ARSENIC AND CHLORIDE DATA FOR FIVE STREAM SITES IN

THE MADISON RIVER DRAINAGE, MONTANA, 1988

By J.R. Knapton and T.M. Brosten

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CONVERSION FACTORS

The following factors can be used to convert inch-pound units in this report
to metric (International System) units.

Multiply inch-pound unit	By	To obtain metric unit
acre-foot	1,233	cubic meter
cubic foot per second (ft^3/s)	0.028317	cubic meter per second
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
pound per day (lb/d)	453.6	gram per day

Temperature can be converted from degrees Celsius (°C) to degrees Fahrenheit (°F)
by the equation:

$$°F = 9/5 \ (°C) + 32$$

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ABSTRACT

Previous studies in the upper Missouri River basin indicate that enriched geothermal waters in Yellowstone National Park contribute large quantities of arsenic to the Madison River. Because arsenic may be acutely or chronically toxic to humans when ingested, it is of concern in the upper Missouri River basin where the water is used for domestic purposes.

Previous data indicate that in passage of water downstream, concentrations of arsenic in the Madison and Missouri Rivers are diluted by tributary inflows. However, insufficient information existed to describe concentrations during runoff at specific locations. As a result, a monitoring network was established to better define arsenic concentrations during the 1988 peak runoff and during periods prior to and following the runoff. In addition to arsenic, samples were analyzed for chloride because of its association with geothermal water and specific conductance because it is a surrogate measure of dissolved-solids concentration. This report presents data acquired during 1988 at five sampling stations in the Madison River drainage.

INTRODUCTION

Previous studies in the upper Missouri River basin (Knapton and Horpestad, 1987; Knapton and Brosten, 1987) indicate that enriched geothermal waters in Yellowstone National Park contribute large quantities of arsenic to the Madison River of southwestern Montana. Arsenic concentrations in nine samples collected from the Madison River near West Yellowstone (station 1) during 1986-87 ranged from 200 to 300 $\mu g/L$ (micrograms per liter) and had a median value of 250 $\mu g/L$. The two previous studies indicated that in passage downstream, tributary water to the Madison and Missouri Rivers dilutes arsenic concentrations; thus, the concentrations of arsenic are inversely related to the quantity of tributary inflow. Arsenic may be acutely or chronically toxic to humans when ingested. Therefore, the U.S. Environmental Protection Agency (1986) has established a maximum concentration of 50 $\mu g/L$ as the primary drinking-water standard. Because water from the upper Missouri River commonly is used for domestic supplies, concern exists regarding arsenic concentrations.

An examination of arsenic data from the previous studies indicated that information during runoff conditions at specific locations was insufficient for proper evaluation. As a result, a monitoring network was established to better define arsenic concentrations during the 1988 peak runoff and during periods prior to and following the runoff. The purpose of this report is to present the data acquired during the 1988 sampling period.

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Sampling stations were established (or reactivated) at three sites on the upper Madison River and near the mouths of two tributaries (fig. 1). Descriptions
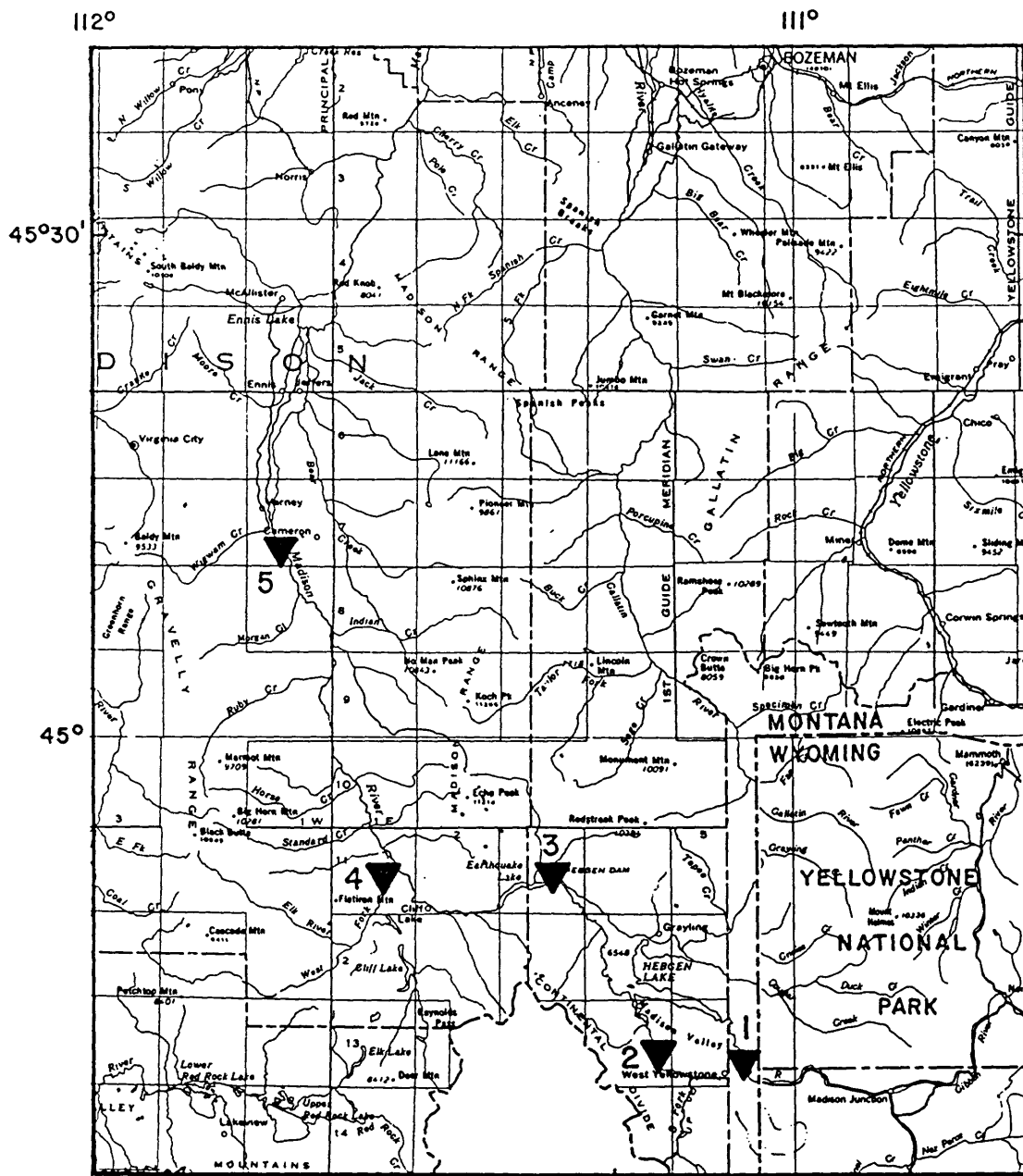
Base from U.S. Geological Survey
State base maps, 1:1,000,000, 1968

0   20 MILES

MONTANA

Map area

WYOMING
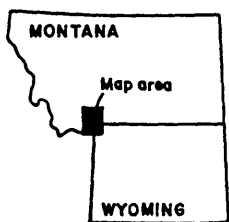
EXPLANATION

4 ▼ NETWORK SAMPLING
       STATION AND NUMBER

Figure 1.--Location of study area and sampling stations.

of the sampling stations, in downstream order, are given in table 1. The number preceding the station name is the station number shown in figure 1. The number following the station name is the formal downstream-order station number assigned by the Geological Survey.

In addition to arsenic, samples were analyzed for chloride and specific conductance. Previous studies have indicated that chloride is associated with geothermal waters (Norton and Friedman, 1985) and specific conductance is a surrogate measure of dissolved-solids concentration. Water discharges, obtained at the time of sampling, were used with arsenic concentrations to calculate arsenic discharge (loading), in pounds per day. Water temperature and air temperature were measured at the time of sampling.

The monitoring program was funded jointly by the U.S. Geological Survey and the Montana Department of Fish, Wildlife and Parks. Sample collection and onsite measurements were done by the Geological Survey. Samples were analyzed in Helena, Montana, by the Chemistry Laboratory Bureau of the Montana Department of Health and Environmental Sciences.

FIELD PROCEDURES

Because samples were to be analyzed for total recoverable arsenic concentration, a representative stream sample of the water-sediment mixture was required. Samples, therefore, were collected either by the "Equal Width Increment" or the "Equal Discharge Increment" method, using modified suspended-sediment samplers (Guy and Norman, 1970). Where streams were shallow enough to allow wading across the stream section, the Equal Width Increment method was used with a US-DH-48 hand-held sampler. Where stream sections were too deep to wade and samples had to be collected from cableways or bridges, the Equal Discharge Increment method was used with a US-D-74 sampler suspended by a cable. Both methods of sampling incorporate depth integration through a series of vertical sections across the stream channel.

The subset samples from all vertical sections were composited and mixed onsite in a Geological Survey churn sample splitter. A representative sample of the water-sediment mixture was withdrawn and preserved by acidification with nitric acid prior to transmittal to the laboratory for arsenic analysis. A second sample for measurement of chloride and specific conductance was withdrawn from the sample splitter in the same manner, but not acidified.

Stream discharge was obtained by direct measurement or, where stream gages were present, indirectly from observed stream stage and stage-discharge rating tables. All methods conformed to documented procedures of the U.S. Geological Survey (Rantz and others, 1982).

Stream temperatures were measured at midstream using field-grade thermometers. Air temperatures also were measured with field-grade thermometers.

LABORATORY PROCEDURES

Arsenic was determined by electrothermal atomic absorption spectrophotometry using a graphite furnace through which the light path of the spectrophotometer

passes. Within the graphite furnace, the sample solution is heated with a small current (drying stage), an intermediate current (charring stage), and a large current (atomizing stage). Nickel nitrate is used as a matrix modifier. The detection limit of the arsenic analysis is 1 µg/L. Analytical precision is given in table 2.

Chloride was determined in the auto analyzer by the colorometric, ferric thiocyanate method. Thiocyanate ions are liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ions, free thiocyanate ions form colored ferric thiocyanate, of which the intensity is proportional to the chloride concentration. The detection limit for this method is 1 mg/L (milligrams per liter). Analytical precision is given in table 2.

Specific conductance was determined by the electrometry method using a cathode-ray tube with wheatstone bridge circuitry in which a variable resistance is adjusted so that it is equal to the resistance of the unknown solution present in a standardized conductivity cell. The reciprocal of the measured resistance is reported as specific conductance, in microsiemens per centimeter (µS/cm). All measurements were made on samples and standards at a temperature of 25 °C. Specific conductance was reported to the nearest whole number. Analytical precision is given in table 2.

As part of the quality assurance plan, about 20 percent of the samples were duplicates. The duplicates were submitted to the laboratory with false station numbers, dates, and times. Results of the arsenic duplicates indicated a median difference in concentration between paired samples of 1 µg/L and a maximum difference of 33 µg/L. The 33 µg/L represented a difference of 9 percent. Paired samples for chloride analysis indicated a median difference of 0.1 mg/L and a maximum difference of 0.5 mg/L, which represented a difference between samples of about 2 percent. The median difference for specific conductance was 6 µS/cm and the maximum difference was 16 µS/cm or 5 percent.

The Chemistry Laboratory Bureau is certified by the U.S. Environmental Protection Agency for water, wastewater, air, and hazardous-waste analyses. The laboratory also participates in the U.S. Geological Survey Standard Reference Sample Program. Internal laboratory quality-control procedures include duplicate analyses for measurement of precision, spiked analyses for checking accuracy, and reference sample analyses used as an external check on standards. Acceptability criteria are given in table 2.

DATA RESULTS

The results of onsite and laboratory measurements are given in table 3. Arsenic concentrations are reported in micrograms per liter and are equivalent to parts per billion. Arsenic discharge was determined by multiplying the water discharge by the concentration of arsenic and a units conversion constant:

$$Qa = Qw \times Ca \times k \tag{1}$$

where
  Qa is arsenic discharge, in pounds per day;
  Qw is the water discharge, in cubic feet per second;
  Ca is arsenic concentration, in micrograms per liter; and
  k is 0.0054, a constant used to convert arsenic discharge to pounds per day.

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Statistical information for arsenic concentrations and arsenic discharge for the three mainstem stations is presented in figures 2 and 3. Minimum and maximum values are indicated by the extent of vertical lines below and above the box, respectively. The 25th and 75th percentiles are represented by the bottom and top borders of the box and the 50th percentile (median) is indicated by the line within the box. Arsenic concentrations and arsenic discharge are shown in figures 4 and 5 for the most upstream location (station 1) and the most downstream location (station 5) for the sampling periods.
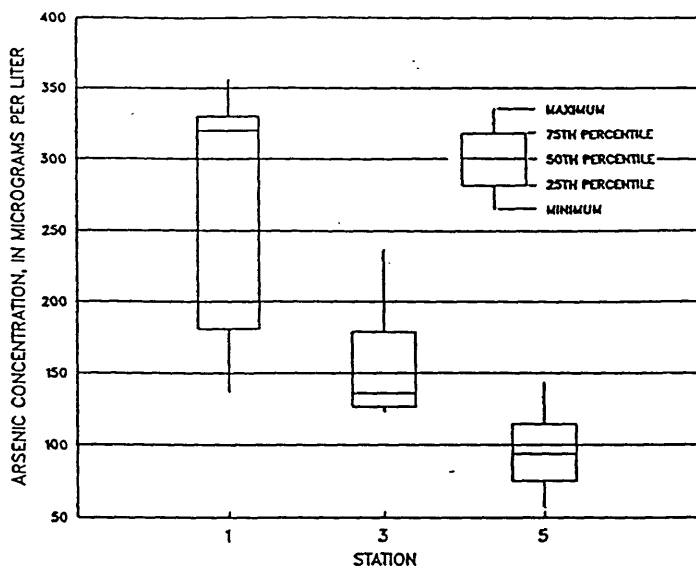
Figure 2.--Statistical summary of total recoverable arsenic concentration for three Madison River stations during 1988.
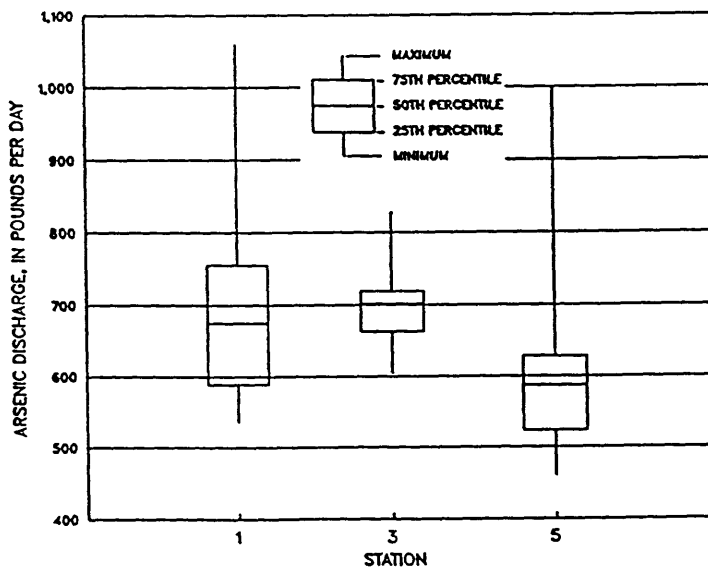
Figure 3.--Statistical summary of total recoverable arsenic discharge for three Madison River stations during 1988.
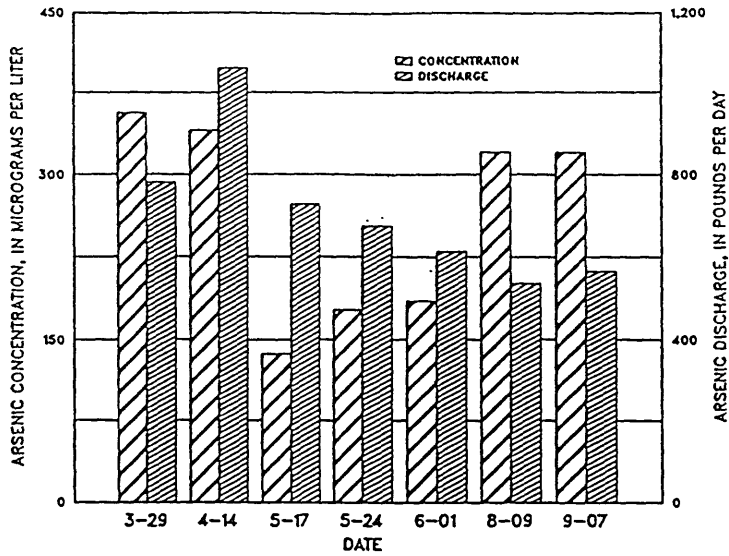
Figure 4.--Total recoverable arsenic concentration and total recoverable arsenic discharge at Madison River near West Yellowstone (station 1) for sampling periods during 1988.
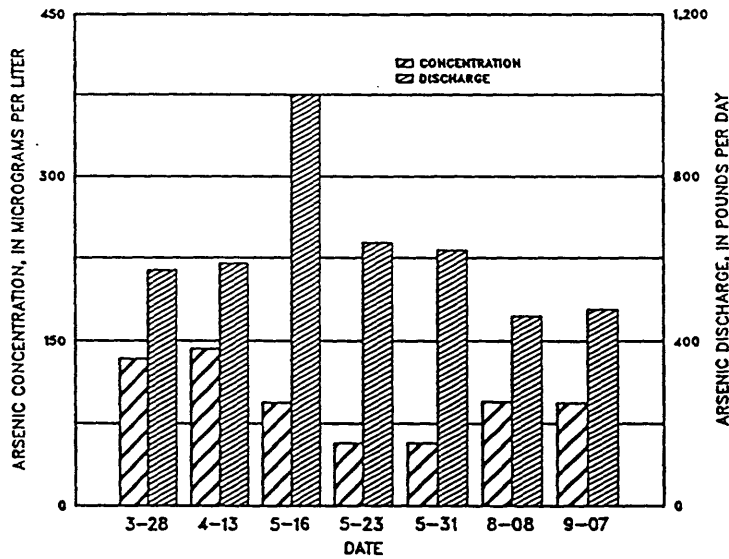
Figure 5.--Total recoverable arsenic concentration and total recoverable arsenic discharge at Madison River near Cameron (station 5) for sampling periods during 1988.

No artificial impoundments exist upstream from station 1 and the Madison River and its tributaries are free flowing. Hebgen Lake (capacity of 385,000 acre-feet) is present between stations 1 and 3 and the much smaller Earthquake Lake exists between stations 3 and 5. If data in this report are used for interpretation, the reader is cautioned to consider the effects of impoundments on the results.

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The impoundments can have a significant effect on both arsenic concentrations and arsenic discharge. Mixing of water within the lakes can cause a dampening of short- and intermediate-term fluctuations in arsenic concentration. Sediments with attached arsenic can fall from suspension in the water column and decrease both the arsenic concentration and the arsenic discharge. In addition, geochemical processes active at the water-bottom sediment interface may further modify arsenic concentration as well as arsenic discharge (Horowitz, 1985). Arsenic discharge also is affected by controlled releases from the impoundments and, although the annual loading may change little, short-term variations are prevalent. As a result of the impoundments, data herein are most useful when consideration is given to longer-term evaluation rather than to the short periods in which sampling runs were made.

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_____1986, Maximum contaminant levels (subpart B of part 141, National interim primary drinking-water regulations): U.S. Code of Federal Regulations, Title 40, Parts 100 to 149, revised July 1, 1986, p. 524-528.

Table 1.--*Descriptions of sampling stations*

[ft, feet; mi, miles]

Station 1--Madison River near West Yellowstone, Mont. (06037500)

LOCATION.--Lat 44°39'25", long 111°04'03", in NE1/4NW1/4SW1/4 sec. 36, T. 13 S., R. 5 E., Gallatin County, Yellowstone National Park, 0.7 mi downstream from Montana-Wyoming State line, 1.5 mi east of West Yellowstone, and 16.4 mi downstream from Gibbon River.

Station 2--South Fork Madison River above Denny Creek, near

West Yellowstone, Mont. (06037700)

LOCATION.--Lat 44°40'50", long 111°11'35" , in NW1/4NW1/4 sec. 25, T. 13 S., R. 4 E., Gallatin County, at bridge on U.S. Highway 20, 2 mi upstream from Denny Creek, and 4.5 mi west of West Yellowstone.

Station 3--Madison River below Hebgen Lake, near Grayling, Mont. (06038500)

LOCATION.--Lat 44°52'00", long 111°20'15", in NE1/4NE1/4NE1/4 sec. 22, T. 11 S., R. 3 E., Gallatin County, Gallatin National Forest, 1,500 ft downstream from Hebgen Dam, 8 mi northwest of Grayling, and 17 mi upstream from West Fork.

Station 4--West Fork Madison River near Cameron, Mont. (06039200)

LOCATION.--Lat 44°53'15", long 111°34'55", in SW1/4NE1/4SE1/4 sec. 10, T. 11 S., R. 1 E., Madison County, on bridge 0.25 mi upstream from mouth, and 22 mi southeast of Cameron.

Station 5--Madison River near Cameron, Mont. (06040000)

LOCATION.--Lat 45°14'00" long 111°45'00", at center of south line of sec. 8, T. 7 S., R. 1 W., Madison County, 30 ft downstream from Varney Bridge, 1.8 mi downstream from Wigwam Creek, and 4.1 mi northwest of Cameron.

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Table 2.—*Laboratory precision, accuracy, and detection limit for arsenic, chloride, and specific conductance*

[μg/L, micrograms per liter; mg/L, milligrams per liter; μS/cm, microsiemens per centimeter at 25 degrees Celsius; ‑‑, no data or insufficient data]

| Parameter | Precision | | Accuracy | | Detection limit |
	Range	Limit	Warning limits (percent recovery)	Acceptance limits (percent recovery)	
Arsenic (Electrothermal atomic absorption spectrophotometry)	1‑5 μg/L	2 μg/L	93‑125	85‑133	1 μg/L
	5‑20 μg/L	3 μg/L	‑‑	‑‑	‑‑
	20‑100 μg/L	5 μg/L	‑‑	‑‑	‑‑
Chloride (EPA 325.2 method)[1]	1‑5 mg/L	.4 mg/L	94‑112	89‑116	1 mg/L
	5‑25 mg/L	.4 mg/L	‑‑	‑‑	‑‑
	25‑50 mg/L	1.9 mg/L	‑‑	‑‑	‑‑
	50‑100 mg/L	2.7 mg/L	‑‑	‑‑	‑‑
Specific conductance (EPA 120.1 method)[1]	.10‑75 μS/cm	11.7 μS/cm	‑‑	‑‑	.10 μS/cm
	75‑560 μS/cm	13.8 μS/cm	‑‑	‑‑	‑‑
	560‑870 μS/cm	35.7 μS/cm	‑‑	‑‑	‑‑
	870‑1,500 μS/cm	64.2 μS/cm	‑‑	‑‑	‑‑

[1]U.S. Environmental Protection Agency, 1983.

Table 3.—Water-quality data for sampling stations

[Abbreviations: ft³/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 °C; °C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; lb/d, pounds per day. Symbol: <, less than]

Date	Time	Stream-flow, instantaneous (ft³/s)	Specific conductance, laboratory (µS/cm)	Temperature, air, onsite (°C)	Temperature, water, onsite (°C)	Chloride, dissolved (mg/L as Cl)	Arsenic, total recoverable (µg/L as As)	Arsenic discharge (lb/d)
Station 1—Madison River near West Yellowstone, Mont. (06037500)
Mar 1988								
29...	1430	407	550	1.0	7.0	73	360	791
Apr								
14...	1030	575	447	8.0	10.0	56	340	1,060
May								
17...	1300	986	217	22.0	13.5	25	140	745
24...	0915	706	315	21.0	16.0	38	180	686
Jun								
01...	0915	614	344	9.0	11.5	39	190	630
Aug								
09...	1400	310	525	25.0	21.0	67	320	536
Sep								
07...	2000	327	558	17.0	16.0	69	320	565

Station 2—South Fork Madison River above Denny Creek,

near West Yellowstone, Mont. (06037700)

Date	Time	Stream-flow, instantaneous (ft³/s)	Specific conductance, laboratory (µS/cm)	Temperature, air, onsite (°C)	Temperature, water, onsite (°C)	Chloride, dissolved (mg/L as Cl)	Arsenic, total recoverable (µg/L as As)	Arsenic discharge (lb/d)
Mar 1988								
29...	1630	80.4	89	.0	7.0	3.4	<1	<.43
Apr								
14...	1130	83.6	105	9.5	8.0	3.7	<1	<.45
May								
17...	1455	214	74	20.0	8.0	2.7	<1	<1.20
24...	1045	180	79	19.5	8.5	2.6	<1	<.97
Jun								
01...	1030	139	86	14.5	7.0	2.8	<1	<.75
Aug								
09...	1545	76.1	91	26.0	14.0	3.4	<1	<.41
Sep								
07...	1945	79.9	95	15.5	11.0	3.7	<1	<.43

Table 3.--Water-quality data for sampling stations--Continued

Date	Time	Stream-flow, instantaneous (ft³/s)	Specific conductance, laboratory (µS/cm)	Temperature, air, onsite (°C)	Temperature, water, onsite (°C)	Chloride, dissolved (mg/L as Cl)	Arsenic, total recoverable (µg/L as As)	Arsenic discharge (lb/d)
Station 3--Madison River below Hebgen Lake, near Grayling, Mont. (06038500)								
Mar 1988								
30...	1015	650	406	.0	4.0	44	210	737
Apr								
13...	1515	647	401	14.0	6.0	44	240	839
May								
17...	1615	960	303	10.0	9.0	30	130	674
23...	1530	956	315	22.0	10.0	32	140	723
31...	1730	982	308	8.0	11.0	29	130	689
Aug								
10...	1000	911	290	23.0	19.0	27	120	590
Sep								
07...	1800	878	310	26.0	16.0	30	150	711
Station 4--West Fork Madison River near Cameron, Mont. (06039200)								
Mar 1988								
28...	1620	40.6	235	5.0	4.0	2.7	2	.44
Apr								
13...	1430	57.4	240	14.0	8.0	3.1	2	.62
May								
16...	1345	305	156	25.0	11.5	2.6	1	1.60
23...	1315	290	169	26.0	8.0	1.9	<1	<1.60
31...	1645	206	194	15.0	8.0	1.4	<1	<1.10
Aug								
08...	1615	44.5	231	25.0	20.5	2.4	<1	<.24
Sep								
07...	1700	45.7	234	27.5	16.0	2.8	1	.25

Table 3.--*Water-quality data for sampling stations*--Continued

Date	Time	Stream-flow, instan-taneous (ft^3/s)	Spe-cific con-duct-ance, labo-ratory (μS/cm)	Temper-ature, air, onsite (°C)	Temper-ature, water, onsite (°C)	Chlo-ride, dis-solved (mg/L as Cl)	Arsenic, total recov-erable (μg/L as As)	Arsenic dis-charge (lb/d)
Station 5--Madison River near Cameron, Mont. (06040000)								
Mar 1988								
28...	1430	789	368	5.5	4.5	31	130	554
Apr								
13...	1230	760	353	15.0	8.5	30	140	575
May								
16...	1120	1,970	296	25.0	11.0	24	94	1,000
23...	1115	2,070	256	20.0	11.5	16	57	637
31...	1500	2,010	238	14.0	8.0	15	57	619
Aug								
08...	1245	898	299	32.0	17.5	22	95	461
Sep								
07...	1430	940	302	27.0	17.0	23	94	477