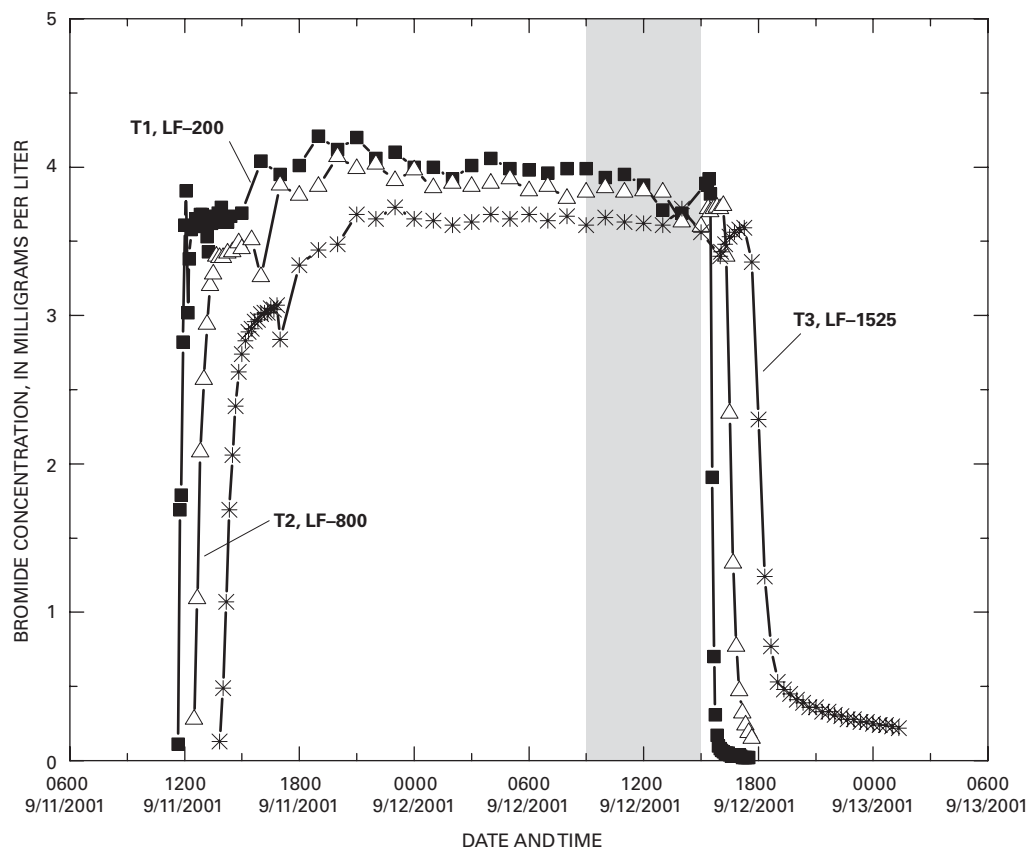


Figure 4. Variation in bromide concentration with time at T1 (LF-200), T2 (LF-800), and T3 (LF-1525), September 11–13, 2001. Shaded region indicates period when synoptic samples were collected in Reaches 1 and 2.

Table 4. Bromide concentrations and streamflow for Lake Fork mass-load study, September 2001.

[mg/L, milligrams per liter; L/s, liters per second; --, no data]

Site	Bromide concentration in synoptic sample ¹ (mg/L)	Revised ² bromide concentration used to calculate streamflow (mg/L)	Streamflow from tracer injection (L/s)	Streamflow measured using velocity meter (L/s)
LF-0	--	3.99	238.5	³ 235
LF-100	3.67	3.99	238.5	--
LF-200	3.71	3.99	238.5	--
LF-323	3.77	Interpolate	238.7	--
LF-390	3.82	Interpolate	238.8	--
LF-455	⁴ 3.89	Interpolate	239.0	245.5
LF-468	3.98	3.98	239.1	263.6
LF-523	3.97	3.97	239.8	--
LF-580	3.88	3.88	245.4	--
LF-668	3.86	3.86	246.8	227.1
LF-780 (outflow)	--	--	--	⁵ 92.3
LF-800	3.82	3.86	156.5	--
LF-887	3.83	3.83	157.9	--
LF-953	3.82	3.82	158.0	156.0
LF-1075	3.70	3.70	163.4	--
LF-1185	3.84	3.69	163.7	--
LF-1287	3.68	3.68	164.2	140.7
LF-1400	3.64	3.64	165.9	--
LF-1525	3.66	--	⁶ 168.3	139.0
LF-2500	--	--	⁷ 181.0	169.3
LF-3500	--	--	--	282.0
LF-3600	--	--	--	⁸ 499.8
LF-5500	--	--	--	906.1
LF-5600	--	--	--	1,402
AR-100	--	--	--	⁹ 2,330

¹Reported concentrations are average values of two analyses except as noted.²Values in bold and italics have been revised as indicated in Appendix 2.³Value is average daily streamflow (8.4 cubic feet per second) reported for the recording stream gage at the site (David Dzurovchin, Colorado State Division of Water Resources, written commun., 2003).⁴Value is average of two analyses of triplicate samples collected at this site.⁵Value is 2 L/s more than the difference in streamflow from tracer injection between adjacent sites because of changes made to bromide concentrations as described in Appendix 2. This value is well within the possible error in the velocity-meter measurement (less than 5 percent) and does not affect the mass-load calculations.⁶Value is sum of streamflow from tracer injection estimated at site LF-1400 and streamflow measured volumetrically at the LF-1495 (Siwatch Tunnel) inflow.⁷Value is the sum of streamflow at LF-1525 and CG-0.⁸Value is the sum of streamflow measured at site LF-3500 and the fish hatchery effluent (FH-0).⁹Value is the sum of streamflow measured at site LF-5600 (the mouth of the Lake Fork) and AR-0 (the Arkansas River upstream from the confluence with Lake Fork).

about 1,400 L/s at the mouth (table 4). Along Lake Fork Creek, the sampled near-stream inflows accounted for about 892 L/s or 71 percent of the observed flow increase (table 5). Reach 5 contributed the greatest increase in flow along Lake Fork Creek (table 5). The increased flow was primarily from Halfmoon

Creek (HC-0), the only sampled inflow in Reach 5. Reaches 1 and 2 contained the smallest amounts of flow increase. The greatest amounts of unsampled flow increases occurred along Reaches 3 and 4 (table 5). The only known unsampled tributary in Reach 4 was Hunt Gulch, which enters Lake Fork Creek a

Table 5. Amount and percentage of sampled and unsampled inflow to Lake Fork Creek during September 2001 synoptic sampling event.

[L/s, liters per second; m, meters; NA, not applicable; <, less than)]

Reach and starting and ending distances	Sampled surface-water inflow (L/s) and percentage of total inflow in reach	Unsampled inflow (L/s)	Total inflow (L/s)	Total in reach as percentage of total gained from Reach 1 through 5
Reach 1 (0–668 m)	6.9 (83 percent)	1.4 (17 percent)	8.3	<1 percent
Reach 2 (800–2,310 m)	17.6 (72 percent)	6.9 (28 percent)	24.5	2 percent
Reach 3 (2,310–4,535 m)	218 (68 percent)	101 (32 percent)	319	25 percent
Reach 4 (4,535–9,115 m)	153 (38 percent)	253 (62 percent)	406	32 percent
Reach 5 (9,115–9,515 m)	496 (100 percent)	NA	496	40 percent
Total	892 (71 percent)	362 (29 percent)	1,254	100 percent

few hundred meters downstream from LF-3600. The remainder of unsampled flow increase in Reaches 3 and 4 represented irrigation-return flow and native ground-water flow. Limited observations in this reach and aerial photographs (fig. 2) indicated abundant beaver activity adjacent to the stream. Because sample spacing was less detailed here than in Reaches 1 and 2, and because Hunt Gulch was not sampled, it is not possible to better estimate the amount of native ground-water flow compared to irrigation-return flow entering Reaches 3 and 4. Reach 6 contained the confluence of Lake Fork Creek and the Arkansas River. The addition of Lake Fork Creek increased stream-flow in the Arkansas River approximately 1.5-fold (table 1).

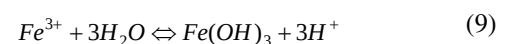
Downstream Trends in Concentration

Downstream profiles of chemical constituents showed several patterns that help interpret the chemical evolution of water along Lake Fork Creek. For some constituents, profiles of both total and dissolved concentrations are shown. Aluminum concentration and loading profiles are considered semiquantitative because of contamination in the blanks (Appendix 1) and likely contamination in the low concentrations in environmental samples observed over most of the study reach. Dissolved concentrations represent inflow samples for all constituents except copper. Appendix 1 details quality issues with the dissolved copper data. Dissolved-inflow concentrations were used because in some inflow samples, low-flow rates made it difficult to exclude bed material from the sample. This material would be included in the analysis of a total-water sample, but is not representative of the composition of the inflow. In addition, some plots also include profiles of Colorado hardness-based acute and chronic toxicity standards for the dissolved constituent.

Profiles of pH, alkalinity, calcium, and sulfate showed increasing values along the study reach (fig. 5A–D). Aluminum, copper, and iron concentrations increased near the middle of the study reach and then decreased by the end of the study reach (fig. 6A–C). The lead profile was similar to those of aluminum, copper, and iron except that lead concentrations increased at the confluence with the Arkansas River (fig. 7A). Cadmium concentrations generally were below the detection limit. Similar to results for lead, however, cadmium showed an increase downstream from the Lake Fork Creek/Arkansas River confluence (fig. 7B). Manganese and zinc concentrations increased most strongly at the beginning and end of the study reach in Reaches 1 and 6 (fig. 8A and B). Additional constituents were included in tables 1–3 but were not part of the data analysis.

pH, Alkalinity, Calcium, and Sulfate Profiles

Values of pH showed a slight increase along the study reach from about 7 (at site LF-0) to about 8 standard units at AR-100 downstream from the confluence (fig. 5A). The pH of inflow samples was generally acidic in Reaches 1 and 2 and near neutral downstream. Inflow samples from Reaches 1 and 2 show an almost bimodal distribution with one group of samples having pH values of about 4 or less and the other group having values of about 6 (fig. 5A). The inflow samples with the lowest pH values were collected from the Dinero tailings-pile toe seep (DP1-01) and near-stream seeps located between 300 and 500 m distance (table 1, fig. 5A). The low pH of the near-stream seeps may indicate that the water is from the Dinero tailings-pile toe seeps. Alternately, pH decreases as amorphous iron minerals precipitate from water:



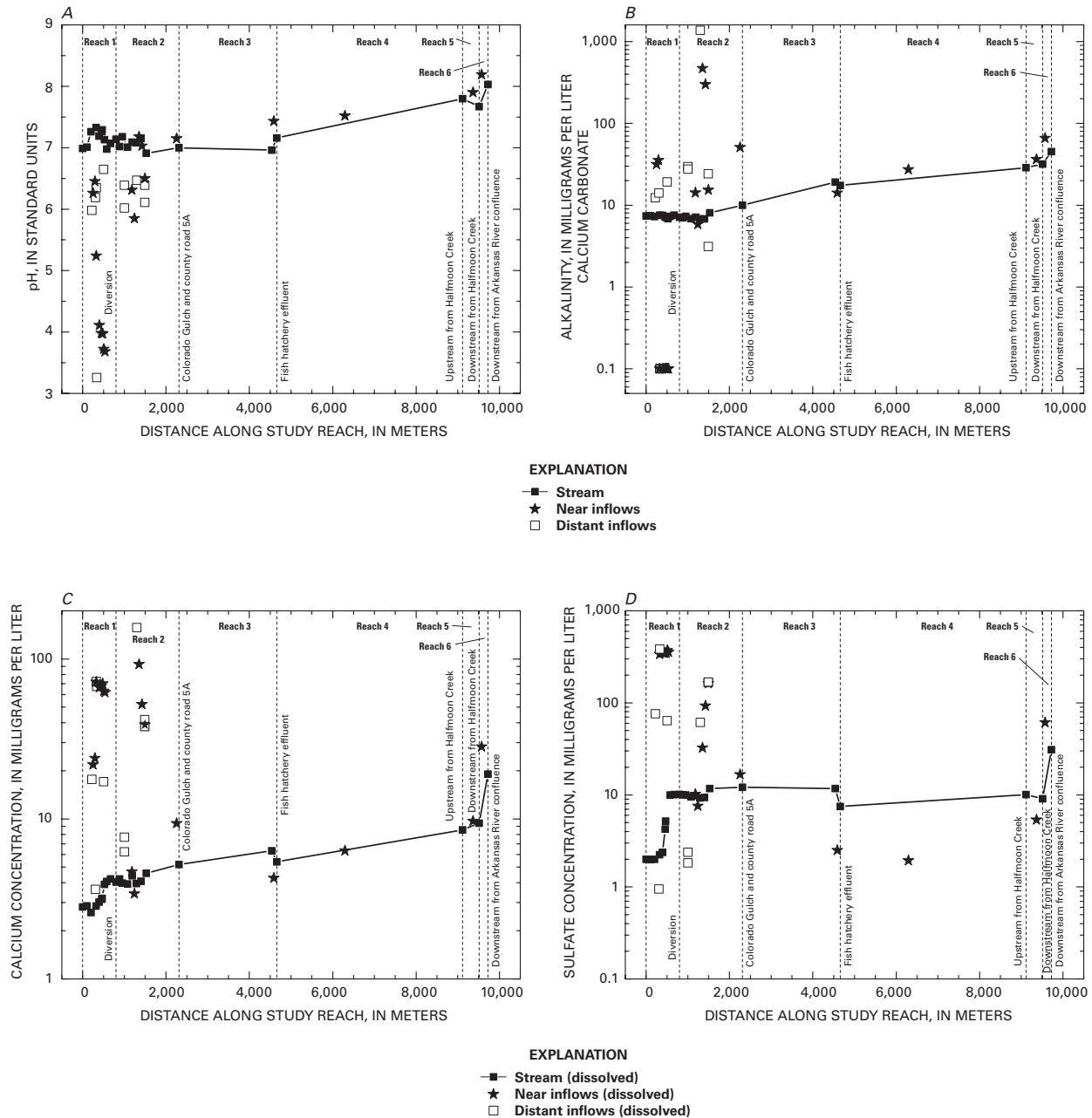


Figure 5. Variation in (A) pH, (B) alkalinity, (C) calcium concentration, and (D) sulfate concentration in stream and inflow samples collected during synoptic sampling, September 12–13, 2001.

Abundant iron staining in some of the near-stream seeps and in the Dinero wetland indicated formation of these minerals was probably increasing the acidity and lowering the pH of water in the wetland. Therefore, pH values may have declined due to formation of amorphous iron minerals as water from the Dinero Tunnel, Nelson Tunnel, Sugarloaf Gulch, and Dinero tailings-piles toe seeps mixed and flowed through the wetland.

Alkalinity generally increased downstream in the study reach (fig. 5B). Alkalinity generally decreased slightly in Reach 1 but increased, except at the fish hatchery effluent (FH-0), over the rest of the study reach. Many of the mildly acidic

inflows in Reach 1 had measurable alkalinity (table 1, fig. 5B), which probably helped buffer the stream from the effects of the most acidic inflows. Throughout most of the study reach, the alkalinity of the inflows was greater than the alkalinity of the stream, which accounts for the downstream alkalinity increase.

Calcium and sulfate concentrations generally increased over the study reach (fig. 5C and D). Sulfate, the major anion of acidic rock drainage, had its greatest concentration increases in Reach 1 and at the confluence with the Arkansas River (Reach 6). In Reaches 1 and 2, calcium and sulfate concentrations in sampled inflows were generally greater than stream

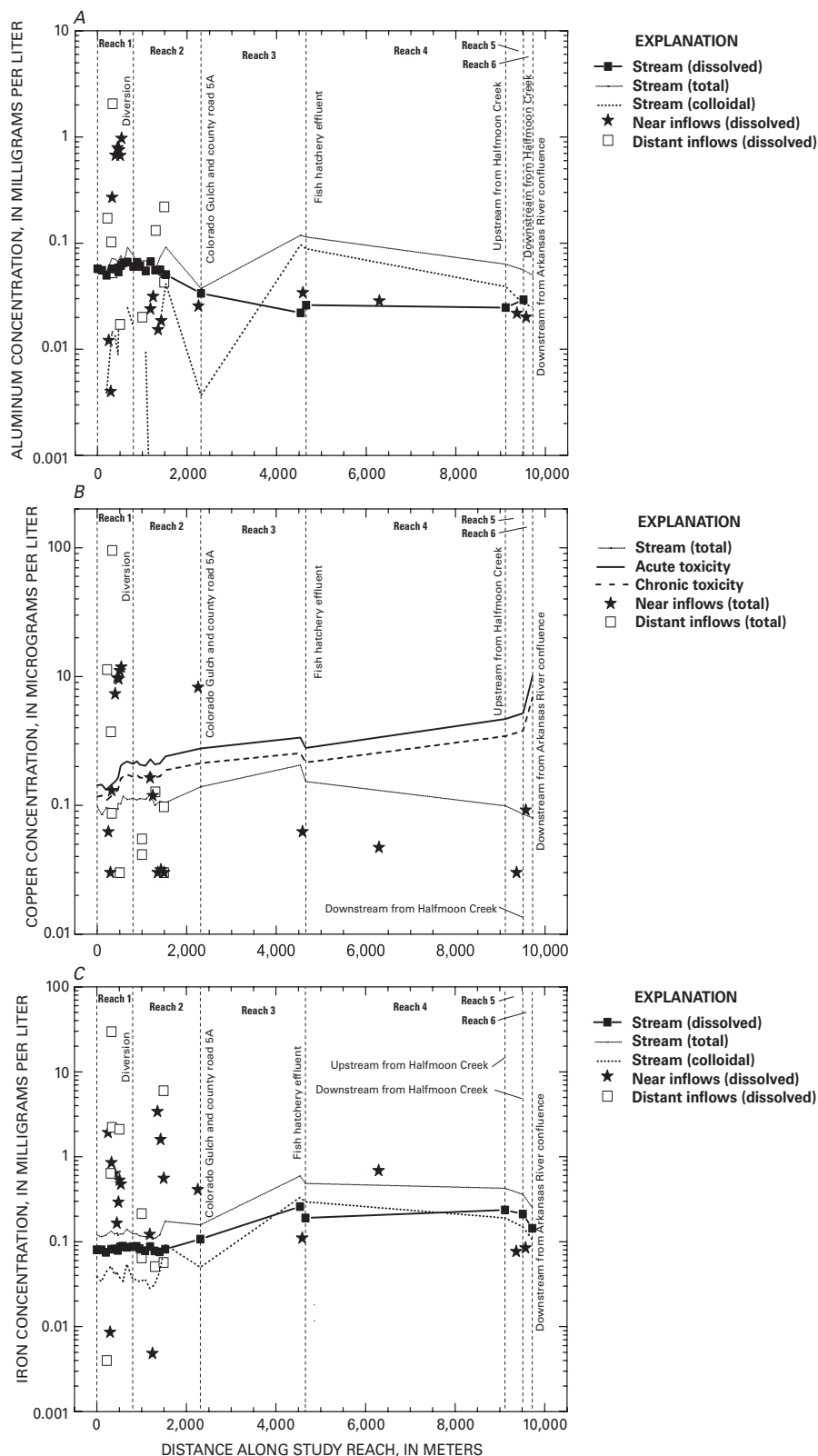


Figure 6. Variation in (A) aluminum concentrations, (B) copper concentrations and Colorado hardness-based acute and chronic toxicity, and (C) iron concentrations in stream and inflow samples collected during synoptic sampling, September 12–13, 2001. Dissolved concentrations represent inflow samples except for copper where total concentrations were used for the inflows. Colloid concentrations are not shown at locations where the total and dissolved concentrations were equal.

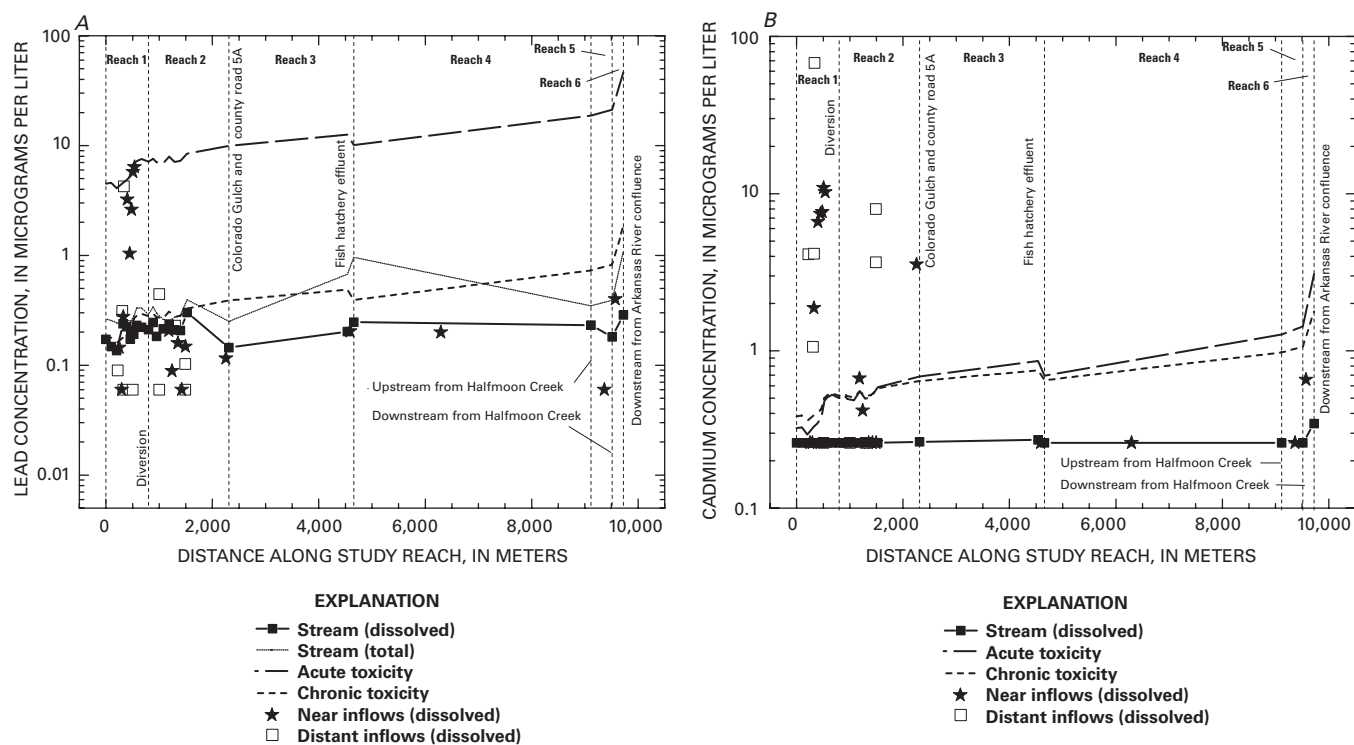


Figure 7. Variation in (A) lead and (B) cadmium concentrations in stream and inflow samples and Colorado hardness-based acute and chronic toxicity in stream samples collected during synoptic sampling, September 12–13, 2001.

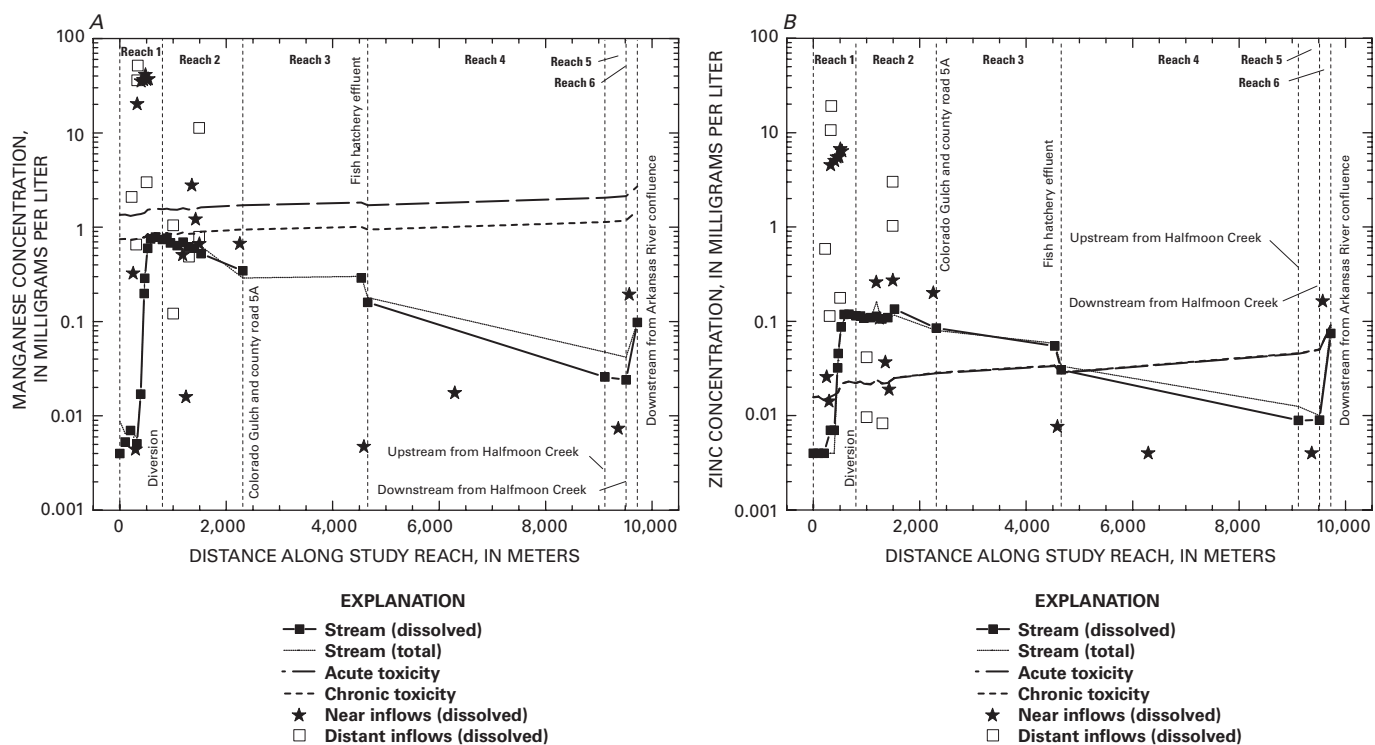


Figure 8. Variation in (A) manganese and (B) zinc concentrations in stream and inflow samples and Colorado hardness-based acute and chronic toxicity in stream samples collected during synoptic sampling, September 12–13, 2001. The acute and chronic toxicity values for zinc plot almost directly on top of one another.

concentrations accounting for the increased stream concentrations occurring over those reaches. Calcium and sulfate concentrations decreased from dilution by the fish hatchery effluent (FH-0) inflow in Reach 3. In contrast, calcium and sulfate concentrations generally increased in Reaches 3 and 4, but inflow concentrations generally were lower than stream concentrations (fig. 5C and D). This observation may indicate that ground water contributing to the stream in these reaches had greater calcium and sulfate concentrations than sampled surface-water inflows.

Aluminum, Copper, and Iron Profiles

Total aluminum concentrations increased near the end of Reach 3 and then decreased through the rest of the study reach (fig. 6A). Inflow concentrations generally were greater than stream concentrations in Reach 1, yet stream concentrations did not increase. It is likely that the formation of solid aluminum phases controlled stream concentrations in Reach 1, although colloidal concentrations were less than “dissolved” concentrations in this reach. Recall, in this study, “dissolved” is operationally defined by a 0.45- μm filter. This filter size probably allowed passage of colloidal material that was smaller than 0.45 μm so that the dissolved fraction contains some component of colloidal material, and the colloidal component is underestimated in figure 6A. At pH values exhibited over the entire study reach, only small amounts of aluminum are truly dissolved as the formation of amorphous aluminum minerals buffers aluminum at low concentrations at pH values greater than 4.5 to 5.0 (Nordstrom and Alpers, 1999).

Total copper concentration increased to the end of Reach 3 and then decreased to the end of the study reach (fig. 6B). Stream total concentrations of copper remained below the Colorado hardness-based toxicity standards (for dissolved copper) throughout the entire study reach. Dissolved copper concentrations are not shown because of contamination problems (Appendix 1). However, because dissolved copper concentrations would be less than or equal to total copper concentrations, toxicity from copper is likely not a problem over the study reach.

Total iron concentrations increased at the end of Reach 3 and then decreased to the end of the study reach (fig. 6C). Similar to aluminum, inflow concentrations generally were greater than stream concentrations in Reach 1 (and much of Reach 2), yet stream concentrations did not increase. It is likely that the formation of amorphous iron minerals (for example, eq. 9) helped maintain low iron concentrations in the stream. In addition, because of the filter size used, the “dissolved” fraction contained colloidal iron particles so that the amount of colloids is underestimated in figure 6C. Total stream iron concentrations were less than the USEPA criterion of 1 mg/L for freshwater aquatic life (U.S. Environmental Protection Agency, 1986).

Lead and Cadmium Profiles

The lead profile is similar to those for aluminum, copper, and iron except that lead concentrations increased downstream from the confluence with the Arkansas River (fig. 7A). Lead concentrations increased slightly in Reach 1 because of inflows that had elevated lead concentrations. Similarly, the increased concentration at the end of the study reach is due to mixing of Lake Fork Creek with the higher concentrations of the Arkansas River. Over the length of the study reach, concentrations of “dissolved” lead were less than 1 $\mu\text{g/L}$ and were also less than Colorado hardness-based chronic and acute toxicity standards (fig. 7A).

Cadmium concentrations were less than the detection limit of 0.26 $\mu\text{g/L}$ for most of the study reach and were less than the Colorado hardness-based acute and chronic toxicity standards for the entire study reach (fig. 7B). However, the data are shown to emphasize that stream concentrations remained low despite inflow from sources that had substantially higher concentrations of cadmium in Reaches 1 and 2. Stream dissolved cadmium concentrations only exceeded the detection limit downstream from the confluence with the Arkansas River because the Arkansas River had a concentration and load of cadmium high enough to maintain concentrations above the detection limit after mixing with Lake Fork Creek.

Manganese and Zinc Profiles

Manganese and zinc concentrations increased by as much as 2 orders of magnitude in Reach 1 because of inflows along this reach (fig. 8A and B). Both metals showed decreases in concentration along Reaches 2 through 5, from dilution and/or removal, and increased concentrations in Reach 6 downstream from the confluence with the Arkansas River. Manganese concentrations were less than Colorado hardness-based toxicity standards throughout the study reach (fig. 8A). However, stream dissolved zinc concentrations were greater than Colorado hardness-based acute and chronic toxicity standards from the middle of Reach 1 until downstream from the input of the fish hatchery effluent (FH-0). Dilution from the fish hatchery effluent, and not increased hardness, caused the stream zinc concentrations to fall below toxic concentrations downstream from the fish hatchery effluent (note that hardness decreased downstream from the fish hatchery effluent from dilution (table 1), so the acute and chronic toxicity standards also decreased at that location). Because zinc is the only metal that exceeded toxicity standards, it is likely elevated zinc concentrations caused some of the observed effects to aquatic life (Nelson and Roline, 1996, 2003) in Lake Fork Creek upstream from the inflow of the fish hatchery effluent.

Mass Loading of Selected Major and Trace Elements

Mass-loading calculations were used to determine the locations and magnitude of the largest sources of loading to Lake Fork Creek. In addition, some metal loads from this study were compared to those from previous studies to determine if recent remediation had changed the sources of loading to the upper Arkansas River. Mass-loading calculations also were used to determine the location and magnitude of natural attenuation along the study reach, to determine the effects of two wetlands on metal loading, and to help understand the effects of discharge from the Leadville National Fish Hatchery on water quality in Lake Fork Creek.

Downstream Trends in Mass Load

The loading profiles exhibit different patterns for different constituents depending on where loading for the constituent occurs and whether reactive removal occurs over the study reach. Elements having similar source areas and geochemical behavior may exhibit similar loading profiles. The load profiles in figures 9 through 13 include the error of the loading measurements in that the cumulative instream load curve does not increment if the error in load at a stream site (eq. 8) is greater than the change in load between the stream site and the next downstream site. In this study, the percent error (calculated as the value in eq. 2 divided by the load at a stream site multiplied by 100) ranged from 5.5 to 12 percent for all elements and stream sites except manganese (14 and 13 percent error at sites LF-5500 and LF-5600) and zinc (16 percent error at stream sites LF-5500 and LF-5600).

Profiles of dissolved-calcium and dissolved-sulfate loads indicate similar patterns typical of elements that are conservatively transported in aquatic systems (fig. 9A–D). The load curves (fig. 9A and B) and the bar graphs showing the change in load (fig. 9C and D) for each sampled stream segment indicate that the primary surface-water inputs of calcium and sulfate in the Lake Fork system were in Reach 1, the fish hatchery effluent, and Halfmoon Creek. There was some input of calcium and sulfate attributed to unsampled sources in Reaches 3 and 4. These sources likely were ground water flowing into the stream and the unsampled flow from Hunt Gulch. There was minimal removal of the constituents except at the end of Reach 1 where water and solutes were removed in the irrigation ditch. The greatest source of loading for each constituent was the Arkansas River.

Profiles of total-aluminum and total-copper loads indicate similar locations for loading and removal of constituents (fig. 10A–D). Both constituents showed some loading at the beginning of the study reach from Turquoise Lake. Loading from surface water and unsampled inputs occurred in Reaches

1 through 6 with loading in Reaches 3 and 6 dominating the profile. Unsampled inflow was particularly significant in Reach 3 and may represent ground-water inflow. Removal occurred at the diversion, but also in Reaches 1 and 2, particularly for aluminum in the stream segment between LF-1525 and LF-2500 that contains the inflow from Colorado Gulch (CG-0 at 2,255 m). Abundant beaver ponds in this reach probably contributed to precipitation, flocculation, and settling of colloidal and particulate material from the water column.

Mass-loading profiles of total iron indicate that most iron loading occurred in Reach 3, and more than one-half of this loading was unsampled inflow—probably ground water (fig. 11A and B). The large amount of surface-water loading in Reach 4 was associated with the Willow Creek inflow at 6,295 m as evidenced by concurrent increases in stream load and inflow load (the load sampled at the Willow Creek site, WC-0) in figure 11A. The only sizable removal of iron occurred from the diversion withdrawal. The lack of iron removal at the near-neutral pH of this stream is somewhat unusual but probably indicates that most of the iron is traveling as colloidal and particulate iron minerals that are readily suspended in the flow rather than as freely dissolved iron. The iron concentration profiles (fig. 6C) support this hypothesis.

Mass-loading profiles of total lead indicate that there were surface-water sources for lead in all reaches, but that unsampled inflow for lead was important in Reaches 3 and 5 (fig. 12A and B). Removal of lead was restricted to the diversion ditch and Reach 4.

Total-manganese and total-zinc profiles demonstrate similar patterns of loading and removal (fig. 13A–D). The greatest loadings for each constituent occurred in Reach 1 and at the confluence with the Arkansas River (Reach 6). The greatest single contributor of the elements in Reach 1 was the Sugarloaf Gulch inflow (LF-537 at 537 m downstream distance). This inflow was the largest surficial discharge from the Dinero wetland, and it contained water from the Dinero and Nelson Tunnels, streamflow from Sugarloaf Gulch, and ground water that discharged to the Dinero wetland. There were some unsampled load sources for each constituent in Reach 1 and for manganese in Reach 3. The greatest removal of manganese and zinc occurred at the diversion ditch and in the stream segment containing the Colorado Gulch (CG-0) inflow (LF-1525 to LF-2500) where beaver ponds facilitated removal of the constituents.

Metal loading summarized by reach (fig. 14) clarifies the main areas of loading for each constituent and areas where constituents exhibit similar loading behavior. The proportion of streamflow contributed by each reach is shown to emphasize where loading for a particular element and reach is disproportional to the amount of streamflow gained in that reach. Calcium and sulfate profiles are the most similar to the streamflow profile and indicate that the primary sources of loading were Reaches 4 and 5. Reach 3 contributed the greatest loads of aluminum (48 percent), copper (34 percent), iron (40 percent), and

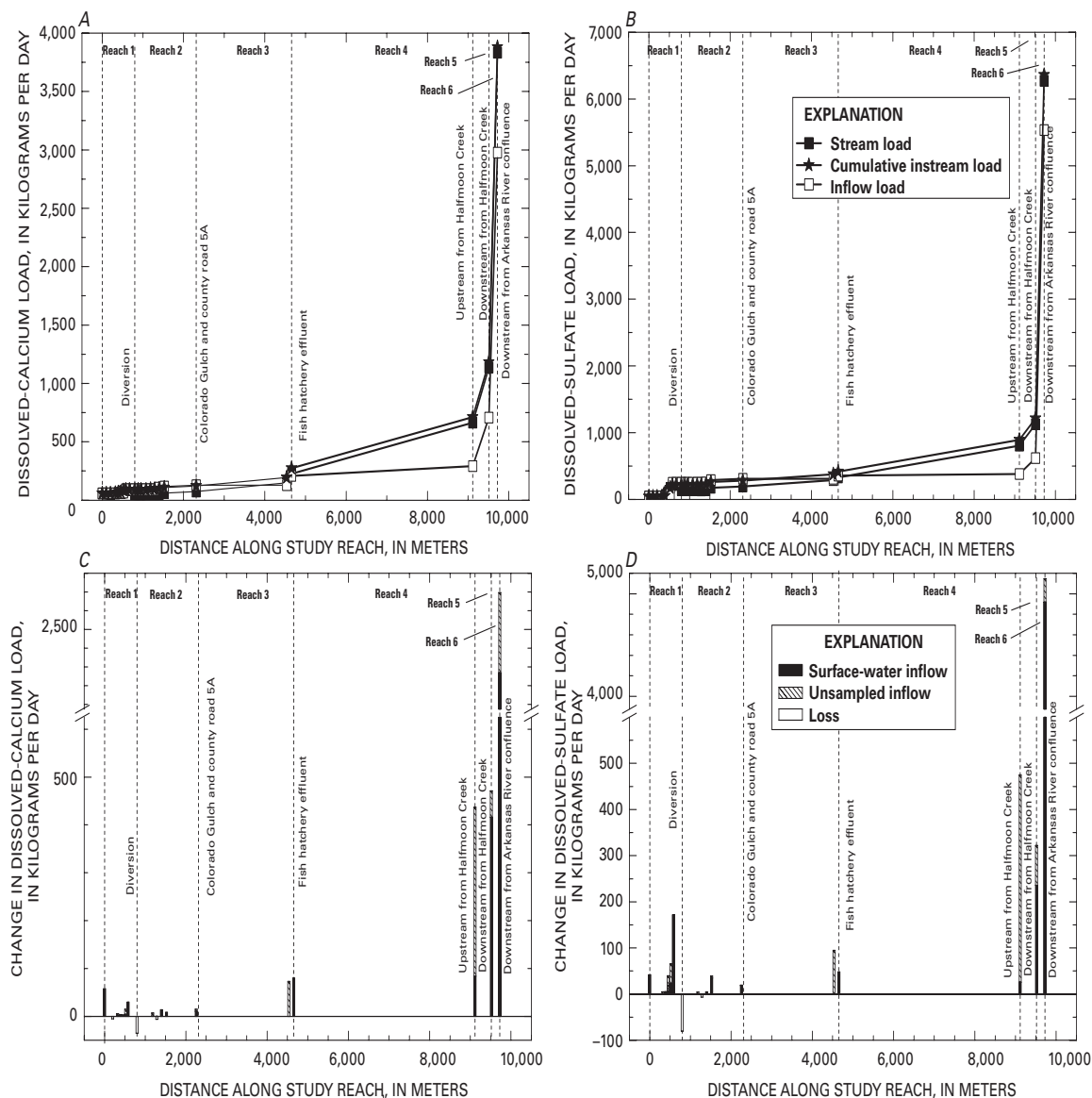


Figure 9. Variation in (A) dissolved-calcium load, (B) dissolved-sulfate load, (C) change in dissolved-calcium load, and (D) change in dissolved-sulfate load during synoptic sampling, September 12–13, 2001.

lead (55 percent); as previously discussed, this loading was unsampled load and probably represents ground-water inflow to the stream. The greatest manganese (80 percent) and zinc loads (77 percent) occurred in Reach 1, which contained the inflow from Sugarloaf Gulch (LF-537 at 537 m), numerous seeps to the stream from the Dinero wetland, and some unsampled inflow that probably represented ground-water inflow to the stream from the Dinero wetland. The three samples collected across the stream width at LF-455 (table 2 and Appendix 1) showed greater metal concentrations along the west bank than in the center or east bank and indicate that most metal load was from the west side of the drainage in this reach.

The proportion of constituent loads contributed to site AR-100 from the Arkansas River upstream from Lake Fork Creek confluence indicates variation in the dominant source for some constituents (fig. 15). More than one-half the load of calcium (70 percent), sulfate (82 percent), manganese (77 percent), lead (78 percent), and zinc (95 percent) in the Arkansas River downstream from the Lake Fork confluence originated in the Arkansas River and upstream tributaries. In contrast, Lake Fork Creek contributed more than one-half the load of aluminum (68 percent), copper (65 percent), and iron (87 percent) to the Arkansas River downstream from the confluence.

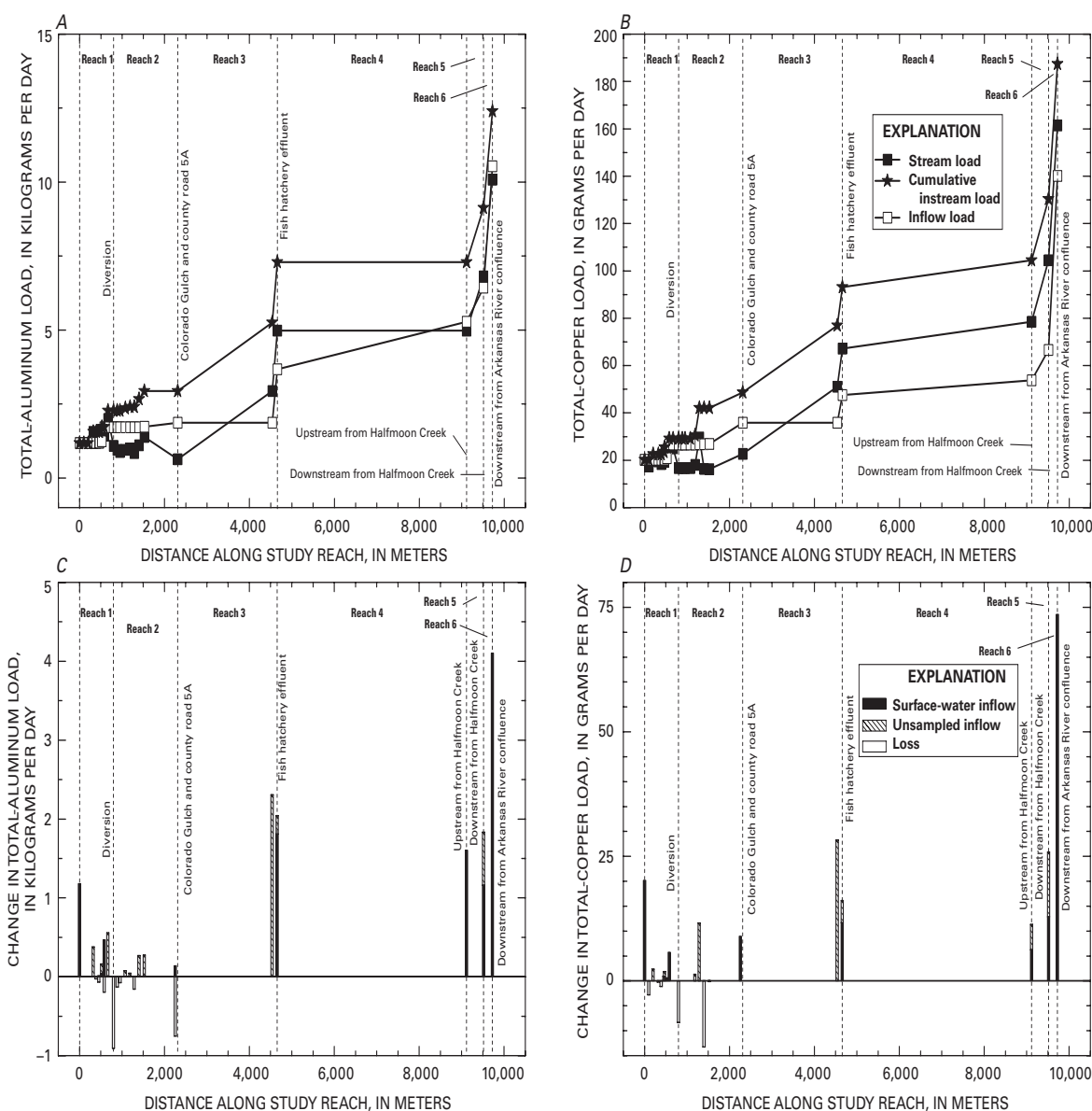


Figure 10. Variation in (A) total-aluminum load, (B) total-copper load, (C) change in total-aluminum load, and (D) change in total-copper load during synoptic sampling, September 12–13, 2001.

A comparison of the results of this study with previous studies may indicate whether the sources of copper, iron, lead, manganese, and zinc loading to the upper Arkansas River Basin have changed in recent years (table 6; Wetherbee and others, 1991; Dash and Ortiz, 1996). Load calculations were made from data collected in other studies to compare with the load measured in Lake Fork Creek at comparable locations and flow regimes during different years. The comparison indicates that copper, iron, lead, manganese, and zinc loads measured in Lake Fork Creek above Halfmoon Creek are within the range of values measured in previous studies under similar streamflow conditions (table 6). This favorable comparison indicates that in Lake Fork Creek, little change has occurred, and our comparison with previous data may be valid. The ratio of loads in Lake Fork Creek above Halfmoon Creek to loads in the upper Arkansas River downstream from the confluence gives an indication of whether conditions in the Arkansas River have changed.

Because of mine-site remediation in Leadville during the 1990s, loads in the Arkansas River may have decreased so that loads in Lake Fork Creek in 2001 would be proportionally greater than before remediation. Considerable mine-site remediation has occurred in the upper Arkansas River Basin since 1992.¹

¹In 1992, two water-treatment plants came on line at two of the major point sources of metals to the Arkansas River: the Yak Tunnel and the Leadville Mine Drainage Tunnel. Since then, several major tailings piles in the Leadville area have been remediated (California Gulch Superfund site; U.S. Environmental Protection Agency <http://www.epa.gov/region8/superfund/co/calgulch/index.html>, accessed July 2005).

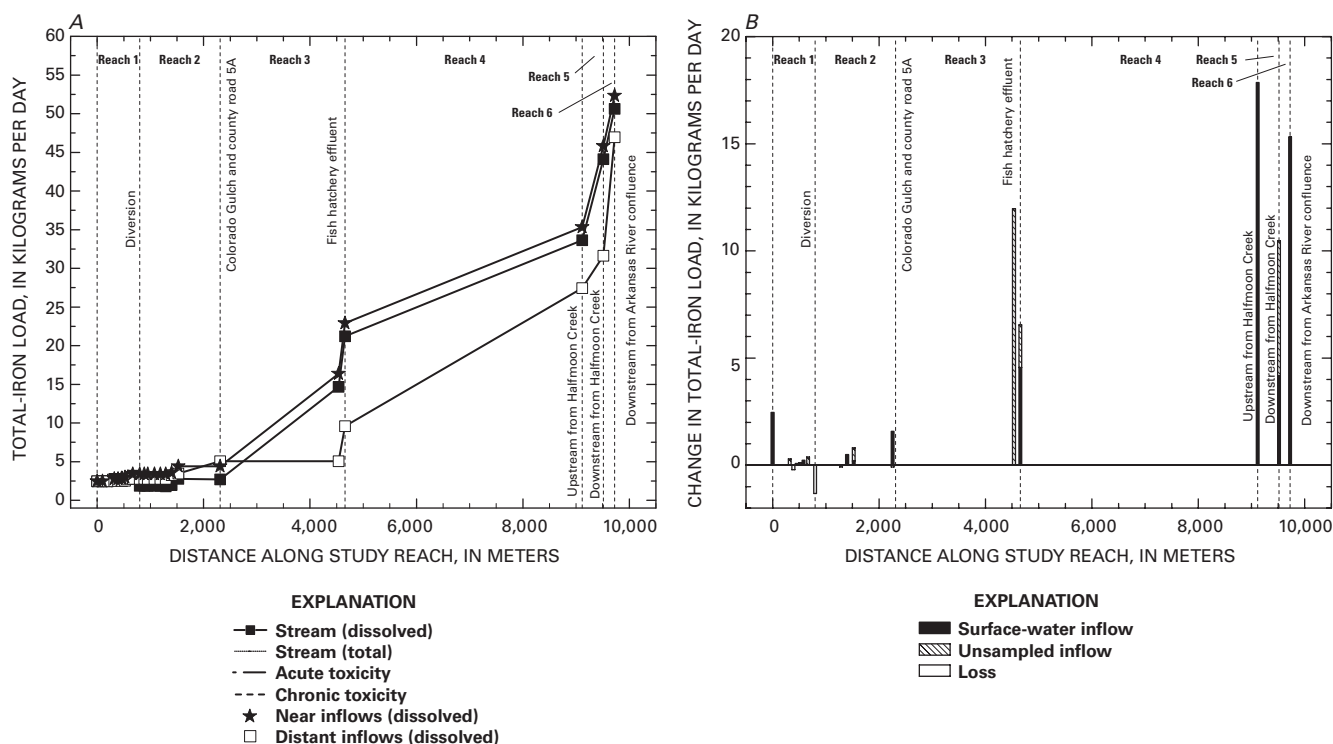


Figure 11. Variation in (A) total-iron load and (B) change in total-iron load during synoptic sampling, September 12–13, 2001.

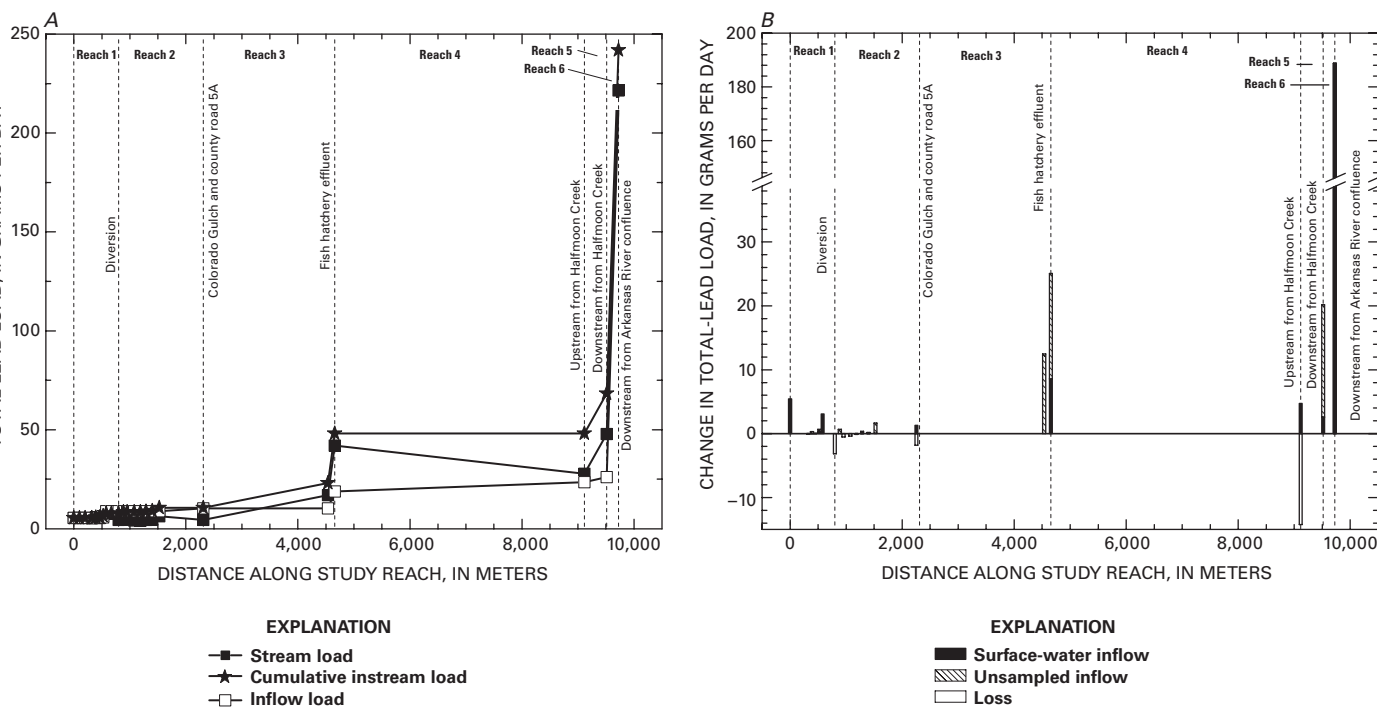


Figure 12. Variation in (A) total-lead load and (B) change in total-lead load during synoptic sampling, September 12–13, 2001.

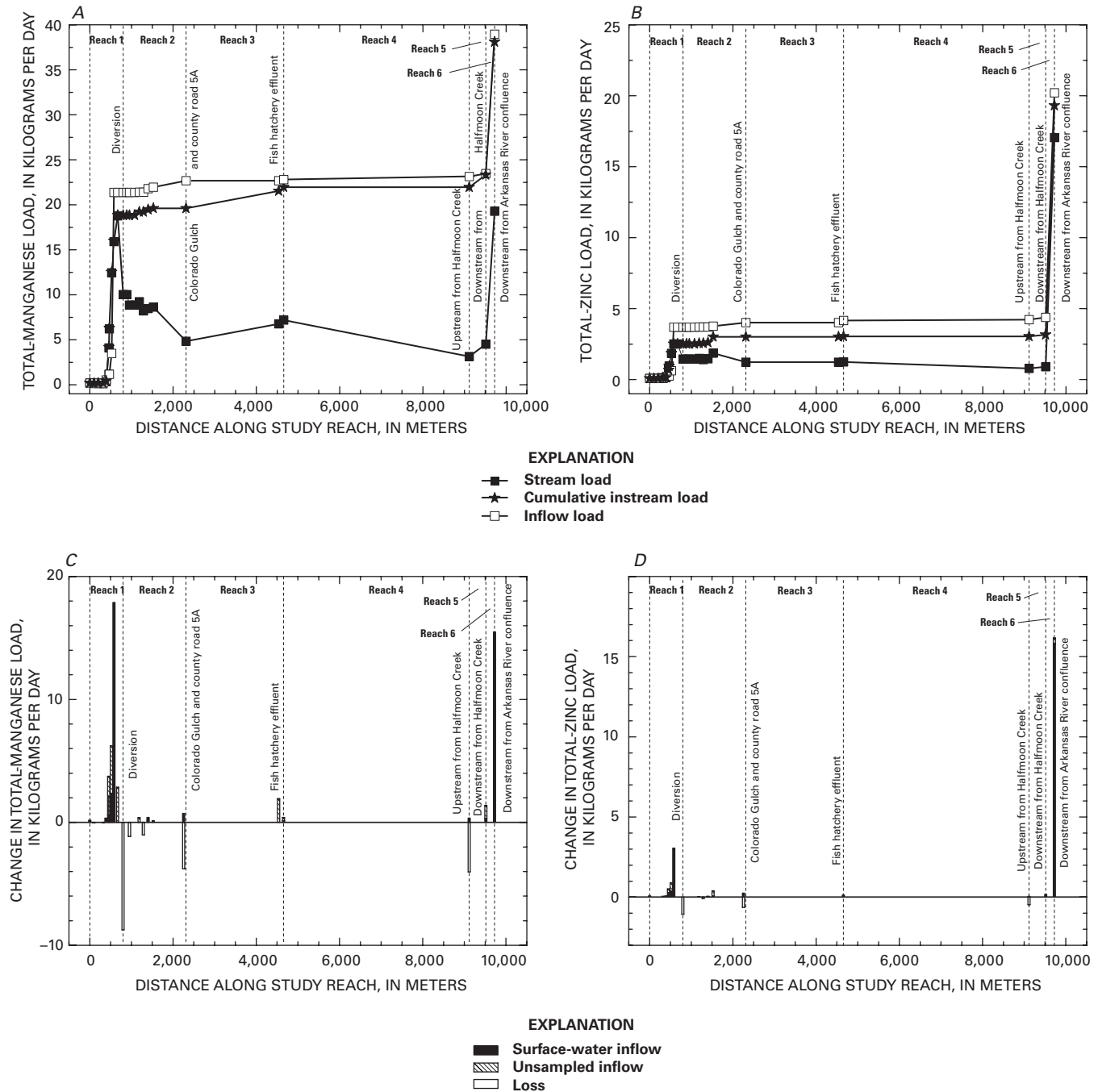


Figure 13. Variation in (A) total-manganese load, (B) total-zinc load, (C) change in total-manganese load, and (D) change in total-zinc load during synoptic sampling, September 12–13, 2001.

Comparison of the percentages (table 6) indicates that only the proportional iron load in Lake Fork Creek is greater than the range of values reported in previous studies under similar flow conditions. Average proportions of copper and zinc in Lake Fork Creek reported in this study are greater than the averages reported in previous studies but are within the range of values used to calculate the averages. Ortiz and others (1998) used additional data from Dash and Ortiz (1996) to indicate that trace-element concentrations decreased significantly at some

sampling sites on the Arkansas River following completion of water-treatment facilities at the Yak Tunnel and Leadville Mine Drainage Tunnel treatment plants. In light of the remediation and these conclusions, it is interesting that Lake Fork Creek has not become a proportionally larger source of metals to the Arkansas River than it was before remediation. However, because the comparisons are made on data collected at different sites, and not precisely at the same streamflow conditions, it is difficult to draw any firm conclusions.

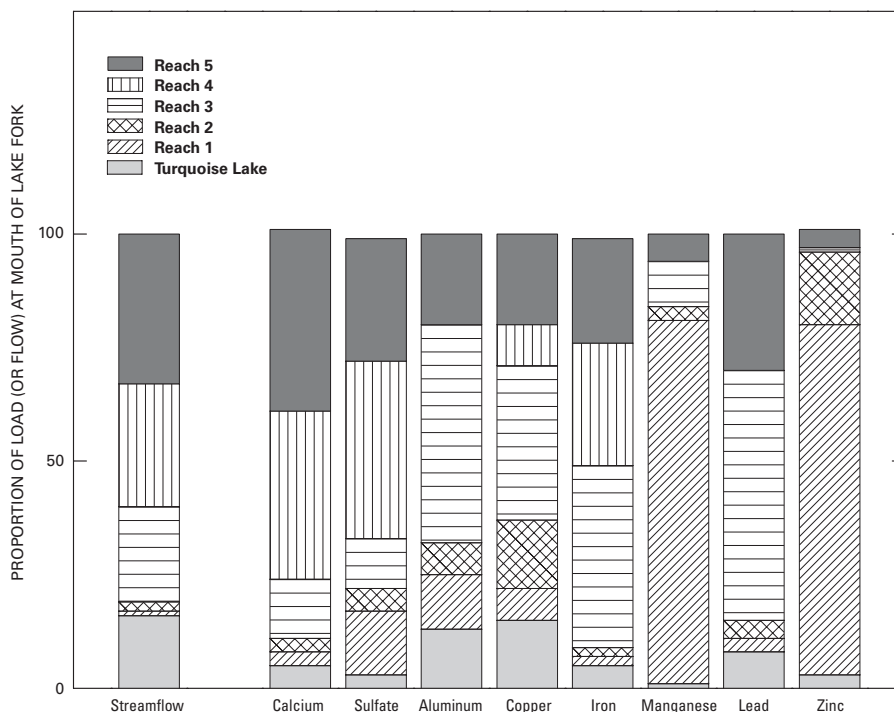


Figure 14. Variation in proportion of streamflow and metal loads contributed by Reaches 1 through 5 of the Lake Fork Creek study area and loads associated with Turquoise Lake that were present at the upstream end of the study reach.

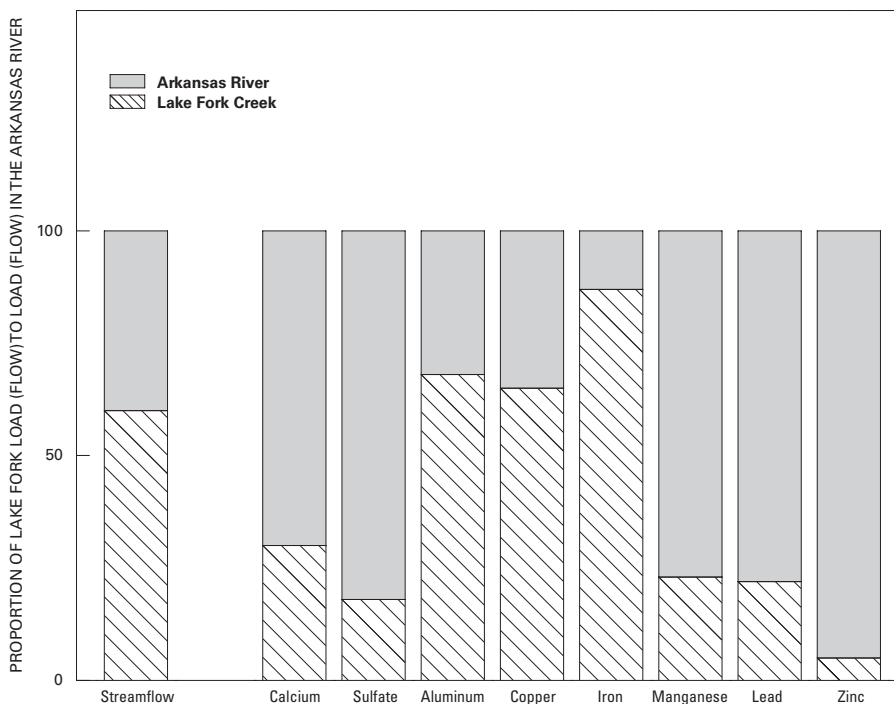


Figure 15. Distribution of metal loading measured in the Arkansas River downstream from the Lake Fork confluence (AR-100) between Lake Fork Creek at the Mouth (LF-5600) compared to the Arkansas River above Lake Fork Creek (AR-0).

Table 6. A comparison of results from this study with previous studies of Lake Fork Creek metal loads and percentage of metal loads contributed by Lake Fork Creek (upstream from Halfmoon Creek) to the load in the Arkansas River downstream from the confluence.

Studies		Copper	Iron	Lead	Manganese	Zinc	Streamflow (cubic feet per second)
		(Load, in kilograms per day)					
This study	Lake Fork Creek load ¹	0.08	34	0.03	3	0.78	32
	Percentage of load in Arkansas River ²	49	66	13	16	5	82
Wetherbee and others (1991) (n=3)	Lake Fork Creek load ³	0.21	28	--	5.1	1.9	30
	(range)	(0.05–0.46)	(15–47)		(2.7–9.4)	(0.5–3.5)	(21–48)
	Percentage of load in Arkansas River ⁴	23	36		19	3	70
	(range)	(3–56)	(19–54)		(5–24)	(1–6)	(60–86)
Dash and Ortiz (1996) (n=2)	Lake Fork Creek load ⁵	0.17	23	0.10	2.7	0.7	28
	(range)	(0.13–0.21)	(21–25)	(0–0.20)	(1.3–4.1)	(0–1.4)	(27–28)
	Percentage of load in Arkansas River ⁶	23	50	15	17	2	84
	(range)	(21–26)	(39–61)	(0–29)	(15–19)	(0–3)	(70–98)

¹Instream load at LF-5500 used to represent the load in Lake Fork Creek above Halfmoon Creek.

²Instream load at AR-100 used to represent the load in the Arkansas River below the confluence.

³Load at Lake Fork Arkansas River near Malta used to represent the load in Lake Fork Creek above Halfmoon Creek. This site is approximately 600 m upstream from LF-5500. There are no major tributaries to Lake Fork Creek between this sampling site and LF-5500. Wetherbee and others (1991), table 15, sampling dates 08/17/1988; 09/16/1988; and 10/16/1988.

⁴Load of Arkansas River at Smith Ranch used to represent the load in the Arkansas River below the confluence. Arkansas River at Smith Ranch is approximately 300 m downstream from AR-100. There are no major tributaries between AR-100 and Arkansas River at Smith Ranch. Data from Wetherbee and others (1991), table 14, sampling dates 08/16/1988; 09/16/1988; and 10/16/1988.

⁵Load at Lake Fork Creek represented by load at Lake Fork Creek above Halfmoon Creek, near Malta. Dash and Ortiz (1996), table 15, sampling dates 10/30/1990; 10/22/1991.

⁶Load at the Arkansas River below the confluence with Lake Fork Creek represented by load at Arkansas River below Empire Gulch near Malta minus the loads at Empire Gulch and Iowa Gulch, Dash and Ortiz (1996), tables 19, 18, and 17; sampling dates as in footnote 5.

Natural Attenuation along Lake Fork Creek

Natural attenuation (removal of load from the water column) varied by constituent and reach along Lake Fork Creek during the September 2001 synoptic sampling event (fig. 16). Calcium, sulfate, and iron were the least reactive constituents and had the least removal. Most removal occurred because of the irrigation withdrawal at the end of Reach 1. Small reductions in constituent loads were observed at the end of Reach 2.

Aluminum and copper loads were reduced by 25 and 20 percent, respectively, over the Lake Fork Creek study reach (fig. 16). Approximately one-half of the removal occurred at the irrigation withdrawal at the end of Reach 1 and at the end of Reach 2. The most likely mechanism responsible for the observed removal of aluminum is formation or flocculation of colloidal aluminum hydroxide phases in the wetland in the last segment of Reach 2. Copper may have coprecipitated with the aluminum phases or may have been associated with other phases, such as manganese minerals and small amounts of iron minerals, which were settling out in that segment.

Manganese, lead, and zinc showed greater natural attenuation than the other constituents studied: 81, 30, and 72 percent, respectively, of their cumulative instream loads were removed by the irrigation withdrawal and stream reactions over the Lake Fork Creek study reach (fig. 16). The similar patterns for manganese and zinc removal in Reaches 1, 2, and 4 may indicate a similar mechanism for their removal. An abundance of manganese oxide crusts was observed coating streambed materials along Lake Fork Creek. Other studies have reported similar findings (Scott and others, 2002). It is likely that manganese oxides precipitate from solution along Lake Fork Creek. Zinc may sorb to, or coprecipitate with, the manganese minerals (Fuller and Harvey, 2000). Lead removal is similar to manganese and zinc removal and occurs in Reaches 1, 2, and 4. Lead may be associated with precipitating aluminum, iron, and manganese phases in Reach 2 and is likely sorbed or coprecipitated with precipitating manganese phases in Reach 4.

Natural attenuation transfers metals from the water column to the streambed. The result helps decrease toxicity within the water column but may decrease the quality of aquatic habitat in the streambed and could provide a means of introducing toxic

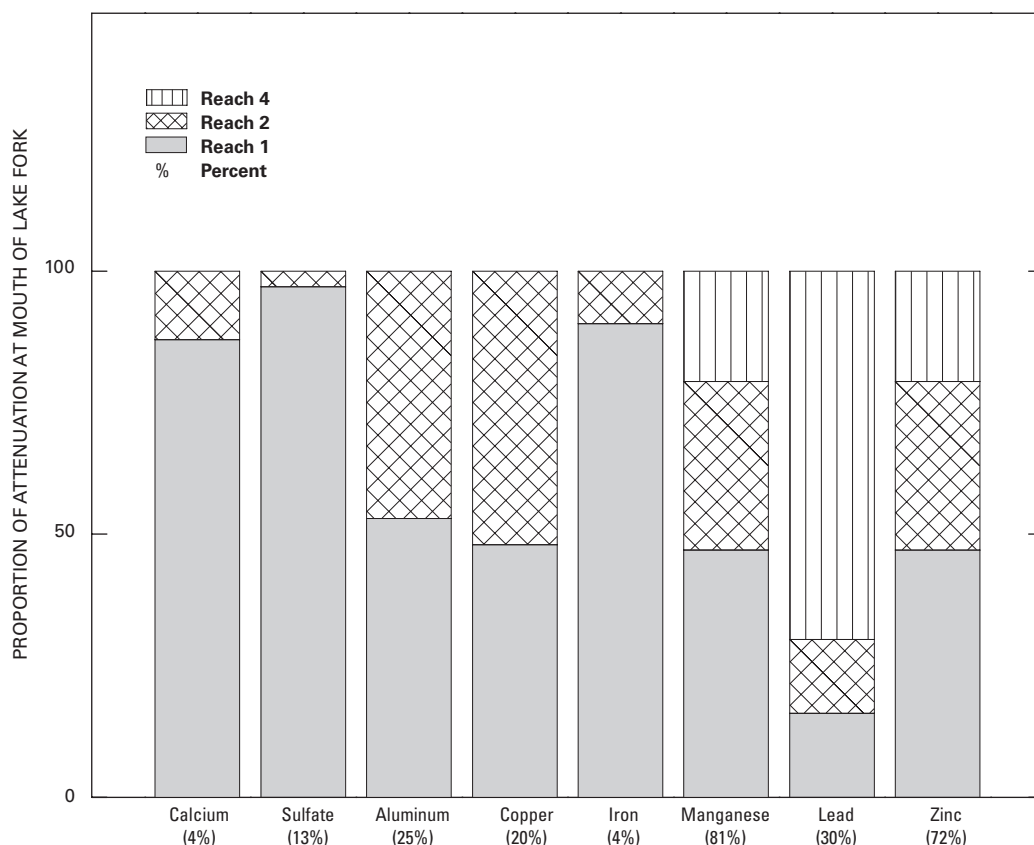


Figure 16. Proportion of metal attenuation that occurred in each reach of Lake Fork Creek during September 12–13, 2001, synoptic sampling. Attenuation over the entire Lake Fork study reach is indicated parenthetically for each bar.

metals into the food web (Besser and others, 2001). Studies of aquatic macrophytes in Lake Fork Creek generally indicate that conditions downstream from the fish hatchery are better than those upstream (Laura Coppock, U.S. Fish and Wildlife Service, oral commun., 2001; Nelson and Roline, 2003). These results indicate that the metal attenuation that occurs in Reach 4 does not substantially degrade aquatic habitat. However, it may be difficult to separate the effects of degraded water quality from those of degraded sediment quality in Lake Fork Creek.

Effects of Wetlands on Metal Loads

Two wetland areas that lie on the west side of and adjacent to the Lake Fork Creek channel intercept flow from several mine-drainage tunnels (fig. 2). The Dinero wetland lies between the Dinero Tunnel and Lake Fork Creek. It receives inflow from the Nelson, Dinero, and Bartlett mine tunnels, from seeps at the eastern edges of the two Dinero tailings piles, and probably from ground water as described later in this section. Flow from the Bartlett Tunnel was not observed to reach the wetland as surface flow but usually infiltrates before reaching either the wetland or Lake Fork Creek. It likely enters the shallow ground-water system of the wetland before discharging to the stream. No drilling was done to confirm this hypothesis, however, and

flow from the Bartlett Tunnel also possibly recharged a deeper ground-water system that did not resurface in the study area. Nonetheless, the metal load from the Bartlett Tunnel was included as an inflow to the wetland, which may overestimate loading into the wetland and will result in a conservative estimate of the remedial effects of the wetland. Similarly, flow from the Nelson Tunnel may not have reached the Dinero wetland, but it was included as input load for the wetland mass balance.

The second wetland area of interest is the Siwatch wetland, which lies between the mouth of the Siwatch Tunnel and Lake Fork Creek (fig. 2). Flow from the Siwatch Tunnel was the only visible flow that entered the wetland. Seeps that may enter the wetland at the base of the Siwatch tailings piles were not included in this analysis. If any seeps exist, the inflow load to the wetland is underestimated by our analysis. Surface water flowed out of the wetland into the Lake Fork channel and was sampled at site LF-1495 (1,495 m) (fig. 2).

The effects of wetlands on metal loads were determined by calculating a rudimentary mass balance. The calculations were simple and did not account for residence time of water in the wetlands but provide an idea of whether the wetlands contributed to natural attenuation of metals. The mass balance was calculated by comparing the total metal loads for all wetland inputs

to the metal load exiting the wetland. For the Dinero wetland, sampled sources of loading into the wetland were the Nelson, Dinero, and Bartlett mine tunnels and the toe seeps at the east ends of the Dinero tailings piles. The mass output from the wetland was calculated as the difference in cumulative instream metal load measured along Lake Fork Creek from 0 to 580 m in Reach 1. This calculation might tend to overestimate natural attenuation occurring in the wetland because some natural attenuation likely occurred in the stream channel along this reach.

The mass-balance calculation for the Siwatch wetland was straightforward. The input to the wetland was the load sampled at the mouth of the Siwatch Tunnel (site ST-0). The output from the wetland was the load sampled where the wetland flow entered Lake Fork Creek (site LF-1495).

Results from the Dinero wetland mass-balance calculation were mixed (fig. 17). First of all, the amount of flow entering the wetland in the five inflows was approximately 7 L/s less than the flow gained by the reach of Lake Fork Creek used in the mass-balance calculation. This result indicates that there was ground-water discharge to the wetland and stream reach whose flow and chemistry were not accounted for by the sampling. Another explanation is that the sampling missed surface-water inputs to the wetland. Some surface-water flow was observed in Sugarloaf Gulch between the Nelson Tunnel and the toe seeps, but this flow was minimal and could not be differentiated from Nelson Tunnel flow. Flow also emanated from a small wetland area upstream from LSG-0 and was sampled at LSG-0. This flow, however, was much less than 7 L/s. No flow was observed in Sugarloaf Gulch upstream from the Nelson

Tunnel during the synoptic sampling. Ground-water discharge within the wetland is the preferred explanation for the missing flow into the wetland.

Results of the mass-balance calculation indicate that the Dinero wetland removed iron, had little effect on zinc mass load, and was a source for, or was releasing, aluminum and manganese in excess of their input to the wetland (fig. 17). The greatest single source of most of these metals to the wetland was the Dinero Tunnel, which accounted for 93, 88, and 88 percent, respectively, of the iron, manganese, and zinc input to the wetland mass balance. The Nelson tunnel was the greatest source of aluminum and accounted for 43 percent of the aluminum input in the wetland mass balance. Aluminum and manganese may have been released from wetland sediments or may have come from ground water that discharged to the wetland. A more detailed mass balance conducted over a longer time period in this wetland reported slightly different results (August and others, 2002). That study indicated that the wetland was a sink for iron, manganese, and zinc in summer months and a source of manganese and zinc in winter months. However, that report did not quantify the tailings pile toe seeps as inputs to the wetland mass balance and, therefore, may have slightly overestimated the outputs from the wetland.

Similar to the Dinero wetland, flow at the outflow of the Siwatch wetland was 0.5 L/s greater than flow entering the wetland from the Siwatch Tunnel. No other surface inflows to the Siwatch wetland were observed. It is likely that ground-water discharge to the wetland represented the missing flow. In contrast to the Dinero wetland, mass loads for all metals considered were lower in the Siwatch wetland output than in the Siwatch

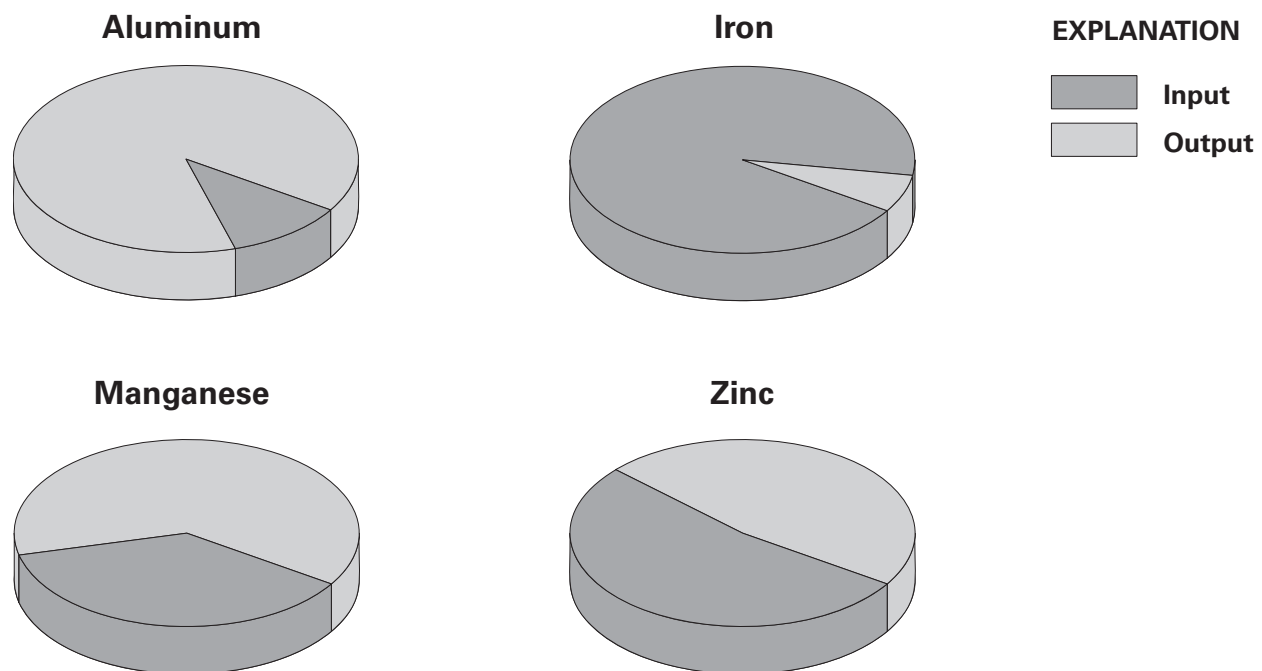


Figure 17. Proportion of metal load input and output for aluminum, iron, manganese, and zinc for the Dinero wetland mass balance.

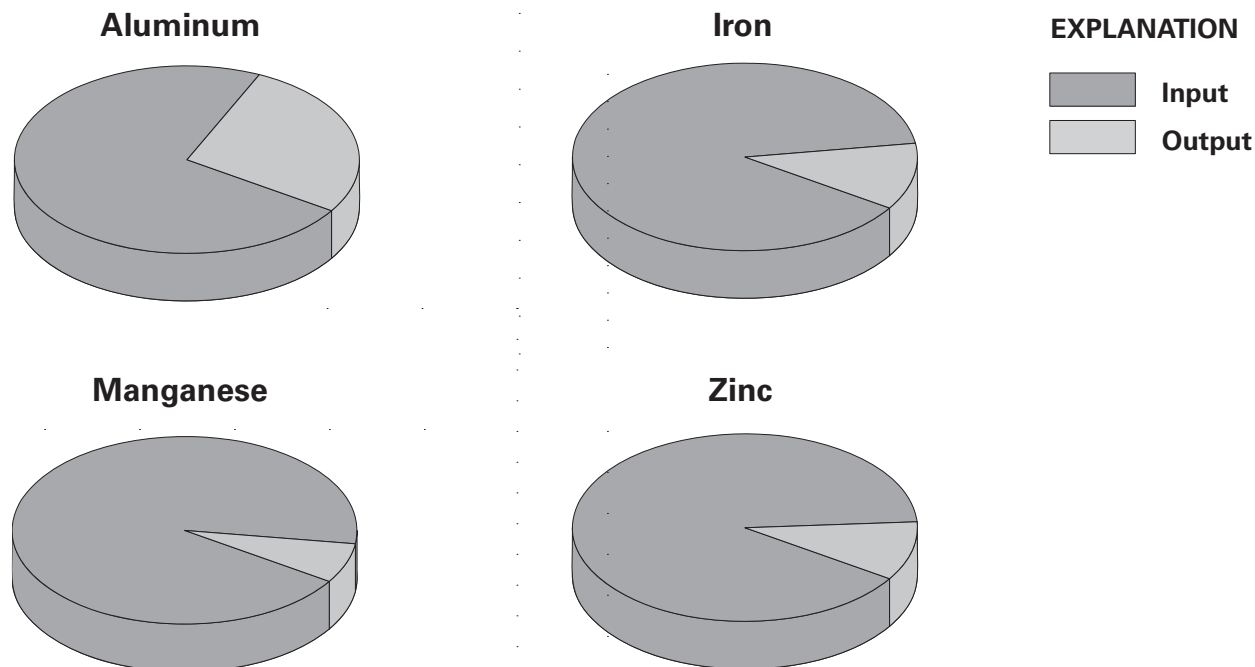


Figure 18. Proportion of metal load input and output for aluminum, iron, manganese, and zinc for Siwatch wetland mass balance.

wetland input (fig. 18). The ability of the Siwatch wetland to reduce metal loads may be due to the difference in chemistry of the water in the wetland. Periscope Pipe Spring (PPS) is located just north of the wetland. It contained the highest alkalinity of any inflow sampled (table 1, fig. 5B—Distant inflow at 1,300 m). Ground-water discharge into the Siwatch wetland may contain some component of Periscope Pipe Spring-type water. Net alkalinity in water greatly enhances the ability of wetlands to treat mine drainage (Walton-Day, 2003; Younger and others, 2002). The ability of the Siwatch wetland to remove manganese and zinc, however, is noteworthy as these two metals are rarely attenuated by natural wetlands (Walton-Day, 2003). Their removal in the Siwatch wetland is unusual and warrants additional investigation. Knowledge of the processes controlling natural remediation in the Siwatch wetland might help land managers preserve the conditions that promote remediation and would also, perhaps, contribute to remediation of additional sources of mine drainage in the watershed.

Effects of Fish Hatchery Effluent

The inflow from the fish hatchery contained the second highest concentration of DOC measured in samples collected on September 12, 2001 (table 7). However, there is no evidence that the higher concentrations of organic matter in the fish

Table 7. Results of dissolved organic carbon and specific ultraviolet analysis of samples collected September 13, 2001.

[DOC, dissolved organic carbon; SUVA₂₅₄, specific ultraviolet absorbance at 254 nanometers]

Sample identification	Distance (meters)	DOC (milligrams per liter)	SUVA ₂₅₄ (liter per milligram carbon per meter)
LF-2500	2,310	2.4	0.035
LF-3500	4,535	2.0	0.034
FH-0	4,585	2.5	0.039
LF-3600	4,655	2.4	0.036
WC-0	6,295	2.6	0.04
LF-5500	9,115	2.0	0.039
HC-0	9,365	0.9	0.022
LF-5600A	9,515	1.7	0.034
LF-5600B	9,515	1.8	0.035
AR-0	9,575	1.3	0.027
AR-100	9,725	1.6	0.031

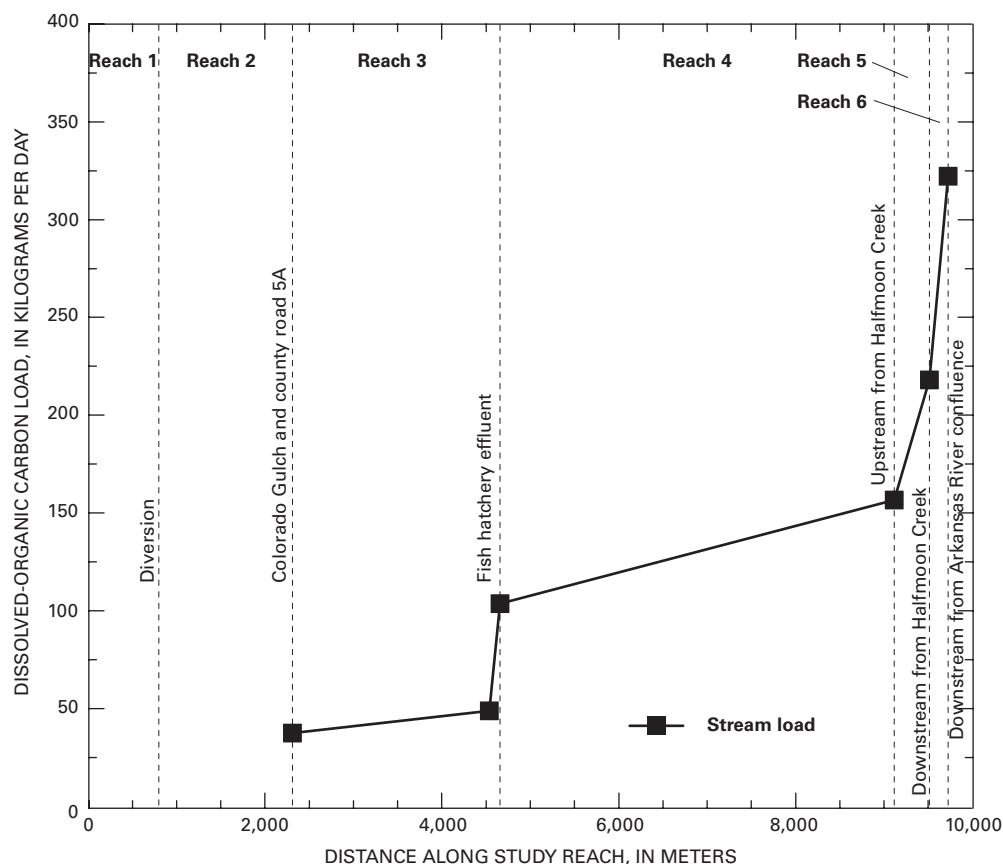


Figure 19. Variation in dissolved-organic carbon load for Lake Fork Creek synoptic sampling, September 13, 2001.

hatchery effluent contribute to the removal of metals previously noted in Reaches 3 and 4. The load of DOC in the Lake Fork increased along these reaches (fig. 19). If metal removal were promoted by interaction with DOC, then DOC loads would decrease along with metal loads.

The results of organic-matter isolation from LF-3500, FH-0, and LF-3600 indicate some changes in the character of the organic matter collected upstream from the fish hatchery effluent (LF-3500) compared to downstream (LF-3600). The sample from LF-3600 contained smaller percentages of trans-

phylic organic acids (TPIA) and low-molecular-weight organic acids (LMW), and a larger percentage of hydrophobic organic neutral compounds (HPON) than sample LF-3500, indicating the effects of mixing with the fish hatchery effluent (FH-0) water, which contained smaller percentages of TPIA and LMW and a larger percentage of HPON than the upstream sample (table 8). The different character of sample FH-0 is most evident in its greater content of HPON, which is composed of relatively undegraded organic matter that would be expected as waste products from the Leadville National Fish Hatchery. It is

Table 8. Results of organic matter isolates from sites LF-3500, FH-0, and LF-3600.

[HPOA, hydrophobic organic acids; TPIA, transphylic organic acids; LMW, low-molecular-weight organic acids; HPON, hydrophobic organic neutral compounds; DOC, dissolved organic carbon, in milligrams per liter; SUVA, specific ultraviolet absorbance, in liter per milligram carbon per meter; %, percent; NR, not reported]

Organic matter fraction	LF-3500			FH-0			LF-3600		
	DOC	SUVA	%	DOC	SUVA	%	DOC	SUVA	%
HPOA	9.8	0.036	46	12.7	0.044	42	11.1	0.039	46
TPIA	4.3	0.029	20	5.1	0.032	17	4.5	0.027	19
LMW	0.7	0.018	29	0.6	0.025	19	0.7	0.013	26
HPON	NR	NR	5	NR	NR	20	NR	NR	7

possible that the greater concentration of organic matter in Lake Fork Creek downstream from FH-0 changed metal speciation and that metal organic complexes were more prevalent in this reach; however, the inverse relation between some metal loads and DOC load in this reach indicates that organic carbon did not contribute to reduction of metal loads. Rather, changes to aquatic biota upstream compared to downstream from the fish hatchery effluent inflow (Nelson and Roline, 1996, 2003; Laura Coppock, U.S. Fish and Wildlife Service, oral commun., 2001) are more likely due to dilution that lowered zinc concentrations below Colorado hardness-based acute and chronic toxicity criteria downstream from FH-0 (fig. 8B).

Summary and Conclusions

A mass-loading study was conducted in Lake Fork Creek in September–October 2001 to illustrate pH and concentration profiles in the creek, determine locations and magnitudes of sources of metal loading to the creek, identify the locations and magnitude of natural attenuation, assess the effects of selected wetlands on metal transport, and evaluate the effect of organic-rich inflow from the Leadville National Fish Hatchery on water quality. The study was done in cooperation with Bureau of Land Management, U.S. Department of Agriculture Forest Service, and U.S. Fish and Wildlife Service. Mass loads were estimated from water-quality data collected during spatially detailed synoptic sampling and streamflow determined from the tracer-injection method, velocity-meter measurement, volumetric measurement, and visual estimates.

Profiles of pH and constituent concentrations (calcium, sulfate, alkalinity, aluminum, cadmium, copper, iron, manganese, lead, and zinc) showed variable patterns over the study reach. Profiles of pH, alkalinity, calcium, and sulfate showed increasing values along the study reach. Aluminum, copper, and iron concentrations increased near the middle of the study reach and then decreased by the end of the study reach. The lead profile was similar to those of aluminum, copper, and iron except that lead concentrations increased at the confluence with the Arkansas River. Cadmium concentrations generally were below the detection limit. But, similar to results for lead, they showed an increase downstream from the Lake Fork Creek/Arkansas River confluence. Manganese and zinc concentrations increased most strongly at the beginning and end of the study reach in Reaches 1 and 6. Stream concentrations did not exceed hardness-based acute and chronic toxicity standards except for zinc starting in the upper parts of the study reach and extending to just downstream from the inflow from the Leadville National Fish Hatchery.

Results of mass-loading calculations indicate that most of the loading of manganese (80 percent) and zinc (77 percent) occurs in the uppermost 800 m of the study reach that contains the Bartlett, Dinero, and Nelson mine tunnels and the Dinero wetland. Reach 3 was the largest source for loading of aluminum (48 percent), copper (34 percent), iron (40 percent), and

lead (55 percent) and contained inflow from the Leadville National Fish Hatchery. The fish hatchery effluent contributed some portion of the loading, but additional loading was from an upstream source, most likely ground water. Attenuation of load along the study reach was important for aluminum (25 percent attenuation), copper (20 percent attenuation), manganese (81 percent attenuation), lead (30 percent attenuation), and zinc (72 percent attenuation). Attenuation primarily occurred at three locations: the irrigation diversion, the beaver pond complex near the mouth of Colorado Gulch, and the stream reach that included the Willow Creek inflow (Reach 4). The most likely attenuation mechanism was precipitation and coagulation of metal oxides and hydroxides (primarily manganese) and sorption or coprecipitation of trace elements with the precipitating phase.

The Arkansas River and its tributaries upstream from Lake Fork Creek were the source of most of the calcium (70 percent), sulfate (82 percent), manganese (77 percent), lead (78 percent), and zinc (95 percent) loads in the Arkansas River downstream from Lake Fork Creek. In contrast, Lake Fork Creek was the major source of aluminum (68 percent), copper (65 percent), and iron (87 percent) loads to the Arkansas River downstream from the confluence. A comparison of these results with results of other studies done before remediation in the Leadville area was inconclusive; this study does not have sufficient data to corroborate water-quality improvements observed in the upper Arkansas River since installation of water-treatment plants on upstream sources of mine drainage in the 1990s.

Mass-balance calculations for aluminum, iron, manganese, and zinc for two sidestream wetlands indicated that the Dinero wetland removed iron from influent mine drainage, had no effect on zinc transport, and was a source for aluminum and manganese. In contrast, the Siwatch wetland removed all four metals from Siwatch Tunnel mine drainage. The difference in behavior of the two wetlands may be due, in part, to greater alkalinity and pH in the Siwatch wetland than in the Dinero wetland. The ability of the Siwatch wetland to remove metals is notable and warrants additional investigation. Knowledge of the processes controlling natural remediation in the Siwatch wetland might help land managers preserve the conditions that promote remediation and would also, perhaps, contribute to remediation of additional sources of mine drainage in the watershed.

Elevated dissolved organic carbon concentrations in the fish hatchery effluent increased DOC concentrations in the sample collected immediately downstream. In addition, organic matter composition in the downstream sample shifted in response to mixing with the different composition of the fish hatchery effluent. However, dissolved organic carbon loads increased along lower stream reaches where metal loads decreased, indicating that metal removal was probably not associated with formation of insoluble metal organic complexes. Observed improvement to aquatic life downstream from the fish hatchery effluent is most likely due to dilution of Lake Fork Creek by the fish hatchery effluent that caused zinc concentrations to fall below toxicity criteria.

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Appendixes

Appendix 1—Quality-Assurance/Quality-Control Procedural Details and Results

Quality Assessment of Analytical Laboratories

Four different analytical laboratories contributed chemical analyses to this study. The University of Southern Mississippi Center for Trace Analysis conducted major cation and trace-element analyses using inductively coupled plasma-mass spectrometry (the method used was a modification of EPA method 200.8, U.S. Environmental Protection Agency, 1994). The USGS Colorado Water Science Center (CWSC) WEBB laboratory conducted alkalinity analyses using titration and gran plot (U.S. Environmental Protection Agency, 1987) on samples having specific conductance less than $67 \mu\text{S}/\text{cm}$. The USGS Utah Water Science Center (UWSC) laboratory conducted alkalinity analyses using titration with a fixed endpoint ($\text{pH} = 4.5$) following EPA method 310.1 (U.S. Environmental Protection Agency, 1983) on samples with specific conductance greater than $67 \mu\text{S}/\text{cm}$ and conducted anion analyses (bromide, chloride, and sulfate) using ion chromatography (Kimball and others, 1999). The USGS Organic Research Project laboratory conducted dissolved organic carbon analyses and organic carbon fractionation (Aiken and others, 1992; Weishaar and others, 2003). The quality of chemical analyses was evaluated using replicate analyses of environmental samples to assess precision, replicate analysis of standard reference materials to assess precision and bias, analysis of blind samples through participation in the USGS standard reference sample program (for example, Woodworth and Connor, 2003) to assess bias, and calculation of charge balance error to assess bias.

The University of Southern Mississippi Center for Trace Analysis and the USGS CWSC WEBB laboratories were approved as production analytical laboratories for the USGS by the USGS Office of Water Quality Branch of Quality Systems (BQS), in accordance with the policy and guidelines described in USGS Office of Water-Quality Memorandum 1998.03 (<http://water.usgs.gov/admin/memo/QW/qw98.03.html>). Laboratory quality-assurance information and quality-control data supporting approval of the two laboratories are maintained by the BQS. Both of these laboratories participated in the USGS Standard Reference Sample Project. During the period that the laboratories performed the analyses presented in this report, the University of Southern Mississippi Center for Trace Analysis scored 3.2 (where 3 is good and 4 is excellent) for analysis of 22 trace elements and major cations and the USGS CWSC WEBB laboratory received an excellent score for alkalinity analysis (Woodworth and Connor, 2003). In addition, a review of the laboratory quality-control data produced by both laboratories during analysis of environmental samples presented in this report indicates that all analyses were in control.

The USGS UWSC has not submitted for approval through the USGS Branch of Quality Systems Laboratory Evaluation Program. Therefore, results of analysis of standard reference materials and environmental precision samples are presented herein (table 9). Quality control of alkalinity analyses was limited and did not include analysis of any samples for bias control. However, results for precision are in excellent control for samples having alkalinity greater than $27 \text{ mg}/\text{L}$ as CaCO_3 . In addition, two replicate samples submitted to both the USGS CWSC WEBB and the USGS UWSC laboratories showed less than 12 percent difference between the laboratories at alkalinities of approximately $25 \text{ mg}/\text{L}$ as CaCO_3 . Finally, charge balance calculations indicated acceptable charge balance (less than 10 percent) for all except six samples (table 1). Therefore, the alkalinity analyses produced by the USGS UWSC laboratory for samples exceeding $67 \mu\text{S}/\text{cm}$ specific conductance are considered in control.

Results for analysis of quality-control samples for bromide, chloride, and sulfate using ion chromatography are presented in table 9. For bromide, the results indicate good control over precision and bias (good control is indicated by 10 percent or less relative standard deviation and bias) in samples having concentrations greater than $1.0 \text{ mg}/\text{L}$. Concentrations less than $1.0 \text{ mg}/\text{L}$ are questionable. All bromide concentrations that were used to calculate streamflow discharge in this study were greater than $3.6 \text{ mg}/\text{L}$ (table 1) and were within control.

Analysis of quality-control samples for chloride concentrations indicated that good precision (less than 10 percent relative standard deviation) was obtained in samples having greater than $0.5 \text{ mg}/\text{L}$, and good bias control (less than 10 percent bias) occurred in samples having concentrations greater than $1 \text{ mg}/\text{L}$. Samples having values less than $1 \text{ mg}/\text{L}$ are not within bias control. Therefore, analyses in this range are qualified as estimated values (table 1). Concentrations of most environmental samples are below the control range and are designated as estimated values in table 1. Chloride is a minor ion in most environmental samples, and chloride analyses were not important in any of the conclusions of this report; therefore, the lack of analytical control is acceptable.

Analysis of quality-control samples for sulfate concentrations indicated that good control of precision and bias was obtained in quality-control samples having concentrations from $10 \text{ mg}/\text{L}$ through $50 \text{ mg}/\text{L}$. Environmental samples having concentrations greater than $50 \text{ mg}/\text{L}$ were diluted to concentrations between 10 and $50 \text{ mg}/\text{L}$ and were reanalyzed. Samples having concentrations less than $10 \text{ mg}/\text{L}$ are qualified as estimated values (table 1). Many samples from the upper 500 m of the study reach have sulfate concentrations less than $10 \text{ mg}/\text{L}$ so that sulfate loads calculated in this reach may be in error. However, because the error occurs in samples having low concentrations of sulfate, the overall effect of the error on sulfate load calculations is small.

Table 9. Statistics for quality-assurance/quality-control samples analyzed using titration (alkalinity) and ion chromatography (bromide, chloride, and sulfate) at the U.S. Geological Survey Utah Water Science Center laboratory.

[Blank samples are laboratory blanks; SRS9 and Check are laboratory precision samples; SR159 and SR161 are environmental precision samples, SR161 was a grab sample collected at LF-1525 and SR159 was a grab sample collected at LF-200; SRL1 and SRL3 are high purity certified standards; SR3 is a calibration standard analyzed as an unknown; SRL101 is an in-house laboratory standard; the number in parentheses after sample name is the number of times the sample was analyzed; % RSD is percent relative standard deviation; MPV is most probable or certified value; % bias is percent bias or difference between MPV and mean value compared to MPV; NA not available; <, less than]

Alkalinity							
Variable	Blank (13)	SRS9 (18)	Check (13)				
% RSD	47	5	3				
MPV	0	NA	NA				
Mean Value	2.55	27.8	265				
% bias	NA	NA	NA				
Bromide							
Variable	Blank (1)	SR161 (5)	SRL1 (20)	SR3 (18)	SR159 (42)	SRL3 (16)	
% RSD	NA	49	2	1	1	4	
MPV	NA	NA	1.0	2.01	NA	10.0	
Mean Value	0.04	0.22	1.02	1.99	3.74	9.90	
% bias	NA	NA	2	<1	NA	-1	
Chloride							
Variable	Blank (34)	SR159 (42)	SRL101 (112)	SRL1 (20)	SR3(18)	SRL3 (16)	SR161 (5)
% RSD	60	25	4	4	1	4	<1
MPV	0	NA	0.505	1	6.00	10	NA
Mean Value	0.09	0.22	0.59	1.01	5.99	10.4	19.2
% bias	NA	NA	17	1	<1	4	NA
Sulfate							
Variable	Blank (21)	SR159 (42)	SRL101 (112)	SRL1 (20)	SR161 (5)	SR3 (18)	SRL3 (16)
% RSD	195	6	7	6	<1	4	4
MPV	0	NA	10.0	10.0	NA	30.0	50.0
Mean Value	0.11	1.89	9.17	9.57	19.1	29.6	51.3
% bias	NA	NA	-9	-4	NA	-1	3

Charge balance error less than 10 percent is acceptable for this study. Charge balance error was less than 7 percent for all but six samples (LF-327, LF-400, LF-448, LF-484, LF-508, and LF-537) that had some of the highest sulfate values and had charge balance error between 10 and 17 percent. It is likely that the error was in the sulfate value as all samples had excess negative charge, elevated sulfate concentrations, and no alkalinity. All sulfate analyses for these samples were repeatedly rerun, and all values used for the charge balance were the lowest obtained. All of these samples were inflow sites, so high bias in the sulfate analyses would only affect the cumulative inflow load calculation, and not the cumulative instream load calculation and would have little to no effect on conclusions presented in this report. Therefore, samples are included in the loading analysis but are highlighted in the data tables (tables 1–3) as having failed charge balance quality criterion.

The USGS Organic Research Project laboratory conducted replicate analyses for all DOC and organic fractionation analyses reported herein. The relative percent difference was less than 10 percent for all analyses except DOC for LF-5500, which had a relative percent difference of 12 percent, and LMW-TPIA analyses for LF-3500 and LF-3600, which had relative percent differences of 17 and 12 percent. The laboratory did not provide an estimate of bias for the analyses because there are no standard reference materials available for organic matter fractionation analysis. The high variability in DOC analysis at LF-5500 does not affect the conclusions of this study as the variation in DOC loads upstream and downstream from LF-5500 (the site above Half-moon Creek) is greater than 12 percent (fig. 19). The large relative percent differences for LMW-TPIA also do not affect the interpretations presented in this report because the LMW-TPIA fraction was a small fraction of the organic matter in the samples analyzed, and it did not vary between samples.

Blanks

Certified inorganic blank water samples obtained from USGS Ocala laboratory were used for field blank samples (LF-BLNKA and LF-BLNKB in tables 1–3). Aliquots of certified inorganic blank water were used to triple-rinse and fill two new 2-L polyethylene jugs, which were transported to the stream. At the stream, one jug of the blank water was used to triple-rinse the

hand-held DH-81 and another new 2-L polyethylene jug. The DH-81 was then filled twice with blank water that was poured into the new 2-L polyethylene jug. The blank sample was then sent back to the central processing location where it was filtered and processed as described for composited synoptic samples in the section “Collection of Water-Quality Samples.”

Analysis of blanks indicated that most analytes were below method detection limits,¹ or that the concentration in the blank was insignificant relative to environmental samples except for aluminum (total and dissolved, table 2), and dissolved copper (table 2) and nickel (table 3). The source of aluminum in the field blanks is unknown. Both the unfiltered and filtered blank samples contained aluminum indicating that (1) the blank water used was contaminated, or (2) that the acid used for sample preservation was contaminated, or (3) that aluminum was introduced into samples from the environment during sample processing. As most of the aluminum concentrations in the environmental samples are low, the load analysis for aluminum is considered semiquantitative. Concentrations greater than 100 µg/L, which is five times the contamination level, are probably reliable. Concentrations of copper and nickel are greater in one filtered blank sample than in the unfiltered sample. In addition, concentrations of copper and nickel are greater in many filtered compared to unfiltered environmental samples. This result is evidence that the filtration units contaminated the samples with trace amounts of Cu and Ni. In earlier studies we had noted Cu contamination in the 10–20 µg/L range (Kimball and others, 1999) and took steps to correct the contamination. Clearly, the contamination has been reduced to submicrogram per liter range but is still significant when values in most environmental samples are in the 1–10 µg/L range, as they are here. Because of the contamination in the filtered samples, graphs and figures show copper data for unfiltered samples only.

Replicates

Five site replicates were collected during the synoptic sampling event. Replicates at LF-200 and LF-5600 were sampling and filtration replicates that were collected within 5 minutes of each other during the synoptic sampling event. Site LF-2500 was sampled on September 12 and was resampled on September 13 to check for variability between the 2 days of the synoptic sampling event. Unfiltered samples were collected at the Dinero Tunnel (DT-0) on September 12 and October 3 to observe shifts in water quality that may have occurred between the two dates and to test whether the October 3 samples collected at a few small inflows to Lake Fork Creek could be included in the mass-loading analysis. Finally, a triplicate was collected at LF-455 to observe chemical variability across the stream channel.

Results of the sampling and filtration replicates (LF-200 and LF-5600) indicate that analyses were within the precision of the results except for a few analyses of total metals content and dissolved metals content where the replicates were close to or less than the detection limit. These results are acceptable. Because both replicates represented the environmental conditions that were being sampled, an average of the replicate analyses was used in data analysis.

Results of the replicate analysis at LF-2500 indicated some variability (up to 31 percent relative standard deviation for the potassium replicates) that may indicate some diel variability occurs in the stream (Nimick and others, 2003). However, replicates for most analytes of interest had percent relative standard deviations within the range of precision for the analytes or less than 11 percent, which is acceptable for data analysis. Because both replicates represented the environmental conditions being sampled, and to help link the data collected over 2 days' time for the loading analysis, an average of the replicate analyses was used in data analysis.

Results of the replicate analysis at DT-0 indicated minimal differences between the samples collected on September 12 and October 3. The additional samples collected on October 3 were ground water from seeps flowing from the Dinero wetland into Lake Fork Creek. Because the ground water in the Dinero Tunnel showed minimal variation over this time period, we assumed that other ground water collected October 3 also would have minimal variation from September 12 and would be suitable for the mass-loading analysis.

Results of the triplicate analysis at LF-455 indicated significant variability up to 95-percent relative standard deviation for total manganese. The samples collected at this site were collected from verticals located near the east bank (LF-455A), center (LF-455B), and west bank (LF-455C) of the channel. At 455 m the channel was divided into three sections having approximately equal discharge. The verticals along which the samples were collected were located at the center of each equal discharge increment. Comparison of the results for this triplicate clearly shows that trace-element concentrations are greater near the west bank than in the center or east bank. This triplicate indicates that the source for these metals is the west bank of the river rather than the east bank. There were no inflows available to be sampled along the east bank, so this triplicate was collected to determine if unsampled ground water was seeping in along the east side. The results indicate that most metals enter Lake Fork Creek in this reach from the Dinero wetland and related sources along the west bank.

¹Method detection limits were estimated as 3 times the standard deviation of the concentration analyzed in laboratory blank samples.

Appendix 2—Bromide Data

Four problems with bromide concentrations in the Lake Fork Creek tracer-injection experiment complicated the calculation of streamflow from the bromide concentration profile. The first problem was increasing concentrations of bromide that occurred at the upstream ends of the tracer-injection reach. The second problem was lower tracer concentration in the synoptic sample at LF-800 than in the downstream site. The third problem was a higher tracer concentration in the synoptic sample from site LF-1185 than at surrounding stream sites. The fourth problem was no decrease in tracer concentration at LF-1525 to indicate the addition of flow from the Siwatch Tunnel inflow.

Profiles of bromide in the stream and at tracer-monitoring sites T1 (200 m), T2 (800 m), and T3 (1,525 m) indicate that there was a gradual decline in plateau-tracer concentration at each site over the duration of the tracer injection (fig. 4). In addition, bromide concentrations exhibited a sharp decrease and partial recovery in concentration between 1200 and 1700 hours on September 12, 2003, at each tracer-monitoring site. The pump rate and bromide concentration exhibit some fluctuation that is probably responsible for some of the observed variability in plateau concentrations. However, the sharp decrease, or dip, in plateau concentrations at each tracer monitoring site indicates at least a 9-percent decrease in the flux of bromide between 1200 and 1700 hours on September 12. Samples were collected periodically from the output of the injection tube to monitor the rate and concentration of tracer injection. Samples collected at 1150 and 1430 hours at the injection site indicated a maximum of 2-percent decline in flux rate. At site T1 (200 m), the concentration dip was apparent between 1200 and 1430 hours. Therefore, there were no injectate samples collected during the time of the concentration dip. The concentration dip was transported to all downstream transport sites (fig. 4) and probably represents a real decrease in pump rate that resulted in a mass flux from the pump lower than that used to calculate the plateau concentration. When the injection was shut down at 1520 hours on September 12, the dip in concentration was starting to recover, as indicated by the bromide concentration profile at T1 (200 m, fig. 4). Alternative explanations for the concentration dip include an increase in streamflow at the injection site or a precipitation event. Outflow from Sugarloaf Dam was not fluctuating that day; the dam operator maintained constant discharge from the dam over the course of the injection. No precipitation occurred over the time period.

Whereas slight fluctuations in pump rate and injection concentration are generally observed over the course of any tracer-injection study, those indicated by the dip are problematic in that synoptic samples were collected at stream sites between 0 and 455 m during passage of the dip through those sites. Consequently, tracer concentration was lower at these sites than downstream (table 4). Tracer concentration should decrease moving downstream from the injection site. Therefore, tracer concentrations in synoptic samples from sites 0–455 m were not representative of tracer concentrations at plateau and were not appropriate for calculation of streamflow.

Instead, using the flow calculated from the median plateau concentration at T1, and assuming no change in streamflow between the injection site and T1, streamflow was interpolated at the sites between 200 and 455 m. The results are shown in table 4 and indicate minor increases in streamflow at the sites between 200 m and 455 m. This result is consistent with field observations that indicated inflow over that reach was from only a few small seeps located on the right bank of the river.

The second problem with bromide concentrations in synoptic samples was that site LF-800 had a bromide concentration lower than those in the upstream and downstream sites (table 4). Therefore, we used the median bromide concentration measured during the period 0 to 1200 hours on September 12 at site T2 (800 m), instead of the concentration measured in the synoptic sample, to calculate streamflow.

The third problem with bromide concentrations was that at site LF-1185, the bromide concentration was larger than in either the upstream or downstream sites (table 4). This elevated analysis was confirmed by reanalysis and may indicate that bromide measured in the inflow site immediately upstream (LF-1180) was sufficient to increase the background bromide concentration. Therefore, streamflow for site LF-1185 was interpolated from streamflow at the adjacent upstream and downstream sites.

The fourth problem with tracer concentrations was that tracer concentration did not decrease at LF-1525 to indicate the water input from the Siwatch Tunnel (LF-1495). During fieldwork prior to the injection, higher specific conductance was noted at the right side of the channel compared to the middle and left side of the channel, but field personnel did not check the depth variation. This observation indicates that the stream was not well mixed at LF-1525. A sampling site farther downstream would have been preferable. However, just downstream from LF-1525, beaver activity interrupted the stream, obliterated the stream channel, and prevented collection of an EWI sample. Therefore, streamflow at LF-1525 was not calculated from the tracer concentration but was the sum of streamflow from the upstream site and streamflow measured volumetrically at LF-1495.