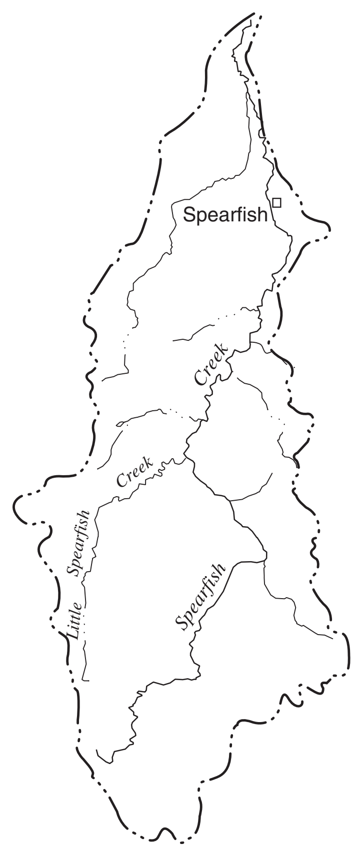
ARSENIC LOADS IN SPEARFISH CREEK, WESTERN SOUTH DAKOTA, WATER YEARS 1989-91

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 95-4080



Prepared in cooperation with the
U.S. ENVIRONMENTAL PROTECTION AGENCY, the
LAWRENCE COUNTY COMMISSION, and the
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AND NATURAL RESOURCES

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By Daniel G. Driscoll and Timothy S. Hayes

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Rapid City, South Dakota

1995

U.S. DEPARTMENT OF THE INTERIOR

BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY

Gordon P. Eaton, Director

For additional information write to:

District Chief
U.S. Geological Survey
1608 Mt. View Rd.
Rapid City, SD 57702

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CONTENTS

ILLUSTRATIONS

TABLES

CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
acre	4,047	square meter
acre	0.4047	hectares
acre-foot (acre-ft)	1,233	cubic meter
acre-foot per year (acre-ft/yr)	1,233	cubic meter per year
cubic foot (ft^3)	0.028317	cubic meter
cubic foot per second (ft^3/s)	0.028317	cubic meter per second
foot (ft)	0.3048	meter
inch (in.)	25.4	millimeter
mile (mi)	1.609	kilometer
pound (lb)	0.4536	kilogram
square mile (mi^2)	259.0	hectare
square mile (mi^2)	2.590	square kilometer

Temperature can be converted to degrees Fahrenheit (°F) or degrees Celsius (°C) by the following equations:

$$°F = 9/5\ (°C) + 32$$

$$°C = 5/9\ (°F - 32)$$

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

Water year (WY): The U.S. Geological Survey defines a water year as the 12-month period which begins October 1 and ends September 30 of the following year. The water year is designated by the calendar year in which it ends; thus, the water year ending September 30, 1991, is called the “1991 water year.”

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ABSTRACT

Numerous small tributaries on the eastern flank of Spearfish Creek originate within a mineralized area with a long history of gold-mining activity. Some streams draining this area are known to have elevated concentrations of arsenic. One such tributary is Annie Creek, where arsenic concentrations regularly approach the Maximum Contaminant Level of 50 µg/L (micrograms per liter) established by the U.S. Environmental Protection Agency. A site on Annie Creek was proposed for inclusion on the National Priorities List by the Environmental Protection Agency in 1991. This report presents information about arsenic loads and concentrations in Spearfish Creek and its tributaries, including Annie Creek.

Stream types were classified according to geologic characteristics and in-stream arsenic concentrations. The first type includes streams that lack significant arsenic sources and have low in-stream arsenic concentrations. The second type has abundant arsenic sources and high in-stream concentrations. The third type has abundant arsenic sources but only moderate in-stream concentrations. The fourth type is a mixture of the first three types.

Annual loads of dissolved arsenic were calculated for two reaches of Spearfish Creek to quantify arsenic loads at selected gaging stations during water years 1989-91. Mass-balance calculations also were performed to estimate arsenic concentrations for ungaged inflows to Spearfish Creek. The drainage area of the upstream reach includes significant mineralized areas, whereas the drainage area of the downstream reach generally is without known arsenic sources.

The average load of dissolved arsenic transported from the upstream reach of Spearfish Creek, which is representative of a type 4 stream, was 158 kilograms per year, calculated for station 06430900, Spearfish Creek above Spearfish. Gaged headwater tributaries draining unmineralized areas (type 1) contributed only 16 percent of the arsenic load in 63 percent of the discharge. Annie Creek (type 2), which has the highest measured arsenic concentrations in the Spearfish Creek drainage, contributed about 15 percent of the arsenic load in about 2 percent of the discharge of the upstream reach. Squaw Creek, which drains another mineralized area, but has only moderate in-stream concentrations (type 3), contributed 4 percent of the arsenic load in 5 percent of the discharge. Ungaged inflows to the reach contributed the remaining 65 percent of the arsenic load in 30 percent of the discharge. The calculated loads from ungaged inflows include all arsenic contributed by surface- and ground-water sources, as well as any additions of arsenic from dissolution of arsenic-bearing solid phases, or from desorption of arsenic from solid surfaces, within the streambed of the upstream reach.

Mass-balance calculations indicate that dissolved arsenic concentrations of the ungaged inflows in the upstream reach averaged about 9 µg/L. In-stream arsenic concentrations of ungaged inflows from the unmineralized western flank of Spearfish Creek probably are generally low (type 1). Thus, in-stream arsenic concentrations for ungaged inflows draining the mineralized eastern flank of Spearfish probably average almost twice that level, or about 18 µg/L. Some ungaged, eastern-flank inflows probably are derived from type 3 drainages, with only moderate arsenic concentrations. If so, other ungaged, eastern-

flank inflows could have in-stream arsenic concentrations similar to those of Annie Creek.

No significant arsenic sources were apparent in the downstream reach of Spearfish Creek. Over the course of the downstream reach, arsenic concentrations decreased somewhat, probably resulting from dilution, as well as from possible chemical adsorption to sediment surfaces or arsenic-phase precipitation. A decrease in arsenic loads resulted from various diversions from the creek and from the potential chemical removal processes.

Because of a large margin of error associated with calculation of arsenic loads for the downstream reach, it is difficult to conclude decisively that chemical removal occurs. It can be concluded, however, that arsenic concentrations do not increase significantly in the downstream reach as a result of interactions with streambed and alluvial sediments. Thus, it also can be concluded that streambed interactions within the channel of Spearfish Creek probably are not a significant source of arsenic within the upstream reach.

INTRODUCTION

Spearfish Creek is the largest drainage basin within Lawrence County (fig. 1). Most of the drainage basin lies within the Black Hills, a small mountain range located in South Dakota and Wyoming. Numerous small tributaries on the eastern flank of Spearfish Creek head within a mineralized area that has a long history of gold-mining activity (fig. 2). Several elements associated with the gold ores have potential to degrade water quality. Anomalous concentrations of arsenic, which are a characteristic of the sediment-hosted, epithermal gold ores present in the Cambrian Deadwood Formation and Tertiary intrusive rocks (Paterson and others, 1988), are of particular concern.

In some northern Black Hills streams, mining activity has degraded water quality. In the case of Whitewood Creek (fig. 1), arsenic concentrations increased because of long-term discharge of arsenic-bearing gold-mill tailings into the creek (Goddard, 1989). Arsenic concentrations approaching or exceeding the Maximum Contaminant Level (MCL) of 50 μg/L (micrograms per liter) for total recoverable arsenic have been documented within Whitewood Creek. The MCL is based upon potential carcinogenic effects from long-term ingestion of arsenic (U.S. Environmental Protection Agency, 1986).

During the 1980's, the northern Black Hills area, particularly Lawrence County, experienced an expansion of mining activity, urbanization, and other resource development. Because of concerns about effects of this development on water quantity and quality, the U.S. Geological Survey (USGS), in cooperation with the Lawrence County Commission and the South Dakota Department of Water and Natural Resources (now the Department of Environment and Natural Resources), began an appraisal of the water resources of Lawrence County in 1988. A network of streamflow-gaging and water-quality sampling stations was established to appraise the quantity and quality of surface water within Lawrence County.

Annie Creek, a small tributary to Spearfish Creek, has been impacted by mining activities (fig. 2). High concentrations of arsenic in the water and sediments of Annie Creek prompted the U.S. Environmental Protection Agency (EPA) to propose, in 1991, that a 5-acre site near the head of Annie Creek be added to the National Priorities List. The EPA subsequently requested USGS technical assistance to determine arsenic conditions in Annie Creek and other tributaries to Spearfish Creek, using data previously collected for the Lawrence County appraisal.

Purpose and Scope

This report presents information about arsenic loads and concentrations during WY 1989-91 for two reaches of Spearfish Creek. Calculated loads of dissolved arsenic at selected gaging stations on Spearfish Creek and its tributaries are included. Estimates of arsenic loads and concentrations for ungaged inflows to Spearfish Creek were made to determine if arsenic conditions in other tributaries are likely to be similar to those of Annie Creek. In addition, a classification of stream types according to geologic characteristics and in-stream arsenic concentrations is presented.

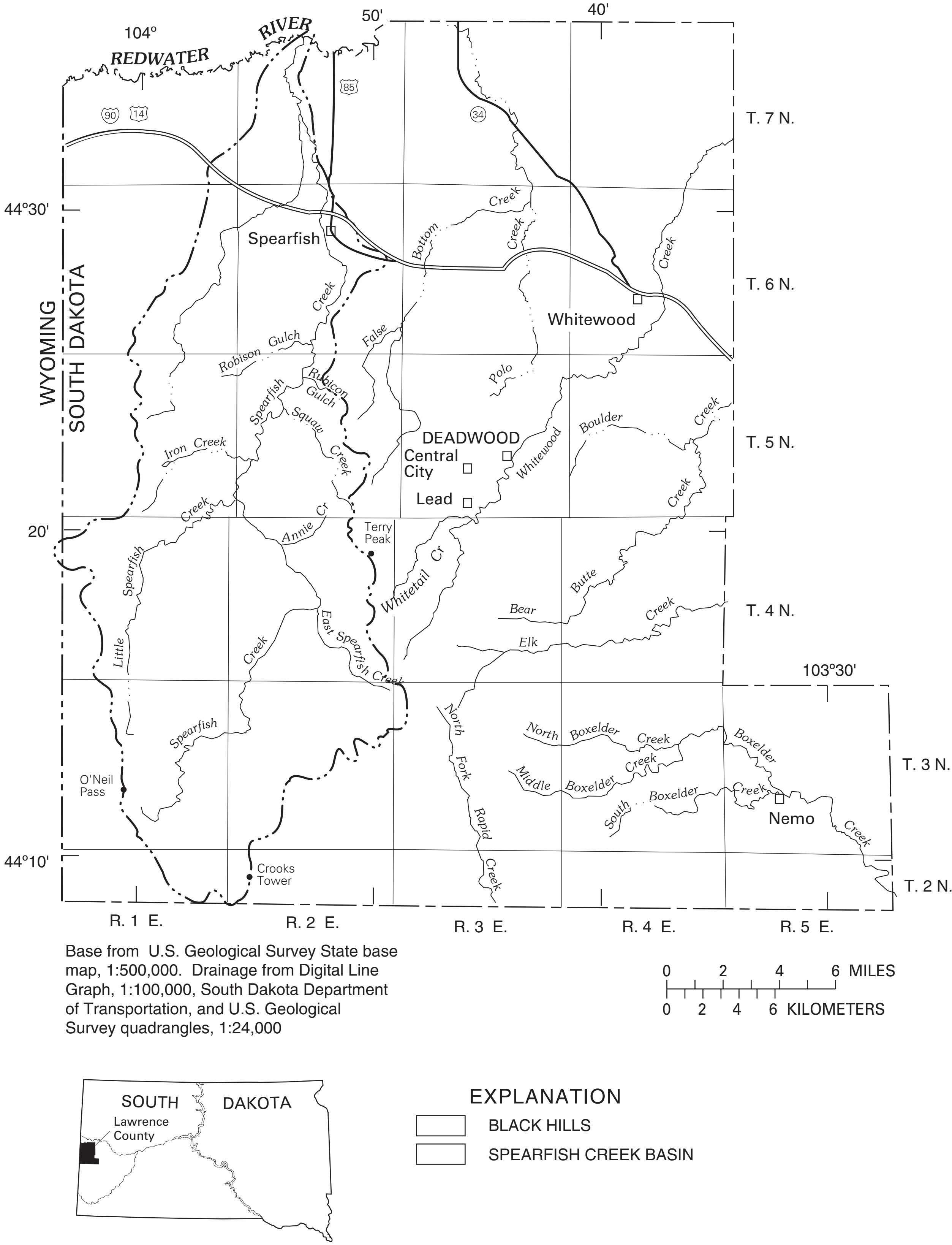
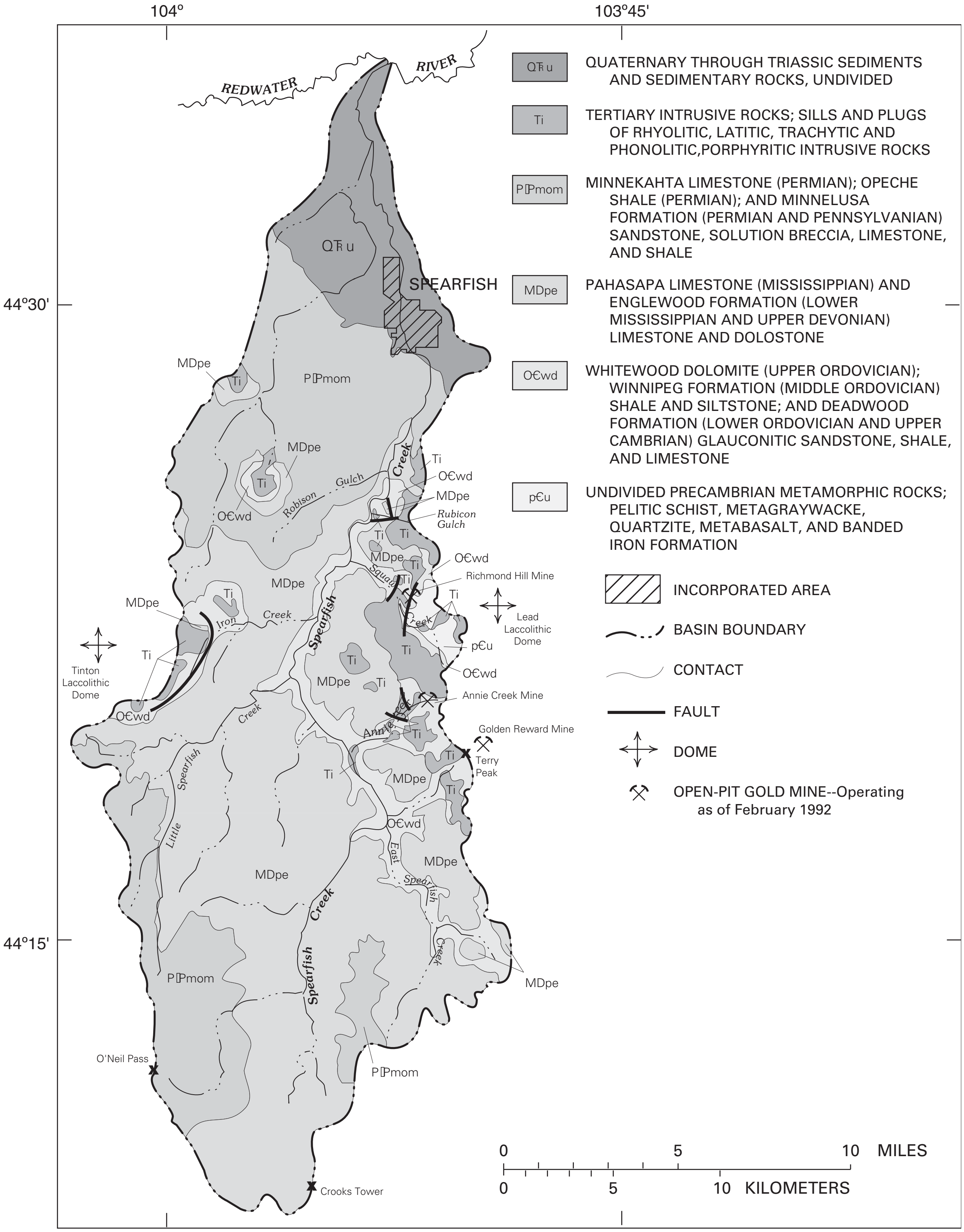


Figure 1. Location of Spearfish Creek in Lawrence County.



Base from U.S. Geological Survey 1:250,000, Rapid City, South Dakota, 1953, revised 1978; and Gillette, Wyoming, Montana, South Dakota, 1955, revised 1975

Geology modified from Ed DeWitt, J.A. Redden, David Buscher, and A.B. Wilson, 1989

Figure 2. Bedrock geology and operating surface gold mines in and adjacent to the Spearfish Creek Basin.

Description of Study Area

The Black Hills of South Dakota and Wyoming are a large domal uplift formed during the Laramide orogeny (Late Cretaceous-Early Tertiary). Spearfish Creek drains an area of slightly greater than 200 mi^2 on the northern slope of the Black Hills. The climate of the Spearfish Creek Basin is influenced by elevation, which ranges from about 3,210 ft above sea level at the creek's confluence with the Redwater River, to 7,137 ft above sea level at Crooks Tower (fig. 2). Mean annual air temperatures decrease with increasing altitude, ranging from 46.9×°F at Spearfish at elevation 3,640 ft to 44.2°F at Lead at elevation 5,350 ft, which is similar to higher elevations within the Spearfish Creek Basin. Annual precipitation increases with elevation, ranging from an average of 21.06 in. at Spearfish to 28.65 in. at Lead (U.S. Department of Commerce, 1990). Generally, most of the annual precipitation falls between March and August. Most runoff occurs between March and June (Addison, 1991) because of increased precipitation, snowmelt, and minimal evapotranspiration.

Land use is diverse within the Spearfish Creek Basin. Land uses at the lower elevations of the basin are primarily urban, suburban, and agricultural. Water from Spearfish Creek is heavily utilized during the summer months for irrigation of cropland, including forage crops for cattle and numerous commercial vegetable gardens. Most of the higher elevation areas south of Spearfish are heavily timbered with ponderosa pine, which is important to an active timber industry. Recreation, including tourism, fishing, skiing, hiking, and cycling, is another important industry. Spearfish Creek harbors naturally reproducing populations of brook and brown trout, as well as a put-and-take rainbow trout fishery. Most of the higher elevation, forested areas are under management by the U.S. Forest Service. Exceptions to this are meadows and bottom lands conducive to agriculture and privately held, patented mining claims, especially in gold-mineralized areas, such as the eastern part of the Spearfish Creek Basin north of Terry Peak.

Gold mining probably has been the most important industry in the overall development of the northern Black Hills. The discovery of gold by the Custer expedition in 1874, near what later became the City of Custer (located about 31 mi southeast of Crooks Tower), led to a gold rush that concentrated around the Deadwood and Lead areas by 1875. Widespread placer-mining activity occurred through about the turn of the century. Underground gold mining by Homestake Mining Company in Lead constituted most of the mining activity in the northern Black Hills from then through about 1980, although numerous small-tonnage mines also were developed along the eastern flank of the Spearfish Creek Basin. Since then, development of heap-leach recovery methods for low-grade gold ores has led to development of several new large-scale, open-pit mines within both the Spearfish Creek Basin and adjacent areas. In 1992, there were two open-pit gold mines operating within the Spearfish Creek Basin--the Annie Creek mine in the headwater area of Annie Creek and the Richmond Hill mine within the headwater area of Squaw Creek (fig. 2). A third open-pit mine, the Golden Reward mine, is located just east of the basin.

AVAILABLE DATA AND CLASSIFICATION OF STREAM TYPES

Discharge and arsenic-concentration data are available for numerous sites within and near the Spearfish Creek Basin. These data are used in subsequent sections of this report for calculation of arsenic loads in two reaches of Spearfish Creek and for classification of stream types according to geologic characteristics and in-stream arsenic concentrations.

Discharge Data

Continuous-record discharge data are available for seven USGS gaging stations in the Spearfish Creek Basin (fig. 3). Abbreviations for station names have been assigned to these sites (table 1) and will be used in lieu of official station names throughout this report. Discharge records for stations listed in table 1 for WY 1989-91 have been published in Water Resources Data, South Dakota (U.S. Geological Survey, 1990-92). Summaries of discharge data for these stations are presented in table 2.

Arsenic Concentrations

Arsenic-concentration data are available for six of the seven stations listed in table 1. Three of the stations are located on the main stem of Spearfish Creek, and three are located on tributaries to Spearfish

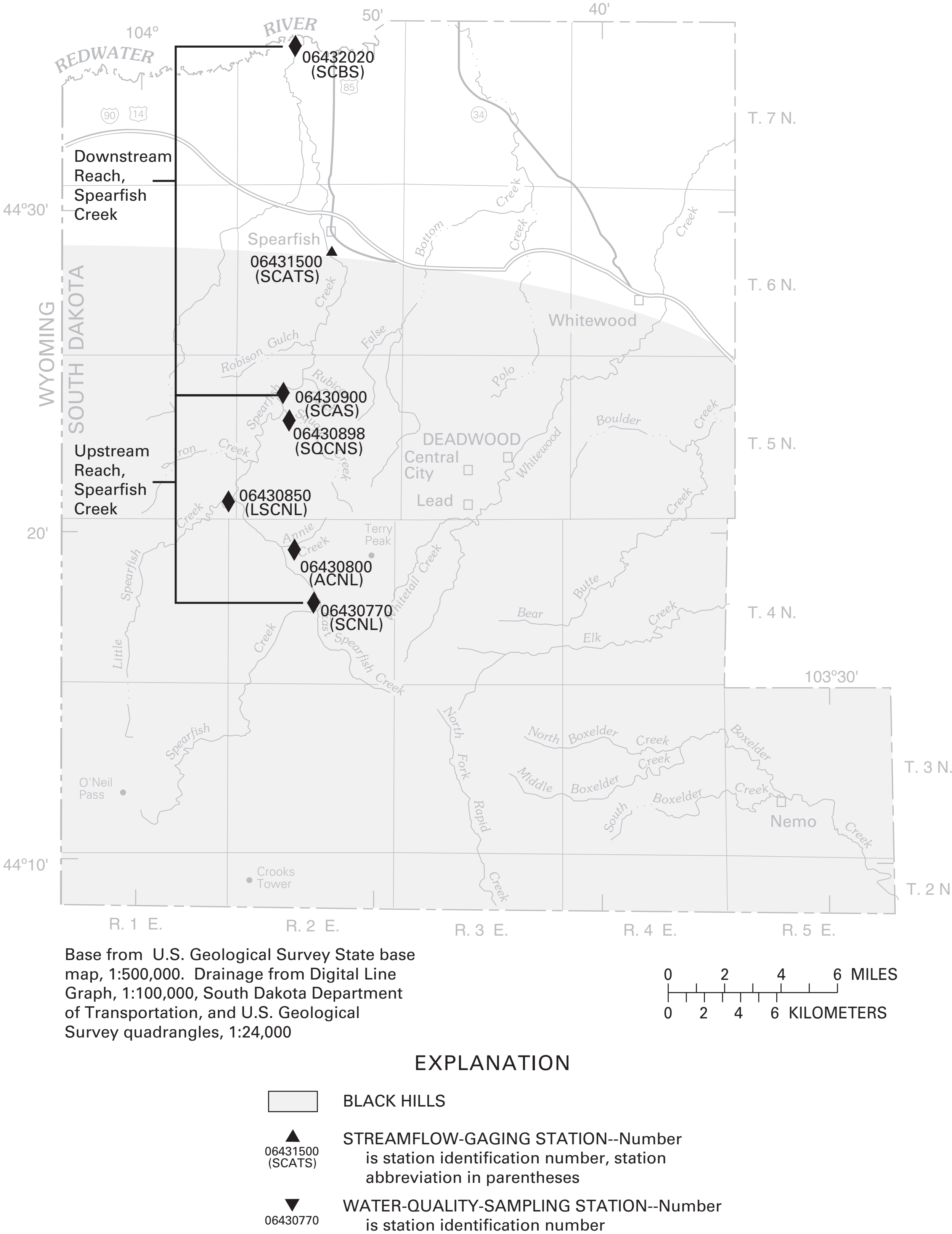


Figure 3. Location of stations within the Spearfish Creek Basin for which continuous-record discharge data and arsenic-concentration data are available.

Table 1. Stations within the Spearfish Creek Basin for which continuous-record discharge data and/or arsenic-concentration data are available

Station identification number	Station name	Station abbreviation	Drainage area (square miles)
06430770	Spearfish Creek near Lead	SCNL	63.5
06430800	Annie Creek near Lead	ACNL	3.55
06430850	Little Spearfish Creek near Lead	LSCNL	25.8
06430898	Squaw Creek near Spearfish	SQCNS	6.95
06430900	Spearfish Creek above Spearfish	SCAS	139
[1]06431500	Spearfish Creek at Spearfish	SCATS	168
06432020	Spearfish Creek below Spearfish	SCBS	204

[1]Arsenic-concentration data not available.

Creek (fig. 3). The discharge and arsenic-concentration data are used for calculating arsenic loads, which are presented later in the report. Summaries of instantaneous discharge at the time of sampling, as well as concentrations of dissolved arsenic and total recoverable arsenic, are presented in table 3.

Arsenic-concentration data also are available for five additional stations in and near the Spearfish Creek Basin (fig. 4). These data are used for classification of stream types according to geologic characteristics and in-stream arsenic concentrations, which are presented in the following section. Summaries of instantaneous discharge at the time of sampling, as well as concentrations of dissolved arsenic and total recoverable arsenic, are presented in table 4.

Table 2. Summary of discharge data for gaging stations within the Spearfish Creek Basin, water years 1989-91

Water year	Station identification number and station abbreviation						
	06430770 SCNL	06430800 ACNL	06430850 LSCNL	06430898 SQCNS	06430900 SCAS	06431500 SCATS	06432020 SCBS
	Mean daily discharge, in cubic feet per second						
1989	15.1	0.68	14.0	2.09	44.7	41.6	40.4
1990	14.2	.87	13.2	2.02	43.6	41.8	39.0
1991	15.2	.88	13.0	2.15	44.6	40.7	40.0
1989-91 mean	14.8	.81	13.4	2.09	44.3	41.4	39.8
	Maximum daily discharge, in cubic feet per second						
1989	25	12	16	36	104	100	98
1990	25	7.8	15	20	94	82	82
1991	30	11	18	29	120	103	122
	Minimum daily discharge, in cubic feet per second						
1989	11	0.00	13	0.20	34	27	1.7
1990	9.0	.05	12	.30	28	26	1.0
1991	7.5	.03	11	.28	25	18	1.6
	10 percent exceedance discharge, in cubic feet per second						
1989-91	19	2.2	15	5.3	59	57	61
	90 percent exceedance discharge, in cubic feet per second						
1989-91	11	0.08	12	0.30	35	32	6.8
	Annual volume, in acre-feet						
1989	10,910	492	10,160	1,520	32,330	30,140	29,260
1990	10,280	628	9,560	1,460	31,590	30,240	28,250
1991	11,040	637	9,420	1,560	32,260	29,450	28,960
1989-91 mean	10,740	586	9,710	1,510	32,060	29,940	28,820

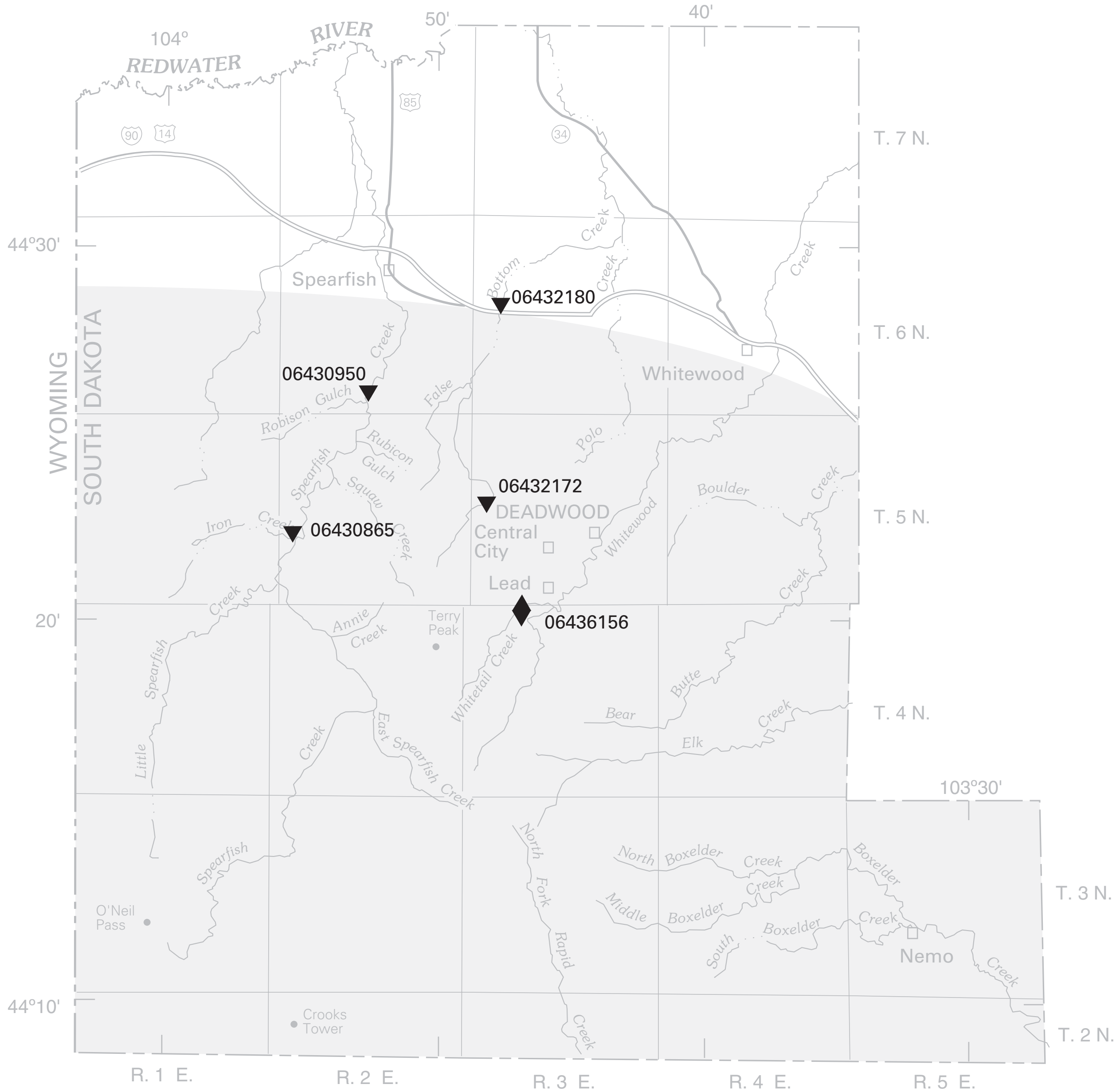
Table 3. Discharge and arsenic data for stations in the Spearfish Creek Basin used for calculating arsenic loads, water years 1988-91

[ft^3/s, cubic foot per second; µg/L, microgram per liter; --, no data available; ---, statistic not computed]

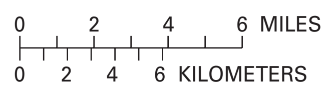
Station number	Station name and abbreviation	Sampling date	Discharge, instantaneous (ft^3/s)	Arsenic, dissolved (µg/L)	Arsenic, total (µg/L)
06430770	Spearfish Creek near Lead (SCNL)	08-02-88	13.9	1	--
		09-07-88	11.0	1	--
		11-29-88	12.8	1	--
		03-06-89	14.6	1	--
		05-23-89	18.7	1	1
		09-07-89	14.5	<1	<1
		11-29-89	16.2	<1	<1
		05-31-90	19.7	<1	<1
		11-28-90	13.3	1	<1
		Number of values	9	9	5
		Mean	14.97	---	---
		Median	14.5	1	<1
		Maximum	19.7	1	1
		Minimum	11	<1	<1
		Standard deviation	2.82	---	---
06430800	Annie Creek near Lead (ACNL)	07-27-88	.16	46	--
		11-29-88	.038	32	--
		03-10-89	.33	27	--
		05-22-89	2.43	27	26
		09-07-89	.06	36	36
		11-29-89	.33	32	28
		04-11-90	1.69	--	15
		05-17-90	6.45	22	27
		08-22-90	.28	48	50
		11-28-90	.063	34	37
		01-15-91	.06	34	--
		02-25-91	.02	37	--
		03-13-91	.01	35	37
		06-20-91	1.65	26	28
		09-05-91	.15	24	34
		Number of values	15	14	10
		Mean	.91	32.9	31.8
		Median	.16	33	31
		Maximum	6.45	48	50
		Minimum	.01	22	15
		Standard deviation	1.71	7.59	9.28
06430850	Little Spearfish Creek near Lead (LSCNL)	11-28-88	13.6	1	--
		03-06-89	14.1	1	--
		05-22-89	14.3	1	1
		09-07-89	13.9	<1	<1
		05-30-90	14.4	1	1
		11-29-90	11.3	<1	<1
		Number of values	6	6	4
		Mean	13.60	---	---
		Median	13.9	1	---
		Maximum	14.4	1	1
		Minimum	11.3	<1	<1
		Standard deviation	1.16	---	---

Table 3. Discharge and arsenic data for stations in the Spearfish Creek Basin used for calculating arsenic loads, water years 1988-91—Continued

Station number	Station name and abbreviation	Sampling date	Discharge, instantaneous (ft^3/s)	Arsenic, dissolved (μg/L)	Arsenic, total (μg/L)
06430898	Squaw Creek near Spearfish (SQCNS)	07-21-88	0.64	4	--
		09-08-88	.26	<1	--
		11-09-88	.75	4	--
		03-07-89	.46	4	--
		05-12-89	12.1	4	4
		09-08-89	.43	3	4
		11-30-89	.75	3	4
		05-29-90	4.80	3	3
		08-23-90	.41	4	4
		11-30-90	.69	4	4
		03-13-91	.49	3	3
		06-20-91	3.34	3	3
		09-05-91	.35	3	4
		Number of values	13	13	9
		Mean	1.96	--	3.7
		Median	.64	3	4
		Maximum	12.1	4	4
		Minimum	.26	<1	3
		Standard deviation	3.34	---	.50
06430900	Spearfish Creek above Spearfish (SCAS)	07-25-88	42.2	4	--
		09-08-88	37.7	4	--
		11-09-88	40.7	3	--
		03-07-89	49.2	3	--
		05-12-89	74.2	5	5
		09-08-89	40.5	2	2
		11-30-89	34.4	2	3
		05-29-90	63.5	4	5
		11-30-90	38.0	4	4
		Number of values	9	9	5
		Mean	46.7	3.4	3.8
		Median	40.7	4	4
		Maximum	74.2	5	5
		Minimum	34.4	2	2
		Standard deviation	13.45	1.01	1.3
06432020	Spearfish Creek below Spearfish (SCBS)	08-04-88	6.77	2	--
		09-15-88	13.2	2	--
		11-28-88	52.0	2	--
		03-09-89	38.8	2	--
		05-31-89	37.3	3	2
		09-11-89	29.0	2	2
		12-01-89	56.5	2	2
		05-31-90	57.3	3	4
		11-26-90	49.0	3	2
		Number of values	9	9	5
		Mean	37.76	2.3	2.4
		Median	38.8	2	2
		Maximum	57.3	3	4
		Minimum	6.77	2	2
		Standard deviation	18.38	.5	.89



Base from U.S. Geological Survey State base map, 1:500,000. Drainage from Digital Line Graph, 1:100,000, South Dakota Department of Transportation, and U.S. Geological Survey quadrangles, 1:24,000



EXPLANATION

▲ 06436156 STREAMFLOW-GAGING STATION--Number is station identification number

▼ 06430950 WATER-QUALITY-SAMPLING STATION--Number is station identification number

Figure 4. Location of selected stations for which additional arsenic-concentration data are available.

Table 4. Discharge and arsenic-concentration data for additional stations, water years 1988-91

[ft^3/s, cubic foot per second; µg/L, microgram per liter; --, no data available; ---, statistic not computed]

Station number	Station name	Sampling date	Discharge, instantaneous (ft^3/s)	Arsenic, dissolved (µg/L)	Arsenic, total (µg/L)
06430865	Iron Creek near Lead	08-03-88	1.52	1	--
		09-08-88	1.48	1	--
		11-15-88	1.27	1	--
		03-07-89	1.30	1	--
		05-11-89	3.19	2	1
		09-11-89	1.09	1	1
		11-29-89	1.48	<1	<1
		05-30-90	2.43	1	1
		11-29-90	1.32	1	<1
		Number of values	9	9	5
		Mean	1.68	---	---
		Median	1.48	1	1
		Maximum	3.19	2	1
		Minimum	1.09	<1	<1
		Standard deviation	.68	---	--
06430950	Spearfish Creek below Robison Gulch, near Spearfish	07-22-88	2.48	3	--
		08-17-88	2.47	3	2
		09-13-88	[1]2.38	4	--
		10-19-88	2.94	1	1
		11-15-88	2.50	3	--
		12-14-88	2.53	3	--
		01-17-89	2.17	3	1
		02-15-89	2.62	3	2
		03-10-89	2.78	3	--
		04-18-89	3.60	4	--
		05-11-89	6.39	4	--
		06-14-89	3.19	3	--
		07-19-89	3.02	3	--
		08-17-89	2.58	3	--
		09-11-89	2.28	3	<1
		10-18-89	2.34	3	<1
		11-20-89	2.52	2	<1
		12-14-89	2.61	2	--
		01-24-90	2.28	2	--
		03-27-90	2.78	3	1
		04-11-90	3.22	3	10
		05-17-90	6.26	2	--
		06-12-90	3.64	3	--
		08-15-90	2.40	3	--
		09-12-90	2.14	3	--
		10-11-90	2.28	2	--
		11-30-90	2.52	3	--
		12-27-90	2.81	2	--
		02-05-91	2.42	3	--
		03-14-91	2.68	2	--
		04-24-91	4.05	3	--
		05-22-91	7.53	3	--
		06-17-91	5.44	3	--
		06-27-91	4.24	3	--
		09-06-91	2.21	3	--

Table 4. Discharge and arsenic-concentration data for additional stations, water years 1988-91—Continued

Station number	Station name	Date	Discharge, instantaneous (ft^3/s)	Arsenic, dissolved (μg/L)	Arsenic, total (μg/L)
06430950	Spearfish Creek below Robison Gulch, near Spearfish—Continued	10-23-91	2.38	2	--
		Number of values	36	36	9
		Mean	3.13	2.8	---
		Median	2.60	3	1
		Maximum	7.53	4	10
		Minimum	2.14	1	<1
		Standard deviation	1.30	.62	---
06432172	False Bottom Creek near Central City	08-03-88	.36	3	--
		09-13-88	.28	3	--
		11-14-88	.41	2	--
		03-08-89	.55	3	--
		05-10-89	12.9	1	4
		09-12-89	.36	2	2
		11-28-89	.70	<1	--
		05-30-90	3.20	1	2
		08-24-90	.29	2	3
		Number of values	9	9	4
		Mean	2.12	--	2.8
		Median	.41	2	2.5
		Maximum	12.9	3	4
		Minimum	.28	<1	2
		Standard deviation	4.15	---	.96
06432180	False Bottom Creek near Spearfish	05-09-89	19.8	2	--
		05-17-90	2.66	5	4
		Number of values	2	2	1
		Mean	---	---	---
		Median	---	---	---
		Maximum	19.8	5	4
		Minimum	2.66	2	4
		Standard deviation	---	---	---
06436156	Whitetail Creek at Lead	08-02-88	1.22	17	--
		09-06-88	.82	16	--
		11-08-88	1.15	13	--
		03-08-89	1.31	12	--
		05-23-89	6.98	11	12
		09-12-89	.91	16	19
		11-28-89	1.24	12	15
		04-10-90	--	11	14
		05-16-90	--	7	7
		08-24-90	1.10	19	20
		11-27-90	.68	12	13
		03-12-91	1.10	13	14
		06-24-91	4.10	12	17
		09-04-91	.78	19	19
		Number of values	12	14	10
		Mean	1.78	13.6	15.0
		Median	1.12	12.5	14.5
		Maximum	6.98	19	20
		Minimum	.68	7	7
		Standard deviation	1.87	3.39	3.94

[1]Estimated.

Stream Types

It is useful to classify four general types of streams in and near the Spearfish Creek Basin. The four types of streams are differentiated by geologic characteristics within their drainage basins (fig. 2) and in-stream arsenic concentrations (tables 3 and 4). A tabulation of stream types and characteristics is presented in table 5.

The first type of stream is one draining areas with unmineralized exposures of the Pahasapa Limestone and Minnelusa Formation. Such drainages lack significant sources of arsenic and generally have arsenic concentrations at or below the detection limit of 1 µg/L. The main headwater tributaries of Spearfish Creek, collectively measured at stations Spearfish Creek near Lead (SCNL) and Little Spearfish Creek near Lead (LSCNL), are examples of this type of stream (fig. 3, table 3).

A second type of stream is one draining mineralized areas where abundant arsenic sources are available and arsenic concentrations generally exceed 10 µg/L. Annie Creek, where arsenic concentrations often approach the MCL of 50 µg/L for total arsenic, is an example of this type of stream (fig. 3, table 3). Whitetail Creek, measured at station 06436156 (at Lead), is another example (fig. 4, table 4). Arsenic concentrations at this station generally are within the same order of magnitude as the MCL, but are somewhat lower than concentrations in Annie Creek. Annie Creek and Whitetail Creek drainages both have deposits of finely crushed, turn-of-the-century-aged, gold-mill tailings and waste-rock dumps in their headwater areas.

A third type of stream is one that drains areas geologically similar to the second type, with abundant sources of arsenic, but with only moderate arsenic concentrations (generally above the detection limit, but an order of magnitude lower than the MCL of 50 µg/L). Squaw Creek, measured at station Squaw Creek near Spearfish (SQCNS), is an example of this type of stream (fig. 3, table 3). False Bottom Creek, measured at station 06432172 (near Central City), is another example (fig. 4, table 4). Measured arsenic concentrations in the two streams range from less than 1 to 5 µg/L. Reasons for the differences in arsenic concentration between the second and third types of streams are not understood. Squaw Creek and False Bottom Creek both drain areas with exposures of the Deadwood Formation and Tertiary intrusive rocks, where gold ores are found at or near the surface, similar to areas drained by Annie and Whitetail Creeks (fig. 2). The Squaw Creek and False Bottom Creek drainages also have deposits of gold-mill tailings and waste-rock dumps. Understanding differences between arsenic concentrations in the second and third type streams will be important to future considerations of arsenic behavior in northern Black Hills streams.

A fourth type of stream is one draining a mixture of mineralized and unmineralized areas and with in-stream arsenic concentrations resulting from a mixture of low-arsenic and higher arsenic water. Spearfish Creek, downstream from the mineralized areas, is an example of this type of stream. Arsenic concentrations at stations Spearfish Creek above Spearfish (SCAS) and Spearfish Creek below Spearfish (SCBS), which range from 2 to 5 µg/L, are a result of this mixture (fig. 3, table 3). Several other streams are preliminarily interpreted to be of this fourth type. One is Iron Creek (fig. 4, table 4), measured at station 06430865 (near Lead), which has significant exposures of mineralized rocks near the Tinton Dome area (fig. 2). It is likely that drainage from the mineralized, headwater area of Iron Creek has moderate (type 3), rather than high (type 2) arsenic concentrations because, after dilution through the remainder of the basin, arsenic concentrations just upstream from the confluence with Spearfish Creek were low (table 4). Another example is Spearfish Creek, measured at station 06430950 (below Robison Gulch). The arsenic concentrations at this site (fig. 4, table 4) were very similar to those at station SCAS (fig. 3, table 3), but the water is of different origin. The entire base flow of Spearfish Creek is diverted just downstream from station SCAS, and returned to Spearfish Creek at a hydroelectric power plant in Spearfish. Thus, the discharge at station 06430950 (table 4) is much less than at station SCAS (table 3). Arsenic concentrations at station 06430950 probably result from a mixture of water from the western flank of Spearfish Creek, with low arsenic concentrations, and water from the eastern flank, with higher concentrations (fig. 2). Some seepage from the power-

Table 5. Classification of stream types in and near the Spearfish Creek Basin according to geologic characteristics and in-stream arsenic concentrations

[μg/L, microgram per liter]

Stream type	Geologic characteristics of drainage basin	Representative in-stream arsenic concentrations (μg/L)	Representative streams
1	Primarily unmineralized, without significant arsenic sources	Low (generally at or below detection limit of 1 μg/L)	Spearfish Creek measured at station 06430770, Spearfish Creek near Lead (SCNL).
			Little Spearfish Creek measured at station 06430850, Little Spearfish Creek near Lead (LSCNL).
2	Primarily mineralized, with abundant arsenic sources	High (generally greater than 10 μg/L)	Annie Creek measured at station 06430800, Annie Creek near Lead (ACNL).
			Whitetail Creek measured at station 06436156, Whitetail Creek at Lead.
3	Primarily mineralized, with abundant arsenic sources	Moderate (generally approaching 5 μg/L)	Squaw Creek measured at station 06430898, Squaw Creek near Spearfish (SQCNS).
			False Bottom Creek measured at station 06432172, False Bottom Creek near Central City.
4	Mixture of mineralized and unmineralized	Low to moderate (generally 1 to 5 μg/L)	Spearfish Creek measured at station 06430900, Spearfish Creek above Spearfish (SCAS).
			Spearfish Creek measured at station 06432020, Spearfish Creek below Spearfish (SCBS).
			Iron Creek measured at station 06430865, Iron Creek near Lead.
			Spearfish Creek measured at station 06430950, Spearfish Creek below Robinson Gulch, near Spearfish.
			False Bottom Creek measured at station 06432180, False Bottom Creek near Spearfish.

diversion dam and pipeline may also contribute to the flow. False Bottom Creek, measured at station 06432180 (near Spearfish), is a final example (fig. 4, table 4). Station 06432180 is located downstream from a reach of sinkholes into the Pahasapa Limestone; hence, there seldom is flow at the station, and the number of samples is limited. The limited available data indicate that the arsenic-concentration characteristics at station 06432180 are similar to those at upstream station 06432172; however, dilution from a substantial limestone-dominated portion of the basin probably occurs during some high flows.

METHODS FOR CALCULATING ARSENIC LOADS

The in-stream loading rate of a given water-borne constituent such as arsenic can be calculated by multiplying discharge by concentration. For a given stream reach, the sum of discharge and the sum of loads (discharge times concentration) into and out of the reach must balance. The constituent concentration in unmeasured tributaries can be calculated by simultaneous solution of these continuity equations for discharge and loading. This method assumes that no change in concentration occurs within the reach because of chemical reactions. Because discharge and concentration generally are not constant, either average values or a method for relating concentration to discharge must be used.

Three stations with both continuous-record discharge and periodic arsenic-concentration data are located on the main stem of Spearfish Creek and collectively define two stream reaches (fig. 3). The upstream reach is bounded by station 06430770, Spearfish Creek near Lead (SCNL) and by station 06430900, Spearfish Creek above Spearfish (SCAS). The downstream reach is bounded by station SCAS and by station 06432020, Spearfish Creek below Spearfish (SCBS). For the reach upstream from station SCAS, continuous-record discharge data and arsenic-concentration data also are available for stations on three tributaries: station 06430800, Annie Creek near Lead (ACNL); station 06430850, Little Spearfish Creek near Lead (LSCNL); and station 06430898, Squaw Creek near Spearfish (SQCNS). Within the reach downstream from station SCAS, additional discharge data are available for station 06431500, Spearfish Creek at Spearfish (SCATS). No other arsenic-concentration data are available, however.

Annual loads of dissolved arsenic for gaged locations are calculated by multiplying annual volume of flow (table 2) by median or mean concentration of dissolved arsenic (table 3). Annual arsenic loads for cumulative ungaged inflow to a reach are estimated by solving the continuity equation for loading for the reach. Ungaged inflow is estimated by solving the continuity equation for discharge. The arsenic concentration for ungaged inflow is estimated by dividing annual load by discharge.

The continuity equation for discharge is stated as:

$$Q(OUT) = Q(IN) \tag{1}$$

where Q(OUT) and Q(IN) are discharge out of and into the reach. As an example, the continuity equation for discharge for the reach of Spearfish Creek upstream from station SCAS is:

$$Q(SCAS) = Q(SCNL) + Q(ACNL) + Q(LSCNL) + Q(SQCNS) + Q(UNGAGED) \tag{2}$$

where Q(UNGAGED) is an unknown representing the cumulative ungaged inflow (both surface and ground water) to the reach. The other terms represent discharge at the respective gaging stations.

Similarly, the continuity equation for loading is stated as:

$$MASS(OUT) = MASS(IN) \tag{3}$$

where MASS(OUT) and MASS(IN) are mass loads out of and into the reach. Again, as an example, the continuity equation for arsenic loads in the reach of Spearfish Creek upstream from station SCAS is:

$$QC(SCAS) = QC(SCNL) + QC(ACNL) + QC(LSCNL) + QC(SQCNS) + QC(UNGAGED) \tag{4}$$

where QC(UNGAGED) is the product of discharge (the unknown from equation 2) and concentration (a second unknown) for ungaged inflow to the reach. The other terms represent the product of discharge and concentration at the respective gaging stations.

The average arsenic concentration for ungaged inflows can then be estimated by dividing the arsenic load, QC(UNGAGED), by the discharge, Q(UNGAGED). As defined, ungaged inflow includes all inflow from ungaged sources. The arsenic load contributed by ungaged inflow, as calculated by this method, includes arsenic derived from bed and alluvial materials along the main stem of Spearfish Creek, as well as arsenic derived from the source areas of the ungaged inflows.

Several options were available for choosing a representative arsenic concentration for calculation of arsenic loads. Mean or median concentrations for either dissolved arsenic or total recoverable arsenic could be used to calculate arsenic loads. Regression equations relating arsenic concentrations to discharge also could be used. In that case, a daily arsenic load would be calculated, based on daily discharge and predicted arsenic concentration, and the annual arsenic load would be calculated by summing the daily arsenic loads.

All arsenic loads presented in this report were calculated using the median or mean concentration for dissolved arsenic. Several factors were considered in making this decision. The data set is larger for dissolved concentrations than for total recoverable arsenic for all stations used in mass-loading calculations (table 3). The data set for dissolved arsenic also spans a larger part of the period of time for which loads are calculated (WY 1989-91) for all stations. Several of the values for dissolved arsenic were for samples collected prior to WY 1989. These samples are included because, in several cases (stations SCNL, SQCNS, and SCBS), they increase the range of applicable discharge values. The maximum instantaneous discharge for which samples were collected was in excess of the 10-percent exceedance discharge for WY 1989-91 (table 2) for all stations except SCBS. For station SCBS, the maximum discharge sampled, 57.3 ft^3/s, was nearly as large as the 10-percent exceedance discharge of 61 ft^3/s. The minimum instantaneous discharge for which samples were collected was less than or equal to the 90-percent exceedance discharge for WY 1989-91 (table 2) for all stations. Thus, values of dissolved arsenic are available for nearly the full range of discharge that occurred during WY 1989-91.

Median concentrations generally were used instead of mean concentrations because the mean is undefined for three stations in table 3 (SCNL, LSCNL, and SQCNS) having censored values (at or below the detection limit of 1 µg/L) for dissolved arsenic. Other methods are available for treatment of censored values (Cohen, 1959; Conover, 1980; Judge and others, 1980; Gilliom and Helsel, 1986; Powell, 1986; Helsel and Cohn, 1988; Travis and Land, 1990; Helsel, 1990). Probability plotting procedures, which model value distributions based on the uncensored data in data sets and yield central tendency parameters for the full distribution, could be used; however, there generally are insufficient data for these stations for such procedures to succeed (Ed Gilroy, U.S. Geological Survey Branch of Systems Analysis, oral commun., March 16, 1991).

The use of regression equations for prediction of daily arsenic concentration as a function of daily discharge was considered for stations ACNL and SCAS. Arsenic concentrations are negatively correlated to discharge for ACNL and positively correlated to discharge for SCAS. The slopes of the regression equations for dissolved arsenic concentrations are significant at the 90-percent level for both stations; however, the relationship between dissolved arsenic concentration and discharge is not well defined for either station, as the r-squared values are 0.28 and 0.39 for ACNL and SCAS, respectively. Thus, it is apparent that other variables, in addition to discharge, significantly affect arsenic concentrations. No significant relationship exists between arsenic concentration and discharge for the other stations; thus, regression equations were not used for calculation of arsenic loads.

For samples collected in and near the Spearfish Creek Basin (tables 3 and 4), most of the total arsenic is in the dissolved form (that is, not associated with a filterable solid). Concentrations for dissolved arsenic generally are as large, or nearly as large, as for total arsenic, which includes both suspended, solid-phase arsenic and dissolved arsenic. Dissolved concentrations exceed total concentrations for several of the analyses, presumably because of analytical errors. Paired analyses for dissolved and total arsenic concentrations are available for 66 samples collected in and near the Spearfish Creek Basin (tables 3 and 4). A regression analysis of total recoverable arsenic concentration as a function of dissolved arsenic concentration was performed for these samples (fig. 5). For this analysis, all censored values were treated as having a concentration of 1 µg/L. The resulting regression equation, with an r-squared value of 0.98, is: Total Arsenic Concentration = 0.15 + 1.06(Dissolved Arsenic Concentration). Thus, loads of total arsenic probably would be very similar to those calculated for dissolved arsenic for the range of discharge that occurred during WY 1989-91.

At high discharges, there could be a substantial difference between concentrations of dissolved and total arsenic concentrations. For the case of nearby Whitewood Creek (fig. 1), Goddard (1989) reported that, under many sets of conditions, much of the arsenic was adsorbed onto a very fine-grained, easily suspended, recently precipitated, ferrihydrite solid phase. At high discharges, the presence of arsenic-laden ferrihydrite commonly caused the total recoverable arsenic concentration to exceed the dissolved arsenic concentration by factors of 2 or more. Whitewood Creek is a very anomalous drainage where arsenic-rich mine tailings were dumped into the creek for over 100 years. Nonetheless, recently precipitated ferrihydrite has been identified within the bed materials of Annie Creek and Squaw Creek, both considered in this report. Thus, under high-flow conditions in some locations, concentrations and loads

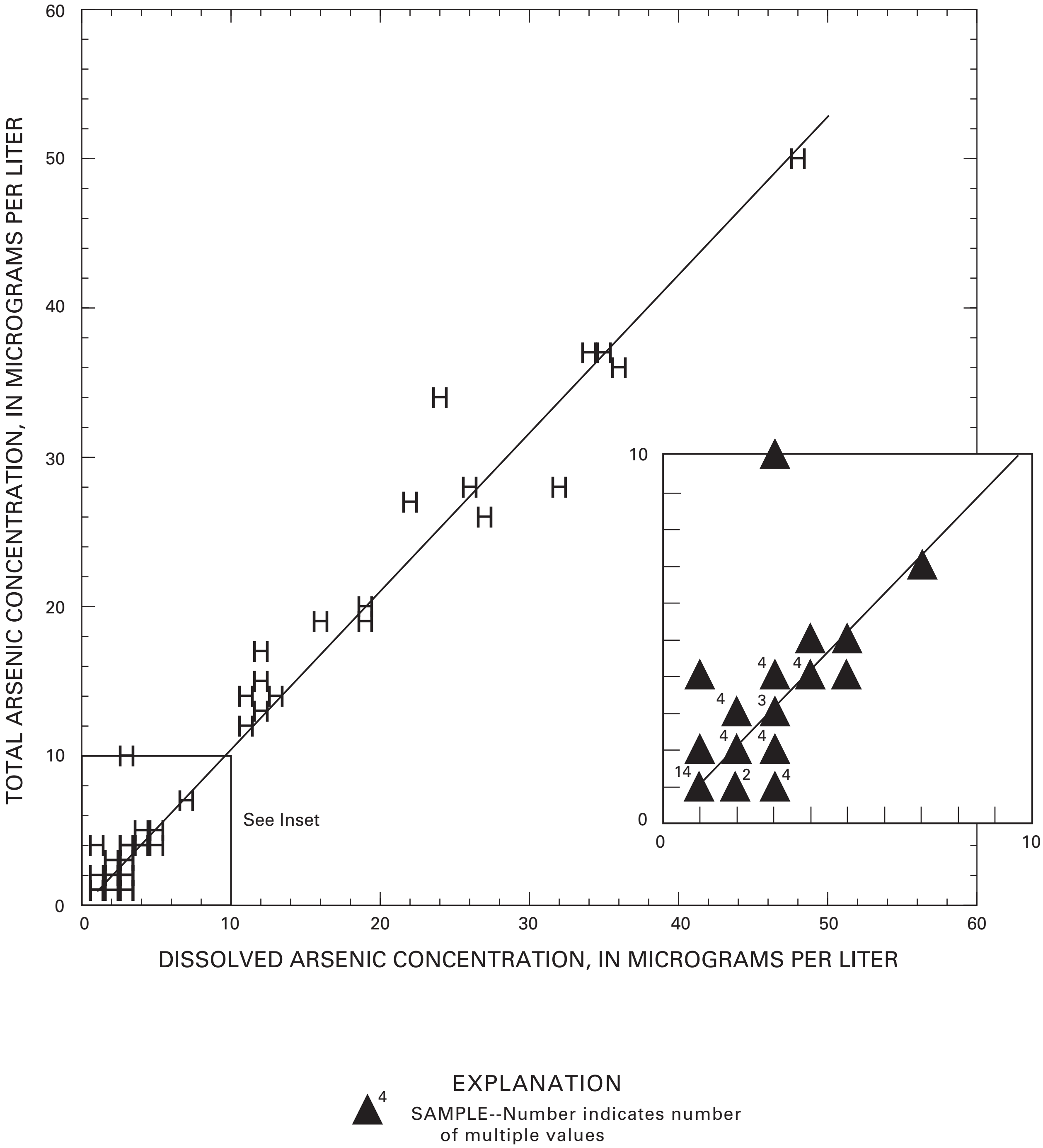


Figure 5. Regression plot of total arsenic concentration as a function of dissolved arsenic concentration for paired samples collected in and near the Spearfish Creek Basin (censored values treated as having concentration of one microgram per liter).

of total arsenic may be considerably larger than those of dissolved arsenic.

ARSENIC LOADS IN SPEARFISH CREEK

Dissolved arsenic loads for two reaches of Spearfish Creek (fig. 3) are presented in the following sections. One reach (hereafter referred to as the upstream reach) is bounded by station 06430770 (SCNL) and station 06430900 (SCAS). The other reach (hereafter referred to as the downstream reach) is bounded by station SCAS and station 06432020 (SCBS). Discharges of ungaged inflows to both reaches are estimated by solving the continuity equation for discharge (eq. 2). Arsenic loads for ungaged inflows are estimated by solving the continuity equation for loading (eq. 4). Concentrations of dissolved arsenic for the ungaged inflows are then determined by dividing the estimated load by the estimated discharge.

Upstream Reach

A summary of calculations of dissolved arsenic loads for the upstream reach of Spearfish Creek is presented in table 6. The average load of dissolved arsenic transported from the upstream reach of Spearfish Creek (calculated for station SCAS) during WY 1989-91 was 158 kg/yr (kilograms per year).

Arsenic loads from the limestone-dominated, headwater tributaries, calculated for stations SCNL and LSCNL (figs. 2 and 3) were small, relative to discharge. The mean load of 13.2 kg/yr at station SCNL represents about 8 percent of the arsenic load in 33 percent of the discharge of the upstream reach, measured at station SCAS (table 6). The mean load of 12.0 kg/yr at station LSCNL represents about 8 percent of the arsenic load in 30 percent of the discharge.

Arsenic loads transported by gaged tributaries originating in mineralized areas (Annie and Squaw

Table 6. Summary of calculations of dissolved arsenic loads, upstream reach of Spearfish Creek, water years 1989-91

[--, information not presented]

Water year	Station number and abbreviation					Ungaged inflows
	06430770 (SCNL)	06430800 (ACNL)	06430850 (LSCNL)	06430898 (SQCNS)	06430900 (SCAS)	
	Median concentration of dissolved arsenic, in micrograms per liter					
1989-91 median	1	33	1	3	4	--
	Annual discharge, in acre-feet per year					
1989	10,910	492	10,160	1,520	32,330	[1]9,250
1990	10,280	628	9,560	1,460	31,590	[1]9,660
1991	11,040	637	9,420	1,560	32,260	[1]9,600
1989-91 mean	10,740	586	9,710	1,510	32,060	[1]9,510
	Annual load of dissolved arsenic, in kilograms per year					
1989	13.5	20.0	12.5	5.6	159	[1]107
1990	12.7	25.6	11.8	5.4	156	[1]100
1991	13.6	25.9	11.6	5.8	159	[1]102
1989-91 mean	13.2	23.8	12.0	5.6	158	[1]103
	Estimated concentration of dissolved arsenic, in micrograms per liter					
1989	--	--	--	--	--	9.4
1990	--	--	--	--	--	8.4
1991	--	--	--	--	--	8.6
1989-91 mean	--	--	--	--	--	8.8

[1] Annual discharge and loads of ungaged inflows = SCAS - SCNL - ACNL - LSCNL - SQCNL.

Creeks) were larger, relative to the discharge of these tributaries. The mean load of 23.8 kg/yr at station ACNL represents about 15 percent of the arsenic load in 2 percent of the discharge. The mean load of 5.6 kg/yr at station SQCNS represents about 4 percent of the arsenic load in 5 percent of the discharge.

The mean arsenic load contributed by ungaged inflows to the upstream reach (located between stations SCNL and SCAS) was 103 kg/yr, representing about 65 percent of the arsenic load in 30 percent of the discharge. Thus, it is apparent that ungaged inflows contributed the majority of the arsenic load to the upstream reach of Spearfish Creek during WY 1989-91.

Estimated concentrations of dissolved arsenic for the ungaged inflows during WY 1989-91 also are presented in table 6. Estimated concentrations ranged from 8.4 to 9.4 μg/L, and averaged 8.8 μg/L (rounded to 9 μg/L for subsequent discussions). The variability in estimated annual concentrations shown in table 6 results primarily from variability in annual discharge. Calculations of arsenic loads also were performed using different methods of selecting representative arsenic concentrations at gaging stations, as discussed in the Methods section. These methods resulted in estimated concentrations for ungaged inflows ranging from about 8 to 11 μg/L. Because the use of other methods had no significant effect on subsequent conclusions, other results are not presented.

Ungaged inflows, which include both surface- and ground-water sources, are identified as the largest source of arsenic to the upstream reach of Spearfish Creek. The actual amount of dissolved arsenic contributed by ungaged tributaries and ground-water inflow could be somewhat different than the estimated average load of 103 kg/yr. There could be additions of arsenic from dissolution of arsenic-bearing solid phases, or from desorption of arsenic from solid surfaces, within the streambed of the upstream reach. Conversely, adsorption or precipitation of dissolved arsenic could be taking place within the upstream reach, thus removing arsenic. The amount of arsenic contributed, or removed, by these mechanisms cannot be quantified.

It is likely that one or more sources of ungaged inflow to the upstream reach of Spearfish Creek have arsenic concentrations considerably higher than the estimated average of 9 μg/L. Ungaged inflows to the upstream reach of Spearfish Creek probably include streams representative of all four types of drainages described in the discussion of stream types. Most tributaries draining the western flank of Spearfish Creek probably are of the first type. Iron Creek, which is the largest ungaged tributary to the upstream reach, is of the fourth type. Although a continuous record of discharge is not available for Iron Creek, the median instantaneous discharge when samples were collected was 1.48 ft^3/s (table 4), which is equivalent to about 1,000 acre-ft/yr, or about 10 percent of the combined discharge of the ungaged inflows (table 6). Streams draining the mineralized areas on the eastern flank probably include primarily the second (high arsenic) and third (moderate arsenic) types. Although several relatively large exposures of Pahasapa Limestone exist in this area, arsenic concentrations in streams draining this area probably are higher than from most Pahasapa Limestone exposures because there are numerous inactive gold mines in this area (DeWitt and others, 1986).

The same mass-balancing concept that was used to estimate arsenic concentrations in the ungaged inflows to Spearfish Creek can be used qualitatively to further examine the possible range of arsenic concentrations that may exist. Assuming that half of the ungaged inflow to the upstream reach is generated from each side of the basin, and that inflow from the western flank has essentially zero arsenic concentration, the arsenic concentration in the eastern tributaries would be twice the estimated, average concentration of 9 μg/L, or about 18 μg/L. Considerable variation in concentration of arsenic-rich streams has been identified (type 2 versus type 3 streams). Thus, it is likely that some of the eastern-sourced streams have arsenic concentrations much lower than 18 μg/L, and consequently, others probably have higher concentrations. Therefore, it is likely that there are other small streams draining the mineralized area on the eastern flank of Spearfish Creek that have arsenic concentrations similar to those of Annie Creek. Again, possible arsenic interactions with streambed sediments within the upstream reach could affect this conclusion. Reconnaissance-level sampling would be necessary to identify tributaries with elevated concentrations of arsenic.

Downstream Reach

The downstream reach of Spearfish Creek has previously been defined as that reach from station SCAS to station SCBS (fig. 3). Data in table 3 indicate that arsenic concentrations in this reach decrease in the downstream direction. Median concentrations of both dissolved and total recoverable arsenic decrease by 50 percent across the reach, and mean concentrations decrease by about one-third. Two possible explanations for this decrease in concentration are: (1) dilution from inflows with low arsenic concentrations; and (2) removal of arsenic from the water. Some dilution probably occurs from tributary inflows to the downstream reach. These tributaries include several perennial springs, which probably originate from the Pahasapa Limestone and/or Minnelusa Formation (Rahn and Gries, 1973), and as such, probably are low in arsenic. Also, arsenic concentrations in the direct runoff from exposures of the unmineralized formations within the drainage area of the downstream reach (fig. 2) probably are low. Examination of table 2 shows that, as a result of various withdrawals, the annual discharge decreases between stations SCAS and SCBS. With both decreasing discharge and concentration, it is apparent that a decrease in the arsenic load must occur across the downstream reach.

The downstream reach of Spearfish Creek is complicated by several diversions that account for some removal of arsenic. Therefore, an extensive water budget had to be developed for the downstream reach before an arsenic budget could be completed. The hydrologic system upon which water budgeting is based is schematically illustrated in figure 6. The entire base flow of Spearfish Creek is diverted immediately downstream from station SCAS. The flow is returned to Spearfish Creek at a hydroelectric plant at the upstream edge of the City of Spearfish. Streamflow data are available for station SCATS, which is located just downstream from the power plant; however, arsenic-concentration data are not available for this station. Additional tributary inflow to Spearfish Creek occurs downstream from the power-diversion dam. Part of this flow generally is diverted from Spearfish Creek for municipal (prior to July 1, 1993) and irrigation supply for the City of Spearfish. The remaining flow of Spearfish Creek typically is lost to sinkholes in the Pahasapa Limestone downstream from the municipal water-supply diversion. Effluent from the Spearfish waste-water treatment plant eventually is diverted outside of the Spearfish Creek Basin. Substantial irrigation diversions occur during the growing season, starting immediately downstream from station SCATS. Some irrigation water is diverted from the basin, but return flow to Spearfish Creek also is common. The City of Belle Fourche (located about 5 mi north of the Redwater River along U.S. Highway 85) diverted an average of 874 acre-ft of water per year during WY 1989-91 (Larry Little, Belle Fourche City Engineer, oral commun., 1992) from a shallow infiltration gallery in the alluvium adjacent to Spearfish Creek between the City of Spearfish and station SCBS. For the discussion that follows, it was assumed that the Belle Fourche supply represents either water withdrawn from Spearfish Creek, or tributary springflow that is prevented from reaching the creek.

Because of the complete streamflow loss that occurs upstream from station SCATS (fig. 6), water budgeting was performed for the reach from station SCATS to station SCBS. This simplified the water budget, but required accounting for arsenic removal resulting from losses in streamflow along the route of the power diversion. It also required the assumption that the arsenic concentration does not change in the streamflow diverted for power generation between stations SCAS and SCATS.

Using the basic water-balance equation, Q(IN) = Q(OUT), the water-balance equation for the downstream reach is:

$$Q(SCATS) + Q(UNGAGED) = Q(SCBS) + Q(IRR) + Q(BF) \quad (5)$$

where Q(UNGAGED) is ungaged inflow; Q(IRR) is irrigation diversions; Q(BF) is diversions for the Belle Fourche water supply; and Q(SCATS) and Q(SCBS) are discharge at the respective gaging stations.

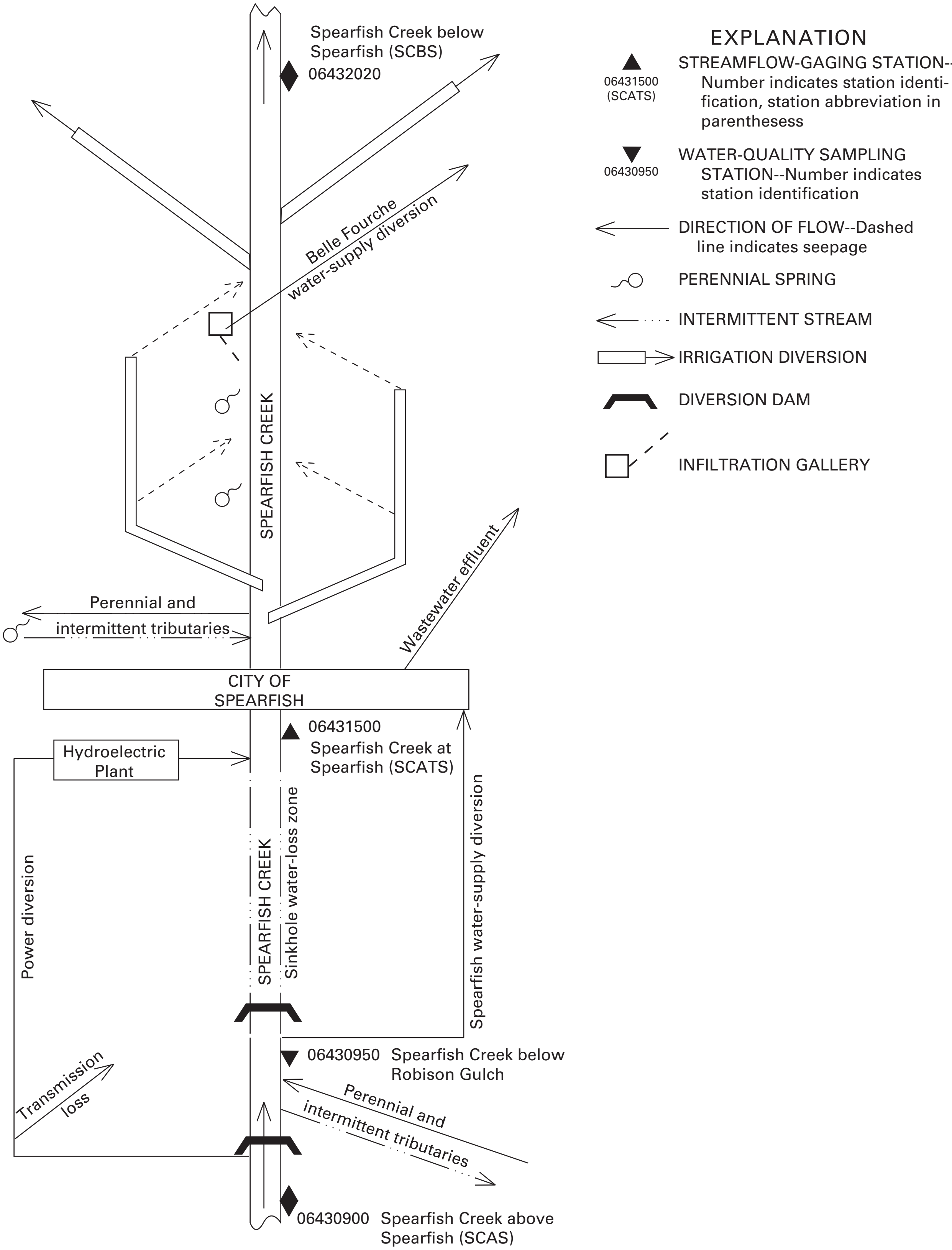


Figure 6. Schematic of hydrologic system for downstream reach of Spearfish Creek.

Equation 5 contains two unknowns, Q(UNGAGED) and Q(IRR); therefore, a second equation is necessary to estimate ungaged inflows. The average monthly and annual discharge for stations SCAS, SCATS, and SCBS for WY 1989-91, along with values calculated from these gaged discharge values are presented in table 7. The monthly differences in discharge between stations SCAS and SCATS (SCATS - SCAS) represent transmission losses along the route of the power-diversion pipeline. The monthly differences between stations SCATS and SCBS (SCBS - SCATS) reflect the combined effects of ungaged inflows and irrigation diversions. These effects are graphically illustrated in figure 7.

Rearranging equation 5 yields:

$$Q(UNGAGED) = Q(SCBS) - Q(SCATS) + Q(IRR) + Q(BF) \quad (6)$$

which, when applied to monthly discharges, and for months with no irrigation withdrawals, reduces to:

$$Q(UNGAGED) = Q(SCBS) - Q(SCATS) + Q(BF). \quad (7)$$

Examination of figure 7 allows identification of months without significant irrigation effects during WY 1989-91. Minor diversions apparently begin in April, when the difference between stations SCBS and SCATS begins to decline, in spite of increased runoff that typically occurs in April. Irrigation diversions peak in July and continue through at least September. The November difference presumably reflects irrigation return flow, and the October difference probably reflects both return flow and minor diversions. The calculated differences between stations SCATS and SCBS (SCBS - SCATS) for the months of December through March are relatively consistent (table 7) and therefore were considered most representative of natural inflows to the downstream reach of Spearfish Creek. The sum of the calculated differences for December through March (1,900 acre-ft) is equal to about 20 percent of the sum of the gaged discharge at station SCAS (9,400 acre-ft) for the same period. Discharge at station SCAS, rather than SCATS, is used to predict Q(UNGAGED), because it is measured before the power diversion and should be unaffected by transmission losses along the route of

Table 7. Average discharge, in acre-feet per month, for downstream Spearfish Creek gaging stations, water years 1989-91

[Abbreviations for station names are: SCAS, Spearfish Creek above Spearfish; SCATS, Spearfish Creek at Spearfish; SCBS, Spearfish Creek below Spearfish]

Month	Gaged discharge			Calculated values	
	06430900 SCAS	06431500 SCATS	06432020 SCBS	SCATS-SCAS	SCBS-SCATS
October	2,430	2,290	2,770	-140	480
November	2,340	2,260	3,020	-80	760
December	2,340	2,140	2,470	-200	330
January	2,390	2,060	2,500	-330	440
February	2,120	1,910	2,390	-210	480
March	2,550	2,300	2,950	-250	650
April	3,110	2,840	3,230	-270	390
May	4,670	4,360	4,390	-310	30
June	3,150	3,050	2,600	-100	-450
July	2,480	2,350	470	-130	-1,880
August	2,280	2,200	407	-80	-1,790
September	2,190	2,180	1,630	-10	-550
Annual total[1]	[2]32,050	[2]29,940	[2]28,830	-2,110	-1,110

[1]Annual totals in acre-feet per year.

[2]Minor differences from values in table 2 may occur because of rounding.

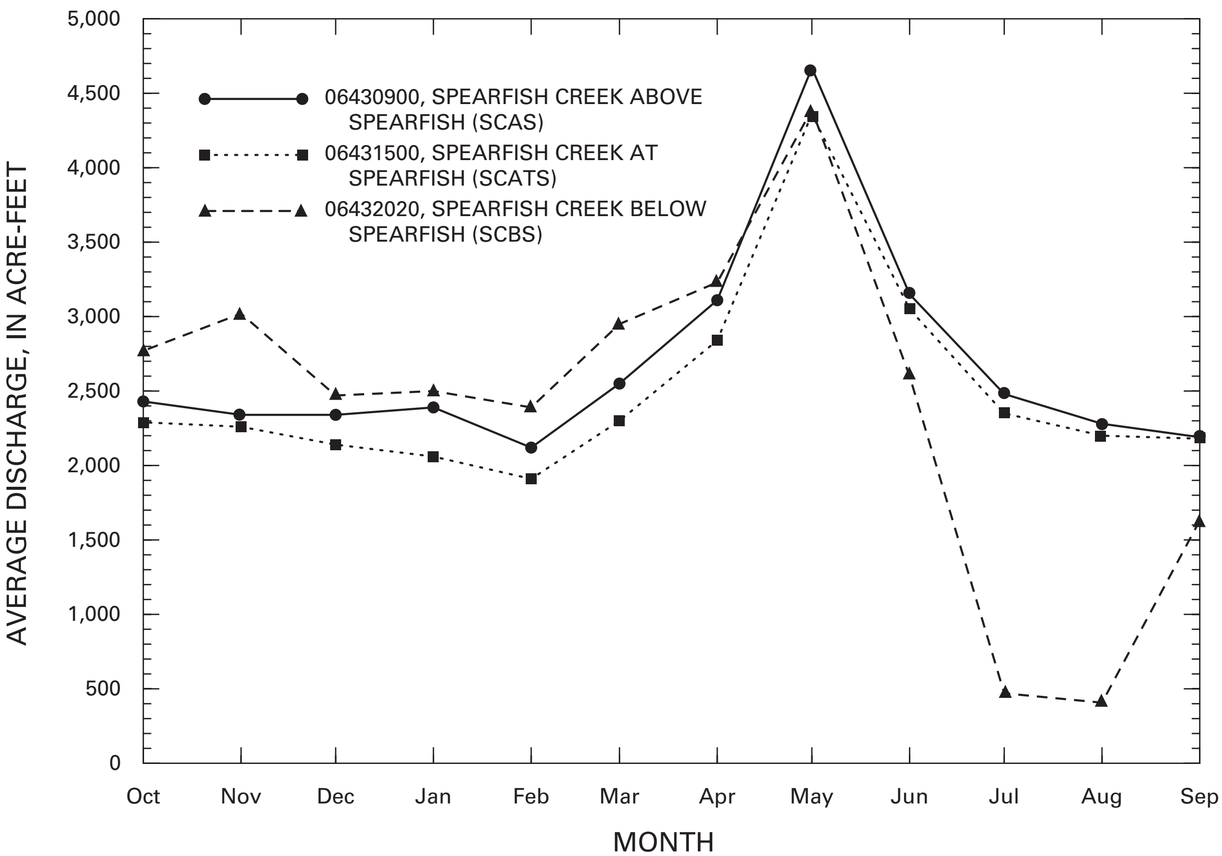


Figure 7. Average monthly discharge for gaging stations on downstream Spearfish Creek, water years 1989-91.

the power diversion. Thus, the naturalized, ungaged inflows may be estimated as:

$$Q(UNGAGED) = 0.2Q(SCAS) + Q(BF) \qquad (8)$$

Solving equation 8 by substituting for Q(SCAS) from table 7 and 874 acre-ft/yr for Q(BF) from previous discussions:

$$Q(UNGAGED) = 0.2(32,050) + 875 = 7,284 \text{ acre-ft/yr}$$

which represents the average, annual ungaged inflow between stations SCATS and SCBS during WY 1989-91. Substituting for Q(UNGAGED) from equation 8, into equation 6:

$$0.2Q(SCAS) + Q(BF) = Q(SCBS) - Q(SCATS) + Q(IRR) + Q(BF) \text{ or}$$

$$Q(IRR) = 0.2(32,050) - 28,830 + 29,940 = 7,520 \text{ acre-ft/yr.}$$

Having solved the water-balance equation, the arsenic budget for the downstream reach of Spearfish Creek can be developed. The mass-balance equation, MASS(IN) = MASS(OUT), is obtained by multiplying each term of equation 5 by the appropriate concentration, thus:

$$QC(SCATS) + QC(UNGAGED) = QC(SCBS) + QC(IRR) + QC(BF). \qquad (9)$$

Because arsenic-concentration data are available for station SCAS rather than for station SCATS, another mass-balance equation is written:

$$QC(SCAS) = QC(SCATS) + QC(TRANS) \qquad (10)$$

where QC(TRANS) is the arsenic load lost in transmission losses along the route of the power- diversion pipeline. Substituting for QC(SCATS) in equation 9:

$$QC(SCAS) - QC(TRANS) + QC(UNGAGED) = QC(SCBS) + QC(IRR) + QC(BF). \qquad (11)$$

Substituting discharge values from table 7 and from previous discussions:

$$32,050C(SCAS) - 2,110C(TRANS) + 7,284C(UNGAGED) = 28,830C(SCBS) + 7,520C(IRR) + 874C(BF) \quad (12)$$

The concentration of the transmission losses is assumed equal to the concentration at station SCAS, immediately upstream from the power-supply diversion. The concentration of the diversions for irrigation and for the Belle Fourche water supply is assumed equal to the average of the concentrations at stations SCAS and SCBS. This assumption is made because the concentration apparently decreased across this reach (table 3). The source of the Belle Fourche municipal supply may be at least partially derived from springflow, which may be of lower concentration than Spearfish Creek. The difference in calculated loads that occurs from the choice of concentration for this relatively minor diversion is negligible, however. Simplifying equation 12, based on these assumptions, results in:

$$29,940C(SCAS) + 7,284C(UNGAGED) = 28,830C(SCBS) + 8,394C(SCAS + SCBS)/2. \quad (13)$$

By substituting known values for arsenic concentration at stations SCAS and SCBS, equation 13 can be solved directly for the concentration of ungaged inflows. For these stations, it is questionable whether the median or mean is most representative of central tendency for dissolved arsenic concentrations (table 3). Thus, equation 13 is solved using both median and mean concentrations of dissolved arsenic, yielding calculated concentrations for ungaged inflows of -5.1 and -1.6 mg/L, respectively. Because both solutions are negative, it is not possible to calculate the arsenic concentration of ungaged inflows; however, it is probable that concentrations are similar to those of type 1 streams, generally at or below the detection limit of 1 mg/L (table 5). It also is apparent that dilution, alone, cannot account for the decrease in arsenic concentration that occurred. Furthermore, accounting for removal of water from Spearfish Creek does not account for all of the arsenic removal that occurred. Thus, it can be concluded that removal of arsenic from the water occurs as a result of some chemical process or processes.

Two possible chemical processes for arsenic removal, by methods other than physical transport, are recognized. The first possibility is the adsorption of arsenic on the surface of sediments in the channel of Spearfish Creek. This also could occur on sediments in the alluvium adjacent to the creek, as a result of interchange of water between the alluvial aquifer and the creek. This process is suggested as a limiting condition to arsenic concentrations along Whitewood Creek (Goddard, 1989). The second possibility is chemical precipitation, again within either the stream channel or alluvial aquifer.

Equation 13 can be modified to account for arsenic removal in addition to that resulting from diversions from Spearfish Creek between stations SCATS and SCBS. The left side of equation 13 represents the arsenic input to the downstream reach, and the right side represents the arsenic output, or the sum of the arsenic loads transported from the reach by Spearfish Creek and various diversions. Assuming the concentration of ungaged inflow is zero and introducing the term Unaccounted Removal (REMOVAL), results in:

$$29,940C(SCAS) = 28,830C(SCBS) + 8,394C(SCAS + SCBS)/2 + REMOVAL. \quad (14)$$

Estimated loads of dissolved arsenic into and out of the downstream reach of Spearfish Creek, calculated by substituting both median and mean concentrations into equation 14, are presented in table 8. The average of results from calculations using median and mean concentrations also are presented in table 8, and will be used as the most reliable estimate of arsenic loads

Table 8. Summary of calculations of dissolved arsenic loads, downstream reach of Spearfish Creek, water years 1989-91

Arsenic input, in kilograms per year	Arsenic output, in kilograms per year	Unaccounted arsenic removal, in kilograms per year
Average annual loads, water years 1989-91, based on median concentrations		
148	102	46
Average annual loads, water years 1989-91, based on mean concentrations		
126	111	15
Average of loads based on median and mean concentrations		
137	106	31

for the downstream reach. During WY 1989-91, about 137 kg/yr of dissolved arsenic was transported into the downstream reach. About 106 kg/yr, representing 77 percent of the arsenic input, can be accounted for in transport from the reach. Thus, about 31 kg/yr, representing 23 percent of the arsenic input, can not be accounted for, except as a result of removal through mechanisms such as adsorption or precipitation.

Results presented in table 8 are based on the assumption that the arsenic concentration of ungaged inflows is zero. Because the ungaged inflows undoubtedly have some finite arsenic concentration, arsenic removal actually is somewhat greater than shown in table 8. At a concentration of 0.5 µg/L, which is comparable to concentrations in the headwater reaches of Spearfish Creek, the ungaged inflows would contribute only 4.5 kg of arsenic in the estimated annual discharge of 7,284 acre-ft. Neglecting this small amount of additional arsenic input results in a more conservative estimate of arsenic removal.

Arsenic concentrations measured in the downstream reach are small enough and sample numbers are few enough that it is valid to question whether or not the data accurately represent actual in-stream conditions. Although sample numbers cannot be addressed, the concentrations can. Analytical error for the hydride-generation atomic adsorption method used by the USGS National Water Quality Laboratory is estimated as plus-or-minus 5 percent for the range of 1 to 15 µg/L (Pritt and Jones, 1989). All of the measured values of arsenic concentration for the downstream reach of Spearfish Creek fall within that range. At the midpoint of the range, the uncertainty calculates to plus-or-minus 0.4 µg/L of either dissolved or total arsenic, such that each individual value and each calculated median or mean could be expressed with an uncertainty of approximately plus-or-minus 0.4 µg/L. Neither the median nor the mean concentrations overlap when expressed with their analytical uncertainties and compared between stations SCAS and SCBS (table 3). However, when the analytical error is applied to the loading calculations, the calculated loads into and out of the reach do overlap when using mean concentrations. Although laboratory analytical uncertainty cannot account for the calculated decline in arsenic concentration between SCAS and SCBS, it may be a factor in calculation of arsenic loads.

Calculations of arsenic loads in the downstream reach are based on numerous assumptions, including estimation of discharge for ungaged inflows and irrigation diversions and estimation of arsenic concentrations for diversions. Some of the irrigation water is diverted from the Spearfish Creek Basin; however, most of the irrigation occurs within the basin, in which case some arsenic is returned to the stream channel in the irrigation return flow. The method of estimating the annual volume of irrigation diversion actually yields the net diversion, or total diversion less return flow, that occurs between stations SCATS and SCBS. Therefore, the implicit assumption is that the arsenic concentration of the return flow is equal to the concentration of the diversions. The actual arsenic concentration of the return flow could increase or decrease, dependent upon processes governed by soil and water chemistry, which are beyond the scope of this report.

The aforementioned assumptions, in combination with analytical and statistical uncertainties, result in a large potential margin of error for calculated arsenic loads for the downstream reach. The margin of error could be large enough that no chemical removal actually occurs. Conversely, the amount of arsenic removed could be somewhat larger than estimated. It is also possible that chemical removal, which is governed by various equilibrium conditions, could occur under some conditions, but not under others. Thus, the estimate of arsenic removal from the downstream reach should be used with caution.

In spite of the uncertainty associated with calculated arsenic loads, one important observation can be made. Although it is difficult to state with certainty that chemical removal of arsenic occurs, it is apparent that arsenic concentrations do not increase as a result of interaction with streambed and alluvial sediments within the downstream reach of Spearfish Creek. Bed sediments and equilibrium conditions for arsenic concentrations within the downstream reach probably are very similar to those within the upstream reach of Spearfish Creek. Thus, it also is unlikely that interaction with streambed sediments is a significant source of arsenic within the upstream reach.

SUMMARY AND CONCLUSIONS

Elevated concentrations of arsenic are recognized as a potential problem in Black Hills streams draining mineralized areas with deposits of gold ore. Arsenic concentrations approaching the MCL of 50 µg/L have been identified in Annie Creek, a tributary to Spearfish Creek with significant gold-ore deposits. Not all mineralized drainages have elevated concentrations of arsenic. The drainage area of Squaw Creek is geologically similar to Annie Creek; however, in-stream arsenic concentrations average only 3 to 4 µg/L. Because of these differences, streams within the study area were classified into four types according to geologic characteristics and in-stream arsenic concentrations.

The first stream type is one draining generally unmineralized areas, such as exposures of the Pahasapa Limestone and Minnelusa Formations, which lack significant arsenic sources and have low in-stream arsenic concentrations (generally at or below the detection limit of 1 µg/L). The headwaters of Spearfish and Little Spearfish Creeks are good examples. The second type includes streams such as Annie Creek, with abundant arsenic in source rocks and with high in-stream concentrations (generally greater than 10 µg/L). The third type includes streams such as Squaw Creek, with abundant arsenic sources, but with only moderate in-stream concentrations (generally approaching 5 µg/L). The fourth type of stream is one draining a mixture of mineralized and unmineralized areas and with in-stream arsenic concentrations reflecting a mixture of low-arsenic and higher arsenic water. Arsenic concentrations in the resulting mixtures generally range from 1 to 5 µg/L, depending on the proportions of the mixture. Spearfish Creek downstream from the mineralized areas is exemplary of the fourth stream type.

Discharge and arsenic-concentration data are available for three gaging stations on the main stem of Spearfish Creek, which define two stream reaches (upstream and downstream from station 06430900, Spearfish Creek above Spearfish). Discharge and arsenic-concentration data also are available for gaging stations on three tributaries within the upstream reach. Mass-balance calculations were performed for both reaches to estimate arsenic loads and concentrations for ungaged inflows to Spearfish Creek. This was done to determine if arsenic concentrations in other tributaries are likely to be similar to those of Annie Creek.

The mean load of dissolved arsenic transported during WY 1989-91 from the upstream reach of Spearfish Creek, calculated for station 06430900, was 158 kg/yr. Relatively small arsenic loads were contributed to the upstream reach by limestone-dominated, headwater tributaries that originate primarily within unmineralized exposures of the Pahasapa Limestone and Minnelusa Formation. The combined, mean arsenic loads at station 06430770, Spearfish Creek near Lead, and station 06430850, Little Spearfish Creek near Lead, were 25.2 kg/yr. These loads resulted from small concentrations in a large discharge and represent about 16 percent of the arsenic load in about 63 percent of the discharge of upstream Spearfish Creek. Arsenic loads transported by gaged tributaries originating in mineralized areas were larger, relative to the discharge of these tributaries. The mean load from Annie Creek of 23.8 kg/yr, calculated for station 06430800, represents about 15 percent of the arsenic load in about 2 percent of the discharge. The mean load from Squaw Creek of 5.6 kg/yr, calculated for station 06430898, represents about 4 percent of the arsenic load in about 5 percent of the discharge.

Arsenic loads contributed by ungaged inflows to the upstream reach (located between stations 06430770 and 06430900) averaged 103 kg/yr during WY 1989-91. This represents about 65 percent of the annual arsenic load to the reach in about 30 percent of the discharge. The calculated loads from ungaged inflows include all arsenic contributed by surface- and ground-water sources, as well as any additions of arsenic from dissolution of arsenic-bearing solid phases, or from desorption of arsenic from solid surfaces, within the streambed of the upstream reach.

The ungaged inflows to upstream Spearfish Creek probably include all four stream types, classified relative to arsenic conditions. Mass-balance calculations indicate that the average concentration of dissolved arsenic for ungaged inflows was about 9 μg/L during WY 1989-91. Presuming that half of the ungaged tributary inflow is generated from each side of the basin, and that western tributaries have, in effect, arsenic concentrations of zero, the arsenic concentration in water from the eastern tributaries would average about 18 μg/L. If some of the ungaged tributaries from the eastern, mineralized areas are of the third or fourth type (with only moderate to low arsenic levels), then arsenic concentrations in other ungaged tributaries would be even higher. Thus, it is possible that some ungaged inflows could have arsenic concentrations similar to those of Annie Creek. Possible arsenic interactions with streambed sediments within the upstream reach could affect this conclusion. Reconnaissance-level sampling would be necessary to identify tributaries with elevated concentrations of arsenic.

Arsenic concentrations decreased during WY 1989-91 within the downstream reach of Spearfish Creek, defined as the reach between station 06430900, Spearfish Creek above Spearfish, and station 06432020, Spearfish Creek below Spearfish. Median concentrations for both dissolved and total recoverable arsenic decreased within the downstream reach by 50 percent (from 4 to 2 μg/L). Mean concentrations decreased by about one-third.

Annual discharge also decreased across the downstream reach during WY 1989-91, because of numerous withdrawals and diversions within the reach. With decreases in both concentration and discharge, it is apparent that the arsenic load transported out of the reach by Spearfish Creek must be smaller than the load entering the reach. After accounting for diversions from Spearfish Creek, arsenic output from the reach still remains smaller than arsenic input to the reach. These conditions result in a negative solution for the concentration of ungaged inflows; thus, the concentration of ungaged inflows cannot be determined. It is concluded; however, that concentrations of ungaged inflows probably are similar to those of type 1 streams, generally at or below the detection limit of 1 μg/L.

Because transport of arsenic out of the downstream reach is less than transport into the reach, it is apparent that removal of arsenic occurs as a result of some chemical process or processes. Two possible chemical processes that could occur are: (1) adsorption of arsenic on sediments within the stream channel, or adjacent alluvium; and (2) chemical precipitation, again within either the stream channel or alluvial aquifer.

Numerous uncertainties exist in calculation of arsenic loads in the downstream reach; thus, it is difficult to conclude decisively that chemical removal of arsenic actually occurs. It can be concluded, however, that arsenic concentrations do not increase significantly in the downstream reach as a result of interactions with streambed and alluvial sediments.

Bed sediments and equilibrium conditions for arsenic concentrations within the downstream reach probably are very similar to those within the upstream reach of Spearfish Creek. Thus, it also is unlikely that interaction with streambed and alluvial sediments is a significant source of arsenic within the upstream reach of Spearfish Creek.

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