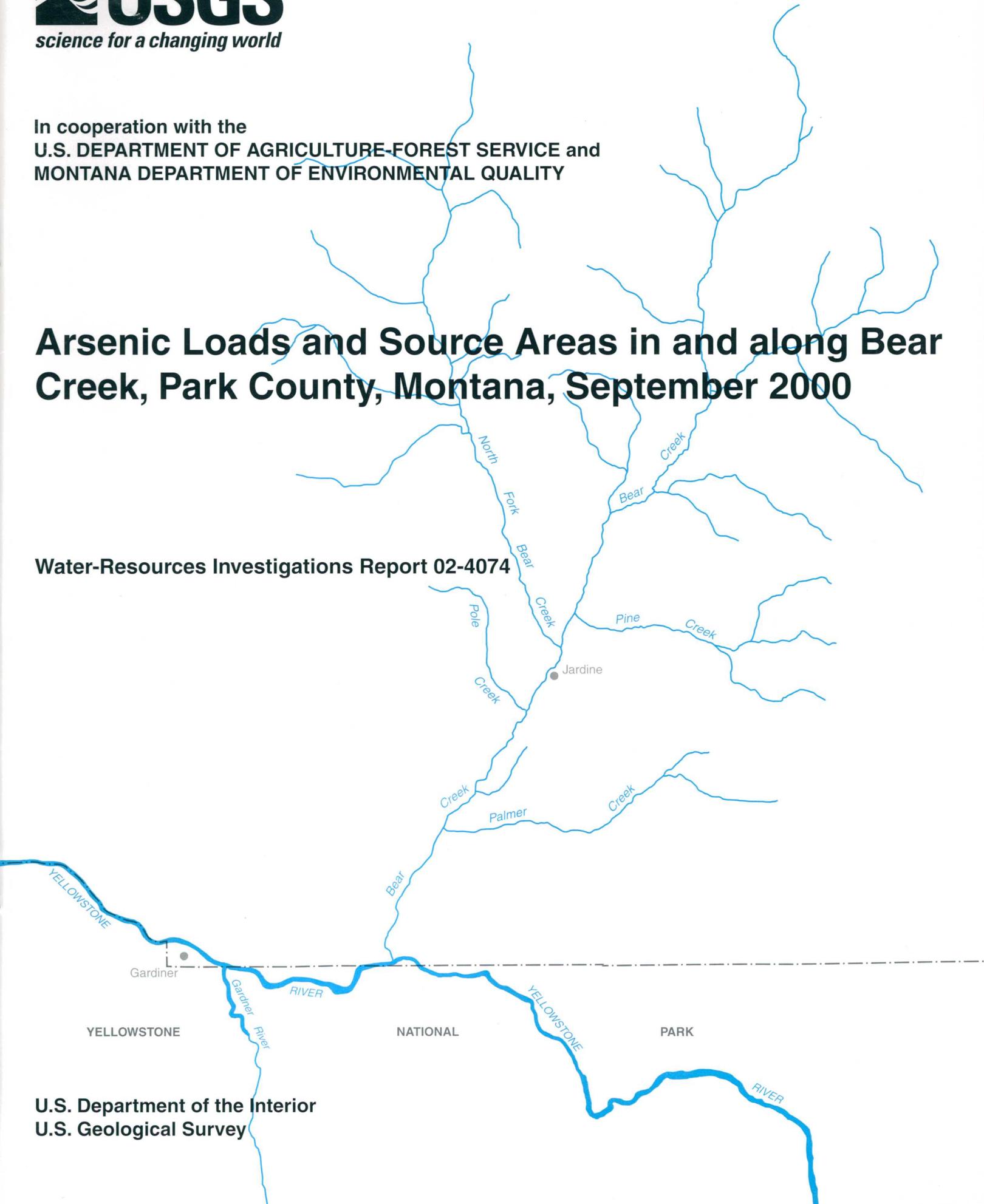


In cooperation with the  
**U.S. DEPARTMENT OF AGRICULTURE-FOREST SERVICE and**  
**MONTANA DEPARTMENT OF ENVIRONMENTAL QUALITY**

# **Arsenic Loads and Source Areas in and along Bear Creek, Park County, Montana, September 2000**

**Water-Resources Investigations Report 02-4074**





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

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**By Joanna N. Thamke, Tricia R. Wotan,  
Thomas E. Cleasby, and David A. Nimick**

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Helena, Montana  
May 2002

**U.S. Department of the Interior**

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**U.S. Geological Survey**

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**CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATED UNITS, AND ACRONYMS**

Multiply	By	To obtain
cubic foot per second (ft <sup>3</sup> /s)	0.028317	cubic meter per second (m <sup>3</sup> /s)
foot (ft)	0.3048	meter (m)
gallon (gal)	3.785	liter
gallon per minute (gal/min, gpm)	0.06309	liter per second (L/s)
inch (in.)	25.4	millimeter (mm)
mile (mi)	1.609	kilometer
pound	453.6	gram

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$^{\circ}\text{F} = 9/5(^{\circ}\text{C})+32$$

**Sea level:** In this report “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviated units and acronyms used in this report:

g/L	grams per liter	MDEQ	Montana Department of Environmental Quality
L	liter	MPDES	Montana Pollutant Discharge Elimination System
L/s	liters per second	NWQL	U.S. Geological Survey National Water Quality Laboratory
µg/L	micrograms per liter	OTN	Old Tailings North
µg/s	micrograms per second	OTS	Old Tailings South
µm	micrometer	RPD	relative percent difference
µS/cm	microsiemens per centimeter at 25 degrees Celsius	SCP	Seepage-Collection Pond
mg/L	milligrams per liter	TSF	Tailings Storage Facility
mg/s	milligrams per second	TVX	TVX Mineral Hill, Inc.
mL/min	milliliters per minute	USDA-Forest Service	U.S. Department of Agriculture-Forest Service
mL/s	milliliters per second	USGS	U.S. Geological Survey

# Arsenic Loads and Source Areas in and along Bear Creek, Park County, Montana, September 2000

By Joanna N. Thamke<sup>1</sup>, Tricia R. Wotan<sup>2</sup>, Thomas E. Cleasby<sup>1</sup>, and David A. Nimick<sup>1</sup>

## ABSTRACT

This report quantifies arsenic loading to Bear Creek and identifies the principal source areas using the results of a tracer-injection and synoptic-sampling study conducted in Bear Creek during September 2000. Arsenic loads were calculated for mainstem sites along the approximately 3-mile long study reach by combining streamflow determined by tracer-injection methods with concentration data determined in synoptic water-quality samples.

Arsenic was the only trace element in Bear Creek that had concentrations greater than the minimum reporting level. Dissolved arsenic concentrations increased from 0.5 to about 11 micrograms per liter ( $\mu\text{g/L}$ ) downstream through the study reach. Although cadmium, copper, lead, and zinc were not detected in any water samples from Bear Creek, these metals were detected in both right- and left-bank inflows downstream from Old Tailings North. Arsenic concentrations were elevated in many right- and left-bank inflows, and ranged from 0.5 to 228  $\mu\text{g/L}$ .

Dissolved arsenic loads in Bear Creek increased by 5,817 micrograms per second ( $\mu\text{g/s}$ ) through the study reach. North Fork Bear Creek contributed only about 1.5 percent (90  $\mu\text{g/s}$ ) of the arsenic load to Bear Creek. Subsurface inflow along a 550-foot subreach near the Former Arsenic Mill accounted for about 36 percent (2,087  $\mu\text{g/s}$ ) of the arsenic load. Inflow from Outfall 001 accounted for about 8 percent (455  $\mu\text{g/s}$ ) of the arsenic load. The remaining 54.5 percent of the arsenic load entering the study reach was attributed to diffuse surface and subsurface inflows.

Based on quantification of arsenic loads in Bear Creek, diffuse surface and subsurface inflows—that probably derive arsenic from natural weathering of the host rock—collectively constitute a large source of

arsenic. Reductions in arsenic loads to Bear Creek could be maximized by remediation efforts that focus on more concentrated source areas, such as the subsurface inflow along the subreach between sites 1,496 and 2,046 (near the Former Arsenic Mill) and on the surface inflow from Outfall 001 (site 3,278).

## INTRODUCTION

Bear Creek is a tributary to the Yellowstone River and is north of Yellowstone National Park and northeast of the town of Gardiner in south-central Montana (fig. 1). This creek flows near Mineral Hill, where arsenic, gold, and tungsten were produced intermittently throughout the twentieth century (Fraser and others, 1969; Amerikanuak, 2000). Bear Creek is classified by the State of Montana as a “B-1” water (Montana Department of Environmental Quality, 2001), suitable for various uses, including drinking water after conventional treatment. However, Bear Creek also is listed as impaired for aquatic life as a result of habitat alteration caused by mining development at Mineral Hill (U.S. Environmental Protection Agency, 2000; Montana Department of Environmental Quality, 2001).

In many parts of the western United States, drainage from inactive or abandoned mine areas and areas of mineralized rock has affected the water quality of streams. In Bear Creek, arsenic is the primary trace element that has affected the surface-water quality. The arsenic in this drainage probably is derived from weathering of naturally occurring arsenopyrite, which is found in waste rock, tailings, and mine adits, as well as in unmined areas. In the early 1980s, dissolved arsenic concentrations in Bear Creek ranged from 10 to 19  $\mu\text{g/L}$  downstream from the Mineral Hill mine when sampled during baseflow conditions (Western Technology and Engineering, Inc., 1980; 1982). Concentra-

<sup>1</sup>U.S. Geological Survey, Helena, Mont.

<sup>2</sup>Environmental Careers Organization, Boston, Mass.

tions of arsenic in Bear Creek upstream from the Town of Jardine were below detection limits, indicating that the elevated levels of arsenic in Bear Creek likely were associated with the mining activity at Mineral Hill (Western Technology and Engineering, Inc., 1982). Despite reclamation in the mid-1990s, dissolved arsenic concentrations (1-10 µg/L) in Bear Creek downstream from the mine continue to be higher than dissolved arsenic concentrations (<1 to <3 µg/L) upstream from the mine during base-flow conditions (Maxim Technologies, Inc., 1999b; 2000a). Substantially higher arsenic concentrations (180–653 µg/L) also occur in water discharged from the 1300-level adit in the mine area (fig. 1) (Montana Department of Environmental Quality, 2001). In addition, very high concentrations of arsenic (as much as 4,800 µg/L) were measured in ground water adjacent to Bear Creek at Mineral Hill (Huntington Engineering & Environmental, Inc. and Camp Dresser & McKee, Inc., 1995; EDE Consultants, 1999; Maxim Technologies, Inc., 1997b; 1999b; 2000a;b).

Although arsenic concentrations have been shown to increase in Bear Creek downstream from mining development, the specific source areas and transport pathways were not well understood. Possible sources of arsenic to Bear Creek include visible surface inflows (such as seepage from waste-rock or tailings piles); discharge from outflow pipes, springs, and tributaries; and subsurface inflow from ground water. The relative contributions of arsenic and metals from mine areas and from areas of mineralized rock have not been quantified. Furthermore, the importance of surface runoff and ground water as pathways for transporting arsenic and metals to Bear Creek is unknown. Property exchange is being planned for the Mineral Hill area by TVX Mineral Hill, Inc. (TVX) and the U.S. Department of Agriculture-Forest Service (USDA-Forest Service) to preserve wildlife habitat. Identifying the primary sources of arsenic can aid resource managers in planning possible remediation activities.

Tracer-injection and synoptic-sampling studies have been useful in characterizing water quality in historically mined areas and providing detailed load profiles along a stream (Kimball and others, 1999; Cleasby and others, 2000; Nimick and Cleasby, 2001). By combining streamflow data obtained by tracer-injection methods and trace-element concentration data obtained

by synoptic water-quality sampling, instantaneous loads can be determined at numerous locations, and sources can be identified. These methods were used to quantify arsenic loads and identify principal source areas along a 15,595-ft study reach of Bear Creek.

## **Purpose and Scope**

The purpose of this report is to quantify arsenic loading to Bear Creek and identify the principal source areas. This report presents the physical and chemical results of the tracer-injection and synoptic-sampling study conducted along lower Bear Creek during September 18-21, 2000. The study reach was 15,595 ft (approximately 3 miles) in length and extended from the tracer-injection site on Bear Creek, 1,456 ft upstream from North Fork Bear Creek, to 1,250 ft downstream from Palmer Creek (fig. 1). This study reach was chosen due to its proximity to the recent and historical mining areas at Mineral Hill. Data were collected at 20 mainstem and 18 surface-inflow sites (table 1). This study was conducted in cooperation with the Montana Department of Environmental Quality (MDEQ) and the USDA-Forest Service.

Arsenic loads in Bear Creek were quantified using streamflow data determined by tracer-injection methods and arsenic-concentration data obtained from laboratory analysis of synoptic samples. Loads contributed by Outfall 001 were determined from these data as well as from supplemental streamflow measurements made by Mineral Hill mine personnel. A downstream profiles of arsenic load provided the spatial information needed to identify the principal source areas of arsenic along Bear Creek.

## **Description of Study Area**

The headwaters of Bear Creek originate at an altitude of about 10,500 ft within the Gallatin National Forest in south-central Montana. Bear Creek is approximately 11 miles long and flows southwest to its confluence with the Yellowstone River at an altitude of 5,260 ft about 1.9 miles east of Gardiner, Mont., and 300 ft north of the Yellowstone National Park boundary. Tributaries of Bear Creek within the study area include Pine Creek, North Fork Bear Creek, Pole Creek, and Palmer Creek. The upper section of the



Base modified from U.S. Geological Survey digital orthophoto quadrangles, 1:40,000, 1998; and U.S. Geological Survey digital data, 1:24,000, 1986 to present. Universal Transverse Mercator Projection Zone 12.

Mine features modified from Frank W. Bergstrom, TVX Mineral Hill, Inc. (written commun., 2001).

Palmer Creek, Pole Creek, and unnamed drainage were dry at their mouth during sampling period.



SITES		EXPLANATION	
T-3	▲ Tracer-monitoring site and number	MINE FEATURES	
15,595	▼ Mainstem surface-water sampling site and number, in feet downstream from tracer-injection site	1.	Former Arsenic Mill (reclaimed)
14,345	▽ Surface-inflow sampling site and number, in feet downstream from tracer-injection site	2.	Old Tailings North
		3.	Old Tailings South
		4.	Tailings Storage Facility
		5.	Seepage-Collection Pond

Figure 1. Aerial photograph of study area with mine features, tracer-monitoring sites, and surface-water sampling sites.

**Table 1.** Sampling site locations in the Bear Creek drainage, Montana

[Site number indicates distance downstream from tracer-injection site, in feet. Type: I, surface-inflow sampling site; M, mainstem sampling site; T, tracer-monitoring site. Site names in brackets are names used for sampling sites in previous studies. The terms right bank and left bank refer to the side of Bear Creek viewed while looking downstream]

Site number (fig. 1)	Type	General site description
0	M	Tracer-injection site (981 feet downstream from Pine Creek, 1,456 feet upstream from North Fork Bear Creek)
1,316	M,T	T-1, at sufficient distance downstream to allow complete mixing of tracer
1,456	I	North Fork Bear Creek, right-bank inflow
1,496	M	40 feet downstream from North Fork Bear Creek
2,046	M	115 feet downstream from Former Arsenic Mill and 590 feet upstream from Jardine Bridge
3,048	M	About 412 feet downstream from Jardine Bridge
3,278	I	Outfall 001, 8-inch diameter discharge pipe, discharged water is from Crevice Tunnel adit and 1300-level adit, left-bank inflow
3,503	M	40 feet above Old Tailings North
3,843	M	Adjacent to Old Tailings North [B4]
3,873	I	Right-bank inflow
4,153	M	Bear Creek
4,207	I	Left-bank inflow from Old Tailings North, inflow visibly colored by iron
5,440	M	Downstream from Old Tailings North
5,873	I	90 feet upstream from Pole Creek (dry), left-bank inflow
6,393	I	Right-bank inflow
6,398	M	Upstream from Old Tailings South
7,493	M	190 feet upstream from diversion ditch
7,683	M <sup>1</sup> ,T	T-2, at diversion ditch, downstream from Old Tailings South
7,818	I	Left-bank inflow near landslide scar
8,013	I	Left-bank inflow
8,448	I	Left-bank inflow
8,688	M	Upstream from Tailings Storage Facility [B3]
9,393	M <sup>1</sup>	Bear Creek
10,398	I	Right-bank inflow
10,758	I	Right-bank inflow
11,586	M	Bear Creek, 40 feet upstream from dry unnamed left-bank drainage from the Tailings Storage Facility and the Seepage-Collection Pond
12,546	M	Bear Creek, downstream
13,039	I	Left-bank inflow
13,468	I	Right-bank inflow
13,498	I	Right-bank inflow
13,850	I	Right-bank inflow
13,950	I	Right-bank inflow
14,093	M <sup>1</sup>	Bear Creek
14,096	I	Right-bank inflow, piezometer located on left bank
14,193	M	About 152 feet upstream from Palmer Creek
14,345	I	Palmer Creek, dry at confluence with Bear Creek, sample collected about 200 feet upstream from mouth, left-bank inflow
14,595	M <sup>1</sup> ,T	T-3, 250 feet downstream from Palmer Creek
15,595	M	1,250 feet downstream from Palmer Creek

<sup>1</sup>Site not sampled during synoptic-sampling event; only ambient chloride concentrations determined.

study reach (between sites 0 and 7,683) has a slope of about 3 percent while the lower section (between sites 7,683 and 15,595) is considerably steeper, with a slope of about 6 percent. The streambed along the entire reach is composed primarily of cobbles, boulders, and bedrock.

Bear Creek streamflow has been measured during base-flow conditions in 1996, 1998, and 1999. The measured streamflow of Bear Creek above Pine Creek during base-flow conditions on September 16, 1996 and 1998 was 17 ft<sup>3</sup>/s. On the same dates in 1996 and 1998, flow at two sites in Bear Creek downstream from an unnamed drainage (located 40 ft downstream from sampling site 11,586), was approximately 23 ft<sup>3</sup>/s (Maxim Technologies, Inc., 1997a; 1999a). On September 20, 1999, the measured streamflow for Bear Creek above Pine Creek was 11 ft<sup>3</sup>/s (Maxim Technologies, Inc., 2000a). On September 20, 1999, Bear Creek streamflow 40 ft below site 11,586 was 21 ft<sup>3</sup>/s (Maxim Technologies, Inc., 2000a).

A USDA-Forest Service ditch (at site 7,683, fig. 1) diverts water from Bear Creek for agricultural purposes from mid-April to early October (R.A. Gardner, USDA-Forest Service, Gardiner Ranger District, oral commun., 2001). The ditch parallels Bear Creek above its right bank through the lower section of the study reach. The legally allotted water withdrawal is 600 inches (15 ft<sup>3</sup>/s), although the actual quantity of water diverted is well below the legal allotment as a result of ditch size and lack of need for this much water (R.A. Gardner, oral commun., 2001). Four streamflow measurements in 1981 ranging from 4.13 to 8.78 ft<sup>3</sup>/s were used to establish the quantity of water diverted from Bear Creek to this ditch (Western Technology and Engineering, Inc., 1982).

Several mining features are located on the east (left-bank) side of the study reach. The Former Arsenic Mill is located between sample sites 1,496 and 2,046. Outfall 001 is a Montana Pollutant Discharge Elimination System (MPDES) discharge pipe that flows from the Mineral Hill mine into Bear Creek at site 3,278, approximately 642 ft downstream from the Jardine bridge. Water discharged from this pipe is a mixture of 1300-level adit and Crevice Tunnel adit water from the Crevice pipeline (fig. 1). The Old Tailings North facility is located near the left bank between sites 3,503 and

5,440. The Old Tailings South facility is located about 500 ft east of the stream between sites 6,398 and 7,683. The Tailings Storage Facility and associated Seepage-Collection Pond are located 600 to 1,000 ft east of the stream near sites 9,393 and 10,398, respectively. An unnamed drainage below the Tailings Storage Facility and the Seepage Collection Pond enters Bear Creek about 40 ft downstream from site 11,586.

The geology of the Bear Creek drainage basin has been described in detail by Seager (1944), Fraser and others (1969), and Johnson and others (1993). Rocks within this area are dominated by Archean quartz-biotite schist associated with biotite schist and iron formations (Johnson and others, 1993). In local abundance, and of economic importance at Mineral Hill, is quartz-cummingtonite schist, which hosts gold and arsenopyrite (Fraser and others, 1969). Also widespread at Jardine are quartz-rich veins containing scheelite, a tungsten-bearing mineral (Seager, 1944). A veneer of Quaternary surficial alluvium, colluvium, glacial till, and glacio-fluvial deposits is present along the bottom of the lower Bear Creek valley (Fraser and others, 1969).

Mining within the Bear Creek drainage began with the discovery of Quaternary placer gold at the mouth of Bear Creek in 1866 (Fraser and others, 1969). As mining progressed into the 1900s, Precambrian vein deposits of gold, and the associated scheelite and arsenopyrite (commercially valuable as tungsten and arsenic trioxide, respectively), were mined and milled intermittently throughout the twentieth century at Mineral Hill near Jardine (Fraser and others, 1969, Amerikanuak, 2000). In 1996, the mining and milling operations at Mineral Hill were halted, and the facility was placed on care and maintenance status (Amerikanuak, 2000). Currently, the Mineral Hill mine is operating under a closure plan, and reclamation has been ongoing since 1994 (Amerikanuak, 2000).

## Acknowledgments

TVX, MDEQ, and the USDA-Forest Service are acknowledged for providing data, maps, and reports of the study area. Patricia J. Belec, Frank W. Bergstrom, and Ronald L. Burke of TVX, shared their knowledge of the study area, flagged sites in the field from previ-

ous studies, and provided discharge data for Outfall 001. Joseph T. Gurrieri of the MDEQ, and Michael J. Burnside, Nancy J. Rusho, Sherman A. Sollid, and Ray TeSoro of the USDA-Forest Service, shared their knowledge of the study area. Ronald A. Gardner of the USDA-Forest Service, Gardiner Ranger District, operated the diversion ditch during this study. In addition, several USDA-Forest Service and U.S. Geological Survey (USGS) employees, as well as one Environmental Careers Organization employee, are acknowledged for their assistance with collection of water-quality and hydrologic data, including: Henry F. Shovic, Wendy A. Urie, and Renee Van Hoven of the USDA-Forest Service; and Michael R. Cannon, Terry L. Heinert, John H. Lambing, Andrew R. Skerda, and Ruth L. Willis of the USGS; and Sharon L. Gelinis, of Environmental Careers Organization.

## METHODS OF DATA COLLECTION

This tracer-injection and synoptic-sampling study was designed to determine streamflow and chemical quality at many mainstem and surface-inflow sites in a short period of time in order to create a nearly instantaneous measure of the loading and downstream transport of arsenic in the study reach. Tracer-injection methods were used to determine streamflow, and synoptic-sampling methods were used to determine chemical quality of water.

A reconnaissance of the study reach was conducted 6 weeks before the start of the tracer-injection and synoptic-sampling study. Sites to be sampled synoptically were selected and marked with flagging, and their distances downstream from the tracer-injection site were measured in the field using a tape measure. Sampling sites on Bear Creek were selected upstream and downstream from visible surface inflows, tailings piles, and other mining-related features that possibly could affect metal loads in the stream. Many visible surface inflows were selected for sampling; however, where several surface inflows were closely spaced, only the largest was selected. To detect possible subsurface inflow, additional mainstem sites were selected in longer subreaches that had no visible surface inflow or mining disturbance.

Sampling sites were numbered according to the site's distance in feet downstream from the tracer-

injection site (site 0). Locations and descriptions of sampling sites are listed in table 1 and shown in figure 1. Right bank and left bank terms used in this report refer to the respective sides of the stream while looking downstream.

Base-flow conditions absent of precipitation runoff were targeted for the tracer study to minimize complications of varying streamflow and short-term loading that might be associated with overland runoff. The USDA-Forest Service ditch diversion gate was closed one week prior to the synoptic tracer sampling event to prevent loss of streamflow and the injected tracer solution from Bear Creek to the ditch.

## Tracer Injection

Streamflow determined by a current-meter measurement near site 2,046 (fig. 1) during the reconnaissance was used to estimate the volume and concentration of tracer solution needed for the tracer injection. Before the start of the tracer injection, an ample volume of tracer solution was prepared in two large polyethylene tanks by mixing 1,000 pounds of sodium chloride (NaCl) with 610 gallons of stream water (from site 0). The tracer solution was circulated between the two tanks to ensure thorough mixing. This mixture ratio produced a concentration of chloride much greater than ambient concentrations in the stream, but less than the concentration at which the solution would be saturated with respect to sodium chloride.

The tracer solution was injected continuously for about 43 hours into Bear Creek at site 0 at a rate that ranged from 901.3 to 907.7 mL/min; the average rate (904 mL/min) was used for calculating streamflow. The injection was started at 1915 hours on September 19 using a positive-displacement pump system controlled and monitored by an electronic data logger. The tracer injection was stopped at 1425 hours on September 21. Six samples of the tracer solution were collected periodically during the injection period to document the tracer concentrations. The chloride concentration of each sample was determined by first measuring the solution density with volumetric glassware and an analytical balance, and then converting density to concentration using data in Weast and Astle (1981). The chloride concentration ranged from 108.9 to

112.3 g/L; the average concentration (110.9 g/L) was used for calculating streamflow.

Water samples for chloride analysis were collected at fixed intervals at three mainstem sites, referred to as tracer-monitoring sites (fig. 1), to document the downstream movement and concentration changes of the injected tracer. Each tracer-monitoring site was sampled prior to the arrival of the tracer to determine the ambient chloride concentration, throughout the injection period to confirm equilibrium conditions, and after the tracer injection to track the return to ambient conditions. These samples were collected manually or with automatic pumping samplers at a single point near midstream (where water was well mixed) and were filtered through 0.45- $\mu$ m capsule filters.

In addition to the tracer-monitoring sites, chloride concentrations were determined at 19 mainstem and 2 surface-inflow sampling sites on September 18-19, 2000, to document ambient chloride concentrations just prior to the tracer injection (table 2). Where stream mixing was good, samples were collected at a single vertical near midstream. At all other sites, equal-width and depth-integrated sampling methods were used, as described by Ward and Harr (1990) and Wilde and others (1998). The samples were filtered onsite through a 0.45- $\mu$ m syringe filter.

### Synoptic Sampling

Synoptic water samples for chemical analysis were collected on September 21, 2000, in acid-washed and stream-rinsed 3-L polyethylene bottles at each sampling site after concentrations of the injected chloride reached equilibrium through the study reach. To reduce the effect of load changes caused by diel variation in streamflow, samples were collected and processed as rapidly as possible. Equal-width and depth-integrated sampling methods were used at all sampling sites. Two teams collected samples; one team sampled water from sites 0 through 9,393, and the second team sampled water from sites 9,393 through 15,595.

Water-quality samples were transported to a central processing location near the middle of the study reach as soon as possible after collection. Field values of specific conductance and pH were determined on an

unfiltered aliquot of each sample. A second, unfiltered aliquot was drawn for analysis of total-recoverable trace elements. Other aliquots were filtered through a 0.45- $\mu$ m capsule filter and analyzed for major ions and trace elements. Sample processing, filtration, and preservation were performed according to procedures described by Ward and Harr (1990), Horowitz and others (1994), and Wilde and others (1998). The USGS National Water Quality Laboratory (NWQL) in Denver, Colo., analyzed water samples using methods described by Fishman and Friedman (1989), Fishman (1993), Garbarino and Taylor (1996), Hoffman and others (1996), and Garbarino and Struzeski (1998). Water-quality data for synoptic samples are reported in table 3.

### Quality Assurance

Data-collection and analytical procedures used in this study incorporated practices designed to control, verify, and assess the quality of sample data. Methods and associated quality control for collection and field processing of water-quality samples are described by Horowitz and others (1994) and Wilde and others (1998).

The quality of analytical results reported for water-quality samples can be evaluated with data from quality-control samples that were submitted from the field and analyzed concurrently in the laboratory with routine samples. These quality-control samples consisted of replicates and blanks, which provide quantitative information on the precision and bias of the overall field and laboratory process. In addition to quality-control samples submitted from the field, internal quality-assurance practices at the NWQL were performed systematically to provide quality control of analytical procedures (Pritt and Raese, 1995). These internal practices included analyses of quality-control samples such as calibration standards, standard-reference-water samples, replicate samples, deionized-water blanks, or spiked samples at a proportion equivalent to at least 10 percent of the total samples analyzed.

Replicate samples were obtained in the field to provide data on precision (reproducibility) for samples exposed to all sources of variability. Precision of analytical results for field replicates is affected by many sources of variability within the field and laboratory

**Table 2.** Chloride concentrations and streamflow at sampling sites in the Bear Creek drainage, Montana, September 2000

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

Site number (fig. 1)	Dissolved chloride concentration, unrounded (mg/L)		Instream tracer concentration <sup>1</sup> (mg/L)	Tracer- calculated streamflow (L/s)	Current-meter measured streamflow <sup>2</sup> (L/s)
	Ambient, pre-tracer injection (Sept. 18-19, 2000)	Synoptic, during tracer injection (Sept. 21, 2000)			
<b><u>Bear Creek</u></b>					
0	0.31	<sup>3</sup> 6.18	5.87	285	--
1,316	.36	6.18	5.82	288	258
1,496	.32	3.91	3.59	466	479
2,046	.30	3.84	3.54	473	--
3,048	.32	3.93	3.61	464	--
3,503	.38	3.74	3.36	498	--
3,843	<sup>4</sup> .46	3.70	3.24	517	--
4,153	.41	3.70	3.29	509	--
5,440	.49	3.74	3.25	515	--
6,398	.51	3.80	3.29	509	--
7,493	.54	3.76	3.22	520	493
8,688	<sup>5</sup> .56	3.74	3.18	527	--
9,393	.57	3.72	3.15	532	--
11,586	.58	3.80	3.22	520	--
12,546	.57	3.74	3.17	528	--
14,093	.57	--	--	--	--
14,193	<sup>6</sup> .57	3.72	3.15	532	--
14,595	.57	<sup>7</sup> 3.69	3.12	537	--
15,595	<sup>6</sup> .57	3.72	3.15	532	487
<b><u>Surface inflows</u></b>					
1,456	.40	<sup>8</sup> 5.57	--	<sup>9</sup> 178	--
3,278	1.42	1.51	--	--	<sup>10</sup> 23.8

<sup>1</sup>Calculated as the difference between ambient and synoptic chloride concentration.

<sup>2</sup>Measurements were conducted on September 21, 2000.

<sup>3</sup>Sample results from this site indicate that tracer injectate was not completely mixed throughout stream at this site; therefore, the chloride concentration from site 1,316 was used for streamflow calculations.

<sup>4</sup>Average of laboratory analyses (0.43 mg/L and 0.50 mg/L).

<sup>5</sup>Sample results from this site indicate possible chloride contamination in sample; therefore, the concentrations from site 7,493 and site 9,393 were averaged for ambient chloride concentration at this site.

<sup>6</sup>Chloride concentration was estimated, using concentrations from nearby sites.

<sup>7</sup>Sample collected by T-3 automatic sampler at 1600 hours.

<sup>8</sup>Increase in chloride concentration over ambient conditions indicated that the North Fork Bear Creek might be receiving tracer injectate from subsurface inflow at this site.

<sup>9</sup>Calculated as the difference between the tracer-calculated streamflows for sites 1,316 and 1,496.

<sup>10</sup>Inflow calculated from measurements provided by Frank Bergstrom (TVX Mineral Hill, Inc., written commun., 2001).

environments, including sample collection, processing (filtration, preservation, transportation, and laboratory handling), and analysis. For this study, replicate samples were sequentially collected in the field at three sites and analyzed separately. Analytical results for field replicates are presented in table 3. Precision of analytical results for any constituent can be determined from the relative percent difference (RPD) of the constituent concentrations in replicate analyses. The RPD is calculated for a constituent by dividing the absolute value of the difference between the two concentrations by the mean of the two concentrations and multiplying

by 100. RPD values for dissolved and total-recoverable trace elements were almost all less than 6 percent, with no systematic exceedance of this value, indicating good precision for analytical results.

Two field blanks were analyzed to identify the presence and magnitude of contamination that potentially could bias analytical results. A field blank is an aliquot of deionized water that is certified as essentially free of the measured trace elements and that is processed through the sampling equipment used to collect stream samples. The blank is then subjected to the

same processing (filtration, preservation, transportation, and laboratory handling) as stream samples. Blank samples were analyzed for the same constituents as those of stream samples to identify whether any detectable concentrations existed. Analytical results for field blanks are presented in table 3. Concentrations of all constituents were less than minimum reporting level, except for one alkalinity value. Consequently, analytical results for the environmental samples are assumed to be free of significant or systematic bias from contamination associated with sample collection and processing.

## TRACER-INJECTION RESULTS

Accurate streamflow measurements are necessary for quantifying the mass of a constituent transported downstream. The tracer-injection method uses conservation-of-mass theory applied to downstream dilution of an injected tracer, such as chloride, and represents an alternative to traditional current-meter methods for determining streamflow. Determination of streamflow using tracer-injection methods is particularly effective in high-gradient mountain streams where traditional methods are hampered by turbulent flow and irregular channel cross sections (Bencala and others, 1990). The tracer-injection method also accounts for the portion of streamflow referred to as underflow, or hyporheic flow, which moves through the gravels and cobbles comprising the bed of the stream. In mountain streams, hyporheic flow can represent a substantial portion of the total streamflow (Kimball, 1997). Hyporheic flow cannot be measured by current-meter methods; therefore, loads might be underestimated using streamflow values obtained by current-meter measurements. Another advantage of the tracer-injection method is that streamflow data can be obtained at many sites more quickly than with current-meter measurements, thus allowing a long study reach to be characterized in less time, minimizing the potential effect of temporal changes in streamflow that could complicate comparisons between sites.

### Downstream Travel and Dilution

During continuous tracer injection, the downstream movement of the tracer solution is documented

by frequent sampling at a few key sites called tracer-monitoring sites. Three tracer-monitoring sites located along the study reach (fig. 1, table 1) were sampled during this study. The first tracer-monitoring site was located at site 1,316 (T1) and was as close to the tracer-injection site as possible to minimize the potential for subsurface inflow to increase streamflow between the sites, but far enough downstream to ensure complete mixing of the tracer solution. Additional tracer-monitoring sites were located at sites 7,683 (T-2) and 14,595 (T-3) on Bear Creek. Samples were collected hourly at tracer-monitoring sites T-1 and T-2; samples were collected every two hours at tracer-monitoring site T-3.

Information on the movement of the chloride tracer is gained by constructing temporal concentration profiles that show the change in chloride concentration with time at each tracer-monitoring site (fig. 2). Ideal temporal concentration profiles of an injected tracer have three distinct regions that show the arrival, plateau (or equilibrium) conditions, and departure of the tracer.

Once the tracer has reached equilibrium at a site, a generally stable plateau concentration ideally will exist until the tracer injection is terminated. Therefore, in a gaining stream system, the plateau concentration decreases downstream as the result of dilution from inflows. Because equilibrium conditions are required for streamflow determinations and load comparisons, data from the tracer-monitoring sites are used to determine whether a relatively stable plateau concentration was reached at each site prior to collection of the synoptic water-quality samples. Chloride concentration remained fairly uniform during the plateau period at all three tracer-monitoring sites (fig. 2). Small changes in chloride concentrations during the plateau period can be caused by natural streamflow variations, variations in the chloride concentration in the injected tracer solution, changes in the tracer injection rate, or variations within analytical precision.

Collection of synoptic samples began about 38 hours after the start of the tracer injection and after the tracer had adequate time to mix and achieve equilibrium. The synoptic-sampling period (shown as the shaded and hatched areas on fig. 2) coincided with periods of relatively constant chloride concentration, indicating that synoptic samples were collected during a period of generally stable streamflow.

**Table 3.** Water-quality data for synoptic samples collected in the Bear Creek drainage, Montana, September 21, 2000

[Site number indicates distance downstream from tracer-injection site, in feet. Abbreviations:  $\mu\text{g/L}$ , micrograms per liter;  $\mu\text{S/cm}$ , microsiemens per centimeter at 25 degrees Celsius;  $\text{mg/L}$ , milligrams per liter. Symbols: <, less than minimum reporting level; --, no data]

Site number (fig. 1)	Time	Specific conductance <sup>1</sup> , field ( $\mu\text{S/cm}$ )	pH, field (standard units)	Hard- ness, total ( $\text{mg/L}$ as $\text{CaCO}_3$ )	Calcium, dissolved ( $\text{mg/L}$ as Ca)	Magnesium, dissolved ( $\text{mg/L}$ as Mg)	Sodium, dissolved ( $\text{mg/L}$ as Na)	Chloride <sup>1</sup> , dissolved ( $\text{mg/L}$ as Cl)	Alkalinity ( $\text{mg/L}$ as $\text{CaCO}_3$ )	Sulfate, dissolved ( $\text{mg/L}$ as $\text{SO}_4$ )
<b><u>Bear Creek</u></b>										
0	0945	66	7.2	24	6.59	1.82	3.2	0.5	34	1.4
1,316	0840	86	6.9	24	6.69	1.84	6.9	6.2	33	1.3
1,496	0900	99	7.1	32	8.19	2.79	6.1	3.9	42	2.7
2,046	0930	96	7.2	32	8.23	2.82	6.1	3.8	41	2.8
3,048	0950	96	7.5	32	8.20	2.83	6.0	3.9	41	2.9
3,503	1030	109	8.0	39	9.28	3.73	6.3	3.7	49	3.9
3,843	1045	111	8.2	39	9.45	3.83	6.4	3.7	49	3.8
4,153	1110	112	8.0	39	9.51	3.81	6.5	<sup>2</sup> 3.7	49	3.9
5,440	1140	114	7.3	39	9.39	3.88	6.2	3.7	49	4.0
5,440 <sup>3</sup>	1141	114	7.3	39	9.55	3.80	6.6	3.7	49	4.0
6,398	1300	112	8.2	40	9.57	3.82	6.5	3.8	49	3.9
7,493	1325	113	8.1	40	9.53	3.85	6.3	3.8	49	3.9
8,688	1425	113	7.9	40	9.64	3.89	6.3	3.7	49	4.1
9,393	0915	110	7.9	40	9.71	3.93	6.4	3.9	49	4.3
9,393	1450	113	8.3	40	9.68	3.90	6.4	3.7	49	4.2
11,586	1100	110	7.7	41	9.85	3.93	6.4	3.8	49	4.2
12,546	1220	110	8.1	40	9.78	3.91	6.3	<sup>2</sup> 3.7	49	4.3
14,193	1630	112	8.1	42	10.3	4.08	6.4	3.7	50	4.4
15,595	1545	113	8.2	43	10.4	4.14	6.4	3.7	51	4.4
15,595 <sup>3</sup>	1550	113	8.1	42	10.2	4.08	6.3	3.7	51	4.4
<b><u>Surface inflows</u></b>										
1,456	0850	109	7.0	42	10.1	4.13	4.8	.6	53	4.9
3,278	1010	402	7.8	184	35.5	23.2	13.2	1.5	198	25.0
3,278 <sup>3</sup>	1011	402	7.9	180	34.3	22.9	13.1	1.1	196	24.1
3,873	1050	331	7.9	144	38.3	11.7	10.7	4.3	147	21.6
4,207	1125	666	4.7	238	57.7	22.8	13.4	16.2	--	287
5,873	1220	411	7.8	196	49.8	17.5	9.3	16.7	135	47.9
6,393	1250	271	7.0	104	27.7	8.47	11.4	12.9	105	8.5
7,818	1345	661	8.3	321	78.8	30.2	10.5	23.3	215	134
8,013	1400	368	8.2	172	40.5	17.2	8.5	4.1	164	29.1
8,448	1410	436	7.9	207	53.2	18.1	8.8	5.5	188	42.5
10,398	1005	116	7.5	79	21.1	6.43	6.3	.8	91	3.5
10,758	1030	119	7.6	49	13.7	3.51	5.9	.6	60	3.4
13,039	1145	424	7.9	205	50.3	19.4	10.6	7.1	171	52.7
13,468	1255	387	8.4	133	28.9	14.8	38.2	1.9	209	14.4
13,498	1300	219	7.8	93	22.7	8.73	10.0	2.9	111	5.1
13,850	1320	319	8.2	143	29.6	16.8	15.5	1.3	178	5.5
13,950	1345	313	7.9	155	29.8	19.6	8.8	.9	178	4.1
14,096	1445	384	7.9	189	40.4	21.5	12.7	1.0	218	5.0
14,345	1510	243	7.8	110	26.1	10.9	6.9	4.3	109	17.1
<b><u>Field blanks</u></b>										
--	0904	<sup>4</sup> 2	5.6	.1	<.02	<.01	<.1	<.3	<.1	<.3
--	1140	<sup>4</sup> 2	6.4	.1	<.02	<.01	<.1	<.3	2	<.3

<sup>1</sup>Specific-conductance values and chloride concentrations in Bear Creek samples are artificially high as a result of the injection of chloride into the stream. Chloride concentrations are rounded to standard reporting levels (see table 2 for unrounded values).

<sup>2</sup>Average of laboratory analyses.

<sup>3</sup>Replicate sample.

<sup>4</sup>Laboratory analysis.

**Table 3.** Water-quality data for synoptic samples collected in the Bear Creek drainage, Montana, September 21, 2000 (Continued)

Arsenic, dissolved (µg/L as As)	Arsenic, total recoverable (µg/L as As)	Cadmium, dissolved (µg/L as Cd)	Cadmium, total recoverable (µg/L as Cd)	Copper, dissolved (µg/L as Cu)	Copper, total recoverable (µg/L as Cu)	Lead, dissolved (µg/L as Pb)	Lead, total recoverable (µg/L as Pb)	Zinc, dissolved (µg/L as Zn)	Zinc, total recoverable (µg/L as Zn)	Site number (fig. 1)
<u>Bear Creek</u>										
0.5	<3	<0.1	<0.1	<1	<1	<1	<1	<1	<1	0
.5	<3	<.1	<.1	<1	<1	<1	<1	<1	<1	1,316
.5	<3	<.1	<.1	<1	<1	<1	<1	<1	<1	1,496
4.9	6	<.1	<.1	<1	<1	<1	<1	<1	<1	2,046
5.9	7	<.1	<.1	<1	<1	<1	<1	<1	<1	3,048
6.7	7	<.1	<.1	<1	<1	<1	<1	<1	<1	3,503
6.8	8	<.1	<.1	<1	<1	<1	<1	<1	<1	3,843
6.8	7	<.1	<.1	<1	<1	<1	<1	<1	<1	4,153
7.1	8	<.1	<.1	<1	<1	<1	<1	<1	<1	5,440
6.8	8	<.1	<.1	<1	<1	<1	<1	<1	<1	5,440 <sup>3</sup>
7.5	8	<.1	<.1	<1	<1	<1	<1	<1	<1	6,398
8.2	9	<.1	<.1	<1	<1	<1	<1	<1	<1	7,493
8.6	10	<.1	<.1	<1	<1	<1	<1	<1	<1	8,688
8.8	9	<.1	<.1	<1	<1	<1	<1	<1	<1	9,393
8.3	9	<.1	<.1	<1	<1	<1	<1	<1	<1	9,393
9.0	10	<.1	<.1	<1	<1	<1	<1	<1	<1	11,586
10.1	10	<.1	<.1	<1	<1	<1	<1	<1	<1	12,546
11.2	11	<.1	<.1	<1	<1	<1	<1	<1	<1	14,193
11.2	12	<.1	<.1	<1	<1	<1	<1	<1	<1	15,595
11.3	12	<.1	<.1	<1	<1	<1	<1	<1	<1	15,595 <sup>3</sup>
<u>Surface inflows</u>										
.5	<3	<.1	<.1	<1	<1	<1	<1	<1	<1	1,456
18.7	22	<.1	<.1	<1	<1	<1	<1	<1	<1	3,278
17.6	21	<.1	<.1	<1	<1	<1	<1	<1	<1	3,278 <sup>3</sup>
5.6	7	<.1	<.1	<1	<1	<1	<1	<1	<1	3,873
.9	--	17	--	4	--	<1	--	55	--	4,207
33.8	120	<.1	<.1	3	5	<1	2	2	7	5,873
228	300	<.1	<.1	3	2	<1	4	<1	<1	6,393
8.5	10	<.1	<.1	1	2	<1	<1	<1	2	7,818
10.6	26	<.1	<.1	1	12	<1	5	<1	15	8,013
10.5	14	<.1	<.1	2	2	<1	<1	1	<1	8,448
18.7	31	<.1	<.1	1	<1	<1	<1	<1	<1	10,398
8.9	15	<.1	<.1	1	2	<1	<1	<1	2	10,758
58.3	59	<.1	<.1	1	1	<1	<1	<1	1	13,039
2.2	4	<.1	<.1	<1	4	<1	1	<1	4	13,468
50.0	105	<.1	<.1	<1	4	<1	3	<1	7	13,498
32.4	32	<.1	<.1	1	1	<1	<1	<1	<1	13,850
64.3	65	<.1	<.1	1	2	<1	<1	<1	1	13,950
94.3	90	<.1	<.1	1	1	<1	<1	<1	<1	14,096
31.7	32	<.1	<.1	1	<1	<1	<1	<1	<1	14,345
<u>Field blanks</u>										
<.2	<3	<.1	<.1	<1	<1	<1	<1	<1	<1	--
<.2	<3	<.1	<.1	<1	<1	<1	<1	<1	<1	--

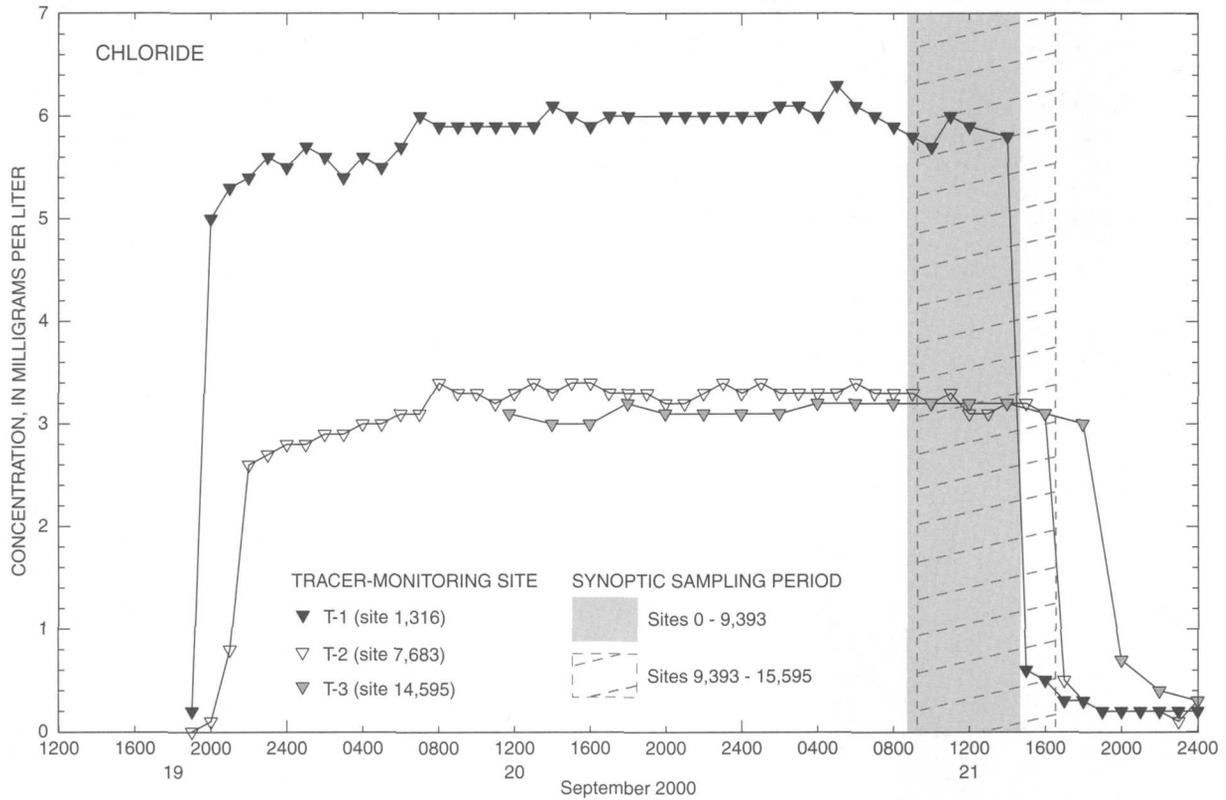


Figure 2. Temporal profiles of chloride concentration at tracer-monitoring sites, Bear Creek, Montana, September 19-21, 2000.

### Determination of Streamflow

Streamflow can be calculated at any mainstem site in the study reach using the instream tracer (chloride) concentration and the concentration and injection rate of the tracer solution. The instream tracer concentration used in these calculations was the difference between the ambient (pre-tracer injection) concentration and the chloride concentration determined in synoptic samples collected during the plateau phase of the tracer injection (table 2).

Using the assumption that chloride is chemically conservative, the mass of the injected tracer was presumed to remain in solution as it traveled downstream. Any decrease in chloride concentration in the mainstem was assumed to be the result of dilution from inflows. For this study, the tracer solution was injected at a rate of 0.0151 L/s, and the average chloride concentration of the tracer solution was 110,900 mg/L.

Thus, the chloride injection rate was 1,675 mg/s. Streamflow at each of the mainstem synoptic-sampling sites was calculated using equation 1:

$$Q_a = (Q_{inj} \times C_{inj}) / (C_a - C_b) \quad (1)$$

where

- $Q_a$  is the streamflow at the mainstem synoptic sampling site, in L/s;
- $Q_{inj}$  is the injection rate of the tracer solution, in L/s;
- $C_{inj}$  is the chloride concentration of the tracer solution, in mg/L;
- $C_a$  is the chloride concentration of the synoptic water sample, in mg/L;
- $C_b$  is the chloride concentration of the pre-tracer injection water sample, in mg/L.

Streamflow values are listed in table 2. Hydrologic sources accounting for flow increases in the sub-

reach between consecutive sites could include visible surface inflows as well as unsampled diffuse seeps and subsurface inflow.

Using the instream chloride concentration from synoptic samples collected on September 21 and equation 1, instantaneous streamflow was calculated for 18 mainstem sites (fig. 3, table 2). Over the length of the study reach, streamflow increased in Bear Creek from 285 L/s at the tracer injection site (site 0) to 532 L/s at site 15,595, representing an increase of 247 L/s. Variations in streamflow between sites 14,193 and 15,595 are considered negligible ( $\pm 5$  L/s). The North Fork Bear Creek accounted for 72 percent (178 L/s) of this increase, and discharge water from Outfall 001 accounted for 10 percent (23.8 L/s) of this increase, leaving 18 percent (45.2 L/s) of the increase attributable to the remaining visible surface inflows and subsurface inflow.

Four current-meter measurements of streamflow in Bear Creek also were made on September 21 (fig. 3, table 2). Because hyporheic flow is included in the streamflow value calculated from the tracer-injection method, the tracer-calculated streamflow was expected to be greater than the streamflow measured by the current meter, which does not measure hyporheic flow. Greater flow was calculated by the tracer-injection method at all sites except for the site downstream from the North Fork Bear Creek (site 1,496). Possibly, the tracer solution at this site, which was 40 ft downstream from the mouth of the North Fork Bear Creek, may not have been fully mixed when the synoptic sample was collected, thereby leading to an underestimation of the tracer-calculated streamflow. At the other sites, the tracer-calculated streamflow ranged from 5 to 12 percent greater than the current-meter streamflow.

## SYNOPTIC-SAMPLING RESULTS

Accurate concentration data collected at numerous locations along a stream reach are as important as accurate streamflow data for compiling a representative spatial profile of constituent loads. Synoptic samples were collected at 17 mainstem sites along Bear Creek and at 18 surface-inflow sites. Samples were analyzed for concentrations of major ions and concen-

trations of dissolved and total-recoverable trace elements (table 3).

### pH and Major-Ion Concentrations

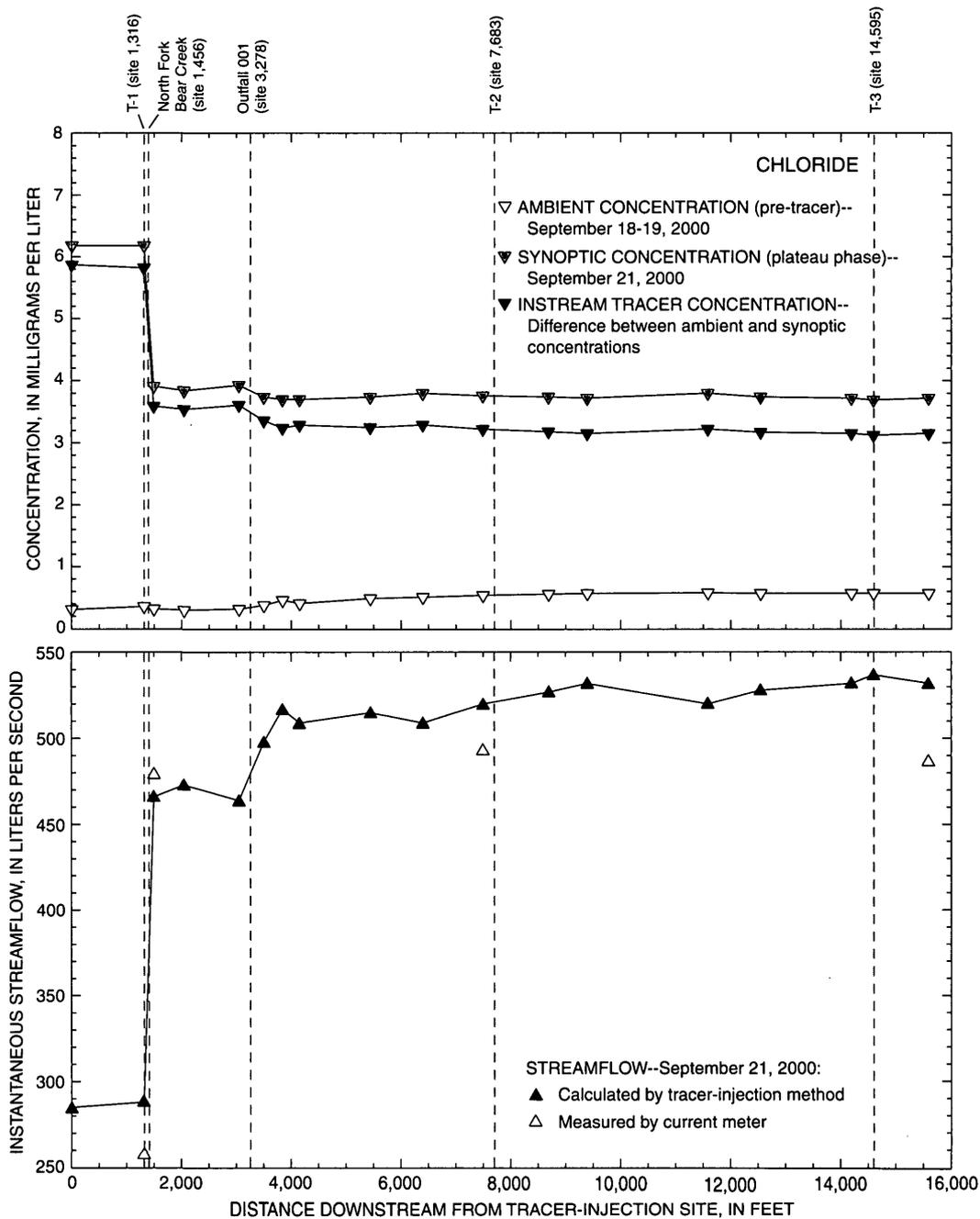
Values of pH in Bear Creek were neutral to slightly basic and remained fairly constant (fig. 4, table 3) through the study reach, ranging from 6.9 (site 1,316) to 8.3 (site 9,393). All inflows contributed near-neutral or basic water to Bear Creek, except for site 4,207 (left-bank inflow from Old Tailings North). This acidic inflow from the Old Tailings North had a pH value of 4.7 and was visibly colored by iron.

Calcium, magnesium, and sulfate concentrations in Bear Creek increased slightly through the study reach, with the largest increases occurring in the upper subreaches between site 1,316 and site 1,496 and between site 3,048 and site 3,503 (fig. 5, table 3). These two increases likely were in response to the higher concentrations of these constituents in the relatively large inflows of North Fork Bear Creek and Outfall 001. Concentrations of calcium, magnesium, and sulfate in most of the other inflows also were greater than concentrations in Bear Creek, but their small flows resulted in only minor increase in the mainstem. Concentrations in left-bank inflows were generally greater than in right-bank inflows.

### Trace-Element Concentrations

Concentrations of selected dissolved and total-recoverable trace elements—arsenic, cadmium, copper, lead, and zinc—were determined from the synoptic samples. Arsenic was mined in the study area and processed at the Former Arsenic Mill (fig. 1) during the early to mid 1900s. In addition to mining wastes, arsenic also is probably derived from the natural weathering of arsenopyrite layers within the schist host rock. Cadmium, copper, lead, and zinc are other trace elements commonly associated with acid drainage from mined areas as well as natural weathering of mineralized rock.

Of the five trace elements, arsenic was the only one that consistently had concentrations greater than minimum reporting levels (fig. 6, table 3). Concentra-



**Figure 3.** Downstream profiles of chloride concentration (top) and streamflow (bottom) at synoptic sampling sites in the Bear Creek drainage, Montana, September 2000.

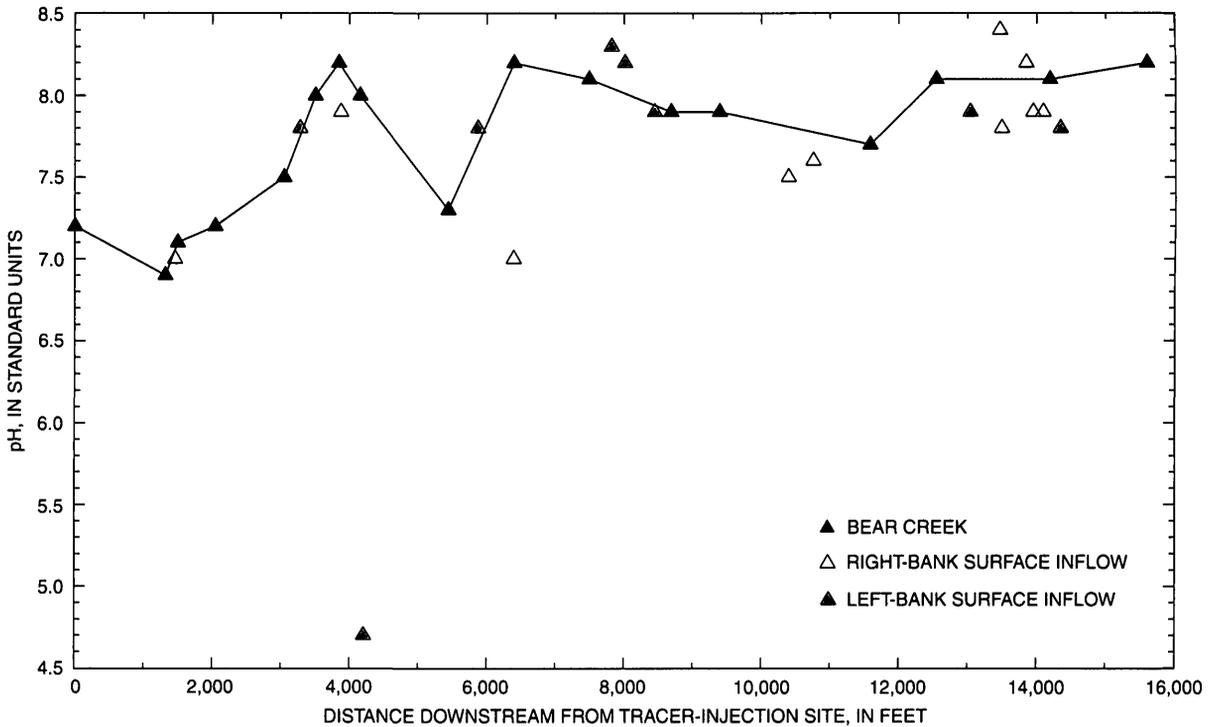
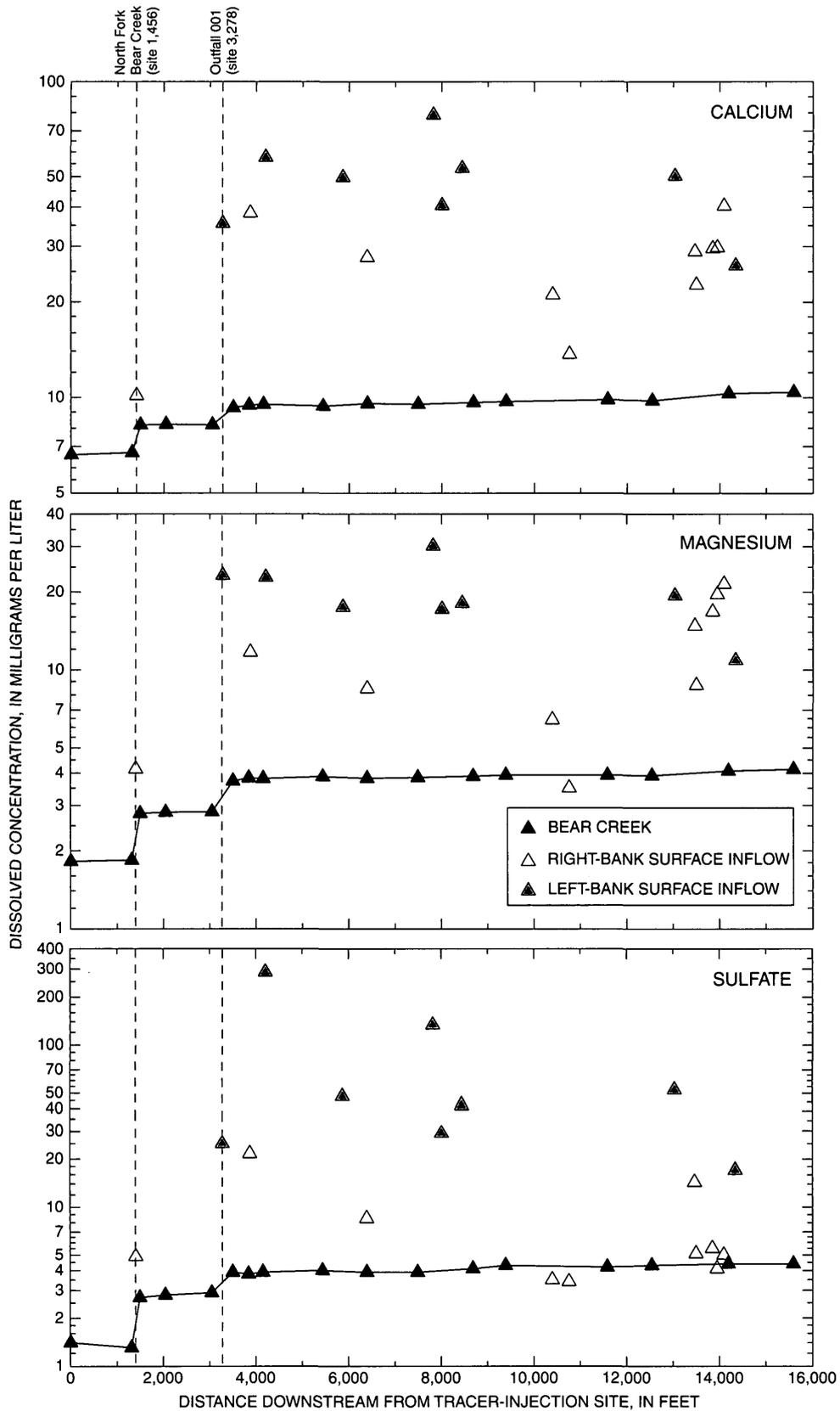


Figure 4. Downstream profile of pH at synoptic sampling sites in the Bear Creek drainage, Montana, September 21, 2000.

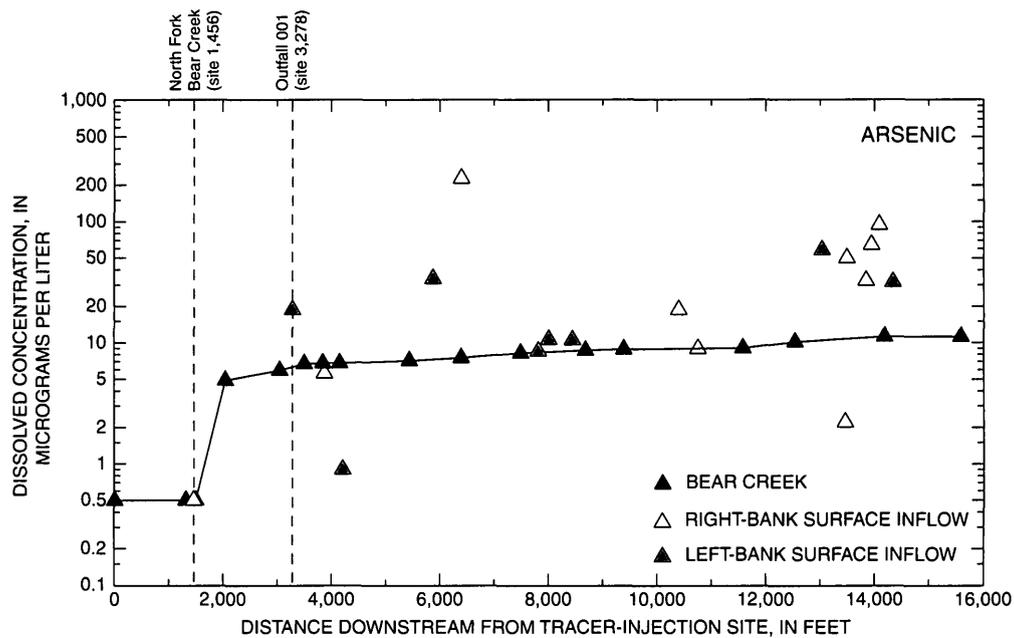
tions of dissolved arsenic were 0.5  $\mu\text{g/L}$  between sites 0 and 1,496 and sharply increased to 4.9  $\mu\text{g/L}$  between sites 1,496 and 2,046. Because site 1,496 is below the confluence with North Fork Bear Creek, it does not appear that this tributary contributed any substantial amount of arsenic. Dissolved arsenic concentrations steadily increased from 4.9  $\mu\text{g/L}$  at site 2,046 to 11.3  $\mu\text{g/L}$  at site 15,595. Dissolved arsenic concentrations in surface inflows ranged from 0.5 to 228  $\mu\text{g/L}$ . Arsenic concentrations were generally similar in surface inflows from both the right and left banks of the study reach, and about two-thirds of the inflows had concentrations higher than the mainstem. The dissolved arsenic concentration (228  $\mu\text{g/L}$ ) in the right-bank inflow at site 6,393 was 2.4 times higher than in any other inflow. The reason for this relatively high concentration is unknown. The only acidic inflow (from the Old Tailings North, site 4,207) to Bear Creek had the lowest arsenic concentration (0.9  $\mu\text{g/L}$ ) of the inflows, other than tributary inflow from North Fork Bear Creek. The concentration profile for total-recoverable arsenic in Bear Creek (not shown) closely follows the profile for dissolved arsenic in both

magnitude and pattern, thereby indicating that most of the arsenic in Bear Creek is dissolved.

Concentrations of cadmium, copper, lead, and zinc were not detected in any samples from Bear Creek (table 3), but were detected in surface inflows generally downstream from Old Tailings North (below site 3,873). The State of Montana aquatic-life standards were equaled or exceeded in only three of the surface inflows (sites 4,207, 6,393, and 13,498) (table 4). Site 4,207 is an acidic inflow from the Old Tailings North and had a dissolved cadmium concentration that exceeded aquatic-life standards for acute toxicity and also had the highest concentration of dissolved zinc in the study reach. In contrast, site 4,207 had low concentrations of arsenic and lead. Concentrations of total-recoverable lead at sites 6,393 and 13,498—both right-bank inflows—equaled or slightly exceeded the aquatic-life standard for chronic toxicity. Dissolved copper concentrations at all of the mainstem sites and several of the inflows were less than minimum reporting level (table 3).



**Figure 5.** Downstream profiles of dissolved concentrations of calcium (top), magnesium (middle), and sulfate (bottom) at synoptic sampling sites in the Bear Creek drainage, Montana, September 21, 2000.



**Figure 6.** Downstream profile of dissolved arsenic concentration at synoptic sampling sites in the Bear Creek drainage, Montana, September 21, 2000.

**Table 4.** Surface-water inflows to Bear Creek, Montana, that equaled or exceeded State of Montana aquatic-life standards, September 21, 2000

[All values reported in micrograms per liter. Aquatic-life standards for cadmium and lead corrected for hardness]

Site number (fig. 1)	Trace element	Concentration in sample	Aquatic-life standard <sup>1</sup>	
			Chronic toxicity	Acute toxicity
4,207	Cadmium, dissolved	17	2	10
6,393	Arsenic, total recoverable	300	150	340
	Lead, total recoverable	4	3	86
13,498	Lead, total recoverable	3	3	74

<sup>1</sup>Montana Department of Environmental Quality (1999).

## QUANTIFICATION OF ARSENIC LOADS

Load is the mass of a constituent transported downstream. For chemically conservative constituents, loads are additive as inflows contribute their load to the load in the receiving stream. For comparative purposes, loads are commonly expressed as a rate of transport in terms of mass per unit time (for example, milligrams per second for an instantaneous load; kilograms per year for an annual load). Instantaneous load, as used in this synoptic study, is calculated as the product of concentration and streamflow at the time of sampling. Instantaneous arsenic loads were calculated for 17 mainstem and 2 surface-inflow sites (table 5). Instantaneous loads of calcium, magnesium, and sulfate were calculated for the same sites to provide a comparison of trace-element and major-ion source areas.

A downstream load profile for a stream can be developed using synoptic streamflow and water-quality data from many sites along a stream. Such a profile can graphically illustrate the spatial distribution of loads and reveal notable differences in loads between sites. Large changes in load effectively identify the location of significant sources or sinks of constituents.

The profiles of instream load (fig. 7) represent the instantaneous constituent loads (table 5) measured at each mainstem sampling site. Instream loads were calculated by multiplying streamflow by constituent concentration. These loads are the net result of contributions from the upstream reach, sampled surface inflows, and any unsampled inflow (diffuse subsurface inflow, primarily ground water), as well as any loss of load caused by streamflow loss, the formation and streambed deposition of colloids, or other geochemical reactions.

The instream-load profiles for dissolved calcium, magnesium, and sulfate (fig. 7) are very similar. Instream loads generally increased in a downstream direction through the study reach, ranging from 1,880 to 5,530 mg/s for calcium, 519 to 2,200 mg/s for magnesium, and 374 to 2,340 mg/s for sulfate. Although concentrations of dissolved calcium, magnesium, and sulfate in most surface inflows were higher than in the mainstem (fig. 5), loads contributed by most inflows did not substantially increase the instream loads in Bear

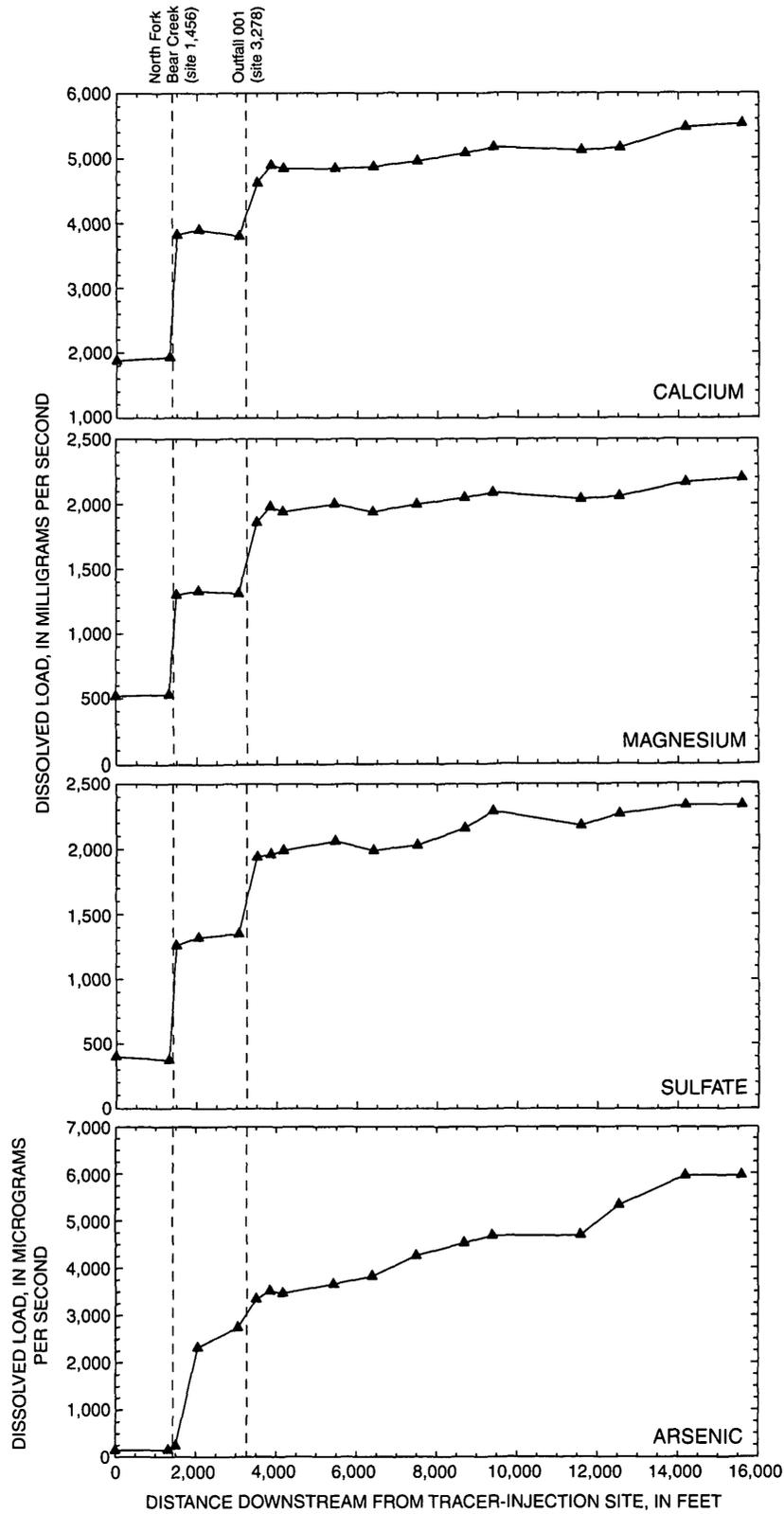
Creek, with two exceptions. The instream load for all three constituents increased sharply at sites 1,496 and 3,503 in response to increased streamflow and associated loads contributed by the North Fork Bear Creek and Outfall 001, respectively. Small decreases in loads in several short subreaches are nearly all less than 5 percent of the instream load and within streamflow and analytical measurement error.

The downstream profile of mainstem dissolved arsenic loads is shown in figure 7. Dissolved arsenic load in Bear Creek increased by 5,817  $\mu\text{g/s}$  through the study reach. Loading to Bear Creek was negligible between sites 0 and 1,496 (less than 2 percent of the load increase), but increased substantially from site 1,496 to site 2,046 near the Former Arsenic Mill. The increase between these two sites accounts for 36 percent of the total loading to Bear Creek in the study reach. Dissolved arsenic loads continued to increase substantially from site 2,046 to site 3,503. Thus, the short (almost 0.5 mi) reach from site 1,496 to site 3,503 contributed about 53 percent of the total increase in the arsenic load of Bear Creek.

In contrast to major-ion loads, the dissolved arsenic load increased steadily in the rest of the study reach (sites 3,503 to 15,595). The increase in arsenic load in this downstream reach was more gradual than in the upstream reach, but substantial, representing 45 percent of the total increase in the dissolved arsenic load of Bear Creek.

## ARSENIC SOURCE AREAS

Bear Creek can be divided into eight subreaches on the basis of patterns in the downstream profiles of arsenic load and locations relative to different mine features or inflows (fig. 8). The subreach extent, possible primary sources of dissolved arsenic in each subreach, and the calculated arsenic loads for the inflows within each subreach are listed in table 6. Streamflow determinations for the North Fork Bear Creek and Outfall 001 (table 2) were used to calculate dissolved arsenic loads for these two inflows. Streamflow was not measured in the other 16 surface inflows; thus, loads from surface and subsurface inflows that entered in the same subreach could not be quantified separately.



**Figure 7.** Downstream profiles of dissolved calcium, dissolved magnesium, dissolved sulfate, and dissolved arsenic loads in Bear Creek, Montana, September 21, 2000.

**Table 5.** Instantaneous loads of selected major ions and arsenic in the Bear Creek drainage, Montana, September 21, 2000

[Site number indicates distance downstream from tracer-injection site, in feet. Abbreviations:  $\mu\text{g/s}$ , micrograms per second;  $\text{mg/s}$ , milligrams per second. Symbols: <, less than]

Site number (fig. 1)	Calcium, dissolved load ( $\text{mg/s}$ )	Magnesium, dissolved load ( $\text{mg/s}$ )	Sulfate, dissolved load ( $\text{mg/s}$ )	Arsenic, dissolved load ( $\mu\text{g/s}$ )	Arsenic, total recoverable load ( $\mu\text{g/s}$ )
<u>Bear Creek</u>					
0	1,880	519	399	143	<855
1,316	1,930	530	374	144	<864
1,496	3,820	1,300	1,260	233	<1,400
2,046	3,900	1,330	1,320	2,320	2,840
3,048	3,800	1,310	1,350	2,740	3,250
3,503	4,620	1,860	1,940	3,340	3,490
3,843	4,890	1,980	1,960	3,520	4,140
4,153	4,840	1,940	1,990	3,460	3,560
5,440	4,840	2,000	2,060	3,660	4,120
6,398	4,870	1,940	1,990	3,820	4,070
7,493	4,960	2,000	2,030	4,260	4,680
8,688	5,080	2,050	2,160	4,530	5,270
9,393	5,170	2,090	2,290	4,680	4,790
11,586	5,120	2,040	2,180	4,680	5,200
12,546	5,160	2,060	2,270	5,330	5,280
14,193	5,480	2,170	2,340	5,960	5,850
15,595	5,530	2,200	2,340	5,960	6,380
<u>Surface inflow</u>					
1,456	1,800	735	872	89	<534
3,278	845	552	595	445	524

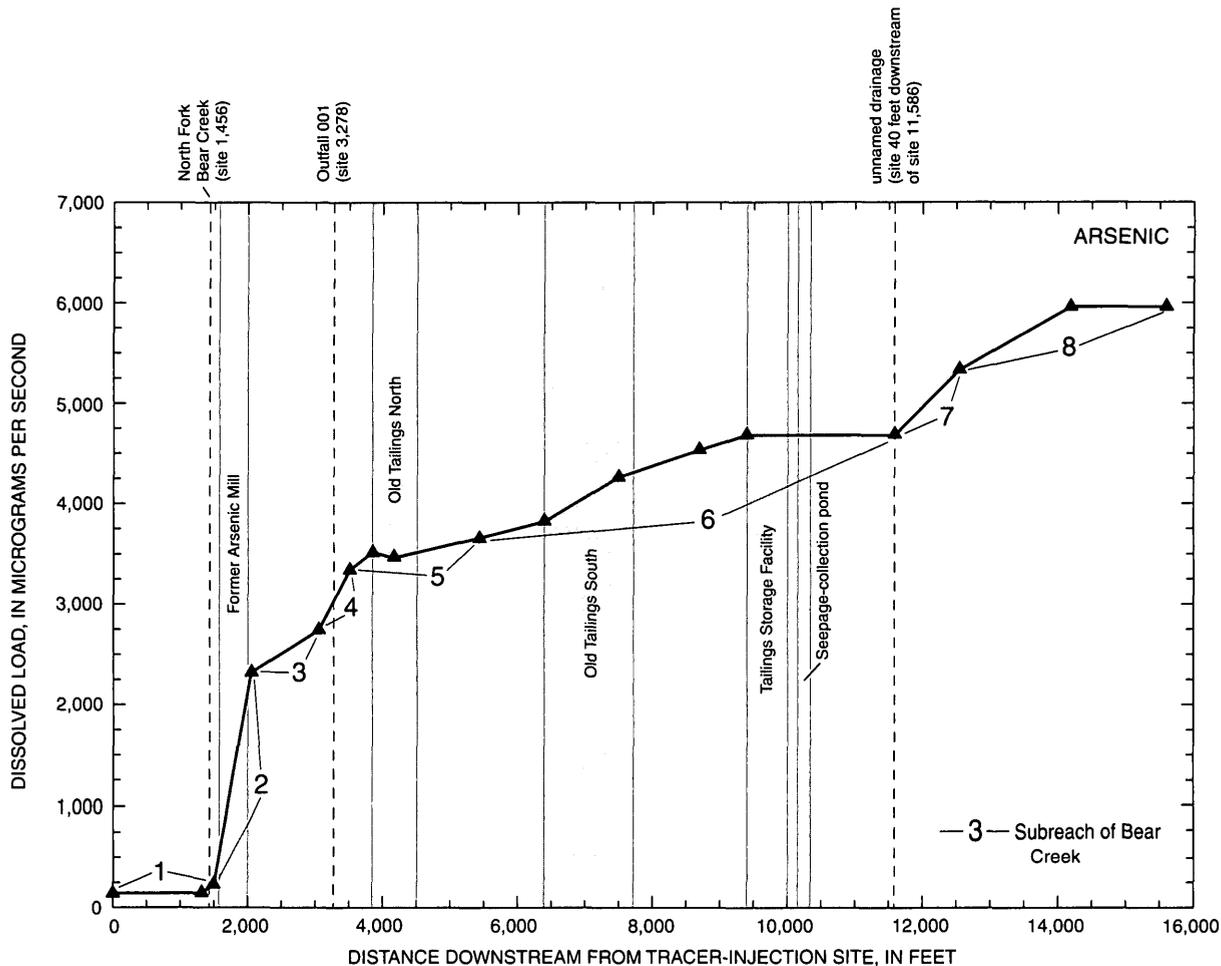
The upstream subreach 1 (between site 0 and site 1,496) received a negligible arsenic load ( $90 \mu\text{g/s}$ ) relative to the total load increase through the study reach ( $5,817 \mu\text{g/s}$ ). Most of the small arsenic load entering this subreach (table 6) likely is from North Fork Bear Creek. Although the concentration of dissolved arsenic in North Fork Bear Creek (site 1,456) was small ( $0.5 \mu\text{g/L}$ ), the streamflow was large ( $178 \text{ L/s}$ ), and therefore accounted for almost all of the arsenic load contributed to this subreach.

Subreach 2 (between site 1,496 and site 2,046) received the largest arsenic load ( $2,087 \mu\text{g/s}$ ) of the entire study reach, and it was contributed entirely from diffuse subsurface inflow because no surface inflows were observed. The increase in tracer-calculated streamflow in the subreach was small ( $7 \text{ L/s}$ ); therefore, the concentration of dissolved arsenic in subsurface inflow within this reach likely was relatively large (averaging nearly  $300 \mu\text{g/L}$ ). However, whether arsenic-rich subsurface inflow came from the right bank, left bank, or both is not known. In this reach, left-bank soils were saturated at the base of the hill-

slope below the Former Arsenic Mill (fig. 1); consequently, the increase in arsenic load in subreach 2 (table 6) might have been caused primarily by subsurface inflow originating from the Former Arsenic Mill.

Subreach 3 flows through the Town of Jardine, between site 2,046 and site 3,048. The entire increase of arsenic load ( $420 \mu\text{g/s}$ ) within this subreach (table 6) is attributed to subsurface inflow because no surface inflows were observed. Arsenic from subsurface inflow within this subreach possibly is from the natural weathering of the host rock (table 6), although mine-related features may contribute to the arsenic loading.

In subreach 4 (between site 3,048 and site 3,503), the dissolved arsenic load increased by  $600 \mu\text{g/s}$ . The only surface inflow in this subreach, Outfall 001, contributed nearly three-quarters ( $445 \mu\text{g/s}$ ) of the arsenic load in this subreach (table 6). Subsurface inflow is assumed to account for the rest of the load ( $155 \mu\text{g/s}$ ) because other visible surface inflows were absent. Arsenic in subsurface inflow likely is derived from the natural weathering of the host rock.



**Figure 8.** Downstream profile of dissolved arsenic loads, subreaches, and mine features in and along Bear Creek, Montana, September 21, 2000.

Subreach 5 (between site 3,503 and site 5,440) flows near Old Tailings North and received a relatively small additional arsenic load (320  $\mu\text{g/s}$ ). The two surface inflows in this subreach (sites 3,873 and 4,207) were small and had low arsenic concentrations (5.6  $\mu\text{g/L}$  and 0.9  $\mu\text{g/L}$ , respectively) and likely contributed little arsenic load. Tailings at Old Tailings North were removed during 1996 and water sampled during 1999 from three wells within Old Tailings North had arsenic concentrations that ranged from 4 to 37  $\mu\text{g/L}$  (Maxim Technologies, Inc., 2000b). Because streamflow was not measured in the surface inflows during synoptic sampling, the relative contributions of dissolved arsenic loads from surface and subsurface inflows could not be quantified separately (table 6). The gradual increase of dissolved arsenic load in this subreach

(fig. 8) is similar to profiles for other subreaches where the primary arsenic source probably is from the natural weathering of host rock. Thus, arsenic loads in subreach 5 are attributed to a combination of surface and subsurface inflows that derive arsenic from either the host rock or residual tailings at Old Tailings North.

Subreach 6 (between site 5,440 and site 11,586) is the longest subreach and received a substantial additional arsenic load (1,020  $\mu\text{g/s}$ ). Two of the seven surface inflows in this subreach had concentrations of dissolved arsenic greater than 30  $\mu\text{g/L}$  (table 3); a right-bank inflow (site 6,393) had a dissolved arsenic concentration of 228  $\mu\text{g/L}$ . Mining claims are present along this subreach, but no surface disturbance by historical or recent mining near this right-bank inflow was

**Table 6.** Possible sources of dissolved arsenic in subreaches of Bear Creek, Montana, September 21, 2000

[Abbreviations: OTN, Old Tailings North; OTS, Old Tailings South; SCP, Seepage-Collection Pond; TSF, Tailings Storage Facility;  $\mu\text{g/s}$ , micrograms per second. Symbol: --, could not be quantified]

Sub-reach	Mine feature or inflow draining to subreach	Possible primary source	Subreach extent, in feet		Dissolved arsenic load, in $\mu\text{g/s}$			
			Up-stream site	Down-stream site	Right-bank inflows	Left-bank inflows	Sub-surface inflow <sup>1</sup>	Com-bined inflow (surface, plus sub-surface)
1	North Fork Bear Creek	North Fork Bear Creek	0	1,496	89	0	1	90
2	Former Arsenic Mill	Subsurface inflow from Former Arsenic Mill	1,496	2,046	0	0	2,087	2,087
3	Town of Jardine	Subsurface inflow from natural weathering of host rock	2,046	3,048	0	0	420	420
4	Outfall 001	Discharge from Outfall 001	3,048	3,503	0	<sup>2</sup> 445	155	600
5	OTN	Natural weathering of host rock or residual tailings at OTN	3,503	5,440	--	--	--	320
6	OTS, TSF, SCP	Natural weathering of host rock	5,440	11,586	--	--	--	1,020
7	Dry drainage below TSF and SCP	Subsurface inflow from TSF/SCP or natural weathering of host rock	11,586	12,546	0	0	650	650
8	Near Palmer Creek	Natural weathering of host rock	12,546	15,595	--	--	--	630
Total gain in dissolved arsenic load								5,817

<sup>1</sup>Calculated as the difference between the gain in instream load between upstream and downstream sites and the sum of the loads in the measured right-bank and left-bank surface inflows within the subreach.

<sup>2</sup>Entire load from Outfall 001.

observed. Even though several mining features are near the left bank of this subreach (Old Tailings South, Tailings Storage Facility, and Seepage-Collection Pond), the profile of dissolved arsenic load (fig. 8) did not indicate any sharp increases, but rather increased consistently and gradually. Such gradual increases in load generally are indicative of non-point sources. Arsenic loads in subreach 6 are attributed to a combination of diffuse surface and subsurface inflows that might derive arsenic primarily from natural weathering of the host rock (table 6).

In the short subreach 7 (between site 11,586 and site 12,546), subsurface inflow is assumed to have contributed the entire additional dissolved arsenic load (650  $\mu\text{g/s}$ ). No visible surface inflows were observed in this subreach; however, a dry drainage from the Tailings Storage Facility and Seepage-Collection Pond area (fig. 1) enters Bear Creek on the left bank 40 ft downstream from site 11,586. Insufficient data exist to

determine if subsurface inflow from this drainage along this tributary channel contributes arsenic to Bear Creek. Thus, arsenic loads entering subreach 7 are attributed to subsurface inflow that derives arsenic from a combination of tailings (from Tailings Storage Facility or Seepage-Collection Pond) and natural weathering of host rock (table 6).

In the most downstream subreach 8 (between site 12,546 and site 15,595), the dissolved arsenic load increased by 630  $\mu\text{g/s}$  and nearly all of the seven surface inflows had arsenic concentrations greater than 30  $\mu\text{g/L}$  (table 3). Five surface inflows were located on the right bank in this subreach. Only one of these right-bank inflows (site 13,468) had an arsenic concentration less than 30  $\mu\text{g/L}$  (2.2  $\mu\text{g/L}$ ). The two left-bank inflows (sites 13,039 and 14,345) had arsenic concentrations of 58.3 and 31.7  $\mu\text{g/L}$ , respectively. The USDA-Forest Service ditch (fig. 1) might contribute flow to the right-bank inflows as water diverted from

Bear Creek leaks into the subsurface and subsequently discharges back to Bear Creek as inflows. Surface disturbance by historical or recent mining along this subreach was not observed. Arsenic in this subreach likely is derived from the natural weathering of the host rock and delivered by a combination of surface inflows and diffuse subsurface inflow (table 6).

Identification of arsenic source areas and their relative contribution of load (table 6) can help guide or prioritize potential remediation efforts. On the basis of findings from this study (table 6), remediation efforts to reduce arsenic from subsurface inflows in subreach 2 near the Former Arsenic Mill and surface inflow in subreach 4 from Outfall 001 (site 3,278) could reduce arsenic loading to the Bear Creek study reach by as much as 44 percent (2,532  $\mu\text{g/s}$ ). Although equally large contributions of arsenic loads (2,545  $\mu\text{g/s}$ ) from surface and subsurface inflows that probably derive arsenic primarily from the natural weathering of host rock are collectively input from the other subreaches, remediation efforts to reduce arsenic loading from these diffuse sources might be difficult or impractical to implement.

## SUMMARY AND CONCLUSIONS

Bear Creek is a tributary to the Yellowstone River and is north of Yellowstone National Park. This creek flows near Mineral Hill, where arsenic, gold, and tungsten have been mined. The quality of water in Bear Creek has been affected by arsenic derived from mine waste, as well as from weathering of naturally occurring arsenopyrite. However, the arsenic loads to Bear Creek from these sources had not been previously quantified. This report quantifies arsenic loading to Bear Creek and identifies the principal source areas. This study was conducted in the Bear Creek drainage during base-flow conditions in September 2000 along an approximately 3-mi (15,595-ft) reach of Bear Creek from 1,456 ft upstream from the North Fork Bear Creek to 1,250 ft downstream from Palmer Creek. Dissolved constituent loads were quantified using streamflow data calculated by tracer-injection methods and water-quality data determined from ambient and synoptic samples. Streamflow increased by 247 L/s through the study reach based on tracer calculations or physical measurement at 18 mainstem and 2 surface-inflow

sites. Synoptic water-quality samples were collected at 17 mainstem and 18 surface-inflow sites.

Instantaneous loads were computed for dissolved calcium, magnesium, and sulfate. While concentrations of dissolved calcium, magnesium, and sulfate in most surface inflows were higher than in the mainstem, loads contributed by these inflows were generally small and did not substantially increase the loads in Bear Creek. However, load contributions from the North Fork Bear Creek and Outfall 001 caused a substantial increase in dissolved calcium, magnesium, and sulfate loads in Bear Creek, primarily as a result of their relatively large streamflow.

Arsenic was the only trace element analyzed in Bear Creek that had concentrations greater than laboratory minimum reporting levels. Concentrations of dissolved arsenic in the mainstem were 0.5  $\mu\text{g/L}$  at the upstream part of the study reach and increased to about 11  $\mu\text{g/L}$  at the downstream part of the study reach. Arsenic concentrations in surface inflows ranged from 0.5 to 228  $\mu\text{g/L}$ ; generally similar concentrations of arsenic occurred in both right- and left-bank inflows.

Concentrations of cadmium, copper, lead, and zinc were not detected in any samples from Bear Creek, but were detected in both right and left-bank inflows downstream from Old Tailings North. Aquatic-life standards were equaled or exceeded in only three of these surface inflows. The only acidic inflow in the study area—from Old Tailings North (site 4,207)—had high concentrations of cadmium, copper, and zinc, but low concentrations of arsenic and lead.

Dissolved arsenic loads in Bear Creek increased by 5,817  $\mu\text{g/s}$  through the study reach. Subsurface inflow along a 550-ft subreach near the Former Arsenic Mill accounted for 36 percent (2,087  $\mu\text{g/s}$ ) of the arsenic loading to Bear Creek in the study area. Inflow from Outfall 001 accounted for an increase in dissolved arsenic load of 445  $\mu\text{g/s}$ , which represented about 8 percent of the arsenic loading to Bear Creek. Natural weathering of the host rock was presumably the primary source of about 44 percent (2,545  $\mu\text{g/s}$ ) of the arsenic loading through five subreaches of Bear Creek: subreach 3 (420  $\mu\text{g/s}$ ), subreach 4 (155  $\mu\text{g/s}$ ), subreach 5 (320  $\mu\text{g/s}$ ), subreach 6 (1,020  $\mu\text{g/s}$ ), and subreach 8 (620  $\mu\text{g/s}$ ). Subsurface inflow that derives arsenic

from a possible combination of tailings from the Tailings Storage Facility or Seepage-Collection Pond and from natural weathering of host rock contributed about 11 percent (650 µg/s) of the dissolved arsenic loading to Bear Creek.

Remediation efforts to reduce arsenic from subsurface inflows near the Former Arsenic Mill and surface inflow from Outfall 001 could reduce arsenic loading to the Bear Creek study reach by as much as 44 percent. Remediation efforts to reduce arsenic from diffuse surface and subsurface inflow that probably derives arsenic from natural weathering of the host rock might be difficult or impractical to implement.

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