SUPPLEMENTAL ARSENIC DATA FOR SELECTED STREAMS IN THE MISSOURI RIVER BASIN, MONTANA, 1987

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

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CONVERSION FACTORS

The following factors may be used to convert inch-pound units published herein to the International System (SI) of units.

Multiply inch-pound unit	By	To obtain SI unit
cubic foot per second (ft^3/s)	0.02832	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

Geothermal waters within Yellowstone National Park contribute arsenic to the Madison River. Arsenic concentrations ranging from 200 to 300 micrograms per liter in the Madison River near the park boundary are diluted downstream by tributary inflows to the Madison and Missouri Rivers. However, significant arsenic concentrations and amounts of arsenic loads are present in the water of the Missouri River as it enters Fort Peck Lake. A monitoring network of 24 stations was operated during 1985 and 1986 in the upper Missouri River basin to measure arsenic concentrations and arsenic discharges. Additional monitoring at nine stations was conducted during March to July 1987 to supplement the data base. This report presents data acquired from the 1987 monitoring period.

INTRODUCTION

Enriched geothermal waters within Yellowstone National Park contribute arsenic to tributaries of the Madison River. As the river flows from the park, arsenic concentrations range from 200 to 300 μg/L (micrograms per liter) (U.S. Environmental Protection Agency, 1972). Although inflows from downstream tributaries to the Madison and Missouri Rivers dilute concentrations, significant amounts of arsenic are present in the water of the Missouri River as it flows into Fort Peck Lake (U.S. Geological Survey, 1976-85). Because 50 μg/L is the maximum allowable limit for arsenic as established by primary drinking-water standards (U.S. Environmental Protection Agency, 1986), concern exists regarding the potential effects on human health.

From November 1985 through October 1986, a monitoring network of 24 sampling stations was operated by the U.S. Geological Survey on the upper Missouri River and selected tributaries to measure arsenic concentrations and determine arsenic discharges. Information from that previous study was published in a report by Knapton and Horpestad (1987). As a supplement to that study, arsenic data were collected from March to July 1987. The purpose of this report is to present the data acquired from the 1987 monitoring period.

Sampling was conducted at nine stations (fig. 1) in 1987, seven of which were on the mainstems of the Madison and Missouri Rivers and two near the mouths of major tributaries. The most upstream mainstem station was Madison River near West Yellowstone (station 2) and the most downstream was Missouri River near Landusky (station 8). The two tributary stations sampled were Jefferson River near Three Forks (station 1) and Musselshell River at Mosby (station 9). Station locations and descriptions are given in table 2.

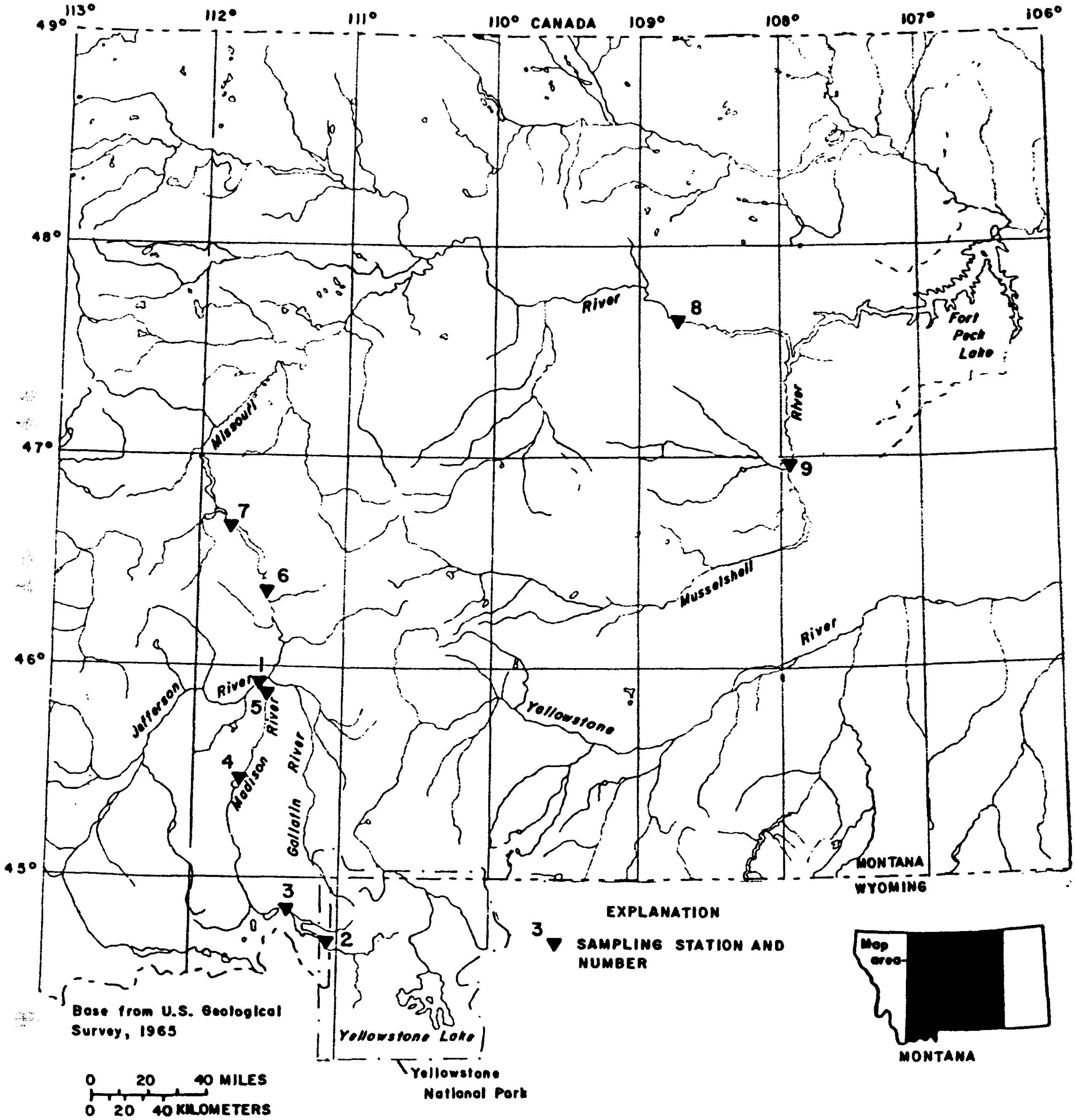

Figure 1.--Location of study area and sampling stations.

The sampling period was selected to include the high flows of spring runoff. Seven samples were scheduled for collection at each station, with sampling times based on streamflow conditions. Samples were analyzed for concentration of total recoverable arsenic; arsenic discharge was calculated from the concentration and stream discharge. In addition to arsenic, specific conductance of the samples was measured as a surrogate determination of dissolved-solids concentration. Stream discharge, water temperature, and air temperature were determined at the time of sample collection.

The monitoring program was funded jointly by the U.S. Geological Survey and the Montana Department of Health and Environmental Sciences (Water Quality Bureau). 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 laboratory analysis was to be performed 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 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 bridge crane and reel. Both methods of sampling enabled 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 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

The samples from individual stations consisted of two bottles each of representative water-sediment mixtures--one acidified and the other untreated. (No additional pretreatment of samples was done either onsite or in the laboratory.) The acidified sample was analyzed for arsenic and reported as total recoverable arsenic. The untreated sample was analyzed for specific conductance.

Arsenic was analyzed by the atomic absorption, spectrophotometric, gaseous hydride method. In a series of steps, all arsenic is reduced to As^{+3}, then combined with sodium borohydride to form gaseous arsine. The arsine is swept by a flow of nitrogen into a quartz cell heated to 900 °C, where concentration is determined by atomic absorption. The detection level for this procedure is 1 µg/L. Analytical precision is given in table 1.

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 1.

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 15 µg/L. The 15 µg/L represented a difference of 6 percent. Paired samples for specific conductance indicated a median difference of 2 µS/cm and a maximum difference of 80 µS/cm, which represented a difference between samples of about 2 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 1.

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:

$$Q_a = Q_w \times C_a \times k \tag{1}$$

where

Q_a is arsenic discharge, in pounds per day;
Q_w is the water discharge, in cubic feet per second;
C_a is arsenic concentration, in micrograms per liter; and
k is 0.0054, a constant used to convert arsenic discharge to pounds per day.

Variations of arsenic concentration and arsenic discharge with time are shown for the most upstream station on the Madison River (fig. 2) and the most downstream station on the Missouri River (fig. 3). Length of time between sample collection ranges from about one-half to 1 month. Although the data points in figures 2 and 3 are connected by lines for visual comparison, the lines may not account for some variations in arsenic concentrations and discharges that could have occurred between times of sample collection.

Arsenic concentrations and arsenic discharges are shown for the seven mainstem stations during selected periods in 1987 (figs. 4 and 5). The April 1-3 sampling (fig. 4) was a relatively stable period of streamflow prior to snowmelt runoff. The June 16-19 sampling (fig. 5) was after the peak snowmelt runoff when reservoirs

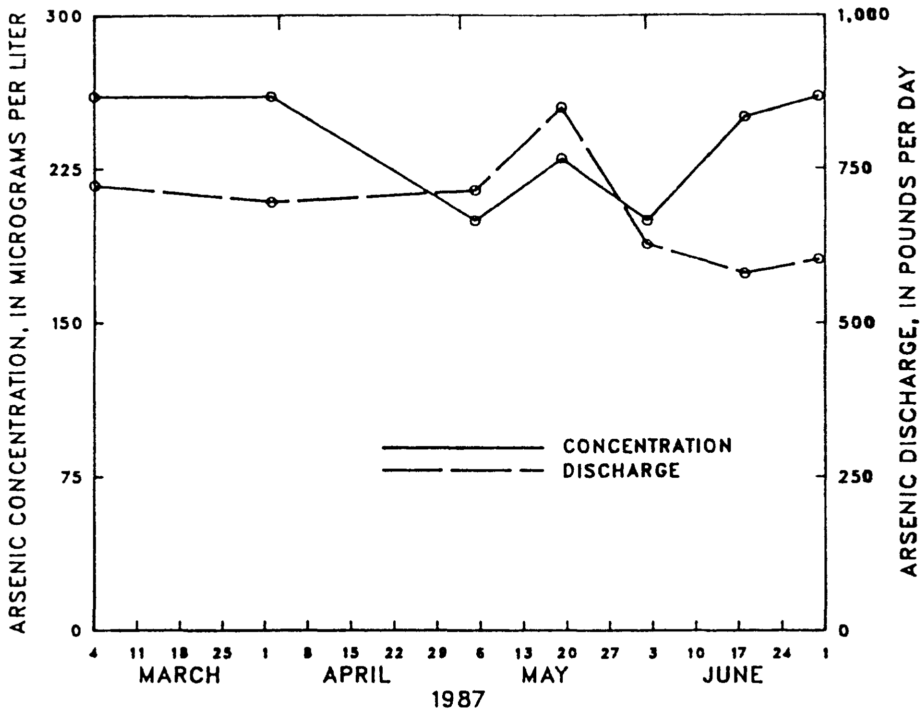

Figure 2.--Total recoverable arsenic concentration and total recoverable arsenic discharge for the Madison River near West Yellowstone (station 2), March 4 through June 30, 1987.

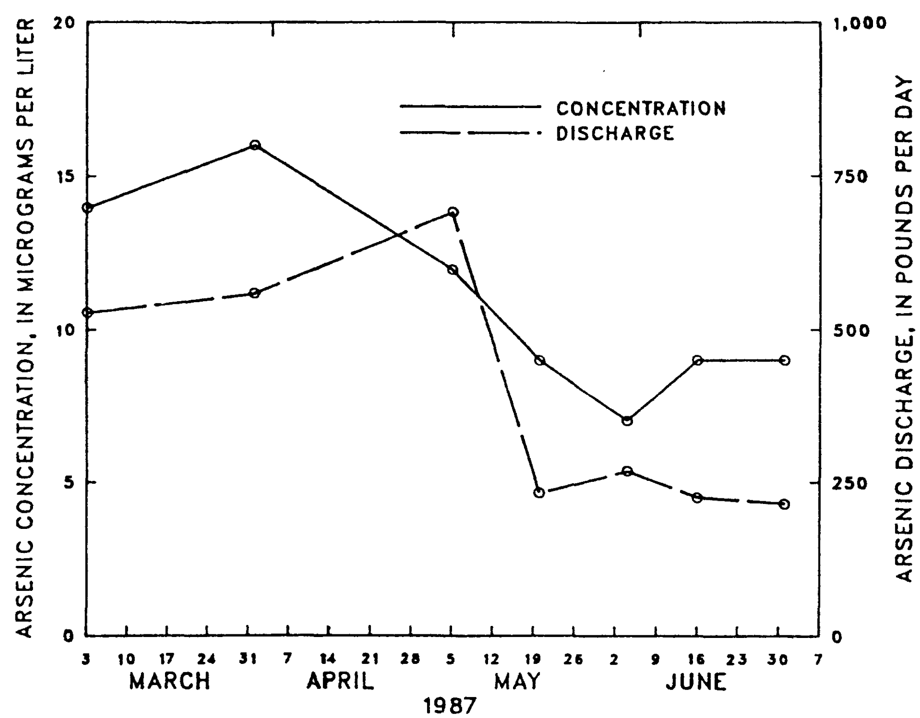

Figure 3.--Total recoverable arsenic concentration and total recoverable arsenic discharge for the Missouri River near Landusky (station 8), March 3 through July 1, 1987.

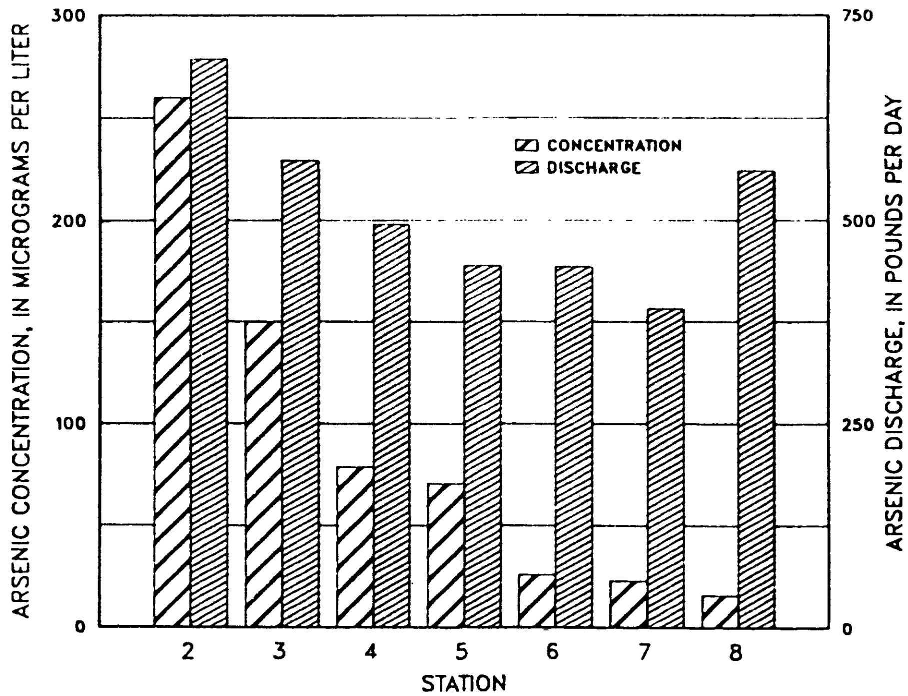

Figure 4.--Total recoverable arsenic concentration and total recoverable arsenic discharge at seven stations on the Madison and Missouri Rivers for samples collected April 1-3, 1987.

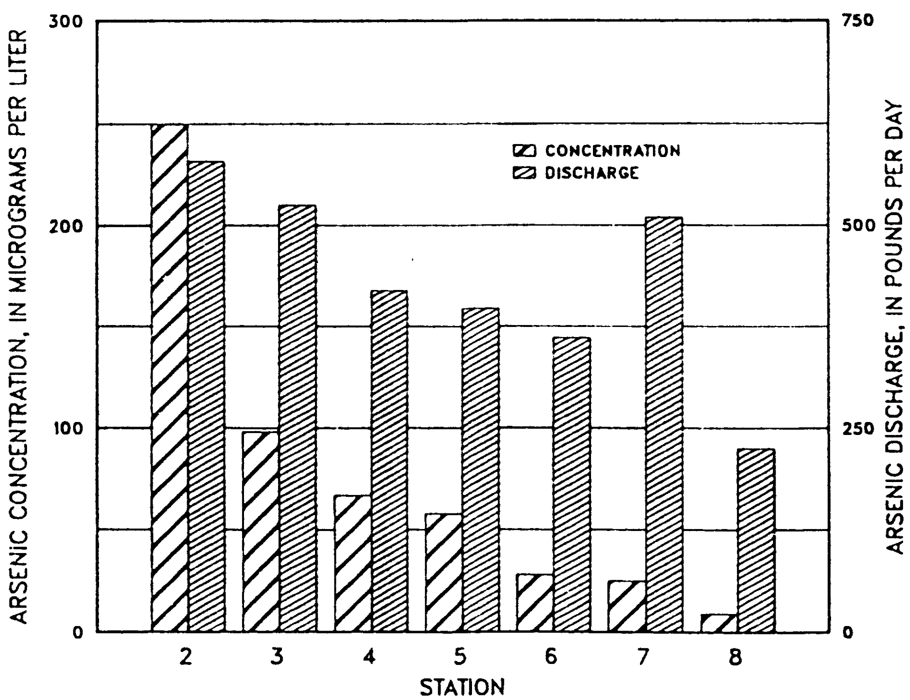

Figure 5.--Total recoverable arsenic concentration and total recoverable arsenic discharge at seven stations on the Madison and Missouri Rivers for samples collected June 16-19, 1987.

were at capacity or filling. The runoff in the upper Missouri River basin during 1987 was considered to be abnormally small, owing to a less than normal mountain snow cover.

Of the seven mainstem stations, only the Madison River near West Yellowstone (station 2) is not affected by a reservoir. Between the most upstream and downstream stations, two reservoirs are present on the Madison River and four on the Missouri River. If data in this report are used for interpretation, the reader is cautioned to consider the effects of impoundments on the results. The reservoirs can have a significant effect on both arsenic concentrations and arsenic discharge. Mixing of waters within the reservoirs can provide a dampening of short- and intermediate-term fluctuations in arsenic concentrations. Geochemical processes active at the water-bottom sediment interface may further modify arsenic concentrations. Controlled water releases from reservoirs can alter natural flow patterns and affect the transport of arsenic that has a direct relationship to stream discharge. As a result of reservoir effects, the 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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Table 1.--*Laboratory precision, accuracy, and detection limits for arsenic and specific conductance*

[µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 °C; --, no data or insufficient data]

Parameter	Precision		Accuracy		Detection limit
	Range	Limit	Warning limits (percent recovery)	Acceptance limits (percent recovery)	
Arsenic (Automated gaseous hydride method)	1-5 µg/L	2 µg/L	--	--	1 µg/L
	5-20 µg/L	3 µg/L	93-125	85-133	--
	20-100 µg/L	5 µg/L	--	--	--
Specific conductance (EPA 120.1 method[1]	0.10-75 µS/cm	11.7 µS/cm	--	--	0.10 µS/cm
	75-560 µS/cm	13.8 µS/cm	--	--	--
	560-870 µS/cm	35.7 µS/cm	--	--	--
	870-1500 µS/cm	64.2 µS/cm	--	--	--

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

Table 2.--*Descriptions of network stations*

[ft, feet; mi, miles]

Station 1--JEFFERSON RIVER NEAR THREE FORKS, MONT. (06036650)

LOCATION.--Lat 45°53'52", long 111°35'45", in SW¼SW¼NW¼ sec. 27, T. 2 N., R. 1 E., Broadwater County, 50 ft downstream from bridge on U.S. Highway 10, and 2.5 mi northwest of Three Forks.

Station 2--MADISON RIVER NEAR WEST YELLOWSTONE, MONT. (06037500)

LOCATION.--Lat 44°39'25", long 111°04'03", in NE¼NW¼SW¼ sec. 36, T. 13 S., R. 5 E., Gallatin County, Yellowstone National Park, 0.7 mi downstream from Montana-Wyoming line, 1.5 mi east of West Yellowstone, and 16.4 mi downstream from Gibbon River.

Station 3--MADISON RIVER BELOW HEBGEN LAKE, NEAR GRAYLING, MONT. (06038500)

LOCATION.--Lat 44°52'00", long 111°20'15", in NE¼NE¼NE¼ 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--MADISON RIVER BELOW ENNIS LAKE, NEAR MCALLISTER, MONT. (06041000)

LOCATION.--Lat 45°29'25", long 111°38'00", in SW¼SE¼NW¼ sec. 17, T. 4 S., R. 1 E., Madison County, 500 ft downstream from Madison powerplant, 1.5 mi downstream from Ennis Lake, and 5.7 mi northeast of McAllister.

Station 5--MADISON RIVER AT THREE FORKS, MONT. (06042600)

LOCATION.--Lat 45°54'05", long 111°31'29", in SE¼NE¼NW¼ sec. 30, T. 2 N., R. 2 E., Gallatin County, at bridge on old U.S. Highway 10, 1.5 mi east of Three Forks, and 3.0 mi upstream from mouth.

Station 6--MISSOURI RIVER AT TOSTON, MONT. (06054500)

LOCATION.--Lat 46°08'46", long 111°25'11", in NW¼SE¼NW¼ sec. 36, T. 5 N., R 2 E., Broadwater County, 2.2 mi southeast of Toston, 4.8 mi upstream from Crow Creek, and 7.8 mi downstream from Sixteenmile Creek.

Station 7--MISSOURI RIVER BELOW CANYON FERRY DAM, NEAR HELENA, MONT. (06058502)

LOCATION.--Lat 46°38'57", long 111°43'39", in SE¼SE¼ sec. 4, T. 10 N., R. 1 W., Lewis and Clark County, at penstock of No. 1 generator at Canyon Ferry Dam, and 15 mi east of Helena.

Station 8--MISSOURI RIVER NEAR LANDUSKY, MONT. (06115200)

LOCATION.--Lat 47°37'51", long 108°41'13", in NW¼NE¼ sec. 31, T. 22 N., R. 24 E., Fergus County, Fort Peck Game Range, 380 ft upstream from bridge on U.S. Highway 191, 0.9 mi upstream from Armells Creek, and 20 mi south of Landusky.

Station 9--MUSSELSHELL RIVER AT MOSBY, MONT. (06130500)

LOCATION.--Lat 46°59'34", long 107°53'34", in NW¼SW¼NW¼ sec. 11, T. 14 N., R. 30 E., Petroleum County, 300 ft upstream from bridge on State Highway 20, 0.3 mi west of Mosby, and 10.9 mi downstream from Flatwillow Creek.

Table 3.--*Water-quality data for network stations*

[ft^3/s, cubic feet per second; µS/cm, microsiemens per centimeter at 25 °C; °C, degrees Celsius; µg/L, micrograms per liter; lb/d, pounds per day; <, less than detection limit]

Date	Time	Stream discharge, instantaneous (ft^3/s)	Specific conductance, laboratory (µS/cm)	Temperature, onsite, air (°C)	Temperature, onsite, water (°C)	Arsenic, total recoverable (µg/L as As)	Arsenic discharge (lb/d)
Station 1--JEFFERSON RIVER NEAR THREE FORKS, MONT. (06036650)							
MAR 1987							
05...	0945	1,350	473	14.0	4.0	3	22
APR							
01...	1200	1,360	469	10.0	7.0	3	22
MAY							
06...	1150	1,510	355	25.0	16.0	3	24
18...	1200	1,450	281	15.0	13.0	4	31
JUN							
02...	1245	2,630	348	15.0	13.0	4	57
17...	1215	1,170	406	21.0	18.5	4	25
29...	1045	680	463	27.0	21.0	4	15
Station 2--MADISON RIVER NEAR WEST YELLOWSTONE, MONT. (06037500)							
MAR 1987							
04...	0915	515	454	0.0	2.0	260	723
APR							
02...	1330	496	456	14.0	11.0	260	696
MAY							
05...	1330	662	366	21.0	17.5	200	715
19...	1115	683	390	25.0	15.0	230	848
JUN							
02...	2000	581	386	14.0	16.0	200	627
18...	1430	429	464	22.5	21.0	250	579
30...	1230	429	473	30.0	23.0	260	602

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

Date	Time	Stream discharge, instantaneous (ft^3/s)	Specific conductance, laboratory (µS/cm)	Temperature, onsite, air (°C)	Temperature, onsite, water (°C)	Arsenic, total recoverable (µg/L as As)	Arsenic discharge (lb/d)
Station 3--MADISON RIVER BELOW HEBGEN LAKE, NEAR GRAYLING, MONT. (06038500)							
MAR 1987							
04...	1040	950	350	0.5	2.5	150	770
APR							
02...	1115	708	351	2.0	4.0	150	573
MAY							
05...	1430	647	264	21.0	5.5	98	342
19...	1340	230	286	15.0	10.0	110	137
JUN							
03...	0730	598	280	1.0	9.0	94	304
17...	1715	993	275	21.5	13.0	98	525
30...	1540	702	275	27.0	19.0	78	296
Station 4--MADISON RIVER BELOW ENNIS LAKE, NEAR MCALLISTER, MONT. (06041000)							
MAR 1987							
04...	1300	1,640	338	15.0	3.0	90	797
APR							
02...	0830	1,160	328	-2.0	3.5	79	495
MAY							
05...	1720	1,160	292	25.0	13.0	76	476
18...	1215	755	278	8.0	12.5	63	257
JUN							
02...	1530	1,160	282	16.0	13.0	45	282
17...	1445	1,160	290	20.0	18.5	67	420
29...	1245	1,070	298	29.0	19.5	59	341

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

Date	Time	Stream discharge, instantaneous (ft^3/s)	Specific conductance, laboratory (µS/cm)	Temperature, onsite, air (°C)	Temperature, onsite, water (°C)	Arsenic, total recoverable (µg/L as As)	Arsenic discharge (lb/d)
Station 5--MADISON RIVER AT THREE FORKS, MONT. (06042600)							
MAR 1987							
05...	1130	1,600	340	17.0	4.0	85	734
APR							
01...	1300	1,160	331	12.0	6.0	71	445
MAY							
06...	1000	1,090	292	23.0	13.5	72	424
18...	1515	705	281	16.0	14.0	65	247
JUN							
03...	1200	1,260	288	20.0	13.0	42	286
17...	1100	1,270	291	17.0	16.5	58	398
29...	1210	983	309	27.0	19.0	62	329
Station 6--MISSOURI RIVER AT TOSTON, MONT. (06054500)							
MAR 1987							
05...	1300	3,720	410	19.0	4.0	38	763
APR							
02...	1730	3,160	411	15.5	7.5	26	444
MAY							
06...	1240	3,120	299	26.0	18.0	22	371
18...	1445	2,670	336	15.5	12.5	24	346
JUN							
02...	1200	5,230	320	13.0	12.0	10	282
18...	1830	2,390	356	13.0	18.5	28	361
29...	1320	1,770	373	29.0	22.0	34	325

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

Date	Time	Stream discharge, instantaneous (ft^3/s)	Specific conductance, laboratory (μS/cm)	Temperature, onsite, air (°C)	Temperature, onsite, water (°C)	Arsenic, total recoverable (μg/L as As)	Arsenic discharge (lb/d)
Station 7--MISSOURI RIVER BELOW CANYON FERRY DAM, NEAR HELENA, MONT. (06058502)							
MAR 1987							
05...	1330	3,800	402	19.0	4.5	27	554
APR							
03...	1045	3,160	386	10.0	4.0	23	392
MAY							
06...	1400	3,700	383	26.0	7.5	27	539
18...	1645	2,320	388	16.0	7.0	28	351
JUN							
02...	1015	2,460	384	10.0	7.5	23	306
19...	0800	3,780	386	10.5	9.0	25	510
29...	1445	3,600	386	31.0	10.0	25	486
Station 8--MISSOURI RIVER NEAR LANDUSKY, MONT. (06115200)							
MAR 1987							
03...	1000	7,000	524	6.0	0.0	14	529
APR							
01...	1330	6,490	809	9.0	7.5	16	561
MAY							
05...	0845	10,700	524	13.0	16.0	12	693
20...	1430	4,800	558	10.0	13.0	9	233
JUN							
04...	0845	7,100	520	15.5	16.0	7	268
16...	0915	4,620	493	22.0	22.5	9	225
JUL							
01...	0915	4,420	510	23.5	22.0	9	215

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

Date	Time	Stream discharge, instantaneous (ft^3/s)	Specific conductance, laboratory (µS/cm)	Temperature, onsite, air (°C)	Temperature, onsite, water (°C)	Arsenic, total recoverable (µg/L as As)	Arsenic discharge (lb/d)
		Station 9--MUSSELSHELL RIVER AT MOSBY, MONT. (06130500)					
MAR 1987							
03...	1330	80	3,710	6.0	1.0	<1	<.43
APR							
02...	1330	125	3,730	13.0	9.5	<1	<.68
MAY							
21...	1400	64	5,200	11.0	13.0	<1	<.35
JUN							
03...	1115	184	2,350	21.0	14.5	<1	<.99
15...	1045	56	3,300	30.0	24.5	<1	<.30
30...	1145	17	2,940	26.5	21.0	<1	<.09