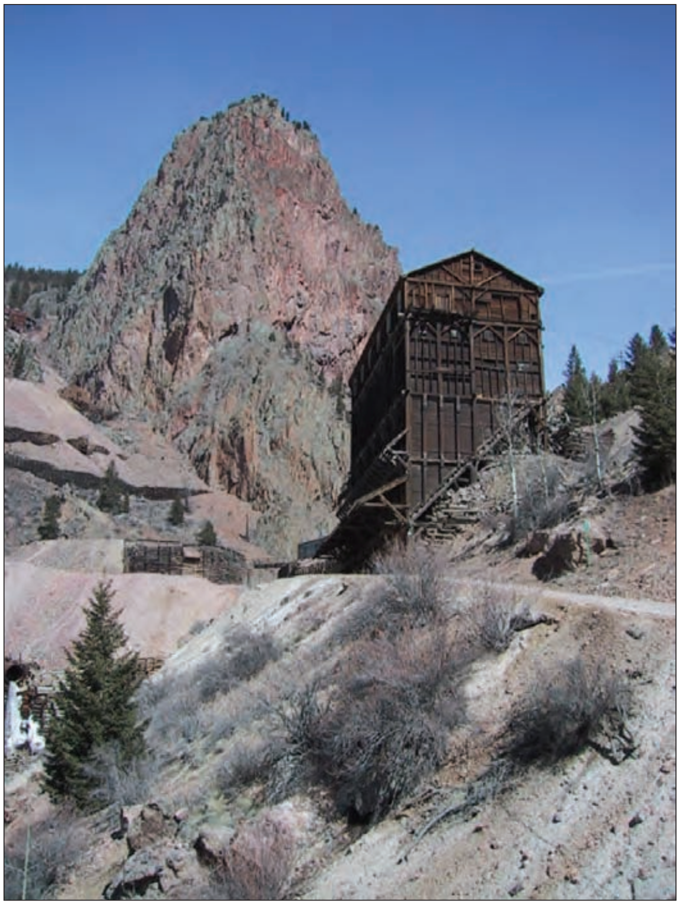
Prepared in cooperation with the
City of Creede, Colorado and the U.S. Forest Service

Evaluation of Metal Loading to Streams near Creede, Colorado, August and September 2000



Scientific Investigations Report 2004–5143

U.S. Department of the Interior
U.S. Geological Survey

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By B.A. Kimball, R.L. Runkel, K. Walton-Day, and B.K. Stover

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Salt Lake City, Utah
2006

U.S. DEPARTMENT OF THE INTERIOR

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U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS, DATUMS, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
kilogram per day (kg/day)	2.2	pound per day (lb/day)
milligram per second (mg/s)	.1901	pound per day (lb/day)
liter per second (L/s)	.0353	cubic foot per second (ft^3/s)
meter (m)	3.281	foot (ft)
micrometer (µm)	.000003281	foot (ft)
milliliter (mL)	.000264	gallon (gal)
square kilometer (km^2)	.03861	square miles (mi^2)

Water temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by using the following equation:

$$°F = 9/5(°C)+32.$$

Horizontal coordinate information is referenced to the North American Datum of 1927 (NAD 27).

Chemical concentration and water temperature are reported only in metric units. Chemical concentration is reported in milligrams per liter (mg/L), micrograms per liter (µg/L), or millimoles per liter (mM/L). Milligrams per liter is a unit expressing the mass of solute per unit volume (liter) of water. For concentrations less than 7,000 milligrams per liter, the numerical value is about the same as for concentrations in parts per million. Specific conductance is reported in microsiemens per centimeter at 25 degrees Celsius (µS/cm).

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ABSTRACT

Decisions about remediation of mine drainage on the watershed scale require an understanding of metal contributions from all sources to be able to choose the best sites for remediation. A hydrologic framework to study metal loading in the Willow Creek watershed, a tributary to the Rio Grande River near Creede, Colorado, was established by conducting a series of tracer-injection studies. Each study used the tracer-dilution method in conjunction with synoptic sampling to determine the spatial distribution of discharge and concentration. Discharge and concentration data were then used to develop mass-loading curves for the metals of interest. The discharge and load profiles (1) identify the principal sources of load to the streams; (2) demonstrate the scale of unsampled, dispersed subsurface inflows; and (3) estimate the amount of natural attenuation. The greatest source of metal loads was from the Nelson Tunnel on West Willow Creek, which contributed 158 kilograms per day of zinc to the stream. Additional loading from other dispersed, subsurface inflows along West Willow Creek added substantial loads, but these were small in comparison to the loads from the Nelson Tunnel. No significant contributions of metal load from potential sources occurred along East Willow Creek. The lack of measurable loading may be a result of previous remedial actions along that stream. The lower Willow Creek section had relatively small contributions of load compared to what had been contributed upstream. This watershed approach provides a detailed snapshot of metal load for the watershed to support remediation decisions and quantifies processes that affect metal transport.

INTRODUCTION

Historical mining near Creede, Colorado, has produced silver, lead, zinc, and gold. Production of metals has been from veins along faults that formed during subsidence of the Creede caldera (Steven and Ratté, 1965). The mining activity in the Willow Creek watershed has affected conditions in the streams. A technical advisory group (TAC) has been working to make decisions about what might be done to improve stream conditions and to lessen the effect of metals in Willow Creek and downstream in the Rio Grande River. To support the decision-making process of the stakeholder group, the U.S. Geological Survey conducted three tracer-injection studies in the Willow Creek watershed in August and September 2000 to assess metal loading.

The Willow Creek watershed covers an area of about 26 km^2. To study metal loading from the headwaters of Willow Creek to the Rio Grande River, the study area was separated into three separate tracer injections (fig. 1). Two injections were upstream from the town of Creede, Colorado. One was in West Willow Creek and started upstream from the Last Chance Mine and continued past the confluence with East Willow Creek to the streamflow-gaging station upstream from Creede. The second injection was in East Willow Creek, starting upstream from the Outlet Mine and continuing past the confluence with West Willow Creek to the same gaging station. The third injection started just downstream from the town of Creede and continued to the mouth of Willow Creek. It also included sampling sites in the Rio Grande River, upstream and downstream from Willow Creek. Much of this lower study reach included braids of Willow Creek and irrigation diversions. Area-velocity discharge measurements were included to supplement the discharge information from the tracer injection in that reach.

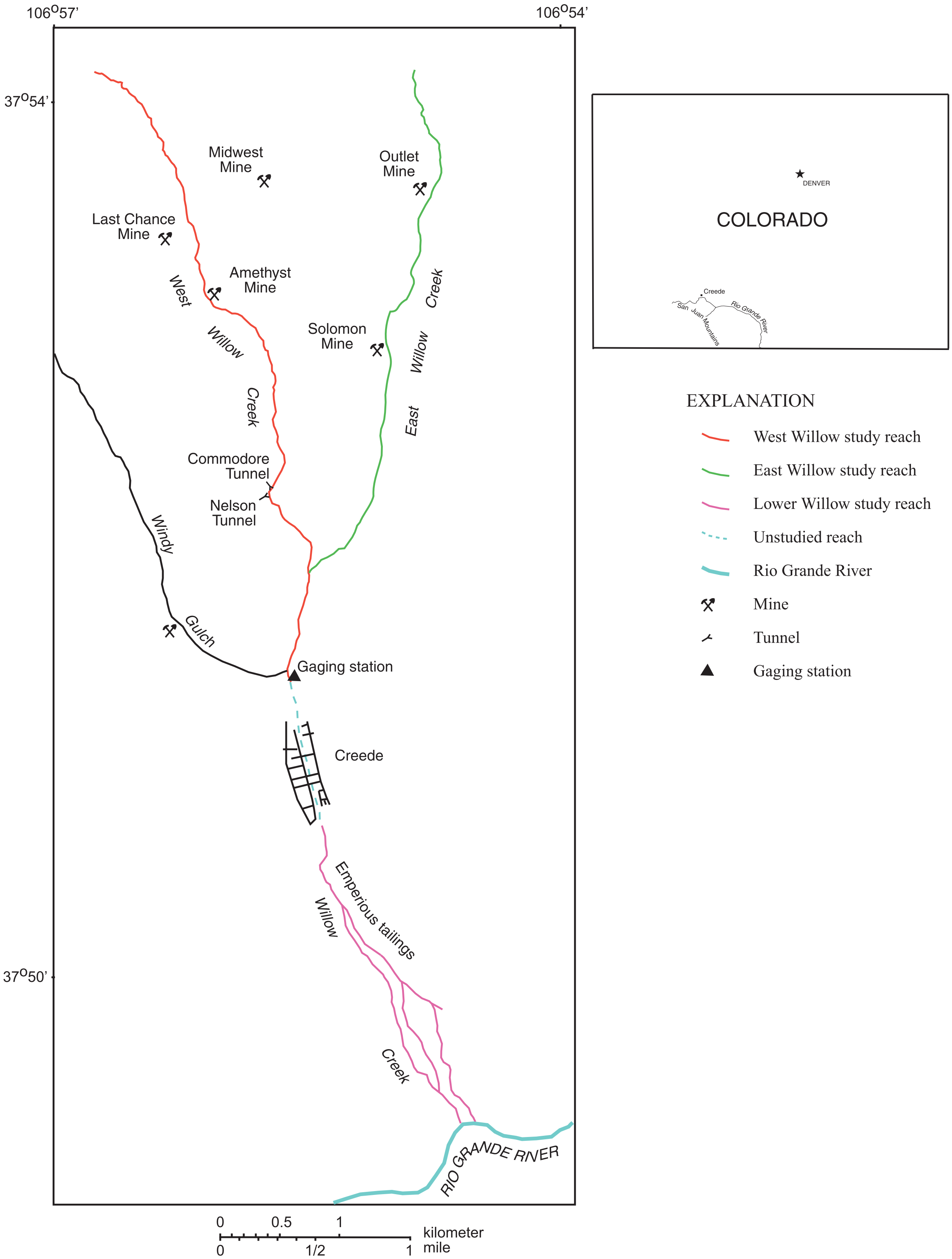

Figure 1. Location of the Willow Creek watershed, indicating study reaches for tracer-injection study reaches and principal mines along the study reach near Creede, Colorado.

Purpose and Scope

This report presents the results of the three tracer injections in Willow Creek. The results will help determine where the greatest metal loading to the stream occurs, the extent of loading from dispersed, subsurface inflow to the stream, and the extent of metal attenuation from physical, chemical, and biological processes. The study treats the major ions calcium (Ca), magnesium (Mg), sodium (Na), sulfate (SO_4), and bicarbonate (alkalinity as $CaCO_3$), and the trace metals aluminum (Al), cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn).

METHODS

Approach

Application of the combined tracer-dilution and synoptic-sampling methods to abandoned mine lands has been developed as part of the U.S. Geological Survey's Toxic Substances Hydrology Program (Bencala and McKnight, 1987; Bencala and others, 1990; Broshears and others, 1993; Kimball and others, 1994; Kimball, 1997; Zellweger, 1994). As described below, the approach includes tracer injections to quantify discharge by tracer-dilution (Kilpatrick and Cobb, 1985) and synoptic sampling to provide spatial concentration profiles of pH and inorganic constituents. Discharge and concentration data are then combined to develop mass-loading curves.

The studies described below were undertaken during low-flow conditions in late summer for two reasons. First, the mass-loading pattern expressed at low flow reflects the importance of metal sources that enter the stream on a continuous basis. Remedial actions that address the sources identified at low flow will therefore improve water quality during the entire year. These sources can include mine waste sources such as waste rock piles, tailings piles, and mine workings and also drainage from adits, tunnels, or ground-water pathways to the stream. Some of these sources contribute water and solutes to the stream as distinct surface inflows, but some contribute water through dispersed, subsurface inflows to the stream. Second, the pattern of metal loading at low flow indicates which sources contribute to high concentrations during the winter months, when the most toxic conditions likely occur (Besser and Leib, 1999). During the low-flow winter months, mine drainage is less diluted by other sources of water, and limits of toxicity are more likely to be exceeded (Besser and others, 2001). Although dissolved metal loads are greater during snowmelt runoff, truly dissolved metal concentrations generally are lower, and the risk to aquatic life is not as great.

Tracer Injections and Stream Discharge

Quantifying discharge in mountain streams by the traditional velocity-area method (Rantz and others, 1982) is compromised because of the roughness of the streambed and the variability caused by pools and riffles (Jarrett, 1992). Further, a substantial percentage of discharge may be flowing through porous areas of the streambed that make up the hyporheic zone (Zellweger and others, 1989). Measurement of discharge with the velocity-area method does not account for flow through the hyporheic zone, and discharge estimates based on the velocity-area method may result in an underestimate of metal loads (Zellweger and others, 1989; Kimball and others, 2002). Another limitation of the velocity-area method for the characterization of metal loads is the time and personnel requirements associated with each discharge measurement. In the studies described below, numerous instream samples were collected during a single day to characterize stream chemistry at steady state. Velocity-area discharge measurements made in conjunction with sample collection at a large number of sites would be difficult, if not impossible.

An alternative means of estimating discharge that was used for this study is the tracer-dilution method (Kilpatrick and Cobb, 1985). With the tracer-dilution method, an inert tracer is continuously injected into the stream at a constant rate and concentration. Given sufficient time, all of the stream, including side pools and the hyporheic zone, becomes saturated with tracer and instream concentration reaches a plateau (Bencala and others, 1990). Decreases in plateau concentration with stream length reflect the dilution of tracer by additional water entering the channel (surface and ground-water inflow). Consideration of this dilution allows for the calculation of discharge at each stream site. Application of the tracer-dilution method addresses both of the problems noted above: (1) the tracer enters porous areas of the streambed such that flow through the hyporheic zone is accounted for; and (2) collection of tracer samples when plateau concentration is achieved provides the ability to obtain discharge estimates at numerous locations during a short period.

Successful implementation of the tracer-dilution method is dependent on several key factors. First and foremost, the injected tracer must be transported through the stream system in a conservative manner; concentrations of the tracer should be unaffected by biogeochemical reactions. Potential tracers include dyes and inorganic salts. The degree to which a given tracer is conservative is often a function of stream pH. Because of the circum-neutral pH of waters within the Willow Creek watershed, a sodium bromide (NaBr) salt was used, and bromide (Br) was used as the conservative tracer. Another key factor is the ability to maintain a constant rate during the continuous tracer injection. For the study described below, tracer injections were controlled with precision metering pumps linked to a Campbell CR-10 data logger. Use of the data logger provides a means to maintain a constant injection rate as battery voltage decreases.

Kilpatrick and Cobb (1985) present a simple mass-balance equation used to determine discharge when fluorescent dyes are used to implement the tracer-dilution method. This equation is also applicable to the Br tracer as background Br concentrations in the Willow Creek watershed are uniform and much lower than that of the injected tracer (Kimball and others, 2002). Stream discharge at any location downstream from the injection site is therefore determined by:

$$Q_D = \frac{Q_{INJ}C_{INJ}}{C_D - C_B} \qquad (1)$$

where

Q_D is stream discharge, in L/s,
Q_{INJ} is the injection rate, in L/s,
C_{INJ} is the injectate concentration, in mg/L,
C_D is the tracer concentration at plateau, in mg/L, and
C_B is the naturally occurring background concentration.

Synoptic Sampling and Analytical Methods

The spatial distribution of metal sources may be characterized by synoptic sampling. Under ideal conditions, samples at all of the sampling locations would be collected simultaneously, providing a description of stream water quality at steady state. Personnel limitations generally preclude simultaneous sample collection, but the synoptic studies described below provide an approximate means of describing steady-state conditions. This approximation is achieved by collecting samples over a relatively short time period (less than 8 hours) and by conducting the studies under low-flow conditions such that the effects of diurnal flow variation are minimized. By approximating steady-state conditions, synoptic sampling provides a spatially intensive “snapshot” of chemistry and discharge that is used to quantify instream loads.

During a synoptic study, samples are collected at a number of stream and inflow sites. Stream sites along the study reach are spaced such that they bracket the sampled inflows and areas of likely subsurface inflow. Subreaches that are bracketed by two adjacent stream sites are referred to as stream segments. The intent of this bracketing is to capture the changes in load that are attributable to visible surface inflow and (or) diffuse subsurface inflow within each segment. At this level of spatial detail, changes in stream chemistry and discharge between stream sampling sites reflect a net metal load for specific segments that incorporates all sources that reach the stream in that segment and instream reactions that affect metal concentrations. Loads for a particular segment cannot always be attributed to specific sources.

For each of the tracer injections described below, stream and inflow samples were collected at numerous predetermined locations, beginning at the downstream end of the study reach and ending upstream of the tracer-injection site. This downstream to upstream sampling order was followed to avoid disturbing streambed materials. Inflow and stream sites that were considered well mixed were sampled by using grab techniques. Sites that were not well mixed were sampled by equal-width integration (Ward and Harr, 1990). Water temperature was measured on site and the collected samples were transported to a central location for further processing. The collected samples were divided into several 125-mL bottles at the central processing location: a raw (unfiltered) unacidified sample (RU), a raw acidified sample (RA), a filtered unacidified sample (FU), a filtered acidified sample (FA), and an ultra-filtered acidified sample (UFA).

Specific conductance and pH were determined from the RU sample within hours of sample collection. Tangential-flow filtration was used with 0.45-µm membranes (FU and FA samples) and 10,000-Dalton molecular weight membranes (UFA sample, giving an effective pore size on the order of 0.001 µm). Metal concentrations for the RA, FA, and UFA samples were determined by inductively coupled plasma-atomic emission spectrometry (Lichte and others, 1987). Anion concentrations were determined from FU samples by using ion chromatography (Kimball and others, 1999). Ferrous iron was determined colorimetrically from the UFA (Kimball and others, 1992), and total alkalinity was determined by titration from the FU samples.

Use of two filtration techniques provides for three different operationally defined concentrations for each metal. The unfiltered sample (RA) provides a measure of the total-recoverable metal concentration (dissolved plus colloidal) and the ultrafiltrate concentration (UFA) is considered the dissolved metal concentration. The 0.45-µm concentration (FA) is used to compare ultrafiltrate concentrations to aquatic standards that are written with 0.45-µm filtration. Colloidal metal concentrations are defined as the difference between the total-recoverable (RA) and the ultrafiltrate metal concentrations (UFA) for stream samples (Kimball and others, 1995).

Mass-Loading Analysis

To quantify load requires accurate discharge and chemical measurements. Profiles of mass load along the study reach use three different views of load. Sampled instream load at individual sampling sites is calculated as:

$$M_a = C_a Q_a \,(0.0864) \qquad (2)$$

where

M_a is the constituent load at location a, in kg/day,
C_a is the concentration of the selected constituent at location a, in mg/L,
Q_a is the discharge at location a, in L/s, and
0.0864 is the conversion factor from mg/s to kg/day.

Sampled instream load is calculated from the total-recoverable concentration of the constituent, but this value for load can be divided between the dissolved and the colloidal load if both filtered and total-recoverable samples are collected. The longitudinal profile of sampled instream load is the basic data from the mass-loading study.

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

$$\Delta M_s = (C_b Q_b - C_a Q_a)(0.0864) \qquad (3)$$

where

ΔM_s is the change in sampled instream load for the segment from a to b, in kg/day,
C_b is the concentration of the selected constituent at location b, in mg/L,
Q_b is the discharge at location b, in L/s,
C_a and Q_a are defined above, and
0.0864 is the conversion factor from mg/s to kg/day.

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. Instream 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 all the increases in load between sampling 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 because it only measures the net loading between sites and does not account for loss resulting from reaction. The cumulative instream load will be greater than the sampled instream load at the end of the study reach if there has been any loss of a constituent to the streambed.

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:

$$\Delta M_i = C_i(Q_b - Q_a)(0.0864) \quad (4)$$

where

ΔM_i is the change in sampled inflow load from location a to b, in kg/day,

C_i is the concentration of the selected constituent at inflow location i, in mg/L,

Q_b and Q_a are defined above, and

0.0864 is the conversion factor from mg/s to kg/day.

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. The cumulative instream and cumulative inflow profiles would be equal if the sampled inflows were 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 that dispersed, subsurface inflow can have higher concentrations of metals than the surface-water inflows in the same stream segment. This causes the profile of cumulative instream load to be greater than the profile of cumulative inflow load and can indicate important areas of unsampled inflow, which is defined as:

$$Unsampled\ inflow = \Delta M_s - \Delta M_i. \quad (5)$$

Unsampled inflow can be calculated for individual stream segments if the segment included a sampled inflow, or for the entire study reach. If the value is negative for the entire study reach, however, it can still be positive for some individual stream segments.

In considering estimates of stream discharge and metal concentration at each stream site, it is possible to predict an 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):

$$Loaderror = (\sqrt{Q_a^2 \Delta C_a^2 + C_a^2 \Delta Q_a^2})(0.0864) \quad (6)$$

where

Q_a is the discharge at the upstream site, in L/s,

ΔC_a is the concentration error at the upstream site, in mg/L,

C_a is the concentration at the upstream site, in mg/L,

ΔQ_a is the discharge error at the upstream site, and

0.0864 is the conversion factor from mg/s to kg/day.

Load error can be 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. Only the changes of instream load that are greater than the load error are included in the longitudinal profiles of sampled instream load and the cumulative instream load.

Principal Components Analysis

Synoptic sampling results in a large number of stream and inflow samples. Classification of these samples into groups of similar chemical characteristics helps highlight their similarities and differences. Because water-rock reactions with altered and unaltered mineral assemblages may lead to particular chemical signatures among inflows to the stream, the classification can help to distinguish different sources and also to recognize geochemical processes.

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

Typically, the first two or three principal components show enough of the variance in the data set to enable the recognition of groups among samples; this is the advantage of using the method for multivariate data. Synoptic samples are plotted by their PCA scores, which are the coordinates of the original data points on the new principal component axes. Adding vectors representing the correlations of original variables with the new principal component axes to the plot of scores creates what is called a biplot. The vectors help identify variations in chemistry among the groups of samples. For the PCA analysis, total-recoverable chemical concentrations, including pH (in millimoles per liter) were used after log transformation. Conversion to millimoles per liter and transformation to logs can maximize the linear relations among solutes that result from stoichiometric chemical reactions. Calculations were done using the U.S. Geological Survey STATPAC programs (Grundy and Miesch, 1985).

EVALUATION OF METAL LOADING

Results from the three tracer injections will be presented individually and the results can be combined for a discussion of watershed implications. A complete listing of the results of chemical analyses for synoptic samples is contained in the appendix. The tracer-injection study reaches in East and West Willow Creeks overlapped downstream from the confluence of the streams and both ended at the discontinued gaging station at the north end of Creede. This allowed for a comparison between the two reaches. The lower study reach started at the south end of Creede. The section of Willow Creek that was not included in a tracer-injection study reach flows through a concrete channel that extends through the town of Creede.

West Willow Creek

The tracer injection in West Willow Creek investigated a 6,602 m section of the Willow Creek watershed, starting upstream from the Last Chance Mine, and continuing past the confluence with East Willow Creek to the gaging station just upstream from the town of Creede (fig. 1). East Willow Creek was the only major surface-water inflow to the study reach, but there were many small seeps, springs, and mine-drainage tunnels. Drainage from the Amethyst Mine, the Commodore Tunnel, and the Nelson Tunnel all entered the study reach. A reconnaissance geologic traverse was mapped in the field for much of this study reach and provides details of the near-stream geology and structure (Bruce Stover, Colorado Division of Minerals and Geology, written commun., 2000).

The 6,602-m study reach was divided into 34 segments by the stream sampling sites (fig. 2). Stream segments bracketed eight major and minor tributary inflows and areas of likely subsurface inflow. Site designations for stream segments came from the previous studies of the stakeholder group: sites WW-A through WW-L, in an upstream direction. Additional sites use the designations for West Willow (WW), East Willow (EW), and lower Willow (LW) along with the measured downstream distance to the site. Downstream distance in East Willow Creek continued past the confluence with West Willow Creek all the way to the Rio Grande River. Distances in West Willow Creek only went as far as the confluence with East Willow Creek. Site designations and information about the sampling sites in West Willow Creek are listed in table 1. In choosing stream-sampling sites, locations were selected that should be sufficiently downstream from inflows to capture both visible tributary inflow and additional subsurface inflow. Only eight stream segments contained sampled inflows; the other segments represented dispersed, subsurface inflow.

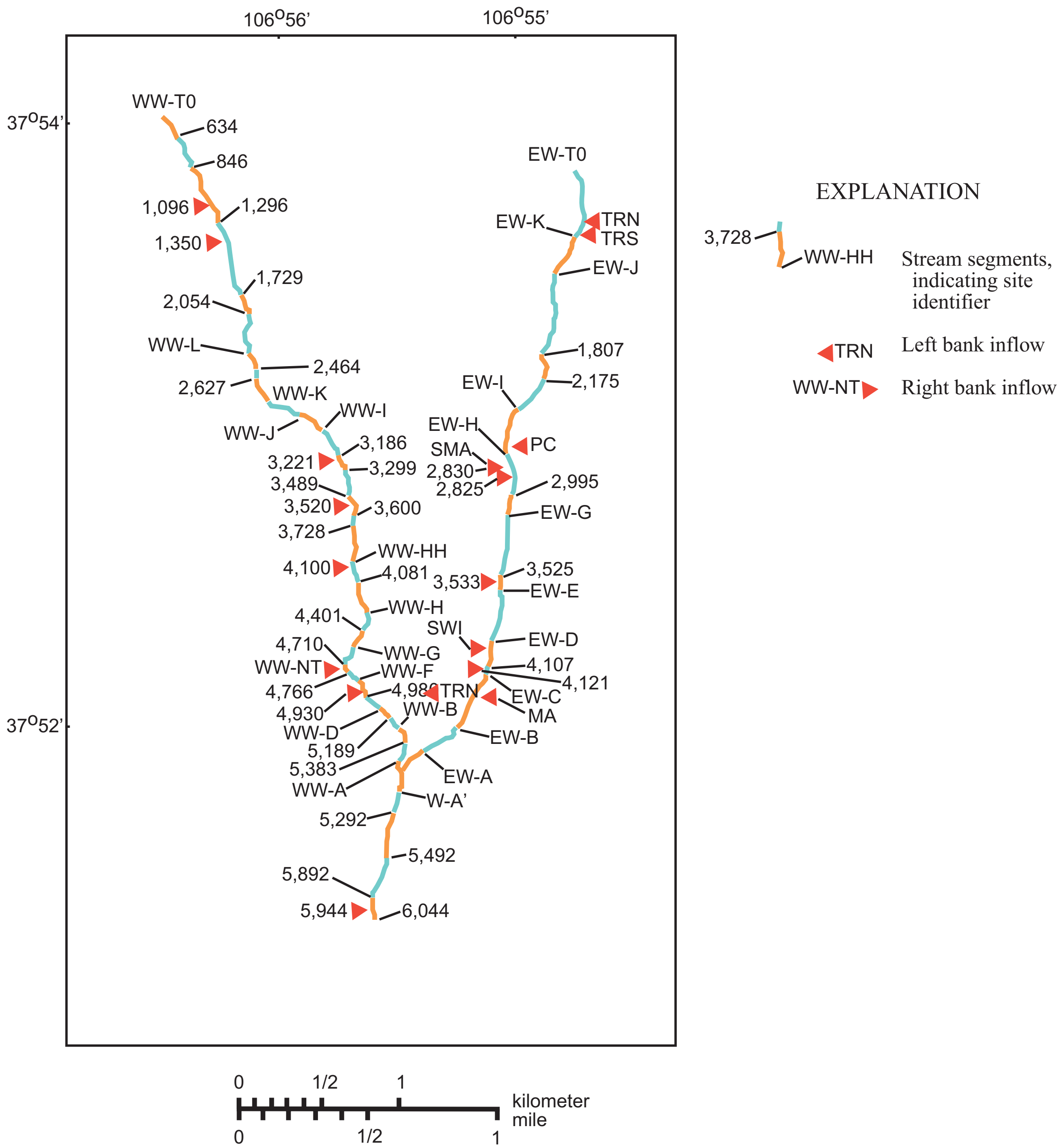

Figure 2. Location of stream segments and inflow samples for East and West Willow Creeks, Colorado. Colors indicate the different stream segments.

Table 1. Sample identification, source, distance along the injection study reach, site description, pH, specific conductance, tracer concentration, and calculated discharge for synoptic samples from West Willow Creek, Colorado, September 2000

Sample identification	Source	Downstream distance, in meters	Site description	pH, in standard units	Specific conductance, in microsiemens per centimeter	Bromide concentration, in milligrams per liter	Calculated discharge, in liters per second
WW-430	Stream	430	T0 - Above injection site	7.91	105	0.09	92
WW-634	Stream	634	T1 - First site below injection site	8.02	111	4.07	92
WW-846	Stream	846	West Willow Creek where gradient increases	8.11	111	4.07	92
WW-1096	Inflow	1,096	Drainage from gully	6.75	58		.10
WW-1296	Stream	1,296	Below rhyolite outcrop	8.09	111	4.07	92
WW-1350	Inflow	1,350	Left bank inflow	6.99	95		.10
WW-1729	Stream	1,729	Stream site to check mixing of tracer	8.08	110	4.07	92
WW-2054	Stream	2,054	Last site in moraine deposits	7.97	111	3.98	95
WW-L	Stream	2,304	Stakeholder site above Last Chance Mine	8.01	111	3.83	100
WW-2464	Stream	2,464	Above Last Chance talus pile	7.86	111	3.83	100
WW-2627	Stream	2,627	Above Amethyst Tunnel	7.93	111	3.83	100
WW-K	Stream	2,667	Below Amethyst Tunnel	7.95	111	3.80	100
WW-J	Stream	2,829	T2 - Above Nelson Creek	7.99	112	3.74	106
NC-E	Inflow	2,847	Nelson Creek above Midwest Mine				
NC-B	Inflow	2,847	Nelson Creek at mouth				
WW-I	Stream	3,021	Below Nelson Creek	7.97	112	3.66	106
WW-3186	Stream	3,186	West Willow Creek above right bank spring at fault	7.94	112	3.55	110
WW-3221	Inflow	3,221	Spring from fault	6.92	101		4
WW-3299	Stream	3,299	West Willow Creek at rhyolite outcrop	7.91	112	3.45	114
WW-3489	Stream	3,489	West Willow Creek at log waterfall	7.87	110	3.41	116
WW-3520	Inflow	3,520	Spring near stream level on right bank	7.13	90		1
WW-3600	Stream	3,600	West Willow Creek at top of cascades	7.96	110	3.38	117
WW-3728	Stream	3,728	West Willow Creek at culvert above Burro Bridge	7.94	110	3.36	118
WW-HH	Stream	3,858	West Willow Creek at Burro Bridge	7.96	110	3.32	120
WW-4100	Inflow	3,885	Water coming off rock face	7.73	32		2
WW-4081	Stream	4,081	West Willow Creek below Burro Bridge	7.94	110	3.27	122
WW-H	Stream	4,245	West Willow Creek in cascades	7.88	109	3.18	126
WW-4401	Stream	4,401	100 meters above old buildings by Commodore Tunnel	7.93	109	3.15	128
WW-G	Stream	4,577	West Willow Creek above Commodore Tunnel	7.91	109	3.09	131
WW-4710	Stream	4,710	Above Nelson Tunnel	7.73	109	3.09	131
WW-NT	Inflow	4,730	Nelson Tunnel discharge	4.45	1,521		22
WW-F	Stream	4,766	West Willow Creek down from Nelson Tunnel (not WW-F)	7.26	328	2.72	153
WW-4866	Stream	4,866	West Willow Creek below culvert	7.37	344	2.63	158
WW-4930	Inflow	4,930	Spring on right bank with aluminum precipitate	5.46	646		5
WW-4980	Stream	4,980	Below Commodore mine dump	7.30	351	2.57	163
WW-D	Stream	5,063	West Willow Creek below mine dump	7.74	349	2.55	164
WW-5189	Stream	5,189	West Willow Creek at point of good mixing	7.77	349	2.55	131

Table 1. Sample identification, source, distance along the injection study reach, site description, pH, specific conductance, tracer concentration, and calculated discharge for synoptic samples from West Willow Creek, Colorado, September 2000—Continued

Sample identification	Source	Downstream distance, in meters	Site description	pH, in standard units	Specific conductance, in microsiemens per centimeter	Bromide concentration, in milligrams per liter	Calculated discharge, in liters per second
WW-B	Stream	5,282	West Willow Creek up from bridge at photo stop	7.75	350	2.55	131
WW-5383	Stream	5,383	West Willow Creek above possible Amethyst Fault	7.72	349	2.53	132
WW-A	Stream	5,540	T3 - West Willow Creek above confluence	7.64	350	2.49	135
EW-A	Inflow	5,614	East Willow Creek near mouth	8.01	53	.03	434
W-A	Stream	5,716	Willow Creek down from confluence	7.82	145	.7	568
EW-5892	Stream	6,450	Willow Creek above pond near Windy Gulch	7.46	147	.7	568
EW-6044	Stream	6,602	Willow Creek down from Windy Gulch at gage	7.59	146	.7	568

Discharge

Precision for the Br analyses was better than 1 percent over the range of concentrations. This allows the detection of very small changes in discharge. In a cascading, cobble-bottom stream like West Willow Creek, an area-velocity measurement might have a precision closer to 20 percent, or as much as 28 L/s. A NaBr tracer with a Br concentration of 145,250 mg/L was injected at a rate of 0.0034 L/s. The systematic decrease of Br concentration downstream from the injection site allowed the calculation of discharge at each of the stream sampling sites (fig. 3). There were no inflows with Br concentrations above the lower detection limit. Thus, with a uniform background concentration of tracer, equation 1 can be used to calculate discharge for the stream sites. The change in discharge for each stream segment represents the combination of surface and subsurface inflow to the stream and is the total inflow discharge for a given stream segment. The increase in discharge along the study reach was 476 L/s. Only about 7 percent of the increase in discharge was from segments that had no sampled inflow. However, subtracting the surface-water inflow from East Willow Creek, about 55 percent of the remaining increase in discharge along West Willow Creek was from unsampled inflow.

The Amethyst Fault intersects West Willow Creek in the vicinity of stream site WW-5189 (Bruce Stover, Colorado Division of Minerals and Geology, written commun., 2000). The Amethyst Fault trends north-northwest and has a dip of 50 to 70 degrees southwest (Steven and Ratté, 1965). Area-velocity measurements made upstream and downstream from the area of the fault indicated a loss of 34 L/s in that segment of the stream. A loss of water would result in a constant tracer constant, and tracer concentrations remained constant in segments WW-D through WW-B. So the tracer pattern is consistent with a measured loss of streamflow. The discharge profile reflects this loss of streamflow at WW-5189 (fig. 3).

Chemical Characterization of Synoptic Samples

Synoptic sampling of inflows provides the range of chemistry affecting the stream and provides a context for understanding the changes in stream chemistry and solute loads. Water-rock interactions with bedrock throughout the watershed can generate inflows that are affected by acid rock drainage as well as inflows that are affected by rocks that have acid-neutralizing capacity. Thus, inflow chemistry can range from acidic and metal-rich to alkaline and essentially metal-free and both kinds of inflow chemistries can affect the stream chemistry.

Streamwater at the injection point in West Willow Creek was a $CaHCO_3$-$CaSO_4$ type water, reflecting the chemical weathering of bedrock in the watershed (Steven and Ratté, 1965). Both major ions and pH remained nearly constant along the study reach from the injection site until the inflow of the Nelson Tunnel at WW-F (fig. 4). At that point, the chemical character changed to a $CaSO_4$ type, and pH was lower. With the inflow of East Willow Creek, at W-A´,

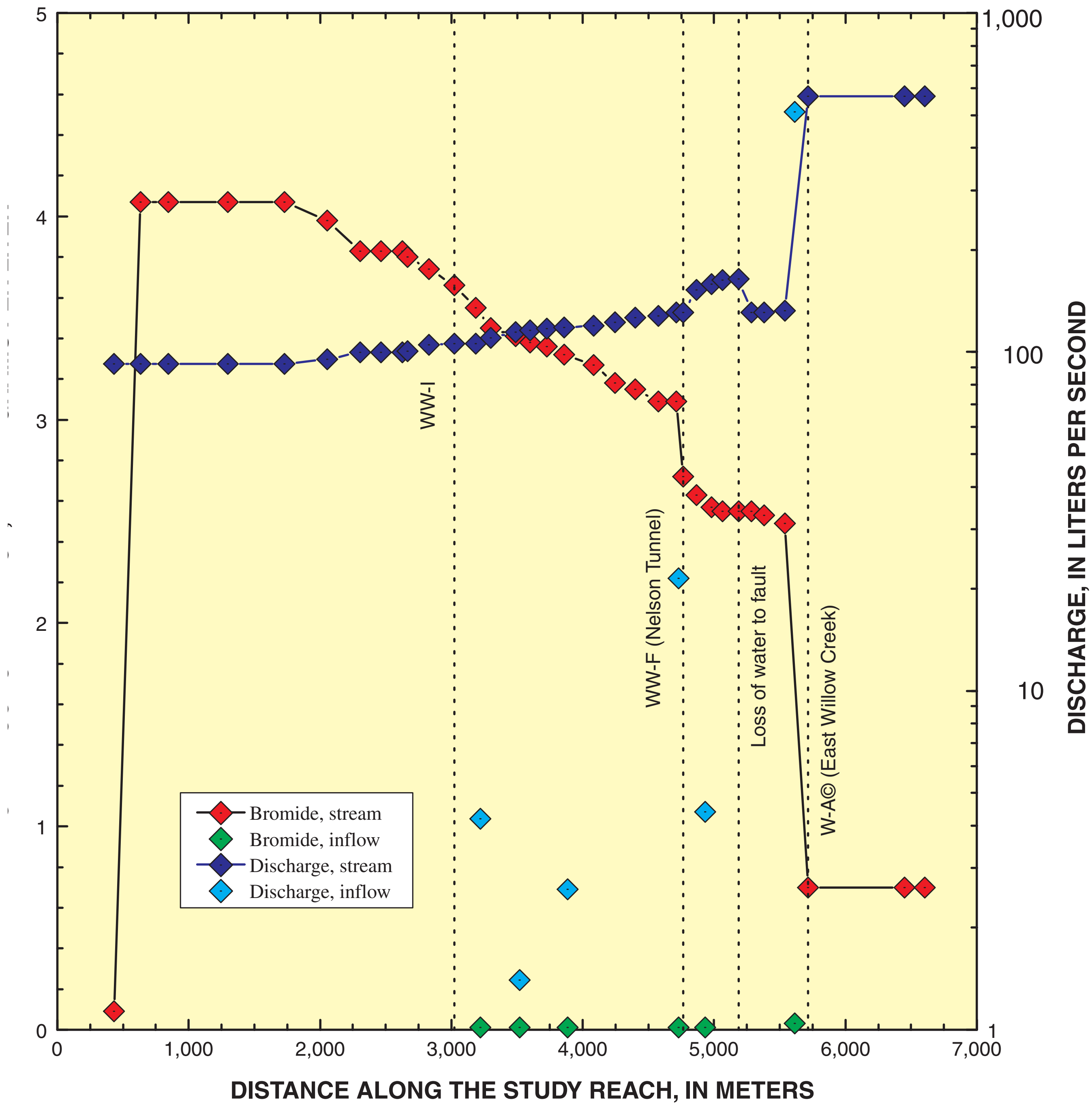

Figure 3. Variaton of bromide concentration and calculated discharge with distance along the study reach, West Willow Creek, Colorado, September 2000.

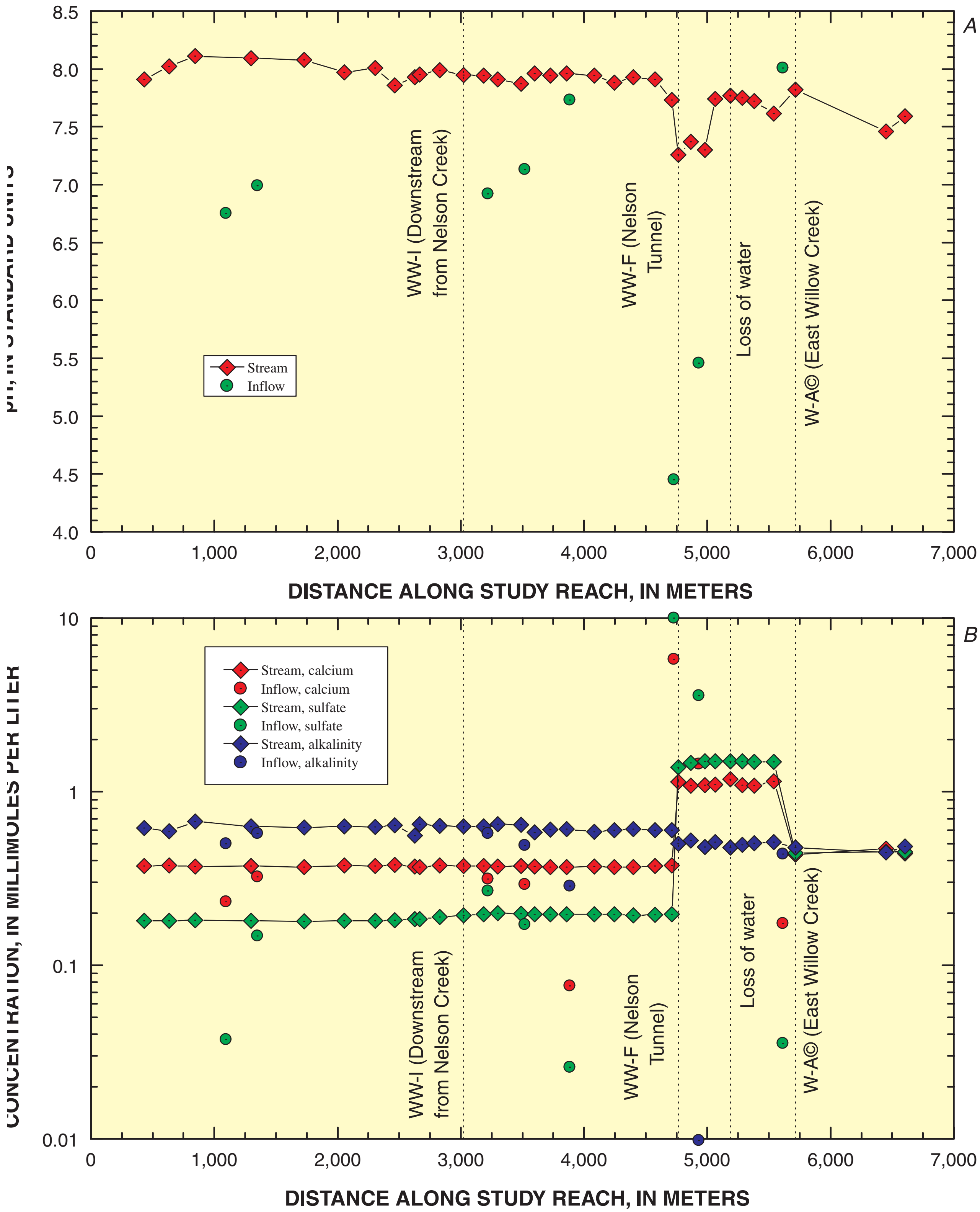

Figure 4. Variation of (A) pH and (B) calcium, sulfate, and alkalinity concentration with distance along the study reach, West Willow Creek, Colorado, September 2000.

pH became more basic again; Ca and SO_4 were diluted, and alkalinity remained nearly constant.

Several metals were present in relatively high concentrations, most notably Fe, Mn, Pb, Sr, and Zn (fig. 5). Dissolved Al, dissolved Fe, and nickel (Ni) mostly were near limits of detection, but colloidal concentrations of Al and Fe were measurable along most of the study reach. Colloidal Pb concentrations generally were higher than dissolved Pb concentrations, but both collodial and dissolved concentrations of Pb were relatively high compared to many streams affected by mine drainage. Although no great variation in major-ion concentrations or pH occurred along the study reach (fig. 4), a substantial difference in metal concentrations upstream and downstream from the Nelson Tunnel did occur, with higher concentrations occurring downstream.

A substantial amount of spatial variation in Al concentrations occurred (fig. 6). From the injection site to the Nelson Tunnel, which entered in segment WW-F, both the ultrafiltrate and 0.45-µm filtered concentrations were less than detection. Only the total-recoverable concentration was measurable, but a considerable amount of analytical variation occurred with the ICP-AES analysis for Al concentrations less than 0.1 mg/L. With the inflow of the Nelson Tunnel at WW-F, total-recoverable and 0.45-µm-filtered concentrations increased, while the ultrafiltrate concentration remained low. Between the Nelson Tunnel inflow and the inflow of East Willow Creek at W-A', a distinct difference occurred between the ultrafiltrate and the 0.45-µm filtered concentrations, indicating the possible distribution in size of the colloidal particles. Downstream from the inflow of East Willow Creek, an even more clear distinction occurred, and the ultrafiltrate and the 0.45-µm filtered concentrations were again near the lower detection limit for analysis.

Ultrafiltrate Fe concentrations essentially were less than detection along the entire study reach (fig. 7). However, the 0.45-µm filtrate concentrations were measurable and followed the pattern of total-recoverable Fe concentrations. The clear distinction between total-recoverable and ultrafiltrate Fe concentrations indicates the presence of colloidal Fe. As with Al, the difference between total-recoverable and 0.45-µm concentrations indicates the size distribution of colloidal particles, but also indicates the importance of ultrafiltration to determine truly dissolved Fe concentrations in a stream affected by mine drainage.

The importance of the Fe and Al colloids is seen by their effect on other metals. Zinc and Cu sorb to the Fe hydroxides (Runkel and others, 1999). The presence of Cu and Zn in the colloidal material could have effects on the chronic toxicity of the stream (Clements, 1994; Besser and others, 2001). Colloidal concentrations contribute to the high concentrations of Cu and Zn in the bed sediments of many streams affected by mine drainage (Kimball and others, 2002).

The pattern of Zn concentration in each of the filtrations differed substantially from the patterns of Al and Fe. Concentrations of Zn were essentially near detection from the beginning of the study reach to the area near the Amethyst Mine, where concentrations increased to more than 0.2 mg/L (fig. 8). Downstream from the inflow of the Nelson Tunnel at WW-4766, Zn concentration increased to more than 10 mg/L. The Nelson Tunnel inflow caused all the filtrate concentrations to increase, and they all decreased with the inflow of East Willow Creek at W-A'. This pattern indicates that Zn occurred in the dissolved, rather than the colloidal, phase. The concentration profile of Mn was very similar to that of Zn, but the concentration of Mn did not increase until inflow of the Nelson Tunnel joined the flow.

All the variations in stream chemistry are summarized in the biplot of principal component scores and loadings (fig. 9). Each of the chemical constituents used in the analysis is represented by an arrow, or vector, in the biplot. Each vector points in the direction of increasing concentration for a given constituent. For example, all the constituents except Fe increase from left to right on the diagram. The value of pH decreases (direction of increasing hydrogen ion concentration) in the direction of WW-NT and WW-4930 (group 6). Thus, the change along the PC1 axis represents the effects of mine drainage, namely, the lowering of pH and the increase of metal concentrations. Changes along the PC2 axis mostly represent variations in Fe concentration, but Al concentration also increases slightly in that direction. Note that total-recoverable Fe was used in the PCA, therefore this includes dissolved plus colloidal concentrations.

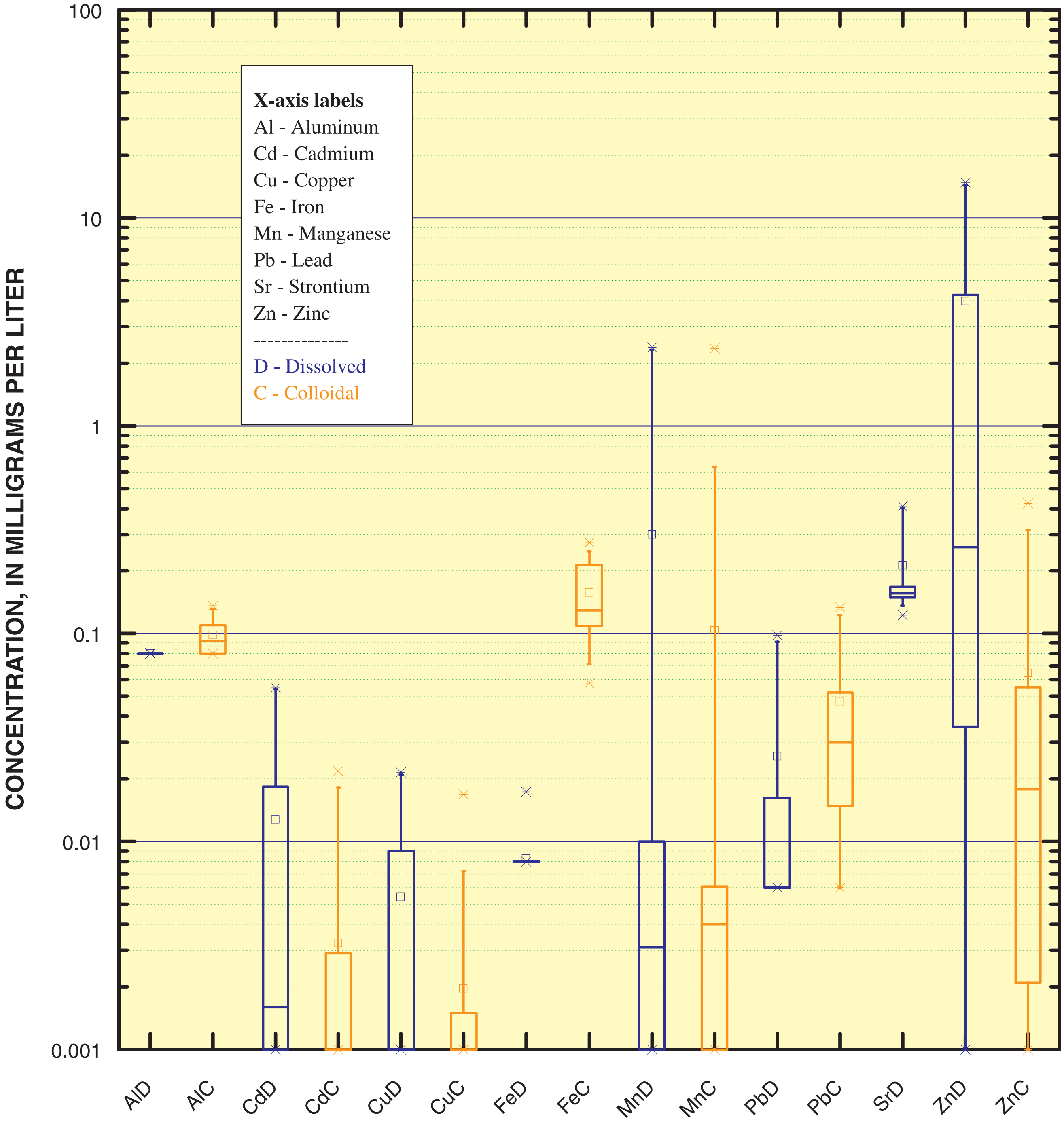

Figure 5. Distribution of dissolved (blue) and collodial (orange) metal concentrations in synoptic stream samples, West Willow Creek, Colorado, September 2000.

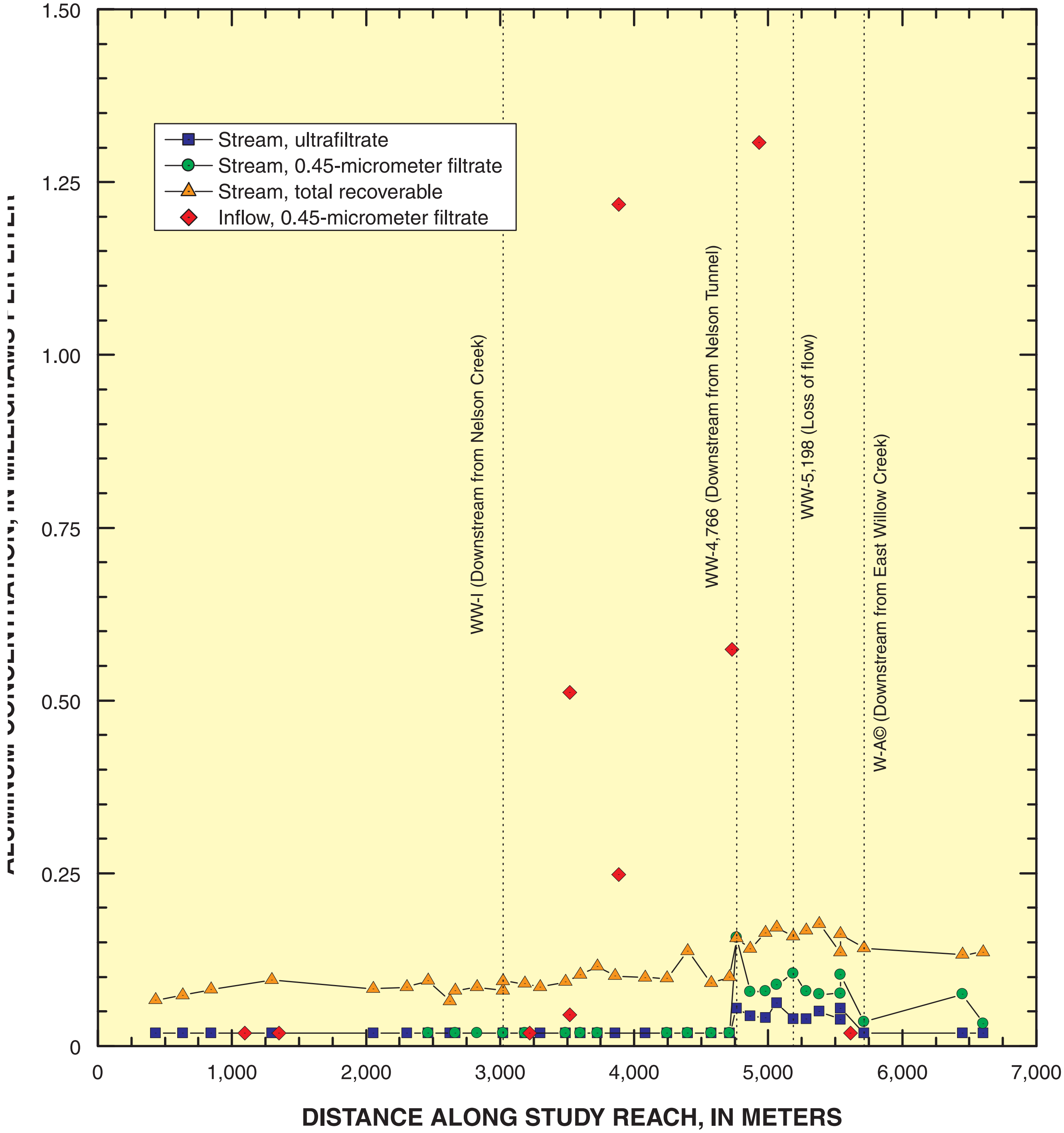

Figure 6. Variation of aluminum concentration in ultrafiltrate, 0.45-µm filtered, and total-recoverable samples with distance along the study reach, West Willow Creek, Colorado, September 2000.

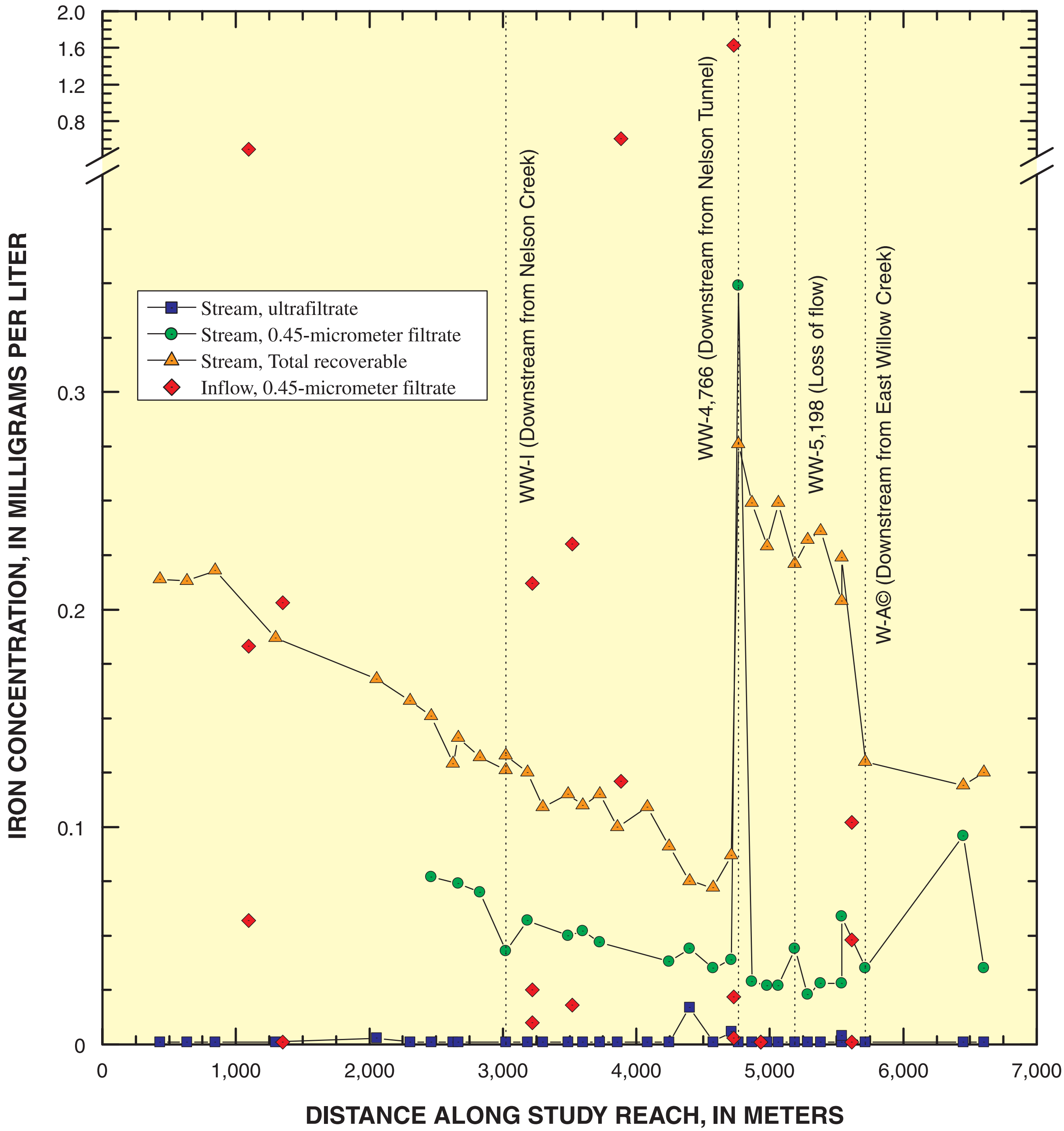

Figure 7. Variation of iron concentration in ultrafiltrate, 0.45-µm filtered, and total-recoverable samples with distance along the study reach, West Willow Creek, Colorado, September 2000.

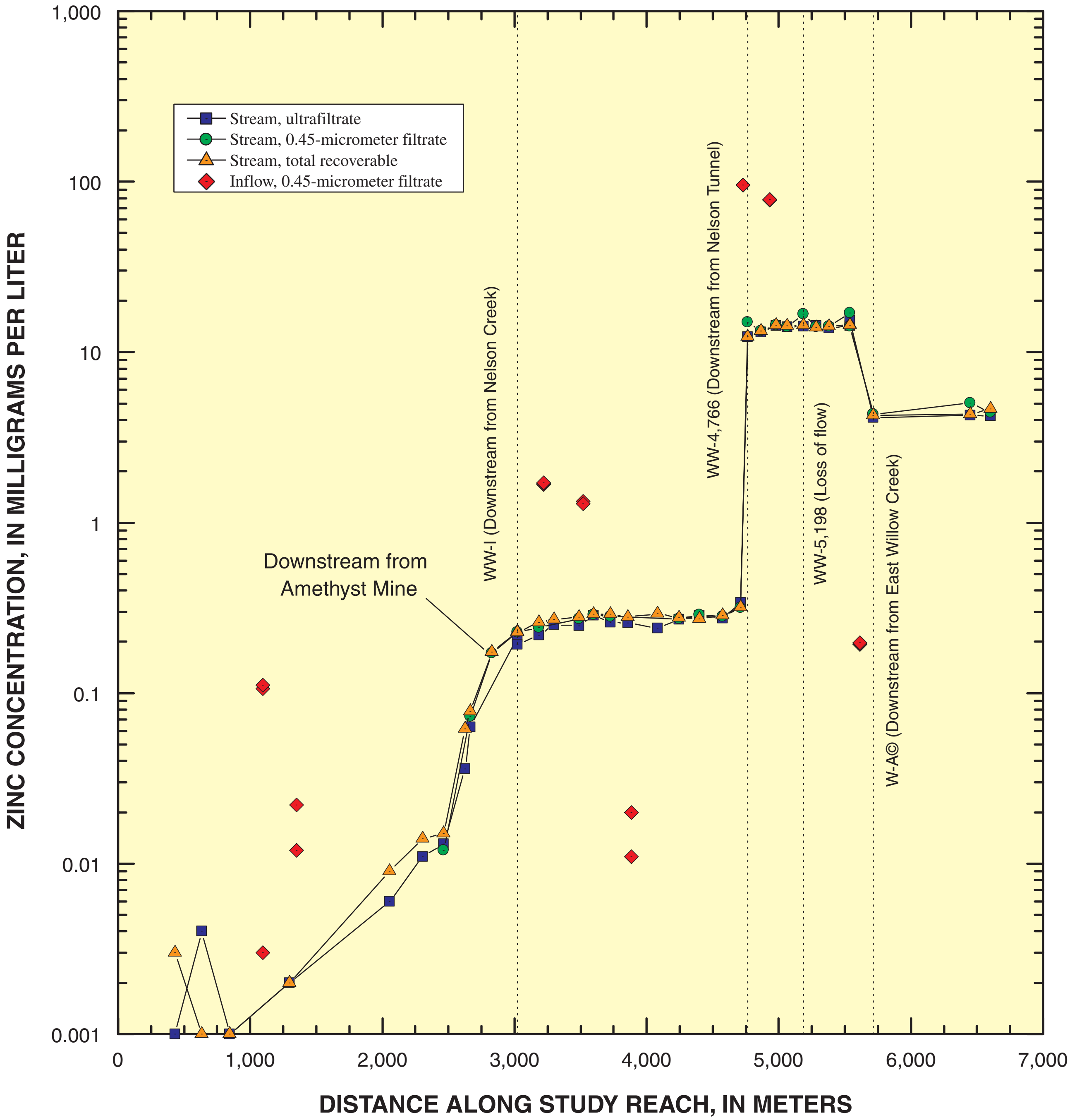

Figure 8. Variation of zinc concentration in ultrafiltrate, 0.45-μm filtered, and total-recoverable samples with distance along the study reach, West Willow Creek, Colorado, September 2000.

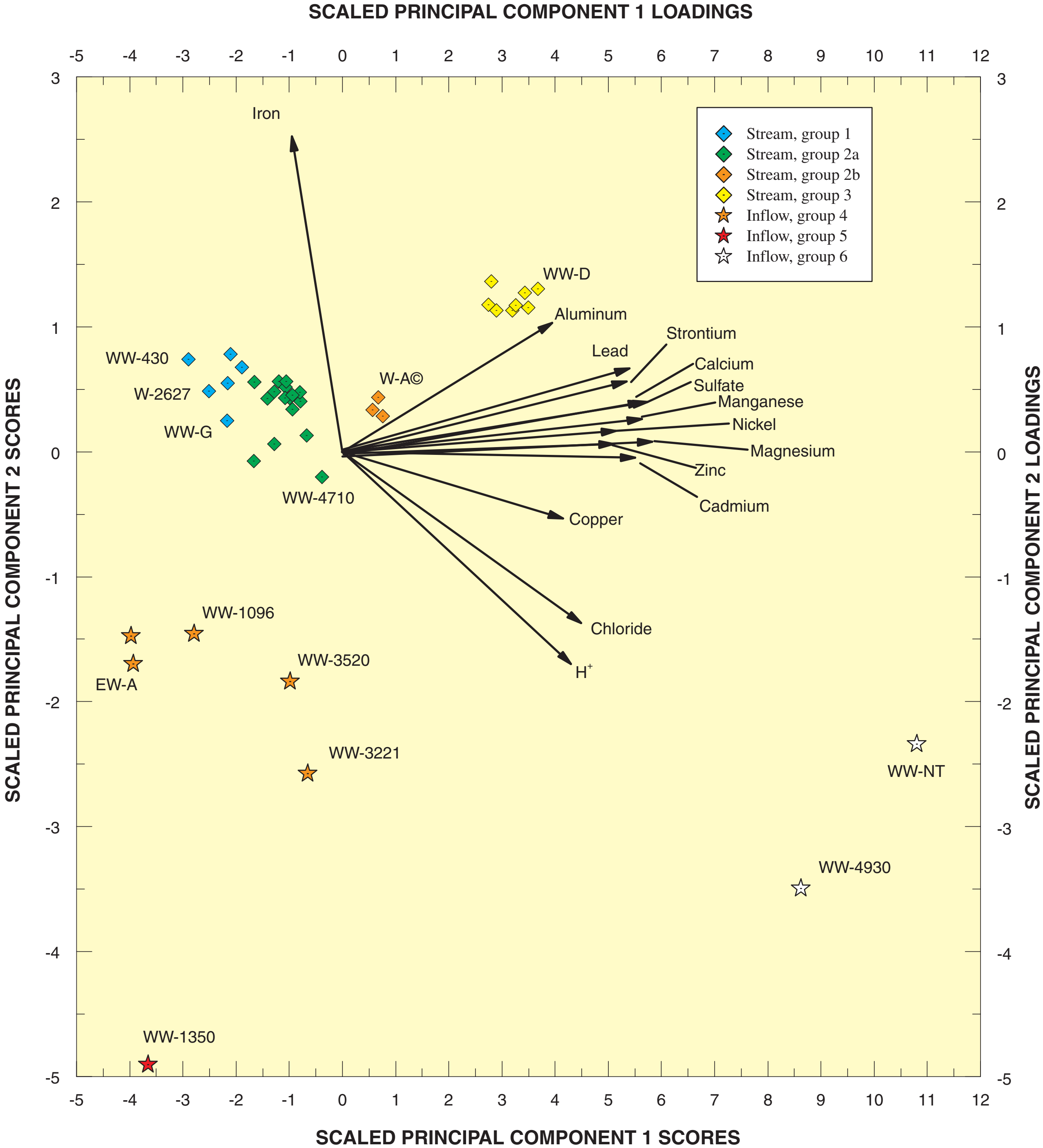

Figure 9. Biplot of principal component scores for synoptic samples and loadings for chemical constituents, West Willow Creek, Colorado, September 2000.

Within this framework of chemical changes, the classification of samples into the different groups indicates important changes along the study reach. Three groups of stream samples and three groups of inflow samples were distinguished (table 2). Stream samples of group 1 have the lowest concentrations of all the stream samples and represent water unaffected by mine drainage. In a sense, this group is like an inflow group, indicating the composition of recharge waters at the head of the stream. Inflows of group 4 also plot far to the left of the biplot and have relatively low concentrations of all the constituents. A unique sample, WW-1350, was sufficiently different to be considered separately as group 5, and had the lowest concentrations of all the constituents, but a lower pH. Two inflow samples make up group 6; these had the highest concentrations and lowest pH values among all the inflow samples. The effects of these inflow groups on the stream samples is evident by changes among groups of stream samples.

Table 2. Median composition of stream and inflow groups distinguished by principal components analysis, West Willow Creek, Colorado, September 2000

[Dis, dissolved; Col, colloidal; mg/L, milligrams per liter; LD, less than detection limit]

Constituent	Phase	Group 1 Stream-headwater samples	Group 2a Stream from Amethyst Mine to Nelson Tunnel	Group 2b downstream from East Willow Creek	Group 3 Stream from Nelson Tunnel to East Willow Creek	Group 4 Inflows—Dilute	Group 5 Inflow WW-1350	Group 6 Inflows—Nelson Tunnel and WW-4930 spring
pH, in standard units	Dis	8.02	7.94	7.59	7.67	7.13	6.99	4.96
Calcium, in mg/L	Dis	14.9	14.9	17.6	43.9	9.27	12.9	145
Magnesium, in mg/L	Dis	1.60	1.65	1.69	3.89	1.30	1.51	12.8
Sodium, in mg/L	Dis	4.15	3.81	4.66	10.1	2.47	2.86	33.2
Chloride, in mg/L	Dis	.160	.170	.220	.278	.260	.240	1.13
Sulfate, in mg/L	Dis	17.3	18.9	43.1	143	3.58	14.2	653
Alkalinity, in mg/L as $CaCO_3$	Dis	31.1	31.0	23.8	25.2	24.5	28.8	.245
Silica, in mg/L	Dis	17.0	17.3	19.2	18.1	17.8	17.3	28.2
Aluminum, in mg/L	Dis	.007	.006	.022	.045	.032	LD	.988
	Col	.061	.090	.120	.115	.032	LD	.988
Cadmium, in mg/L	Dis	.001	.001	.018	.038	.003	LD	.388
	Col	LD	LD	.003	.002	.003	LD	.388
Copper, in mg/L	Dis	LD	.004	.008	.005	.004	LD	.278
	Col	LD	LD	LD	LD	.004	LD	.278
Iron, in mg/L	Dis	LD	LD	LD	LD	.024	LD	.007
	Col	.186	.109	.125	.233	.024	LD	.007
Manganese, in mg/L	Dis	.021	.035	.636	2.42	.038	.038	13.1
	Col	LD	.003	.005	LD	.038	.038	13.1
Nickel, in mg/L	Dis	LD	LD	LD	LD	LD	LD	.009
	Col	LD	LD	LD	LD	LD	LD	.009
Lead, in mg/L	Dis	LD	LD	.012	.081	.004	LD	1.30
	Col	.001	.026	.047	.117	.004	LD	1.30
Strontium, in mg/L	Dis	.159	.152	.137	.395	.114	.113	1.24
	Col	LD	.005	.007	LD	.114	.113	1.24
Zinc, in mg/L	Dis	.002	.253	4.22	14.1	.194	.012	86.9
	Col	LD	.015	.122	.162	.194	.012	86.9

The first effect on stream samples is seen by the change from group 1 to group 2a. This change occurred downstream from the Last Chance Mine (WW-2304) and occurred in stream samples collected from upstream of the Amethyst Mine to the sample collected upstream from the Nelson Tunnel, WW-4710. A second group of stream samples with slightly higher concentrations is classified as group 2b and included the three samples collected downstream from the confluence of East and West Willow Creeks. The greatest shift in concentration among the stream samples occurred downstream from the inflow of the Nelson Tunnel (WW-NT). At that point, the samples shift to the higher concentrations measured in group 3. Thus, the stream samples change systematically to the right on the biplot with increasing concentrations from group 1 in the recharge area, to group 2a near the Amethyst Mine, to group 3 downstream from the Nelson Tunnel. Then the shift is back to the left, to group 2b, downstream from the confluence with East Willow Creek. This shift is in the direction of the East Willow sample, EW-A.

Load Profiles

Transferring chemical data into a hydrologic context provides information that can be useful for remediation decisions and for quantifying the physical, chemical, and biological processes that affect metal transport and availability. This hydrologic context comes from detailed spatial profiles of load that are possible from combining the tracer-injection study with synoptic sampling for chemistry. As defined in the “Methods” section, load profiles provide the sampled instream load, which yields the data on net loading or attenuation for each stream segment. These data can be used to calculate the cumulative instream load, which gives the best estimate of the total loading for an element in a study reach. An evaluation of how well the sampled inflows account for the cumulative instream load comes from the cumulative inflow load. The cumulative instream load is calculated from total-recoverable concentrations, but sampled instream load can be calculated by using the dissolved or colloidal concentrations. This permits an evaluation of instream chemical reactions.

A summary of load calculations for selected metals in West Willow Creek is listed in table 3. Values in table 3 come from the load profiles of each solute. The five stream segments that have the greatest loading are indicated in each column. Concentrations of Cu and Ni were too low to be able to calculate load profiles, therefore, they are not included in table 3.

As an example of how the profiles are used, the load profile of Al (fig. 10) shows five different curves, as described in the “Methods” section. Cumulative instream load is the best estimate of the total quantity of a metal entering the stream along the study reach, which was 9.17 kg/day for total Al. Cumulative inflow load shows whether or not the sampled inflows account for that total instream load. For Al, the cumulative inflow load was only 33 percent of the cumulative instream load. Subtracting the inflow load from the instream load gives the unsampled load, which was 67 percent for Al. The difference between the cumulative instream load and the total instream load, including both dissolved and colloidal load, is the amount of attenuation along the study reach. This was 27 percent of the cumulative instream load for Al. Only a small part of that attenuation was from the loss of load at WW-5189 because Al concentrations were low.

Cumulative instream loads varied considerably among these solutes (table 3). Because SO_4 is a product of pyrite oxidation as well as the oxidation and dissolution of other metal-bearing sulfide minerals, it commonly has a much greater load than any of the metals. However, SO_4 can be added to the stream through dissolution reactions of gypsum or anhydrite, which may be present as accessory minerals. Among the metals, Zn and Mn have substantially greater loads than the others. In fact, the cumulative instream load of Zn is one of the highest of all the watersheds in the Rocky Mountains where tracer-injection studies have been used to quantify loadings (Kimball and others, 1994; Kimball and others, 1999a; Kimball and others, 1999b; Cleasby and others, 2000; Kimball and others, 2001; Kimball and others, 2002).

Table 3. Summary of load calculations, West Willow Creek, Colorado, September 2000

[Loads reported in kilograms per day, except for percent values; italicized bold numbers in parentheses indicate rank for the five greatest loads of each constituent]

Segment ID	Distance, in meters	Aluminum	Cadmium	Iron	Manganese	Lead	Strontium	Zinc	Sulfate
WW-430 (T-0)	430	***(3)***0.527	0.015	***(3)***1.71	0.193	0.014	***(2)***1.27	0.022	***(4)***139
WW-634	634	.056	.003	-.015	-.018	.015	.065	.016	-.239
WW-846	846	.067	-.008	.040	-.002	-.020	-.140	-.033	.638
WW-1296	1,296	.115	.018	-.244	.168	.045	.110	.009	-1.04
WW-1729	1,729	.000	.000	.000	.000	.000	.000	.000	.000
WW-2054	2,054	-.086	-.011	-.115	-.023	.073	.041	.056	4.02
WW-L	2,304	.059	-.002	-.015	.071	.054	-.000	.054	8.04
WW-2464	2,464	.075	-.003	-.060	.062	-.016	.104	.007	.259
WW-2627	2,627	-.257	-.001	-.187	.087	-.150	-.155	.400	2.33
WW-K	2,667	.140	.017	.107	-.228	***(5)***.203	.112	.143	1.24
WW-J	2,829	.000	.000	.000	.000	.000	.000	.000	.000
WW-I	3,021	.098	.023	-.035	.057	.145	-.030	1.42	17.2
WW-3186	3,186	.067	.008	.004	-.018	.043	.097	.385	8.30
WW-3299	3,299	-.018	.000	-.115	.162	-.072	.027	.196	10.2
WW-3489	3,489	.087	.004	.075	-.152	.036	-.002	.117	.540
WW-3600	3,600	.114	.006	-.041	-.037	.031	.100	.145	1.10
WW-3728	3,728	.127	-.002	.061	.259	-.002	.001	.032	1.48
WW-HH	3,858	-.126	-.001	-.141	-.136	-.083	-.090	-.090	2.83
WW-4081	4,081	.001	.029	.120	-.020	.009	.042	.219	3.53
WW-H	4,245	.025	-.023	-.158	-.041	.071	.101	-.087	6.29
WW-4401	4,401	***(4)***.443	-.056	-.161	.062	-.284	-.084	.152	.093
WW-G	4,577	-.486	.000	-.017	.204	-.071	.110	.073	6.73
WW-4710	4,710	.099	.069	.169	-.197	***(3)***.315	.201	.624	1.61
WW-F	4,766	***(2)***.934	***(1)***.475	***(2)***2.65	***(1)***28.4	***(1)***2.26	***(1)***3.04	***(1)***158	***(1)***1,540
WW-4866	4,866	-.134	-.195	-.221	***(2)***4.93	.062	***(5)***.448	***(4)***19.8	***(2)***174
WW-4980	4,980	***(5)***.374	***(5)***.137	-.184	***(3)***2.87	.166	.160	***(3)***21.2	***(5)***98.4
WW-D	5,063	.134	***(3)***.297	***(5)***.312	-.583	.133	.125	-1.10	17.0
WW-5189	5,189	-.646	-.407	-1.04	-6.24	-.846	-1.18	-39.7	-417
WW-B	5,282	.101	***(4)***.214	.133	-3.26	***(4)***.176	.056	-.411	1.24
WW-5383	5,383	.125	.020	.069	.074	.044	-.064	-.100	11.2
WW-A	5,540	-.288	-.076	-.211	***(5)***1.76	-.160	.279	1.3	25.0
W-A	5,716	***(1)***5.22	***(2)***.387	***(1)***3.90	3.44	***(2)***.913	***(3)***2.00	***(2)***36.2	***(3)***433
EW-5892	6,450	-.461	-.010	-.545	-.633	-.506	-.712	3.91	23.1
EW-6044	6,602	.177	.118	***(4)***.319	***(4)***2.64	.113	***(4)***.663	***(5)***15.5	4.91
Cumulative instream load		9.17	1.84	9.66	45.5	4.92	9.16	269	2,540
Cumulative inflow load		3.07	.890	2.68	37.5	3.29	6.55	215	2,200
Percent inflow load		33	48	28	82	67	72	80	87
Attenuation		2.5	.790	3.51	11.6	2.21	2.47	41.6	418
Percent attenuation		27	43	36	25	45	27	15	16
Unsampled inflow		6.10	.950	6.98	8.00	1.63	2.61	54.0	340
Percent unsampled inflow		67	52	72	18	33	28	20	13

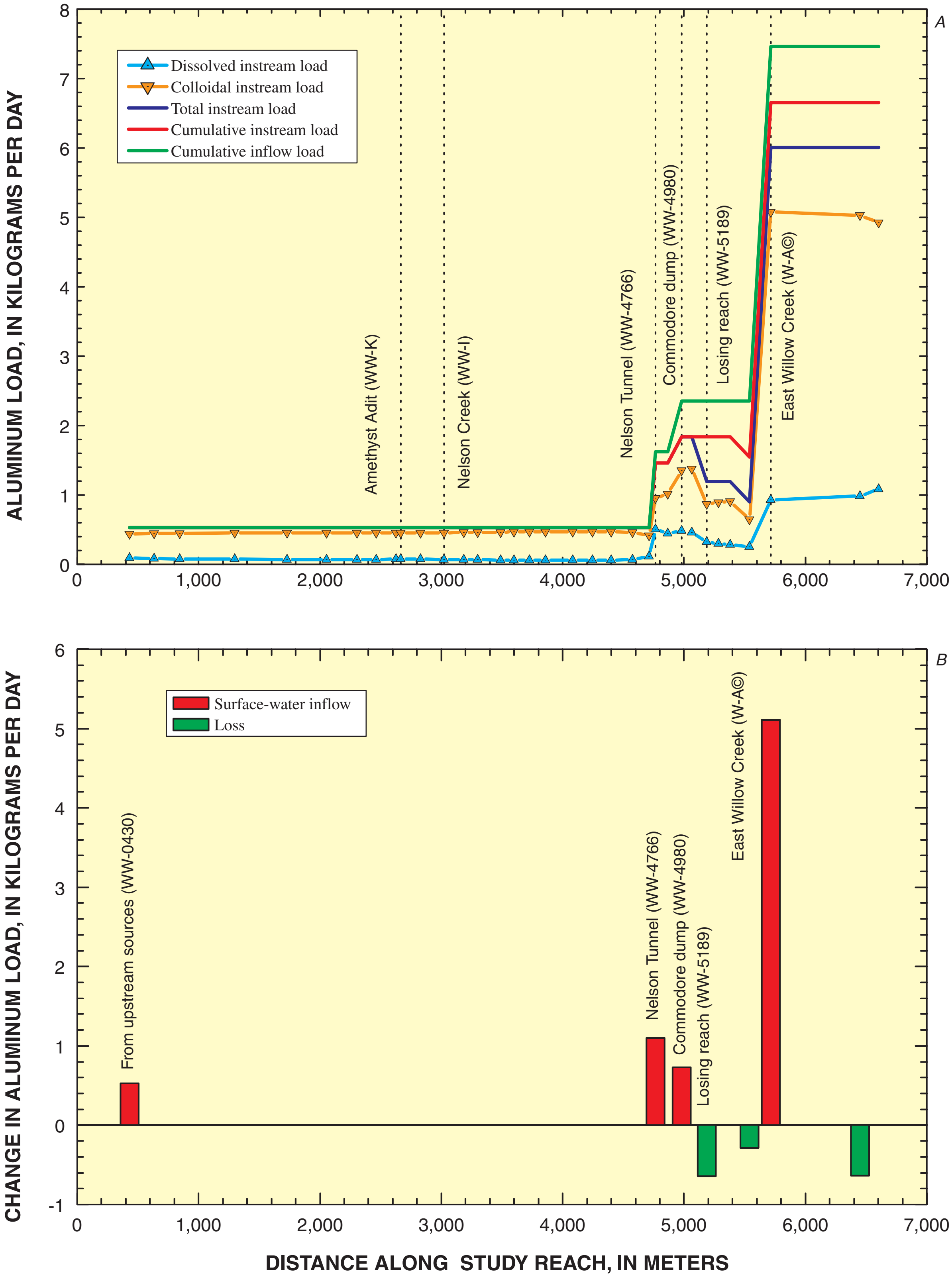

Figure 10. (A) Variation of aluminum load with distance and (B) changes in aluminum load for individual stream segments, West Willow Creek, Colorado, September 2000.

Differences in the amount of unsampled inflow were noted among the solutes. The unsampled inflows of Mn, Sr, Zn, and SO_4 were much smaller than those of Al and Fe (table 3). This grouping is consistent with the geochemical behavior of these solutes. Aluminum and Fe are among the most reactive constituents and Mn, Zn, and SO_4 are less reactive. Thus, Mn, Zn, and SO_4 were not lost from the aqueous phase during transport to the stream from metal sources away from the stream. For this same reason, Zn and SO_4 had the least amount of attenuation in the stream. Attenuation of Mn was measurable, but much less than attenuation of Al, Cd, Fe, and Pb. Given these general characteristics of loading, the loading profiles mostly fall into two groups that include Mn, Zn, and SO_4 in one group and Al, Fe, and Cd in another. Strontium and Pb had characteristics of both groups.

Loading profiles for Mn (fig. 11), Zn (fig. 12), Sr (fig. 13), and SO_4 (fig. 14) are dominated by loading from the Nelson Tunnel (accounted for at stream site WW-F), and the substantial loading in the two stream segments just downstream from the Nelson Tunnel (WW-4866 and WW-4930). The inflow at WW-4866 was “unsampled” inflow for Mn, Zn, and SO_4 (figs. 11B, 12B, and 14B). White Al precipitate in a sampled inflow in segment WW-4930 coated logs and rocks before the inflow entered the stream. Both Sr and SO_4 have sources from non-ore minerals, and their loading profiles indicate sources upstream from the beginning of the study reach.

Although substantial loads of Al (fig. 10) and Fe (fig. 15) were added to West Willow Creek by the Nelson Tunnel discharge, East Willow Creek also had substantially greater loads of these solutes. East Willow Creek also was an important source for Cd (fig. 16) and Pb (fig. 17). Much of the cumulative instream load for Fe came from unsampled inflow, similar to the load for Al. If the loads come from dispersed, subsurface inflow, the Al and Fe can enter the stream before being removed if they have remained soluble in the subsurface. Once in the stream, however, they have a tendency to precipitate and form colloidal particles. This is evident by the relatively large percentage of Al and Fe that were removed by attenuation. Slightly greater percentages of Cd and Pb were removed, and this was most likely through sorption to the Fe colloidal material that was formed.

Principal Locations of Mass Loading

Net instream load for each stream segment allows for a ranking of segments according to their contribution of mass to the stream. Mass of a constituent, not its concentration in an inflow, determines the real effects on the stream (Kimball and others, 2002). The change in mass for any stream segment can be divided by the cumulative instream load to give a percentage of the total load contributed by each segment. However, this percentage may be affected by a net loss of solute for a stream reach. For example, stream segments with sampled inflows may have a positive inflow load and yet may have a negative instream load because chemical reactions are fast enough to remove the solutes before transport to the downstream end of the stream segment.

Two clear patterns emerge from these loadings (table 3). First, the Nelson Tunnel (accounted for at WW-F) contributed the greatest loads of Cd, Mn, Pb, Sr, Zn, and SO_4. Generally, this was greater than 50 percent of the load along the study reach. For some of these solutes, the Nelson Tunnel contributed about 10 times the load contributed by any other stream segment. Not only did the Nelson Tunnel contribute the majority of load for most solutes, but there were also substantial loads contributed for Cd, Mn, Pb, Zn, and SO_4 in the two segments downstream from the Nelson Tunnel (WW-4866 and WW-4980). These loads could result from leakage of Nelson Tunnel discharge into the large waste-rock pile at the Commodore Mine and then discharge of this leakage to the stream.

The second pattern is that Al and Fe, and to some extent Pb and Sr, are substantially contributed in the stream segment that includes East Willow Creek (W-A'). For each of these solutes, except Sr, this contribution was mostly transformed to the colloidal phase within the stream segment W-A'. The majority of this load, however, was unsampled inflow. It is not clear if this unsampled inflow came from the discharge of East Willow Creek, or perhaps upwelling of water from the drainage of East Willow, West Willow, or both.

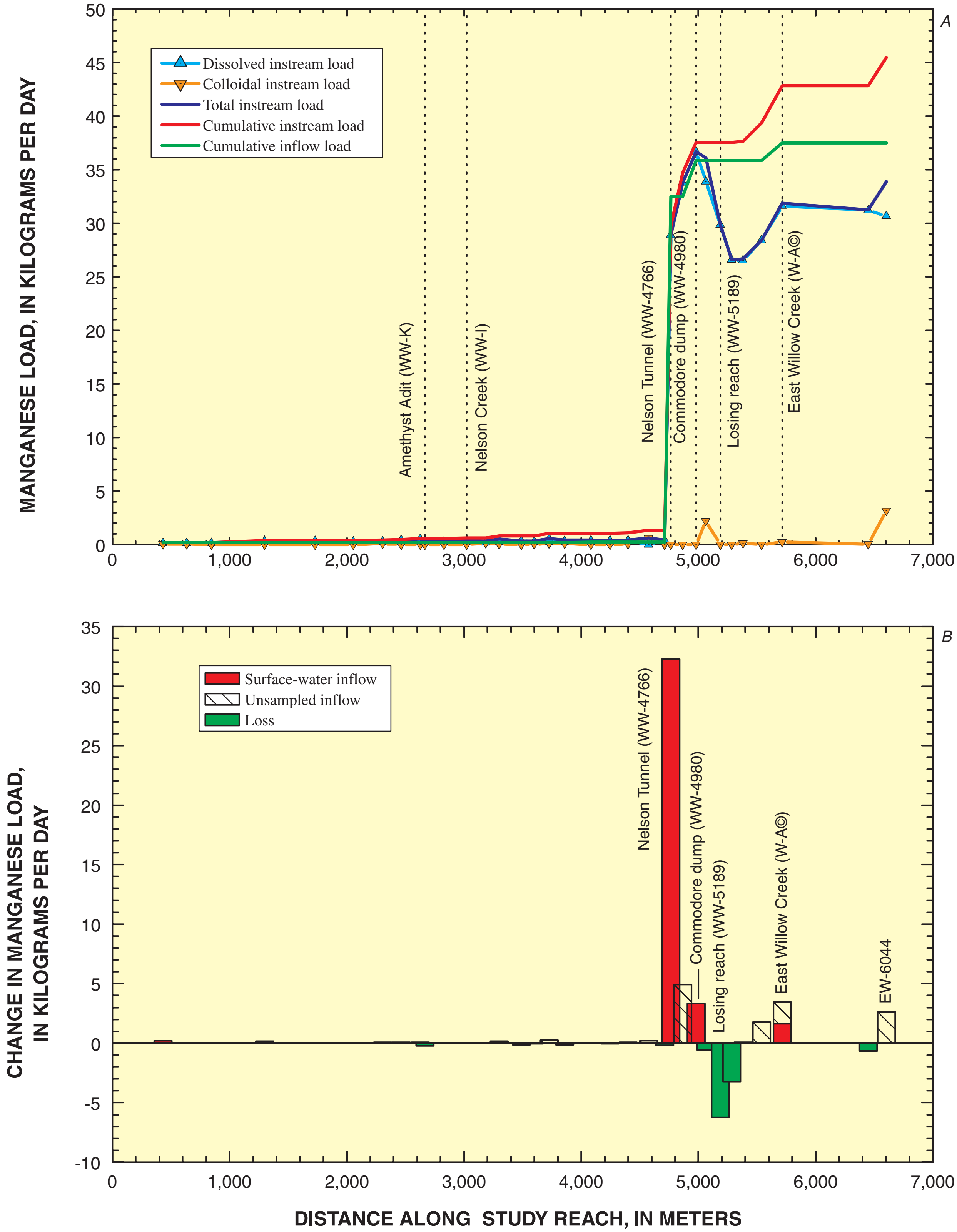

Figure 11. (A) Variation of manganese load with distance and (B) changes in manganese load for individual stream segments, West Willow Creek, Colorado, September 2000.

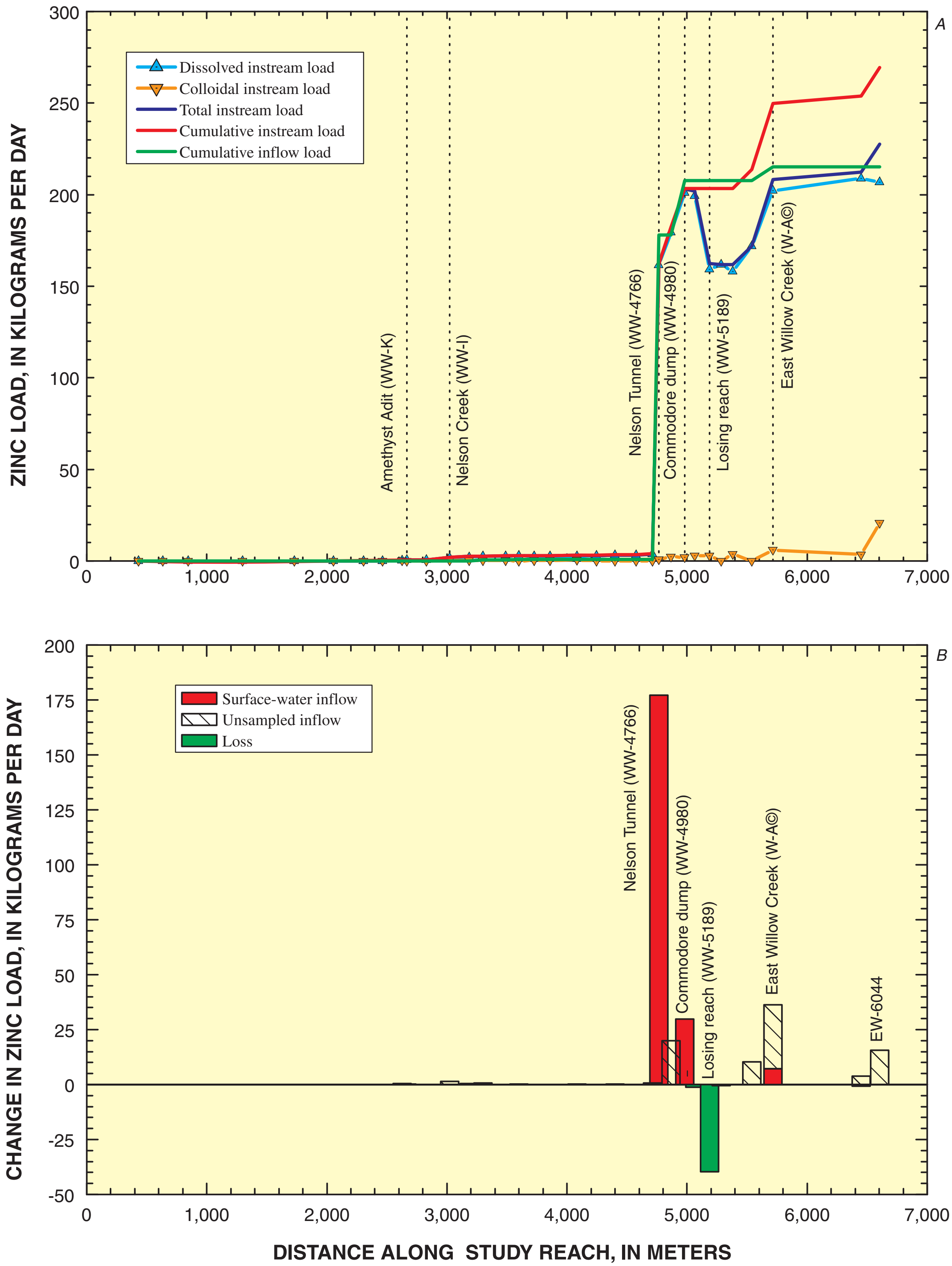

Figure 12. (A) Variation of zinc load with distance and (B) changes in zinc load for individual stream segments, West Willow Creek, Colorado, September 2000.

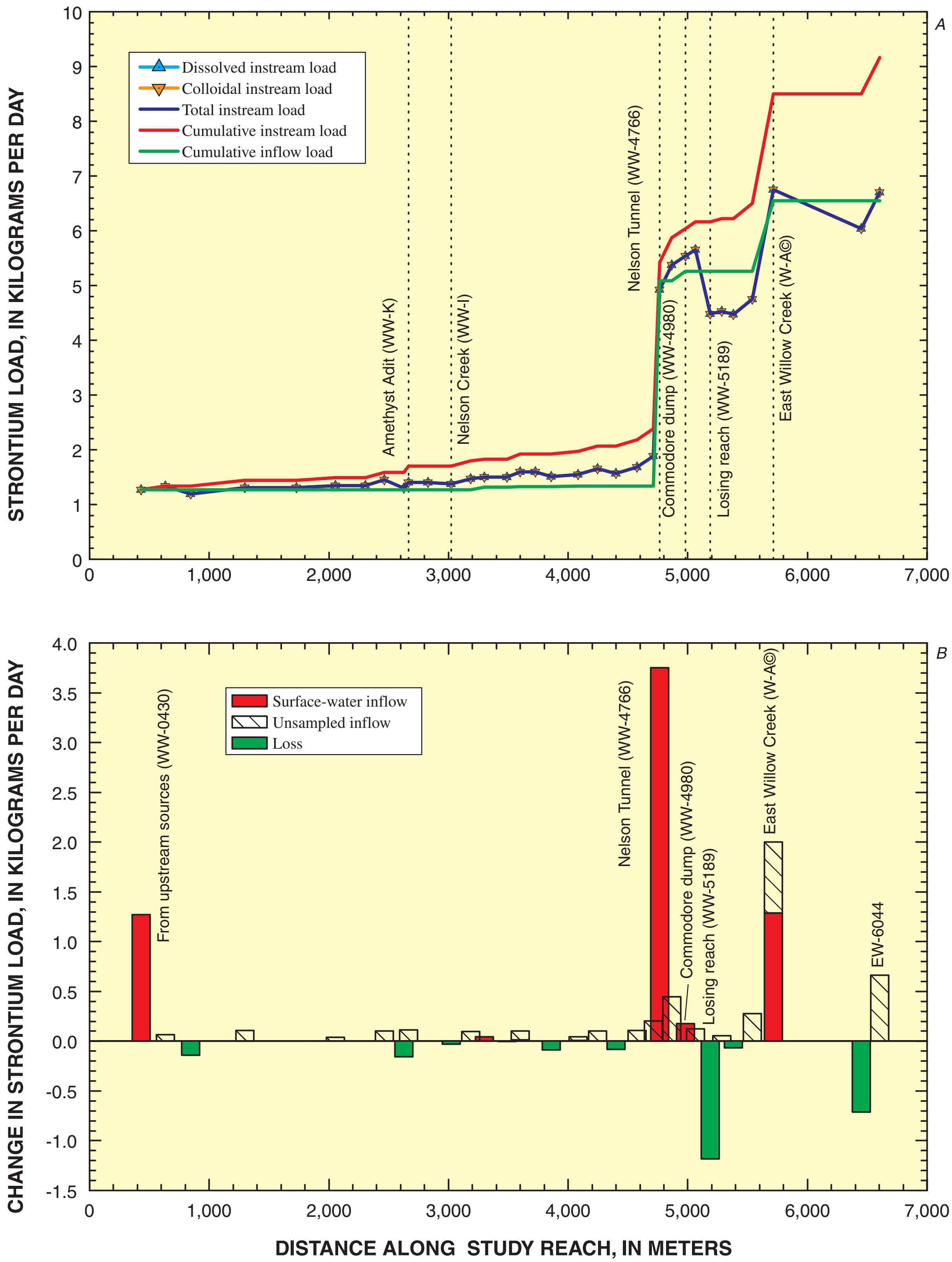

Figure 13. (A) Variation of strontium load with distance and (B) changes in strontium load for individual stream segments, West Willow Creek, Colorado, September 2000.

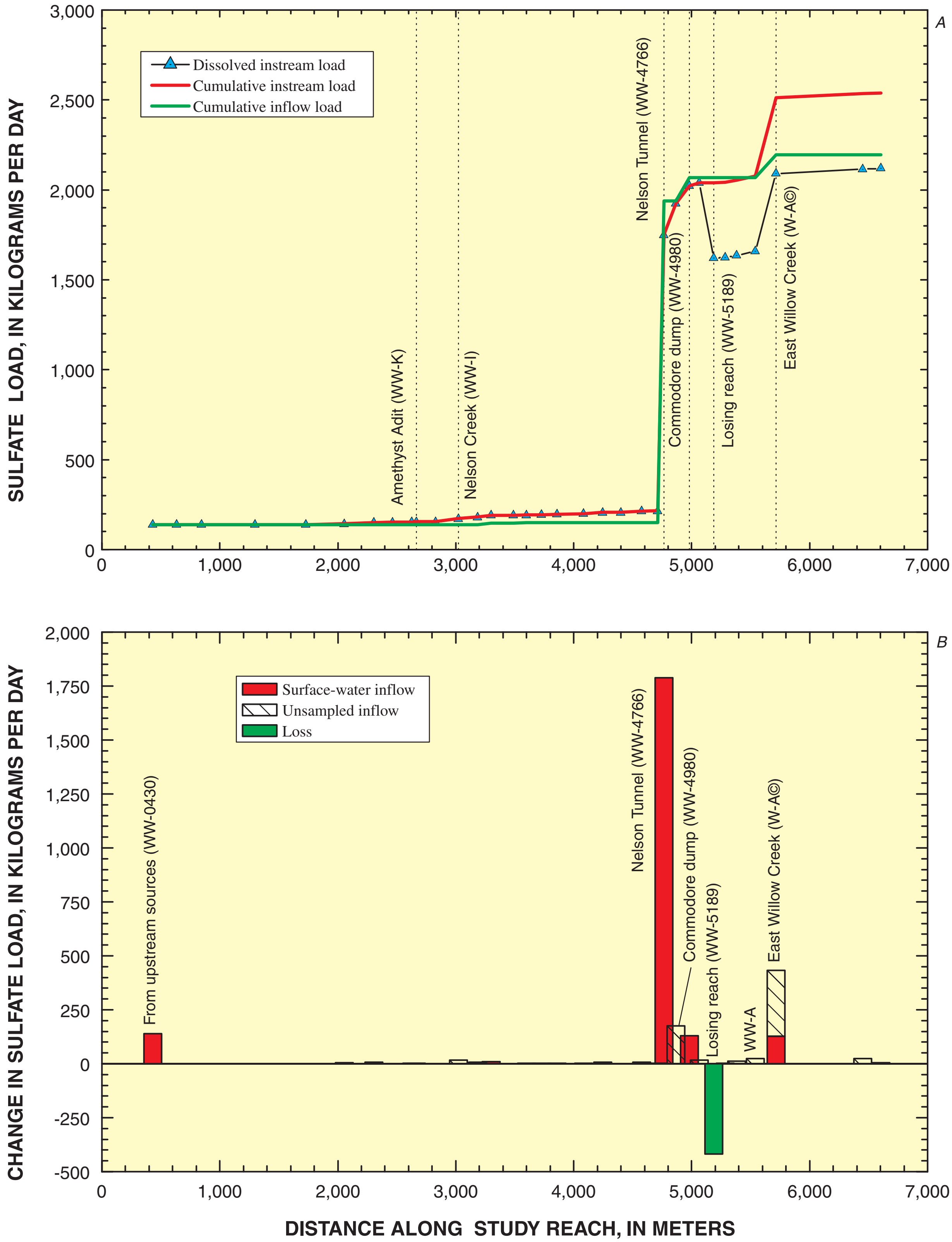

Figure 14. (A) Variation of sulfate load with distance and (B) changes in sulfate load for individual stream segments, West Willow Creek, Colorado, September 2000.

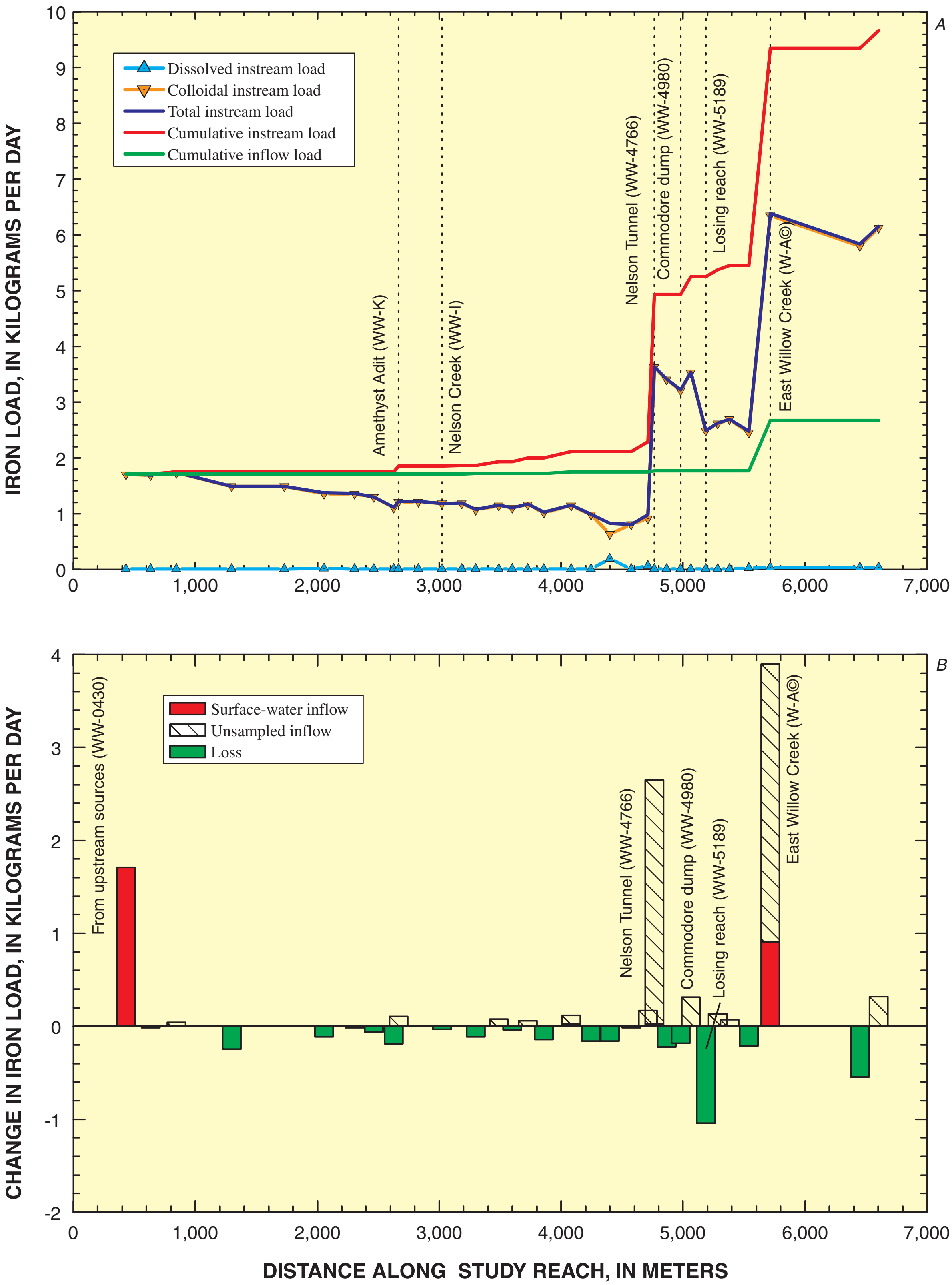

Figure 15. (A) Variation of iron load with distance and (B) changes in iron load for individual stream segments, West Willow Creek, Colorado, September 2000.

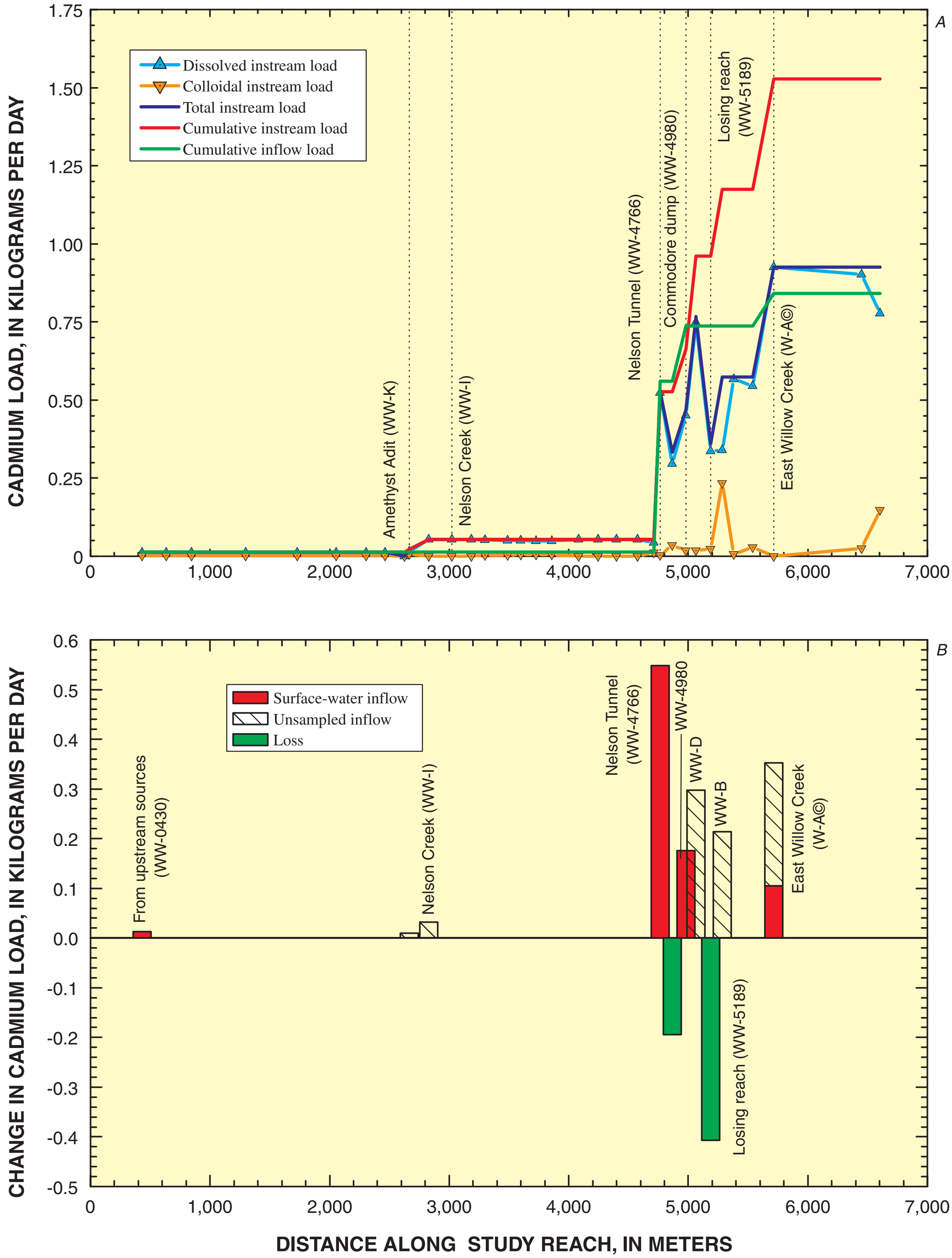

Figure 16. (A) Variation of cadmium load with distance and (B) changes in cadmium load for individual stream segments, West Willow Creek, Colorado, September 2000.

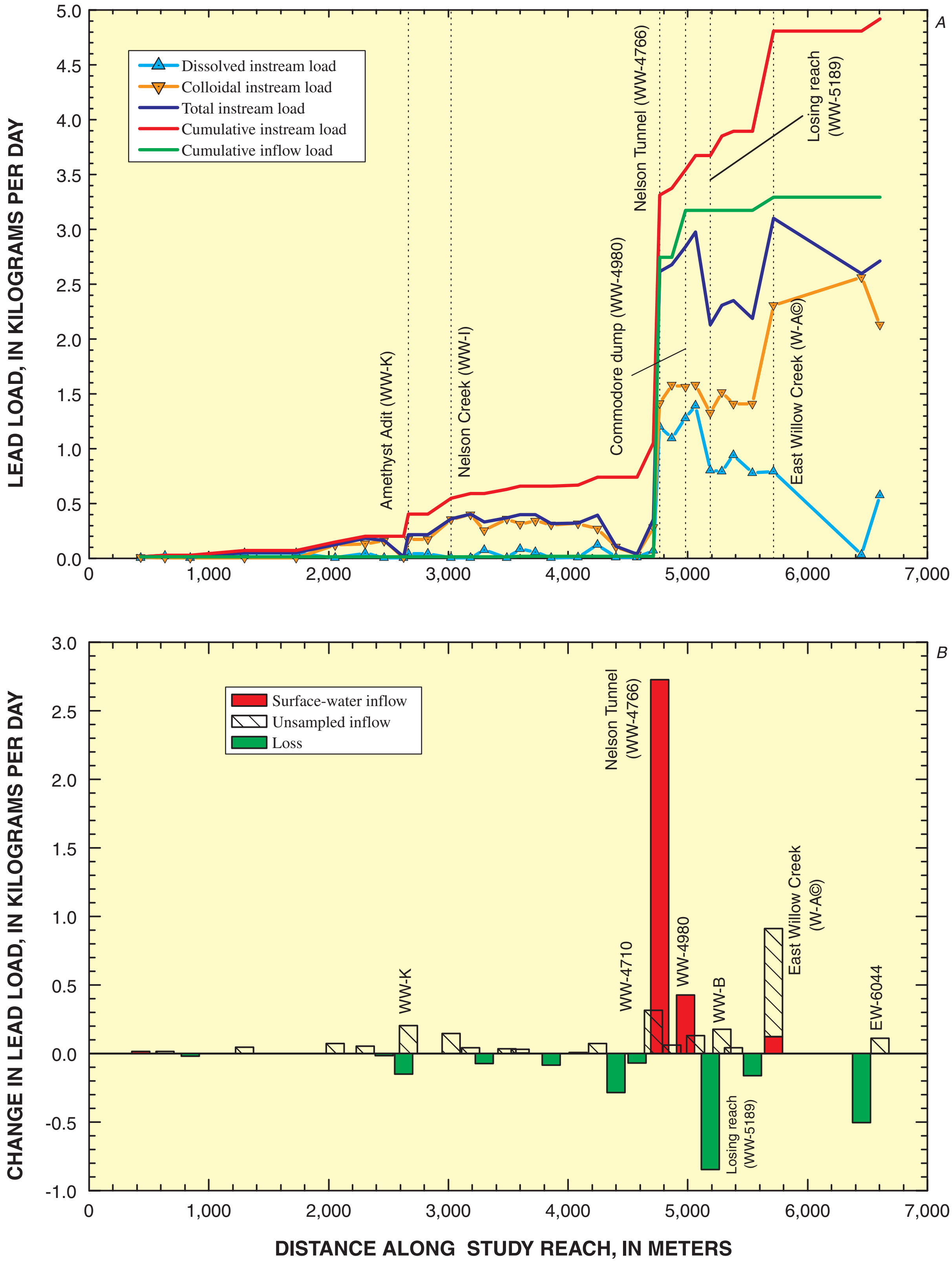

Figure 17. (A) Variation of lead load with distance and (B) changes in lead load for individual stream segments, West Willow Creek, Colorado, September 2000.

Unsampled Inflow

There were three locations with considerable amounts of unsampled inflow (figs. 10-17). The first was segment WW-4866, downstream from the Nelson Tunnel. Unsampled inflow of Mn, Sr, Zn, and SO_4 occurred in this segment. As noted above, this unsampled inflow was likely from infiltration of Nelson Tunnel discharge and subsequent discharge downstream. It also could be from an alternative pathway from the mine workings to the stream. The second location was at the confluence of East and West Willow Creeks, segment W-A'. The unsampled inflow was greatest for Al, Fe, and Pb in that segment. Loading from subsurface water in this segment could be from East or West Willow, or both. Data from these tracer studies cannot distinguish between the two sources. The third location of unsampled inflow was in the last segment of the study reach, EW-6044. This loading could represent subsurface inflow from Windy Gulch and was most important for Mn, Sr, and Zn. It is not possible to distinguish the inflow between Windy Gulch and other possible sources because it could also be from mine wastes within the Willow Creek drainage. Most of the alluvial material near the end of the canyon has been reworked and could contain source material.

Attenuation of Load

Attenuation of metal loads ranged from a high of 45 percent for Pb, to 15 percent for Zn (table 3). In an Fe-rich system where there is abundant formation of Fe colloids, it is common to see substantial metal attenuation (Kimball and others, 1994). In West Willow Creek, pH was greater than 7.0, even downstream from metal-rich inflows. At this pH, it would be reasonable to expect substantial sorption of metals to the iron hydroxide colloids. Yet, relatively little attenuation occurred. After the inflow of the Nelson Tunnel discharge and the two subsequent stream segments that had substantial unsampled inflow, some attenuation of Cd, Fe, Mn, and Zn occurred in segments WW-5189, WW-B, WW-5383, and WW-A. Subsequently, downstream from the inflow of East Willow Creek, in segments W-A' and EW-5892, attenuation of Fe, Mn, Pb, and Sr was measurable. No attenuation of SO_4 occurred, however, which is consistent with the pH value greater than 7.5 in these stream segments.

East Willow Creek

Load profiles from West Willow Creek indicated increases in the load of some constituents in the segment that included the inflow of East Willow Creek. To determine where these loads originated in East Willow Creek, a tracer injection was used to identify possible sources in that drainage.

The East Willow Creek tracer injection covered a 6,044-m section of the Willow Creek watershed, starting upstream from the Outlet Mine and continuing past the confluence with West Willow Creek to the gaging station just upstream from the town of Creede (fig. 2). There were no major inflows to the stream along the study reach, but discharge did increase from some discharge of dispersed, subsurface flow and mine-drainage tunnels. The Solomon Mine was the principal mine drainage entering the stream in the study reach.

The 6,044-m study reach was divided into 21 segments by the stream sampling sites (fig. 2). Stream segments bracketed 12 inflow samples, but there likely were areas of subsurface inflow also bracketed by stream samples. Segment designations, downstream distance, and information about the sampling sites are listed in table 4. Only 9 stream segments contained sampled inflows; the other 12 segments had no sampled inflow.

Discharge

A NaBr tracer with a Br concentration of 151,250 mg/L was injected at a rate of 0.004 L/s. The systematic decrease of Br concentration downstream from the injection site allowed the calculation of discharge at each of the stream sampling sites (fig. 18). The increase in discharge along the study reach was from 341 L/s at the injection site to 619 L/s at the downstream gage. West Willow Creek accounted for 199 L/s of the increase, or 72 percent. Discharge increased by 79 L/s upstream from the confluence with West Willow Creek, and 39 percent of that increase was from segments that had no sampled inflows.

Table 4. Synoptic sampling sites, East Willow Creek, Colorado, August 2000

[Distance, in meters along the study reach; dashed line indicates samples that were collected upstream from the confluence with West Willow Creek]

Site designation	Source	Distance, in meters	Site description	pH, in standard units	Discharge, (in liters per second
EW-T0	Stream	947	Upstream from injection site	7.90	341
TRN	Inflow	1,079	Left bank drainage through culvert	7.78	.10
TRS	Inflow	1,129	Spring discharging from hill	7.57	.10
EW-K	Stream	1,157	East Willow Creek upstream from Outlet Mine	7.91	341
EW-J	Stream	1,447	T1-East Willow Creek downstream from Outlet Mine	7.90	348
EW-1807	Stream	1,807	Along road to check for ground-water inflow	7.92	350
EW-2175	Stream	2,175	In canyon to check for ground-water inflow	8.03	350
EW-I	Stream	2,405	Upstream from Solomon and Ridge Mines	7.95	353
PC	Inflow	2,695	Pipe on left bank	7.18	4.4
EW-H	Stream	2,735	Upstream from Solomon wetland	7.91	358
SMA	Inflow	2,790	Solomon adit	4.71	.10
EW-2830	Inflow	2,811	Spring discharge from Solomon Tunnel	7.02	2.25
EW-2825	Inflow	2,825	Drainage from Solomon ponds along road	5.68	2.25
EW-2995	Stream	2,995	T2 - Stream downstream from Solomon ponds	7.95	363
EW-G	Stream	3,135	Downstream from Solomon tailings	8.01	367
EW-3525	Stream	3,525	Upstream from spring on right bank at base of talus	7.79	373
EW-3533	Inflow	3,533	Spring from talus slope	7.33	6.23
EW-E	Stream	3,602	East Willow Creek as valley gets constricted	7.90	380
EW-D	Stream	3,970	East Willow Creek upstream from old diversions	7.93	385
SWI	Inflow	4,015	Discharge at concrete diversion structure	7.33	5.74
EW-4107	Stream	4,107	Upstream end of culvert	7.62	391
EW-4121	Inflow	4,121	Small spring downstream from culvert	7.33	7.39
EW-C	Stream	4,157	East Willow Creek upstream from Mammoth adit	7.73	398
MA	Inflow	4,183	Pipe upstream hill discharging Mammoth adit flow	7.66	17.3
EW-B	Stream	4,613	East Willow Creek upstream from North Creede site	7.62	416
EW-A	Stream	4,968	T3-East Willow Creek near mouth	7.67	419
WW-A	Inflow	5,056	West Willow Creek near mouth	7.23	199
W-A	'Stream	5,158	Willow Creek downstream from confluence	7.45	618
EW-5292	Stream	5,292	Willow Creek in reaction zone	7.34	618
EW-5492	Stream	5,492	Willow Creek upstream from braids and dam	7.47	618
EW-5892	Stream	5,892	Willow Creek upstream from pond near Windy Gulch	6.79	618
EW-5944	Inflow	5,944	Drainage from right bank pond near Windy Gulch	7.06	1.07
EW-6044	Stream	6,044	Willow Creek at Army Corps of Engineer gage	7.12	619

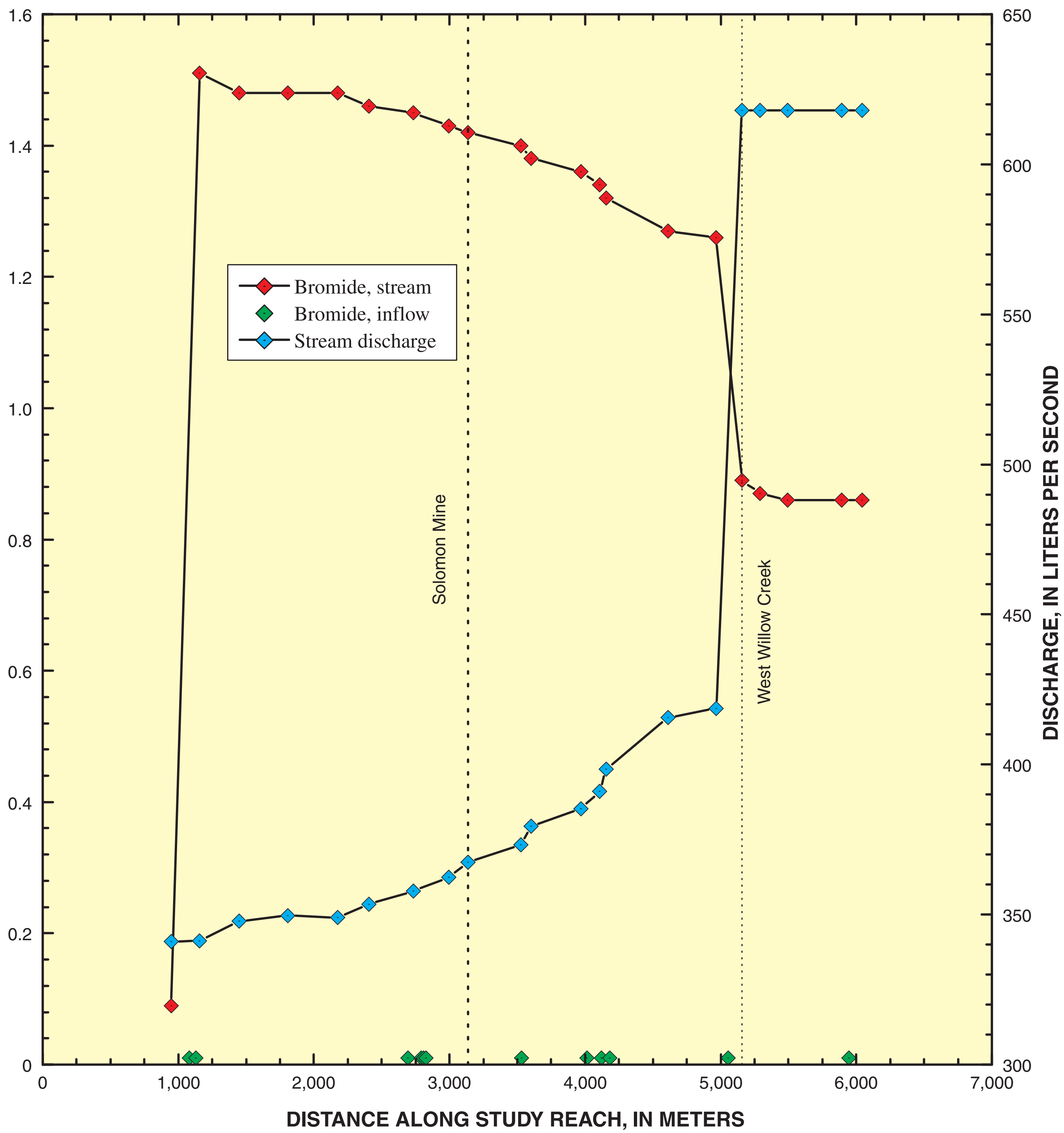

Figure 18. Variation of bromide concentration and calculated discharge, East Willow Creek, Colorado, August 2000.

Chemical Characterization of Synoptic Samples

Analysis of synoptic samples collected along East Willow Creek indicates that the pH along the study reach to the confluence with West Willow Creek was near 8.0 (fig. 19A) and that the principal ions were Ca, Na (not shown in figure), and HCO_3 (fig. 19B). These major ions result mostly from weathering of non-ore minerals. In these upper reaches, the SO_4 concentration of East Willow Creek is very low, indicating little effect from sulfide minerals. Downstream from the confluence with West Willow Creek, pH was less than 7.5 and the dominant ions were Ca and SO_4. The sample at W-A' represents the mixing of East and West Willow Creeks.

Metal concentrations were high in some of the synoptic samples, but considerably lower than in West Willow Creek (fig. 20). Concentrations of dissolved Zn were the highest among the metals, with a maximum concentration of 4.1 mg/L, and a median of 0.11 mg/L. Colloidal concentrations of Al, Fe, and Pb were greater than the dissolved concentrations. Colloidal Zn concentration was not higher than dissolved Zn concentration, but was greater than detection in many of the stream samples. Concentrations of dissolved Cu were greater than those of colloidal Cu; only a few samples indicated measurable colloidal Cu.

Although metal concentrations were high in the sample from the Solomon Mine adit, no substantial change in the stream concentrations along East Willow Creek occurred downstream from the adit. Concentrations of Zn increased downstream from the area of the Solomon Tunnel, but this increase was small in comparison to the increase downstream from the confluence for West Willow Creek (fig. 21).

Concentrations of Mn were similar to those of Zn. Although Mn concentrations were high in samples collected at the Solomon Mine adit (SMA), instream concentrations did not increase greatly until the confluence with West Willow Creek. In contrast to this, concentrations of Al and Fe were low (fig. 22). Concentrations of Fe and Al also were high in samples collected from the Solomon Mine adit, but these concentrations did not affect the stream concentrations. This could be from the effects of the constructed wetland, or because there is little hydrologic input from the adit to the stream.

These trends in composition are summarized by the groups of inflows and stream samples in a biplot of PCA results (fig. 23). Vectors for the constituents fall into two groups that are distinguished by those constituents that increase from the inflow of West Willow Creek (Ca, Mg, SO_4, Cd, Sr, pH, Zn, Na, Pb, and Cl), and those that vary to some degree in East Willow Creek (Fe, Al, and Cu). Within this framework, there are only two groups of stream samples. Group 1 includes all the samples in East Willow Creek upstream from West Willow Creek, and the inflows TRN and TRS, which had a chemistry similar to that of the stream samples. These samples vary somewhat in their Fe and Al concentrations, and there is some variation in Zn, but overall there is not a great amount of variation along that part of East Willow Creek. Group 2 includes those stream samples that are downstream from the confluence, and this group is shifted to the right on the biplot, indicating the increase in all those constituents that are dominant in West Willow Creek. The shift is toward the West Willow sample, WW-A.

The highest concentrations of metals, including Al, Fe, and Cu, were measured in the sample collected from the Solomon Mine adit (SMA, group 4). EW-2825 (group 5) originated from the same source but had lower metal concentrations because the adit water had passed through constructed wetlands before the sample was collected. EW-2830 (group 2) originated from the Solomon Mine but was collected from a spring that issued near the stream, downstream from the Solomon adit and the constructed wetlands. It was not clear if that water drained from the adit or from the wetlands, but the sample had lower concentrations of metals than did sample EW-2825. Despite high concentrations of metals, these inflows had little effect on the stream chemistry. There was only a slight shift toward SMA among stream samples of group 1; group 1 samples that plot to the right generally were collected downstream from the Solomon Mine area. This mostly reflects the increase in Zn concentration, as mentioned above. A lack of the shift indicates that the Solomon Mine and the associated inflows had little influence on the stream chemistry. The only major shift in the stream chemistry came downstream from the confluence with West Willow Creek (group 2). The sample from Windy Gulch, EW-5944, was distinguished by low concentrations of Al, Fe, and Cu, but relatively high concentrations of other metals.

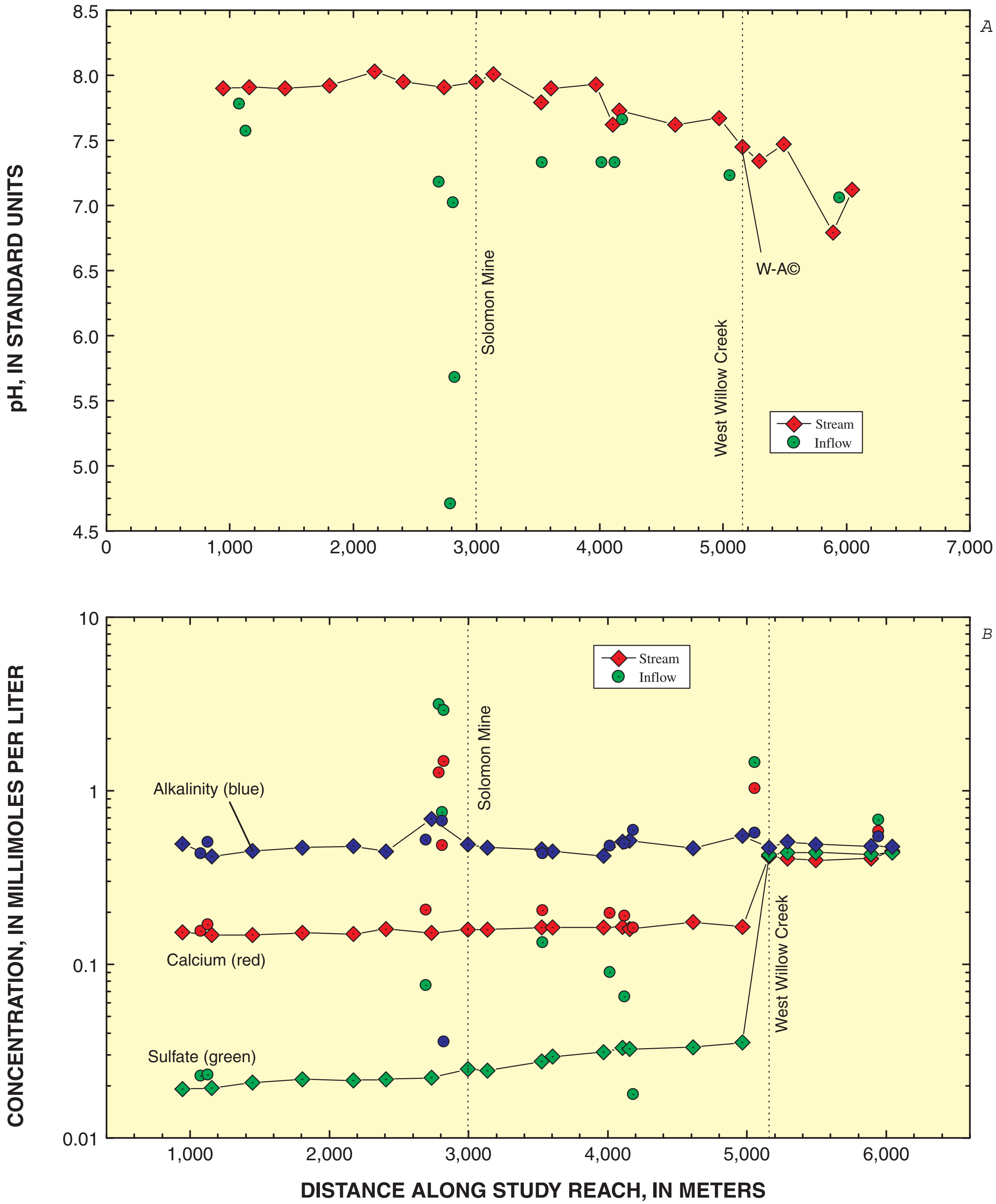

Figure 19. Variation of (A) pH and (B) calcium, sulfate, and alkalinity concentration with distance along the study reach, East Willow Creek, Colorado, August 2000.

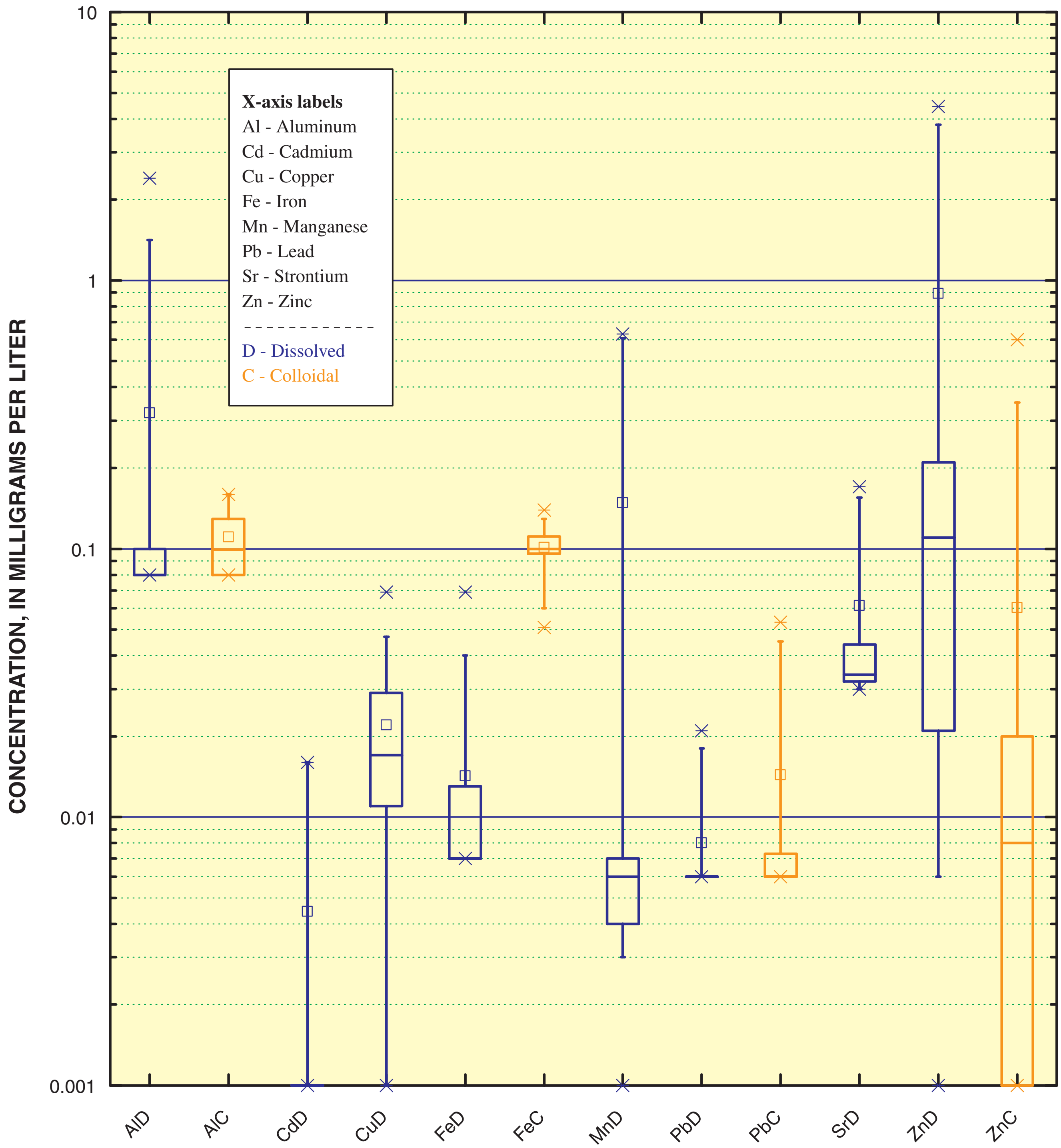

Figure 20. Distribution of dissolved (blue) and collodial (orange) metal concentration in synoptic stream samples, East Willow Creek, Colorado, August 2000.

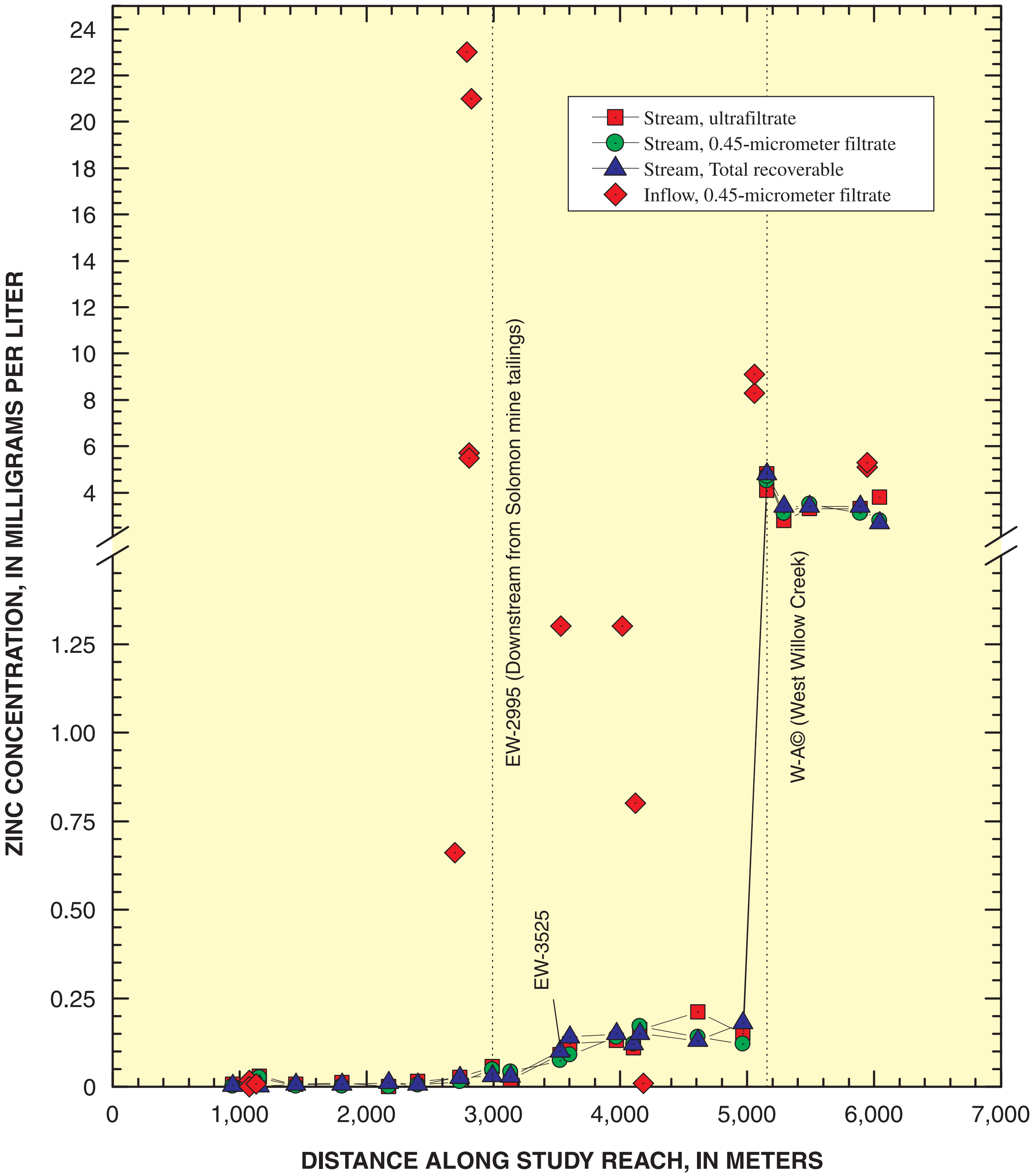

Figure 21. Variation of zinc concentration with distance along the study reach, East Willow Creek, Colorado, August 2000.

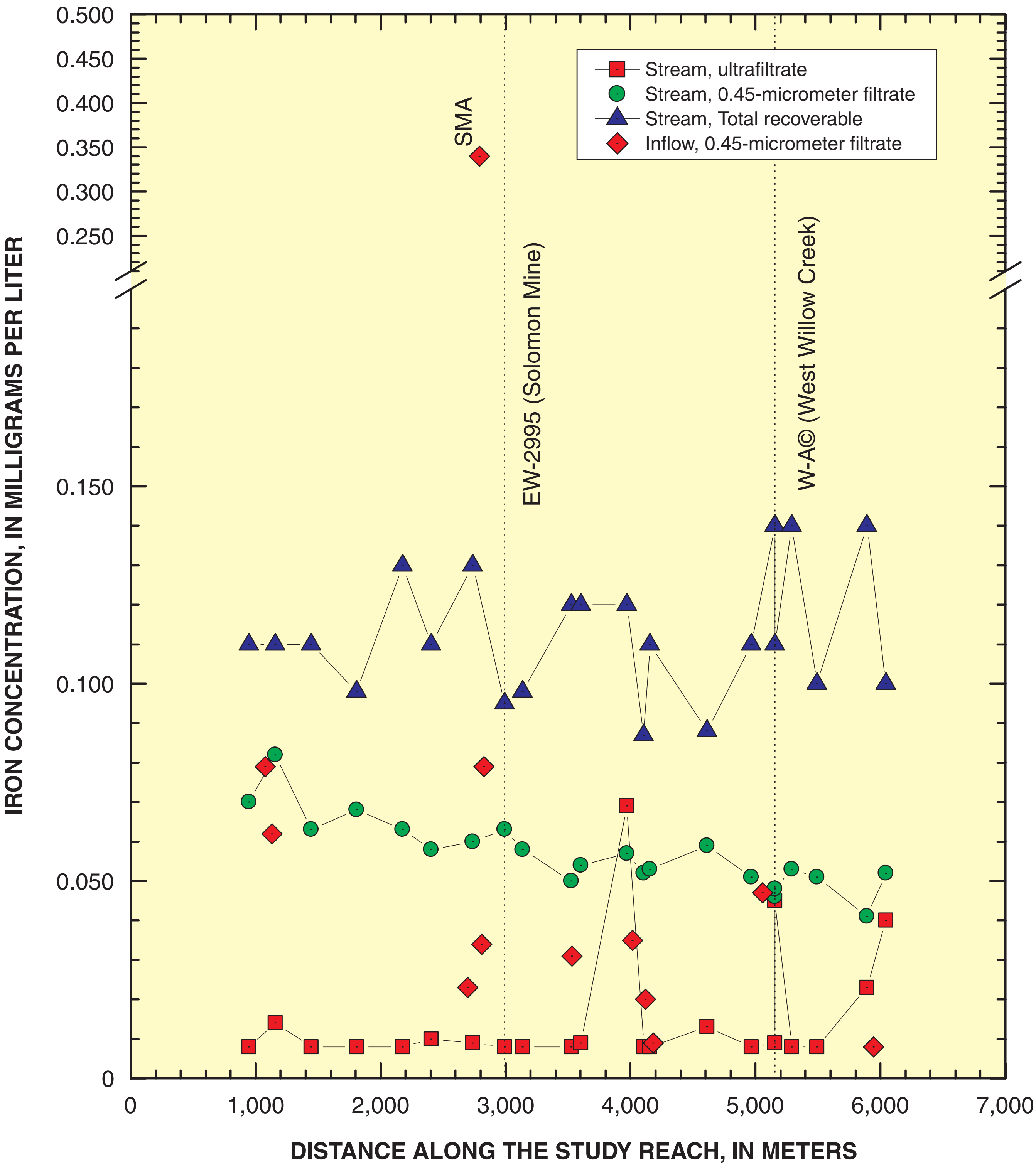

Figure 22. Variation of iron concentration with distance along the study reach, East Willow Creek, Colorado, August 2000.

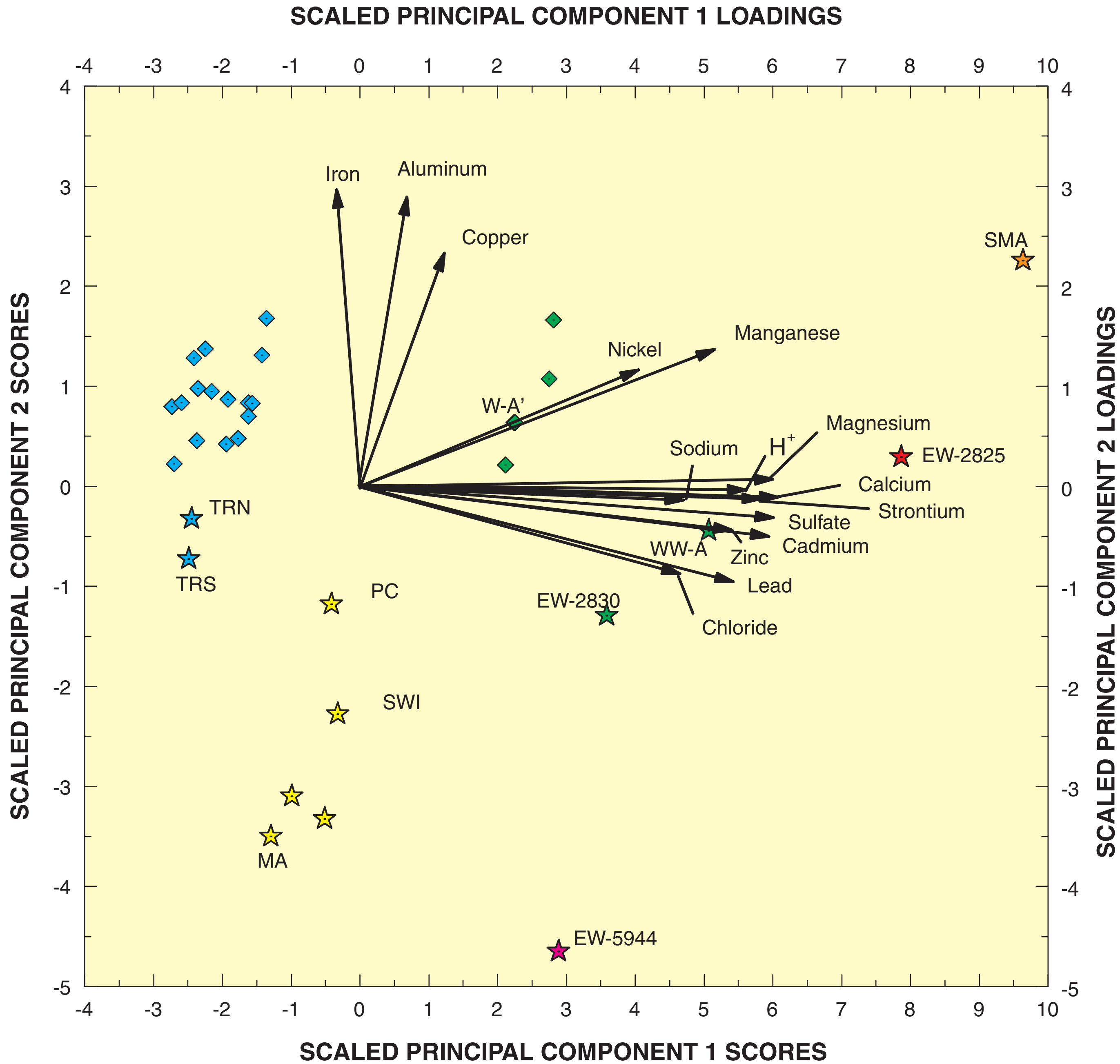

Figure 23. Biplot indicating classification of synoptic samples from East Willow Creek, Colorado, August 2000.

For both stream (diamonds) and inflow (stars) samples, groups are indicated by color: Group 1 (blue), group 2 (green), group 3 (yellow), group 4 (orange), group 5 (red), and group 6 (magenta).

Load Profiles

Load profiles for solutes in East Willow Creek are presented for the entire study reach (table 5). To compare the summary values for cumulative instream load in table 5 to the inflow values in table 2, the sum should only be through EW-A. For example, the cumulative instream load for Al along the East Willow Creek study reach was 7.94 kg/day, but 2.38 kg/day of that total was added by West Willow Creek in segment W-A'. Therefore, the load from East Willow Creek would be only 5.56 kg/day. Copper is not included in the summary because concentrations were too close to the detection limit.

Load profiles for East Willow Creek had two patterns. First, those elements that had very little loading along the study reach upstream from EW-A included SO_4 (fig. 24), Sr (fig. 25), Mn (fig. 26), and Zn (fig. 27). Load profiles of these elements indicate that essentially all of the load came from West Willow Creek. The sample from WW-A accounted for all the increase in SO_4 (fig. 24B), Sr (fig. 25B), and Mn (fig. 26B). Part of the increase in Zn was unsampled inflow (fig. 27B). This could indicate the occurrence of substantial subsurface inflow that had high Zn concentrations from West Willow Creek.

Load profiles for Al (fig. 28) and Fe (fig. 29) were very different from those of the first group. The cumulative loads at the mouth of East Willow Creek were comparable to the loads from West Willow Creek, and so downstream from the confluence, both these loads essentially doubled. The mass balance between the two tracer-injection studies was very good. For both Al and Fe the load was transported in the colloidal phase, unlike SO_4, Sr, Mn, and Zn, which were transported in the dissolved phase.

Although the Solomon Mine area provided an increase in the Al load, the majority of Al was contributed upstream from the study reach. A considerable load of Fe also was contributed upstream from the study reach, but very little was contributed by the Solomon Mine. The small loading of Al and the lack of loading for other metals except Zn could be a result of the passive wetlands at the Solomon adit. No historical data are included in this study to enable a comparison, but the stakeholder group has collected data that may help evaluate the influence of the wetland.

Principal Locations of Mass Loading

Only Al and Fe had significant loadings in the study reach upstream from West Willow Creek (table 5). However, the magnitude of the Al and Fe loads in comparison to those of West Willow Creek were about equal (figs. 28 and 29). Among the other solutes, only Zn had any substantial loading, but the Zn load was very small in comparison to the loading from West Willow Creek. Thus, in comparison to West Willow Creek and the portion of Willow Creek downstream from the confluence, the study reach of East Willow Creek upstream from the confluence with West Willow Creek was not a significant contributor to metal and SO_4 loads.

Unsampled Inflow

For the entire study reach, most of the unsampled inflow occurred downstream from the confluence with West Willow Creek. The reach upstream from the confluence accounted for only a small portion of the overall load of any metal, and the unsampled inflow ranged from less than 1 percent for Mn and SO_4 to 49 percent for Fe.

Attenuation of Metals

Attenuation ranged from less than 1 percent for Fe to 28 percent for Zn in East Willow Creek (table 5). However, the magnitude of loads was so small in comparison to West Willow Creek that it was not comparable.

Lower Willow Creek

The tracer injection in lower Willow Creek investigated a 2,912-m section of the Willow Creek drainage, starting near the end of the engineered section of the stream at the south end of Creede, and continued to the Rio Grande River downstream from the confluence with Willow Creek (fig. 30). The hydrology of this stream reach was complicated by braids in the stream, and samples did not represent a longitudinal profile of stream segments as they did in East and West Willow Creeks. However, it was possible to calculate mass balance for important aspects of the study reach. Sample sites for the Lower Willow injection reach as well as important field and discharge

Table 5. Summary of load calculations, East Willow Creek, Colorado, August 2000

[Loads reported in kilograms per day, except percentages; italicized bold numbers in parentheses indicate rank for the five greatest loads of each constituent]

Segment name	Distance, in meters	Aluminum	Cadmium	Iron	Manganese	Lead	Strontium	Zinc	Sulfate
East Willow Creek									
EW-T0	947	***(1)***3.39	***(4)***0.048	***(2)***3.22	0.109	0.048	***(3)***0.943	0.197	***(3)***53.9
EW-K	1,157	.002	.0	.002	.030	.0	-.058	.678	.916
EW-J	1,447	.066	.001	***(5)***.062	.033	.001	.017	-.644	5.57
EW-1807	1,807	.019	.0	.018	.001	.0	.065	.122	2.44
EW-2175	2,175	-.006	.0	-.006	.099	.0	-.002	-.022	-.720
EW-I	2,405	.044	.0	.042	-.158	.0	.073	.148	1.70
EW-H	2,735	.044	.0	.042	.165	.0	-.080	.324	2.04
EW-2995	2,995	.046	.0	.043	-.037	.001	.106	1.00	9.30
EW-G	3,135	.049	.0	.046	-.028	.001	-.017	-.887	-.884
EW-3525	3,525	***(3)***1.41	.012	.055	***(5)***.207	***(4)***.2365	.081	***(3)***2.30	11.2
EW-E	3,602	.084	.001	.059	-.059	-.022	.052	1.374	7.00
EW-D	3,970	.079	-.011	.055	-.028	-.212	-.048	.403	7.08
EW-4107	4,107	-.554	.0	.054	-.140	.0	.051	-.939	7.23
EW-C	4,157	***(5)***.088	.001	***(4)***.070	.152	.001	-.012	***(5)***1.48	.985
EW-B	4,613	***(4)***.207	***(5)***.014	***(3)***.163	-.068	.002	***(5)***.410	***(4)***2.04	7.19
EW-A	4,968	.034	-.012	.027	-.023	***(3)***.273	-.278	-1.06	8.03
Downstream from confluence with West Willow Creek									
W-A	5,158	***(2)***2.38	***(1)***.828	***(1)***3.53	***(1)***31.8	***(1)***3.39	***(1)***5.64	***(1)***250	***(1)***2,070
EW-5292	5,292	.0	***(2)***.138	.0	***(3)***.534	-.350	***(4)***.534	-74.8	***(2)***60.3
EW-5492	5,492	.0	-.011	.0	-.534	-.460	.0	.0	***(5)***9.08
EW-5892	5,892	.0	-.038	.0	***(4)***.497	***(2)***.380	.0	.0	-52.3
EW-6044	6,044	.0	***(3)***.124	.0	***(2)***.534	***(5)***.066	***(2)***1.60	***(2)***21.4	***(4)***52.3
Cumulative instream load		7.94	1.17	7.48	34.2	4.40	11.0	281	2,320
Cumulative inflow load		6.48	.98	3.79	37.7	2.40	7.63	158	2,560
Percent inflow load		82.0	84	51	110	55	69	56	110
Attenuation		.560	.07	<.01	1.08	1.04	.58	78	54.0
Percent attenuation		7	6	< 1	3	24	5	28	2
Unsampled inflow		1.46	.19	3.69	< 1	2.00	3.37	123	< 1
Percent unsampled inflow		18.0	16	49	< 1	45	31	44	< 1

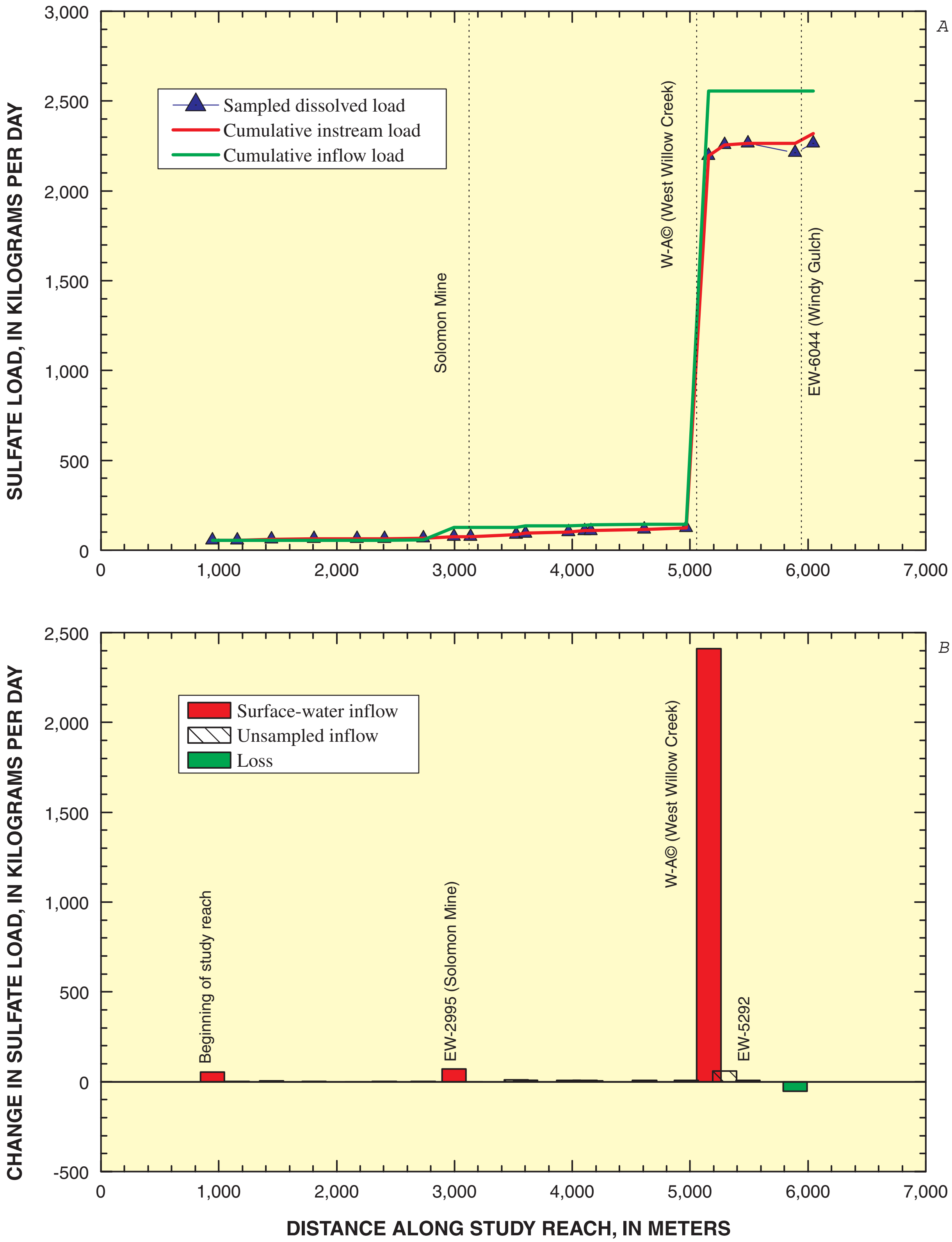

Figure 24. (A) Variation of sulfate load with distance and (B) changes in sulfate load for individual stream segments, East Willow Creek, Colorado, August 2000.

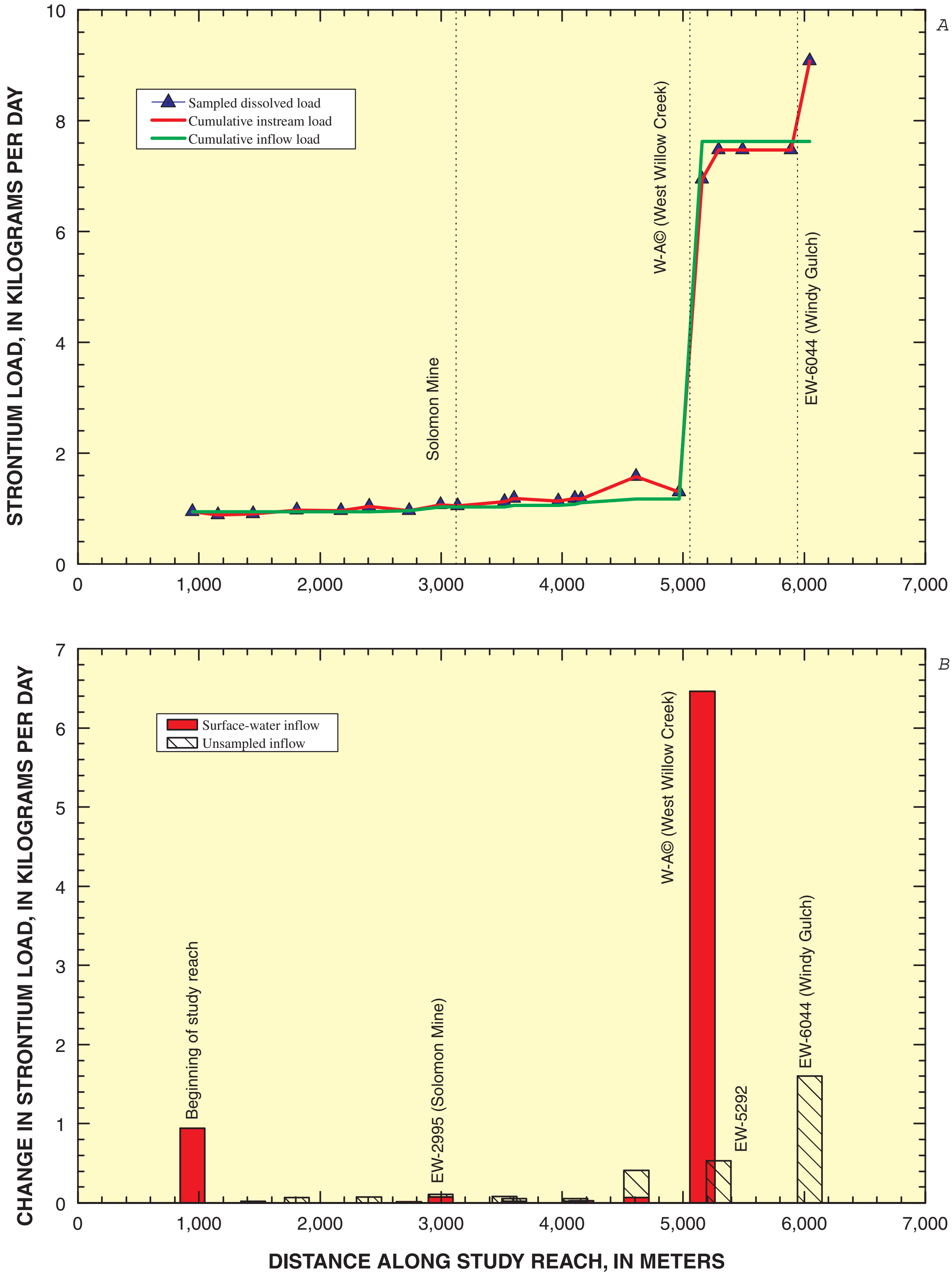

Figure 25. (A) Variation of strontium load with distance and (B) changes in strontium load for individual stream segments, East Willow Creek, Colorado, August 2000.

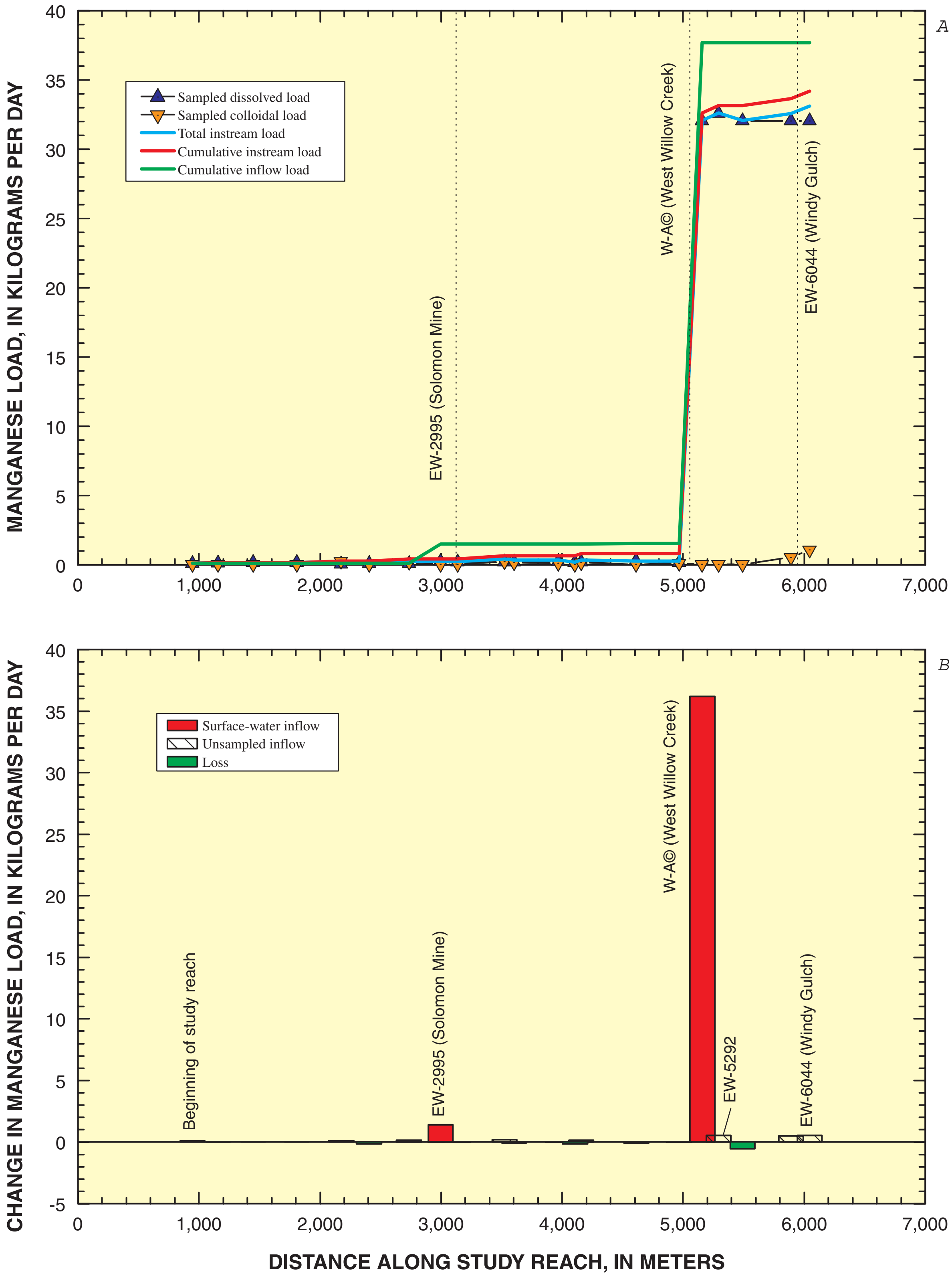

Figure 26. (A) Variation of manganese load with distance and (B) changes in manganese load for individual stream segments, East Willow Creek, Colorado, August 2000.

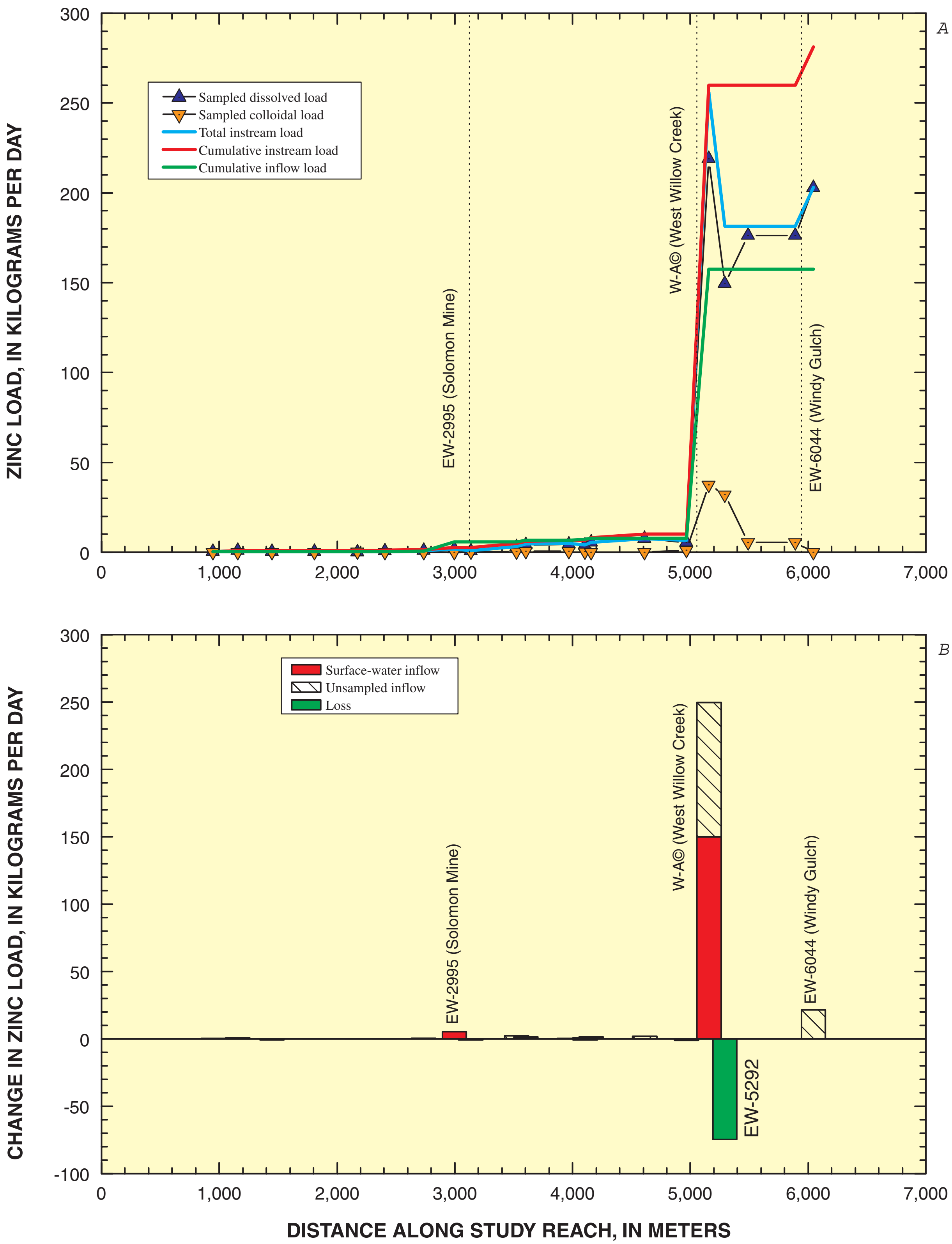

Figure 27. (A) Variation of zinc load with distance and (B) changes in zinc load for individual stream segments, East Willow Creek, Colorado, August 2000.

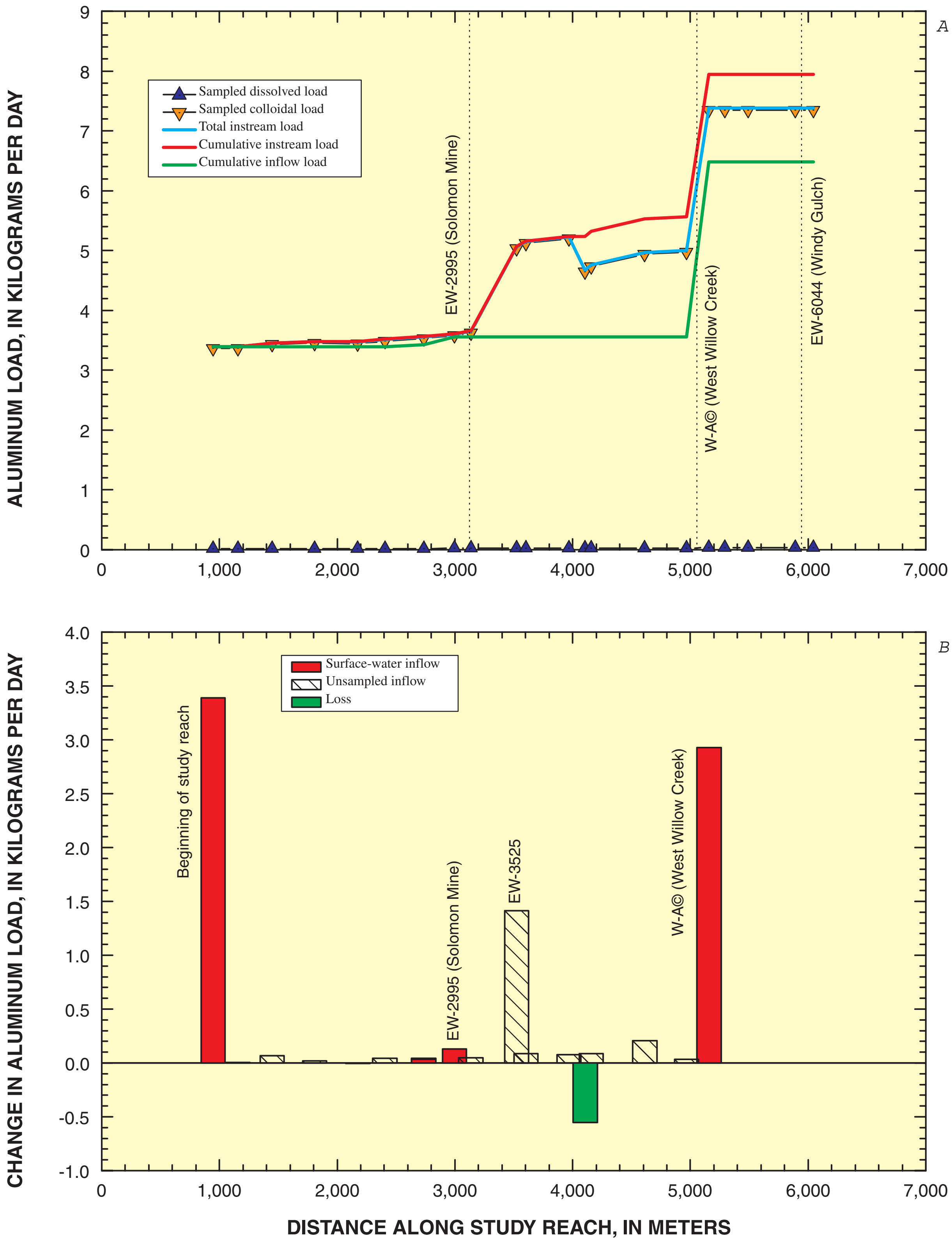

Figure 28. (A) Variation of aluminum load with distance and (B) changes in aluminum load for individual stream segments, East Willow Creek, Colorado, August 2000.

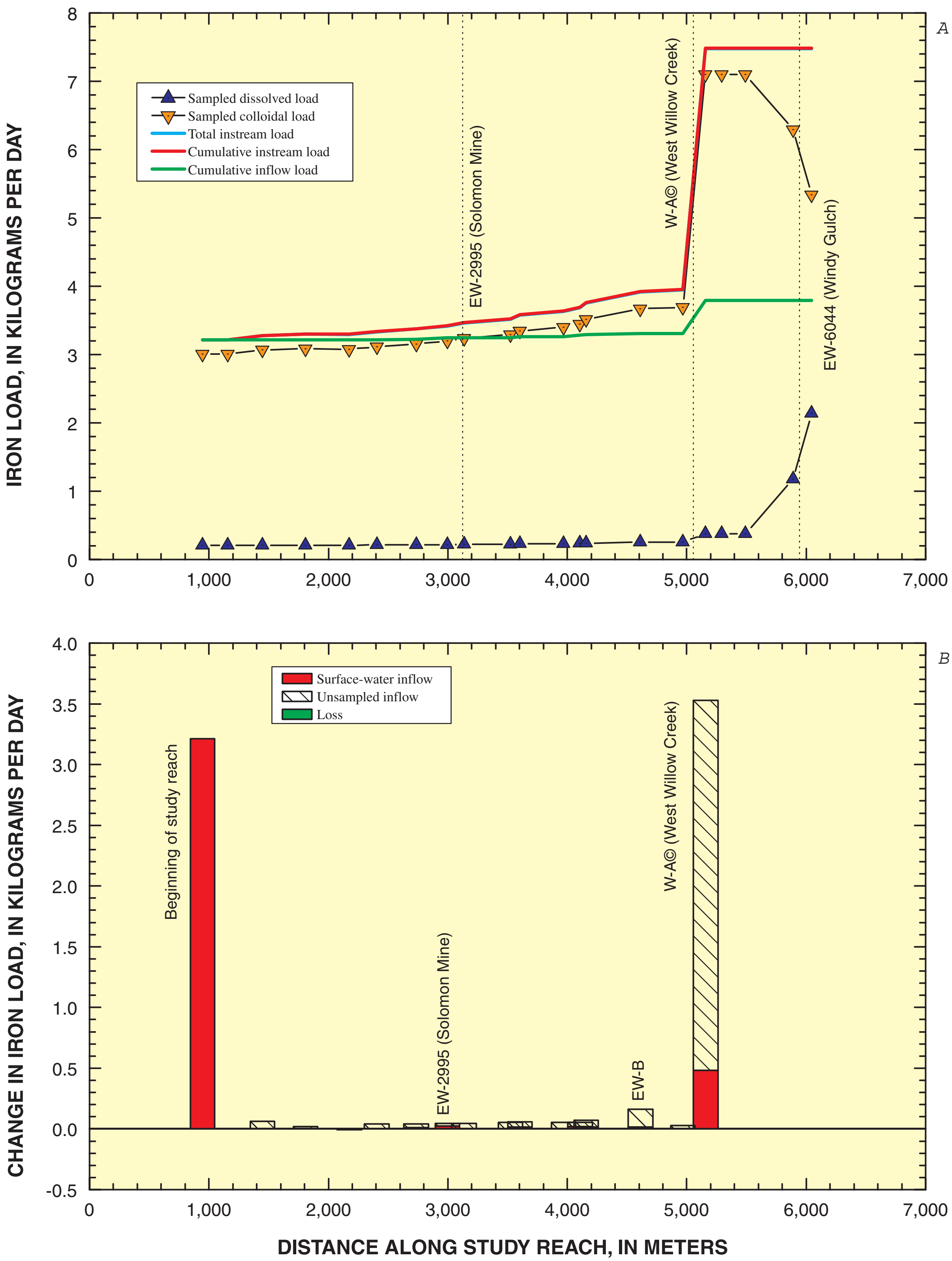

Figure 29. (A) Variation of iron load with distance and (B) changes in iron load for individual stream segments, East Willow Creek, Colorado, August 2000.

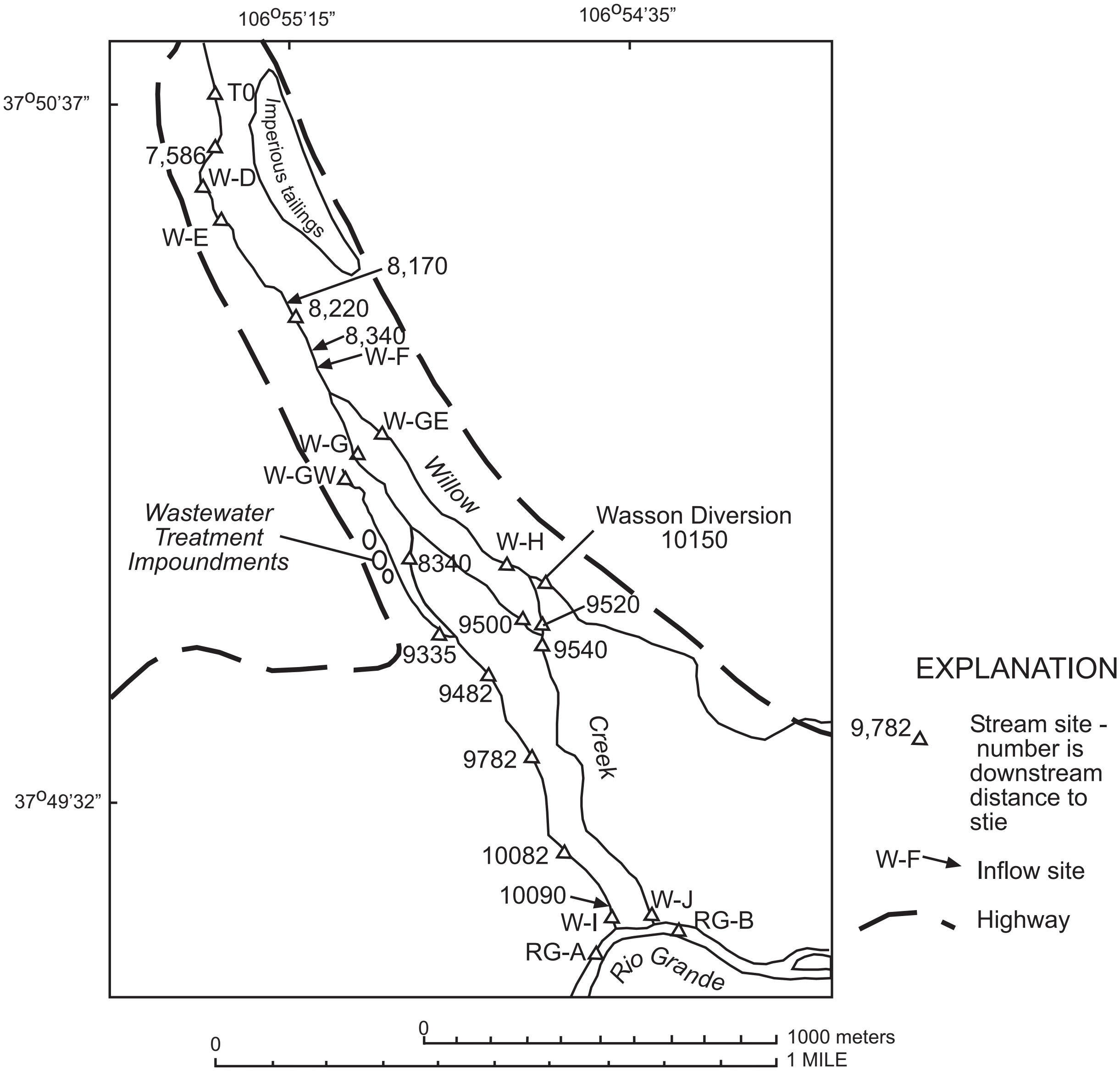

Figure 30. Location of synoptic sampling sites, lower Willow Creek, near Creede, Colorado, August 2000.

data are listed in table 6. Inflow from the Creede sewage treatment plant may have occurred along the west side of the study reach. Along the east side, acidic inflow was likely from the Imperious tailings (fig. 30). Otherwise, only a few obvious inflows along the study reach were observed. A diversion of 29 percent of the water occurred at the Wasson gate (LW-10150). Although this resulted in a loss of mass, it was possible to account for this in the load calculations.

Discharge

A NaBr tracer with a Br concentration of 151,900 mg/L was injected at a rate of 0.0043 L/s. Straightforward application of equation 1 for determining discharge was not possible because of extensive braiding that occurs in this lower reach. Numerous discharge estimates based on traditional velocity-area measurements (Rantz and others, 1982) were therefore combined with tracer-dilution data to provide a description of discharge. Discharge estimates for sites above the braided area (W-D, W-E, and LW-8220) were first calculated by using equation 1. Velocity-area measurements were then used to assign discharge to a number of additional sites (LW-9500, LW-9520, LW-9540, W-H, LW-10150, W-I, and W-J). Discharges at the remaining sites were given by:

$$Q_D = \frac{Q_U(C_U - C_D)}{C_D - C_L} \qquad (7)$$

where:

Q_U = stream discharge at the upstream site, in L/s,
C_U = the tracer concentration at the upstream site, in mg/L,
C_D = the tracer concentration at the downstream site, in mg/L, and
C_L = the inflow concentration (of water entering between two stream sites).

For example, discharge at W-I, which is downstream from LW-10082, was estimated from the upstream discharge at LW-10082 (Q_U), the upstream concentration at LW-10082 (C_U), the downstream concentration at W-I (C_D), and the inflow concentration at LW-10090 (C_L) (fig. 31).

Chemical Characterization of Synoptic Samples

Concentrations along the study reach are difficult to track because the braiding of the stream caused variations to a simple longitudinal profile. There were essentially three different longitudinal paths through the study reach, defined as follows:

1. From the injection site, path 1 follows the eastern braid to W-H, and then a part goes to LW-9520 and from there to the mouth of Willow Creek at W-J.
2. From the central braid, at W-G, the stream continues to the mouth of Willow Creek at W-I.
3. On the west side of the study reach, a stream starts upstream from W-G West, passes the Sewage Treatment Plant (STP), and joins path 2 at LW-9482.

The stream was mostly a calcium sulfate type water in all of the braids. The Rio Grande River near Willow Creek was a calcium bicarbonate type. Values of pH were generally between 7.0 and 7.5 (fig. 32). The effect of acidic inflows may have started at LW-8220, but values just downstream were again near 7.5. pH in the Rio Grande River was higher than in the study reach of Willow Creek.

Concentrations of Al, Fe, Mn, and Zn were relatively high along the study reach (fig. 33). Both Al and Fe were present mostly as colloids. There was some colloidal Zn, but concentrations of dissolved Zn were much higher. The spatial variation of metals gives an indication of the importance of the Imperious tailings and other sources. The pattern of SO_4 concentration indicates that concentrations were higher in the east braid (path 1) than in the central braid (fig. 34). This could be from the inflow of W-F and LW-8340. However, the concentration of SO_4 in the west braid (path 3) was substantially higher. The source of this SO_4 is not clear because this braid started just upstream from the sampling site. Water entering the Rio Grande River along path 1 had a higher SO_4 concentration than along path 2, but they were not very different.

The pattern of Mn was different from that of SO_4 (fig. 35). There was a distinction between concentrations in the east and middle braids (paths 1 and 2), but concentrations in the west braid (path 3) were lower. Concentrations of Zn were similar to those of SO_4 because the west braid (path 3) had higher Zn concentrations than the other two paths (fig. 36).

Table 6. Synoptic sampling sites, lower Willow Creek, Colorado, August 2000

[—, no data]

Segment identification	Source	Distance, in meters	Site description	pH, in standard units	Specific conductance, in micro-siemens per centimeter	Discharge, in liters per second	Smoothed bromide, in milligrams per liter
LW-T0	Stream	7,443	Upstream from injection	7.46	137	582	0.04
LW-7586	Stream	7,586	At the end of the channel at railroad bridge	7.31	143	582	.73
W-D	Stream	7,716	Down from trailer park sewage disposal	7.39	142	582	1.02
W-E	Stream	7,830	T1 - Up from braided reach	7.43	141	588	1.05
LW-8170	Inflow	8,170	Stream return flow—may have tailings seepage	7.50	139	—	—
LW-8220	Stream	8,220	Where braids come back together	6.84	145	599	1.03
LW-8340	Inflow	8,340	Seep with Ulothrix algae	3.42	2,050	—	.01
W-F	Inflow	8,450	Seep from tailings	2.95	2,770	—	.01
W-G	Stream	8,725	Stream in middle braid 170 m before split	7.46	144	304	1.01
W-G-East	Stream	8,725	East channel	7.40	149	263	.99
W-G-West	Stream	8,725	West channel with little flow	7.17	176	31.7	.94
LW-9075	Stream	9,075	T2 - Right part of middle braid	7.49	143	250	.89
LW-9335	Inflow	9,335	Seepage from sewage treatment plant	7.46	172	55.4	.01
LW-9482	Stream	9,482	Down from sewage treatment plant	7.45	146	305	.87
LW-9500	Stream	9,500	Upstream from Wasson return	7.28	148	40.3	.87
LW-9520	Inflow	9,520	Wasson return	7.11	149	99.1	
LW-9540	Stream	9,540	Down from Wasson return	7.10	149	148	.87
LW-9782	Stream	9,782	Right part of middle braid	7.38	147	308	.88
LW-10082	Stream	10,082	Another right part of the middle braid	6.74	149	322	.88
LW-10090	Inflow	10,090	Flow along base of high berm	6.96	166	—	.01
W-H	Stream	10,100	Wasson gate	7.21	150	265	.88
LW-10150	Stream	10,150	Irrigation diversion	—	—	—	—
W-I	Stream	10,324	Stream near mouth of upstream braid	7.37	147	333	.82
W-J	Stream	10,324	Stream near mouth of downstream braid	7.42	147	163	.60
RG-A	Stream	10,350	Rio Grande River up from Willow Creek	8.13	80	7,074	.29
RG-B	Stream	10,355	Rio Grande River down from Willow Creek	7.45	82	7,570	.04

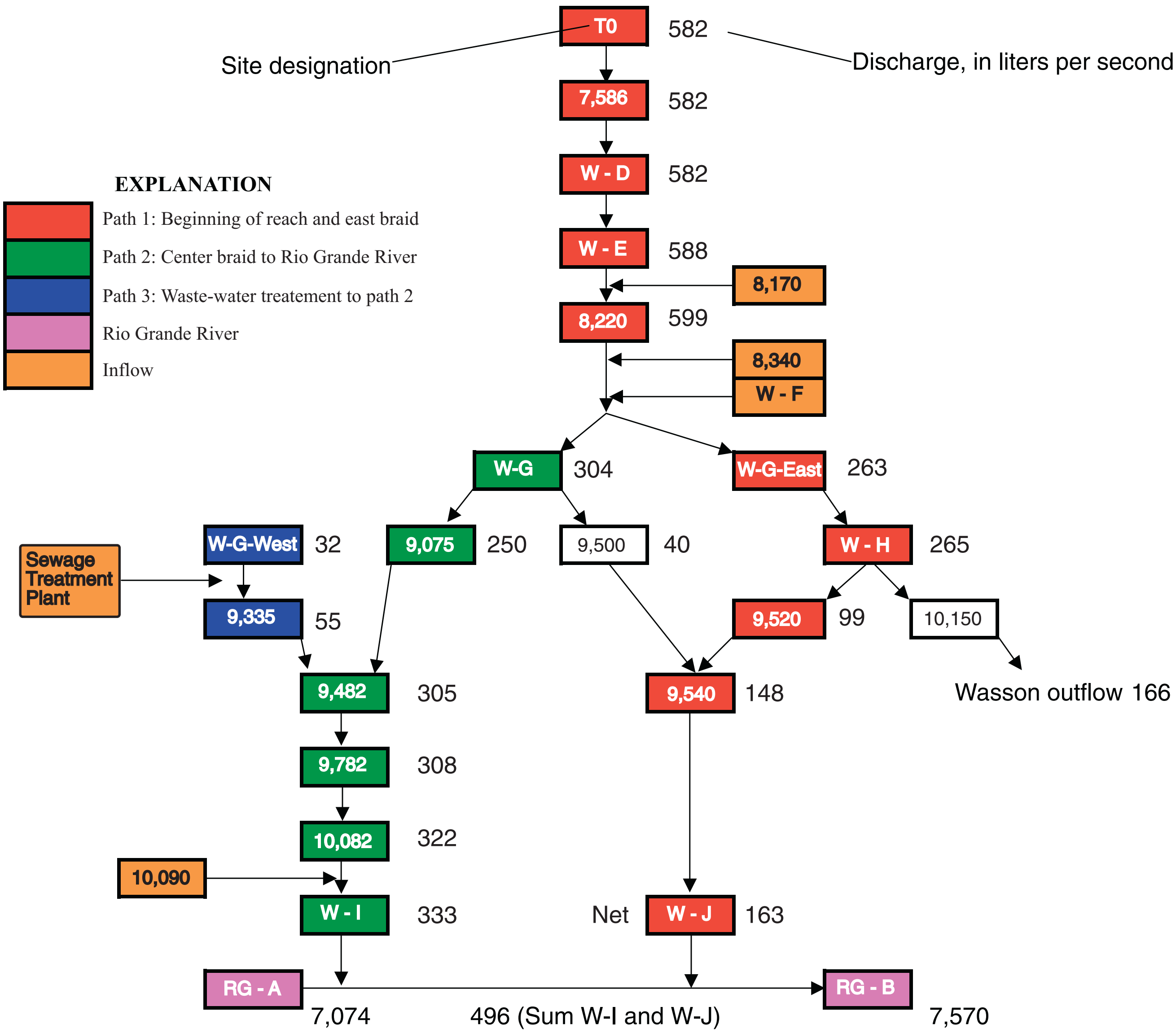

Figure 31. Discharge at sampling sites along the study reach, lower Willow Creek, Colorado, August 2000.

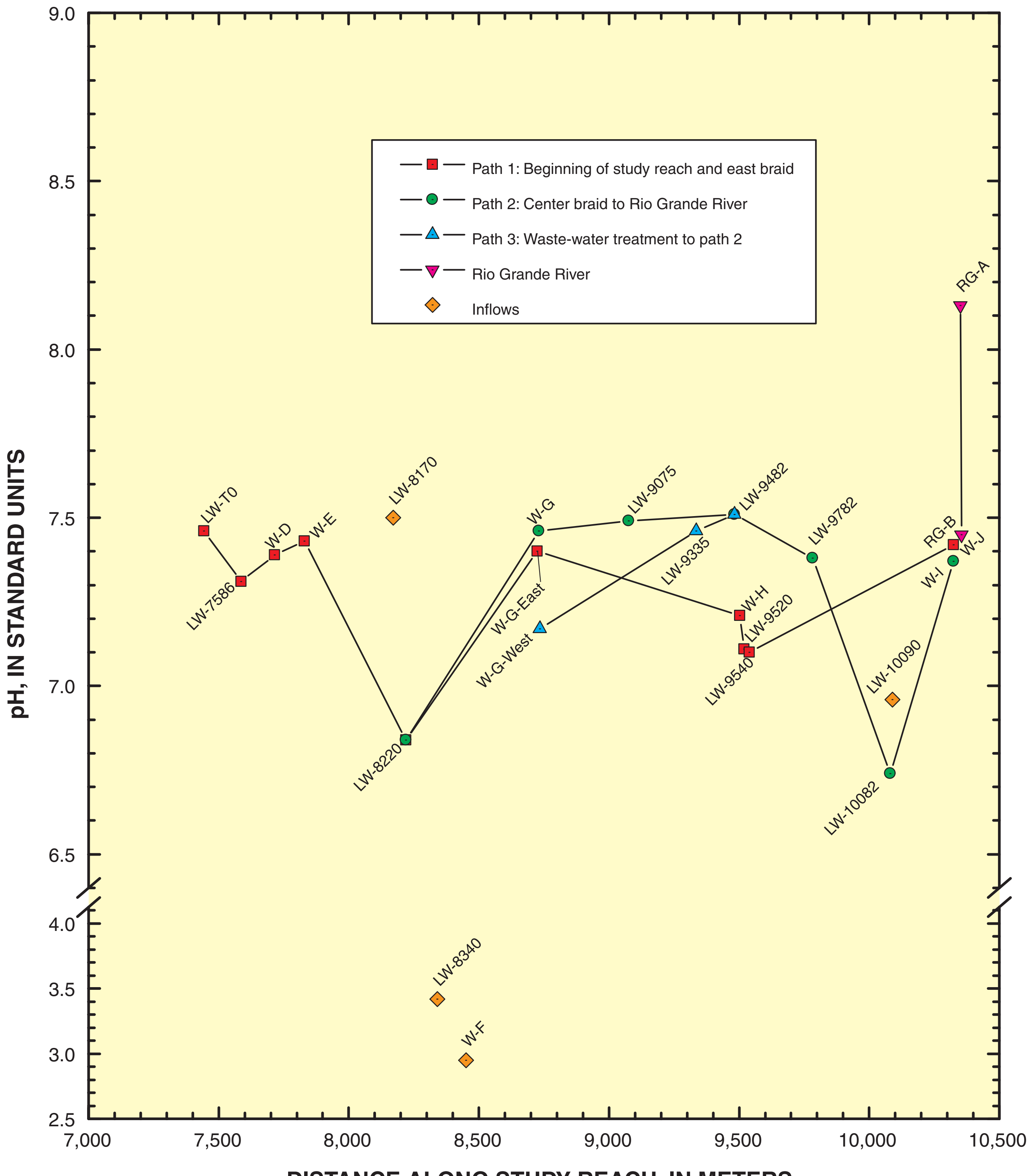

Figure 32. Variation of pH with distance along the study reach, indicating paths of braids, lower Willow Creek, Colorado, August 2000.

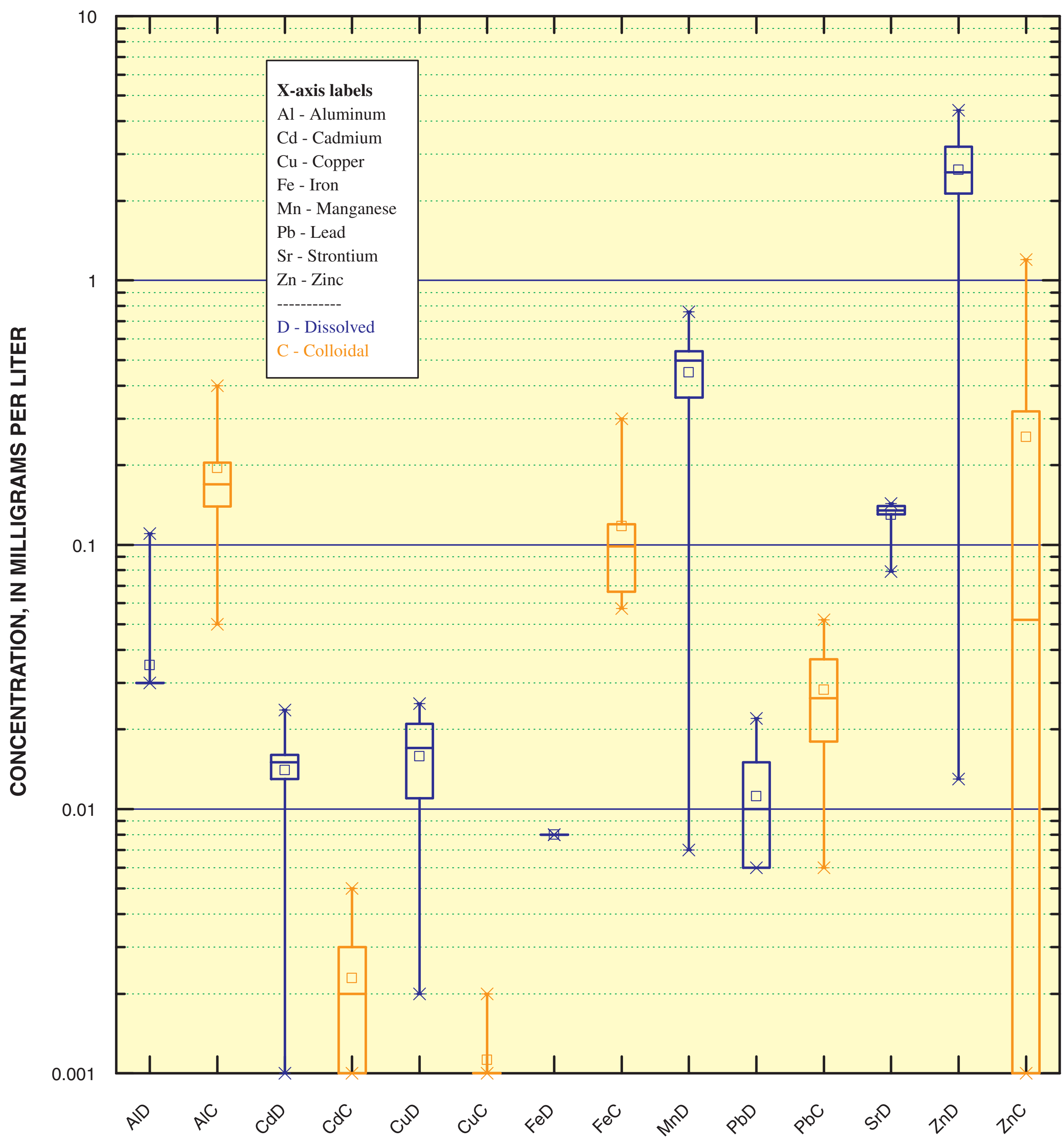

Figure 33. Distribution of selected dissolved (blue) and colloidal (orange) metal concentrations, lower Willow Creek, Colorado, August 2000.

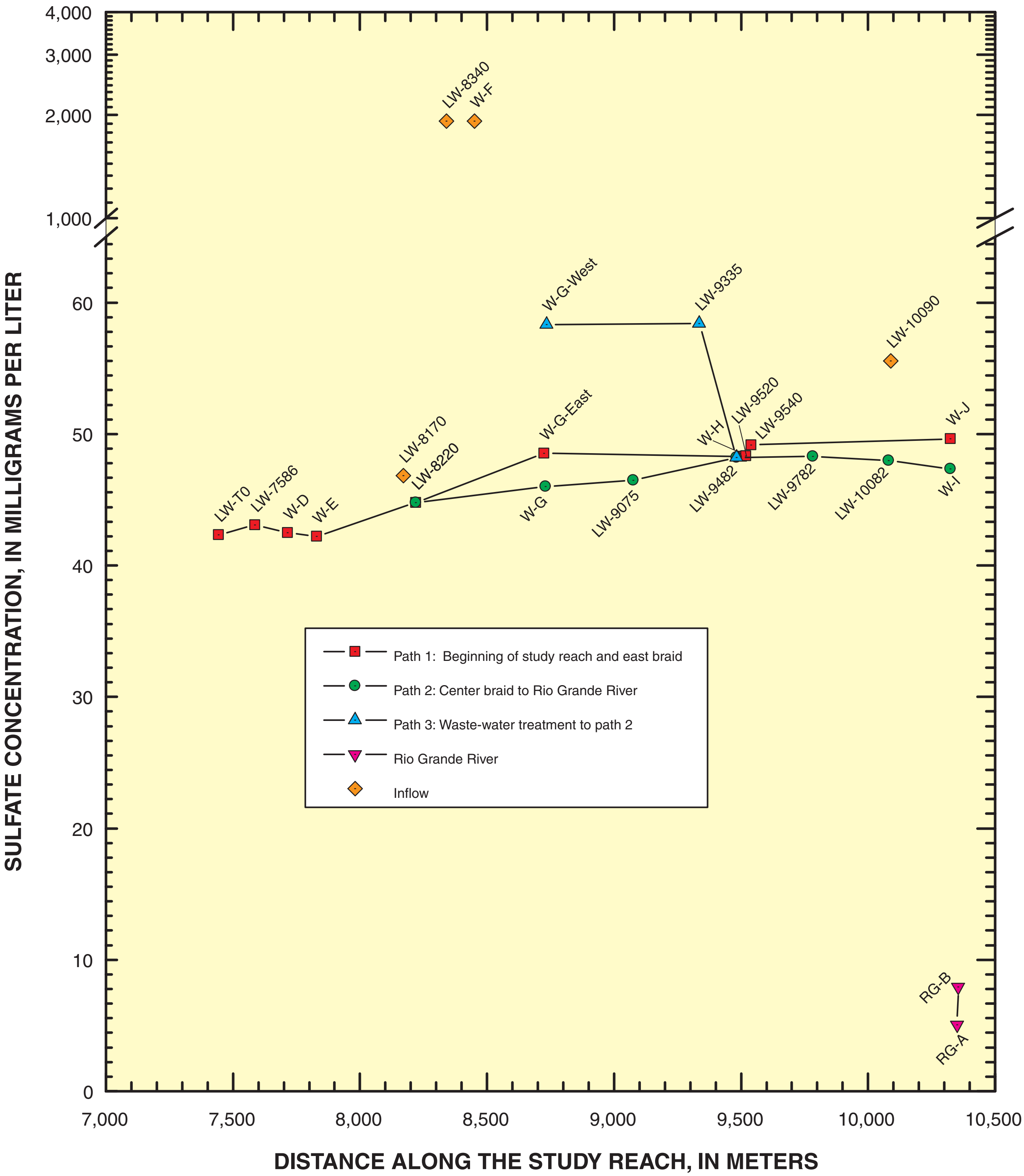

Figure 34. Variation of sulfate concentration with distance along the study reach, indicating paths of braids, lower Willow Creek, Colorado, August 2000.

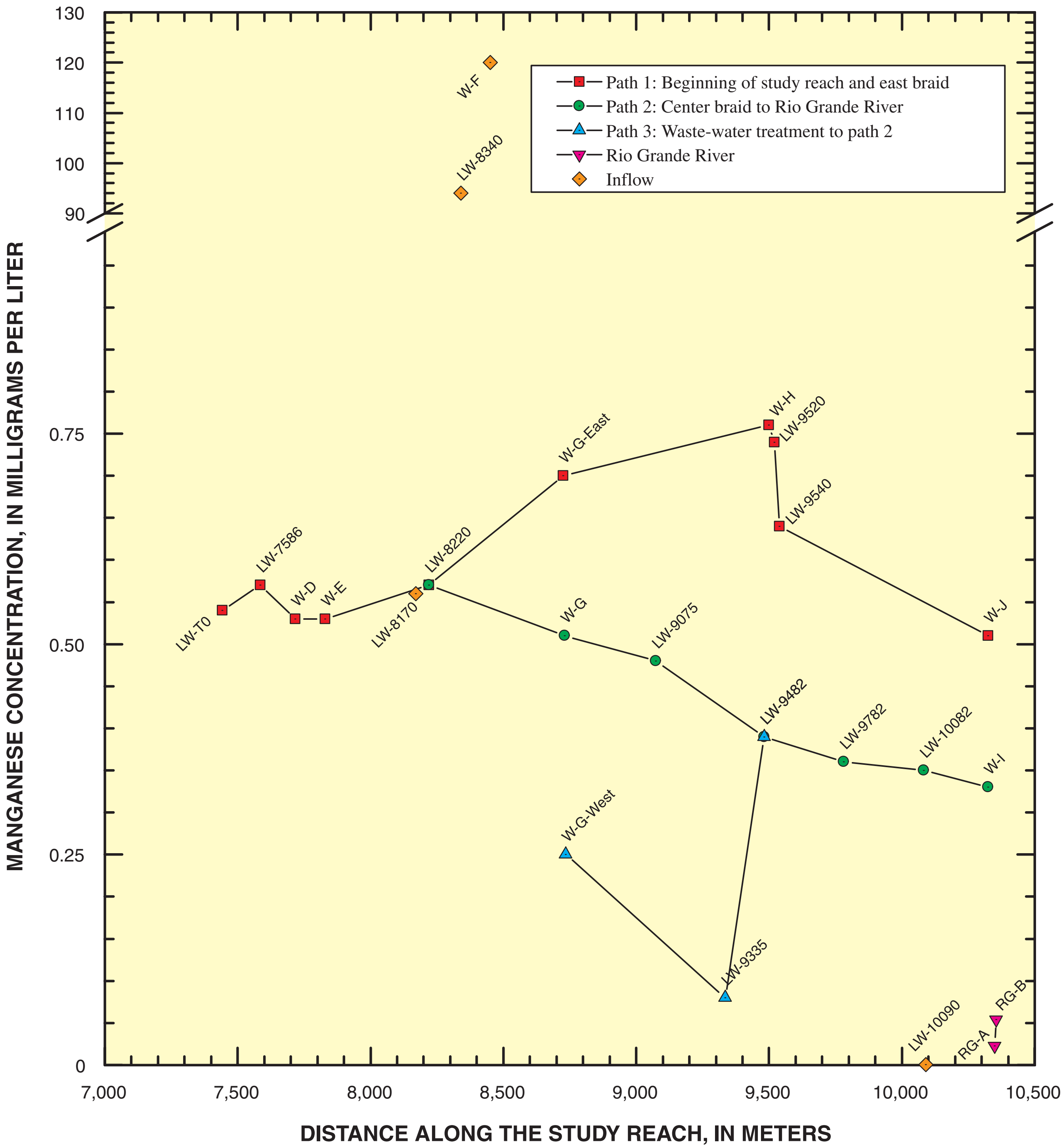

Figure 35. Variation of manganese concentration with distance along the study reach, indicating paths of braids, lower Willow Creek, Colorado, August 2000.

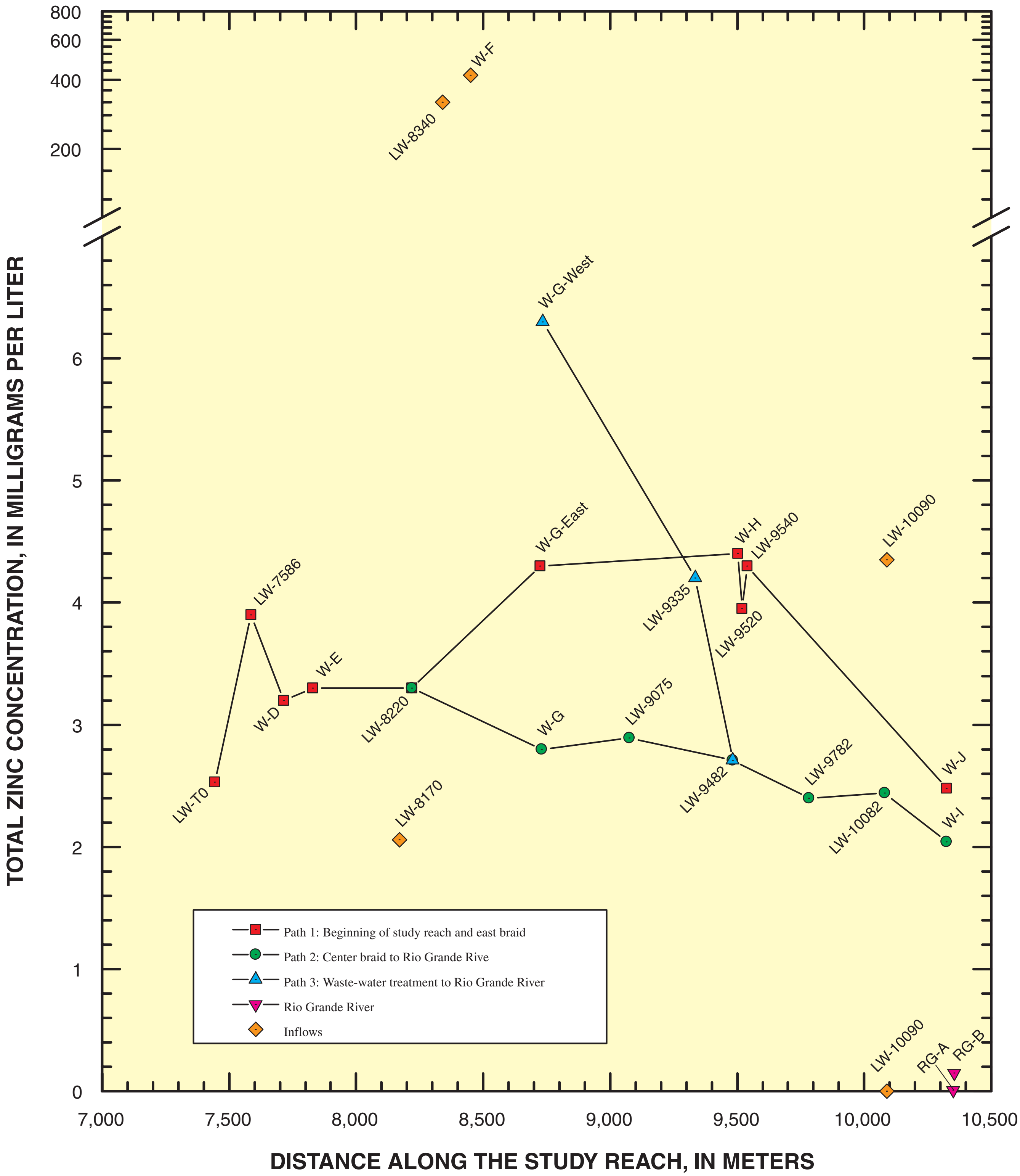

Figure 36. Variation of zinc concentration with distance along the study reach, indicating paths of braids, lower Willow Creek, Colorado, August 2000.

Load Profiles

Patterns of loading are difficult to display in a longitudinal view for the lower Willow Creek study area. With the braiding in the stream, loads are split and at other places, they recombine. To avoid the complexity of such a plot, the loads are presented in a schematic map view, similar to the presentation of discharge. It is also difficult to present a summary of loading calculations that is similar to those for West and East Willow Creeks. However, some load calculations help identify the effect of this study reach on loads to the Rio Grande River (table 7). The first calculation is the sum of W-I and W-J. The net gain through the study reach takes this sum, adds the load leaving by the Wasson diversion, and subtracts the load at LW-8220, upstream from the beginning of braiding. Finally, the net gain for the Rio Grande River is from the difference between loads at RG-A and RG-B.

The overall effect of the lower Willow study reach was a net loss of Fe, Mn, and Zn, and a net gain of Al and SO_4. Overall, however, there appeared to be a net gain of Al, Fe, Mn, Zn, and SO_4 to the Rio Grande River between the two sampling sites. Without the longitudinal profiles of load, it is difficult to determine if this increase was from unsampled inflow, but it most likely was ground-water contribution to the Rio Grande River from sources within the Willow Creek watershed.

To interpret the load diagrams for the lower Willow study, strontium can be viewed as a conservative solute through the study reach. Strontium concentration did not vary by more than a few hundredths of a milligram per liter. With that assumption, the percentage of Sr load at W-G and W-G-East was 51 (3.70 of 7.25) and 44 (3.19 of 7.25) percent, respectively, of the load at LW-8220 (fig. 37). If other metals have different percentages, particularly at W-GE, then we might assume that there was some loading along the east braid, most likely from the Imperious tailings. The same reasoning might be used at other sites, but this one is of particular interest for metal loading. For SO_4 loading, the percentages are comparable: 52 percent for W-G and 48 percent for W-G-East (fig. 38). For Mn (fig. 39) and Zn (fig. 40) loads, however, the percentages are reversed, and W-G only accounts for 46 and 43 percent, respectively. Thus, there is some indication of loading in this small reach of stream because of the highly acidic inflows of W-F and LW-8340.

SUMMARY—IMPLICATIONS FOR REMEDIATION

Metal loading in the Willow Creek watershed was quantified by establishing the hydrologic framework for chemical synoptic sampling in a series of tracer injections. Mass-loading results have shown that there is not a substantial contribution from any of the possible sources in lower Willow Creek, although the loads from sources upstream of Creede, Colorado, mostly are transported to the Rio Grande River through the lower Willow Creek area. Load profiles from West Willow Creek indicate that the greatest loading of metals in the Willow Creek watershed comes from the Nelson Tunnel inflow, accounted for at sampling site WW-F. This is a particularly substantial loading for Zn and other metals. Other stream segments, just downstream from WW-F, contribute substantial amounts of metals, including additional Zn load. It is possible that these secondary loadings result from water that leaks into the waste-rock pile and enters the stream farther down the drainage. Any remediation plan should account for those secondary sources, whether they are part of the Nelson Tunnel loading or not. East Willow Creek is not a significant source of metal loads. This could be a result of previous,

Table 7. Change in load through study reach of lower Willow Creek, Colorado, August 2000

[All values reported in kilograms per day; <, less than]

Calculation	Aluminum	Cadmium	Copper	Iron	Manganese	Strontium	Zinc	Sulfate
Sum of load from two braids of Willow Creek	7.3	0.6	0.8	2.7	17.0	6.0	93.7	2,062
Net gain through study reach (including Wasson diversion)	1.1	0	.4	-.9	-1.1	.8	-14.2	436
Net gain in the Rio Grande River	13.4	.5	-13.9	19.0	21.3	4.7	89.7	2,088
Unsampled inflow to Rio Grande River	6.1	< 1	< 1	16.3	4.3	< 1	< 1	22

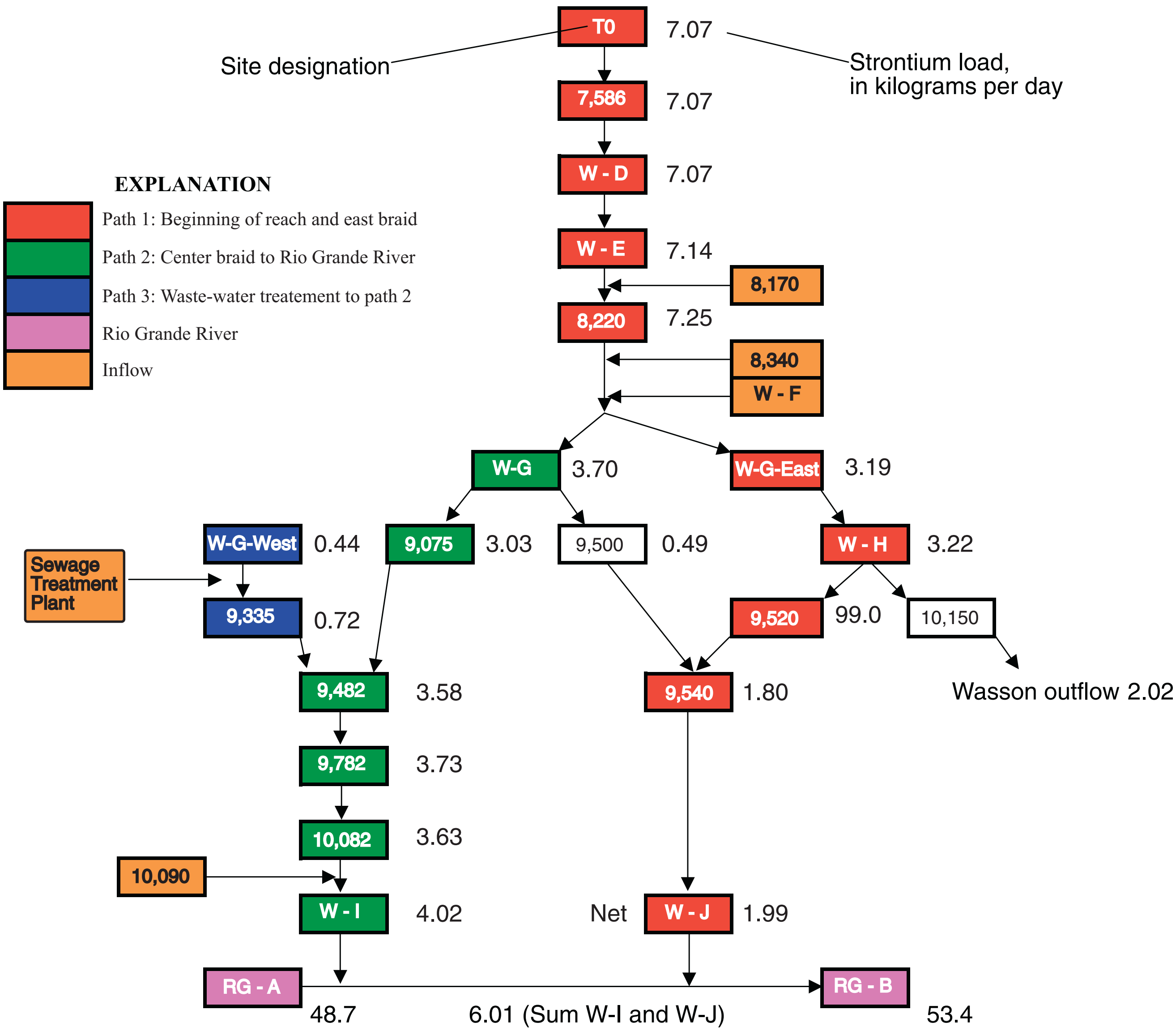

Figure 37. Total strontium load at synoptic sampling sites, lower Willow Creek, Colorado, August 2000.

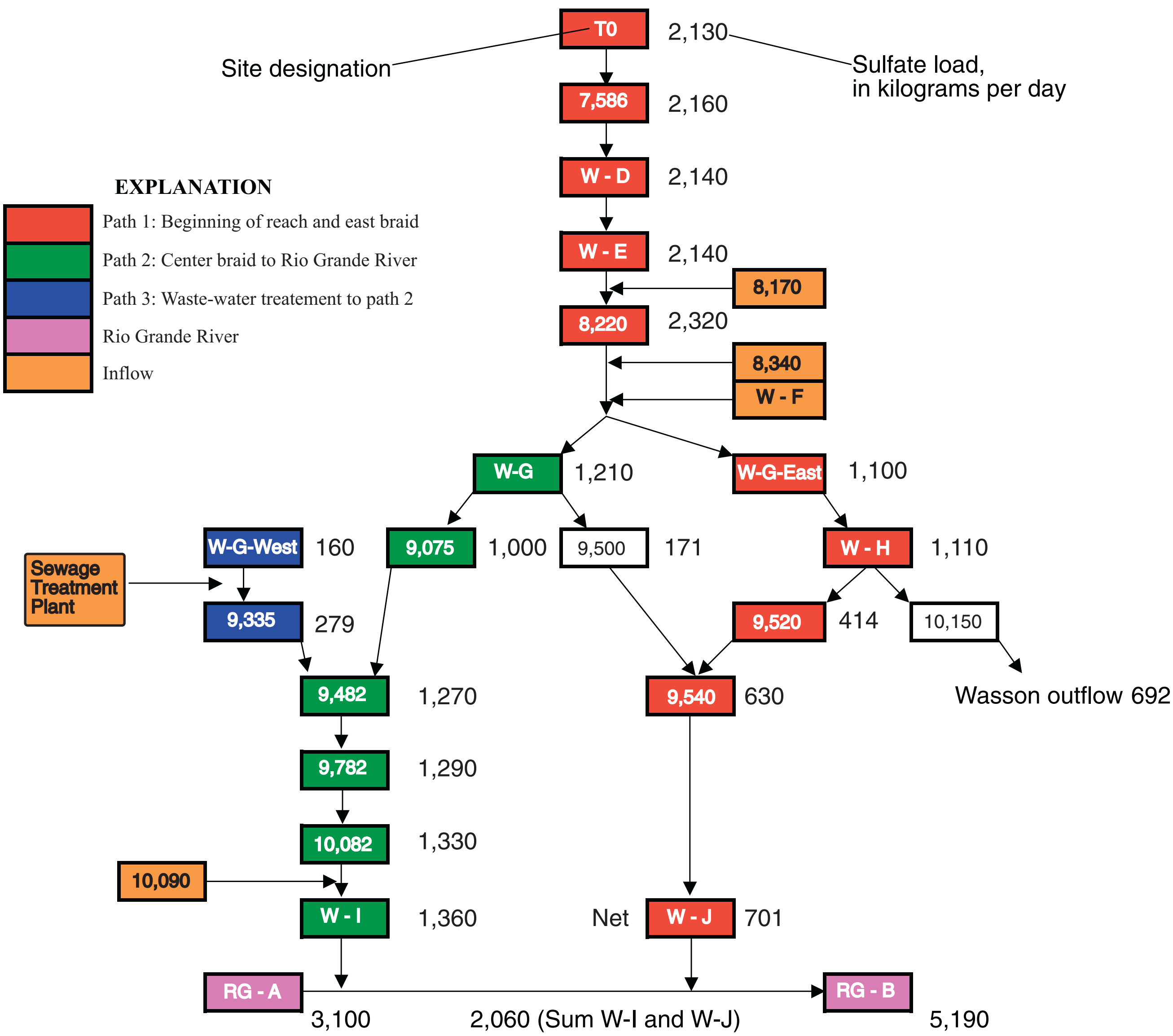

Figure 38. Total sulfate load at synoptic sampling sites, lower Willow Creek, Colorado, August 2000.

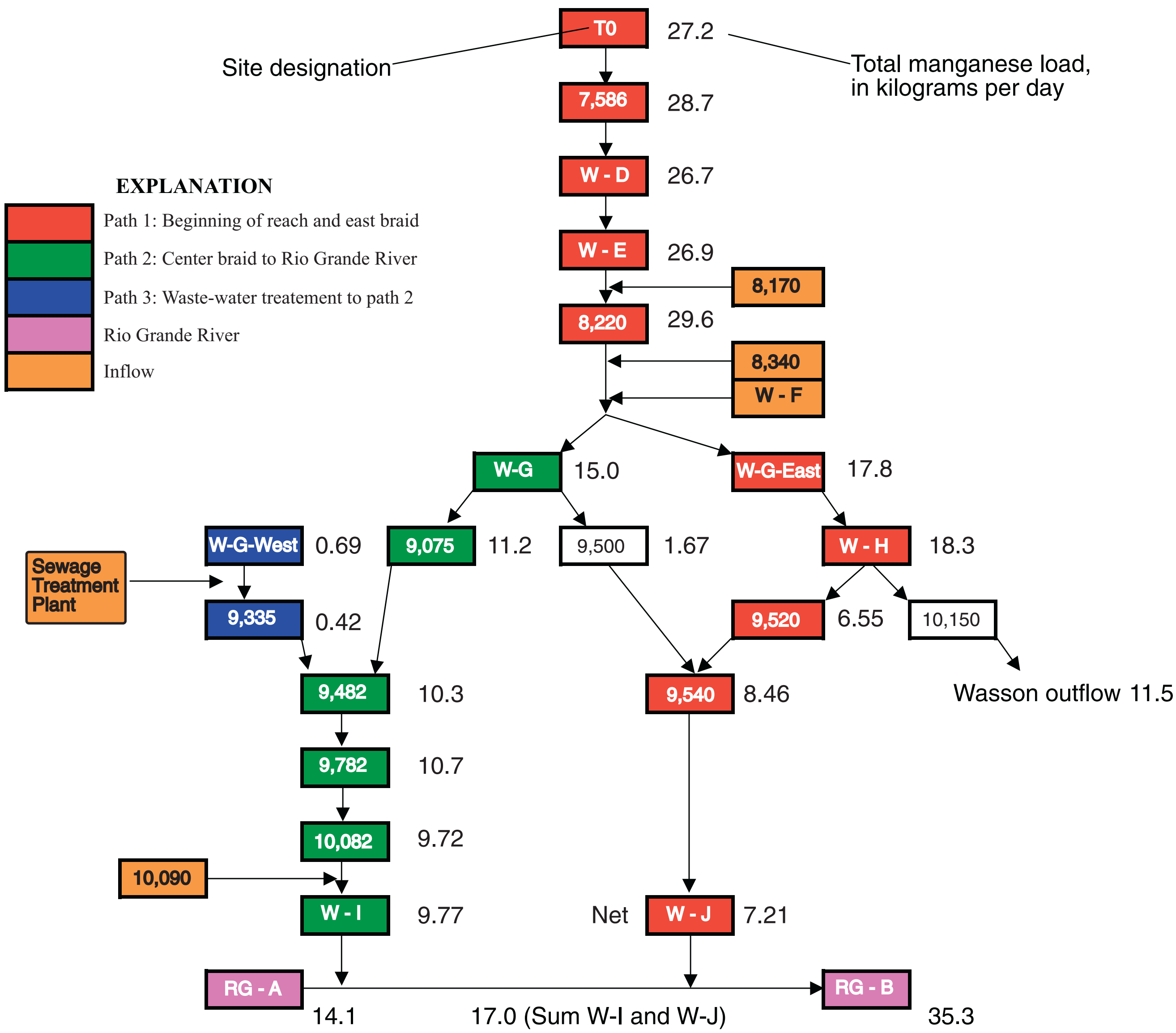

Figure 39. Total manganese load at synoptic sampling sites, lower Willow Creek, Colorado, August 2000.

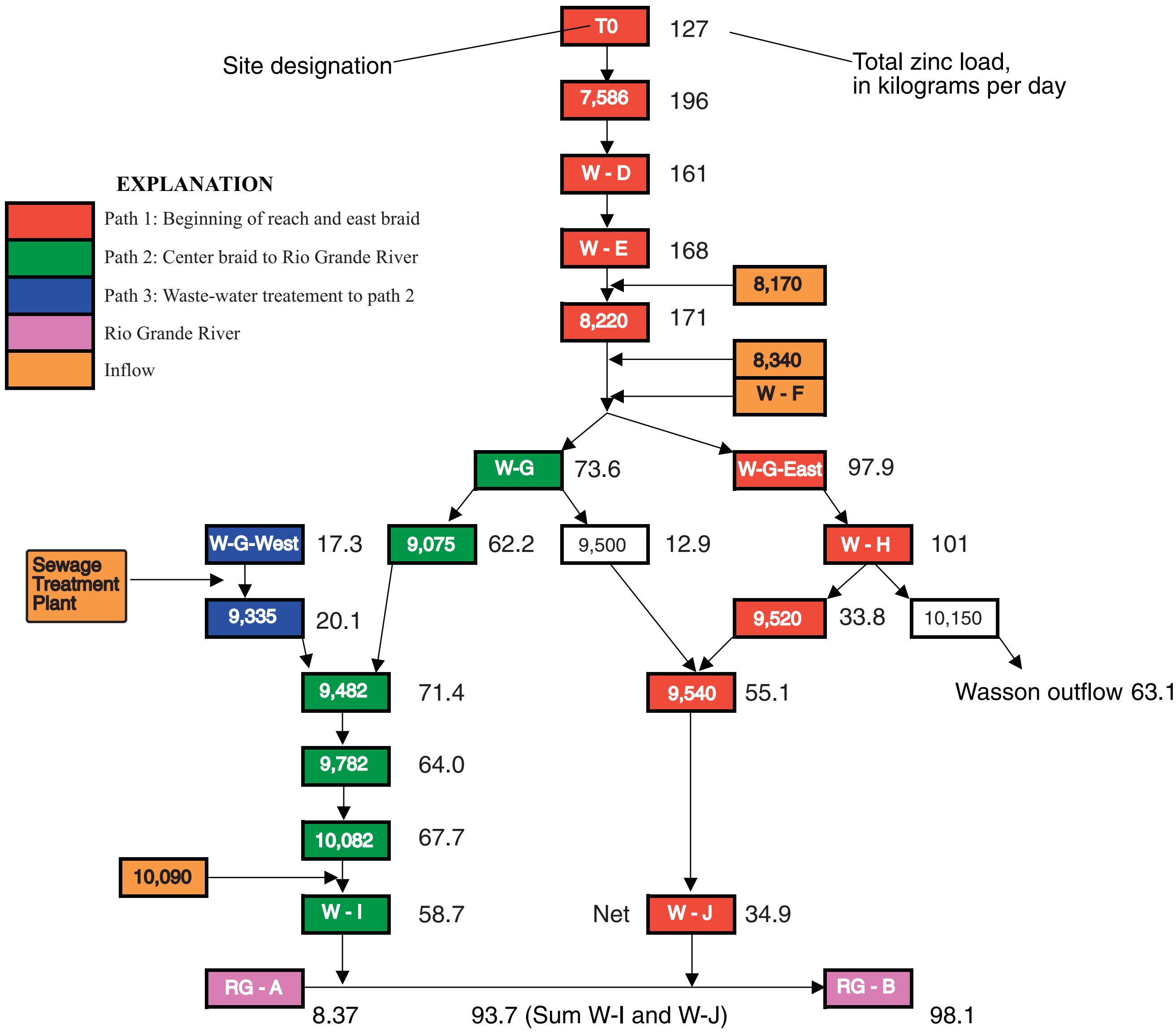

Figure 40. Total zinc load at synoptic sampling sites, lower Willow Creek, Colorado, August 2000.

remediation efforts in that drainage. In summary, these tracer-injection studies have given a watershed picture of the metal-loading in streams near Creede, Colorado. Metal loading is dominated by the inflow from the Nelson Tunnel, however, there also were dispersed, subsurface inflows that add substantial loads.

REFERENCES CITED

Bencala, K.E., and McKnight, D.M., 1987, Identifying in-stream variability: Sampling iron in an acidic stream, *in*, Averett, R.C. and McKnight, D.M., eds., Chemical Quality of Water and the Hydrologic Cycle: Chelsea, Mich., Lewis Publishers, Inc., p. 255-269.

Bencala, K.E., McKnight, D.M., and Zellweger, G.W., 1990, Characterization of transport in an acidic and metal-rich mountain stream based on a lithium tracer injection and simulations of transient storage: Water Resources Research, v. 26, p. 989-1000.

Besser, J.M., Brumbaugh, W.G., May, T.W., Church, S.E., and Kimball, B.A., 2001, Bioavailability of metals in stream food webs and hazards to brook trout (*Salvelinus fontinalis*) in the upper Animas River watershed, Colorado: Archive of Environmental Contamination and Toxicology, v. 40, p. 48-59.

Besser, J.M., and Leib, K.J., 1999, Modeling frequency of occurrence of toxic concentrations of zinc and copper in the upper Animas River, *in* Morganwalp, D.W., and Buxton, H.T., eds., U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting, Charleston, S.C., March 8-12, 1999, v. 1, Contamination from Hardrock Mining: U.S. Geological Survey Water-Resources Investigations Report 99-4018A, p. 75-81.

Broshears, R.E., Bencala, K.E., Kimball, B.A., and McKnight, D.M., 1993, Tracer-dilution experiments and solute-transport simulations for a mountain stream, Saint Kevin Gulch, Colorado: U.S. Geological Survey Water-Resources Investigations Report 92-4081, 18 p.

Cleasby, T.E., Nimick, D.A., and Kimball, B.A., 2000, Quantification of metal loads by tracer-injection and synoptic sampling methods in Cataract Creek, Jefferson County, Montana, August 1997: U.S. Geological Survey Water-Resources Investigations Report 00-4237, 39 p.

Clements, W.H., 1994, Benthic invertebrate community responses to heavy metals in the upper Arkansas River basin, Colorado: Journal of the North American Benthological Society, v. 13, no. 1, p. 30-44.

Daultrey, S., 1976, Principal components analysis: Concepts and techniques in modern geography No. 8: London, Institute of British Geographers, 50 p.

Grundy, W.D., and Miesch, A.T., 1985, Brief descriptions of STATPAC and related statistical programs for the IBM personal computer: U.S. Geological Survey Open-File Report 87-411-A, 34 p.

Jarrett, R.D., 1992, Hydraulics of mountain rivers, *in* Yen, B.C., ed., Channel Flow Resistance Centennial of Manning's Formula: International Conference of the Centennial of Manning's and Kuichling's Rational Formula: Littleton, Colo., Water Resources Publications, p. 287-298.

Joreskog, K.G., Klovan, J.E., and Reyment, R.A., 1976, Geological factor analysis: New York, Elsevier Scientific Publishing Co., 178 p.

Kilpatrick, F.A., and Cobb, E.D., 1985, Measurement of discharge using tracers: Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 3, Chap. A16.

Kimball, B.A., 1997, Use of tracer injections and synoptic sampling to measure metal loading from acid mine drainage: U.S. Geological Survey Fact Sheet FS-245-96.

Kimball, B.A., Bencala, K.E., and Broshears, R.E., 1994, Geochemical processes in the context of hydrologic transport: Reactions of metals in St. Kevin Gulch, Colorado, *in*, Dutton, A., ed., Toxic Substances in the Hydrologic Sciences: Minneapolis, Minn., American Institute of Hydrology, p. 80-94.

Kimball, B.A., Callender, E., and Axtmann, E.V., 1995, Effects of colloids on metal transport in a river receiving acid mine drainage, Upper Arkansas River, Colorado, U.S.A.: Applied Geochemistry, v. 10, p. 285-306.

Kimball, B.A., McKnight, D.M., Wetherbee, G.A., Harnish, R.A., 1992, Mechanisms of iron photoreduction in a metal-rich, acidic stream, St. Kevin Gulch, Colorado, U.S.A.: Chemical Geology, v. 96, p. 227-239.

Kimball, B.A., Nimick, D.A., Gerner, L.J., and Runkel, R.L., 1999a, Quantification of metal loading in Fisher Creek by tracer injection and synoptic sampling, Park County, Montana, August 1997: U.S. Geological Survey Water-Resources Investigations Report 99-4119, 40 p.

Kimball, B.A., Runkel, R.L., and Gerner, L.J., 1999b, Quantification of metal loading in French Gulch, Summit County, Colorado, using a tracer-injection study: U.S. Geological Survey Water-Resources Investigations Report 98-4078, 38 p.

Kimball, B.A., Runkel, R.L., and Gerner, L.J., 2001, Quantification of mine-drainage inflows to Little Cottonwood Creek, Utah, using a tracer-injection and synoptic sampling study: Environmental Geology, v. 10, p. 1390-1404.

Kimball, B.A., Runkel, R.L., Walton-Day, K., and Bencala, K.E., 2002, Assessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling: Cement Creek, Colorado, USA: Applied Geochemistry, v. 17, p. 1183-1207.

Lichte, F.E., Golightly, D.W., and Lamothe, P.J., 1987, Inductively coupled plasma-atomic emission spectrometry: U.S. Geological Survey Bulletin 1770, 10 p.

McKinnon, T.E., 2002, Sources and seasonal variability of metal and arsenic concentrations in the surface water of the Clark Fork River Basin, Montana: University of Montana Master's thesis.

Rantz, S.E., and others, 1982, Measurement and computation of streamflow: Volume 1. Measurement of stage and discharge: U.S. Geological Survey Water-Supply Paper 2175, 631 p.

Runkel, R.L., Kimball, B.A., McKnight, D.M., and Bencala, K.E., 1999, Reactive solute transport in streams: A surface complexation approach for trace metal sorption: Water Resources Research, v. 35, no. 12, 3829-3840.

Steven, T.A., and Ratté, J.C., 1965, Geology and structural control of ore deposition in the Creede District, San Juan Mountains, Colorado: U.S. Geological Survey Professional Paper 487, 90 p.

Taylor, J.R., 1997, An introduction to error analysis: The study of uncertainties in physical measurements, 2nd edition: Sausalito, California, University Science Books, 327 p.

Ward, J.R., and Harr, C.A., 1990, Methods for collection and processing of surface-water and bed-material samples for physical and chemical analyses: U.S. Geological Survey Open-File Report 89-140, 71 p.

Zellweger, G.W., 1994, Testing and comparison of four ionic tracers to measure stream flow loss by multiple tracer injection: Hydrological Processes, v. 8, p. 155-165.

Zellweger, G.W., Avanzino, R.J., and Bencala, K.E., 1989, Comparison of tracer-dilution and current-meter discharge measurements in a small gravel-bed stream, Little Lost Man Creek, California: U.S. Geological Survey Water-Resources Investigations Report 89-4150, 20 p.

APPENDIX—RESULTS OF CHEMICAL ANALYSES FOR SYNOPTIC SAMPLES COLLECTED NEAR CREEDE, COLORADO

The appendix consists of two tables available as PDF files. These files are linked from their titles below.

Table A-1. Physical properties of synoptic samples collected near Creede, Colorado, August and September 2000

Table A-2. Concentration of chemical constituents in synoptic samples collected near Creede, Colorado, August and September 2000

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B.A. Kimball and others—Evaluation of Metal Loading to Streams near Creede, Colorado, August and September 2000—Scientific Investigations Report 2004–5143

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