



**QUANTIFICATION OF METAL LOADING
IN FISHER CREEK BY TRACER INJECTION
AND SYNOPTIC SAMPLING, PARK COUNTY,
MONTANA, AUGUST 1997**

Water-Resources Investigations Report 99-4119

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
kilogram (kg)	2.2046	pound
liter (L)	0.26417	gallon
meter (m)	3.2808	foot
micrometer (μm)	0.0000032808	foot
milligram (mg)	0.000002205	pound
milliliter (mL)	0.00022642	gallon

Water temperature is reported in degrees Celsius ($^{\circ}\text{C}$), which can be converted to degrees Fahrenheit ($^{\circ}\text{F}$) by the following equation:

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

Chemical concentration and water temperature are reported only in metric units. Chemical concentration is reported in grams per liter (g/L), milligrams per liter (mg/L), or micrograms per liter ($\mu\text{g/L}$). Milligrams per liter is a unit expressing the mass of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 milligram per liter. 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 ($\mu\text{S/cm}$).

QUANTIFICATION OF METAL LOADING IN FISHER CREEK BY TRACER INJECTION AND SYNOPTIC SAMPLING, PARK COUNTY, MONTANA, AUGUST 1997

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ABSTRACT

Acid mine drainage from abandoned and inactive mines affects the water quality of the upper reaches of Fisher Creek, Montana. A sodium chloride tracer was added to the stream for 29.5 hours to provide a hydrologic context for synoptic sampling of metal chemistry in the stream and its inflows. The detailed profile of stream discharge obtained from the sampling helped to indicate those areas of Fisher Creek where most of the metal loading occurred. Inflows to the stream can be divided between visible surface inflows, which were sampled, and subsurface inflows, which were not sampled, but the effects of both types of inflows on the stream load were quantified. Substantial loads were attributed to both sources. These results indicate that treatment of large visible inflows, particularly the Glengary adit, could still leave metal concentrations in Fisher Creek at levels that may adversely affect aquatic life.

INTRODUCTION

Acid mine drainage from abandoned and inactive mines affects the water quality of Fisher Creek, Montana, a headwater tributary of the Clark's Fork of the Yellowstone River. Planning is in progress for possible clean-up actions to alleviate water-quality degradation in Fisher Creek. Clean-up actions would be more effective and cost-efficient if the primary sources of acid water and metal loads were known and if important instream geochemical processes were well understood.

Metal concentrations in Fisher Creek and its main tributaries have been documented by periodic water-quality sampling (Amacher and others, 1995). Discharge measurements available for a limited number of sites allow calculation of metal loads (M.C. Amacher, U.S. Forest Service, oral commun., 1997).

However, more closely spaced sampling sites are needed for detailed remediation planning.

Spatial variations of pH and toxic metals in streams affected by acid mine drainage are the result of the interaction of hydrologic and geochemical processes (Bencala and McKnight, 1987; Kimball and others, 1994; Broshears and others, 1995). In several streams affected by acid mine drainage, sources of acid and metals have been identified and quantified by combining tracer-injection methods and spatially intensive synoptic water-quality sampling (Kimball and others, 1994; Kimball, 1997; Kimball and others, 1999). By combining discharge, determined through tracer dilution, with synoptic metal concentrations, these studies have provided the mass-balance information needed to define load profiles for metals. The detailed load information also helps decipher key geochemical processes that affect pH and metal concentrations in the stream.

Purpose and Scope

This report has two principal objectives. The first objective is to identify and quantify the principal sources of metal loads to Fisher Creek within the study reach. This is accomplished through a study that combines tracer injection and synoptic sampling. Some of the sources are visible inflows such as drainage from adits and other mine-related features and other sources are from diffuse subsurface inflows to the stream. The second objective is to describe geochemical processes that affect metal concentrations in the stream.

Description of Study Area

Fisher Creek is an alpine stream near Cooke City, Montana, that originates at an altitude of more than 3,000 m (fig. 1). The principal source of stream water is snowmelt runoff, which mostly occurs from May

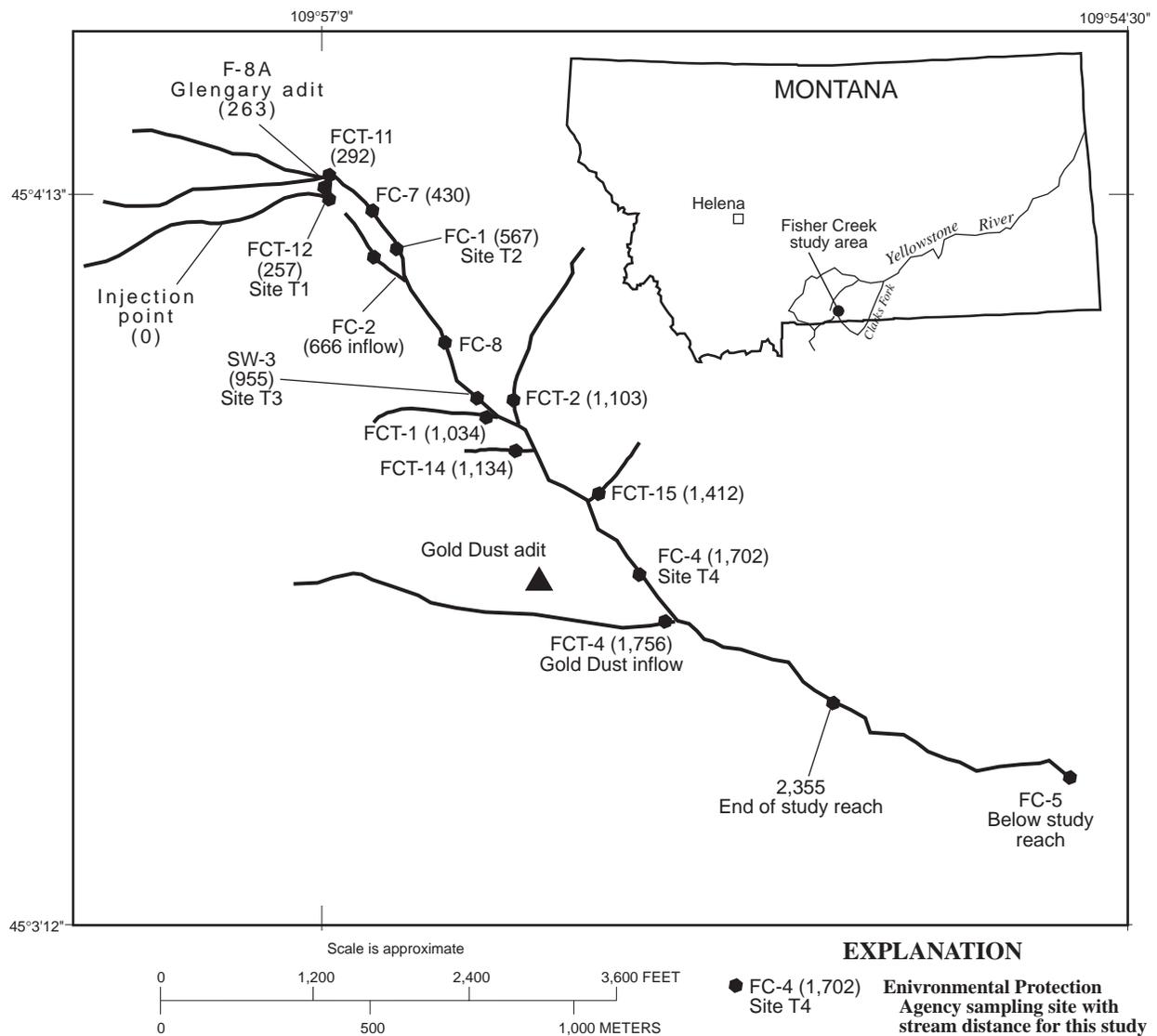


Figure 1. Location of selected surface-water sampling sites along Fisher Creek, Montana.

through July. The stream receives acid mine drainage from the Glengary adit and several seeps and springs. Pools, riffles, and cascades in this small, shallow stream cause rapid mixing of inflows.

Sampling and Analysis

The tracer-injection study was done in a 2,355-m reach of Fisher Creek for 5 days in August 1997. The tracer injection began at 1130 on August 18 and continued until 1700 on August 19 (table 1). For reporting results, 1130 is the beginning of the experiment time, or 0.0. Subsequent times are reported as decimal hours.

The injection site was about 263 m upstream from the Glengary adit, in the branch labeled FCT-12, so that drainage from the adit could be quantified as tributary inflow to the stream. A second branch of Fisher Creek, labeled FCT-11, enters the stream 29 m downstream from the Glengary adit inflow and was treated as a tributary. The 2,355-m reach was divided into 42 segments for synoptic sampling. Sampling sites were located upstream and downstream from selected inflows to allow mass-balance calculations for each inflow. Additional stream sampling sites were located in some of the longer areas without visible inflows to detect any subsurface inflow. The longest of these segments was 120 m, but most of the segments were about 60 m or less. A total of 23 inflow sampling sites was

Table 1. Sequence of tracer-injection activities and sampling in Fisher Creek, Montana, August 1997

[mL/min, milliliters per minute; mg/s, milligrams per second]

Date	Time	Experiment time (hours)	Activity	Pump rate (mL/min)	Injection rate (mg/s)
8/16/97	0900		Reconnaissance of stream and inflows to establish sampling sites and measure downstream distances from the injection site.		
8/17/97	0900		Reconnaissance of sites and flow-meter discharge measurements at sites T2 through T5.		
8/18/97	1130	0.0	Start of tracer injection; start of sampling for the tracer arrival at the downstream transport sites.	215.4	544.6
	1700	5.5	Started autosamplers at sites T3, T4, and T5.		
	2146	10.27	Pump #1 failed and pump #2 started with a slightly higher injection rate.	236.9	599.0
8/19/97	0800	20.5	Synoptic sampling of stream and inflow sites.		
	1002	22.53	Connected new battery to pump #2, causing a slight increase in flow rate.	291.2	736.1
	1700	29.5	End of tracer injection; start of sampling for the tracer departure at the downstream transport sites.		
8/20/97			Continued sampling with autosamplers at downstream transport sites.		
	1200	48.5	End of sampling.		

chosen to represent the range of pH and specific conductance of water entering the stream. Sampling sites and inflow locations are referenced by their distance downstream from the injection site. A previous study (Amacher and others, 1995) used the Glengary adit as a zero point for measuring meters downstream, so the distances in this study are 263 m longer than in that study.

Tracer Sampling

A tracer solution of sodium chloride (NaCl; 149.4 +/- 2.2 g/L as Cl) was injected into Fisher Creek. During the 29.5-hour injection, variations in the pump rate resulted in changes of the injection rate to the stream (table 1). It was necessary to account for the variations of the injection rate to interpret the downstream tracer concentrations. The arrival of the NaCl pulse and the development of a plateau concentration

were observed at five locations, transport sites T1 through T5. These sites ranged from 257 to 2,355 m downstream from the injection site (fig. 1). Numerous samples were collected at all five transport sites to observe the arrival and departure of the tracer. Autosamplers collected tracer samples at T3, T4, and T5 throughout the night. Water samples for tracer analysis were filtered through 0.45- μ m in-line capsule filters upon collection. Analytical methods are indicated in table 2.

Synoptic Sampling

During the plateau period, water samples were collected at the synoptic sites, which included the transport sites. Water samples for metal and anion analysis were collected from the stream and inflows in acid-washed polyethylene bottles. At a temporary field laboratory, splits of each sample were processed for the

Table 2. Analysis of synoptic samples collected in Fisher Creek, Montana, August 1997
[μm , micrometer]

Analysis	Field treatment	Analytical method
Filtered ferrous iron	Filtered (0.45 μm), unacidified	Bipyridine, colorimetric method for ferrous iron
pH, specific conductance	Unfiltered, unacidified	Ion-sensitive electrode
Chloride tracer concentrations and sulfate	Filtered (0.45 μm), unacidified	Ion chromatography
Filtered metal concentrations	Filtered (0.45 μm), acidified	Inductively coupled argon plasma-atomic emission spectrometer--(ICP-AES)
Total-recoverable metal concentrations	Unfiltered, acidified	ICP-AES with standard U.S. Environmental Protection Agency digestion for total-recoverable concentrations

different analyses (table 2). Filtration was with 0.45- μm in-line capsule filters to meet regulatory requirements of the U.S. Environmental Protection Agency (EPA). This filtration provided an operational definition of dissolved metal concentrations, not a truly dissolved metal concentration (Kimball and others, 1995). These concentrations are referred to as filtered, rather than dissolved, to emphasize this operational definition for metals.

Chemical Analysis

Ferrous iron, pH, and specific conductance were measured in the field on the same day the samples were collected. Chloride and SO_4 were analyzed by the U.S. Geological Survey at the Utah District Office. Quality assurance methods and results for precision of the anion analyses are presented in the appendix. For samples with concentrations of Cl greater than about 60 mg/L the precision was 5.4 percent. For the majority of the stream, however, the precision of Cl analysis was 2.4 percent. This allows the detection of much smaller changes in discharge than could be accomplished with a flow-meter measurement.

Metals were analyzed by an EPA contract laboratory, and quality assurance procedures for the contract were followed. A flat value of 5 percent precision was assumed for the metals data.

Equations

When a constant-rate injection is continued for a sufficient length of time, an equilibrium condition develops in which a tracer-plateau concentration occurs at each downstream site. The injection rate and injection

concentration are known, so the downstream concentration of the tracer in the stream provides for a calculation of stream discharge at the first sampling point downstream from the injection site:

$$Q_A = \frac{Q_{Inj}(C_{Inj} - C_0)}{(C_A - C_0)} \quad (1)$$

where Q_A is the stream discharge at the first downstream site,
 C_{Inj} is the tracer concentration in the injection solution,
 Q_{Inj} is the rate of the tracer injection into the stream,
 C_A is the tracer concentration at the first site downstream from the tracer injection, and
 C_0 is the background tracer concentration upstream from the injection site.

The discharge at the first site downstream from the injection, Q_A , is used to calculate the discharge at the next site, and each subsequent sampling site by using the equation:

$$Q_B = \frac{Q_A(C_A - C_I)}{(C_B - C_I)} \quad (2)$$

where Q_B is the discharge at the downstream site,
 Q_A is the upstream discharge,
 C_A is the upstream tracer concentration,
 C_I is the tracer concentration in water entering the stream between sites A and B, and
 C_B is the tracer concentration at the downstream site.

Where there was no inflow sample between consecutive stream sites, the median C_I concentration for all the inflow samples was substituted for C_I . The increase of discharge for each of the 42 segments was the difference between the upstream and downstream discharge for each segment and could be due to visible surface inflows and subsurface inflow.

It is helpful to compare the variations of the different concentration profiles among all the metals. Variation of a metal concentration in a stream should be viewed relative to some defined measure. The instream metal concentration generally will reach some value that is between the maximum and minimum concentrations of inflows (Bencala and McKnight, 1987). There can be a wide range of concentrations among the metals from mine drainage. Normalization of concentrations relative to the sampled range of inflow concentrations renders the various metals more comparable. Instream concentrations are normalized by the equation (Bencala and McKnight, 1987):

$$C_{NORM} = \frac{(C_S - C_{MIN}^I)}{(C_{MAX}^I) - C_{MIN}^I} \quad (3)$$

where C_{NORM} is the normalized concentration relative to the range of inflow concentrations,

C_S is the instream concentration at a given distance downstream from the injection,

C_{MIN}^I is the minimum inflow concentration for the metal, and

C_{MAX}^I is the maximum inflow concentration for the metal.

This ratio of concentrations will be 1.0 if the instream concentration is equal to the maximum inflow concentration and will be 0.0 if the instream concentration is equal to the minimum inflow concentration.

During the plateau condition, synoptic sampling provided a spatially intensive “snapshot” of the instream conditions that included chemistry and discharge. Logistically, taking the snapshot of several kilometers of a stream required sampling over a period of hours. Load (mg/s) is the product of concentration (mg/L) and discharge (L/s) and can be calculated for any stream site. For site A, load would be $Q_A C_A$ (fig. 2). The instream change in mass between the upstream site A and the downstream site B, ΔM_S , is calculated from the equation:

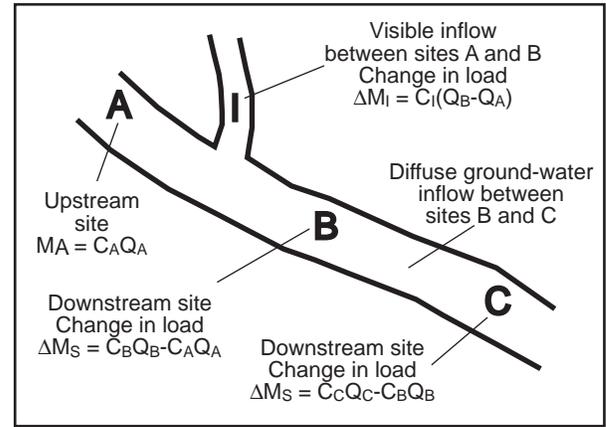


Figure 2. Schematic diagram showing mass-balance calculation around an inflow to a stream.

$$\Delta M_S = (Q_B C_B - Q_A C_A) \quad (4)$$

where ΔM_S is the net change in stream load between sites A and B,

Q_B is the discharge at site B,

C_B is the metal concentration at site B,

Q_A is the discharge at site A, and

C_A is the metal concentration at site A.

There are two ways to account for ΔM_S between stream sites. If a sampled inflow concentration, C_I , represents the concentration of all the water entering between sites A and B, then the change in mass also can be calculated from:

$$\Delta M_I = C_I(Q_B - Q_A) \quad (5)$$

where ΔM_I is the net change in stream load between sites A and B, assuming that C_I represents all the water entering the stream between sites A and B. This is called the “sampled inflow load” for this study.

Alternatively, if there was no visible inflow, but a subsurface contribution to the load between sites A and B caused an increase in load, then the average inflow concentration for the segment can be calculated by rearranging equation 5 to solve for C_I to represent the ground-water concentration. If the metal was removed by chemical reaction between A and B, however, the calculated value of C_I will be an underestimate of the average inflow concentration. To resolve the fraction of ground-water and surface-water contributions, more information is needed about the ground water. This limitation represents a best approach at this time.

A negative value of ΔM_S represented the mass of metal removed from the stream by instream processes. Any removal can mask inflows that occur in the area.

Effects of instream processes are most evident when the sampled instream load is compared with a cumulative total load. This load is calculated by summing all the positive values of ΔM_S . For each stream segment, however, ΔM_S represents a net change in load, so that it may represent some loss of mass. Thus, the cumulative total load represents a minimum estimate of the total load. These possibilities are summarized as follows:

Condition	Probable explanation
$\Delta M_S = \Delta M_I$	The value of C_I represents the concentration of all the water entering the stream.
$\Delta M_S > \Delta M_I$	Subsurface inflow has a concentration greater than C_I .
$\Delta M_S < \Delta M_I$	Could indicate two conditions: (1) load is lost through chemical reaction within the subreach or (2) subsurface inflow has a concentration less than C_I .
$\Delta M_S < 0$	There is a net loss of load through chemical reaction within the stream subreach.

TRACER INJECTION

A load analysis must be based on accurate discharge measurements. Tracer-injection studies typically provide a more accurate discharge for loading analysis than flow-meter measurements for cobble-bottomed, mountain streams (Kimball, 1997). The calculation of arrival time is described using data from site T5.

Arrival Time

An injected tracer moving downstream without dispersion or transient storage would arrive at a downstream site with a very sharp concentration front. On a graph of concentration versus time, this front would look like a box, going from a background concentration near zero to the plateau concentration instantly. Likewise, the concentration would decrease sharply from the plateau to the background concentration after the injection stopped. As a result of dispersion and, more importantly, transient storage, the arrival of a tracer is spread out over time so there is a shoulder on the front edge of the box and a tail after the box (Stream Solute Workshop, 1990).

By convention, the arrival time at a site is defined as the time at which the instream-tracer concentration

reaches half of the plateau concentration (Zellweger and others, 1988). Residence time between two sites is the difference in arrival times. The breakthrough time, also by convention, is defined as the time when the instream tracer concentration is double the pre-injection concentration.

Because of the drop in altitude of more than 50 m from the injection site to the first transport site T1, the arrival time for traveling the 257 m was expected to be about 20 minutes. However, the arrival of the tracer was profoundly delayed. A possible explanation of this delay is a flow path through alpine soils near the injection site. More than 4 hours passed before the transient storage capacity of the soils was filled and the plateau was reached at site T1.

Not only was the tracer delayed, but problems with the pumps resulted in three different pump rates (table 1). From the start of the injection at 1130 until 2146 on August 18, the pump rate was 215 mL/min, delivered by pump #1. From 2146 hours on August 18, when pump #1 failed, pump #2 delivered a rate of 237 mL/min until 1002 on August 19. At that time, a new battery was connected to pump #1 causing the flux to increase to 291 mL/min. This rate remained steady until the end of the injection at 1700 on August 19. Even with the complications, however, the arrival times and plateau concentrations of the tracer could be calculated at the transport sites.

Data for site T5 are used to demonstrate how tracer arrival times and plateau concentrations were calculated and how adjustments were made to account for the changes in pump rate (fig. 3). Solid vertical lines represent the start of the injection, the start of pump #2, changing the pump #2 battery, and the end of the injection. The clearest signal in the concentration data for site T5 was the breakthrough at 3.17 hours in response to the initial tracer injection. The dashed vertical line in figure 3 after each pump event represents this time interval. This 3.17-hour interval compared very well with the decrease in tracer concentration after the injection was stopped.

Different plateau concentrations should have been observed for each of the three pump rates. However, no clear plateau levels occurred because of the temporal overlap of the tracer movement caused by each change in rate. At 13.2 hours, the tracer at site T5 may have been close to the first plateau level. However, this plateau is not well defined because the tracer concentration increased in response to the increased flux caused by the switch to pump #2. A second plateau at 2.75 mg/L is evident at about 23 hours. Similar to the

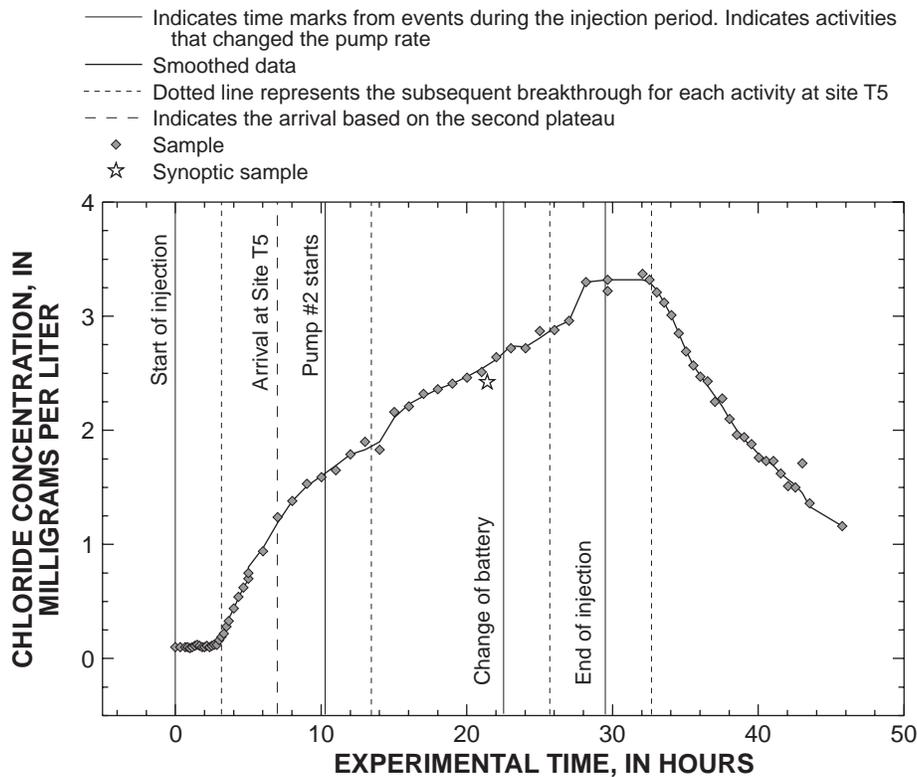


Figure 3. Variation of chloride concentration with time at transport site T5.

first plateau, the second plateau occurred about 13 hours after the change in pump rate. The third plateau may have been near 3.3 mg/L and occurred between about 28 and 32 hours. This plateau started only about 6 hours after the related change in pump rate so it is not clear whether this plateau is real. The second plateau level is considered the most definitive because it occurred during the longest period of constant pump rate.

Using the second, most probable plateau level of 2.75 mg/L and the ratio of the injectate fluxes for the first and second levels, the first plateau level would be:

$$2.75 \text{ mg/L} \left(\frac{544.6}{599.0} \right) = 2.5 \text{ mg/L.} \quad (6)$$

The time at which half of 2.5 mg/L reached site T5 was 7 hours. This represents the residence time for the entire study reach. From site T2 to site T5, the residence time was only about 3 hours; retention of tracer upstream from site T2 accounted for the other 4 hours.

This same reasoning was followed to find the second plateau concentration and the arrival time for sites T1 through T4. The tracer data for all the transport sites are shown in figures 3 to 7. Because the tracer was delayed upstream from site T1, the arrival times at sites

T1 and T2 almost occurred after the manual tracer sampling ended on August 18. Arrival times at sites T3, T4, and T5 were sampled because autosamplers collected samples through the night. A summary of the transport information for each of these sites is listed in table 3, along with adjusted plateau and synoptic Cl concentrations and discharge calculations at the sites.

Discharges calculated from the tracer concentrations were greater than those calculated by flow-meter measurements on August 17. At sites T2 and T3, the values were comparable. At sites T4 and T5, the tracer-determined discharges were much greater. This difference might indicate that there was more hyporheic flow at downstream sites. However, because there was rain at night between the flow-meter and the tracer-dilution measurements, the difference might also have been affected by the storm, but this kind of difference would likely have been observed at the upstream sites as well.

Discharge Profile of the Stream

A detailed discharge profile for a stream can be developed using the tracer concentrations in each synoptic sample. Calculation of these discharges for a

Table 3. Transport information, chloride concentrations, and discharge calculations at transport sites downstream from the tracer-injection site, August 18-19, 1997, Fisher Creek, Montana

[mg/L, milligrams per liter; L/s, liter per second; NM, no measurement]

Transport site	Distance from injection site (m)	Pre-injection chloride (mg/L)	Synoptic chloride (mg/L)	Plateau chloride (mg/L)	Arrival time (hours)	Residence time between sites (hours)	Plateau discharge (L/s)	Flow-meter discharge (L/s)
T1	257	0.09	238	201	4.88	4.88	3.0	NM
T2	567	.30	19.8	19.8	5.86	.98	30	23
T3	955	.21	12.2	11.2	6.15	.29	54	44
T4	1,702	.07	4.2	4.3	6.49	.34	141	77
T5	2,355	.11	2.4	2.75	7.00	.51	227	133

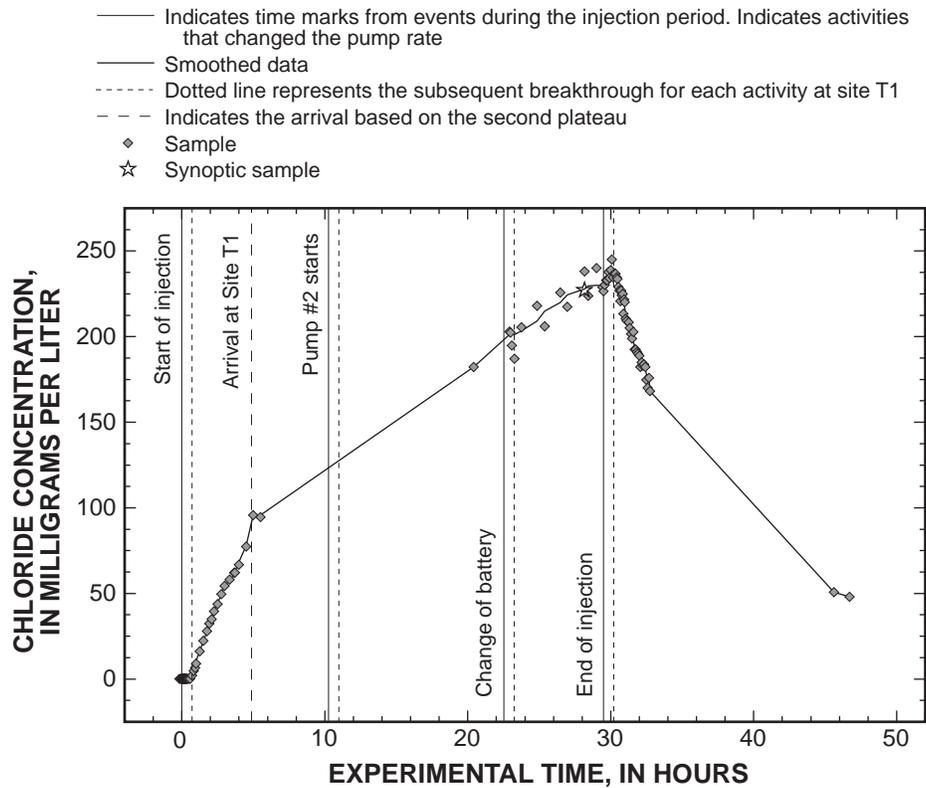


Figure 4. Variation of chloride concentration with time at transport site T1.

- Indicates time marks from events during the injection period. Indicates activities that changed the pump rate
- Smoothed data
- Dotted line represents the subsequent breakthrough for each activity at site T2
- - - Indicates the arrival based on the second plateau
- ◇ Sample
- ☆ Synoptic sample

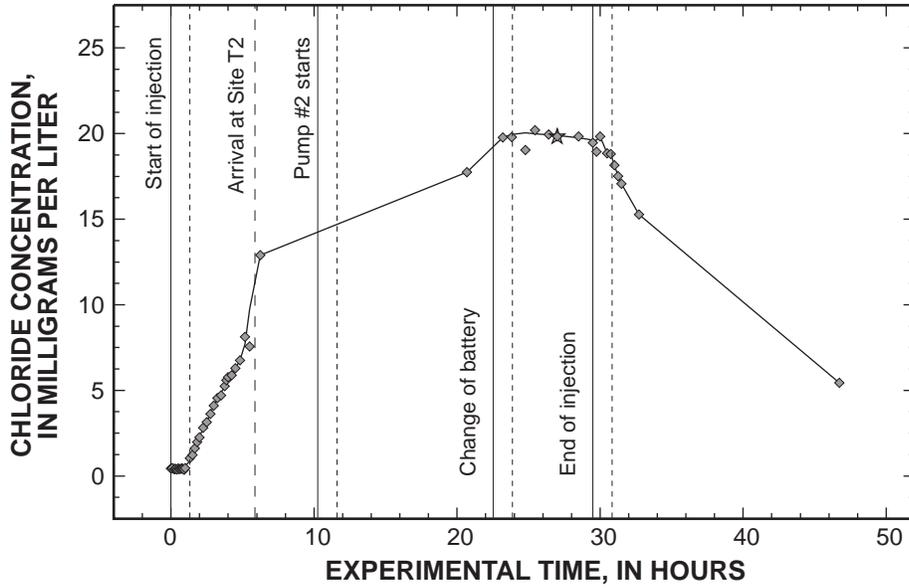


Figure 5. Variation of chloride concentration with time at transport site T2.

- Indicates time marks from events during the injection period. Indicates activities that changed the pump rate
- Smoothed data
- Dotted line represents the subsequent breakthrough for each activity at site T3
- - - Indicates the arrival based on the second plateau
- ◇ Sample
- ☆ Synoptic sample

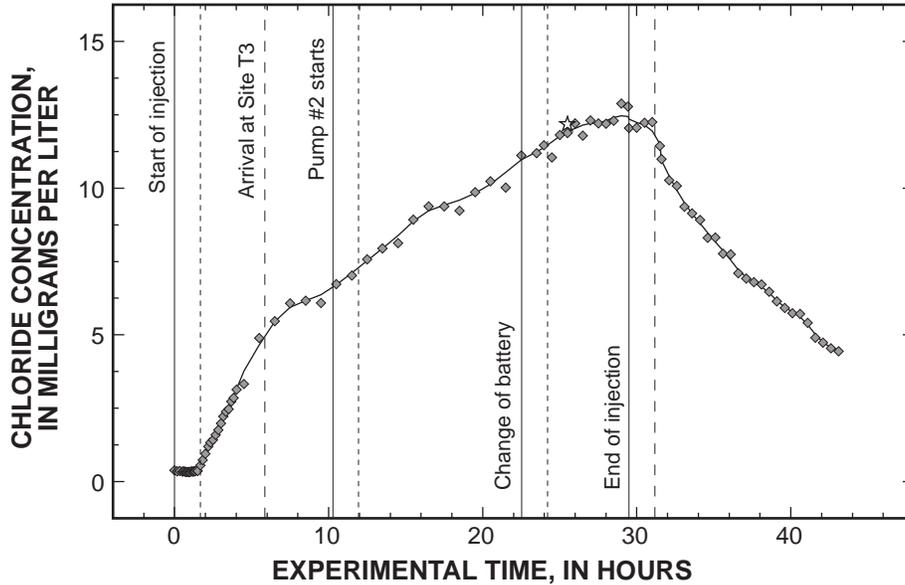


Figure 6. Variation of chloride concentration with time at transport site T3.

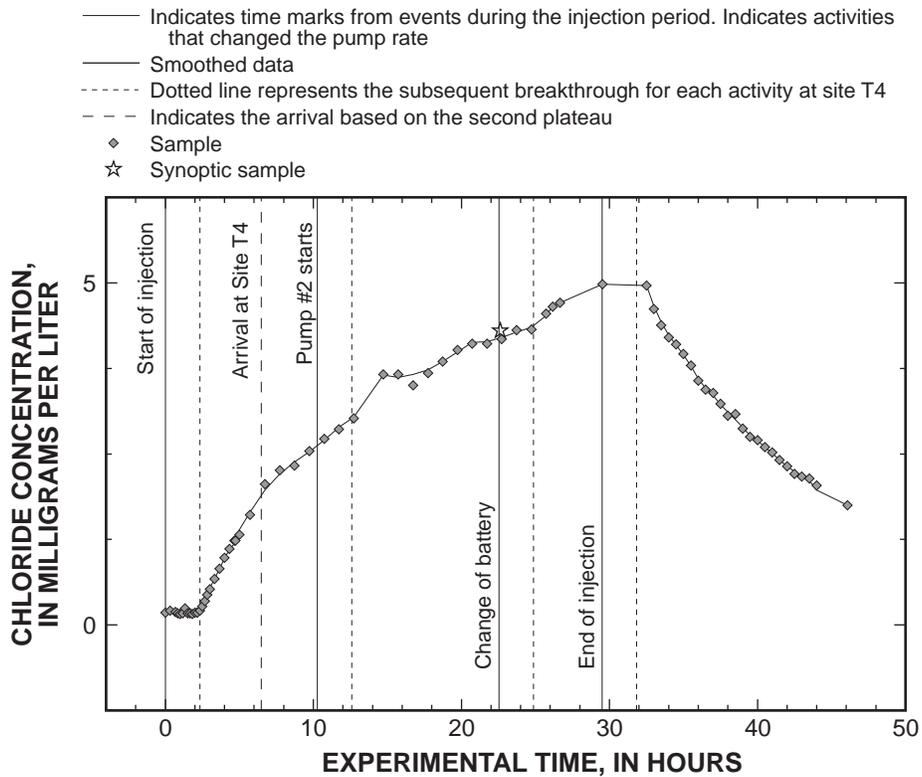


Figure 7. Variation of chloride concentration with time at transport site T4.

tracer-injection study depends on two conditions. First, the tracer concentration in the stream should be consistently higher than the concentration in the inflows. This condition was realized with the instream Cl concentration during the synoptic sampling (fig. 8a). None of the inflows had a Cl concentration greater than 0.25 mg/L and the median was 0.13 mg/L. Second, the tracer concentration in each synoptic sample should represent the steady-state plateau concentration at that sampling site. The variation of the injection rate prevented this condition at some sites. As noted above, the second plateau level was better defined and therefore was used for calculating discharge. Cl concentrations in some synoptic samples needed to be adjusted because the second plateau level was moving downstream as synoptic samples were being collected in an upstream order. The synoptic Cl concentration was greater than the second plateau at site T1, comparable at sites T2, T3, and T4, and less than the plateau level at site T5. Although the concentration differences between plateau and synoptic Cl concentrations were small, they resulted in a substantial difference in discharge calculations (fig. 8b).

Synoptic Cl concentrations downstream from site T4 were adjusted by calculating the difference between

synoptic and plateau concentrations at sites T4 and T5. Differences at the two points were regressed against the sample collection time, and then a shift was calculated for all the individual sampling times at all the synoptic sites between T4 and T5. This temporal correction accounted for the shift, which was greatest in the morning and grew smaller as samples were collected upstream.

The difficulty with the pumps could not be foreseen, but if the delay in the tracer arrival could have been anticipated, an extra day of injection would have been allowed before the synoptic sampling began so that all the sites would have had more time at the plateau concentration. Any future injection site in Fisher Creek should be downstream from the soils that caused the delay in the tracer.

The total gain of water downstream from site T1 was 227 L/s. The segments with visible inflows accounted for 65 percent of this flow, leaving 35 percent attributable to small seeps and subsurface inflows. Almost 60 percent of the gain occurred in just eight stream segments, including both visible and subsurface inflows. The largest visible inflows occurred at 1,103 m (FCT-2); 2,116 m (a wetland inflow); 292 m (FCT-11),

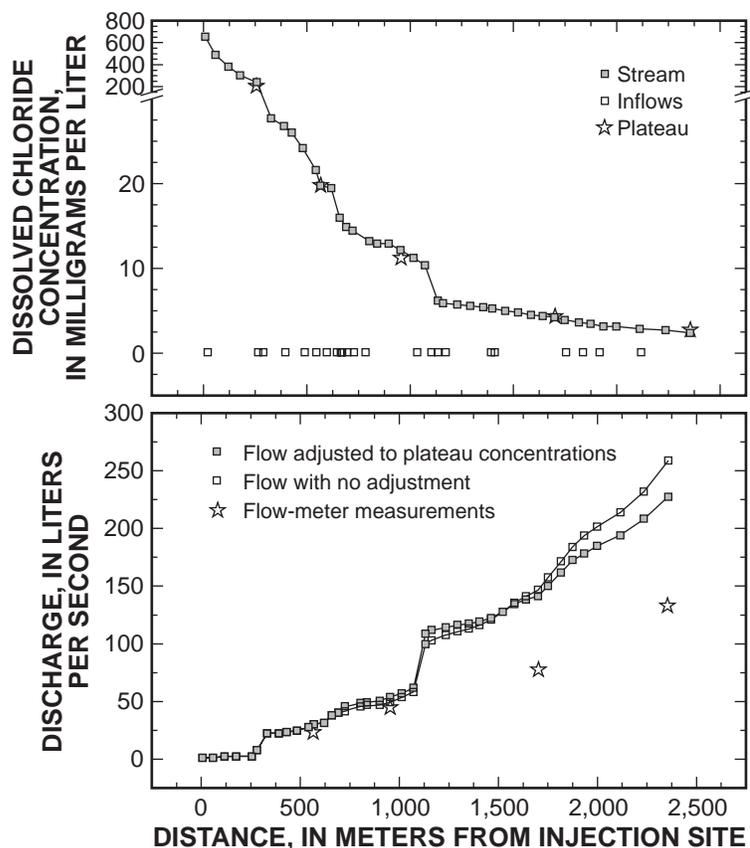


Figure 8. Variation of (a) chloride concentration and (b) calculated discharge with distance in Fisher Creek, Montana, during synoptic sampling, August 19, 1997.

1,756 m (FCT-4), 1,834 m (a wetland inflow); and 645 m (FC-2, drainage from a mine waste-rock pile just below the Glengary adit). The Glengary adit, at 263 m, added only 4.8 L/s, but had a profound effect on the metal concentrations.

Substantial subsurface inflow also occurred in many stream segments. The greatest subsurface inflow (28 L/s) occurred between 1,462 m and 1,750 m. This inflow was significant because of the metal loads that it contributed to Fisher Creek. Other substantial subsurface inflows occurred between 1,936 m and 2,000 m and between 2,235 m and 2,355 m. Both of these were nonacidic inflows that affected the metal chemistry downstream.

SYNOPTIC SAMPLING

Results of chemical analysis of water from the synoptic sampling sites are listed in tables 4 and 5. Data are sorted in downstream order within groups of stream and inflow sites to emphasize the downstream changes.

Inflows

The chemical character of water in Fisher Creek changed in response to the chemistry of inflows. The downstream profile of pH provides an overview of the changes, indicating three important divisions for the study reach (fig. 9). First, upstream from the Glengary adit, Fisher Creek was acidic, indicating that there were sources of acid drainage. Natural weathering of the intrusive porphyritic rock high in the watershed may have been the source of this acid drainage. Acidic inflows downstream, however, had much more effect on the stream chemistry. The second geochemical division began at 263 m, where the Glengary adit inflow caused the lowest pH and the highest metal concentrations in Fisher Creek. This division extended downstream to about 1,715 m. A combination of acidic and near-neutral pH inflow in this second division, resulted in the gradual increase of pH. In the final division of the stream, downstream from 1,715 m, pH increased sub-

Table 4. Characteristics of water and concentrations of major ions in water from synoptic-sampling sites, Fisher Creek, Montana, August 19, 1997

[Trib, stream=0, inflow=1; Distance, distance from injection site, in meters; EPA name, U.S. EPA designation for sites; Temp, water temperature, in degrees Celsius; pH, in standard units; specific conductance, K_{sc}, in microSiemens per centimeter at 25 degrees Celsius; all major ions in milligrams per liter]

Trib	Distanc\$	EPA nam\$	Tim\$	T\$mp	pH	K _{sc}	Calcium	Magn\$sium	Sodium	Chlorid\$	Sulfat\$
0	10		1620	12.7	4.30	2,190	2.57	0.57	404	652	40.1
0	60		1605	14.4	4.18	1,589	2.82	.56	288	480	36.3
0	120		1555	14.4	4.07	1,293	2.92	.50	227	383	41.1
0	180		1550	13.8	3.94	1,024	3.39	.58	171	303	40.6
0	280		1527	10.0	3.08	1,322	40.2	11.7	47.8	77.1	376
0	330		1520	13.5	3.12	600	18.7	5.02	17.2	27.6	204
0	390		1515	13.5	3.10	578	18.7	4.96	17.1	26.8	196
0	430	FC-7	1503	13.5	3.20	593	18.6	4.95	16.6	25.9	195
0	482		1500	14.0	3.17	565	18.5	4.88	15.8	23.5	190
0	542		1445	14.1	3.12	522	18.1	4.69	14.5	21.7	183
0	567	FC-1	1430	15.0	3.14	501	17.5	4.48	13.5	20.0	177
0	618		1422	13.8	3.19	495	16.9	4.40	13.3	18.3	172
0	659		1417	14.4	3.27	436	15.4	3.99	11.1	16.5	167
0	692		1355	15.4	3.28	407	15.0	3.94	10.7	15.0	163
0	725		1242	15.0	3.21	390	14.7	3.84	10.4	14.1	158
0	802		1320	16.4	3.33	370	14.0	3.70	9.77	13.4	154
0	840		1315	17.0	3.34	370	13.9	3.63	9.59	13.0	150
0	900		1306	16.6	3.41	362	13.6	3.54	9.36	12.7	148
0	955	SW-3	1300	17.6	3.42	354	13.2	3.47	9.07	12.1	147
0	955	SW-3	1300	17.6	3.42	354	13.5	3.52	9.20	12.3	148
0	1,015		1215	14.8	3.41	350	13.2	3.49	8.94	11.3	144
0	1,072		1206	13.3	3.45	312	12.0	3.16	7.94	10.4	136
0	1,132		1151	12.1	3.62	208	9.55	2.39	5.34	6.11	104
0	1,161		1142	11.9	3.62	194	9.27	2.28	5.10	6.09	104
0	1,232		1124	11.8	3.65	195	9.00	2.20	4.90	5.64	95.0
0	1,292		1117	10.6	3.53	197	8.86	2.15	4.83	5.50	71.2
0	1,352		1110	10.6	3.84	187	8.79	2.17	4.75	5.39	72.3
0	1,402		1055	9.3	3.79	175	8.62	2.34	5.17	5.24	69.2
0	1,462		1043	9.0	3.82	165	8.79	2.17	4.68	5.03	67.9
0	1,522		1035	10.2	3.80	164	8.81	2.15	4.62	4.77	67.5
0	1,582		1030	13.8	3.79	152	8.49	2.04	4.25	4.51	67.8
0	1,642		1022	9.5	3.73	164	8.53	2.02	4.19	4.33	63.2
0	1,702	FC-4	1008	8.5	3.65	160	8.50	2.07	4.18	4.16	83.6
0	1,750		1003	7.9	4.00	150	8.43	2.04	4.05	3.90	76.9
0	1,816		950	7.5	4.21	156	11.5	2.81	3.82	3.58	77.9
0	1,876		940	7.0	4.14	152	12.8	3.34	4.15	3.34	77.4
0	1,936		925	6.6	4.51	157	13.3	3.45	4.20	3.18	76.9
0	2,000		920	6.2	4.54	150	13.4	3.48	3.81	3.05	76.8
0	2,115		912	5.9	4.66	148	13.2	3.37	3.73	2.89	89.0
0	2,235		905	6.1	5.90	136	14.9	3.49	3.29	2.67	52.7
0	2,355		855	6.6	5.61	135	14.9	3.49	3.29	2.42	48.0

Table 4. Characteristics of water and concentrations of major ions in water from synoptic-sampling sites, Fisher Creek, Montana, August 19, 1997-Continued

Trib	Distance	EPA name	Time	Temp	pH	K _{sc}	Calcium	Magnesium	Sodium	Chloride	Sulfate
1	21		1610	11.9	4.90	38	3.04	.27	1.09	0.04	14.7
1	263	F-8A	1535	2.9	3.00	1,402	58.1	17.3	4.13	.11	601
1	292	FCT-11	1523	16.2	3.76	132	7.00	1.53	1.01	.00	64.1
1	397		1510	11.5	3.97	93	7.93	1.60	1.08	.04	49.9
1	492		1450	12.7	6.22	109	13.2	2.78	2.15	.18	33.9
1	550		1442	8.5	5.70	75	8.05	1.47	2.19	.20	21.5
1	599		1425	19.7	6.33	66	5.99	1.00	3.65	.04	15.7
1	645		1420	17.5	3.27	310	10.1	2.96	3.09	.29	114
1	666		1410	11.9	3.61	289	11.3	4.20	4.54	.09	123
1	670		1403	19.9	3.75	130	4.54	1.77	3.33	.06	68.4
1	699		1347	16.2	5.78	47	4.48	.85	1.78	.06	17.0
1	729		1337	14.1	6.49	42	4.60	.80	1.70	.06	5.71
1	786		1325	13.8	4.44	47	2.09	.74	1.86	.04	26.7
1	1,034	FCT-1	1210	13.6	6.25	37	3.43	1.06	1.30	.06	22.4
1	1,103	FCT-2	1200	10.0	6.45	46	5.53	1.07	.89	.04	9.43
1	1,134	FCT-14	1146	11.5	3.85	84	3.70	1.09	1.73	.05	47.9
1	1,172		1128	10.1	6.37	39	4.83	.68	1.21	.03	10.3
1	1,394		1100	8.4	6.16	29	2.85	.56	1.60	.14	2.76
1	1,412	FCT-15	1050	7.7	6.37	81	11.9	1.54	.87	.00	14.0
1	1,756	FCT-4	1000	8.3	6.74	241	32.6	8.08	1.59	.02	101
1	1,834		945	7.9	6.76	350	44.2	15.1	6.52	.08	138
1	1,917		930	7.8	6.27	169	23.4	4.68	1.05	.03	69.5
1	2,116	FCT-13	910	5.6	7.20	164	25.9	4.21	.96	.11	35.9

Table 5. Metal concentrations in samples from Fisher Creek, Montana, August 19, 1997

[All concentrations in micrograms per liter; Trib, 0=stream sites, 1=inflow site, 9=field blank; Distance, distance from injection site, in meters]

Trib	Distance	Aluminum, filtered	Aluminum, total	Arsenic, filtered	Arsenic, total	Barium, filtered	Barium, total	Cadmium, filtered	Cadmium, total	Copper, filtered	Copper, total	Iron, filtered	Iron, total	Lead, filtered	Lead, total
0	10	1,380	1,410	< 3	< 3	37	40	< 3	< 3	726	726	117	192	< 2	3
0	60	1,260	1,250	< 3	< 3	39	38	< 3	< 3	595	570	214	235	3	5
0	120	1,550	1,540	< 3	< 3	58	56	< 3	< 3	664	646	120	139	6	7
0	180	2,330	2,380	< 3	< 3	85	85	< 3	< 3	970	973	70	102	7	9
0	257	3,210	3,170	< 3	< 3	107	105	< 3	< 3	1,230	1,190	51	64	8	9
0	280	10,400	10,200	6	4	40	40	< 3	< 3	4,070	3,990	45,500	45,700	23	25
0	330	4,900	5,010	< 3	< 3	36	38	< 3	< 3	1,650	1,640	14,400	17,100	8	10
0	390	4,910	4,820	< 3	< 3	37	36	< 3	< 3	1,650	1,590	13,500	15,700	9	10
0	430	4,800	4,640	< 3	< 3	36	35	< 3	< 3	1,610	1,510	14,100	14,400	9	10
0	482	4,560	4,450	< 3	< 3	36	35	< 3	< 3	1,530	1,450	12,700	13,200	8	10
0	542	4,170	4,090	< 3	< 3	33	33	< 3	< 3	1,400	1,330	11,200	11,500	8	9
0	567	3,880	3,980	< 3	< 3	32	34	< 3	< 3	1,300	1,320	9,970	10,400	7	7
0	618	3,810	4,090	< 3	< 3	32	35	< 3	< 3	1,270	1,350	8,900	10,100	6	7
0	659	3,620	3,730	< 3	< 3	30	31	< 3	< 3	1,210	1,260	7,990	8,520	6	7
0	692	3,550	3,690	< 3	< 3	29	31	< 3	< 3	1,230	1,270	7,080	7,620	7	7
0	725	3,460	3,690	< 3	< 3	28	31	< 3	< 3	1,190	1,260	6,830	7,410	6	7
0	802	3,230	3,360	< 3	< 3	27	30	< 3	< 3	1,120	1,150	6,110	6,500	5	7
0	840	3,180	3,340	< 3	< 3	27	29	< 3	< 3	1,100	1,150	5,940	6,340	5	4
0	900	3,110	3,230	< 3	< 3	27	29	< 3	< 3	1,070	1,120	5,570	5,920	5	5
0	955	3,000	3,160	< 3	< 3	26	28	< 3	< 3	1,040	1,090	5,170	5,610	5	6
0	955	3,050	3,160	< 3	< 3	27	29	< 3	< 3	1,050	1,080	5,310	5,570	5	6
0	1,015	3,000	3,160	10	< 3	26	29	< 3	< 3	1,040	1,080	5,170	5,540	5	5
0	1,072	2,620	2,790	9	< 3	28	30	< 3	< 3	921	970	4,400	4,760	4	5
0	1,132	1,670	1,740	8	< 3	21	23	< 3	< 3	580	606	2,710	2,940	< 2	3
0	1,161	1,610	1,800	8	< 3	22	25	< 3	< 3	548	614	2,520	2,860	2	3
0	1,232	1,540	1,830	8	< 3	21	25	< 3	< 3	528	578	2,390	2,690	< 2	4
0	1,292	1,520	1,660	9	< 3	21	23	< 3	< 3	510	561	2,270	2,560	< 2	2
0	1,352	1,480	1,600	9	< 3	20	23	< 3	< 3	500	538	2,200	2,390	< 2	3
0	1,402	1,590	1,620	7	< 3	23	24	< 3	< 3	537	555	2,260	2,440	< 2	< 2
0	1,462	1,380	1,520	11	< 3	22	23	< 3	< 3	477	493	1,910	2,200	< 2	2
0	1,522	1,370	1,390	10	< 3	22	21	< 3	< 3	474	461	1,810	2,000	< 2	3
0	1,582	1,310	1,390	< 3	< 3	21	22	< 3	< 3	437	473	1,660	1,970	< 2	2
0	1,642	1,320	1,380	< 3	< 3	21	21	< 3	< 3	440	461	1,590	2,000	< 2	3
0	1,702	1,320	1,380	< 3	< 3	21	22	< 3	< 3	439	455	1,580	1,840	< 2	3
0	1,750	1,270	1,380	< 3	< 3	20	22	< 3	< 3	427	464	1,480	1,800	< 2	3
0	1,816	1,120	1,270	< 3	< 3	21	22	< 3	< 3	374	396	997	1,550	< 2	2
0	1,876	1,120	1,160	< 3	< 3	23	22	< 3	< 3	380	375	766	1,470	< 2	3
0	1,936	1,090	1,100	< 3	< 3	23	24	< 3	< 3	370	366	703	1,390	< 2	4
0	2,000	1,040	1,050	< 3	< 3	25	22	< 3	< 3	364	346	627	1,290	< 2	3
0	2,115	1,010	1,050	< 3	< 3	25	22	< 3	< 3	357	342	554	1,250	< 2	3
0	2,235	89	887	< 3	< 3	27	25	< 3	< 3	271	280	397	1,020	< 2	3
0	2,355	61	878	< 3	< 3	27	26	< 3	< 3	253	284	355	1,000	< 2	< 2
1	21	213	228	< 3	< 3	25	24	< 3	< 3	< 4	< 4	< 14	38	3	5
1	263	14,100	13,400	6	6	9	7	< 3	< 3	5,550	5,290	69,400	67,600	33	33
1	292	1,950	2,230	< 3	< 3	35	36	< 3	< 3	365	363	1,750	2,400	< 2	4
1	397	155	199	< 3	< 3	17	17	< 3	< 3	43	41	61	99	< 2	< 2
1	492	< 35	62	< 3	< 3	13	12	< 3	< 3	< 4	< 4	< 14	< 14	< 2	< 2
1	550	51	105	< 3	< 3	11	10	< 3	< 3	10	< 4	22	28	< 2	< 2
1	599	< 35	105	< 3	< 3	13	14	< 3	< 3	5	20	54	283	< 2	< 2
1	645	3,280	3,400	< 3	< 3	19	20	< 3	< 3	1,200	1,220	2,600	2,650	4	5
1	666	3,160	3,440	< 3	< 3	13	15	< 3	< 3	1,940	2,070	5,990	16,900	< 2	< 2
1	670	2,280	2,350	< 3	< 3	28	30	< 3	< 3	1,340	1,360	384	1,010	< 2	< 2
1	699	49	88	< 3	< 3	8	8	< 3	< 3	7	10	39	122	< 2	< 2
1	729	< 35	69	< 3	< 3	8	10	< 3	< 3	6	12	< 14	72	< 2	2
1	786	353	429	< 3	< 3	52	55	< 3	< 3	323	346	< 14	36	< 2	< 2
1	1,034	< 35	120	11	< 3	46	49	< 3	< 3	182	208	< 14	< 14	< 2	< 2
1	1,103	< 35	100	9	< 3	11	13	< 3	< 3	4	8	< 14	24	< 2	< 2
1	1,134	1,390	1,590	8	< 3	35	39	< 3	< 3	375	403	25	36	< 2	< 2
1	1,172	< 35	118	9	< 3	10	12	< 3	< 3	< 4	5	< 14	61	< 2	< 2
1	1,394	< 35	92	10	< 3	8	10	< 3	< 3	< 4	5	< 14	58	< 2	< 2
1	1,412	< 35	46	8	< 3	19	18	< 3	< 3	< 4	< 4	< 14	< 14	< 2	< 2
1	1,756	< 35	62	< 3	< 3	26	28	< 3	< 3	< 4	< 4	< 14	< 14	< 2	< 2
1	1,834	< 35	61	< 3	< 3	32	34	< 3	< 3	4	4	< 14	< 14	< 2	< 2
1	1,917	< 35	51	< 3	< 3	32	31	< 3	< 3	< 4	< 4	< 14	< 14	< 2	< 2
1	2,116	41	35	< 3	< 3	47	44	< 3	< 3	< 4	< 4	< 14	< 14	< 2	< 2
9	Field blank	< 35	62	< 3	< 3	< 1	< 1	< 3	< 3	< 4	< 4	< 14	< 14	< 2	< 2
9	Field blank	< 35	76	8	< 3	< 1	< 1	< 3	< 3	< 4	< 4	< 14	< 14	< 2	< 2

Trib	Distance	Manganese, filtered	Manganese, total	Nickel, filtered	Nickel, total	Selenium, filtered	Selenium, total	Silver, filtered	Silver, total	Thalium, filtered	Thalium, total	Vanadium, filtered	Zinc, filtered	Zinc, total
0	10	43	44	6	23	<3	<3	<4	<4	7	<4	<4	29	50
0	60	77	74	7	26	<3	<3	5	<4	6	<4	<4	32	90
0	120	82	80	<6	13	<3	<3	<4	<4	6	<4	<4	33	49
0	180	100	104	<6	16	<3	<3	<4	<4	<4	<4	<4	40	71
0	257	121	118	<6	15	<3	4	<4	<4	<4	<4	<4	48	54
0	280	58	63	<3	5	<4	<4	<4	<4	6	6	<4	465	445
0	330	1,500	1,490	28	36	<3	4	<4	<4	<4	<4	<4	190	208
0	390	1,500	1,440	31	28	<3	<3	6	<4	6	4	<4	191	248
0	430	1,470	1,380	29	31	<3	6	<4	<4	<4	<4	<4	186	199
0	482	1,400	1,320	22	29	<3	4	<4	<4	4	<4	<4	180	183
0	542	1,290	1,200	25	28	<3	3	<4	<4	<4	<4	<4	168	174
0	567	1,190	1,160	23	22	<3	<3	<4	<4	5	<4	<4	156	178
0	618	1,140	1,180	20	22	<3	<3	<4	<4	4	<4	<4	151	209
0	659	992	999	22	22	<3	<3	<4	<4	<4	<4	<4	151	176
0	692	961	966	18	26	<3	<3	<4	<4	<4	<4	<4	150	161
0	725	932	951	18	18	<3	<3	<4	<4	<4	<4	<4	144	171
0	802	874	868	17	17	<3	<3	<4	<4	<4	<4	<4	137	154
0	840	863	860	19	15	<3	<3	<4	<4	<4	<4	<4	134	158
0	900	838	837	14	16	<3	<3	<4	<4	<4	<4	<4	132	141
0	955	810	812	17	19	<3	<3	<4	<4	<4	<4	<4	129	150
0	955	822	805	11	14	<3	<3	<4	<4	<4	<4	<4	130	143
0	1,015	802	802	16	14	<3	<3	5	<4	7	<4	<4	128	138
0	1,072	701	707	12	14	<3	<3	<4	<4	<4	<4	<4	113	138
0	1,132	443	442	<6	15	<3	<3	<4	<4	5	<4	<4	73	78
0	1,161	421	437	<6	7	<3	<3	<4	<4	<4	<4	<4	71	106
0	1,232	401	417	<6	8	<3	<3	<4	<4	7	<4	<4	69	86
0	1,292	391	404	9	15	<3	<3	<4	<4	<4	<4	<4	66	78
0	1,352	383	390	9	14	<3	<3	4	<4	6	<4	<4	67	75
0	1,402	390	397	6	12	<3	<3	<4	<4	<4	<4	6	69	87
0	1,462	345	357	<6	<6	<3	<3	<4	<4	5	<4	<4	59	93
0	1,522	341	339	<6	8	<3	<3	<4	<4	<4	<4	<4	60	77
0	1,582	325	345	8	<6	<3	<3	<4	<4	5	<4	<4	55	70
0	1,642	327	337	<6	11	<3	<3	<4	<4	<4	<4	<4	55	66
0	1,702	325	333	14	12	3	<3	<4	<4	4	<4	<4	55	76
0	1,750	317	338	11	15	<3	<3	<4	<4	5	<4	<4	54	66
0	1,816	281	288	9	7	<3	<3	<4	<4	5	<4	<4	53	79
0	1,876	277	277	<6	10	<3	<3	<4	<4	4	<4	<4	54	62
0	1,936	272	268	7	8	<3	<3	<4	<4	<4	<4	<4	54	71
0	2,000	266	254	<6	7	<3	<3	<4	<4	6	<4	<4	51	60
0	2,115	259	253	<6	7	<3	<3	<4	<4	<4	<4	<4	51	59
0	2,235	219	208	<6	13	<3	<3	<4	<4	<4	<4	<4	43	57
0	2,355	218	211	<6	<6	<3	<3	<4	<4	5	<4	<4	44	53
1	21	38	38	9	9	<3	3	7	<4	<4	<4	<4	29	59
1	263	3,860	3,790	58	63	<3	5	<4	<4	6	6	<4	465	445
1	292	1,500	1,440	31	28	<3	<3	6	<4	6	<4	<4	191	248
1	397	34	35	<6	<6	<3	<3	<4	<4	<4	<4	<4	14	104
1	492	<2	4	8	9	<3	<3	<4	<4	<4	<4	<4	10	23
1	550	8	5	8	<6	<3	<3	<4	<4	<4	<4	<4	6	47
1	599	10	10	<6	<6	<3	<3	<4	<4	<4	<4	<4	8	41
1	645	452	451	17	21	<3	<3	<4	<4	<4	<4	<4	165	199
1	666	610	629	16	25	<3	<3	<4	<4	<4	<4	<4	162	195
1	670	243	233	19	13	<3	<3	<4	<4	<4	<4	8	84	108
1	699	13	14	<6	<6	<3	<3	<4	<4	<4	<4	<4	<3	12
1	729	<2	<2	<6	<6	<3	<3	<4	<4	<4	<4	<4	13	40
1	786	38	37	<6	10	<3	<3	<4	<4	<4	<4	<4	13	44
1	1,034	5	6	<6	<6	<3	<3	<4	<4	5	<4	<4	11	25
1	1,103	<2	2	<6	<6	<3	<3	<4	<4	<4	<4	<4	4	35
1	1,134	218	223	<6	6	<3	<3	<4	<4	5	<4	<4	75	99
1	1,394	<2	2	<6	<6	<3	<3	<4	<4	<4	<4	<4	<3	16
1	1,172	<2	<2	<6	<6	<3	<3	<4	<4	<4	<4	<4	<3	32
1	1,412	<2	<2	<6	<6	<3	<3	<4	<4	<4	<4	<4	<3	22
1	1,756	5	6	7	11	3	<3	<4	<4	<4	<4	<4	51	63
1	1,834	<2	<2	<6	<6	<3	<3	<4	4	4	<4	<4	17	36
1	1,917	<2	<2	<6	<6	<3	<3	<4	<4	<4	<4	<4	5	18
1	2,116	<2	<2	<6	<6	4	<3	<4	<4	4	<4	<4	<3	6
9	Field blank	<2	<2	<6	<6	<3	<3	<4	<4	<4	<4	<4	<3	11
9	Field blank	<2	<2	<6	<6	<3	<3	<4	<4	<4	<4	<4	<3	19

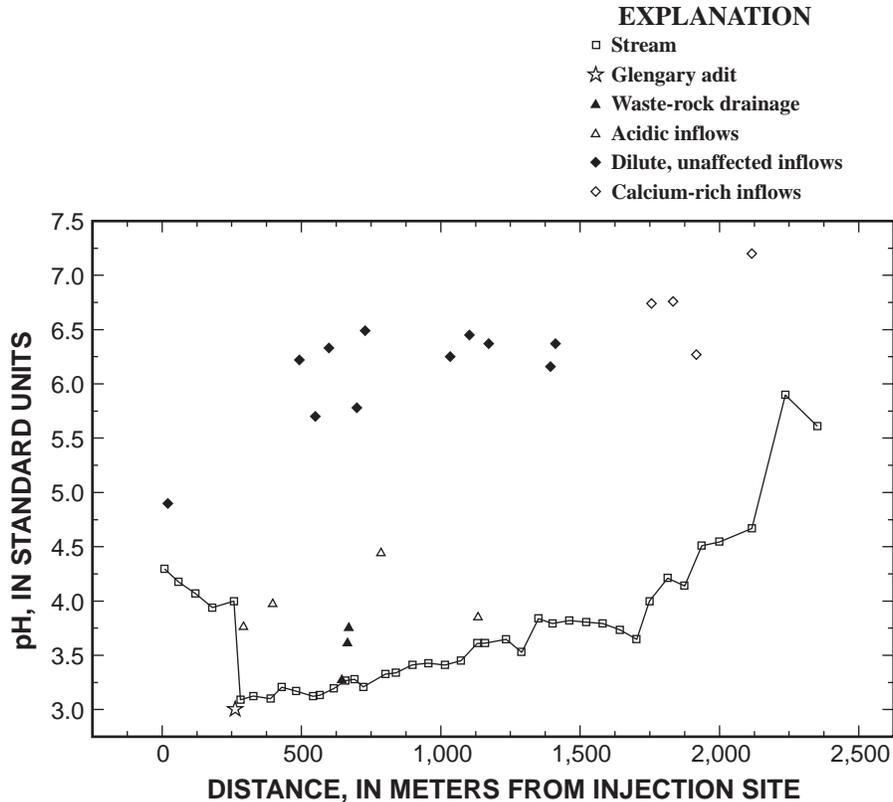


Figure 9. Variation of stream and inflow pH with distance from the injection site, Fisher Creek, Montana, August 19, 1997.

stantially, to a pH greater than 5.0, in response to the inflow of neutral pH water from the wetland and water draining carbonate rocks.

Inflow sampling sites were chosen to represent the range of chemistry that could be affecting the stream. The pH and chemistry of the 23 inflow samples indicated 5 groups of inflow chemistry (table 6). Three of these groups had pH values less than 5.0. The most unique inflow was from the Glengary adit; no other inflow was as acidic or had concentrations of metals that were as high. A second group of acidic inflows had substantially elevated metal concentrations and an average pH less than 4.0. All three inflows of this group drained the waste-rock pile just below the Glengary adit and entered Fisher Creek near 670 m. A third group of inflows had a slightly less acidic pH and lower metal concentrations. They clearly contained metals, however, and may have represented more natural drainage of the porphyritic country rock. The sample from 21 m, upstream from the Glengary adit, may have represented such natural acidic drainage.

Two groups of inflows had higher pH. The first group included inflows that had low metal concentra-

tions; these inflows appeared unaffected by mining ("Dilute catchment water," table 6). They occurred along much of the study reach between 492 m and 1,412 m and caused the gradual increase of pH from 3.08 at 280 m to 4.00 at 1,750 m (fig. 9). A second higher pH group occurred downstream from 1,750 m ("Calcium-rich," table 6). These inflows caused substantial increases in pH and a higher calcium (Ca) concentration. This group included the inflow from the Gold Dust Mine and inflows at the start of the wetland area.

Stream Sites

Sources of Metals

Metal content of the water in Fisher Creek was dominated by Ca, iron (Fe), aluminum (Al), magnesium (Mg), copper (Cu), and zinc (Zn). Natural and acidic weathering of the bedrock, particularly limestone that crops out in the watershed, produces Ca and Mg. The high concentrations of Al result from the

Table 6. Chemical characteristics of inflow groups from Fisher Creek, Montana, August 1997

[All concentrations are average values for filtered samples in the groups, in micrograms per liter, unless indicated]

Inflow group	Glengary adit	Drainage from waste-rock pile	Acidic water	Dilute catchment water	Calcium-rich water	Overall average
Number of samples	1	3	5	10	4	23
pH, in standard units	3.00	3.54	4.18	6.21	6.74	5.38
Specific conductance, in micro-siemens per centimeter at 25 degrees Celsius	1,402	243	79	57	231	175
Sulfate	584	101	39	15	85	69
Calcium	58,100	8,647	4,752	6,486	31,525	12,990
Magnesium	17,300	2,977	1,045	1,181	8,018	3,276
Sodium	4,130	3,653	1,354	1,734	2,531	2,144
Aluminum	14,100	2,907	812	38	36	1,192
Copper	5,550	1,493	222	23	4	495
Iron	69,400	2,991	373	21	14	3,500
Manganese	5,740	435	115	5	3	334
Nickel	104	17	7	6	6	12
Zinc	679	137	35	7	19	61

acidic attack on aluminosilicate minerals in the watershed. The source of the other metals is the oxidation of sulfide minerals in the mineralized rock, waste rock from mining, and tailings from processing. There were detectable levels of arsenic, barium, lead, nickel, selenium, thorium, and vanadium; each of these likely originated in mineralized rocks. There was no detectable concentration of cadmium. The major anion was SO_4 , which also originates from oxidation of pyrite and other sulfide minerals. Bicarbonate was important only at the most downstream sites, which were in the wetland area. During the injection, concentrations of Na and Cl were greater than the natural ions in the upper section of the study reach; under normal conditions, Na concentration would be only a few mg/L and Cl concentration would be less than 1 mg/L.

Major Metals

Comparison of metal-concentration patterns is facilitated by normalization using equation 3 (Bencala and McKnight, 1987). Each of the metals showed substantial spatial variability (figs. 10a and 10b). The downstream profiles of Ca, Cu, and Fe concentrations showed different patterns related to their respective sources and geochemical behavior. Calcium was

derived from both mining and non-mining sources. The pattern of Ca after the addition from the Glengary adit reflects weathering from non-mining sources. The pattern of Cu represents the other metals, such as Al, manganese (Mn), and Zn. The patterns of Ca and Cu were very similar with two exceptions. First, concentrations of Cu were relatively greater upstream from the Glengary adit, which may result from natural drainage of the porphyry deposit in the watershed. Second, the Ca concentration increased downstream from 1,750 m. Inflows on the right bank (looking downstream) drain limestone outcrops. Iron also is derived from mine drainage but showed a different behavior. Like Ca and Cu concentrations, the Fe concentration increased downstream from the Glengary adit, but after the inflow of FCT-11, the Fe concentration dropped to a value lower than the Ca and Cu concentrations, indicating that it was removed by chemical reaction.

Both ferrous iron (Fe(II)) and filtered Fe were measured in the synoptic water samples (table 5). Ferric iron (Fe(III)) was assumed to be equal to the difference between the filtered Fe and Fe(II) concentrations. Filtration with 0.45- μm filters likely allowed colloidal-sized Fe(III) particles to be analyzed as part of the filtered Fe concentration. Although dissolved Fe(III) has been measured in other streams using ultrafiltration

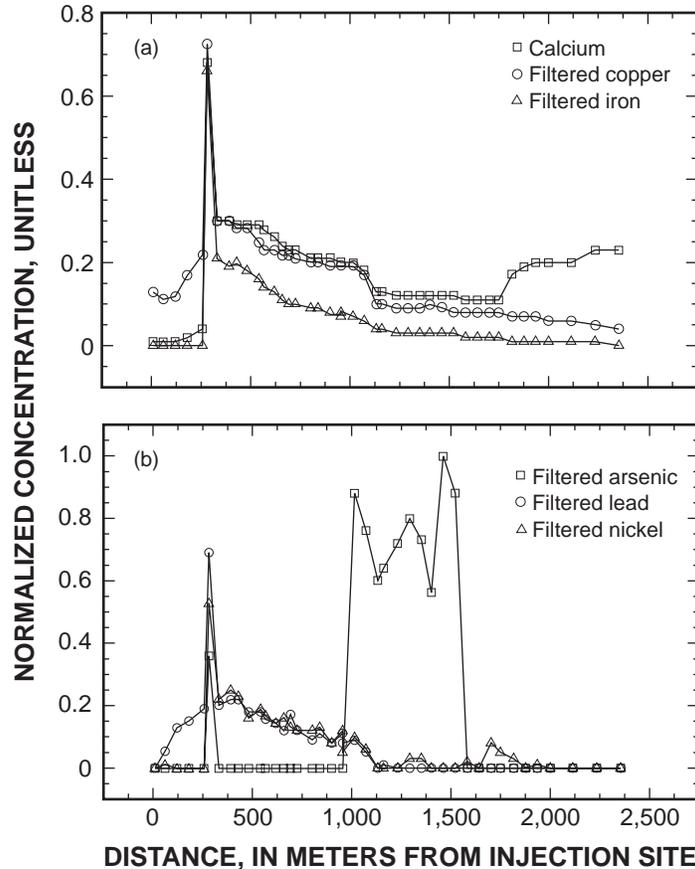


Figure 10. Variation of normalized concentrations of (a) calcium, filtered copper, and filtered iron; and (b) filtered arsenic, filtered lead, and filtered nickel, with distance from the injection site, Fisher Creek, Montana, August 19, 1997.

(Kimball and others, 1992; 1994), it is not possible to state it was present in Fisher Creek using 0.45- μm filtration. For these samples, Fe(II) may be a better measure of truly dissolved Fe concentrations.

Most of the Fe entered the stream as Fe(III) at the Glengary adit, and the decrease in concentration downstream resulted from the settling of aggregated colloidal Fe and photoreduction of Fe(III). The percentage of Fe(II) increased downstream from the inflow of the Glengary adit from 12 percent to a maximum of 91 percent at 2,235 m (fig. 11). Because samples were collected over several hours, the downstream pattern could have been affected by daily variations. If there had been an effect during the daylight hours, it would have been the opposite of this trend; higher Fe(II) percentages would have occurred upstream in the samples collected after 1200 (McKnight and others, 1988). The increase in the percentage of Fe(II) with transport

downstream likely represents loss of Fe(III) by precipitation of Fe mineral phases.

Minor Metals

The metals that occur in trace concentrations indicate details about the sources and processes that affect the metals (fig. 10b). Filtered arsenic (As) concentrations were greater than detection immediately downstream from the Glengary adit and then occurred again downstream from most of the metal-rich inflows to the stream. Arsenic occurs as an anionic species in natural waters, which causes it to behave differently than a metal in water. Although the increased pH between 1,015 m and 1,522 m might have caused the increase in As concentration by desorption of As from Fe colloids, there was no evidence of colloidal As. Also, the abrupt decrease downstream would not be consistent. High concentrations of filtered lead (Pb)

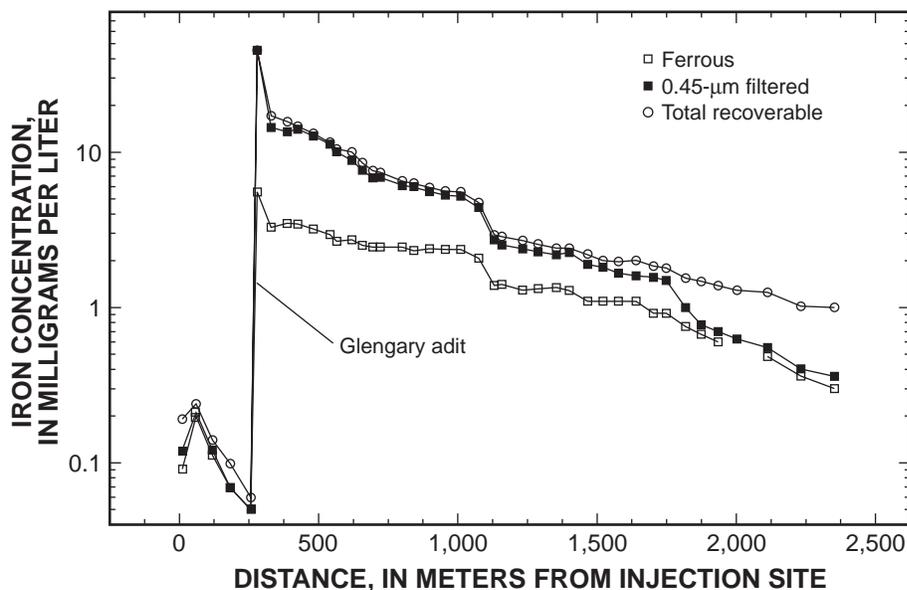


Figure 11. Variation of ferrous, filtered, and total-recoverable iron with distance from the injection site, Fisher Creek, Montana, August 19, 1997.

mostly resulted from the inflow of the Glengary adit, but similar to filtered Cu, there was a relatively high concentration upstream from the adit that could be the result of natural acidic drainage. Concentrations of filtered nickel were clearly part of the mine drainage contribution from the Glengary adit, but there was also a small increase at 1,702 m that could indicate mine drainage in that part of the stream.

These patterns of metal concentrations could be the result of physical or chemical processes. Only by viewing the various processes in a hydrologic context can their effects be determined.

QUANTIFICATION OF LOADING

The sampled instream load contains information about the contribution of each stream segment and about the net effects of chemical and physical processes affecting metal transport (Broshears and others, 1995; Kimball and others, 1994). Interpretation of the sampled instream load is facilitated by comparison to the cumulative total load and the cumulative inflow load. The cumulative total load indicates the mass that enters the stream disregarding any loss from chemical or physical processes and is the sum of net gains for stream segments from equation 4.

Loads of Major Ions

Calcium

Although the highest Ca concentration occurred just downstream from the Glengary adit (fig. 10a), the load of Ca in the stream at that point was only a small part of the total load at the bottom of the study reach (fig. 12a). This points out the substantial difference between the load profile and the concentration profile. The sampled instream load for Ca closely follows the cumulative total load because there were no chemical processes that removed Ca in this setting. Most of the total load came from the inflows downstream from 1,750 m (62 percent), but the Glengary adit, FCT-2, and FCT-11 contributed 20 percent of the load. About 65 percent of the Ca loading came from visible inflows to Fisher Creek, so that the cumulative inflow load mostly followed the cumulative total load (fig. 12a).

The load attributed to each stream segment is illustrated by the bar graph (fig. 12b). There are three different kinds of bars. The load that can be attributed to visible inflows (eq. 5) is indicated, and if the sampled instream load increased by more than the load from a visible inflow (ΔM_S was greater than ΔM_I , table 3), then the difference is shown by the bar labeled subsurface inflow. Finally, if there is a net loss for a stream segment, that loss is indicated. One special condition

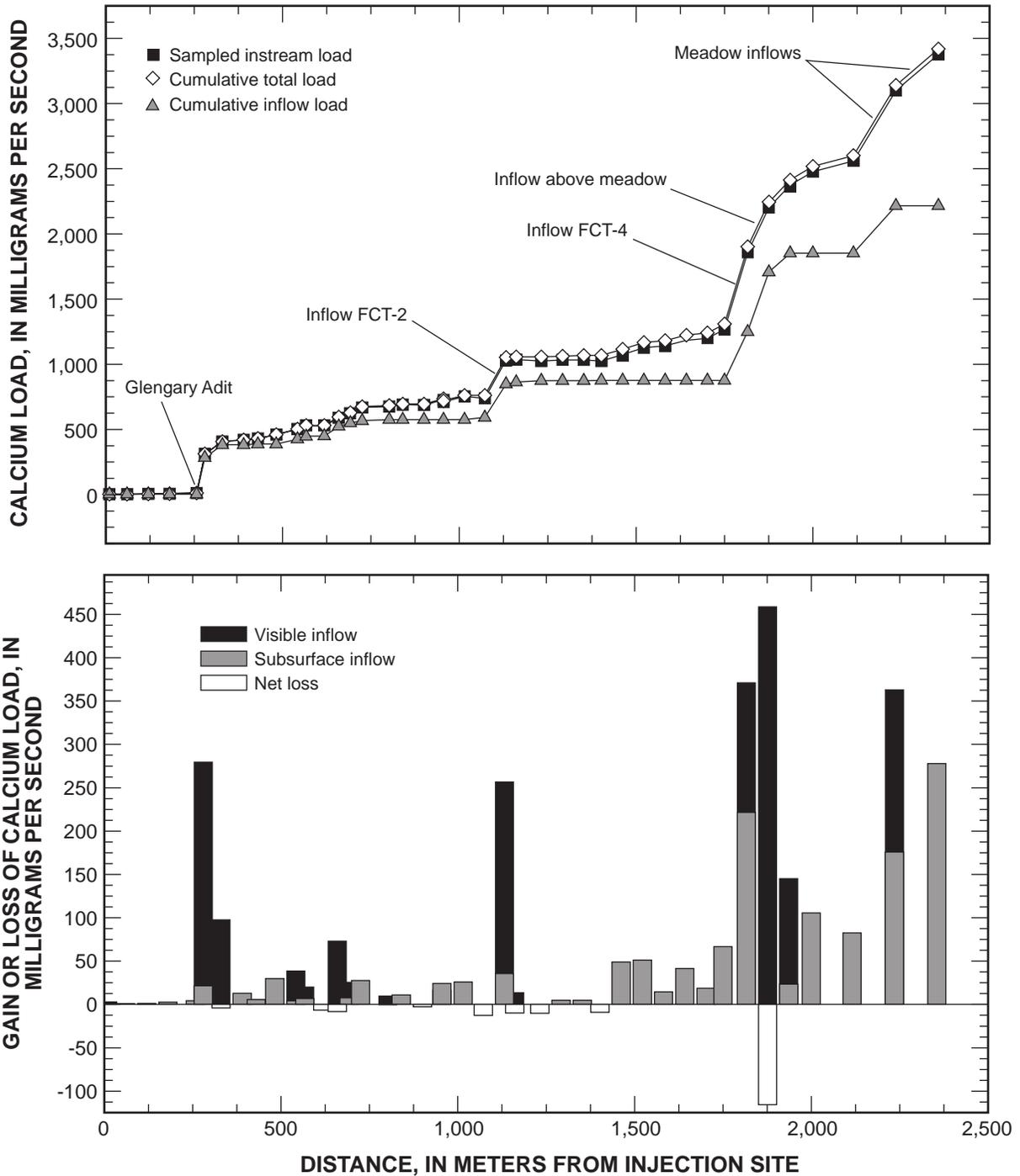


Figure 12. (a) Sampled instream load, cumulative total load, and cumulative inflow load of calcium, and (b) net gain or loss of calcium load, Fisher Creek, Montana, August 19, 1997.

occurred in a few stream segments. If there was a net loss for a segment and there was also a visible inflow, then bars were shown for each. The total loss for the stream segment likely is greater than the amount shown for the net loss in this situation. The bars in figure 12b and subsequent load figures present details for individual stream segments.

Sulfate

There are two important contrasts between the loads of Ca and SO₄. First, there was a much larger difference between the cumulative total load and the cumulative inflow load; the cumulative inflow load only accounted for about 58 percent of the cumulative total load of SO₄ (fig. 13a). Part of this difference was logistic because fewer of the small inflows were sampled farther from the principal sources of metal inflow. To account for mass loading in stream segments without sampled inflows, the change in discharge for the segment was multiplied by an estimate of inflow concentrations that were estimated from concentrations of nearby sampled inflows. This increased the estimate of cumulative inflow load by 3.48 mg/s, making it 58 percent instead of 43 percent of the cumulative total load.

The 42-percent difference in the cumulative total and the cumulative inflow loads can indicate that subsurface water entering the stream had SO₄ concentrations that were higher than the SO₄ concentration in the sampled inflows. Second, there was a substantial difference between the cumulative total load and the sampled instream load of SO₄. The most likely cause for this difference was chemical reactions that affected the SO₄ load. Removal of SO₄ could be through sorption to Fe-hydroxide colloids at low pH or coprecipitation of SO₄ as part of Fe-oxyhydroxysulfate minerals (Bigham and others, 1990; Bigham and others, 1996; Brady and others, 1986). The greatest loss of SO₄ load occurred downstream from 2,115 m (fig. 13b).

Loads of Metals

Patterns of metal loads from mine drainage were more comparable to SO₄ than to Ca because of the substantial number of dispersed subsurface inflows and the reactive chemistry that affected their transport. The extent of chemical reaction was greatest for Fe, but also significant for Al, Cu, Mn, and Zn.

Iron

Thermodynamically, Fe should readily precipitate within the pH range of Fisher Creek to form colloidal-sized, hydrous Fe oxide solids (Lindsay, 1979; Pankow, 1991). Through a sequence that includes precipitation to form nanometer-sized particles, aggregation to form micrometer-sized particles, settling of aggregated colloids, and entrapment by biofilm on cobbles, these colloidal Fe solids coat the streambed of Fisher Creek (Grundl and Delwiche, 1993). Many streams affected by mine drainage have a characteristic ochre-colored streambed from this process. This pattern of Fe loss has been documented in St. Kevin Gulch, Colorado, where a rate constant for the first-order removal of Fe was determined (Kimball and others, 1994). Accumulation of Fe precipitate on the streambed can affect the physical habitat of aquatic organisms and also can create a source of chronic toxicity because of the metals that readily sorb to the Fe colloids.

The mass-load profile of filtered Fe was very different from the profiles of Ca, SO₄, and the other filtered metals (fig. 14a). Because of the reactive behavior of Fe, it is very difficult to account for the total inflow of Fe. It is possible that Fe was removed fast enough to cause a net loss in almost every segment of the stream; there were few positive values of ΔM_S (fig. 14b). Thus, the actual amount of Fe lost from streamwater could have been greater than the difference between the cumulative total load and the sampled instream load might indicate (fig. 14).

Steps in the removal of Fe from the stream are illustrated by looking at the load profiles of Fe(II), filtered, and total-recoverable Fe (fig. 14). First, the Glen-gary adit and FCT-11 were two large point sources of Fe to the stream at about 300 m. As this large input of Fe was transported downstream, Fe(III) precipitated in the water column as Fe colloids, aggregated, and settled from the stream or was entrapped by biofilm. This results in the continuous decrease in filtered and total-recoverable Fe loads. The nearly constant difference between these two loads, continuing for about 1,000 m of the stream, indicates a constant process of precipitation, aggregation, and removal. With the pH change downstream from 1,750 m and an increase of Fe load, the formation of Fe colloids accelerated. More colloidal Fe was in the water column, as indicated by a greater difference between filtered Fe and total-recoverable Fe loads. The rate of settling, however, did not seem to change because there was little change in the decrease of total-recoverable Fe load with distance. As the fil-

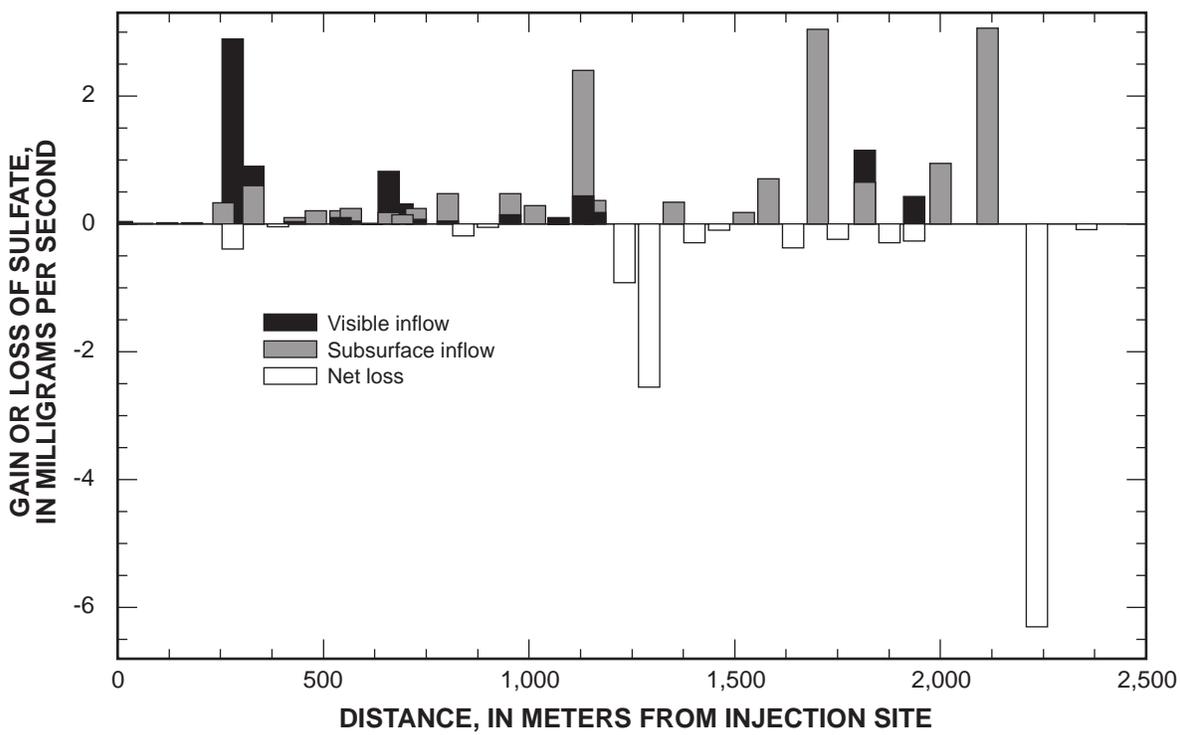
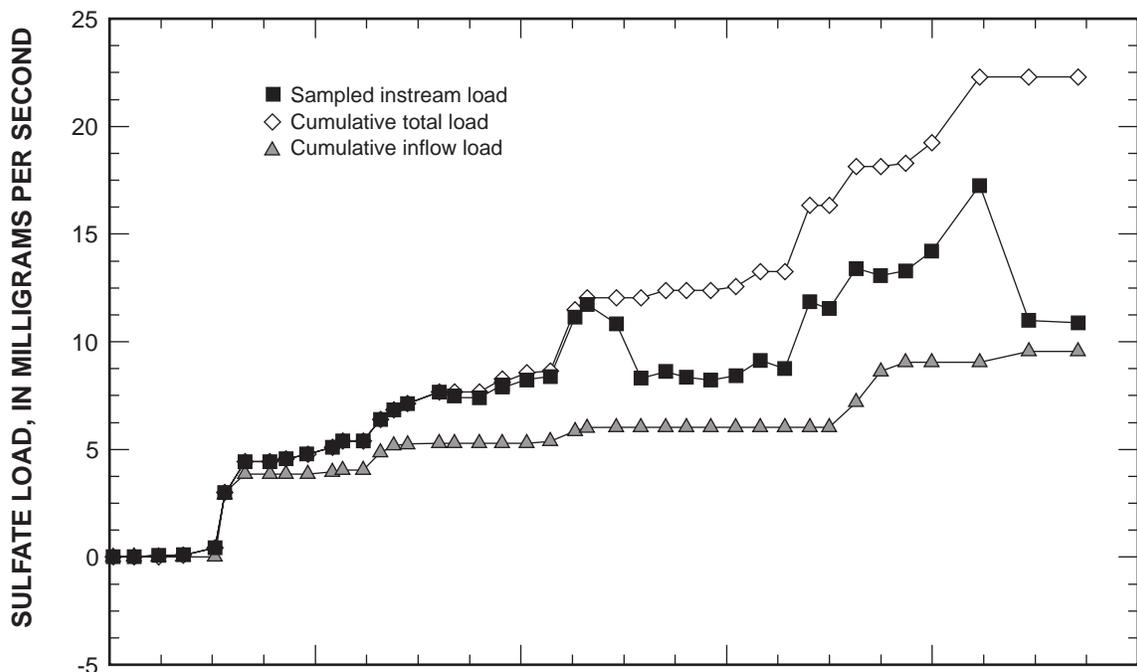


Figure 13. (a) Sampled instream load, cumulative total load, and cumulative inflow load of sulfate, and (b) net gain or loss of sulfate load, Fisher Creek, Montana, August 19, 1997.

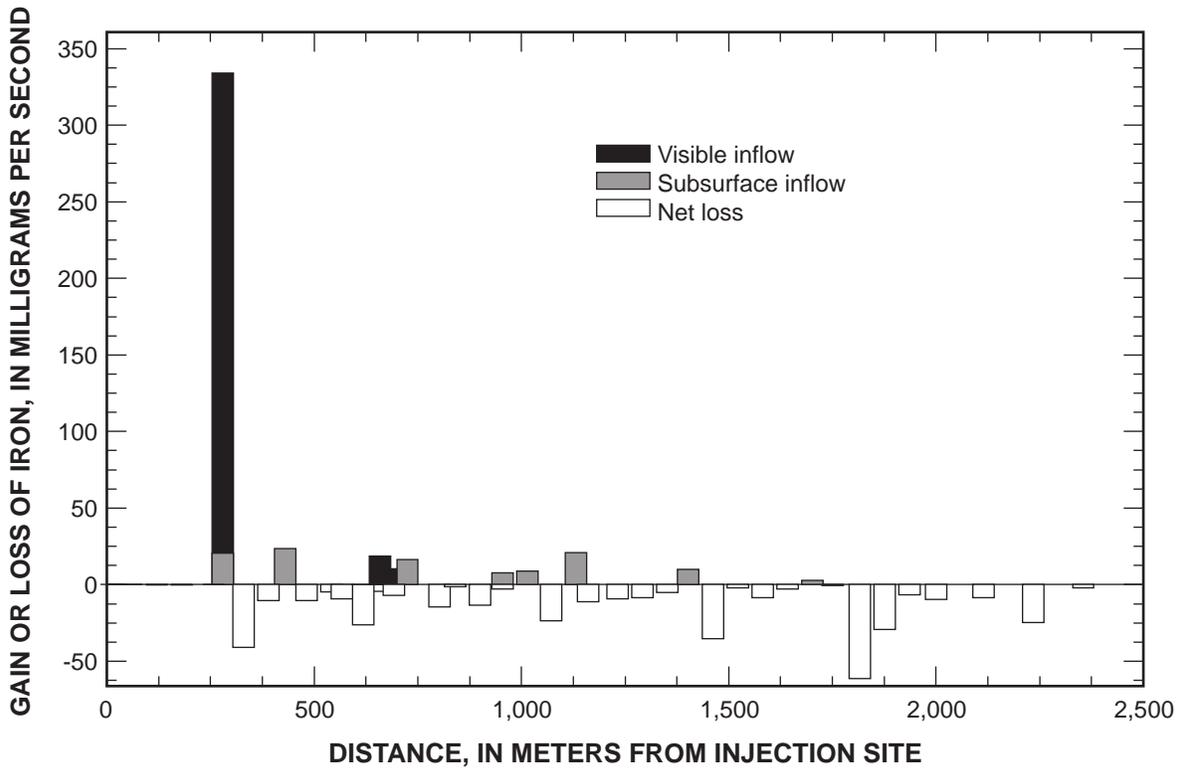
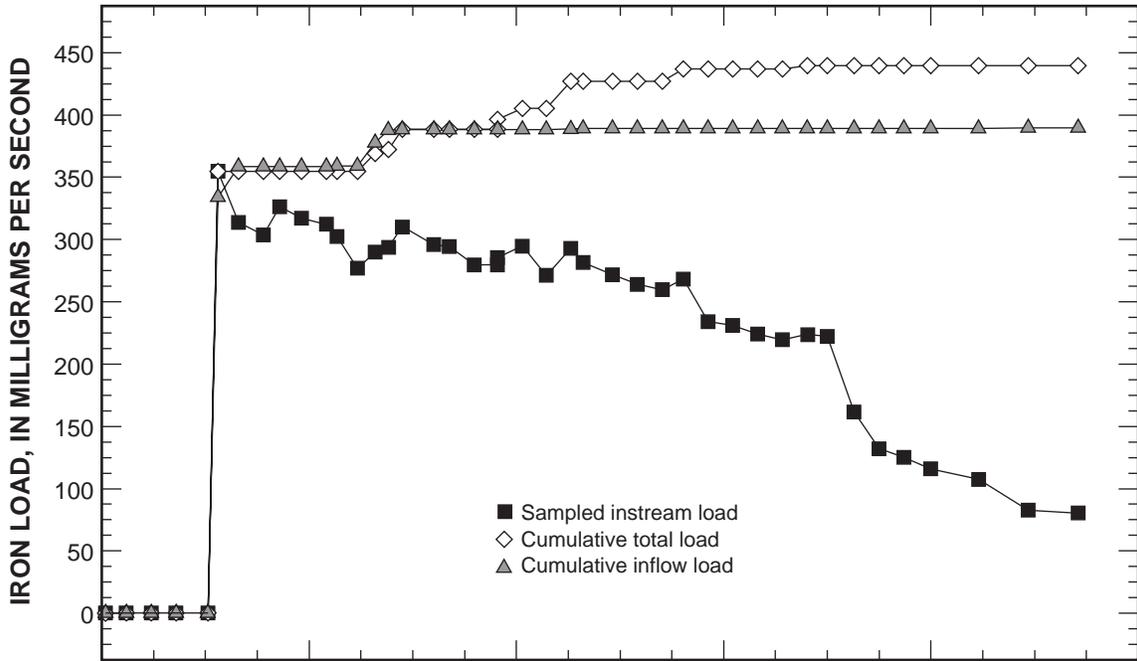


Figure 14. (a) Sampled instream load, cumulative total load, and cumulative inflow load of iron, and (b) net gain or loss of iron, Fisher Creek, Montana, August 19, 1997.

tered Fe load reached the level of the Fe(II) load, the Fe(II) decreased along with the filtered Fe, possibly indicating that Fe(II) was converted to Fe(III) and then precipitated as Fe colloids.

Fe-rich colloids that settle to the streambed or are trapped by algae on streambed cobbles, are flushed by snowmelt runoff the following year. This was the likely cause of large increases in colloidal loads of metals in the Animas River, Colorado, during snowmelt runoff (Church and others, 1997).

Aluminum, Copper, Manganese, and Zinc

The most striking difference between the profile of Ca load and the profiles of metal loads is the relative importance of the different sources. Sources of Ca load occur all along the study reach, but a large part of the metal loads comes from the Glengary adit and other mine-related sources in the first 700 m of the study reach (figs. 15, 16, 17, and 18). About 60 percent of the Al, Cu, Mn, and Zn loads can be accounted for by the concentrations in the samples of the visible inflows, and almost all of these loads entered Fisher Creek in the upper 700 m. This means the cumulative inflow load is much closer to the cumulative total load for these metals than for SO_4 . The remaining 40 percent was from diffuse subsurface inflows. Considering this diffuse source, the reduction of metal loads in Fisher Creek might be limited unless there were a way to reduce loads from the diffuse sources as well as reducing loads from the Glengary adit and nearby mining wastes. For example, the load of Cu from the Glengary adit was 28 mg/s, which was 32 percent of the total load at the end of the study reach (fig. 15). A decrease of 32 percent of the load may not reduce Cu to concentrations that would be low enough for a healthy fish population. Also, eliminating inflow of the Glengary adit would increase the pH of Fisher Creek, and reduce the load of Fe, changing the dynamics of Cu sorption to Fe colloids. With these chemical complexities, the exact amount of reduction in Cu for eliminating a particular source needs to be estimated by a reactive solute-transport simulation; it is not a simple mass-balance question.

Loads for filtered Al, Cu, Mn, and Zn showed the same general pattern. The major loads from the Glengary adit and nearby mining wastes initially dominate the load profiles. Transport of that load was conservative for each metal to about 800 m. From 802 m to 1,582 m, the sampled instream load and the cumulative total loads diverged because of net losses in some

stream segments as a result of chemical reactions. These decreases in load occurred downstream from neutral inflows that raised the instream pH. The decreases could have resulted from sorption of the metals to the Fe colloids or from coprecipitation with the Fe colloids. Amacher and others (1994) have shown a marked increase in the Cu concentration in the streambed Fe precipitates in this same area of Fisher Creek. None of the total-recoverable metal concentrations increased in this reach (table 6), indicating that there must have been sorption directly to bed material. After the instream metal loads decreased, each metal load subsequently increased between 1,582 m and 1,750 m. This area had no visible inflows; the increased load must represent metal-rich, subsurface inflow. The source of this metal-rich inflow was not apparent and should be investigated further.

The loading of Al was different from the other metals downstream from the inflow at 2,116 m (fig. 16a). With the increase in pH, Al precipitated, as indicated by the sharp decline in load. There was visible evidence of precipitation on the streambed cobbles along the right bank downstream from the inflow. The load of Cu also decreased in that reach, most likely as a result of sorption of Cu onto the Fe and Al precipitates rather than by precipitation of a solid phase. If Cu and other metals are stored on the streambed with Fe colloids, they could be flushed by the next snowmelt runoff.

Mass-load profiles of Mn (fig. 17) and Zn (fig. 18) were similar. For both, the Glengary adit was the principal source of the metal load. The largest losses occurred in the area from 1,402 m to 1,462 m and from 2,115 m to 2,235 m, both in response to inflows that had high pH. Between 1,750 m and 1,936 m the load of Zn increased due to subsurface inflows, but the Mn load did not increase. This could indicate a mineralogical difference between the source of metals in that area and the source of the Glengary adit.

Despite the differences in details among the mass-load profiles, the metal loads collectively indicate five areas where most of the metal loads entered the stream. The net gain or loss of metals in each stream segment is summarized in table 7. For each metal, the five largest increases are shaded to point out the principal areas of loading. The first area was between 257 m and 330 m, including the Glengary adit and the FCT-11 tributary. The second area was between 618 m and 725 m, where streams that drain waste-rock piles enter Fisher Creek. The third important area was between 1,072 m and 1,132 m, which receives the discharge

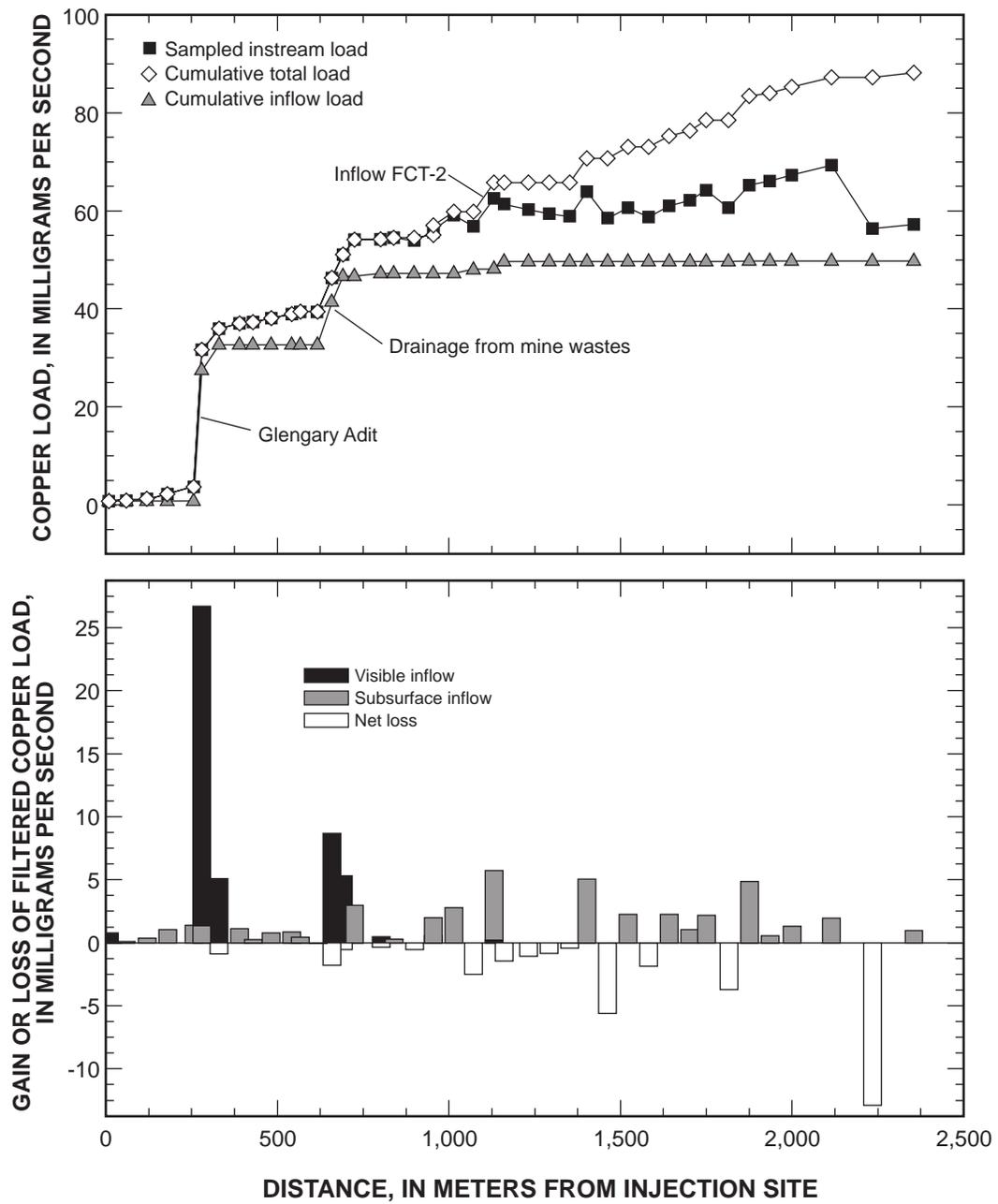


Figure 15. (a) Sampled instream load, cumulative total load, and cumulative inflow load of filtered copper, and (b) net gain or loss of filtered copper load, Fisher Creek, Montana, August 19, 1997.

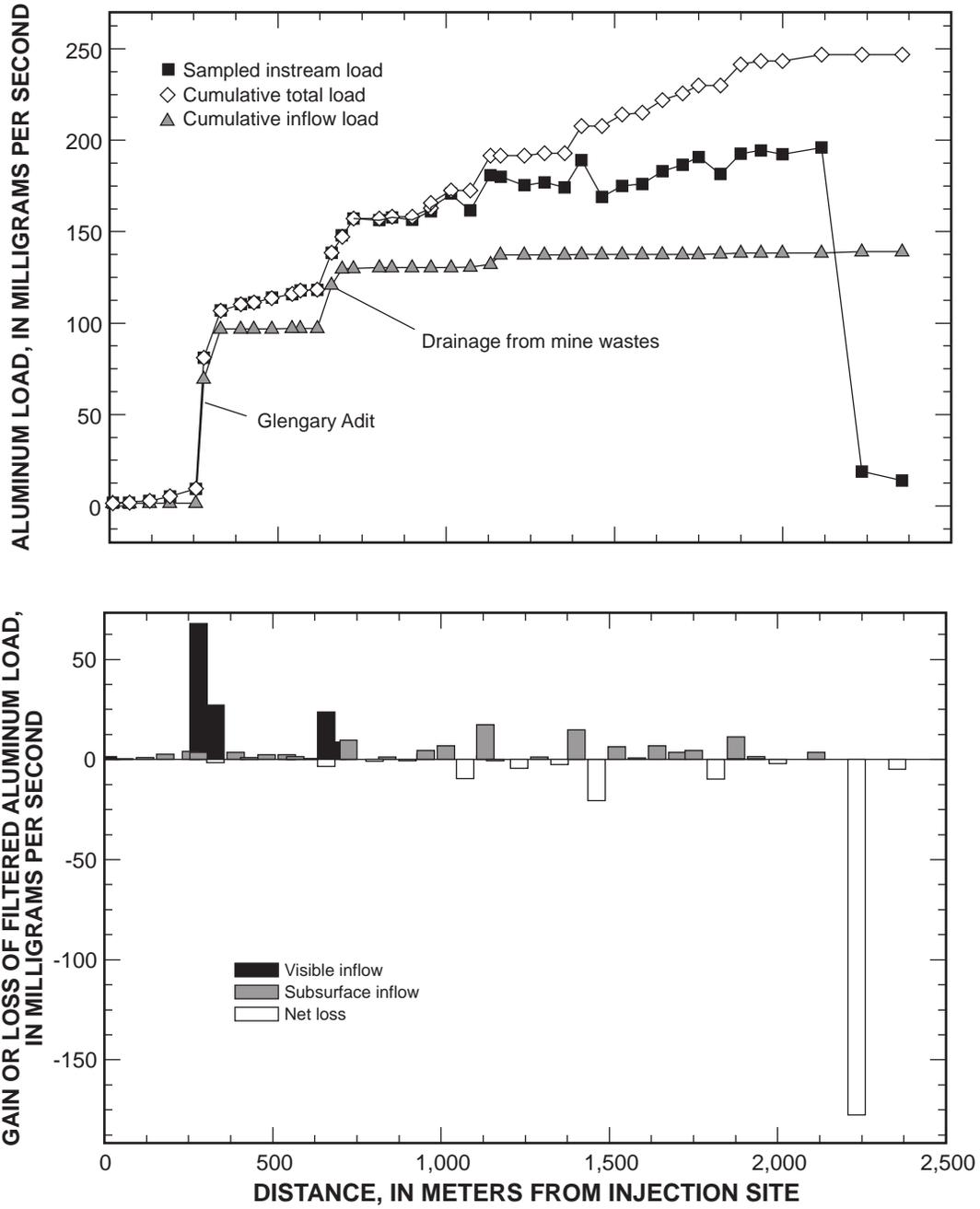


Figure 16. (a) Sampled instream load, cumulative total load, and cumulative inflow load of filtered aluminum, and (b) net gain or loss of filtered aluminum load, Fisher Creek, Montana, August 19, 1997.

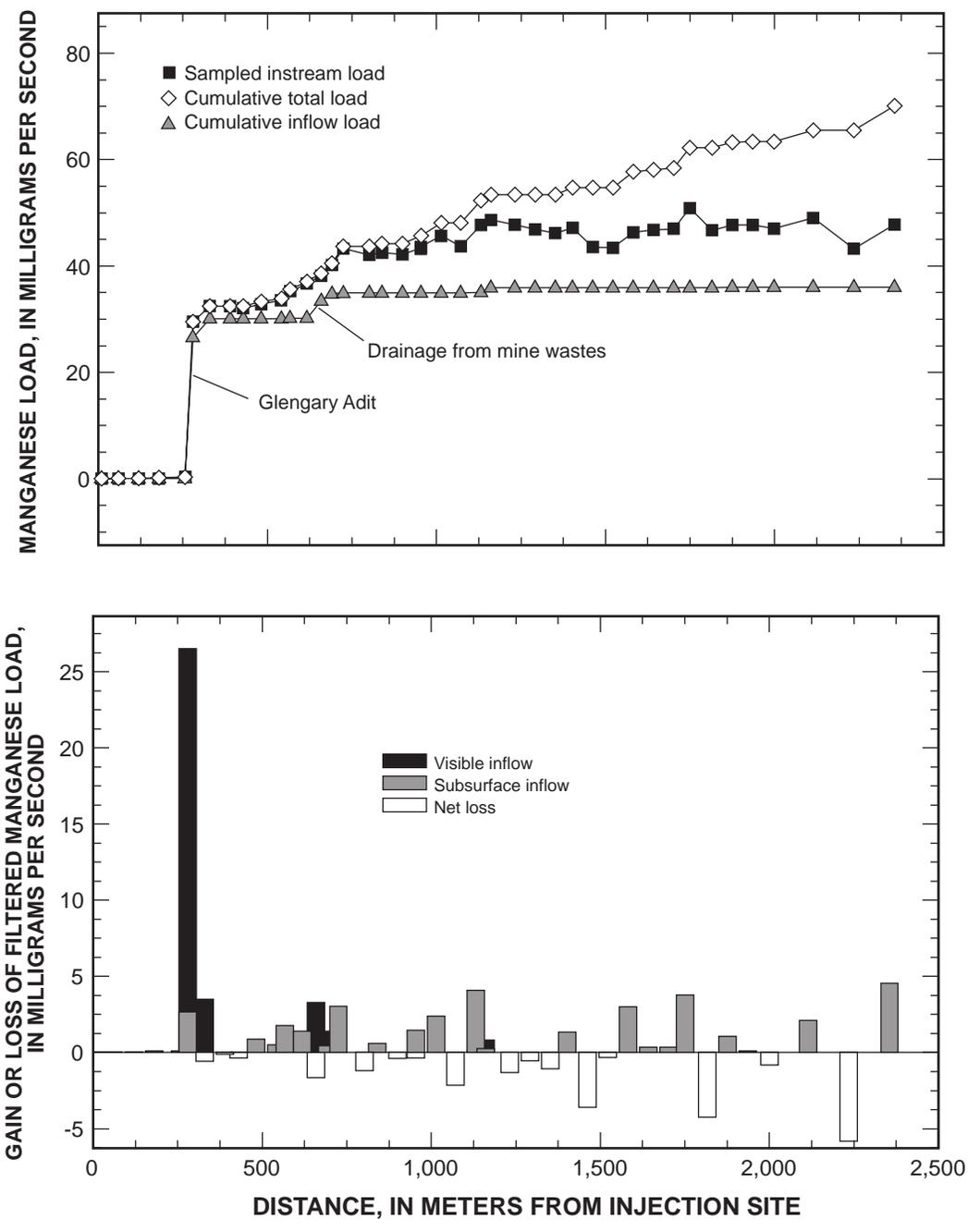


Figure 17. (a) Sampled instream load, cumulative total load, and cumulative inflow load of filtered manganese, and (b) net gain or loss of filtered manganese load, Fisher Creek, Montana, August 19, 1997.

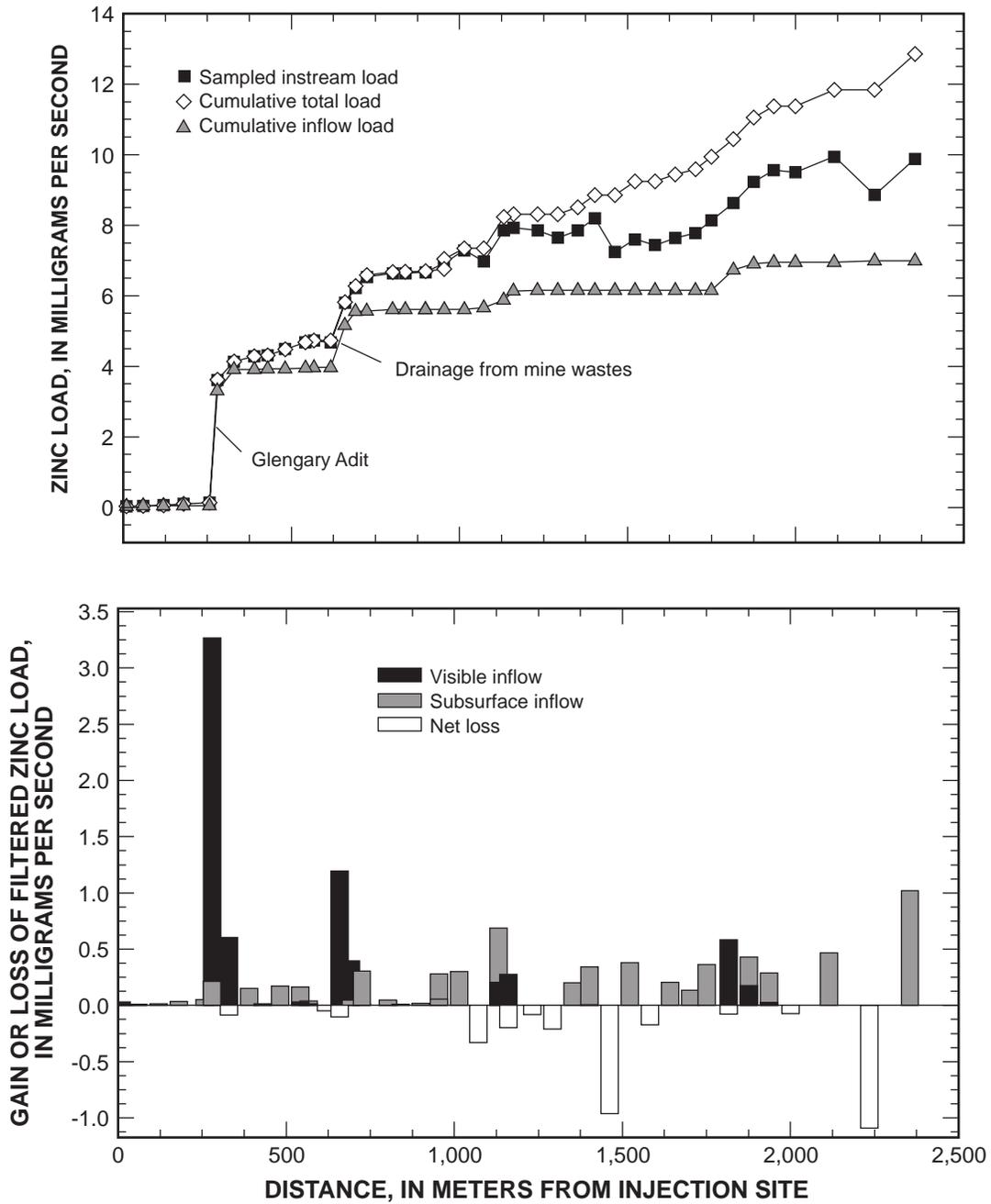


Figure 18. (a) Sampled instream load, cumulative total load, and cumulative inflow load of filtered zinc, and (b) net gain or loss of filtered zinc load, Fisher Creek, Montana, August 19, 1997.

Table 7. Net gain or loss of selected metals and sulfate in stream segments of Fisher Creek, Montana, August 1997

[All values are in milligrams per second]

Distance (m)	Calcium	Sulfate	Aluminum	Copper	Iron	Manganese	Zinc
10	2.80	0.04	1.50	0.79	0.13	0.05	0.03
60	1.37	.01	.36	.09	.19	.06	.02
120	1.24	.02	1.01	.35	-.09	.04	.01
180	2.54	.02	2.59	1.04	-.06	.10	.03
257	4.37	.33	4.11	1.39	-.01	.11	.05
280	301	2.50	71.5	28.1	355	29.2	3.48
330	94.0	1.50	25.7	4.22	-4.98	2.92	.51
390	12.8	-.04	3.58	1.13	-1.35	-.10	.15
430	11.3	.13	1.03	.28	23.8	-.34	.02
482	29.7	.21	2.33	.79	-1.48	.89	.17
542	42.9	.31	2.46	.85	-4.66	.52	.19
567	27.0	.29	1.61	.46	-9.38	1.78	.06
618	-6.58	.00	.50	-.04	-26.4	1.42	-.05
659	65.0	1.01	2.32	6.90	14.3	1.62	1.09
692	33.1	.45	8.78	4.74	3.34	1.86	.45
725	45.2	.30	9.83	3.01	16.41	3.11	.32
802	9.64	.52	-.89	.14	-14.6	-1.20	.09
840	11.1	-.19	1.22	.29	-1.43	.60	.01
900	-2.65	-.05	-.68	-.53	-13.3	-.39	.02
955	24.2	.47	4.53	1.98	7.56	1.47	.28
955	16.2	.14	2.70	.54	-2.81	-.37	.05
1,015	26.0	.29	6.88	2.78	8.96	2.40	.30
1,072	-12.6	.10	-9.47	-2.50	-23.4	-2.13	-.33
1,132	293	2.83	19.0	5.92	21.7	4.19	.89
1,161	3.88	.55	-.55	-1.44	-11.2	1.07	.08
1,232	-1.06	-.92	-4.38	-1.06	-9.19	-1.30	-.08
1,292	4.95	-2.55	1.31	-.85	-8.32	-.53	-.21
1,352	4.76	.34	-2.48	-.43	-4.92	-1.06	.20
1,402	-9.10	-.29	15.0	5.04	9.94	1.33	.35
1,462	48.8	-.10	-2.52	-5.59	-35.5	-3.60	-.96
1,522	51.2	.18	6.36	2.26	-2.21	-.32	.38
1,582	14.6	.71	.89	-1.87	-8.33	3.02	-.18
1,642	41.4	-.37	6.92	2.26	-2.69	.35	.21
1,702	18.7	3.05	3.55	1.04	2.86	.34	.13
1,750	66.8	-.24	4.48	2.19	-.68	3.78	.36
1,816	592.8	1.80	-9.81	-3.72	-61.3	-4.24	.50
1,876	343.2	-.29	11.6	4.92	-29.4	1.10	.61
1,936	168.7	.16	1.60	.58	-6.48	.11	.32
2,000	105.7	.95	-2.10	1.32	-9.45	-.83	-.07
2,115	82.6	3.06	3.60	1.94	-8.49	2.11	.46
2,235	539	-6.30	-177	-12.9	-24.9	-5.82	-1.09
2,355	278	-.09	-4.88	.97	-2.12	4.56	1.02

from the largest visible inflow, FCT-2. A fourth area with substantial inflow was between 1,582 m and 1,750 m, where increased load was mostly from subsurface inflow and not visible inflows. Finally, the area from 1,876 m to 1,936 m had a considerable increase of load for Ca, Al, and Cu. This area likely drains carbonate outcrops on the right side of the canyon. The sources of Al and Cu are not clear, however, because drainage from the Gold Dust Mine does not appear to enter the inflow in this area.

SUMMARY

Acid mine drainage from past mining affects the water quality of Fisher Creek, Montana. To effectively plan for remediation requires detailed knowledge of the sources of the mine drainage, how the drainage from the sources enters the stream, and what natural attenuation may remove the metals once they are in the stream. The U.S. Geological Survey, in cooperation with the U.S. Environmental Protection Agency, conducted a tracer injection and synoptic sampling study to provide the information.

A chloride tracer injection allowed the calculation of discharge for synoptic samples along a 2,355-m reach of Fisher Creek. The study reach began upstream from the Glengary adit and ended in a downstream wetland, just upstream from site FC-5. The load profiles were calculated using discharge, calculated from the dilution of the tracer, and concentration data from detailed synoptic sampling. Loads of aluminum, copper, iron, manganese, and zinc greatly increased from the inflow of the Glengary adit. Downstream from the adit, metal transport was without substantial chemical reaction until the inflow of a tributary with higher pH (FCT-2), which caused instream pH to rise. Chemical reaction also decreased the loads of copper and aluminum in the wetland area, near the end of the study reach. At the higher pH, aluminum changed from the filtered phase to colloidal solids and started settling from the stream. Chemical reactions substantially affected the load profile of iron along the entire study reach. The copper and zinc load profiles indicated the significance of ground-water inflows near the bottom of the study reach.

Calculating the cumulative total load and the cumulative inflow load helps indicate the extent of metal removal and the likely sources of ground-water inflow. Removal of metal loads from the stream has two important consequences. First, the metals are stored in iron colloids each summer and then are

flushed by snowmelt runoff, likely causing a large increase of colloidal metal load for many kilometers downstream. Second, accounting for the total load facilitates the illustration of individual sources of metal loads.

The similarity of load profiles for the metals points out the impacts of mine drainage on Fisher Creek. A large part of the metal loads comes from the inflow of the Glengary adit, but substantial loads of each metal also occurred at other locations. Some loads came from diffuse subsurface inflow. Eliminating only a single source, without considering all principal sources, may not reduce instream concentrations to levels that do not adversely affect aquatic life.

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APPENDIX

Ion-Chromatograph Analytical and Quality Assurance Procedures

Chloride and sulfate were analyzed by the U.S. Geological Survey (USGS) Utah District laboratory using a Dionex 2002I ion chromatograph (IC) with an AS4A column, an AG4A guard, and a conductivity detector. All samples were filtered in the field through 0.45- μ m filters before analysis on the IC.

A typical analytical run included 64 samples. Of those 64, only 39 (about 61 percent) were actual environmental samples. The remaining 25 samples (39 percent) included calibration standards, laboratory-certified standards and standard reference samples, site-specific standard reference samples, and blanks. Occasionally, analytical runs included fewer than 64 samples. In these cases, the percentage of environmental samples decreased relative to the percentage of other samples.

Six calibration standards were placed at the beginning of every run. External laboratory-certified standards were analyzed every fifth sample, a total of 11 in a run of 64. A USGS laboratory standard reference sample was analyzed at the beginning and end of every run. Standards were collected from Fisher Creek at several times during the tracer injection so that site-specific standard reference samples represented both background and plateau, or at least elevated Cl conditions. Appropriate site-specific standard reference samples were analyzed every tenth sample, a total of 5 in a run of 64. One laboratory blank consisting of reagent-grade deionized water was analyzed at the end of every run.

Analytical procedures followed by the Utah District laboratory are outlined by Brinton and others

(1996). Three different volume sample loops were used in the determination of Cl and SO₄ concentration with three different sets of calibration standards (table 8).

Background Cl concentrations and lower-level SO₄ concentrations were determined using the 250- μ L sample loop. Most samples were analyzed on the 50- μ L loop, which provided the best middle-range results. The 10- μ L loop was used when Cl or SO₄ concentrations exceeded upper limits of calibration for the 50- μ L sample loop or when they exceeded the upper limits of calibration for the 10- μ L sample loop and sample dilutions were required.

Laboratory-certified standards and USGS laboratory standard reference samples were analyzed so that short- and long-term accuracy and precision could be evaluated. Accuracy is defined as a measure of agreement between the measured concentration of an analyte and the actual concentration. The percentage error for Cl between the measured medians and the certified or most probable values was within 5 percent for five out of the six standard reference samples analyzed. The percentage error for SO₄ between the measured medians and the certified or most probable values was within 5 percent for four out of the six standard reference samples. Those with a difference greater than 5 percent were within 10 percent (table 9).

The overall relation between measured median concentrations and certified or most probable values for Cl and SO₄ in laboratory standard reference samples SR15, SR16, SR17, M102, and M140 have been plotted in figures 19 and 20. Standard reference samples M102 and M140 depart from the most probable values, while the median concentrations of others indicate reasonable accuracy. It should be remembered that the median concentrations do not reflect the actual scatter of results (fig. 21).

Table 8. Sample-loop volumes and minimum and maximum chloride and sulfate concentrations of each corresponding set of calibration standards for water samples from Fisher Creek, Montana, August 1997

[μ L, microliters; mg/L, milligrams per liter; Min., minimum; Cl, chloride; Max., maximum; SO₄, sulfate]

Volume of sample loop (μ L)	Min. Cl (mg/L)	Max. Cl (mg/L)	Min. SO ₄ (mg/L)	Max. SO ₄ (mg/L)
250	0.00	1.00	0.00	25.0
50	.00	6.00	.00	150
10	.00	60.1	.00	300

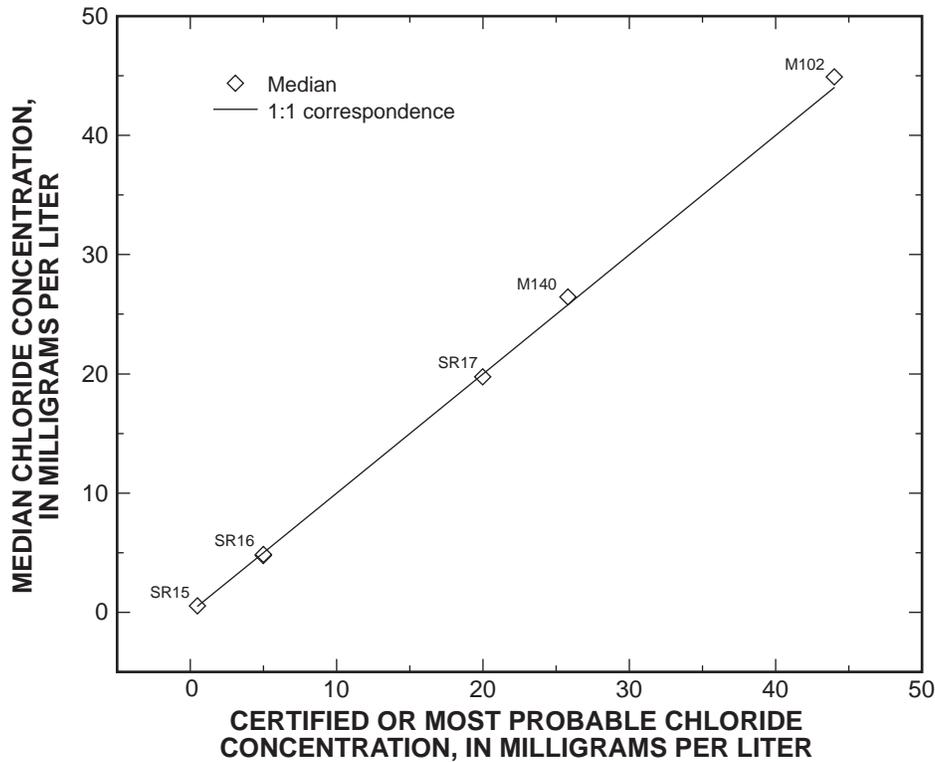


Figure 19. Relation of measured chloride concentration with certified or most probable concentration.

Standard reference sample M140 was analyzed only on the 10- μ L loop. Accuracy declines when the volume on the column declines. Standard reference sample M102 was analyzed predominately on the 50- μ L loop. Because the most probable values for Cl and SO₄ are outside the linear range of calibration for this loop, the sample is diluted at a ratio of approximately 1:10. Accuracy is generally poorer for samples that have been diluted.

Precision is defined as “a measure of the expected reproducibility of a method when it is repeated on a homogeneous sample under controlled conditions, regardless of whether or not the measured concentrations are widely displaced from the true concentration” (Brinton and others, 1996). Mathematically, the precision of a standard, s , can be defined as:

$$P_s = (SD_c)(t_{9n-(1, 0.99)}), \quad (7)$$

where SD_c is the standard deviation of the concentrations for the n duplicates and

t is the student t-statistic at the 99 percent confidence interval for $n-1$ degrees of freedom.

Because standard deviations become higher as the analyte concentration becomes higher, percent precision is perhaps a more comparable measure of precision. Percent precision is defined as:

$$\% P = (P_s/LCV)(100),$$

or

$$\% P = (P_s/MPV)(100), \quad (8)$$

where $\%P$ is the percent precision,
 P_s is the precision calculated above,
 LCV is the laboratory-certified value, and
 MPV is the most probable value.

The percent precision reported in table 8 reflects the overall percent precision for that standard reference sample, loop, and analyte for the time the Fisher Creek samples were being analyzed. Although daily percent precision would likely be better, reproducibility of results for the length of time it takes to complete the analyses for an experiment is more important if daily data are to be merged and compared as a single data set.

Percent precision for Cl is less than 10 percent for five out of the six standard reference samples. Percent precision ranges from 5.04 percent for M140 to 14.12 percent for M102. Percent precision for SO_4 is larger and indicates much greater variability in results, possi-

bly a result of (1) changing pH of the sample as it is carried into the column by a sodium-carbonate and bicarbonate eluant, and (or) (2) ongoing precipitation of iron in the autosampler and IC plumbing. Percent precision ranges from 4.87 percent for M140 to 33.08 for SR16 (on the 10- μ L loop).

Site-specific standards were collected and analyzed to better evaluate analytical precision on site-specific matrices. Although percent precision could not be calculated, precision (P_c) indicates less variability for Cl and greater variability for SO_4 (table 8).

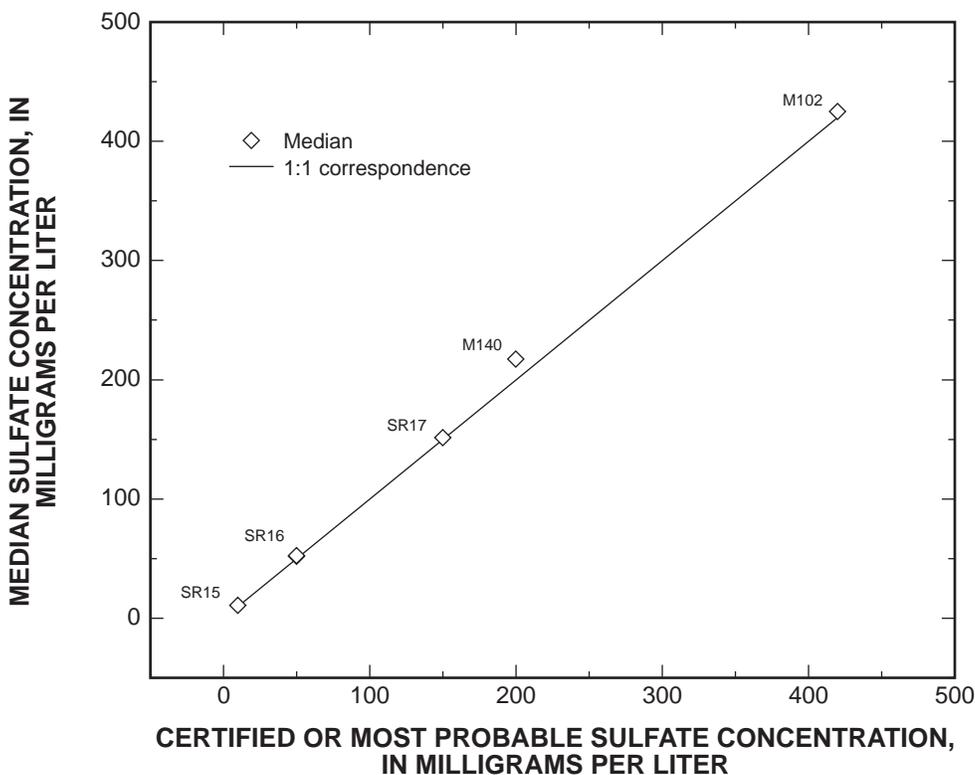


Figure 20. Relation of measured sulfate concentration with certified or most probable concentration.

Table 9. Analysis of chloride and sulfate accuracy and precision from certified standards and standard reference samples from Fisher Creek, Montana, August 1997

[N, number of analyses; LCV, laboratory certified value; MPV, most probable value; %Error, percent error; t(n-1,0.99), student-t value for 99 percent probability; P_c, precision; %Precision, percent precision]

Sample name	Source	Loop	N	Analyte	LCV or MPV	Median	% Error	Standard deviation	Minimum	Maximum	t (n-1, 0.99)	P _c	% Precision
SR15	Lab	250	27	Cl	0.50	0.53	5.7	0.02	0.50	0.56	2.479	0.0496	9.92
	Lab	250	28	SO4	10.00	10.86	8.6	.85	9.58	12.43	2.473	2.1021	21.02
SR16	Lab	10	13	Cl	5.00	4.78	4.4	.10	4.63	4.94	2.681	.2681	5.36
	Lab	10	13	SO4	50.00	52.38	4.8	6.17	49.13	66.52	2.681	16.5418	33.08
SR16	Lab	50	74	Cl	5.00	4.88	2.4	.16	4.56	5.23	2.383	.3813	7.63
	Lab	50	74	SO4	50.00	52.28	4.6	6.90	39.51	66.73	2.383	16.4427	32.89
SR17	Lab	10	72	Cl	20.00	19.78	1.1	.45	19.01	20.96	2.384	1.0728	5.36
	Lab	10	72	SO4	200.00	217.32	8.7	12.32	197.06	248.65	2.384	29.3709	14.69
M102	USGS	50	18	Cl	44.00	44.89	2.0	2.42	41.62	49.40	2.567	6.2121	14.12
	USGS	50	18	SO4	420.00	425.08	1.2	19.93	394.68	461.14	2.567	51.1603	12.18
M140	USGS	10	16	Cl	25.80	26.46	2.6	.50	25.57	27.29	2.602	1.3010	5.04
	USGS	10	16	SO4	150.00	151.33	.9	2.81	146.56	157.00	2.602	7.3116	4.87
SR120	Site	10	32	Cl	none	3.39	NA	.10	3.14	3.51	2.423	.2325	NA
	Site	10	32	SO4	none	120.86	NA	8.58	113.11	143.32	2.432	20.8768	NA
SR120	Site	50	35	Cl	none	3.25	NA	.09	3.10	3.45	2.443	.2222	NA
	Site	50	35	SO4	none	111.11	NA	7.30	102.41	136.13	2.443	17.8441	NA
SR121	Site	250	12	Cl	none	.32	NA	.06	.25	.46	2.718	.1670	NA
	Site	250	12	SO4	none	59.14	NA	2.28	57.03	62.30	2.718	6.1988	NA

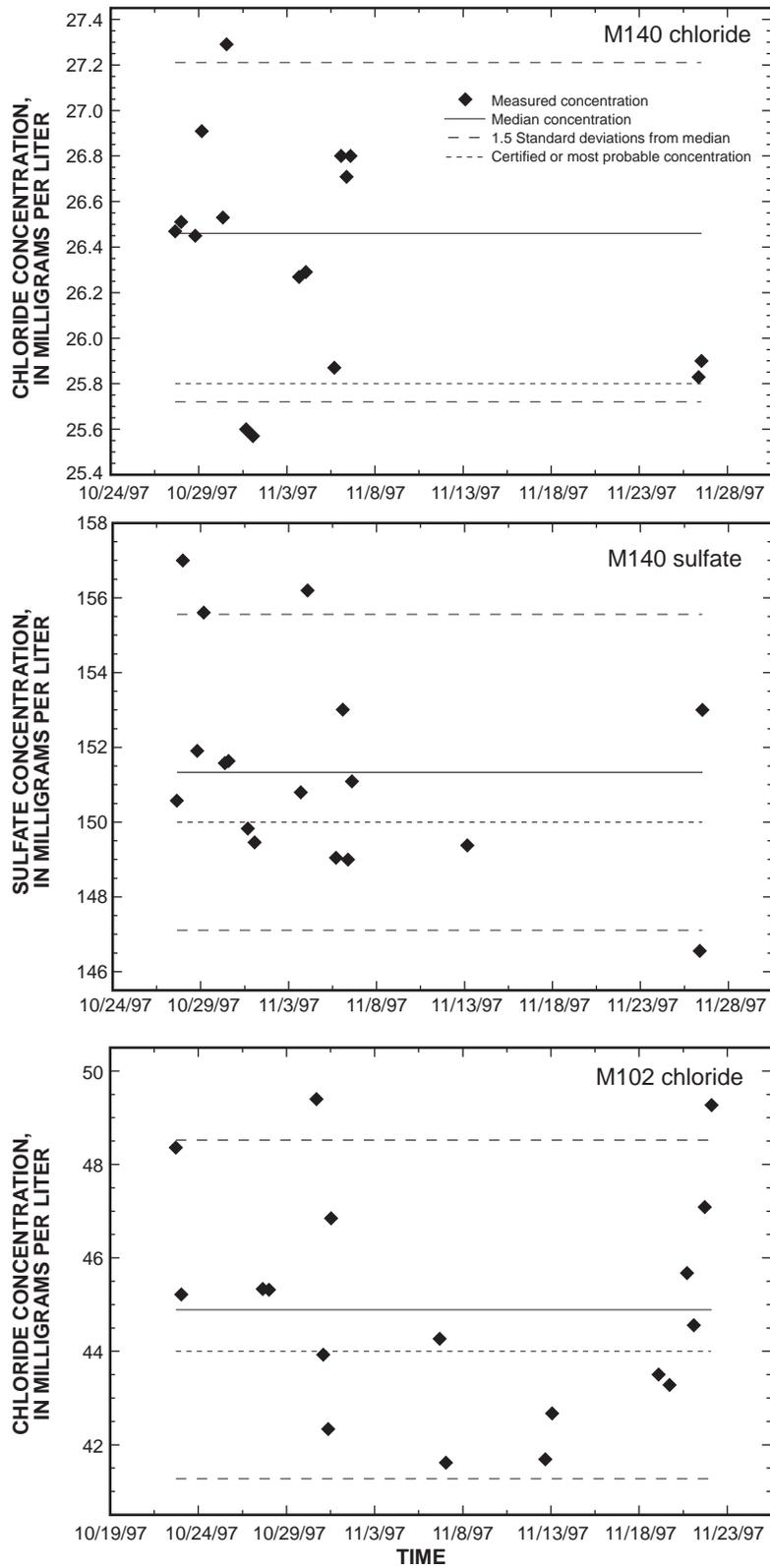


Figure 21. Variation in concentration of chloride and sulfate with time in standard reference samples.

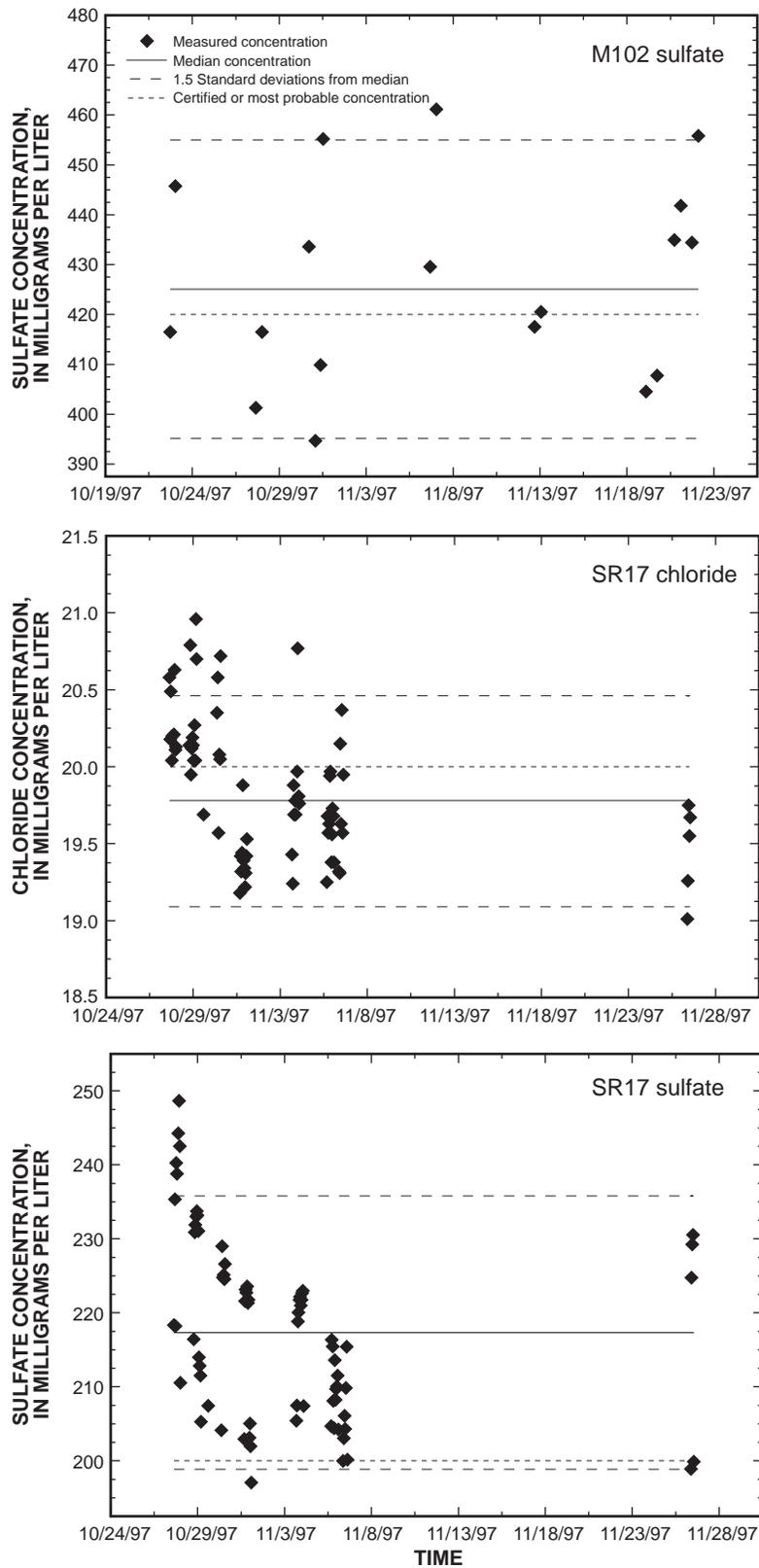


Figure 21. Variation in concentration of chloride and sulfate with time in standard reference samples—Continued.

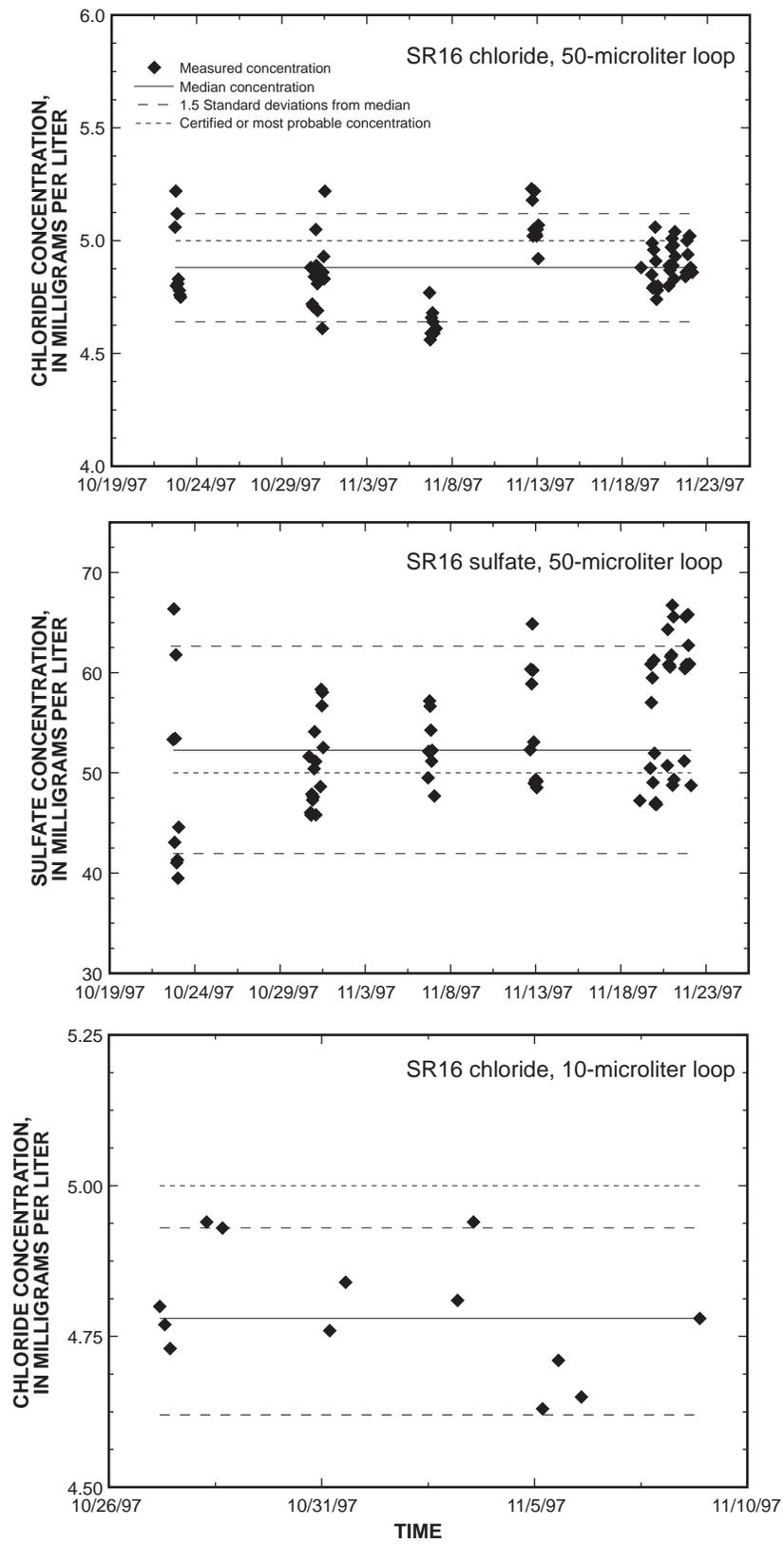


Figure 21. Variation in concentration of chloride and sulfate with time in standard reference samples—Continued.

