COMPOSITION, DISTRIBUTION, AND HYDROLOGIC EFFECTS OF CONTAMINATED SEDIMENTS RESULTING FROM THE DISCHARGE OF GOLD MILLING WASTES TO WHITEWOOD CREEK AT LEAD AND DEADWOOD, SOUTH DAKOTA

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CONVERSION FACTORS

For readers who may prefer to use metric units rather than inch-pound units, the conversion factors and abbreviations for the units used in this report are listed below:

Multiply	By	To obtain
acre	4,047	square meter
acre	0.4047	hectare
inch	25.4	millimeter (mm)
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
pound (lb)	0.4536	kilogram
ton	907.2	kilogram
gallon (gal)	3.785	liter
gallon per minute (gal/min)	0.06308	liter per second
cubic foot per second (ft^3/s)	0.02832	cubic meter per second

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ABSTRACT

Between 1876 and 1977, as much as 100 million tons of mining and milling wastes derived from gold-mining activities were discharged into Whitewood Creek and its tributaries at Lead and Deadwood, South Dakota. An unknown, but substantial proportion of these wastes were deposited on the flood plains along Whitewood Creek and the Belle Fourche River either as thick deposits adjacent to meanders or as extensive, thinner overbank deposits. The wastes mostly are fine-ground mill tailings that originally contained 7 to 8 percent iron-sulfide minerals, including the mineral arsenopyrite (FeAsS), as well as metallic mercury and cyanide compounds added during the milling process. The potential hazard of the wastes caused the U.S. Environmental Protection Agency to list an 18-mile reach of Whitewood Creek and the adjacent flood plain as an Interim Priority Site under the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA).

Mineral composition and chemical characteristics of contaminated-sediment (mixture of wastes and naturally occurring sediment) samples collected from the flood plains along Whitewood Creek and the Belle Fourche River indicate that, although most of the sulfide minerals originally present apparently have been weathered to secondary oxides and hydroxides, the arsenic concentration is as much as 11,000 µg/g (micrograms per gram). Comparisons between natural, uncontaminated-sediment samples and contaminated-sediment samples indicate that arsenic is the most anomalous trace constituent; uncontaminated-sediment samples had a mean arsenic concentration of 9.2 µg/g, whereas contaminated-sediment samples had a mean arsenic concentration of 1,920 µg/g.

Results of a stratified, random, sediment-sampling program indicate that most of the near-surface sediments on the flood plains along Whitewood Creek and the Belle Fourche River are contaminated by arsenic. On the flood plain along Whitewood Creek downstream from the junction with Gold Run, 82 percent of the near-surface sediment samples contained anomalously large concentrations of arsenic; the mean arsenic concentration was 1,400 µg/g with a maximum concentration of 11,000 µg/g. Although the arsenic concentrations were anomalously large in 71 percent of the sediment samples collected from the Belle Fourche River flood plain, the mean arsenic concentrations gradually decreased downstream from about 1,300 µg/g just downstream from the junction with Whitewood Creek to about 400 µg/g near the mouth. There was less arsenic contamination of the Cheyenne River flood plain where arsenic in near-surface sediment samples averaged about 70 µg/g.

Appreciable surface-water contamination caused by the contaminated sediments is confined to Whitewood Creek and a reach of the Belle Fourche River downstream from the junction with Whitewood Creek. As expected, the most significant contaminant is arsenic. In Whitewood Creek, the dissolved-phase concentrations vary from about 20 to 80 µg/L (micrograms per liter) during the year in response to variations in ground-water inflow and dilution. The suspended-phase arsenic concentrations vary from about 20 to 8,000 µg/L during the short term in response to rapid changes in suspended-sediment concentration. The relations among discharge, suspended-sediment concentration, and total-recoverable arsenic concentrations indicate that total-recoverable arsenic concentrations exceeded the criteria of 200 milligrams per liter recommended by the U.S. Environmental Protection Agency for livestock water about 32 percent of the time in Whitewood Creek during the study.

Ground-water contamination in the alluvial aquifers along Whitewood Creek and the Belle Fourche River is limited to areas in direct contact with large deposits of contaminated sediments. Aquifer-wide contamination evidently is prevented by the slow oxidation rate of sulfide minerals in the contaminated sediments combined with the carbonate buffering capacity of the natural, uncontaminated sediments. Arsenic is the only constituent in ground water directly attributable to the wastes that exceeds a primary drinking-water standard established by the U.S. Environmental Protection Agency. The dissolved-arsenic concentration was larger than the standard of 50 µg/L in water from 4 of 36 sampled wells and had a maximum concentration of 280 µg/L. Solubility of arsenic compounds at the pH-Eh conditions measured in the alluvial aquifer indicates that dissolved-arsenic concentrations are controlled not by the solubility of these compounds, but rather by some other process such as sorption-desorption equilbria with metallic hydroxides.

INTRODUCTION

For about 100 years, since the original discovery of gold at Deadwood in 1875 until the late 1970's, huge volumes of mining and milling wastes were discharged into Whitewood Creek and its tributaries at Lead and Deadwood, South Dakota. The wastes were transported down Whitewood Creek to the Belle Fourche River, then to the Cheyenne River, and then to the Missouri River (fig. 1). However, a substantial proportion of these wastes was deposited on the flood plains along Whitewood Creek and the Belle Fourche and Cheyenne Rivers.

Most of the wastes consist of finely ground mill tailings. The composition of the mill tailings is similar to the iron-magnesium silicate and carbonate mineralogy of the ore bodies. The mill tailings also contain metallic sulfide minerals associated with the gold ore. Iron-sulfide minerals--pyrrhotite, pyrite, and arsenopyrite--are common; arsenopyrite (FeAsS) is associated with the gold ore at Lead. Mill tailings being discharged to Whitewood Creek in June 1971 contained a daily load of 2,735 tons of suspended solids including 9.5 tons of arsenic (U.S. Environmental Protection Agency, 1973) presumably in the form of arsenopyrite. If these loads are considered typical of daily discharges during the period of modern mining operations (since about 1920), then about 75 million tons of suspended solids including 270,000 tons of arsenic have been discharged to Whitewood Creek since 1920. In addition, earlier processing of ore by stamp mills, also contributed large quantities of wastes to Whitewood Creek.

In addition to the potentially hazardous materials contained in the ore, and thus discharged with the mill tailings, mercury and cyanide used in the milling processes also are present in the wastes. Gold was recovered from milled ore by mercury amalgamation from the earliest days of mining operations through 1970. Metallic mercury was added to the ore during the grinding phase of the operation and was recovered using copper amalgamators. Some mercury was not recovered during the processing and is present in the wastes. Sampling in 1970 by the U.S. Environmental Protection Agency (1971) indicated a daily discharge of 12 to 40 lb of mercury to Whitewood Creek. The U.S. Environmental Protection Agency (1973a) detected concentrations of mercury in sediment samples collected from "tailings-like" deposits that ranged from 0.1 to 4.1 μg/g (micrograms per gram) and averaged 0.6 μg/g. This contrasted to a "background" concentration of mercury in uncontaminated sediment of 0.1 μg/g. Cyanidation, or the recovery of gold using dilute solutions of calcium cyanide, was begun in 1901 and is still (1984) the process used for gold recovery. Cyanide contamination of Whitewood Creek and the Belle Fourche River was a serious problem in the past (total cyanide concentration in Whitewood Creek ranged from 0.6 to 9.1 mg/L (milligrams per liter) and averaged 2.6 mg/L (South Dakota Department of Health, 1960a)) and is still (1984) readily detectable in the contaminated sediments along Whitewood Creek.

From the beginning of the large-scale, gold-recovery operations at Lead in the late 1800's, to about the mid-1950's, disposal of milling wastes into Whitewood Creek was an acceptable practice. As people became more aware of environmental degradation, and the human-health problems that could result from such disposal, studies were begun to quantify the Whitewood Creek contamination problem, to determine if human health was being adversely affected, and to seek solutions. The first systematic studies undertaken by the South Dakota Department of Health (1960a, b) quantified the suspended-solids and cyanide loads discharged to Whitewood Creek, recommended further study, and reported that a comprehensive water-pollution-control program was needed if any beneficial use was to be made of water from Whitewood Creek and a substantial reach of the Belle Fourche River. A study by the South Dakota Department of Game, Fish and Parks (Thilenius, 1965) determined that aquatic bottom organisms were not present in Whitewood Creek downstream from the waste discharges or in the Belle Fourche River for 60 mi downstream from the junction with Whitewood Creek. In 1970-71, a series of studies by the U.S. Environmental Protection Agency (1971) were undertaken to document and characterize the discharge of mill tailings to Whitewood Creek, and to determine the magnitude and extent of the resultant pollution on surface water, ground water, and aquatic life in the Cheyenne River basin. Of major concern during these studies was the possible serious environmental hazard created by mercury contamination. The U.S. Environmental Protection Agency (1971; 1973b) determined that mercury concentrations in fish from the Cheyenne River arm of Lake Oahe exceeded 0.5 part per million. A study by the University of South Dakota (Heisinger and others, 1974) determined that without restrictions on fish consumption, persons eating fish from the Cheyenne River arm would accumulate mercury in their body tissue slightly in excess of "safe" levels. These studies and the increasing knowledge of the environmental hazards of mercury led to the discontinuance of mercury in the gold-recovery operations in December 1970.

One common conclusion of all these pollution studies was that Whitewood Creek and the Belle Fourche and Cheyenne Rivers would remain contaminated until the discharge of milling wastes was discontinued. To comply with new environmental laws, the Homestake Mining Co., the sole operator of mining operations at Lead since about 1890, implemented the Grizzly Gulch Tailings Disposal Project. A 230-ft high earth and rockfill dam was constructed across Grizzly Gulch, a steep, narrow canyon about 3 mi south of the mine and mill area, to create an impoundment area for tailings storage. The tailings-disposal system became operational on December 1, 1977, and no discharge of mill tailings into Whitewood Creek has occurred since that time.

Problem

The contamination of Whitewood Creek and the downstream rivers was alleviated by the discontinuance of mill-tailings discharge in 1977. However, there is concern by Federal, State, and local officials, and local land owners that the huge deposits of contaminated sediments along these streams were continuing to seriously degrade surface water and ground water in the Cheyenne River basin. Because the contaminated sediments were deposited by natural surface-water flow, the sediments are subject to resuspension and downstream movement, particularly during periods of high discharge when contaminated sediments could enter the streams by streambed scouring, inundation of normally dry streamside deposits, or by overland runoff. Surface-water samples collected from the Belle Fourche and Cheyenne Rivers during the years since discontinuance of mill-tailings discharge to Whitewood Creek, continue to contain unusually large concentrations of arsenic, iron, and manganese. Of particular concern is the possible contamination of the alluvial aquifers under the flood plains along Whitewood Creek and the Belle Fourche and Cheyenne Rivers. A number of farms and ranches obtain irrigation and stock water from the streams and domestic and stock water from wells completed in the alluvial aquifers; this water may be hazardous to livestock and people if it contains substantial concentrations of contaminants. During a study by Stach and others (1978), arsenic concentrations ranging from 2.5 to 1,530 μg/L (micrograms per liter) were detected in ground water from areas with large deposits of contaminated sediments. They concluded that the arsenic was derived from bacterial action solubilizing arsenic from arsenophrite. In the winter of 1974-75, about 50 Holstein dairy cattle, which were part of a dairy operation located adjacent to Whitewood Creek, died of unknown causes. Later, a study by the South Dakota State University, Department of Veterinary Science (Bergeland and others, 1976) concluded the cattle had died of arsenic toxicosis due to consumption of corn silage that had been contaminated with mining wastes during silo-filling operations.

The conclusions of the two studies were challenged by representatives of Homestake Mining Co. However, the evidence from these and other studies indicated a possible environmental problem along Whitewood Creek. This undefined hazard caused the U.S. Environmental Protection Agency to list an 18-mi reach of Whitewood Creek and the adjacent flood plain as an Interim Priority Site, under the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA).

Before an accurate evaluation of the potential hazard could be made, it was necessary to conduct systematic investigation of the hydrologic effects of the contaminated sediments. Therefore, in the fall of 1982, the South Dakota Department of Water and Natural Resources asked the U.S. Geological Survey to conduct a 2-year study of the potential problem. The study area, shown in figure 1, included the streams and adjacent flood plains of the following: Whitewood Creek from southeast of the mining area at Lead to the mouth, the Belle Fourche River from west of the junction with Whitewood Creek to the mouth, and the Cheyenne River from south of the junction with the Belle Fourche River to Lake Oahe.

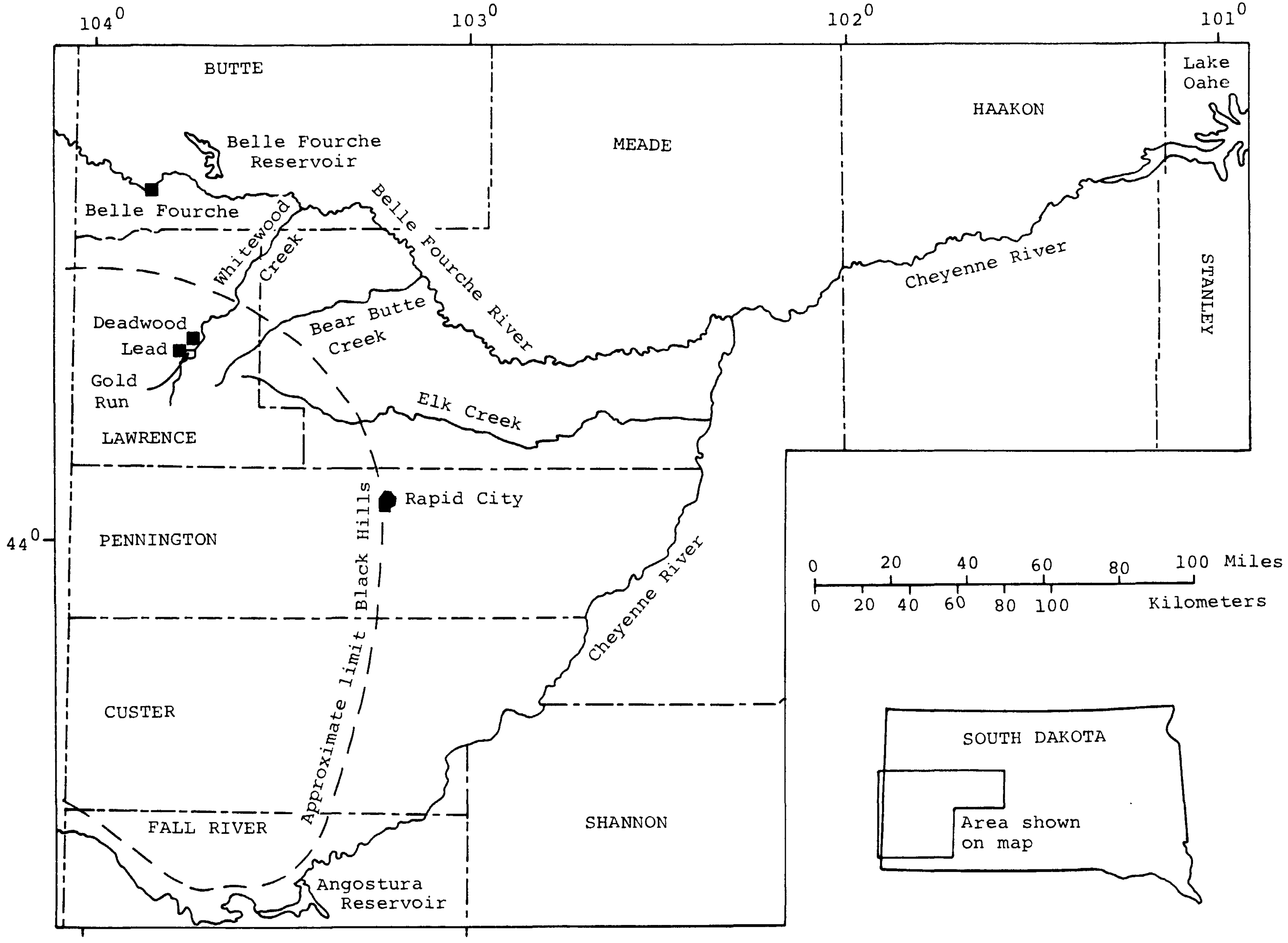

Figure 1.--Location of study area in South Dakota.

Objectives and Methods of Study

The objectives of the study were to determine the composition and distribution of the contaminated sediments, and the extent and rate of movement of surface- and ground-water contamination in the study area. The investigation included four main elements:

1. Definition of the mineral composition and the physical and chemical characteristics of the contaminated sediments. Thirteen uncontaminated-sediment samples and 95 contaminated-sediment samples were collected in the study area. All the samples were analyzed for chemical composition. Selected samples were analyzed for mineral composition and physical characteristics.

2. Determination of the areal extent of contamination on the flood plains of Whitewood Creek and the Belle Fourche and Cheyenne Rivers. The large size of the study area precluded on-the-ground mapping and the use of remote-sensing techniques was not effective due to vegetative cover and mixing of the wastes with natural sediments. A geochemically based, random, sediment-sampling program was conducted that allowed inferences to be made regarding the distribution of the contaminated sediments by determining the distribution of arsenic.

3. Documentation of the movement of contaminated sediments or any resultant leachate in the surface flow of Whitewood Creek and the Belle Fourche and Cheyenne Rivers. Monitoring programs were established that: (1) Collected data on water chemistry and suspended-sediment concentration, (2) defined the discharge and water-chemistry profile of the study reaches, and (3) determined temporal variations in water chemistry and suspended-sediment concentration.

4. Identification of any ground-water contamination of the alluvial aquifers caused by leaching of contaminated sediments on the flood plains along Whitewood Creek and the Belle Fourche and Cheyenne Rivers. Thirty-nine wells specifically designed for ground-water monitoring were drilled into the alluvial aquifers in areas likely to be affected by leachate and 36 wells were sampled seasonally; 3 wells were not sampled because 2 were dry and 1 was destroyed. This phase of the study was directed toward detecting contamination of the alluvial aquifers rather than investigating the transport of solutes within the aquifers.

Purpose and Scope of Report

This report presents the data-collection techniques, summary tables of the data, and the interpretive conclusions reached during the study. The intent is to describe the extent and magnitude of contamination resulting from the mining and milling wastes discharged to Whitewood Creek. Several aspects that could effect water use in the basin, such as the large selenium concentration in ground water, but that are not related to the mining activities, are not discussed in detail.

Extensive descriptions of data-collection techniques are included because of the undefined nature of the contamination problem. Individual data measurements are not included because of the enormous quantity of data collected during the study. However, summary tables, which include statistical analysis of the data, are included and generally were used as the basis for the conclusions. Some individual data measurements are necessary to support the analysis; therefore, some data measurements are included in several figures and tables, or are described in the text. All data collected during the study are available from the U.S. Geological Survey office in Rapid City, South Dakota, or from the U.S. Geological Survey's WATSTORE computer-data storage system.

Acknowledgments

Many people provided data, or technical and professional help, to the author during the course of this study. Margot Nielson, Keith O. Schwab, and Linda Haas of the U.S. Environmental Protection Agency provided assistance with the laboratory and drilling contracts. George Tomas Manthey of the South Dakota Department of Water and Natural Resources provided information on previous studies, effluent data, and participated in the report review. A good working relationship was maintained between Homestake Mining Co. and the U.S. Geological Survey throughout the investigation due largely to discussions with Frederick D. Fox and Terry Mudder. Work by and discussions with John A. Cherry, Francois M. Morel, Jerald L. Schnoor, and Jim V. Rouse were instrumental in formulating the concepts of the ground-water geochemistry.

Appreciation is extended to the many residents and land-owners throughout the study area for providing gaging-station and monitoring-well sites, and for permitting access to sediment and surface-water sampling sites. Without the helpful attitude of the many residents along Whitewood Creek and the Belle Fourche and Cheyenne Rivers, the successful completion of this study would not have been possible.

COMPOSITION OF THE CONTAMINATED SEDIMENTS

Contaminated sediments on the flood plains along Whitewood Creek and the Belle Fourche River occur in deposits that can be easily identified by color, texture, and other characteristics. The deposits normally consist of well-sorted, fine-grained particles with generally laminar bedding. The deposits have three distinct lithologies. The first, limited in extent to the more steeply sloping reaches between and near the towns of Lead and Whitewood, is a reddish-brown, cemented, conglomerate-like deposit. The second is a brown to red, fine-grained silty sand. The third, nearly identical in appearance to milling wastes now produced by the mining operations at Lead, is a medium to dark gray, fine-grained, sand-silt mixture. The texture is similar to that of the second lithology and the color difference is related to the degree of weathering the sediments have undergone. The reddish-brown and dark gray sediments commonly are found alternating in complex patterns within a deposit. Color banding commonly occurs along the edges of the dark gray sediments and in concentric rings around tree roots or worm holes. The color banding is an indication that oxidation of the wastes is occurring at exposed surfaces with the consequent formation of secondary iron minerals. However, it is not known if the different lithologies are the result of substantial variations in the mineral, physical, or the chemical composition of the material.

Data Collection

Ninety-five samples were collected from deposits of visually identified contaminated sediments present in the study area. Sampling included the brown to red sands, associated by other investigators (U.S. Environmental Protection Agency, 1973) with early mill-tailings discharges, and the gray silt considered characteristic of more recent mill-tailings discharges. Most contaminated-sediment samples were collected from shallow trenches dug into streambank deposits rather than from the ground surface. The trenching allowed visual inspection of the cross section of the deposit. Generally, if several visually distinct sediments were present at one location, each was sampled. The remaining contaminated-sediment samples were collected from pits or drill cores. Most of the samples were collected from deposits along the Belle Fourche River. Contaminated sediments were extensively sampled along Whitewood Creek by F. M. Fox Associates and these data were made available to the U.S. Geological Survey. No visually identified contaminated sediments were found along the Cheyenne River. The 13 uncontaminated-sediment samples were collected from the streambank between 1 and 5 ft above the normal water surface.

To understand the geochemical processes occurring within the contaminated sediments, it is necessary to identify the minerals in the sediments. The numerous mineralogical data available for the Precambrian Homestake Formation were not used for this identification because these data reflect in-situ conditions within the ore body and may not reflect changes in mineralogical composition that may have occurred during transport and storage of the sediments in the flood plains.

To determine the suite of minerals present in the contaminated sediments, 46 of the 95 samples were subsampled and analyzed by X-ray diffraction. This method was used rather than optical methods because optical methods are hindered by the weathered condition of the mineral grains. The X-ray analyses were made at Old Dominion University, Department of Geophysical Sciences, Norfolk, Virginia.

Seventeen of the 95 contaminated-sediment samples were subsampled for particle-size analysis. The samples were analyzed by the U.S. Geological Survey sediment laboratory at Iowa City, Iowa, following standard U.S. Geological Survey procedures (Guy, 1969).

All 95 contaminated-sediment samples were analyzed for the constituents listed in table 1. Analyses were made at contract laboratories specified by the U.S. Environmental Protection Agency, using the methods listed in table 1. Desolution treatment prior to analysis was done using standard methods of the U.S. Geological Survey (Skougstad and others, 1979) to determine acid-soluble metals and minor elements. Desolution involved preliminary treatment with hydrogren peroxide to destroy organic matter, followed by digestion using hot, dilute (less than 1 molar) hydrochloric acid for 30 minutes.

Mineral Composition

Although various geologic formations were mined in the Lead and Deadwood district, most of the ore mined was from the Precambrian Homestake Formation (Noble and Harder, 1948). The Homestake Formation is a sideroplesite-quartz schist [$(Fe, Mg) CO_3$] containing some biotite, chlorite, and graphite (Noble, 1950). The Homestake has been extensively metamorphosed (Noble and Harder, 1948) and cummingtonite [$(MgFe)_7 Si_8 O_{22} (OH)_2$] erratically to completely replaces sideroplesite in and near the ore body (Slaughter, 1968).

The ore bodies are almost completely chloritized parts of the sideroplesite or cummingtonite schists of the Homestake Formation (Noble, 1950). Quartz masses and veins are abundant and the iron-sulfide minerals, pyrrhotite (Fe_xS), pyrite (Fe_2S) and arsenopyrite (AsFeS) are common, comprising 7 to 8 percent of the ore (Noble, 1950).

Table 1.--Constituents and analytical methods for solids samples

Constituents	Analytical method	References
Total recoverable arsenic	Atomic absorption, hydride	Digestion: Nygaard and Lowry, 1982. Analysis: U.S.Geological Survey I-5062-78[1].
Total recoverable metals (calcium, magnesium, sodium, potassium, cadmium, chromium, copper, iron, lead, manganese, nickel, silver, and zinc)	Inductively coupled argon plasma	Digestion: U.S. Geological Survey I-5485-78[1], Analysis: U.S. Environmental Protection Agency, 1980.
Total recoverable mercury	Atomic absorption, spectrometric	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-5462-78[1].
Total selenium	Atomic absorption, hydride	Digestion: Nygaard and Lowry, 1982. Analysis: U.S. Geological Survey I-5667-78[1].
Total cyanide	Colormetric, barbituric acid	Digestion: Included as part of analysis. Analysis: U.S. Environmental Protection Agency, 1974.

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[1] Skougstad and others, 1979.

Less common minerals include ankerite $[Ca\ (Mg, Fe)\ (CO_3)_2]$, calcite ($CaCO_3$), dolomite $[CaMg\ (CO_3)_2]$, biotite $[K(Mg, Fe)_3AlSi_3O_{10}(OH)_2]$, garnet $[(Ca, Fe, Mg, Al)_5Si_3O_{12}]$, albite ($Na\ Al\ Si_3O_8$), galena ($PbS$), sphalerite ($ZnS$), chalcopyrite ($CuFeS_2$), specularite ($Fe_2O_3$), magnetite ($Fe_3O_4$), and native gold (Slaughter, 1968). There is an association of gold with quartz, chlorite, and arsenopyrite.

Although individual carbonate minerals are relatively rare, as a group they may be a substantial constituent of the ore. There is considerable variability in the carbonate-mineral content due to the heterogeneous nature of the ore bodies. For example, reported ore analysis indicates that sideropleiste comprises from 0 to 42 percent, ankerite comprises from 0 to 30 percent, and dolomite comprises from 0 to 18 percent of individual ore samples, although these minerals normally are present in the range of from 1 to 2 percent (G. C. Nelson, Homestake Mining Co., oral commun., 1985). Unfortunately, there are insufficient data to allow accurate estimates of the total proportion of carbonate minerals present in the mined ore. However, carbonate minerals are abundant in some ore samples, indicating they may be a major constituent in the mill wastes.

When considering possible effects on the environment, the important aspects of the ore-body composition are: (1) Iron-sulfide minerals are abundant and have the potential of producing sulfuric acid when oxidized, (2) carbonate minerals such as sideroplesite, ankerite, dolomite, and calcite are sometimes abundant and these minerals have the potential of buffering the sulfuric acid produced by weathering of iron-sulfide minerals, (3) arsenopyrite is associated with the gold and so is preferentially mined and becomes a common constituent in the wastes, and (4) metallic-sulfide minerals other than those of iron are present, but only in trace quantities.

The results of the mineral-composition analysis of contaminated sediments are listed in table 2. About 75 percent of the contaminated sediments consists of silicate minerals derived from the chloritized schists of the Homestake Formation. Most of the remaining contaminated sediments, about 22 percent, consists of clay minerals thought to be derived from weathering of the parent silicate minerals. Less than 3 percent consists of reactive iron-sulfide and carbonate minerals.

The iron-sulfide minerals are not as common in the contaminated sediments as they are in the ore. Pyrite was detected in only 5 of the 46 samples analyzed and was never present in quantities greater than 1 percent by weight. Cherry and others (1986) reported pyrite detection in 2 of 9 samples collected from massive contaminated-sediment deposits along Whitewood Creek. These results contrast with the 7 to 8 percent in the ore as reported by Noble (1950).

Possible explanations for the lack of sulfide minerals in the contaminated sediments are: (1) The original sulfide minerals have been oxidized to secondary iron minerals in the near-surface deposits where most of the contaminated-sediment samples were collected; (2) the analytical method, which included treating the samples to remove ferric-hydroxide coatings from grains, destroyed or did not detect the sulfide minerals; (3) the sulfide minerals were attacked by the cyanide solutions used in gold recovery and so are not present in the discharged wastes as crystalline solids; or (4) the sulfide minerals were preferentially segregated during downstream transport and so are not as common in the contaminated sediments as in the unsegregated wastes. Metallic sulfide minerals are, in general, heavier than the silicate minerals and, it would seem, be more likely to be deposited. Although the cyanide solutions will attack sulfide minerals and may be responsible for removal of specific sulfide minerals such as those of copper, sulfide minerals such as pyrite and arsenopyrite are rather

Table 2.--Minerals present in visually identified contaminated-sediment samples as determined by X-ray diffraction analysis

[Majority of samples treated to remove amorphous-iron grain coatings]

Identified mineral	General chemical composition	Number of samples	Number of positive identifications	Mean percent by weight
Quartz	SiO_2	46	46	53
Feldspar	$(K,Na)AlSi_3O_8$ - $CaAl_2Si_2O_8$	46	46	9
Amphioboles[1]	$(Mg,Fe)_7Si_8O_{22}(OH)_2$ - $CaNa(Mg,Fe)_4(AlFeTi)_3\ Si_6O_{22}(O,OH)_2$	46	43	8
Chlorite	$(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_8$	46	44	5
Hypersthene	$(Fe,Mg)SiO_3$	46	27	1
Pyroxenes[2]	$Ca(Mg,Fe,Al)(Si,Al)_2O_6$	46	27	<1
Micas	$KAl_3Si_3O_{10}(OH)_2$ - $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	46	26	<1
Calcite	$CaCO_3$	46	6	<1
Pyrite	FeS_2	46	5	<1
Hematite	Fe_2O_3	46	4	<1
Siderite	$FeCO_3$	46	1	<1
Dolomite	$CaMg(CO_3)_2$	46	1	<1
Semectite	$(Al,Mg,Fe)_2(Si_3Al)O_{10}(OH)_2(Ca,Na,K)$	46	43	12
Illite	$(K,Na,H_3O)_2(Al,Mg,Fe)_4(Si_7Al)O_{20}(OH)$	46	46	5
Kaolinite	$Al_2Si_2O_5(OH)_4$	46	30	3
Mixed-layer clays	Variable	46	33	2
Vermiculite	$(Mg,Fe)_3(Si,Al,Fe)_4O_{10}(OH)_3 \cdot 4H_2O$	46	6	<1

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[1] Includes cummingtonite, a monoclinic amphibole.

[2] All pyroxenes except hypersthene.

insoluble and should not be significantly affected (Julian and Smart, 1904). The possible analytical problem is somewhat harder to discount because the samples were treated to remove iron coatings; minerals that may be present in trace quantities are difficult to detect using X-ray diffraction. It seems likely, however, that the majority of the sulfide minerals originally present in the ore have been weathered into secondary oxides and that the metallic ions present in the contaminated sediments do not exist as crystalline solids, but are adsorbed onto the oxides and clays present in the sediments.

Carbonate minerals, also common in the ore, are rare in the contaminated-sediment samples. Calcite was detected in only 6 of the 46 samples, and siderite and dolomite were detected only once. These results are different than those reported by Cherry and others (1986), who detected calcite in 5 of 9 samples, siderite in 4 of 9 samples, and dolomite in 4 of 9 samples. Both the rarity of carbonate minerals in the contaminated-sediment samples analyzed during this study, and the contrast of these data with those reported by Cherry and others (1986), may be caused by the different locations from which the sample groups were collected. The samples analyzed during this study were collected from trenches in streamside deposits and from core obtained from thin deposits on the flood plain along the Belle Fourche River. Almost all the samples were collected at depths of less than 5 ft from the land surface and many were from areas that were inundated yearly by the Belle Fourche River. Calcite and other soluble carbonate minerals may have been removed by solution, a process that would be hastened by acids produced during sulfide-mineral oxidation. The results reported by Cherry and others (1986) are for samples from cores collected while drilling into thick, extensive, meander-fill deposits along Whitewood Creek. The interior of these deposits may not be subject to repeated saturation and soluble minerals could persist for long periods. Also detected in 8 of the 9 samples described by Cherry and others (1986) were substantial quantities of gypsum; gypsum was not detected in any of the samples analyzed during this study. This again could be the result of the near-surface location of the samples collected for this study. However, it also is possible that the iron-removal treatment used during the analysis removed both gypsum and calcite from the samples, thus creating the apparent rarity of soluble carbonate minerals in the samples analyzed during this study.

Physical Characteristics

Almost all the mill wastes discharged to Whitewood Creek consist of rock particles crushed to sand size or smaller by the various milling methods. During the early mining activity, prior to about 1920, the ore was crushed by stamp mills, resulting in relatively coarse sand-size particles. Later, more modern rod and ball mills were installed that pulverized the ore resulting in a greater percentage of finely ground rock particles. In 1959, the mill-processed ore contained 44 percent slimes--rock particles finer than 0.075 mm (millimeter) with 85 percent finer than 0.045 mm (South Dakota Department of Health, 1960a). During the early mining period, all the mill tailings were discharged as wastes, but as the underground workings became deeper, a percentage of the coarse fraction (sand-size particles) was retained and used as backfill in the mine. Because of this, the physical characteristics of the discharged milling wastes changed from mostly sand-size particles during the first 40 years to mostly silt-size particles during the more modern period of discharge.

Because the mill wastes were transported and deposited by surface streams, it could be expected that there would be some particle-size partitioning. In general, finer particles would have remained in suspension and be transported downstream, perhaps to the Missouri River. As a result, the streamside deposits along Whitewood Creek and the Belle Fourche River would contain a smaller percentage of finer particles than was originally contained in the discharged mill wastes.

Seventeen of the 95 visually identified contaminated-sediment samples were selected for particle-size analysis. Of these, nine samples were collected from hand-dug trenches along the Belle Fourche River and eight samples were collected from drill cores. The samples represented a cross section of the different visual characteristics of the contaminated sediments.

The contaminated sediments are well sorted, consisting mostly of fine to very-fine sand-size and silt-size particles. Considering the entire group of samples, about 44 percent of the particles were fine to very-fine sand size (between 0.062 and 0.25 mm), and about 39 percent were silt size (between 0.002 and 0.062 mm). Clay-size particles (less than 0.002 mm) comprised slightly less than 10 percent of the total. Within this broad classification, there was a large variation among samples. For example, one sample contained 21 percent sand-size and 79 percent silt-size particles, whereas another contained 87 percent sand-size, 9 percent silt-size, and 4 percent clay-size particles.

There appears to be some correlation between particle-size distribution and the visual characteristics of the contaminated sediments. Many of the dark gray, unoxidized contaminated-sediment samples consisted mostly of particles less than 0.062 mm, whereas most of the reddish-brown, oxidized contaminated-sediment samples consisted of larger sand-size particles. However, this is not a definitative correlation and two sets of paired samples (two samples collected from a single deposit, only inches apart, and with different visual characteristics) had nearly identical particle-size distributions.

Chemical Composition

The chemical constituents that may adversely affect the environment are present in the contaminated sediments only in trace quantities. Although metallic-sulfide minerals identified in the ore are known to contribute arsenic, iron, manganese, and other trace constituents to the contaminated sediments, the mineral composition of the samples gave little evidence of occurrence or concentrations of the trace constituents. However, chemical analysis is much more sensitive and, therefore, delineated the trace-constituent concentrations and differentiated these concentrations with respect to trace-constituent concentrations in natural, uncontaminated sediments. Summaries of the solids chemistry data obtained during the study are divided into uncontaminated-sediment and contaminated-sediment data groups in tables 3 and 4. Comparison between the data in these two tables indicates which constituents are more prevalent in the contaminated sediments, and the arithmetic mean concentrations of the constituents indicate the concentrations that would occur in a typical sample. A graphical comparison of the trace-constituent concentrations (fig. 2) allows an easy visual comparison of the uncontaminated-sediment and contaminated-sediment chemistry data.

Table 3.--Statistical summary of chemical constituents in uncontaminated-sediment samples collected from the flood plain along the Belle Fourche River upstream from the mouth of Whitewood Creek

[<, less than value shown]

Constituent	Number of samples	Arithmetic mean concentration (micrograms per gram)	Standard deviation (micrograms per gram)	Minimum concentration (micrograms per gram)	Maximum concentration (micrograms per gram)
Calcium[1]	13	19,400	10,400	8,330	40,900
Magnesium[1]	13	2,680	740	1,440	3,970
Sodium[1]	13	926	520	258	2,110
Potassium[1]	13	515	393	174	1,490
Arsenic[2]	13	9.2	5.2	4	20
Cadmium[1]	13	[3] .12	.15	[4] <.05	.52
Chromium[1]	13	[3] 4.0	2.5	[4] <.5	9.5
Copper[1]	13	10.7	3.3	5.5	16
Cyanide[2]	13	[3] <.5	0	[4] <.5	[4] <.5
Iron[1]	13	23,700	20,900	11,200	86,600
Lead[1]	13	13.4	4.3	5.7	23
Manganese[1]	13	550	480	298	2,090
Mercury[1]	13	<.1	0	[4] <.1	[4] <.1
Nickel[1]	13	13.5	5.5	7.9	27
Selenium[2]	13	[3] 1.0	.1	[4] <1.0	1.5
Silver[1]	13	[3] 1.6	1.4	[4] <.5	5.5
Zinc[1]	13	55	20	31	108

[1] Total-recoverable concentration.
[2] Total concentration.
[3] May not be significant, some values less than detection limit.
[4] Less than detection limit.

Table 4.--Statistical summary of chemical constituents in contaminated-sediment samples collected from visually identified contaminated-sediment deposits on the flood plain along Whitewood Creek

[<, less than value shown]

Constituent	Number of samples	Arithmetic mean concentration (micrograms per gram)	Standard deviation (micrograms per gram)	Minimum concentration (micrograms per gram)	Maximum concentration (micrograms per gram)
Calcium[1]	95	9,350	3,400	395	17,800
Magnesium[1]	95	5,610	3,880	110	16,800
Sodium[1]	94	636	780	35	4,200
Potassium[1]	95	1,530	820	50	3,580
Arsenic[2]	95	1,900	1,240	350	8,200
Cadmium[1]	95	[3]11.6	14.3	[4]<.05	97
Chromium[1]	95	[3] 6.6	4.1	[4]<.5	18
Copper[1]	95	[3]46	25	[4]<5.0	156
Cyanide[2]	95	[3].87	.67	[4]<.5	5.5
Iron[1]	95	56,700	21,400	9,250	114,000
Lead[1]	94	24	20	<5.0	104
Manganese[1]	95	1,520	2,980	33	28,900
Mercury[1]	95	[3].79	.64	[4]<.1	2.9
Nickel[1]	94	[3]12	9.9	[4]<2.0	40
Selenium[2]	95	[3]1.5	.89	[4]<1.0	6.0
Silver[1]	95	[3]9.4	28	[4]<.5	274
Zinc[1]	92	41	21	<.5	115

[1] Total-recoverable concentration.
[2] Total concentration.
[3] May not be significant, some values less than detection limit.
[4] Less than detection limit.

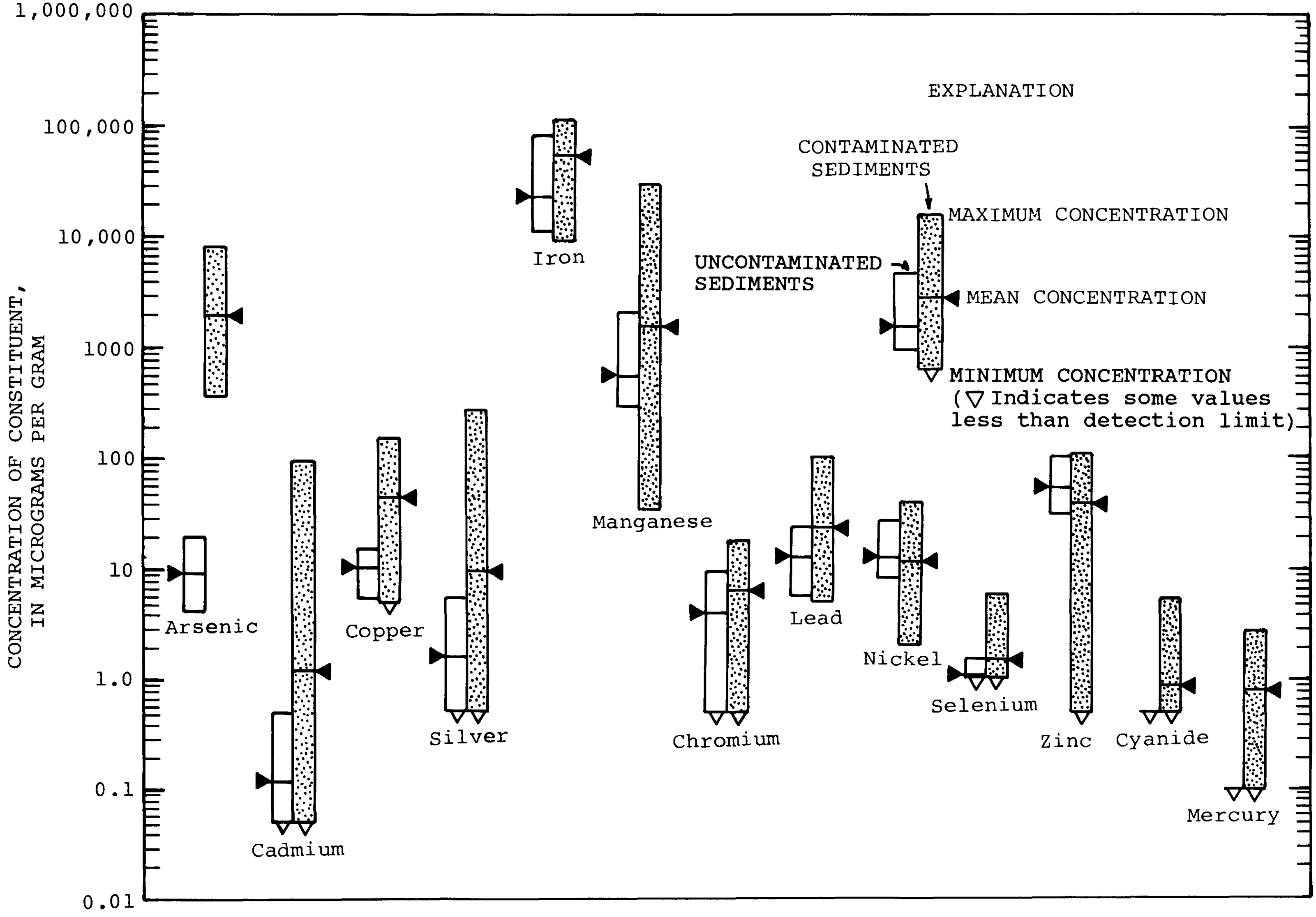

Figure 2.--Trace-constituent concentrations measured in uncontaminated-sediment samples and in visually identified contaminated-sediment samples collected from the flood plains along the Belle Fourche River and Whitewood Creek.

The contaminated sediments have larger concentrations of magnesium and potassium, a similar concentration of sodium, and a smaller concentration of calcium compared to the uncontaminated sediments. The magnesium and potassium probably are derived from the decomposition of the feldspars, amphiboles, and micas that are common in the mining and milling wastes. Sodium also is a common cation in the silicate minerals, but because it generally is more soluble than magnesium or potassium, it may be removed from the contaminated sediments at a faster rate. The concentration of calcium in the contaminated sediments is less than in the uncontaminated sediments, but this probably is because of the greater abundance of calcium in western South Dakota rather than the depletion of calcium from the contaminated sediments. Natural sources of calcium in the study area include limestone (Madison Limestone, Minnelusa Formation, Minnekahta Limestone all of late Paleozoic age), gypsum-rich shale (Spearfish Formation of Permian and Triassic age), and calcareous shale (Belle Fourche Shale, Greenhorn Formation, Carlile Shale, Niobrara Formation, and Pierre Shale all of Cretaceous age). The difference in calcium concentration, and to a lesser extent, the differences in magnesium and potassium concentrations, between those measured in uncontaminated sediments and in contaminated sediments may be substantial. However, the constituent concentrations that occur in the contaminated sediments are well within the expected range. A report on element concentrations in soils and other surficial materials of the conterminous United States (Shacklette and Boerngen, 1984) listed the following arithmetic mean concentrations: calcium, 9,200 µg/g; magnesium, 4,400 µg/g; sodium, 5,900 µg/g; and potassium, 15,000 µg/g.

The concentration of arsenic and several other trace constituents are from several times to several orders of magnitude larger in the contaminated sediments than in the uncontaminated sediments. The trace-constituent concentrations measured in the contaminated sediments (fig. 2) can be divided into four groups based on their anomalies with respect to concentrations in uncontaminated sediments. Arsenic, cadmium, copper, and silver are trace constituents known to be associated with the ore and have arithmetic mean concentrations ranging from 4 times (copper) to 200 times (arsenic) larger in the contaminated sediments than in the uncontaminated sediments. Iron and manganese also are trace constituents known to be associated with the ore minerals, but there are many other sources of iron and manganese in the environment, and the concentrations in the contaminated sediments are only several times larger than those in the uncontaminated sediments. Chromium, lead, nickel, selenium, and zinc are not concentrated in the ore, and there are no substantial differences between the concentrations in the contaminated sediments and in the uncontaminated sediments. Cyanide and mercury are trace constituents contributed largely by ore processing and were detected in many of the contaminated sediment samples, but the concentrations were never more than the detection limit in the uncontaminated-sediment samples. Application of the Wilcox rank-sum and the Kruskal-Wallis statistical tests indicated that statisically significant (at the 0.05 significance level) differences exist in the concentrations for all trace constituents, except lead and nickel, between the contaminated sediments and the uncontaminated sediments.

Arsenic is by far the most anomalous trace constituent in the contaminated sediments. The 13 uncontaminated-sediment samples collected from the flood plain along the Belle Fourche River upstream from the mouth of Whitewood Creek had an arithmetic mean concentration of 9.2 µg/g arsenic, whereas the 95 contaminated-sediment samples had an arithmetic mean concentration of 1,900 µg/g arsenic. The large concentrations of arsenic in the contaminated sediments are derived from the decomposition of the arsenopyrite (FeAsS) present in the ore.

The arithmetic mean concentration of 9.2 µg/g arsenic determined for the uncontaminated sediments during this phase of the study is typical of non-mineralized areas. Results of an extensive sampling program described later in this report indicated an arithmetic mean concentration of 8.3 µg/g arsenic for 71 uncontaminated-sediment samples randomly collected from the flood plains along the Belle Fourche and Cheyenne Rivers upstream from possible contamination. These values are comparable to arithmetic concentrations of arsenic in other uncontaminated materials determined by other investigators. Shacklette and Boerngen (1984) reported an arithmetic mean concentration of 7.2 µg/g arsenic and a maximum concentration of 97 µg/g arsenic for 1,318 samples of soils and other surficial materials collected from across the conterminous United States. Schultz and others (1980) reported an arithmetic mean concentration of 14 µg/g arsenic and a maximum concentration of 490 µg/g arsenic for 202 samples collected from the Pierre Shale in the Northern Great Plains.

The arithmetric mean concentration of 1,900 µg/g arsenic determined for the contaminated sediments is comparable to that expected based on reported mineral-composition analysis of ore materials. Noble (1950) reported 0.75 percent arsenopyrite in the ore, which converts to about 3,500 µg/g arsenic in the mining and milling wastes. An analysis of ore made in 1958 (South Dakota Department of Health, 1960a) indicated 0.25 percent arsenopyrite or about 1,200 µg/g arsenic. Undoubtedly the quantity of arsenopyrite in the ore, and therefore, the quantity of arsenic in the mining and milling wastes, changed as different levels of the mine were developed and the ore was mined and milled.

There are other natural and man-induced sources of arsenic in the study area, but these are considered unimportant when compared to the quantity contained in the mine and mill wastes. It seems likely that if the mining operations at Lead had not taken place, the natural weathering of the sulfide minerals at the site would have resulted in anomalously large concentrations of arsenic in the sediments of the Whitewood Creek basin. The arsenic concentration in soils directly overlying arsenic-sulfide deposits commonly ranges from 100 to 2,000 µg/g (Hawkes and Webb, 1962; National Research Council, 1977). It is impossible to determine the quantities of arsenic present in and along Whitewood Creek and the downstream river system before mining. However, natural erosion of the ore deposit only could have exposed a minute fraction of the material that was exposed by the mining operation. Sediment samples from the flood plain along Whitewood Creek upstream from the major waste discharge site (Gold Run), but still within the general area affected by mineralization had arsenic concentrations larger than those determined for other uncontaminated sites within the Cheyenne River basin, but still had an arithmetic mean concentration of 56 µg/g. A number of pesticides sometimes used on agricultural lands also contain arsenic compounds. Arsenic concentrations from 100 to 2,000 µg/g have been detected in soils on which pesticides containing arsenic compounds have been recently applied (National Research Council, 1977). Although it is likely that pesticides containing arsenic compounds have been used in the Cheyenne River basin, there is no indication or reason to expect that these pesticides have ever been applied in large enough quantities to substantially effect the hydrologic system. It is apparent that the arsenic contained in the contaminated sediments is a direct result of the decomposition of arsenopyrite originally contained in the ore and discharged as a constituent of the mining and milling wastes.

Cadmium, copper, and silver have substantially larger concentrations in the contaminated sediments than in the uncontaminated sediments (tables 3 and 4, fig. 2). Of these, cadmium was the most anomalous with arithmetic mean concentrations of

0.12 µg/g in the uncontaminated sediments and 11.6 µg/g in the contaminated sediments. The cadmium is clearly associated with the mining and milling wastes although cadmium minerals are not identified in the ore bodies. The only important cadmium mineral is greenockite (CdS), which is not described in the Homestake deposit, but cadmium commonly is associated with lead and zinc in sulfide minerals containing those constituents (Hawkes and Webb, 1962). In the Homestake ore bodies, cadmium apparently is associated with arsenic because these constituents correlate in the contaminated sediments (table 5). Copper and silver are constituents known to be asociated with the ore mineralogy. Chalcopyrite ($CuFeS_2$) is reported in the ore (Noble, 1950), and copper is present in the mill feed due to inclusion of copper blasting wire (F. D. Fox, Homestake Mining Co., oral commun., 1985). Silver is recovered at the Homestake Mine as a by-product of the gold-recovery operations. Copper and silver have no significant correlation with arsenic or one another, although silver has a significant positive correlation with manganese (table 5).

Iron and manganese are more common in the contaminated sediments than in the uncontaminated sediments (tables 3 and 4, fig. 2). There is no doubt that both iron and manganese are contributed to the contaminated sediments by ore-body minerals, however, these constituents are rather common in the environment and have numerous other sources in the Cheyenne River basin. Iron contributed by the decomposition of iron-sulfide minerals common in the ore, is only about twice as concentrated in the contaminated sediments as in the uncontaminated sediments. Iron is a common constituent in soils and other surficial materials and arithmetic mean concentrations reported by other investigators (Shacklette and Boerngen, 1984; Schultz and others, 1980; Hawkes and Webb, 1962) range from 26,000 to 40,000 µg/g, values not appreciably different from the arithmetic mean concentration of 57,100 µg/g determined for the contaminated-sediment samples. Shacklette and Boerngen (1984) and Schultz and others (1980) reported arithmetic mean concentrations for manganese of 550 and 720 µg/g, which compares with the arithmetic mean concentration of 550 µg/g determined for uncontaminated sediment during this study. The arithmetic mean manganese concentration of 1,520 µg/g in the contaminated sediments is only about twice the arithmetic mean manganese concentration of 720 µg/g reported by Schultz and others (1980) and is much less than the maximum concentration of 34,600 µg/g they reported.

Chromium, lead, nickel, selenium, and zinc are trace constituents that are not concentrated in the contaminated sediments (tables 3 and 4, fig. 2). Chromium, nickel, and selenium are not associated either with the ore mineralogy or the ore processing. Lead and zinc minerals [galena (PbS; sphalerite (ZnS)] are known to occur in the ore body (Noble, 1950) but apparently are quite rare.

Concentrations of the final two trace constituents examined during the study, cyanide and mercury, are much larger in the contaminated sediments than in the uncontaminated sediments (tables 3 and 4, fig. 2). The source of the cyanide is the cyanide leaching used since the early 1900's in the gold-recovery operations. In the past, cyanide was discharged to Whitewood Creek as part of the mill wastes in concentrations ranging from 0.60 to 9.1 mg/L with an average of 2.6 mg/L (South Dakota Department of Health, 1960a). The majority of cyanide discharged to the stream probably existed as various metallocyanide complexes considering the numerous metallic-sulfide minerals present and the affinity of cyanide for metallic ions. Many cyanide complexes are readily soluble and most of the cyanide was likely in the dissolved state. However, some cyanide complexes were adsorbed on particulate matter and so are contained in the contaminated sediments.

Table 5.--Correlations among chemical constituents in 95 visually identified contaminated-sediment samples for which coefficients are greater than +0.50

	Calcium	Magnesium	Sodium	Potassium	Arsenic	Cadmium	Chromium	Copper	Cyanide	Iron	Lead	Manganese	Mercury	Nickel	Selenium	Silver	Zinc
Calcium	1.00																
Magnesium		1.00															
Sodium			1.00														
Potassium				1.00													
Arsenic					1.00												
Cadmium					.67	1.00											
Chromium				.65			1.00										
Copper		.52						1.00									
Cyanide									1.00								
Iron		.53								1.00							
Lead											1.00						
Manganese												1.00					
Mercury										.54			1.00				
Nickel														1.00			
Selenium															1.00		
Silver												.95				1.00	
Zinc		.65				.65											1.00

Mercury was detected in 86 of the 95 contaminated-sediment samples, and was less than the detection limit of 0.1 µg/g in all uncontaminated-sediment samples. An arithmetic mean concentration of 0.79 µg/g mercury was determined for the contaminated sediments. The anomalous mercury concentration in the contaminated sediments is the result of mercury in the ore and the unrecovered elemental mercury from ore processing.

About one-half of the mercury in the contaminated sediments could be accounted for by mercury contained in the ore. Mahrholz and Slaughter (1967) reported that the concentrations of mercury in gold ores mined at Lead generally ranged between 0.2 and 0.3 µg/g and rarely were as much as 2.0 µg/g. The U.S. Environmental Protection Agency (1971) reported a concentration of 0.57 µg/g mercury in ore entering the Homestake mill. Prior to late 1970, gold recovery in the Lead and Deadwood areas involved the use of elemental mercury for amalgamation and the unrecovered mercury from the process was known to contribute mercury to the mill wastes (U.S. Environmental Protection Agency, 1971; 1973). Unfortunately, the available chemical-analysis data for solid-waste discharge to Whitewood Creek in the past generally are incomplete, making it difficult to estimate the quantity of mercury discharged to Whitewood Creek due to the amalgamation process.

DISTRIBUTION OF THE CONTAMINATED SEDIMENTS

Data Collection

Flood-plain deposits that consist entirely or almost entirely of contaminated sediments have color, texture, and other characteristics that enable them to be visually identified. However, in many areas the contaminated sediments are covered by veneers of uncontaminated sediment or vegetation, and so are hidden from easy identification. In addition, if the wastes are widely dispersed within the contaminated sediments, the contamination is not visually apparent.

Infrared aerial photographs were taken by the U.S. Environmental Protection Agency in 1980 in an attempt to map the contaminated sediments on the flood plains along Whitewood Creek and a reach of the Belle Fourche River. This attempt was unsuccessful because most of the contaminated sediments were covered by uncontaminated sediments and vegetation. Ground mapping is not practical due to the large size of the study area and the problems with uncontaminated-sediment cover and the incorporation of contaminated sediments into uncontaminated sediments.

A geochemically based, random, sediment-sampling program was conducted that, while not providing delineated areas of contaminated sediments, allows inferences about how the contaminated sediments are distributed through the shallow flood-plain deposits of the Whitewood Creek-Belle Fourche River-Cheyenne River system. The sampling design that was used for this phase of the study is a stratified hierarchical analysis of variance, which is illustrated schematically in figure 3. The design was modified from one proposed by Chappel (1980) for a geochemical study in Colorado.

Level 1 of the design consisted of 43 subreaches, each 5 mi in length. Two subreaches were located on each stream upstream from any possible contamination in order to determine the constituent concentrations in uncontaminated sediments. To further define these concentrations, subreaches were established upstream from the mouths of Bear Butte Creek, a tributary to the Belle Fourche River, and Elk Creek, a tributary to the Cheyenne River (fig. 1).

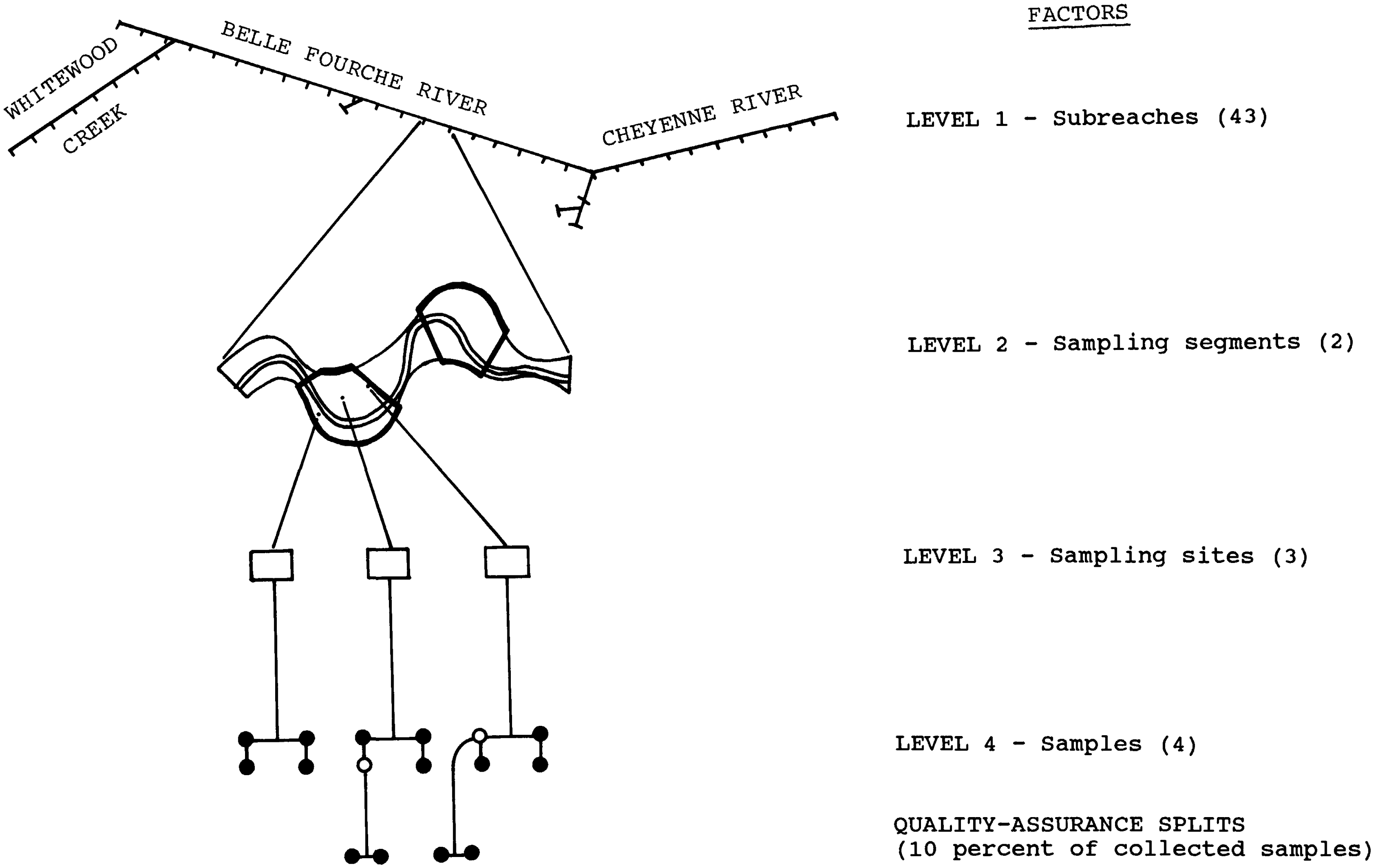

Figure 3.--Design of geochemically based, random, sediment-sampling program using a stratified, hierarchical, analysis of variance.

Level 2 in figure 3 represents two 1-mi-long segments randomly chosen from the five segments in a subreach. Within the segment, three sampling sites (level 3 in fig. 3) were randomly selected on the flood plain using a grid with a 200-ft spacing. At each sampling site, four samples (level 4 in fig. 3) were collected for determination of small-scale variability and variability with depth. Two surface (top 0.1 ft) samples were collected 100 ft apart, spaced parallel with the trend of the river, and two near-surface samples were collected 1.0 ft below the surface samples.

In order to evaluate the analytical component of the variance, 10 percent of the samples were randomly selected for duplicate analysis. Determination of analytical error is necessary for confidence in conclusions reached at higher levels.

Arsenic was chosen as an indicator of contamination due to the association of gold ore with arsenophyrite and resultant large concentrations of arsenic in the wastes discharged to Whitewood Creek. An investigation by the U.S. Environmental Protection Agency (1973) measured arsenic, copper, mercury, and zinc concentrations in sediments collected along stream reaches upstream and downstream from the waste-discharge point. They concluded that arsenic, copper, and mercury were present in concentrations substantially greater than background concentrations in areas contaminated by wastes. Of these three constituents, arsenic concentrations were the most anomalous and were several orders of magnitude greater than background concentrations. Samples collected by the U.S. Geological Survey during this study further defined the trend of anomalous concentrations of arsenic in the contaminated sediments.

Sediment samples collected during this phase of the sampling program were analyzed for total-recoverable arsenic concentration. The chemical analyses were performed at contract laboratories specified by the U.S. Environmental Protection Agency using the atomic absorption, hydride method (table 1).

Arsenic Distribution

To delineate areas that have unusually large, or anomalous, arsenic concentrations it is first necessary to estimate the naturally occurring, or background, concentrations of arsenic. In the previous section, an arithmetic mean concentration of 9.2 µg/g arsenic was determined for the 13 uncontaminated-sediment samples, all of which were collected from the flood plain along the Belle Fourche River upstream from the mouth of Whitewood Creek. The much larger data base available from this phase of the study, 168 samples, yields an arithmetic mean concentration of 20.8 µg/L arsenic. The difference in the arithmetic mean concentrations was the result of including a few samples from the contaminated flood plain of Whitewood Creek that had arsenic concentrations of 100 to 670 µg/g. Arithmetic means are sensitive to a few unusually large values and tend to be misleading when considering naturally occurring concentration distributions. Other investigators (Hawkes and Webb, 1962; Shacklette and Boerngen, 1984) reported that there is a tendency for trace-constituent concentrations in natural materials to have lognormally distributed populations. For this reason, a geometric mean is a better measure of the central tendency than the arithmetic mean. The geometric mean concentration for arsenic in the 168 sediment samples collected from all the uncontaminated reaches is 10.9 µg/g. A separate geometric mean concentration of 19.3 µg/g arsenic, based on 36 samples, was calculated for the uncontaminated flood plain along Whitewood Creek due to the mineralized nature of the area.

In order to determine a threshold concentration, above which the concentration is considered anomalous, the variation about the mean needs to be taken into account. In lognormal distributions, the geometric deviation measures this scatter much as the way standard deviation represents scatter about an arithmetic mean. The deviation, either geometric or standard, commonly is used to estimate a threshold concentration, above which the constituent concentration is considered anomalous. In the case of lognormally distributed populations, DxM^2 is used (D = geometric mean; M = standard deviation, in log units). Only 2 percent of the data values would be expected to be larger than the DxM^2 value if data is lognormally distributed. Applying this calculation to the 168 samples collected throughout the Cheyenne River basin results in a threshold concentration of 46 µg/g arsenic. A separate threshold concentration of 223 µg/g arsenic was calculated for the uncontaminated flood plain along Whitewood Creek to allow for the mineralized nature of the area.

A comparison of these threshold arsenic concentrations with measured arsenic concentrations in the sediment samples collected on the flood plains along Whitewood Creek and the Belle Fourche River (fig. 4) indicates that the surface sediments on the flood plains along these streams are contaminated with arsenic. Within the areas affected by wastes (downstream from Gold Run), arsenic concentrations in the sediment are sometimes two orders of magnitude larger than those in sediment upstream from Gold Run. This contrast is particularly apparent along the Belle Fourche River (fig. 4). The contrast along Whitewood Creek is not as distinct because of the larger background concentrations caused by the naturally mineralized nature of the Whitewood Creek basin.

Also shown in figure 4 is the large variability of the arsenic data within sampling segments. Factors that affect the arsenic concentration reported for an individual sample, and therefore, that affect sample variability, include: (1) Variation in the arsenic concentration in the waste discharge, (2) degree of mixing with natural alluvium, (3) particle-size variations, and (4) site-location, sample-collection, sample-handling, and laboratory-analysis errors. Site-location errors are only important when a site thought to be within the flood plain is outside the actual flood plain. Because abrupt breaks in slope generally mark the boundaries of the flood plain, making it easy to map, these errors should be minimal. Every effort was made to prevent cross contamination between samples during collection. Analysis of blind duplicate samples will detect errors in sample handling and laboratory analysis; results of these analyses are shown in figure 5. Although there is some scatter, the variability in concentrations usually was less than 100 percent, much less than the two orders of magnitude variability between individual samples. Assuming sample-collection errors to be unbiased, the random sample-collection program will (if sufficient samples are collected) reflect the distribution of the arsenic in the flood-plain sediments.

To make meaningful conclusions about the distribution of arsenic in the study area, it is necessary to group large numbers of samples together and to consider the statistical differences between these groups. The most logical grouping of data is by flood-plain segments; the frequency distributions for the eight different flood-plain segments sampled during the study are shown in figure 6. Most obvious is the distinction between total-recoverable-arsenic concentrations for uncontaminated and contamined flood-plain segments. Assuming a threshold concentration of 223 µg/g arsenic for the flood plain along Whitewood Creek and 46 µg/g arsenic for the flood plains along the Belle Fourche and Cheyenne Rivers, then 82 percent of the flood plain along Whitewood Creek downstream from Gold Run, 71 percent of the flood plain along the Belle Fourche River downstream from the mouth of Whitewood Creek, and 47 percent of the flood plain along the Cheyenne River downstream from the mouth of

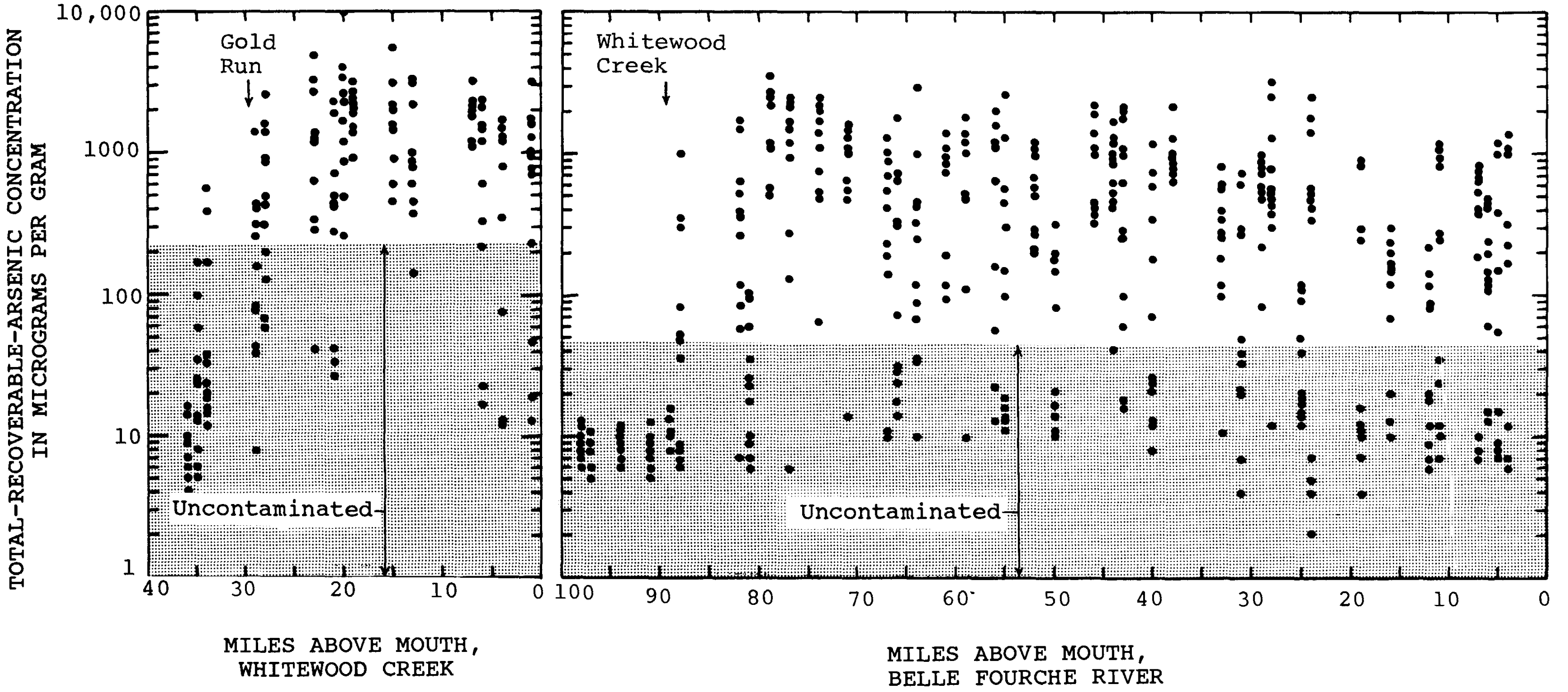

Figure 4.--Arsenic concentrations measured in sediment samples collected from the flood plains along Whitewood Creek and the Belle Fourche River.

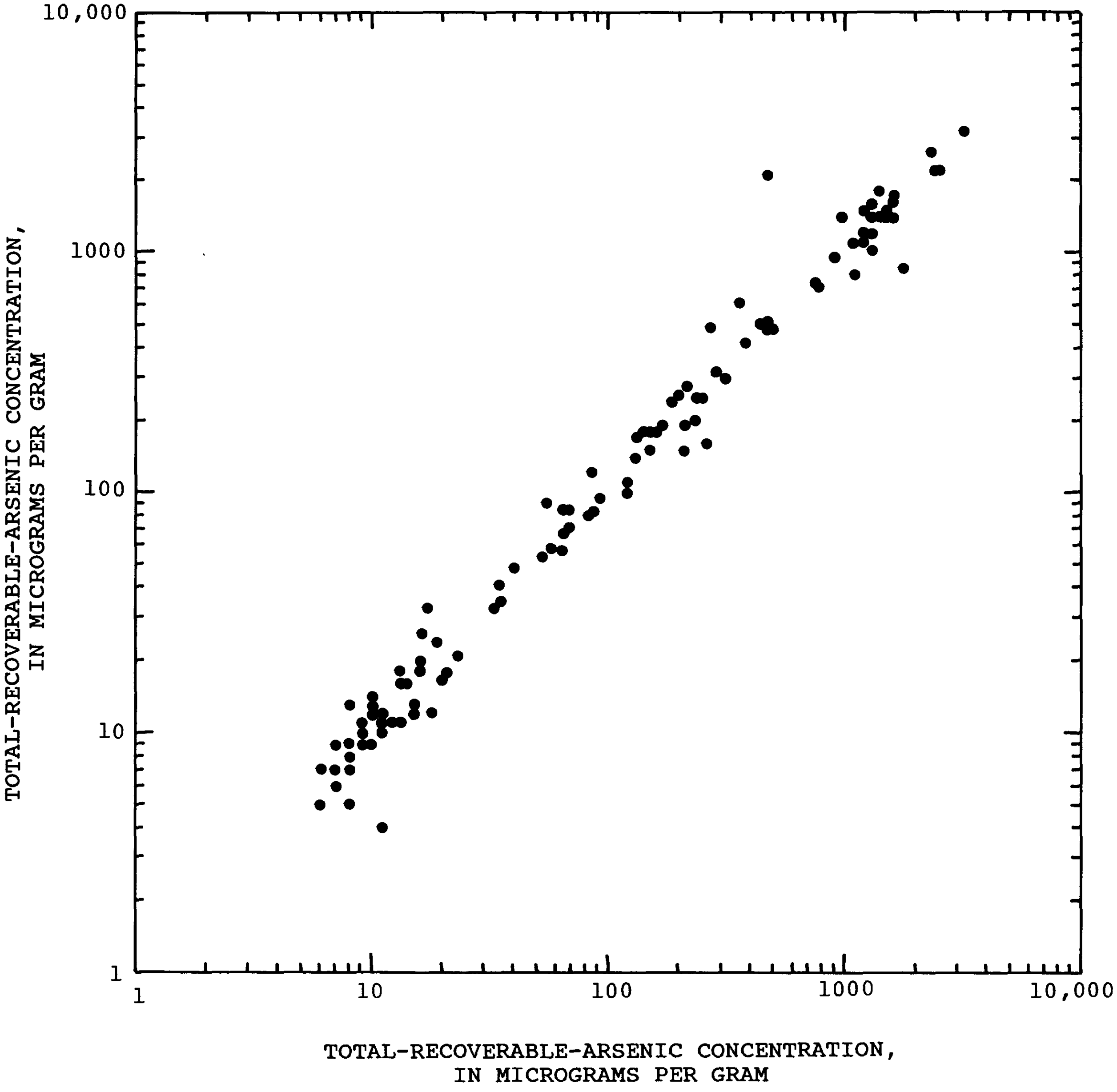

Figure 5.--Total-recoverable-arsenic concentrations measured in duplicate samples.

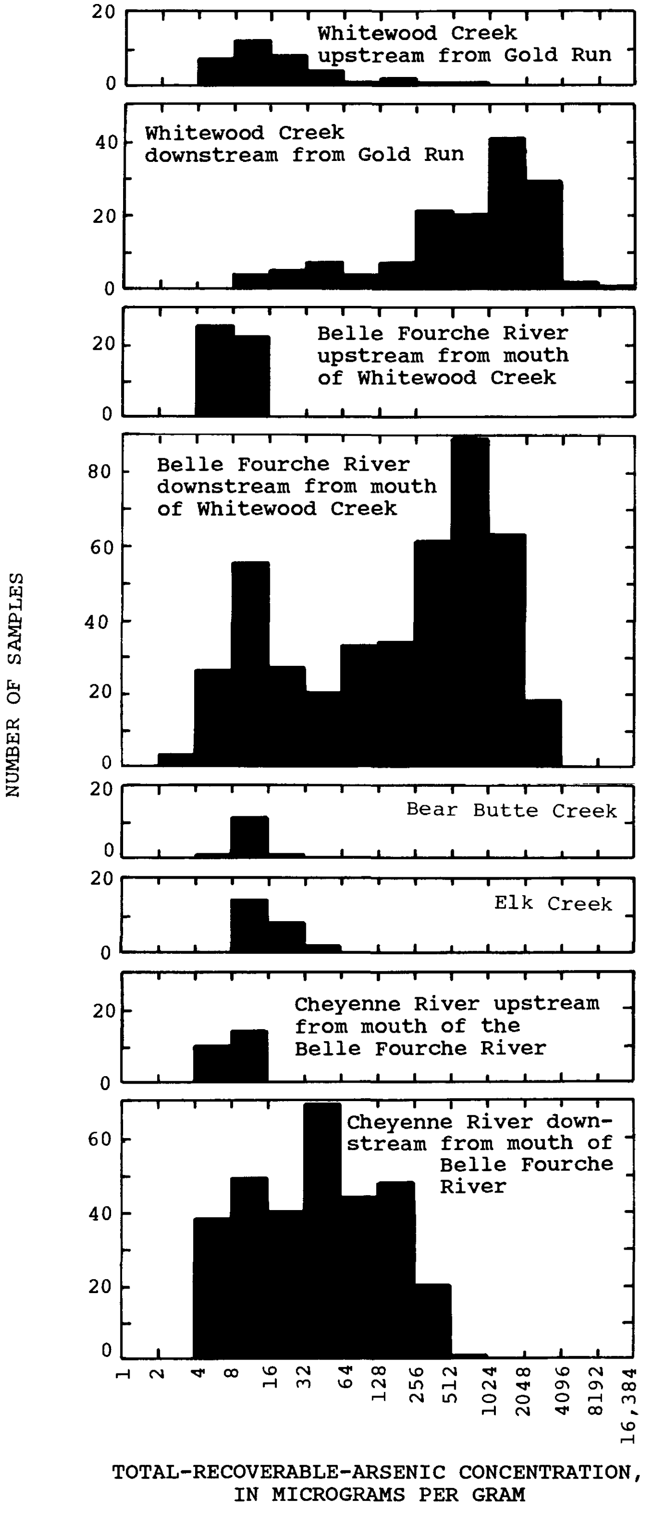

Figure 6.--Frequency distributions of total-recoverable-arsenic concentrations in sediment samples collected from the flood plains along Whitewood Creek, the Belle Fourche River, Bear Butte and Elk Creeks, and the Cheyenne River.

the Belle Fourche River are contaminated by arsenic. The magnitude of the contamination is considerably less for the flood plain along the Cheyenne River than for the flood plains along Whitewood Creek and the Belle Fourche River.

Further subdivision of the samples into groups obtained from 10-mi-long flood-plain segments indicates a general decrease in the extent and magnitude of arsenic contamination in the downstream direction along the Belle Fourche and Cheyenne Rivers. A summary of both arithmetic and geometric analyses of the arsenic concentrations in sediment samples by 10-mi-long flood-plain segments is presented in table 6. Although geometric (log transformed) analysis is superior when investigating significance of background concentrations, arithmetic analysis is superior when investigating the magnitude of contamination. Arithmetic means are the estimate of geochemical abundance of the constituent under consideration, in this case arsenic, rather than the typical concentration of the constituent in a group of samples. Considering then the arithmetic means listed in table 6, the most contaminated flood-plain segments are along Whitewood Creek, and between river miles 70 and 80 along the Belle Fourche River. A graphical representation (fig. 7) of the arithmetic-analysis data listed in table 6 indicates the general decrease of arsenic contamination downstream along the Belle Fourche River.

With such a large data set, many other groupings of data are possible, with each confirming or discounting some hypothesis. For example, other investigators reported that arsenic concentrations measured in sediments were larger at the land surface than at depth at sites along Whitewood Creek (Cherry and others, 1986). Comparing the arithmetic mean concentrations of arsenic for surface samples to the arithmetic mean concentrations of arsenic for subsurface samples (fig. 8) does indicate a bias towards larger concentrations of arsenic at the land surface along Whitewood Creek and several reaches of the Belle Fourche and Cheyenne Rivers. This may be due to the tendency for fluvial sediments to contain a greater percentage of smaller particles at the land surface. However, the deviations about these means are very large. Although it is likely that in general the concentration of arsenic will decrease with depth, the samples collected during this phase of the study were all collected on or near the land surface and analysis of the data does not confirm the trend. As shown in figure 8, the location along the river is more determinate of arsenic contamination than the depth at which the samples were collected.

Because the maximum arsenic concentrations were measured in sediment samples collected from the flood plain along Whitewood Creek for about 20 river miles upstream from the mouth and from the flood plain along the Belle Fourche River for about 20 river miles downstream from the mouth of Whitewood Creek, environmental damage resulting from arsenic in flood-plain sediments could be maximum in this area. If biological and environmental investigations do not determine any serious effects on these parts of the flood plains along Whitewood Creek or the Belle Fourche River, it is unlikely any other area of the Cheyenne River system will be affected. A possible exception would be the bottom sediments and water of Lake Oahe, which were not investigated during this study. Contamination of surface or ground water also could be prevalent along the downstream reaches of Whitewood Creek.

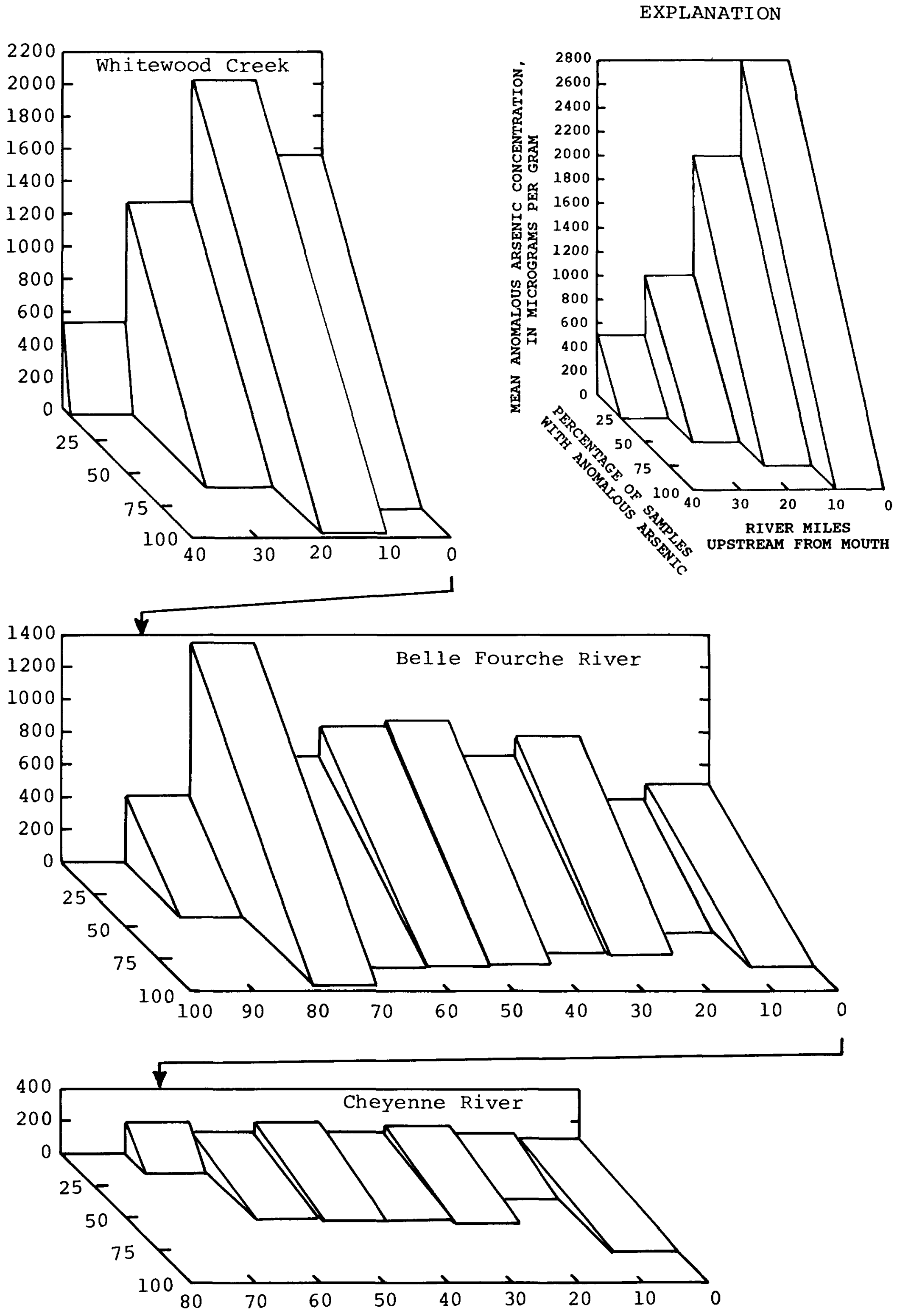

Figure 7.--Extent and magnitude of mean anomalous arsenic concentrations in sediment for 10-mile-long flood-plain segments along Whitewood Creek and the Belle Fourche and Cheyenne Rivers.

Table 6.--Summary of arithmetic and geometric analyses for concentrations of total-recoverable arsenic in sediments from the flood plains of Whitewood Creek, the Belle Fourche River, Bear Butte and Elk Creeks, and the Cheyenne River

Stream	Type of flood-plain segment[1]	Location of flood-plain segment[2]	Approximate area of flood-plain segment[3]	Number of samples	Concentration range	Mean	Deviation	Number of samples with anomalous concentration[4]
Whitewood Creek	U	31-40	1.3	36	4-670	55.6	127	2
	C	21-30	.7	47	8-4,900	826	1,010	29
	C	11-20	1.9	46	140-11,000	1,940	1,760	44
	C	1-10	2.0	48	12-3,200	1,220	900	37
Belle Fourche River	U	91-100	3.9	47	5-13	8.5	2.3	0
	C	81-90	3.6	44	6-1,700	183	372	19
	C	71-80	4.9	44	6-3,500	1,300	824	42
	C	61-70	1.9	48	10-2,900	500	566	37
	C	51-60	1.6	48	10-2,600	683	616	39
	C	41-50	1.7	48	10-2,200	696	660	38
	C	31-40	3.7	48	4-2,200	465	496	34
	C	21-30	2.6	48	2-3,200	572	703	35
	C	11-20	5.2	48	4-1,200	221	342	26
	C	1-10	6.4	47	6-1,400	330	378	32
Bear Butte Creek	U	1-10	--	13	4-22	12.2	3.9	0
Elk Creek	U	1-10	--	24	8-52	16.6	10.2	1
Cheyenne River	U	71-80	6.9	24	6-12	8.0	1.5	0
	C	61-70	7.7	48	5-500	35.8	91	7
	C	51-60	7.8	43	5-450	73.3	94	22
	C	41-50	7.8	46	5-490	109	137	24
	C	31-40	7.6	48	6-420	80.1	85	25
	C	21-30	7.8	48	6-530	99.6	121	26
	C	11-20	8.3	38	5-400	61.9	130	13
	C	1-10	7.6	48	8-280	81.3	62	36

1/ U, uncontaminated, upstream from possible contamination by wastes; C, contaminated, within area of possible contamination by wastes.

2/ River miles upstream from mouth.

3/ Square miles.

4/ Values that exceed $\bar{x} + 2SD$ where $\bar{x}$ is arithmetic mean and SD is standard deviation for uncontaminated samples. Data set for uncontaminated flood-plain segment along Whitewood Creek used to determine anomalous values for contaminated flood-plain segments along Whitewood Creek; data set for all uncontaminated flood-plain segments used to determine anomalous values for contaminated flood-plain segments along all other streams.

5/ Log-transformed data.

6/ Values that exceed $M \times D^2$ where M is geometric mean and D is geometric deviation of uncontaminated samples. Data set for uncontaminated flood-plain segment along Whitewood Creek used to determine anomalous values for contaminated flood-plain segments along Whitewood Creek; data set for all uncontaminated flood-plain segments used to determine anomalous values for contaminated flood-plain segments along all other streams.

Arithmetic analysis			Geometric analysis[5]					
Percentage of samples with anomalous concentration[4]	Mean anomalous concentration[4]	Anomalous deviation[4]	Mean	Deviation	Number of samples with anomalous concentration[6]	Percentage of samples with anomalous concentration[6]	Mean anomalous concentration[6]	Anomalous deviation[6]
6	530	198	19.3	3.4	2	6	510	1.5
62	1,270	1,070	360	4.5	32	68	840	2.3
96	2,020	1,760	1,430	2.3	45	98	1,510	2.1
77	1,560	725	591	5.6	38	79	1,320	1.8
--	--	--	8.2	1.3	0	--	--	--
43	407	488	41	5.5	19	43	217	3.2
95	1,360	792	867	3.6	42	95	1,080	2.2
82	642	572	212	4.9	37	82	429	2.7
81	837	583	303	5.4	39	81	608	2.5
79	874	630	285	5.8	38	79	617	2.6
71	649	479	170	6.2	34	71	475	2.4
73	778	722	189	7.0	35	73	527	2.6
54	397	387	62	5.7	26	54	260	2.5
81	480	372	109	6.4	32	81	346	2.4
--	--	--	11.5	1.4	0	--	--	--
4	52	0	14.6	1.6	1	4	52	0
--	--	--	7.9	1.2	0	--	--	--
15	187	183	13.3	2.9	6	13	146	2.6
51	133	104	41.0	3.2	21	49	109	2.0
52	193	145	46.6	4.1	24	52	145	2.2
52	136	85	44.0	3.3	25	52	117	1.8
54	170	127	48.4	3.6	26	54	134	2.0
34	144	201	29.7	3.0	13	34	96.1	2.2
75	100	61	60.6	2.3	36	75	86.8	1.7

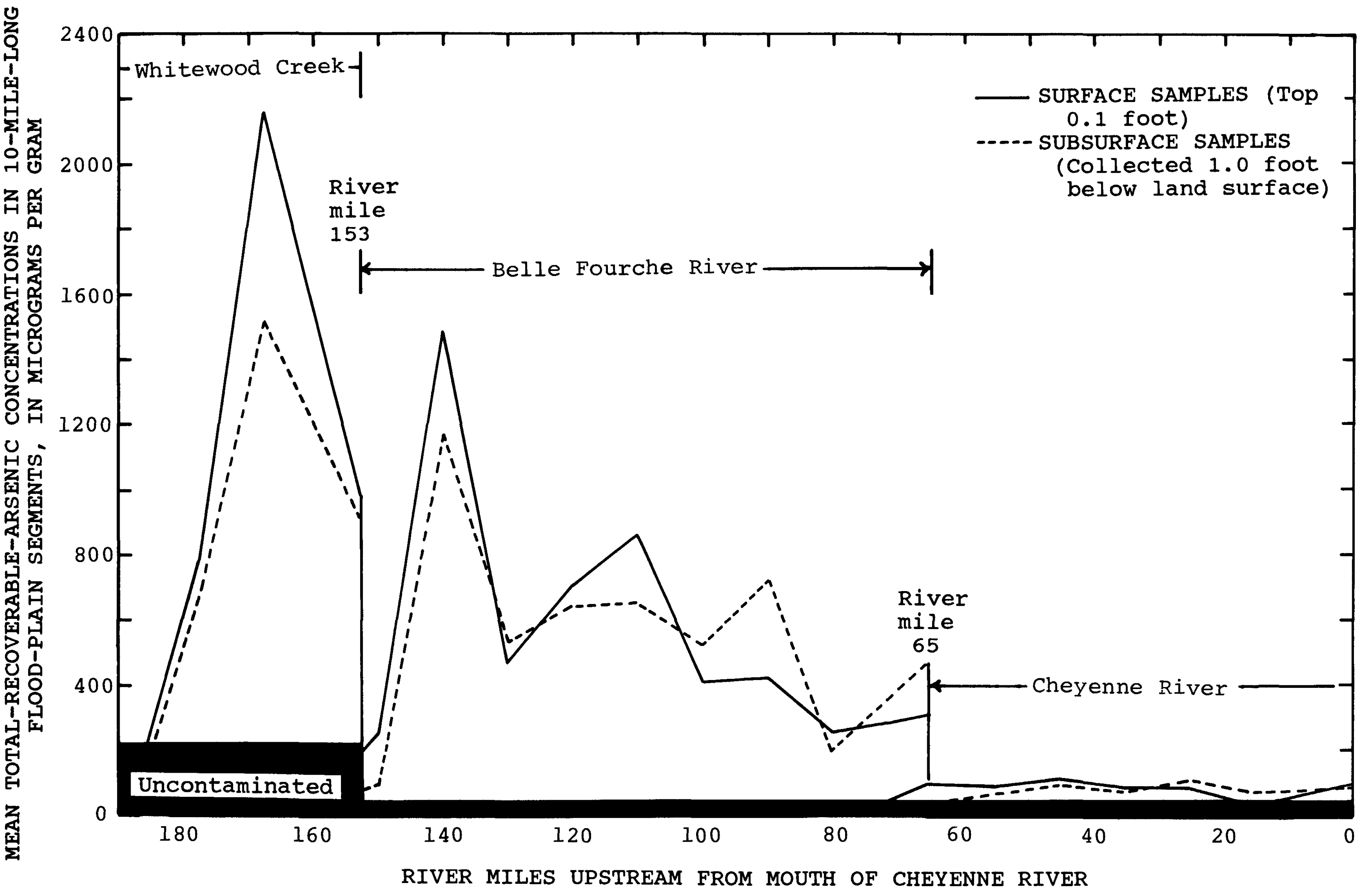

Figure 8.--Mean total-recoverable-arsenic concentrations in surface and subsurface sediment samples collected from the flood plains of Whitewood Creek and the Belle Fourche and Cheyenne Rivers.

EFFECTS OF THE CONTAMINATED SEDIMENTS ON SURFACE-WATER QUALITY

Data Collection

Resuspension of contaminated sediments from streambank deposits and inflow of leachate from the alluvial aquifers affects the water quality of Whitewood Creek and the Belle Fourche and Cheyenne Rivers. To document the magnitude of effects, 11 streamflow-quality monitoring stations were established along the study reach. The stations are listed in table 7 and are located in figure 9. The data-collection program was designed to determine temporal and downstream variations in water chemistry and sediment concentration both within and upstream from the stream reaches affected by wastes. In addition, discharge and water-quality properties were measured and water samples were collected at 43 sites along Whitewood Creek and the Belle Fourche and Cheyenne Rivers twice during the study.

Samples to define the naturally occurring concentrations of the major ions and trace constituents were collected at the following sites: Belle Fourche River near Fruitdale, Whitewood Creek above Lead, and Cheyenne River near Wasta; all sites are upstream from the reaches affected by wastes (table 7, fig. 9). Between 12 and 24 samples were collected at each of these sites from January 1983 to August 1984. To further define naturally occurring concentrations, surface-water samples occasionally were collected from Bear Butte Creek and Elk Creek, tributaries to the Belle Fourche and Cheyenne Rivers. Physical and chemical characteristics determined by analysis of samples from these sites are considered to represent the natural conditions of surface water in the study area.

Data on the variation in water chemistry and sediment concentration resulting from changing hydrologic conditions were obtained from sites on Whitewood Creek and the Belle Fourche and Cheyenne Rivers. The sites--Whitewood Creek above Whitewood, Whitewood Creek near Whitewood, Whitewood Creek above Vale, Belle Fourche River at Vale, Belle Fourche River near Sturgis, Belle Fourche River near Elm Springs, Cheyenne River near Plainview, and Cheyenne River at Cherry Creek--are located within the reaches affected by contaminated sediments (table 7, fig. 9). Monthly samples were collected at each of these sites from January 1983 to August 1984. Comparison of data collected at these sites with data collected at sites upstream from the reaches affected by wastes were used to determine the degree of surface-water contamination caused by the contaminated sediments.

One objective of the study was to determine the water chemistry and sediment concentration in the study reach during periods of high discharge. The contaminated sediments are subject to resuspension and downstream movement during periods of high discharge when contaminated sediments can enter the flow by streambed scouring, inundation of streamside deposits, and by overland runoff. High discharge in streams in western South Dakota usually is caused by runoff from intense, short duration thunderstorms; the resultant periods of high discharge also usually are of short (several hours) duration. Due to the logistical difficulty of collecting samples during short periods of high discharge, automatic-sampling equipment was installed at four sites. Three of the sites--Whitewood Creek above Whitewood, Whitewood Creek above Vale, and Belle Fourche River near Sturgis--are located along the contaminated reach, whereas the fourth site--Belle Fourche River near Fruitdale--is located upstream from any possible contamination.

Table 7.--Sites at which periodic surface-water samples were collected, January 1983 to August 1984

Site number1/	Station name2/	U.S. Geological Survey station number3/	Location
1	Belle Fourche River near Fruitdale	06436000	44°41'27" 103°44'14" T8N R3E Sec. 3NW¼NE¼
2	Whitewood Creek above Lead	06436150	44°18'07" 103°46'57" T4N R3E Sec. 17NW¼SE¼
3	Whitewood Creek above Whitewood	06436180	44°26'32" 103°37'44" T6N R4E Sec. 33NE¼NE½
4	Whitewood Creek near Whitewood	06436190	44°32'30" 103°34'16" T7N R4E Sec. 25SE¼NE¼
5	Whitewood Creek above Vale	06436198	44°37'04" 103°28'52" T8N R5E Sec. 35NE¼NW¼
6	Belle Fourche River at Vale	06436250	44°38'10" 103°25'37" T8N R6E Sec. 19SE¼NE¼
7	Belle Fourche River near Sturgis	06437000	44°30'47" 103°08'11" T6N R8E Sec. 3SE¼NW¼
8	Belle Fourche River near Elm Springs	06438000	44°22'11" 102°33'56" T5N R13E Sec. 29NE¼NE¼
9	Cheyenne River near Wasta	06423500	44°04'52" 102°24'03" T1N R14E Sec. 2NE¼NW¼
10	Cheyenne River near Plainview	06438500	44°31'16" 101°59'34" T7N R18E Sec. 31NE¼SW¼
11	Cheyenne River at Cherry Creek	06439300	44°36'10" 101°29'24" T7N R22E Sec. 5NE¼NW¼

1/ Site number refers to number shown in figure 9.

2/ U.S. Geological Survey policy is to refer to nearest official post office.

3/ Since October 1, 1950, all U.S. Geological Survey streamflow stations are assigned a station number based on the drainage basin and the downstream direction along the main stem. The first two digits (06) refer to the Missouri River basin, the second pair refer to the Cheyenne-Belle Fourche (43) system or the upper Cheyenne (42) system.

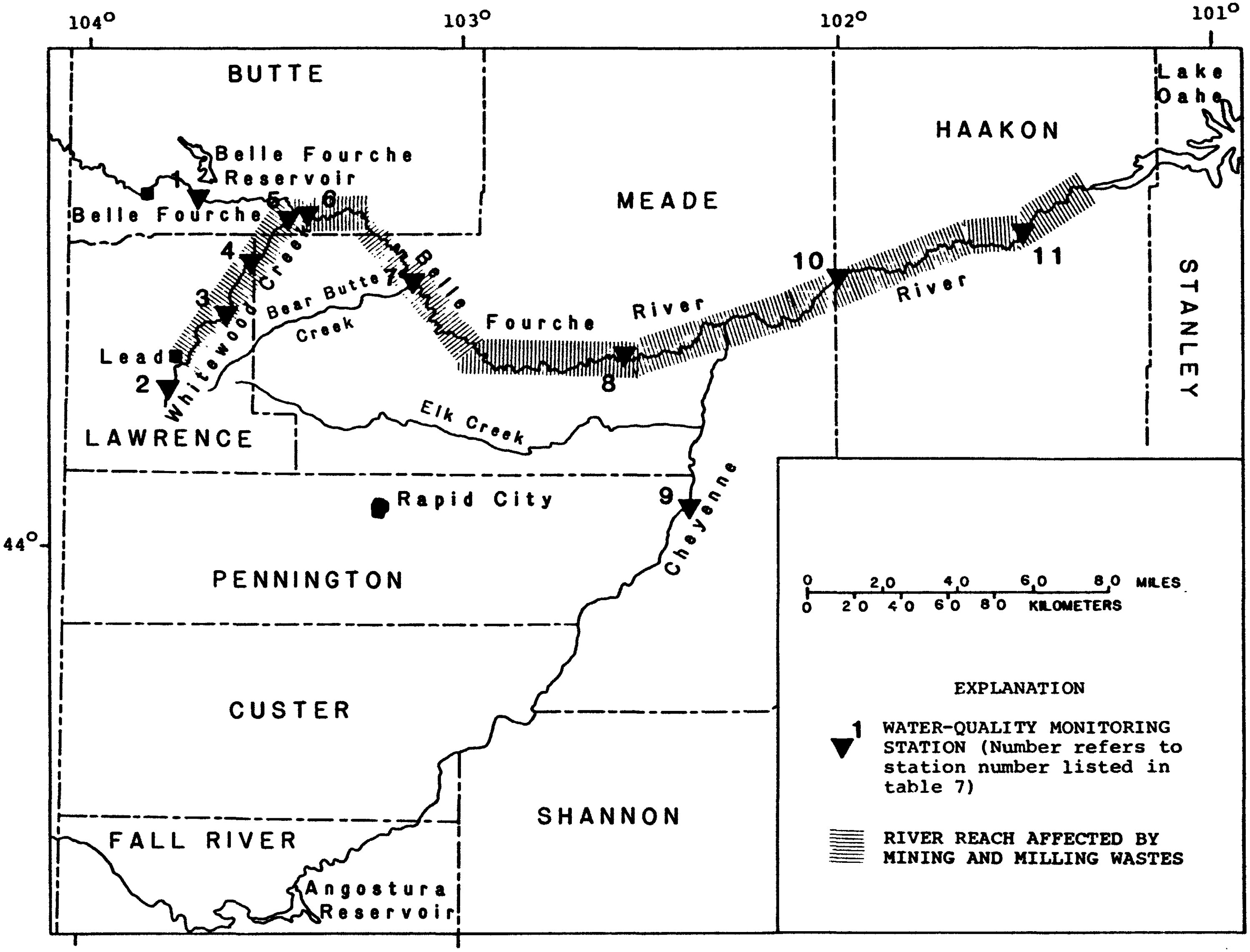

Figure 9.--Location of sites at which periodic surface-water samples were collected, January 1983 to August 1984.

The techniques used in the collection and processing of surface-water samples followed procedures normally used by the U.S. Geological Survey. The procedures used to collect and process surface-water samples for chemical and physical analysis varied, depending on whether they were obtained manually or by use of automatic-sampling equipment. Manually collected samples for inorganic and suspended-sediment analyses were obtained by wading the stream and collecting depth-integrated aliquots with a sampling rod that held two 2-liter bottles equipped with sampling nozzles. Aliquots were collected at from 10 to 25 equally spaced verticals across the channel and were composited in a U.S. Geological Survey sample-splitting churn. Samples collected by use of automatic-sampling equipment (Manning Environmental Corporation[1/] Model S-4051) were automatically delivered into new, one-gallon plastic containers and immediately chilled to 4 °C. Field personnel removed and composited the samples in a U.S. Geological Survey sample-splitting churn. Samples for raw-water analyses were filled from the churn. Bottles for dissolved constituents were filled by pumping the water from the churn with a peristaltic pump and filtering the water through a 0.45-µm (micrometer) cellulose filter. Samples to be analyzed for dissolved trace metals and major cations were preserved with nitric acid. Samples to be analyzed for dissolved mercury were placed in glass bottles and preserved with chromic acid. Samples to be analyzed for cyanide were preserved with NaOH and put on ice.

Surface-water samples were analyzed for the constituents and properties listed in table 8. Analyses were performed at contract laboratories specified by the U.S. Environmental Protection Agency using the methods listed in table 8.

Factors That Affect Surface-Water Quality

The chemical constituents that are present in surface water are largely derived from solution of minerals in rocks and soils with which the water has been in contact. In systems that are undisturbed by humans, relations exist between drainage-basin geology and surface-water composition. These relations may be simple and uncomplicated, such as the case of a small stream draining an area of a single geologic formation. Or, as is more common, the situation may be more complex because of effects of various geologic formations, mixing of water of varying compositions, and chemical reactions within the water, such as cation exchange or adsorption of dissolved ions on suspended sediment. Add to this complexity human-produced effects such as discharge regulation, urban and agricultural runoff, and municipal and industrial waste discharge, and the situation becomes exceedingly complex.

The chemical characteristics of water in Whitewood Creek and the Belle Fourche and Cheyenne Rivers is the result of this complex interaction between natural and human-induced factors. As commonly is the case, the major-ion chemistry is dominated by the geology of the study area, whereas many trace constituents can be attributed directly or indirectly to human activities in the study area.

Whitewood Creek originates as ground-water discharge from the Madison Limestone. The water in the upstream reach of Whitewood Creek is a calcium bicarbonate type that is characteristic of water in contact with carbonate rocks. Downstream, the quality of Whitewood Creek changes as the quality is affected first by the Spearfish Formation, a unit that contains considerable gypsum, and then by the extensive, black,

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[1/] Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 8.--Constituents and properties, and analytical methods for surface-water samples

Constituent or property	Analytical method	References
Dissolved metals (calcium, magnesium, sodium, potassium, cadmium, chromium, copper, iron, lead, manganese, nickel, silver, and zinc)	Inductively coupled argon plasma	Digestion: Included as part of analysis. Analysis: U.S. Environmental Protection Agency, 1980.
Total-recoverable metals (calcium, magnesium, sodium, potassium cadmium, chromium, copper, iron, lead, manganese, nickel, silver and zinc)	Inductively coupled argon plasma	Digestion: U.S. Geological Survey I-3485-78. Analysis: U.S. Environmental Protection Agency, 1980.
Dissolved arsenic	Atomic absorption, hydride	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-1062-7[1].
Dissolved selenium	Atomic absorption, hydride	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-1667[1].
Total-recoverable arsenic	Atomic absorption, hydride	Digestion: Nygaard and Lowry, 1982. Analysis: U.S. Geological Survey I-3062-78[1].
Total selenium	Atomic absorption, hydride	Digestion: Nygaard and Lowry, 1982. Analysis: U.S. Geological Survey I-5667-78[1].
Dissolved cyanide	Colormetric, barbituric acid	Digestion: Included as part of analysis. Analysis: U.S. Environmental Protection Agency, 1974.
Total cyanide	Colormetric, barbituric acid	Digestion: Included as part of analysis. Analysis: U.S. Environmental Protection Agency, 1974.
Dissolved mercury	Atomic absorption, spectrometric	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-1462-78[1].
Total-recoverable mercury	Atomic absorption, spectrometric	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-3463-78[1].
Total alkalinity (as carbonate-bicarbonate)	Titrimetric (pH 8.3-4.5)	Standard methods[2].
Dissolved sulfate	Colormetric, complexometric methylthymol blue	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-2822-77[1].
Dissolved chloride	Colormetric, ferric thlocyanate	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-1187-78[1].
Dissolved solids	Gravimetric, residue on evaporation at 180 °C	Standard methods[2].
Laboratory pH	Electrometric, glass electrode	Standard methods[2].
Laboratory specific conductance	Electrometric wheatstone bridge	Standard methods[2].

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[1] Skougstad and others, 1979.

[2] Exact method dependent on method chosen by laboratory. Several analtyical methods will result in acceptable values.

marine shale that underlies the downstream reach of Whitewood Creek and the reaches of the Belle Fourche and Cheyenne Rivers in the study area. Weathering of these formations adds some calcium and considerable sodium and sulfate to the streams. The change from calcium to sodium as the principal cation occurs gradually downstream as dissolution of gypsum present in the Spearfish Formation, and to a lesser extent in the shale, continues to add calcium to the water. The change from bicarbonate to sulfate occurs much more quickly and sulfate is the dominant surface-water anion everywhere except in the upstream reach of Whitewood Creek.

Sulfate is important because it is the only major ion that is present in sufficient concentrations to possibly limit water use. Mean concentrations of dissolved sulfate increase from 7 mg/L at site 2, Whitewood Creek above Lead (fig. 9), to 360 mg/L at site 5, Whitewood Creek above Vale (fig. 9), to in excess of 1,000 mg/L at most sites on the Belle Fourche and Cheyenne Rivers. Except during high discharge, sulfate exceeds the secondary drinking-water standard of 250 mg/L (U.S. Environmental Protection Agency, 1979) everywhere in the study area except in the upstream reach of Whitewood Creek. Corresponding to the downstream increase in dissolved sulfate is a downstream increase in dissolved solids. Again, with the exception of periods of high discharge, dissolved-solids concentration exceeds the secondary drinking-water standard of 500 mg/L (U.S. Environmental Protection Agency, 1979) everywhere in the study area except in the upstream reach of Whitewood Creek.

Although major-ion chemistry is the result of natural processes, many trace constituents that result from human activities in the basin also are present in the water of Whitewood Creek and the Belle Fourche and Cheyenne Rivers. Most of these constituents are undesirable or toxic to livestock and people, and so can affect water use or damage the environment. These constituents enter the water by direct discharge to the streams, as is the case with municipal and industrial waste discharge, and by indirect means such as runoff from agricultural and urban areas.

Delineation of the extent and magnitude of surface-water contamination caused by the contaminated sediments is complicated by the other sources of contamination present in the study area. Some sources are of little importance to this study because they contribute constituents not associated with the contaminated sediments. These include the discharge from the Lead/Deadwood municipal sewage-treatment plant at Deadwood and runoff from agricultural or stock-impoundment areas. These sources contribute organic matter and nutrients to the streams, that, although they may produce undesirable effects, are not important to this study.

Several point sources of contaminants are present that contribute constituents identical to those derived from the contaminated sediments. The most substantial of these is the Homestake Mining Co. effluent discharge to Gold Run at Lead. The effluent results from mine dewatering and disposal of some of the mill-circuit water (F. D. Fox, oral commun., 1983), and contains dissolved cyanide, arsenic, and metals. In the case of dissolved cyanide and copper, the quantity contributed to Whitewood Creek by the effluent is a large proportion of the constituent load of the stream. However, during the fall of 1984, a new water treatment system became operational and should decrease the dissolved cyanide and copper loads considerably. The city of Whitewood municipal sewage lagoon also contributes dissolved arsenic and metals to Whitewood Creek although the effects may not be important due to the slow discharge rate. The estimated effects of these discharges on the concentrations of specific constituents will be discussed later in the report.

Effects of Contaminated Sediments

Magnitude of Contamination

Because one objective of the study was to determine the possible effects of the contaminated sediments on surface-water quality, a detailed analysis was made only for those constituents known to be associated with contaminated sediments. Arsenic, cadmium, copper, cyanide, iron, manganese, mercury, and silver can be directly related to the contaminated sediments. Sufficiently large concentrations of any of these constituents may effect water use by exceeding standards for drinking water, stock and irrigation water, or aquatic life. A summary, by sampling site, of the concentrations for these constituents is presented in table 9. Caution needs to be used when interpreting the mean concentrations listed in this table, particularly for the total or total-recoverable data. Sites 1, 3, 5, and 7 were selected for high-discharge sampling and a large percentage of the total number of samples were collected during high discharge. This biases the data toward concentrations during high discharge, even though high discharge only occurs during a small percentage of the year. However, the mean and maximum concentrations listed in table 9 are an indicator of what constituents may be of concern.

The data listed in table 9 indicate that effects of the contaminated sediments are largely confined to Whitewood Creek and the reach of the Belle Fourche River downstream from the mouth of Whitewood Creek. The furthest downstream reaches of the Belle Fourche River, and all reaches of the Cheyenne River, are not seriously affected. Arsenic, cadmium, manganese, and silver generally increase in concentration downstream along Whitewood Creek. Concentrations are maximum at site 5, Whitewood Creek above Vale, near the mouth of Whitewood Creek, and then decrease downstream along the Belle Fourche River. Copper, cyanide, and mercury generally decrease in concentration downstream along Whitewood Creek and the Belle Fourche River and the maximum concentrations were from samples collected at site 3, Whitewood Creek above Whitewood. Iron is somewhat indeterminate, total-recoverable iron increases in concentration downstream along Whitewood Creek, whereas dissolved iron decreases in concentration.

Hydrogeochemical Processes

Trends of increasing or decreasing constituent concentration along Whitewood Creek are related to the primary source of the constituent. Constituents primarily derived from contaminated sediments generally increase in concentration downstream along Whitewood Creek as the large deposits of contaminated sediments along Whitewood Creek add leachate and sediment to the water. Constituents primarily derived from point sources in the Lead/Deadwood area generally decrease in concentration downstream along Whitewood Creek due to dilution, adsorption, or biodegradation.

The most important constituent derived from the contaminated sediments is arsenic. Undetected or seldom present in measurable concentrations at sites 1, 2, and 9, which are upstream from the contaminated sediments, maximum concentrations of dissolved arsenic occur in the downstream reach of Whitewood Creek. Detected only twice in 53 samples collected from sites 1, 2, and 9 (fig. 9, table 9), dissolved arsenic was detected in 76 of the 82 samples collected from sites 3, 4, and 5 along the downstream reach of Whitewood Creek. The largest dissolved arsenic concentrations were measured at sites 4 and 5, with a mean concentration of 34 µg/L and a maximum concentration of 82 µg/L. Total-recoverable arsenic, which includes both the dissolved

Table 9.--Summary of selected constituent concentrations in water samples from Whitewood Creek and the Belle Fourche and Cheyenne Rivers, January 1983 to August 1984

[Cyanide concentrations are milligrams per liter; all other concentrations are micrograms per liter. Mean, arithmetic mean of concentrations more than detection limits; N, number of samples with constituent concentration more than detection limit; (TN), total number of laboratory analysis; Range, range of concentrations; ND, never detected. Detection limit varies between sample sets]

Site number1/	Station name	Arsenic, dissolved	Arsenic, total recoverable	Cadmium, dissolved	Cadmium, total recoverable	Copper, dissolved	Copper, total recoverable
		Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range
1	Belle Fourche River near Fruitdale	ND/0 (25) <1-<50	22/13 (25) <1-110	ND/0 (25) <1-<10	3/3 (25) <1-<100	3/2 (25) <2-<50	3/1 (17) 3-<50
2	Whitewood Creek above Lead	5/1 (16) <1-<50	21/3 (16) <1-<50	ND/0 (16) <1-<10	ND/0 (16) <1-<10	ND/0 (16) <2-<50	ND/0 (14) <2-<50
3	Whitewood Creek above Whitewood	18/30 (34) <10-<50	460/34 (35) 29-1,900	3/4 (35) <1-<10	9/13 (35) <1-25	54/18 (35) <2-300	310/28 (32) 28-1,100
4	Whitewood Creek near Whitewood	34/18 (19) 17-75	119/19 (19) 31-580	4/2 (19) <1-<10	5/5 (19) <1-<10	74/6 (19) <2-350	140/8 (17) 7-350
5	Whitewood Creek above Vale	34/28 (29) 17-82	1,230/29 (29) 24-7,900	4/3 (29) <1-<10	25/9 (29) <1-100	14/6 (29) <2-64	270/14 (25) <50-1,100
6	Belle Fourche River at Vale	18/14 (17) 8-43	51/17 (17) 14-260	ND/0 (17) <1-<10	3/3 (17) <1-<10	52/2 (17) <2-100	98/2 (15) <2-100
7	Belle Fourche River near Sturgis	12/22 (27) <2-<50	360/21 (25) <10-2,400	9/1 (25) <1-<10	11/6 (25) <1-19	2/4 (27) <2-<50	85/7 (19) <5-120
8	Belle Fourche River near Elm Springs	8/14 (22) <2-13	44/12 (16) 8-260	1/1 (22) <1-<10	2/1 (16) <1-<10	3/8 (22) 2-<50	120/1 (14) <2-120
9	Cheyenne River near Wasta	2/1 (12) <2-<50	29/8 (12) 1-150	ND/0 (12) <1-<10	10/1 (12) <1-10	ND/0 (12) <5-<50	190/1 (12) <5-190
10	Cheyenne River near Plainview	4/2 (13) <2-<50	18/9 (13) 2-<50	ND/0 (13) <1-<10	4/1 (13) <1-<10	3/1 (13) 3-<10	ND/0 (12) <5-<50
11	Cheyenne River at Cherry Creek	6/9 (19) <1-<50	26/10 (13) 1-130	3/2 (19) <1-<10	5/1 (13) <1-<10	5/8 (19) 4-<50	110/1 (12) <5-110

Table 9.--Summary of selected constituent concentrations in water samples from Whitewood Creek and the Belle Fourche and Cheyenne Rivers, January 1983 to August 1984--Continued

	Cyanide, dissolved	Cyanide, total recoverable	Iron, dissolved	Iron, total recoverable	Manganese, dissolved	Manganese, total recoverable	Mercury, dissolved	Mercury, total recoverable	Silver, dissolved	Silver, total recoverable
Site number	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range	Mean/N(TN) Range
1	0.05/2 (25) <0.01-<3.0	0.03/3 (25) <0.01-<2.0	23/11 (25) 3-50	9,300/25 (25) 17-76,800	183/25 (25) 23-572	670/25 (25) 192-2,440	ND/0 (24) <0.2-<0.5	0.4/3 (24) <0.2-<0.5	ND/0 (25) <3-<100	ND/0 (25) <3-<100
2	ND/0 (16) <0.01-<2.0	ND/0 (16) <0.01-<2.0	18/4 (15) 5-28	1,030/14 (14) 150-5,900	12/7 (16) 5-20	65/13 (16) 14-410	ND/0 (15) <0.2-<0.5	0.5/1 (15) <0.2-0.5	ND/0 (16) <3-<10	ND/0 (16) <3-<10
3	0.39/29 (35) <0.01-6.1	0.40/31 (35) <0.01-6.2	41/16 (33) 5-100	31,600/35 (35) 30-200,000	210/35 (35) 52-753	1,490/35 (35) 106-6,720	0.2/1 (32) <0.2-<0.5	2.6/24 (35) <0.2-11	4/1 (35) <3-<10	24/14 (34) <3-56
4	0.30/15 (19) <0.01-3.7	0.44/15 (19) <0.01-5.6	38/7 (18) 4-88	4,470/18 (18) 421-16,000	160/19 (19) 52-288	310/19 (19) 89-704	0.2/1 (18) <0.2-<0.5	0.6/4 (18) <0.2-0.7	4/1 (19) <3-<10	ND/0 (19) <3-<50
5	0.14/22 (29) <0.01-1.8	0.19/22 (29) <0.01-2.0	27/12 (28) 5-61	39,100/27 (28) 510-290,000	260/29 (29) 76-495	2,430/29 (29) 88-17,500	0.3/1 (27) <0.2-<0.5	2.1/14 (27) <0.2-7.0	4/5 (29) <3-<10	43/4 (29) <3-120
6	0.29/7 (17) <0.01-1.6	0.29/7 (17) <0.01-1.7	18/3 (17) <2-<50	2,360/17 (17) 500-14,000	270/17 (17) 52-1,000	360/17 (17) 120-1,100	0.3/1 (16) <0.2-<0.5	0.3/1 (16) <0.2-<0.5	3/1 (17) <3-<10	ND/0 (17) <3-<10
7	0.08/7 (25) <0.01-0.24	0.07/11 (27) <0.01-<1.0	21/10 (27) <2-60	30,000/25 (25) 100-220,000	160/24 (27) 3-820	980/25 (25) 50-5,760	0.3/1 (23) <0.2-<0.5	0.6/16 (26) <0.1-2.6	4/2 (27) <3-<10	ND/0 (25) <3-<10
8	0.06/1 (16) <0.01-0.06	0.06/1 (16) <0.01-<0.10	17/11 (22) <2-50	9,490/16 (16) 150-130,000	95/20 (22) 5-730	370/16 (16) 30-3,100	0.2/4 (21) <0.1-<0.5	0.4/2 (15) <0.2-0.5	ND/0 (22) <1-<10	ND/0 (16) <3-<10
9	ND/0 (12) <0.01-<3.0	ND/0 (12) <0.01-<3.0	ND/0 (11) <10-<50	13,900/11 (12) <50-130,000	15/6 (12) 6-30	730/11 (11) 30-6,000	0.3/2 (11) <0.2-<0.5	0.5/3 (11) <0.2-0.7	ND/0 (12) <5-<10	ND/0 (12) <5-<10
10	ND/0 (12) <0.01-<0.01	ND/0 (13) <0.01-<1.0	ND/0 (13) <2-<50	5,350/13 (13) 100-32,000	50/8 (13) <10-150	190/13 (13) 30-800	0.4/3 (12) <0.2-0.5	0.3/1 (12) <0.2-<0.5	ND/0 (13) <3-<10	ND/0 (13) <3-<10
11	0.02/1 (12) <0.01-0.02	ND/0 (12) <0.01-<1.0	8/6 (19) <3-<50	9,770/13 (13) 100-89,000	50/12 (19) 5-150	380/13 (13) 34-2,900	0.6/8 (19) <0.2-2.0	0.8/5 (13) <0.2-2.0	ND/0 (19) <3-<10	ND/0 (13) <3-<10

1/ Refers to site number shown in figure 9 and listed in table 7.

and suspended components, also is present in large concentrations in the downstream reach of Whitewood Creek. Total-recoverable arsenic was detected in 82 of 83 samples collected at sites 3, 4, and 5 along the downstream reach of Whitewood Creek; the maximum concentration was 7,900 µg/L at site 5. Arsenic commonly was detected in the Belle Fourche River downstream from Whitewood Creek but the magnitude of contamination was much less. Arsenic was only occasionally detected in the Cheyenne River.

Cadmium and silver also are derived from the contaminated sediments, and, like arsenic, maximum concentrations of these constituents occur in the downstream reach of Whitewood Creek. However, the mean and maximum concentrations for these constituents are much less than those for arsenic. Dissolved cadmium was detected in only 9 of 83 samples with a maximum concentration of 7 µg/L, whereas dissolved silver was detected in only 7 of 83 samples with a maximum concentration of 4 µg/L. Unlike arsenic, both these constituents are relatively insoluble in aerated water and equilibrium concentrations for these constituents are in the range of the detection limits, 1 to 10 µg/L (Hem, 1970). Total-recoverable cadmium and silver were detected more frequently but only in samples containing large concentrations of suspended sediment. The maximum total-recoverable cadmium and silver concentrations, 100 µg/L and 120 µg/L, were from a sample collected at Whitewood Creek above Vale (site 5), which had a suspended-sediment concentration of 10,600 mg/L.

Although copper is present in the contaminated sediments, the maximum concentration of copper in Whitewood Creek was measured at site 3, Whitewood Creek above Whitewood, due largely to the effects of the Homestake Mining Co. effluent discharge. In Whitewood Creek, water samples with substantial concentrations of dissolved copper, more than about 10 µg/L, also have substantial concentrations of dissolved cyanide, generally more than 0.1 mg/L. The sample containing the maximum concentration of dissolved copper, 350 µg/L, had a dissolved-cyanide concentration of 3.7 mg/L, the maximum measured during the study. Correlation coefficients between the concentrations of dissolved copper and dissolved cyanide are 0.90 for 35 samples collected at site 3, Whitewood Creek above Whitewood, and 0.94 for 19 samples collected at site 4, Whitewood Creek near Whitewood, indicating a direct relation between the constituents. Cyanide is a strong complexing agent with copper and any dissolved cyanide discharged to, or present in, Whitewood Creek would quickly form either iron or copper metallocyanide complexes. Copper metallocyanide complexes are soluble, and are recovered in the laboratory analysis for dissolved copper. The source of the copper for forming the copper metallocyanides comes from: (1) Copper-sulfide minerals present in the ore, (2) copper wire used in mining and incorporated in the ore, and (3) copper from contaminated sediments present in the stream. Whatever the source, without the increased solubility created by the cyanide, the solubility limits of copper in aerated, alkaline water (the conditions in Whitewood Creek) would limit dissolved-copper concentrations in Whitewood Creek to the range of 1 to 10 µg/L.

Iron and manganese are both common constituents of the contaminated sediments and large concentrations usually are detected in Whitewood Creek and the Belle Fourche River. These constituents also are abundant in natural rocks and soils and so are present in detectable concentrations at sites upstream from contaminated sediments. The solubility of iron in aerated, alkaline surface water is negligible and water at equilibrium cannot contain concentrations of uncomplexed dissolved iron greater than about 10 µg/L. However, as is the case with copper, iron can complex with cyanide and so is sometimes present in concentrations as much as 100 µg/L at the sites along the downstream reach of Whitewood Creek. Samples with substantial concentrations of dissolved iron also contain substantial concentrations of dissolved cyanide and copper. As would be expected, samples containing substantial concentrations of suspended sediment also contain substantial concentrations of total-recoverable iron. Manganese is considerably more soluble than iron in aerated, alkaline surface water and so the concentrations of dissolved manganese are about 5 to 10 times greater than the concentrations of dissolved iron at all sampling sites. Along the downstream reach of Whitewood Creek, dissolved-manganese concentrations average about 220 µg/L whereas dissolved-iron concentrations average about 36 µg/L. Dissolved manganese apparently is derived from the solid phase manganese present in the contaminated sediments and incorporated in the stream-channel material, and the concentrations in Whitewood Creek agree with what would be expected based on the solubility of manganese in surface water.

The only substantial source of cyanide to Whitewood Creek is the Homestake Mining Co. effluent discharge at Lead. The concentration of cyanide in the effluent is quite variable, ranging from less than 0.01 to 11 mg/L (F. D. Fox, oral commun., 1985), and the concentrations of cyanide in Whitewood Creek are, therefore, also quite varible, ranging from less than 0.01 to 6.2 mg/L. Most of the measured cyanide concentrations in Whitewood Creek were in the range of 0.01 to 0.2 mg/L with almost all the constituent in the dissolved phase. A seasonal trend occurs with the largest cyanide concentrations in the spring, resulting from increased cyanide present in the Homestake Mining Co. effluent discharge during this period (F. D. Fox, oral commun., 1985). Cyanide concentrations decrease quickly downstream along the study reach. An example is the dissolved-cyanide concentrations measured in the April 1984 sample set. Dissolved-cyanide concentrations decreased from 7.1 mg/L at Whitewood Creek above Whitewood, to 3.7 mg/L at Whitewood Creek near Whitewood, to 1.8 mg/L at Whitewood Creek above Vale, to 1.6 mg/L at Belle Fourche River at Vale, and to 0.24 mg/L at Belle Fourche River near Sturgis.

Mercury is contributed to Whitewood Creek and the Belle Fourche River by the contaminated sediments present along these streams. Although concentrations of total-recoverable mercury occasionally are more than the detection limit at sites 1 and 2, both the percentage of concentrations more than the detection limit and the measured concentrations are larger within the contaminated reaches. Along the downstream reach of Whitewood Creek, total-recoverable mercury was detected in 42 of 80 samples, and had a mean concentration of 2.6 µg/L and a maximum concentration of 11.0 µg/L at site 3, Whitewood Creek above Whitewood. Total-recoverable-mercury concentrations decreased downstream along Whitewood Creek from this site, a trend difficult to explain. Mercury is known to be present in the contaminated sediments and is not thought to be contributed by sources in the Lead/Deadwood area. It is possible that contaminated sediments within the reach between Deadwood and site 3, Whitewood Creek above Whitewood, are the primary source of mercury to Whitewood Creek. During recent placer-mining operations along this reach of Whitewood Creek, the miners reportedly found visible quantities of elemental mercury (R. D. Townsend, South Dakota Department of Water and Natural Resources, oral commun., 1984). The concentrations of dissolved mercury are uniformally small throughout the study area due to its negligible solubility and dissolved mercury was detected in only 22 of 218 surface-water samples. However, unlike any of the other trace constituents, dissolved mercury was more commonly detected along the Cheyenne River where maximum concentrations occurred, again a trend difficult to explain.

The concentrations of arsenic, cadmium, mercury, and silver vary considerably during the year as a result of natural processes acting on the contaminated sediments.

The dissolved concentrations vary by as much as several hundred percent during the year as a result of variations in ground-water inflow and dilution. The total or total-recoverable concentrations vary by as much as several orders of magnitude during short periods in response to rapid changes in suspended-sediment concentration. These fluctuations of constituent concentrations are related to both short-term and seasonal fluctuations of discharge typical of small streams in semiarid western South Dakota. Analysis of discharge fluctuation, and the relations between discharge, suspended-sediment concentration, and the dissolved and total-recoverable concentrations of constituents, provide insight into the hydrogeochemical processes controlling the surface-water chemistry, and will allow estimations of the significance of the contamination. Because the downstream reach of Whitewood Creek is the most seriously affected reach of surface water in the study area, the data collected from this reach of Whitewood Creek were analyzed in detail using regression analysis.

The discharge variation of Whitewood Creek is largely the result of snowmelt during March, April, and May and runoff from thunderstorms common from May to August. A distinct high-discharge period resulting from snowmelt during late April and early May is seen on the hydrographs of mean daily discharge for the 1983 and 1984 water years for two sites along the downstream reach of Whitewood Creek (figs. 10 and 11). Snowmelt also can increase the discharge, particularly at the most downstream site, Whitewood Creek above Vale, during the winter in response to brief, warm periods. Discharge during the summer is unpredictable with rainfall runoff causing large variations during periods ranging from 1 day to several weeks. Intense rains in June 1984, resulted in the large discharge peaks shown in figure 11 and the maximum instantaneous discharge, 980 ft^3/s, of Whitewood Creek during the study was measured on June 10 as a result of these storms. Although natural processes are responsible for most of the discharge variation measured in Whitewood Creek, stream discharge also is affected by variations in wastewater discharge by the Homestake Mining Co. at Lead and in discharge from the Lead/Deadwood municipal sewage-treatment plant at Deadwood as well as by minor withdrawals for irrigation of about 800 acres.

The magnitude and variation of discharge measured in Whitewood Creek may also be shown in duration curves. The discharge-duration curves for sites 3 and 5 on Whitewood Creek are shown in figure 12. A discharge-duration curve depicts the percentage of time specific discharges were equaled or exceeded. For example, at site 5, Whitewood Creek above Vale, the mean daily discharge equaled or exceeded 100 ft^3/s about 12 percent of the time (44 days a year), 200 ft^3/s about 4 percent of the time (15 days a year), and 300 ft^3/s about 1 percent of the time (4 days a year). Because the concentrations of many water-quality constituents are related to stream discharge, discharge-duration data are useful in predicting the duration or recurrence interval of the concentration of a particular constituent.

Of the four constituents derived primarily from the contaminated sediments, only arsenic occurs principally in the dissolved phase and is present in detectable concentrations in the downstream reach of Whitewood Creek. As previously discussed, the minimal solubility of cadmium, silver, and mercury in an aerated, alkaline surface water prevents any detectable dissolved-phase concentrations of these constituents in the water. Concentrations of dissolved arsenic can range from 100 to 10,000 µg/L (Hem, 1970); these concentrations are much larger than those measured in water samples from Whitewood Creek. Therefore, it does not appear that maximum dissolved-arsenic concentrations are controlled by arsenic solubility but rather by other processes.

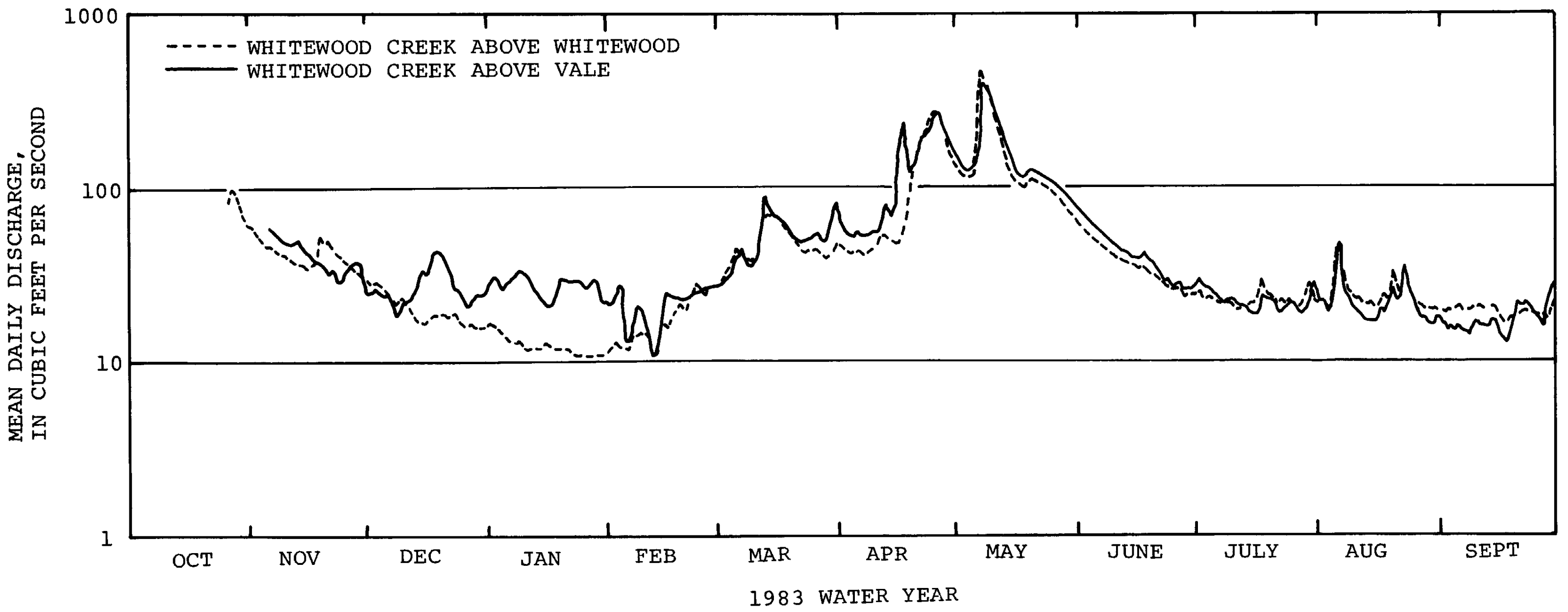

Figure 10.--Mean daily discharge measured during the 1983 water year at sites 3 and 5, Whitewood Creek above Whitewood and Whitewood Creek above Vale.

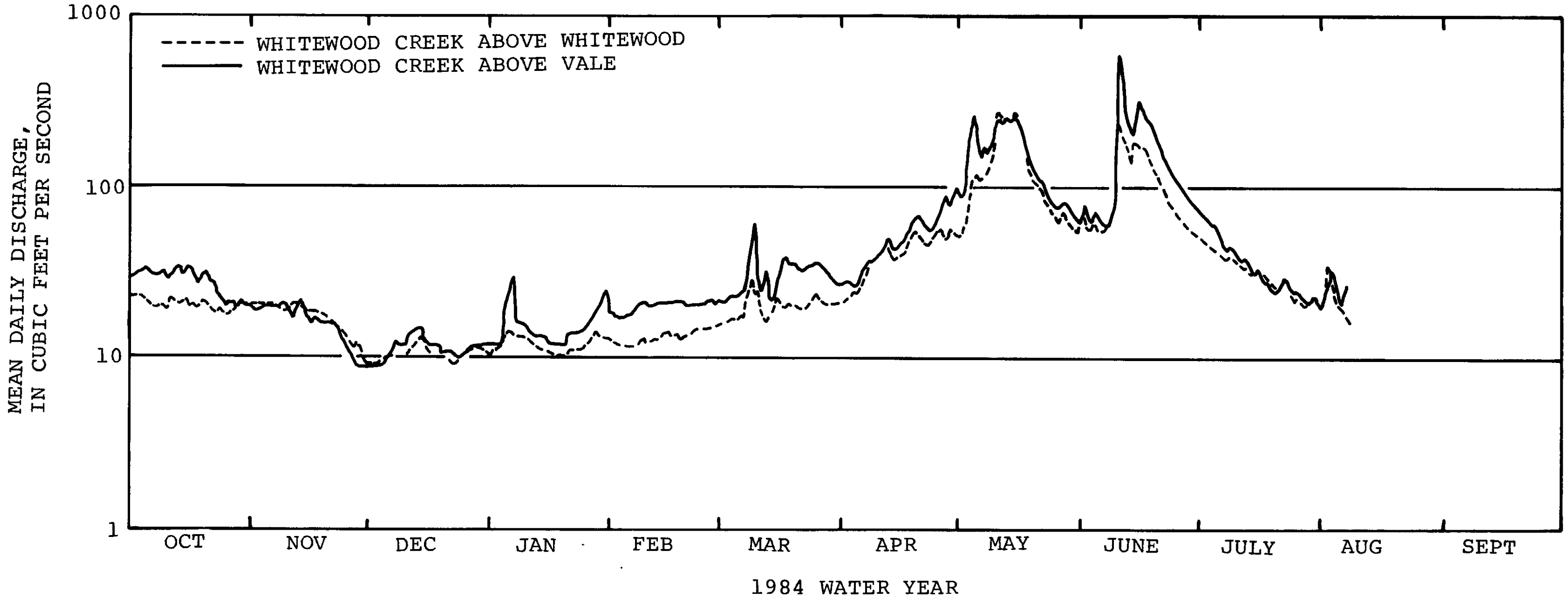

Figure 11.--Mean daily discharge measured during the 1984 water year at sites 3 and 5, Whitewood Creek above Whitewood and Whitewood Creek above Vale.

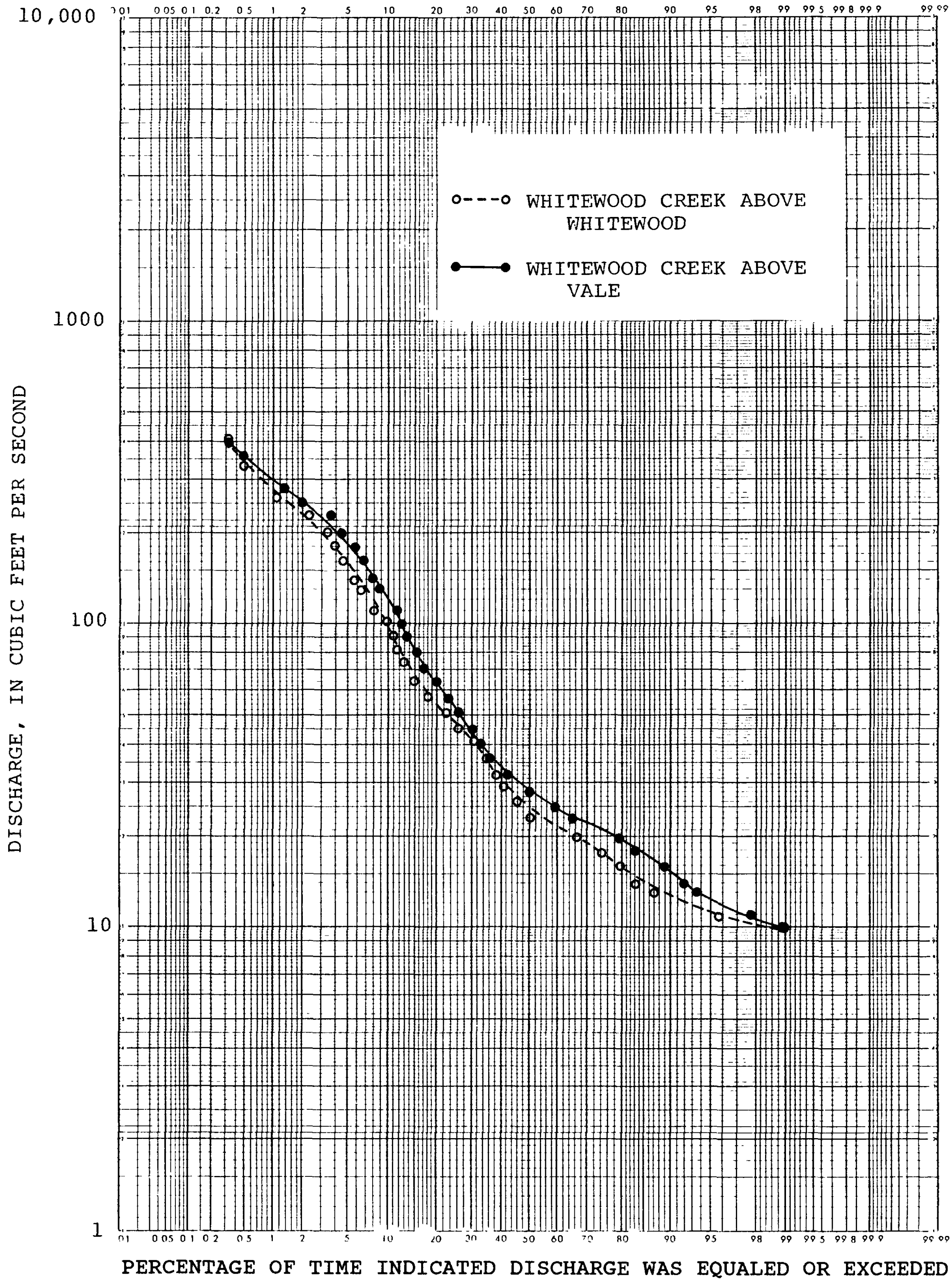

Figure 12.--Discharge-duration curves at sites 3 and 5, Whitewood Creek above Whitewood and Whitewood Creek above Vale, for mean daily discharge, November 1982 to August 1984.

Dissolved arsenic can enter the water in a stream by direct solution or desorption of ions from solid material entrained in the water or present in the stream bed, or by inflow of ground water containing dissolved arsenic. If dissolved arsenic primarily was derived from solid-phase arsenic adsorbed on suspended sediment, there could be positive correlation between dissolved and total-recoverable arsenic concentrations. This, however, is not the pattern. Samples with concentrations of total-recoverable arsenic as much as 7,900 µg/L, have concentrations of dissolved arsenic generally ranging from 20 to 30 µg/L. There is a negative correlation between dissolved and total-recoverable arsenic concentrations at sites along the downstream reach of Whitewood Creek. However, there is some desorption during periods of high discharge that is evidenced by the large dissolved-arsenic loads present during these periods. If the source of the dissolved arsenic is from ground-water inflow, and not related to contaminated sediments entering the stream during periods of high discharge, then the stream discharge would dilute the dissolved-arsenic concentration and a negative correlation will exist between dissolved and total-recoverable concentrations. Why arsenic is not solubilized from the large quantities of suspended sediment sometimes entrained in the water is likely the result of ion sorption on metallic hydroxides. Compounds such as ferric hyroxy-arsenate will form in the presence of arsenic and iron (Hem, 1970); these compounds are almost insoluble and will not release arsenic or iron back into solution in an aerated, almost-neutral surface water.

Both dilution and variation in ground-water inflow are responsible for the periodic variations in dissolved-arsenic concentration in the downstream reach of Whitewood Creek (figs. 10, 11, and 13). The smallest dissolved-arsenic concentrations occur during the spring, a period of sustained high discharge. This would be expected if the primary source of dissolved arsenic is ground-water discharge and is not runoff related. The largest instream concentrations of dissolved arsenic, in the range of 40 to 80 µg/L, occur in the late spring and early summer, shortly after the period of high discharge. During the same period, ground-water discharge to the stream also would be maximum due to release of bank storage and recharge that occurred during the spring. The downstream reach of Whitewood Creek is a gaining reach throughout most of the year, but the largest volumetric gains occur during the spring and early summer.

Other evidence indicates that ground-water inflow is a major source contributing dissolved arsenic to Whitewood Creek. First, water in the alluvial aquifer along Whitewood Creek is known to contain dissolved arsenic in concentrations ranging from 50 to 500 µg/L, based on ground-water sampling during this and other studies (Cherry and others, 1986). Samples collected from two seeps discharging to the creek in the reach downstream from site 3, Whitewood Creek above Whitewood, in late June 1984, contained dissolved-arsenic concentrations of 181 and 498 µg/L. Second, discharge and arsenic data from two gain-loss surveys conducted along Whitewood Creek downstream from site 2, Whitewood Creek above Lead (fig. 14), indicate that during the period of minimum ground-water inflow during the fall, discharge, dissolved-arsenic concentration, and dissolved-arsenic load generally do not increase downstream from site 3, whereas during the period of maximum ground-water inflow in the spring, discharge, dissolved-arsenic concentration, and dissolved-arsenic load generally increase downstream from site 3.

It seems likely that discharge of arsenic contaminated ground water to the Belle Fourche River also occurs. The resultant instream concentrations along the Belle Fourche are less than those in Whitewood Creek because dissolved-arsenic concentrations in the ground water are less, 20 to 200 µg/L, as determined during this study, and the discharge in the river is considerably larger, diluting the arsenic.

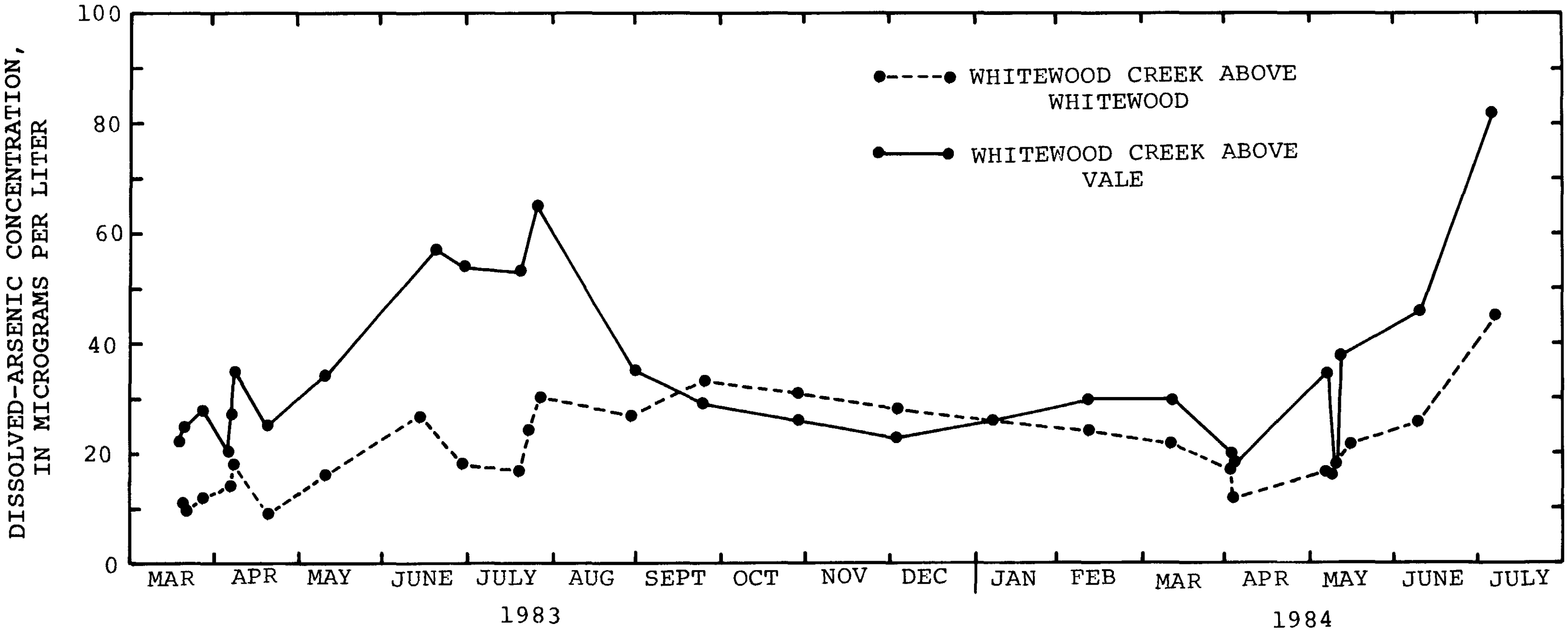

Figure 13.--Dissolved-arsenic concentrations at sites 3 and 5, Whitewood Creek above Whitewood and Whitewood Creek above Vale, March 1983 to July 1984.

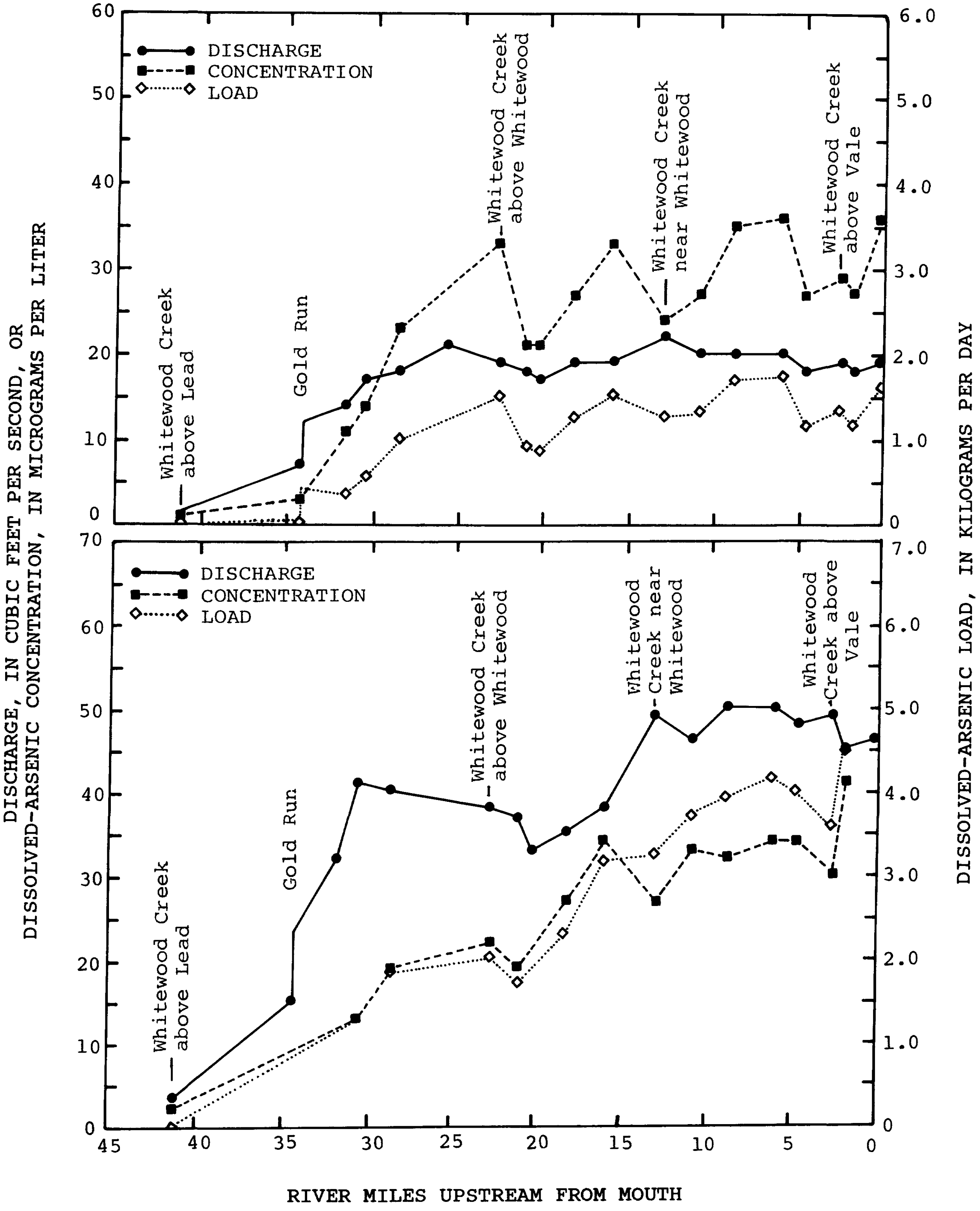

Figure 14.--Discharge, dissolved-arsenic concentration, and dissolved-arsenic load for Whitewood Creek in October 1983 (top graph) and April 1984 (bottom graph).

Other constituents are undoubtedly contributed to the streams by discharge from the alluvial aquifers. Cadmium, mercury, and silver have such negligible solubilities, even in the ground water, that concentrations of these constituents were not more than the detection limits in the sampled seeps. Other constituents, such as iron, while readily soluble in some ground water, have negligible solubilities in aerated water and precipitate when reaching the land surface. The two seeps sampled along Whitewood Creek had dissolved-iron concentrations of 4,400 and 6,850 µg/L, and wells drilled through massive deposits of contaminated sediments near the mouth of Whitewood Creek yielded water with dissolved-iron concentrations as much as 206,000 µg/L (Cherry and others, 1986). Yet, dissolved iron only is present in the surface water in detectable concentrations (more than 50 µg/L) if complexed with cyanide.

One water-quality parameter that is almost always related to discharge is suspended-sediment concentration. Higher discharge results in increases in water velocity and the transport capacity of the stream due to increased turbulence. The relation among stream discharge, mean downstream water velocity, and the vertical component of current (turbulence) is pronounced in steep-gradient, rough-bottom streams such as Whitewood Creek. Unfortunately, the relation between discharge and suspended-sediment concentration for a specific site may not have a pronounced correlation due to the complicated set of factors acting on the land surface of the drainage basin and throughout the channel system upstream from the site. The relations between discharge and suspended sediment at two sites on Whitewood Creek are shown in figures 15 and 16. Data collected at the upstream site, Whitewood Creek above Whitewood, are scattered and not well correlated, whereas data collected at the downstream site, Whitewood Creek above Vale, are grouped and better correlated.

Streams that are affected by metal contamination usually transport a substantial fraction of their metal load absorbed on suspended sediment, and relations between suspended-sediment concentration and total or total-recoverable metal concentrations usually have a significant correlation. The suspended sediment/total-recoverable iron, and suspended sediment/total-recoverable arsenic relations for the downstream site on Whitewood Creek are shown in figures 17 and 18. The graphical correlation for iron is linear when plotted on log scales because iron has minimal solubility and almost all the iron is absorbed onto or associated with suspended sediment; the graphical correlation for arsenic is curved at the lower end due to the presence of dissolved-phase arsenic that is included in total-recoverable analysis data. The lines shown in the figures are best fit using the method of least squares and are in the form of a power equation. The constant used in the linear equation for arsenic is the mean dissolved-arsenic concentration measured during the study at the site for samples that had a suspended-sediment concentration of less than 1,000 mg/L.

Equations describing the relations between suspended-sediment and total-recoverable-constituent concentrations, and between suspended-sediment concentration and discharge, can be used in conjunction with discharge-duration data as a predictive tool. The equations of the least-squares fit lines and their respective correlation coefficients between suspended-sediment and total-recoverable-constituent concentrations for the constituents of greatest interest at two sites on Whitewood Creek are listed in table 10. After considering the limitations of the data base, particularly the limited correlation between suspended-sediment concentration and discharge at site 3, Whitewood Creek above Whitewood, and assuming the conditions present during the study will represent those that will occur in the future, these equations can be used to estimate the percentage of time that the constituent concentrations in Whitewood Creek will exceed criteria applicable to uses of untreated water, such as livestock watering or irrigation. For example, the criteria for arsenic

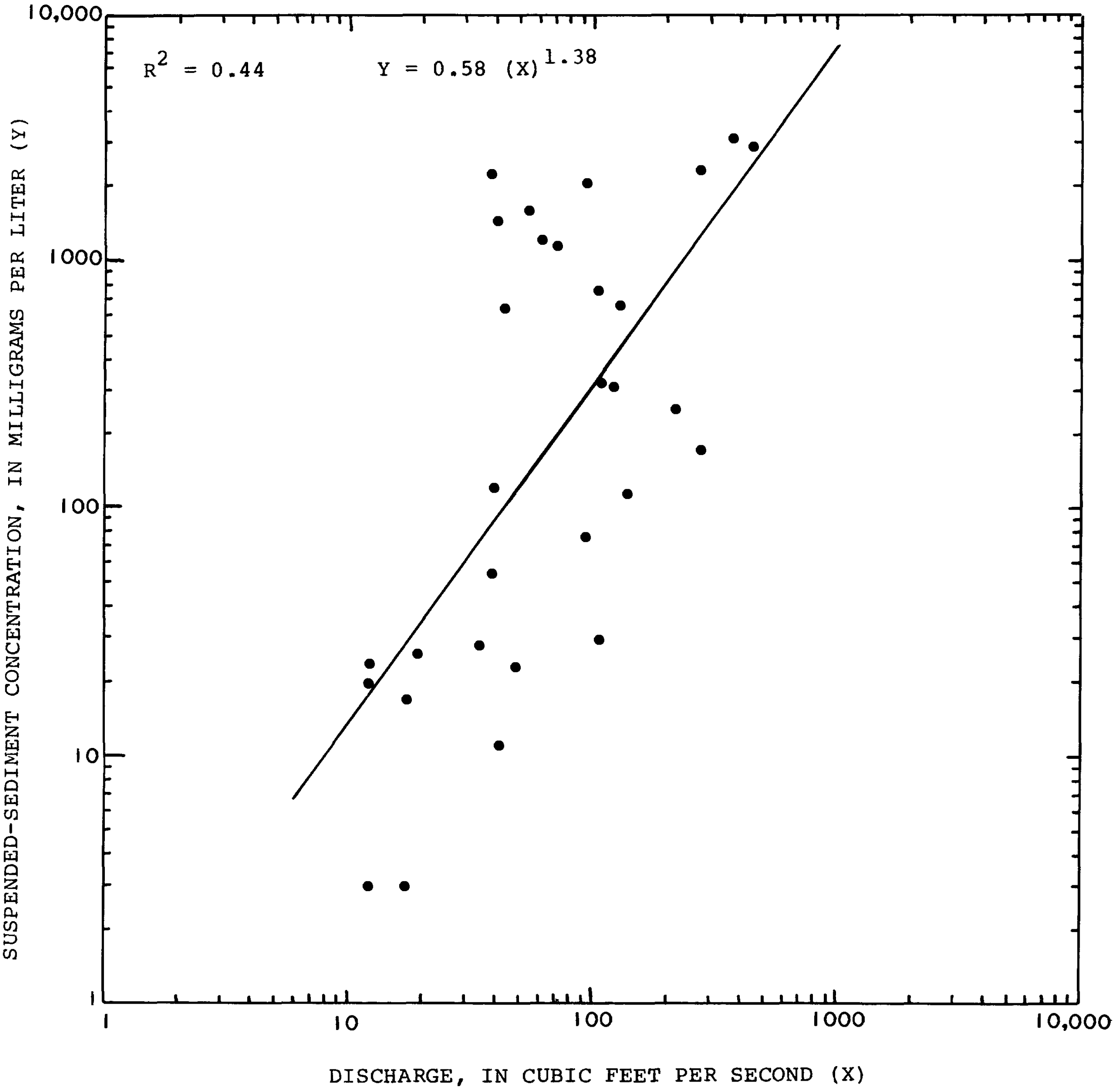

Figure 15.--Graphical and mathematical relations between discharge and suspended-sediment concentration at site 3, Whitewood Creek above Whitewood, April 1983 to July 1984.

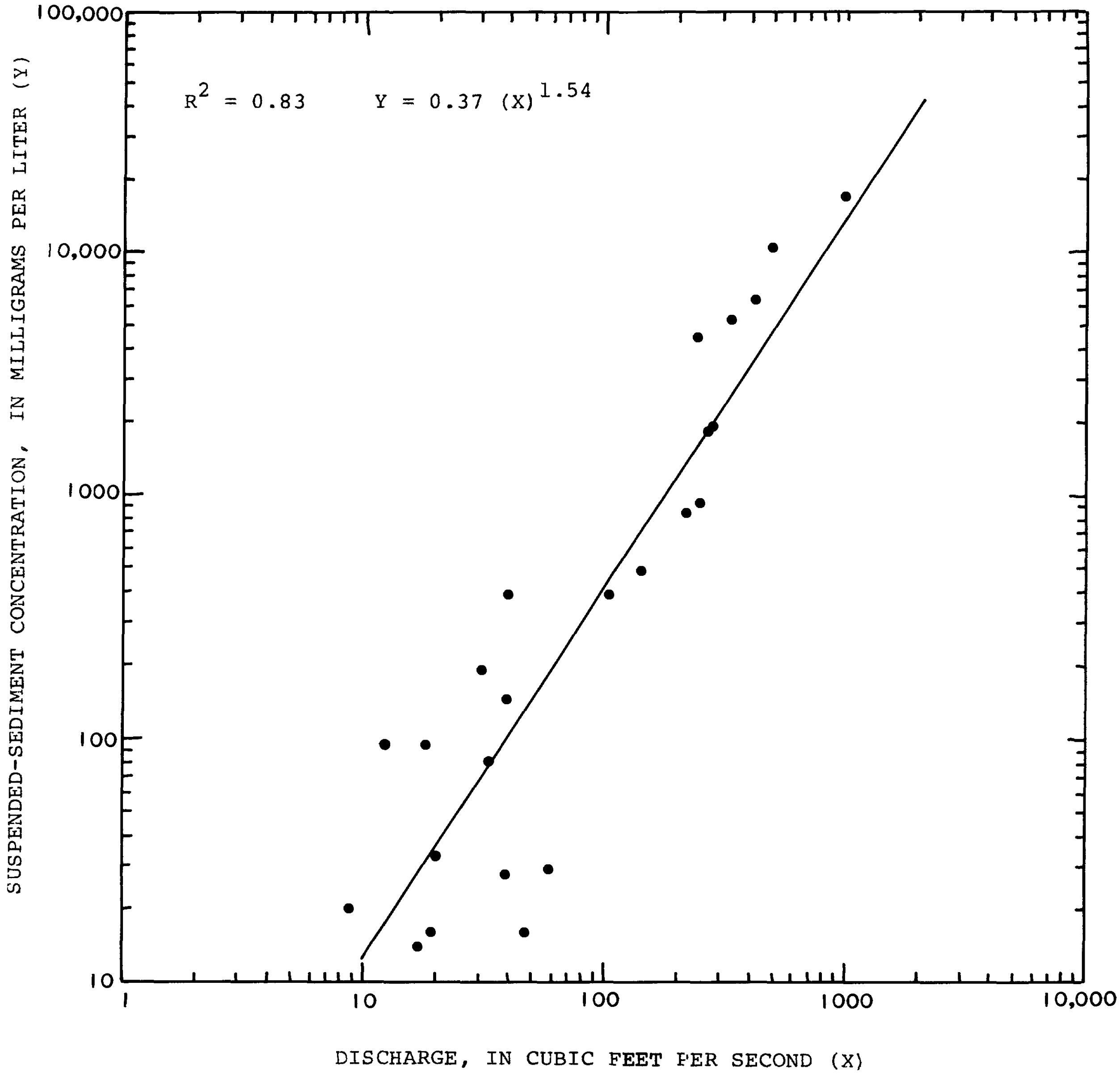

Figure 16.--Graphical and mathematical relations between discharge and suspended-sediment concentration at site 5, Whitewood Creek above Vale, April 1983 to July 1984.

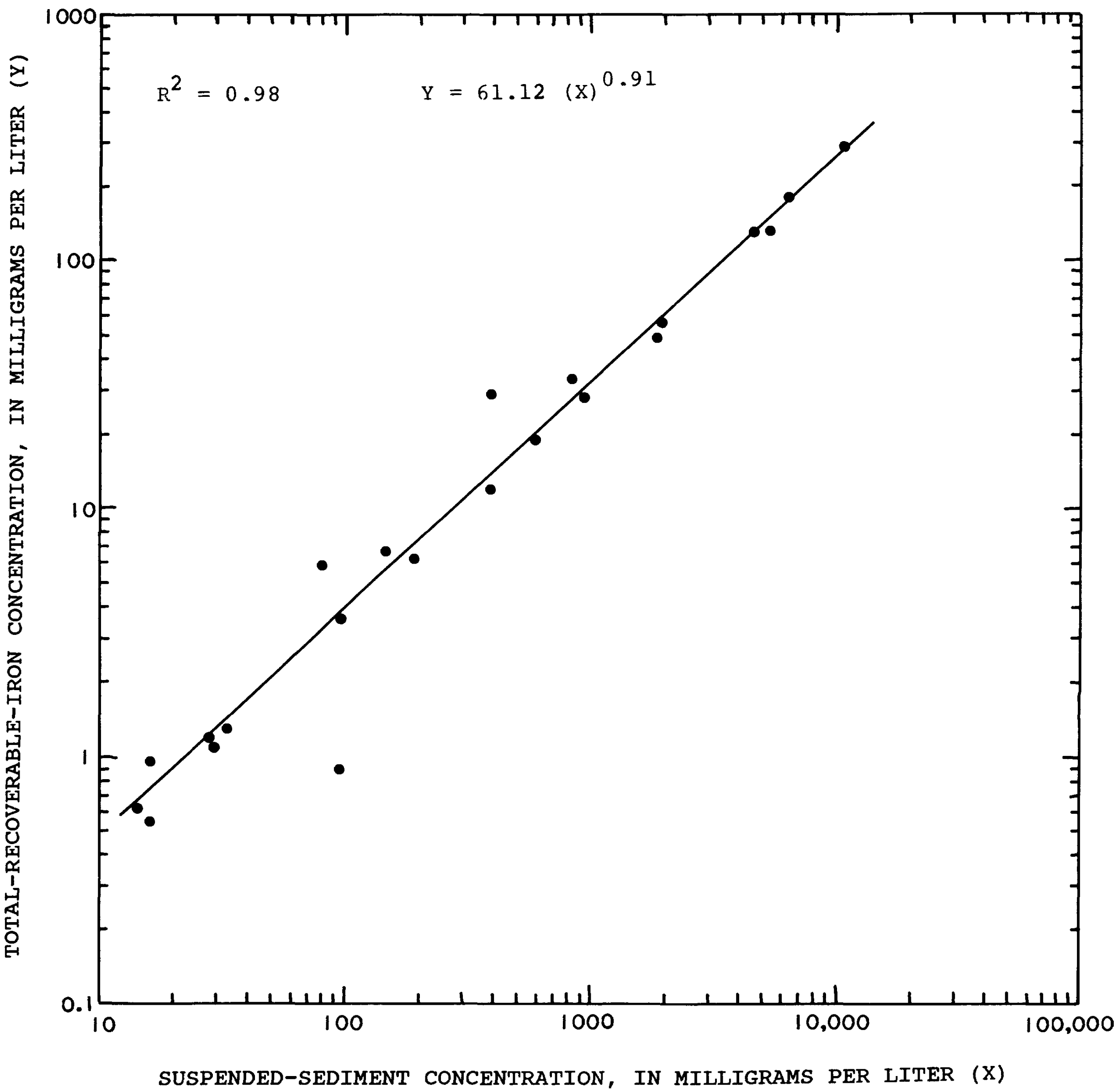

Figure 17.--Graphical and mathematical relations between suspended-sediment and total-recoverable-iron concentrations at site 5, Whitewood Creek above Vale, April 1983 to July 1984.

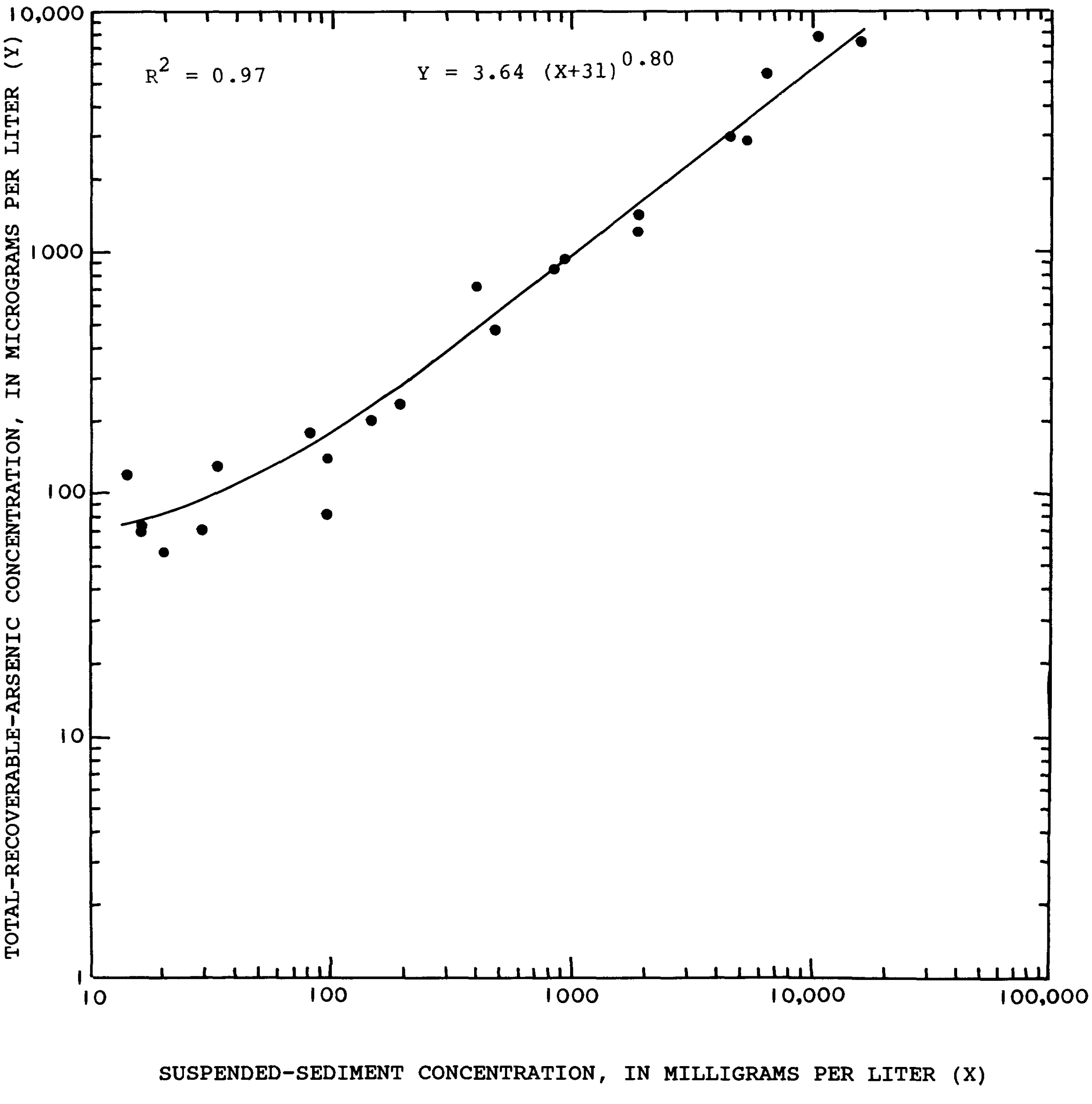

Figure 18.--Graphical and mathematical relations between suspended-sediment and total-recoverable-arsenic concentrations at site 5, Whitewood Creek above Vale, April 1983 to July 1984.

Table 10.--Equations of the least-square fit lines between concentrations of suspended-sediment and selected constituents, and corresponding correlation coefficients, for data collected at sites 3 and 5, Whitewood Creek above Whitewood and Whitewood Creek above Vale

Site name	Constituent	Equation[1/]	Number of data points	Correlation coefficient
Whitewood Creek above Whitewood	Arsenic	$Y = 1.93(X+19)^{0.85}$	31	0.94
	Cadmium	$Y = 0.53(X)^{0.39}$	12	.47
	Iron	$Y = 131(X)^{0.85}$	30	.95
	Manganese	$Y = 1.80(X+100)^{1.01}$	31	.96
	Mercury	$Y = 0.02(X)^{0.66}$	23	.65
	Silver	$Y = 0.28(X)^{0.63}$	13	.63
Whitewood Creek above Vale	Arsenic	$Y = 3.64(X+31)^{0.80}$	22	.97
	Cadmium	$Y = 0.62(X)^{0.48}$	8	.78
	Iron	$Y = 61.12(X)^{0.91}$	21	.98
	Manganese	$Y = 2.32(X+200)^{0.92}$	23	.96
	Mercury	$Y = 0.04(X)^{0.50}$	14	.81
	Silver	$Y = 1.17(X)^{0.28}$	7	.28

[1/] Y is the total-recoverable-constituent concentration, in micrograms per liter, and X is the suspended-sediment concentration, in milligrams per liter.

of 0.2 mg/L (U.S. Environmental Protection Agency, 1976) in water for livestock will be exceeded about 32 percent of the time in the downstream reach of Whitewood Creek.

Because of the large short-term variability in suspended-sediment concentration, and the corresponding large short-term variability in total-recoverable-constituent concentration at a particular sampling site, constituent concentrations alone cannot be used to determine downstream changes in water-quality characteristics. Also, differences in average constituent values may not be statistically significant due to differences in sample numbers and the different conditions during which the samples may have been collected. A more useful analytical procedure is to compare the equations describing the relations between suspended-sediment and constituent concentrations because this will eliminate the effects of sample numbers and timing and varying suspended-sediment concentration.

Although arsenic, iron, and manganese concentrations correlate well with suspended-sediment concentration, the other metals correlate poorly. Many investigators have determined that grain size is an important factor in controlling the retention and transport of trace metals (Horowitz, 1984). The major factor may be physical because fine silt and clay-sized sediments have large surface areas per unit weight as opposed to coarse silt and sand-sized sediments. Because particle surfaces are substrates on which trace metals can be adsorbed, sediments containing greater percentages of finer sediments can transport larger concentrations of trace metals. It is possible that the poor correlations between suspended sediment and some of the trace metals is the result of variations in particle-size distribution between samples.

A limited number of particle-size distributions were determined for suspended-sediment samples collected from Whitewood Creek and the distributions are shown in figure 19. A large variation between individual samples is indicated, a trend expected in a small turbulent stream in which variations in discharge result in major variations in a stream velocity and turbulence.

The few particle-size distribution data do not allow a rigorous analysis of how particle size affects the suspended-sediment chemistry. However, analysis of the data does demonstrate that variation of particle-size distribution contributes to variations between suspended-sediment concentration and trace-metal concentration for individual samples. Horowitz (1984) presented a method in which only the size fraction less than 0.016 mm is considered as contributing to the chemical composition of the sediment. To apply the method, the suspended-sediment concentration and total-recoverable-constituent concentration are used to calculate the constituent concentration per unit weight of suspended sediment. A "standardization" factor is then calculated by dividing the percentage of sample with particle size less than 0.016 mm into 100. The "standardization" factor and the constituent concentration per unit weight of suspended-sediment are then multiplied together to yield a standardized data value. This method was applied to mercury data collected at two sites on Whitewood Creek and the results are listed in table 11. The variations in mercury concentrations between individual samples are decreased by this procedure, indicating that the size fraction less than 0.016 mm is important in the transport of mercury. The data also indicate that mercury is a more abundant sediment contaminant at the upstream site on Whitewood Creek, a trend indicated by the slope differential in the mercury equations listed in table 10.

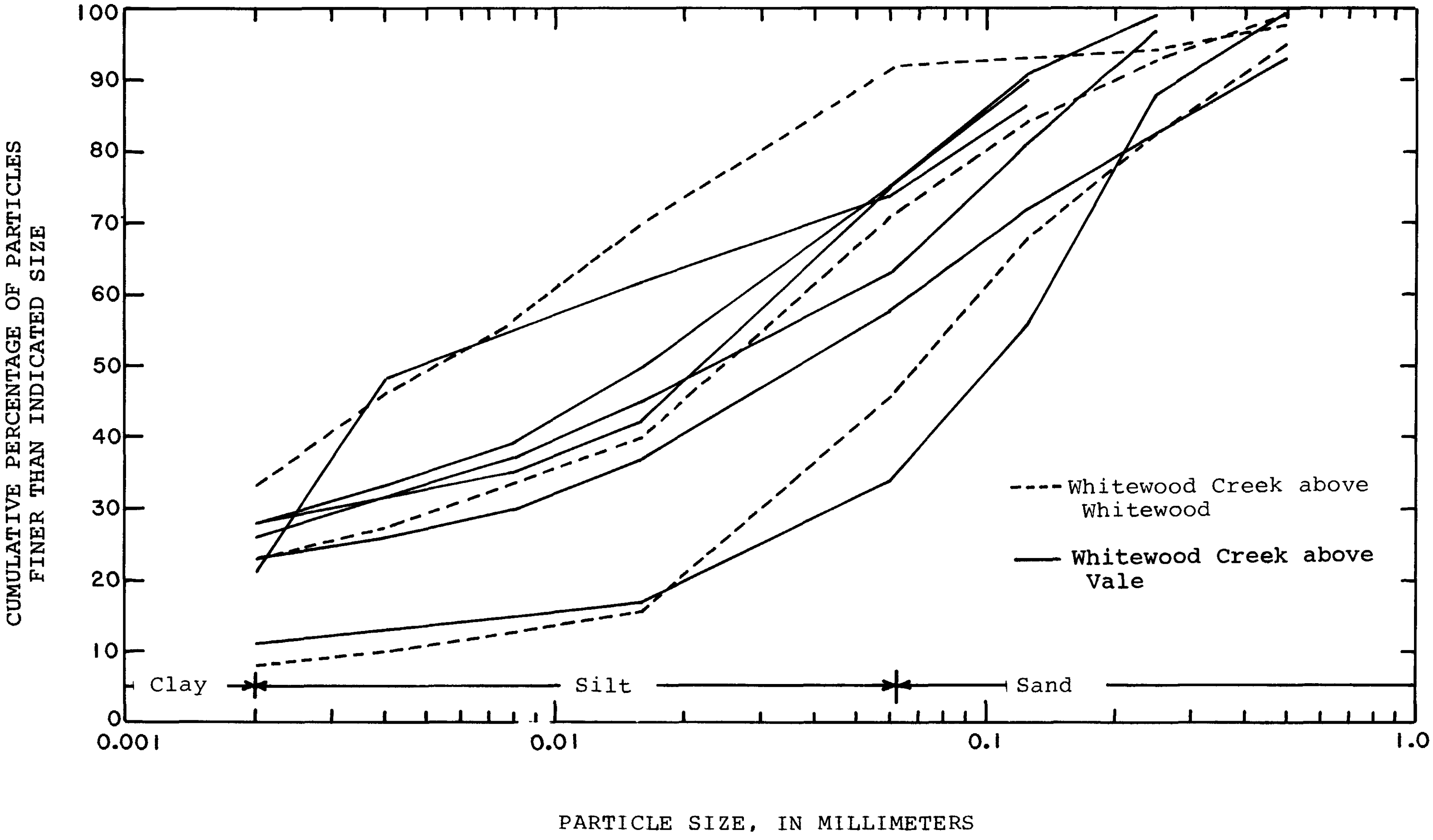

Figure 19.--Particle-size distribution of suspended sediment at sites 3 and 5, Whitewood Creek above Whitewood and Whitewood Creek above Vale.

Table 11.--Conversion of total-recoverable-mercury concentration to mercury concentration per unit weight of sediment and correction of these data for differences in particle-size distribution using a method by Horowitz (1984)

			Water		Sediment		
Site	Sample date	Sample time	Suspended-sediment concentration (milligrams per liter)	Mercury concentration (micrograms per liter)	Mercury concentration (micrograms per gram)	Percent finer than 0.016 millimeter	Standardized mercury concentration (micrograms) per gram)
Whitewood Creek above Whitewood	5- 6-83	2230	2,970	11	3.7	70	5.29
	6- 9-84	2130	2,340	2.2	.94	40	2.35
	6-14-84	0400	3,160	2.3	.73	16	4.56
Whitewood Creek above Vale	5- 7-83	0645	10,600	7.0	.66	50	1.32
	5- 7-83	1045	6,290	4.7	.75	45	1.67
	5- 3-84	1745	4,500	2.8	.62	42	1.48
	6- 9-84	2130	838	.7	.84	62	1.35
	6-10-84	0230	16,900	4.6	.27	37	.73
	6-14-84	0830	5,350	1.5	.28	17	1.65

EFFECTS OF THE CONTAMINATED SEDIMENTS ON GROUND-WATER QUALITY

Alluvial Aquifer System

Most of the Whitewood Creek valley and all of the Belle Fourche and Cheyenne River valleys within the study area are occupied by shallow alluvial aquifers in contact with the surface streams. The alluvium is discontinuous and of limited extent in the deep, narrow canyon upstream from site 3, Whitewood Creek above Whitewood, and generally increases in thickness and lateral extent downstream through the study area. The alluvium generally is less than 30 ft thick over most of the study area although it is as much as 70 ft thick along the Cheyenne River. An alluvial-fan deposit exists at the mouth of the Whitewood Creek canyon, near the town of Whitewood, and is more than 50 ft thick, but is of limited areal extent. Data collected during this study indicate that saturated thickness ranges from 0 to 10 ft along Whitewood Creek and the Belle Fourche River, to as much as 60 ft along the Cheyenne River.

The alluvium is underlaid by relatively impermeable Cretaceous shale, except for the reach of Whitewood Creek near and upstream from site 4, Whitewood Creek near Whitewood. Between that site and Deadwood, the discontinuous alluvium is underlaid by a number of sandstone, limestone, and shale formations including the Deadwood Formation (Cambrian and Ordovician), the Madison Limestone, the Minnelusa Formation, and the Inyan Kara Group, all of which are major aquifers in the Black Hills area. Because the Black Hills is a major recharge area for the Madison Limestone, many surface streams in the Black Hills lose some or all of their flow to the Madison. However, there is no measurable streamflow loss to the Madison Limestone, or any of the other aquifers, along Whitewood Creek (K. D. Peter, U.S. Geological Survey, written commun., 1984). It is possible that fine-grained wastes have sealed the fractures in the Madison preventing or decreasing streamflow infiltration. Upstream from Deadwood to within a mile of the headwaters, the alluvium along Whitewood Creek is underlaid by crystalline rocks that contain and transmit only minute quantities of water in near-surface fractures. The headwaters part of the Whitewood Creek basin is underlaid by the Deadwood Formation and the Madison Limestone. Discharge from the Deadwood and Madison forms the perennial flow of Whitewood Creek.

The shale units underlying the alluvium throughout most of the study reach do not substantially affect flow in the alluvial aquifer, thereby simplifying the conceptional flow system. There is undoubtedly some flow through the weathered shale directly underlying the alluvium, and Cherry and others (1986) reported hydraulic-conductivity values ranging from 10^{-6} to 10^{-4} cm/s (centimeters per second) for shallow shale zones along Whitewood Creek. However, the hydraulic conductivity of the alluvium is much greater, with an arithmetic mean value of 1×10^{-2} cm/s (Cherry and others, 1986) and flow into and through the alluvium is much more important. Springs and seeps occur at the contact between alluvium and the underlying shale where the contact is exposed.

Data Collection

Large deposits of contaminated sediments occur nearly everywhere along Whitewood Creek and the Belle Fourche River and in most places lie directly over the uncontaminated sediments that comprise the alluvial aquifers. Arsenic and trace metals, if solubilized by infiltrating water, could be transported from the contaminated sediments into and through the alluvial aquifers. Although there are a number of domestic and stock wells drilled into the alluvium, most of these wells are some distance from large deposits of contaminated sediments. To adequately determine if there is substantial ground-water contamination, specifically designed monitoring wells were drilled in locations likely to be contaminated.

The monitoring wells were drilled in groups of 2 to 6 wells in order to determine the direction of ground-water flow. To avoid duplication of effort with the investigation of ground-water chemistry that was being conducted along Whitewood Creek (Cherry and others, 1986), all but 4 of the 39 wells were drilled along the Belle Fourche and Cheyenne Rivers. The location of well groups and the number of wells in each group are shown in figure 20. The well-group numbers, well-identification numbers, land ownership, and general well-completion information are listed in table 12.

The wells were drilled using a hollow-stem auger with a 4-inch inside diameter. Continuous core was collected throughout the drilling using a 5-ft long, 4-inch diameter, split-spoon type sampler implaced through the hollow-stem auger and driven down simultaneously with the auger. Recovery of core varied greatly with the nature of the material being drilled and varied from about 100 percent in unsaturated, fine-grained sediment to less than 10 percent in saturated, coarse gravels. The well drilling took place under the direct supervision of U.S. Geological Survey personnel who collected samples and maintained detailed well logs. Sediment samples were collected at the land surface prior to the start of drilling and at least one sediment sample was obtained from every 5-ft core section. These samples were collected, handled, and analyzed using the techniques and laboratory methods previously described in the sediment-composition section of this report. Complete well logs, including sampled intervals, and well-completion information for each well are available from the U.S. Geological Survey. Chemical-analysis data for individual samples are available in the U.S. Geological Survey's WATSTORE data-storage system.

The wells were cased and completed using techniques that minimized down-hole contamination of the aquifer with contaminated sediments from surface deposits. The screen and casing (schedule 60 PVC with flush, screw-type joints) were implaced down through the center of the hollow-stem auger and a sand pack (washed silica sand) was installed around the screened interval as the auger was slowly withdrawn. Above the sand pack, a bentonite seal was installed, also as the auger was being withdrawn. The auger was then fully withdrawn and the remaining open hole filled with cuttings. To protect the finished well, a 5-inch steel surface casing with lockable cap was cemented in place over the casing.

Prior to the collection of water samples for chemical analysis, the water levels were allowed to stabilize, the wells were developed by surging, and the water levels were allowed a second period of stabilization. It was planned to conduct the well development shortly after completion of the drilling, however, severe winter weather and deep snow made it impossible to reach the remote well locations between the end of November 1983, shortly after completion of the drilling, and early January 1984. In January, the wells were developed by surging with nitrogen gas. Well development was conducted to remove any material that may have settled out on the bottom of the well casing and to improve well yield by cleaning the sand pack. Nitrogen gas was used rather than compressed air to avoid as much as possible the introduction of oxygen into the aquifer surrounding the well. After development, the water levels were allowed to stabilize for a minimum of 3 weeks before the first set of water samples was collected.

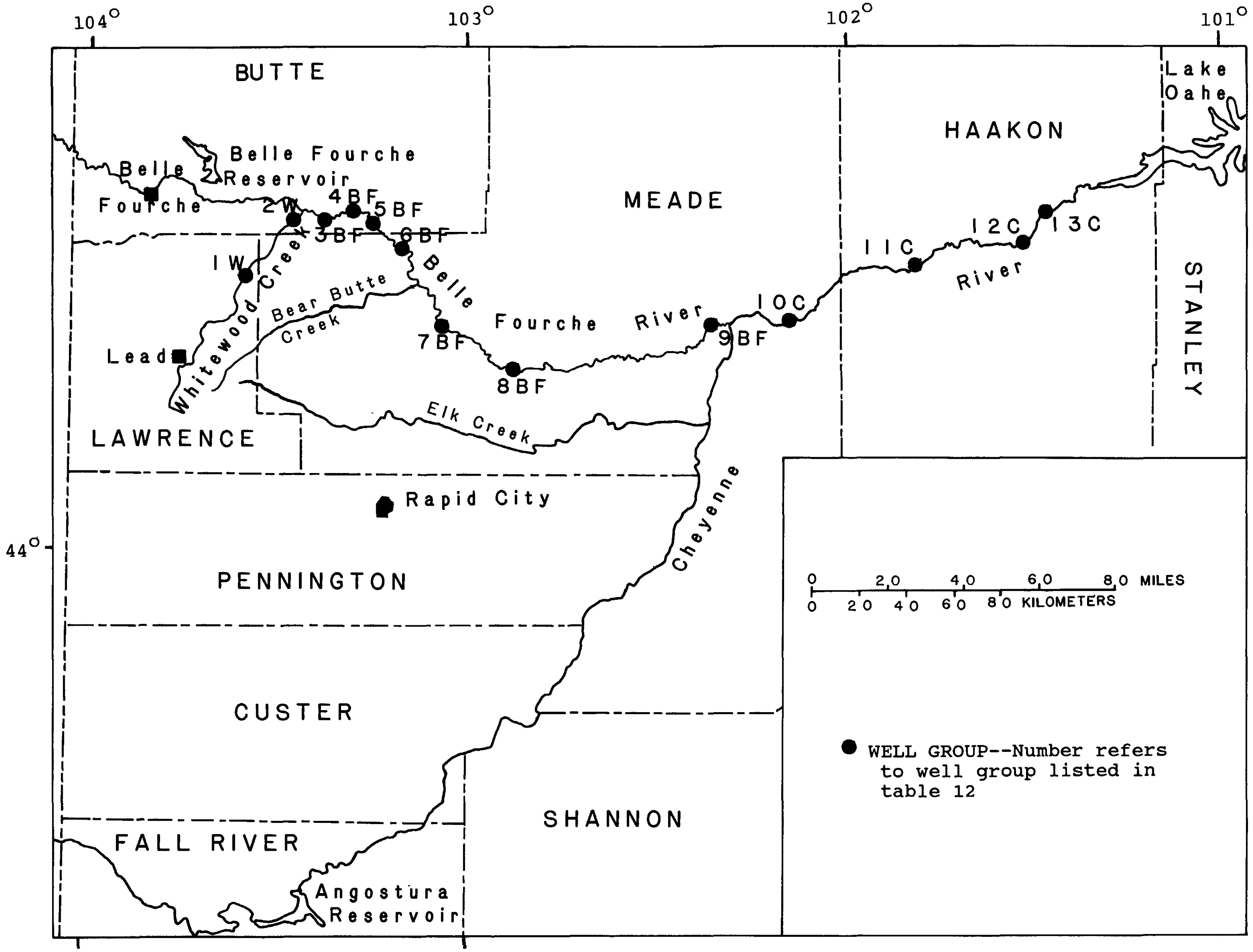

Figure 20.--Location of well groups from which water samples were collected.

Table 12.--Well-group numbers, well-identification numbers, land ownership, and general well-completion information for monitoring wells completed in the alluvial aquifers along Whitewood Creek and the Belle Fourche and Cheyenne Rivers

Well-group number[1]	Well-identification number[2]	Land ownership	Date drilled	Depth of well (feet)	Depth to water below land surface[3] (feet)	Screened interval below land surface (feet)	Depth below land surface of intervals yielding visibly contaminated drill cuttings (feet)
1W	442803103381701	Whitewood Custom Treaters	11- 2-83	21.8	17.0	11.5-21.8	None.
	442806103381601	do.	11- 2-83	15.2	--	5.4-15.2	None.
2W	443801103272601	Doug Simmons	11- 9-83	8.6	8.0	6.5-8.6	0-1, 3-5
	443758103272301	do.	11-10-83	12.1	10.0	11.1-12.1	0-2, 4.5-7.0
3BF	443743103233101	Empire Friends Church	10-30-83	15.3	7.4	8.2-15.3	11.2-15.0
	443739103233101	do.	10-30-83	16.5	9.2	10.4-16.5	11.0-12.0
	443737103233201	do.	10-31-83	14.0	9.5	10.4-14.0	0-6.4, 9.4-12.4
	443746103232201	do.	11- 8-83	12.1	6.5	7.1-12.1	None.
	443743103232201	do.	11- 9-83	15.0	11.0	11.8-15.0	0.5-1.0
	443740103232301	do.	11- 9-83	14.0	6.7	9.0-14.0	0-6.7, 8.7-10.7
4BF	443849103200901	H. L. Brunner and Sons	9- 1-83	16.1	9.0	2.2-16.1	2.1-6.0
	443846103200901	do.	10-28-83	15.7	13.3	13.6-15.7	None.
5BF	443811103162401	Lee Dutton	10-25-83	15.2	8.3	9.6-15.2	1.0-2.0, 3.0-5.0
	443812103160801	do.	10-25-83	18.6	8.9	10.6-18.6	0-2.0, 3.0-7.0, 9.0-12.0
	443818103155801	do.	10-26-83	16.2	8.7	9.8-16.8	1.0-2.2
	443828103155801	do.	10-26-83	20.7	11.1	12.2-20.7	0-1.0
6BF	443433103104701	Thomas Casteel	10-31-83	10.5	5.5	6.4-10.5	0-2.1, 5.0-7.0
	443445103103601	do.	10-31-83	20.1	13.6	14.7-20.1	None.
	443456103102501	do.	11- 1-83	10.1	9.5	8.1-10.1	1.0-7.0
7BF	442412102595701	Kenny McNenny	10-18-83	16.8	15.8	13.7-16.8	None.
	442413102595401	do.	10-19-83	15.7	14.5	12.5-15.7	1.0-2.1
	442413102595101	do.	10-19-83	7.0	6.4	4.8-7.0	1.0-1.7, 4.7-5.0
8BF	442048102491801	Ed Mushitz	10-27-83	16.5	16.3	14.9-16.5	None.
	442046102491801	do.	10-27-83	10.9	9.9	9.3-10.9	0-0.50
	442043102491901	do.	10-28-83	9.4	8.6	7.3-9.4	1.0-1.8, 3.8-6.7
9BF	442343102231401	Alfred Ameson	10-17-83	16.0	14.0	10.9-16.0	1.0-2.2
	442356102225901	do.	10-17-83	15.5	13.1	12.4-15.5	None.
	442405102230601	do.	10-18-83	8.3	7.1	5.5-8.3	1.0-1.9, 4.0-5.0
10C	442616102090701	William Stone	10-16-83	12.0	9.1	10.4-12.0	None.
	442640102090201	do.	10-16-83	11.7	8.0	10.2-11.7	None.
	442621102082701	do.	10-16-83	24.4	11.6	14.1-24.4	None.
11C	443416101423501	Paul Elshere	10-14-83	21.0	11.7	21.0-13.4	None.
	443429101425301	do.	10-14-83	32.1	11.0	27.0-32.1	None.
	443429101425201	do.	10-15-83	19.0	11.0	14.0-19.0	None.
12C	443603101275801	Frank Halligon	10-12-83	17.7	9.5	11.7-17.7	None.
	443613101282301	do.	10-13-83	24.2	11.6	14.0-24.2	None.
	443618101283201	do.	10-13-83	16.3	9.1	11.2-16.3	None.
13C	444116101174501	Cole Briggs	10-11-83	23.8	8.5	13.9-23.8	None.
	444121101174801	do.	10-11-83	28.3	9.5	18.2-28.3	None.

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[1] Well-group number refers to number shown in figure 20.

[2] Permanent U.S. Geological Survey well-identification number: latitude, longitude, and two-digit sequence number.

[3] On date drilled.

Water samples were collected from the monitoring wells using one of two methods, depending on the saturated thickness of the alluvium at the well site and the yield of the well. A Johnson SP-81 submersible sampling pump with teflon impellers and sampling line was used if the saturated thickness and yield was sufficient so that a minimum of 4 ft of water remained in the casing while pumping about 1 gal/min. If there was insufficient water in the well to use the submersible sampling pump, then a portable peristaltic pump was used to obtain the sample. At three sites there was insufficient water in the well to use even a peristaltic pump and no sample was collected.

Use of the Johnson SP-81 was the preferred method of sampling the wells due to its larger capacity and was used whenever possible. The capacity of the pump, about 1 gal/min, made it possible to measure water-quality properties in a specially designed flow-through chamber. The chamber, made of lucite and PVC, was designed to accommodate standard measurement probes. Temperature was measured to the nearest 0.5 °C with a Yellow Springs Instrument (YSI) model 32 FL conductance meter and YSI model 3220 thermister. Specific conductance was measured to three significant places with a YSI model 32 FL conductance meter and a YSI model 3403 glass cell. The pH was measured to 0.05 standard unit with an Orion model 401A meter and a Sargent-Welch glass combination pH electrode. The Eh was measured to the nearest 0.05 volt with an Orion model 401A meter and an Orion combination platinum electrode. Dissolved-oxygen concentration was measured to the nearest 0.1 mg/L with a YSI model 54 dissolved-oxygen meter and a YSI model 5739 oxygen-temperature probe. Calibration of the thermistor was checked against an American Society for Testing and Materials certified mercury thermometer. Calibration of the specific-conductance instrument was checked weekly against standard solutions. The pH and dissolved-oxygen instruments were calibrated daily and checked at each site.

Water samples from wells with sufficient yield to allow the use of the SP-81 submersible pump were collected only after pumping the well until the specific conductance, pH, and dissolved-oxygen concentration of the discharge water stabilized. These values generally stabilized within 10 minutes because the SP-81 submersible pump could pump about one casing volume from the well every 2 minutes depending on the saturated thickness penetrated. However, ground-water samples were never collected before at least 10 casing volumes of water had been discharged. Samples were collected from a tube attached to the discharge line of the down-hole pump just below the measurement chamber. This line was connected to a peristaltic pump and then to a 0.45-µm membrane-filter apparatus. The peristaltic pump was used to provide driving force for filtering so that back pressure on the down-hole pump could be avoided. The entire set-up of submersible pump, pump line, measurement chamber, sampling line and filter apparatus was purged of air before data collection began.

The pumping capacity of the peristaltic pump was insufficient to allow use of the measurement chamber. Therefore, specific conductance and pH were measured in aliquots of the discharge water at 5-minute intervals if there was sufficient water in the well to allow continuous pumping. The instruments and calibration procedures used were the same as those previously described. Although the capacity of the peristaltic pump was only about 0.15 gal/min, the small volume of water in the well bore, less than 1 gal, made it possible to discharge at least five casing volumes before samples were collected. The sampling line and filter apparatus was purged of air before data collection began.

Ground-water samples were filtered through a 0.45-µm membrane filter using a peristaltic pump to provide the necessary pressure. Samples were analyzed for the constituents and properties listed in table 13. Arsenic- and iron-speciation analyses were performed on selected samples. Analyses were performed at contract laboratories specified by the U.S. Environmental Protection Agency using the methods listed in table 13.

Factors That Affect Ground-Water Quality

The composition of water in an alluvial aquifer can be affected by the composition of the recharge water and the composition of underlying rock units. In many situations, alluvial aquifers existing along perennial streams are recharged by the streams, and the composition of the water may be nearly identical to that of the surface water. Underlying units may contribute constituents by direct discharge of water to overlying alluvial material, or, if the underlying unit is almost impermeable, by contact of water in the alluvial aquifer with the underlying unit at the interface.

Along the study reach, the major-ion chemistry of the water in the alluvial aquifers is the result of cumulative effects of the underlying shale units. As the ground water moves over the top of the underlying weathered shale, constituents characteristically derived from marine shale, particularly sulfate, are added to the water resulting in large concentrations of these constituents in the water of the alluvial aquifers throughout the study area. Calcium and sodium are the predominant cations, with sodium usually more abundant. Sulfate is by far the predominant anion, and is present in concentrations ranging from about 1,000 to more than 6,000 mg/L. Corresponding to the large concentrations of sulfate are large concentrations of dissolved solids. Ground water containing large concentrations of dissolved sulfate discharging to the surface streams is responsible for the increasing concentrations of sulfate in the surface water.

Both sulfate and dissolved-solids concentrations in samples from the alluvial aquifers are large enough to limit water use throughout the study area. Sulfate concentrations are 4 to 25 times more than the secondary drinking-water standard of 250 mg/L (U.S. Environmental Protection Agency, 1976) and it would seem unlikely that the alluvial aquifers would be used as continuous domestic supplies. Water containing less than 14,000 mg/L dissolved solids can be successfully used as a livestock supply if the major ions are sodium, calcium, and sulfate (Hem, 1970). Sodium and dissolved-solids concentrations may be large enough in some places to prevent the use of the water for irrigation.

Delineation of the extent and magnitude of ground-water contamination resulting from the contaminated sediments is complicated by several factors. Sulfate is largely derived from the underlying shale bedrock although some sulfate is undoubtedly contributed to the ground water by weathering of pyrite contained in the contaminated sediments. Other than isotopic analysis, beyond the scope of this study, there is no way to determine what percentage of sulfate is natural and what percentage is contributed by the contaminated sediments. Although it has been determined that the large concentrations of arsenic and some other trace constituents can only occur in the ground water as a result of the contaminated sediments present in the study area, it may not be apparent at some particular location whether the large concentrations of other constituents are due to contaminated sediments at the location or to infiltrating surface water.

Table 13.--Constituents and properties, and analytical methods for ground-water samples

Constituent or property	Analytical method	References
Dissolved metals (calcium, magnesium, sodium, potassium, cadmium, chromium, copper, iron, lead, manganese, nickel, silver, and zinc)	Inductively coupled argon plasma	Digestion: Included as part of analysis. Analysis: U.S. Environmental Protection Agency, 1980.
Dissolved arsenic	Atomic absorption, hydride	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-1062-7[1].
Dissolved selenium	Atomic absorption, hydride	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-1667[1].
Dissolved cyanide	Colormetric, barbituric acid	Digestion: Included as part of analysis. Analysis: U.S. Environmental Protection Agency, 1974.
Dissolved mercury	Atomic absorption, spectrometric	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-1462-78[1].
Total alkalinity (as carbonate-bicarbonate)	Titrimetric (pH 8.3-4.5)	Standard methods[2].
Dissolved sulfate	Colormetric, complexometric methylthymol blue	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-2822-77[1].
Dissolved chloride	Colormetric, ferric thiocyanate	Digestion: Included as part of analysis. Analysis: U.S. Geological Survey I-1187-78[1].
Dissolved solids	Gravimetric, residue on evaporation at 180 °C	Standard methods[2].
Dissolved iron (Fe^{+2}, Fe^{+3})	Colormetric, ferrozine	Digestion: Included as part of analysis. Analysis: Unpublished report[3].
Dissolved arsenic (AS^{+3}, AS^{+5})	Colormetric, molybdate	Digestion: Included as part of analysis. Analysis: Unpublished report[3].
Laboratory pH	Electrometric, glass electrode	Standard methods[2].
Laboratory specific conductance	Electrometric wheatstone bridge	Standard methods[2].

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[1] Skougstad and others, 1979.

[2] Exact method dependent on method chosen by laboratory. Several analtyical methods will result in acceptable values.

[3] Analytical methods may be obtained from U.S. Geological Survey, Rapid City, South Dakota.

Effects of Contaminated Sediments

Magnitude of Contamination

Arsenic, cadmium, copper, silver, manganese, iron, cyanide, and mercury are the constituents of concern due to their known association with the mill-waste discharge. A summary of the measured concentrations for these constituents in ground water is listed in table 14. Cadmium and cyanide were never present in concentrations more than the detection limits, whereas copper and silver were only rarely detected. The dissolved-silver concentration of 31 µg/L measured in water from a well along the Belle Fourche River is uncorrelated with other samples from the same well and likely represents sample contamination or laboratory error. Thus, the only constituents directly related to the contaminated sediments that normally are present in ground water in concentrations more than the detection limits are arsenic, iron, manganese, and mercury.

Dissolved arsenic in ground water was more than the detection limit of 2 µg/L in 30 of 101 samples and had a maximum concentration of 280 µg/L. Only four of the wells sampled during the study yielded water with arsenic concentrations more than the primary drinking-water standard of 50 µg/L (U.S. Environmental Protection Agency, 1977), although three other wells yielded water with arsenic concentrations ranging from 20 to 50 µg/L. These wells were located along Whitewood Creek or the upstream one-half of the contaminated reach of the Belle Fourche River. During the investigation of the Whitewood Creek deposits by Cherry and others (1986), monitoring wells drilled in areas covered by large deposits of contaminated sediment yielded water containing dissolved-arsenic concentrations ranging from 30 to 780 µg/L. All the monitoring wells yielding water containing dissolved-arsenic concentrations larger than 50 µg/L are completed in the alluvium, or mixtures of alluvium and contaminated sediments, directly under large deposits of contaminated sediment. Arsenic contamination of ground water is apparently not widespread, but rather is limited to areas in the vicinity of large deposits of contaminated sediments.

Dissolved iron and manganese were present in most ground-water samples collected during the study, and the concentrations usually were many times more than secondary standards for drinking water. Dissolved iron was in excess of the secondary standard of 300 µg/L in 39 of the 101 samples; dissolved manganese was in excess of the secondary standard of 50 µg/L (U.S. Environmental Protection Agency, 1976) in 86 of the 101 samples. However, both iron and manganese are considered non-toxic to aquatic life, livestock, and people at concentrations normally present in water and the secondary standards for drinking water are based on esthetic qualities rather than on possible health effects.

Samples that contained considerable concentrations of iron also had considerable concentrations of manganese, generally more than 1,000 µg/L, and iron usually was the prevalent ion. In samples from wells located near or in large deposits of contaminated sediments, iron concentrations commonly ranged from 1,000 to 10,000 µg/L and had a maximum concentration of 150,000 µg/L, whereas manganese concentrations commonly ranged from 500 to 5,000 µg/L and had a maximum concentration of 35,000 µg/L. Several wells along the Cheyenne River yielded water containing manganese in excess of 1,000 µg/L but small concentrations of iron.

Mercury was more than the detection limit of 0.2 µg/L in 36 of 100 samples, but was never present in concentrations more than the primary drinking-water standard of 2 µg/L (U.S. Environmental Protection Agency, 1977). The maximum dissolved-

Table 14.--Summary of selected constituent concentrations in water samples from monitoring wells along Whitewood Creek and the Belle Fourche and Cheyenne Rivers

[Cyanide concentrations are milligrams per liter; all other concentrations are micrograms per liter. Mean, arithmetic mean of concentrations more than detection limits; N, number of samples with constituent concentration more than detection limit; Range, range of concentrations; ND, never determined. Detection limit varies between sample sets]

Well-group number1/	Number of wells	Number of samples	Arsenic, dissolved	Cadmium, dissolved	Copper, dissolved	Silver, dissolved	Manganese, dissolved	Iron, dissolved	Cyanide, dissolved	Mercury, dissolved
			Mean/N Range	Mean/N Range	Mean/N Range	Mean/N Range	Mean/N Range	Mean/N Range	Mean/N Range	Mean/N Range
1W	2	0	--	--	--	--	--	--	--	--
2W	2	4	162/4 48-320	ND/0 <10-<100	ND/0 <2-<100	ND/0 <3-<30	14,800/4 4,800-35,000	51,800/4 11,000-150,000	ND/0 <0.01	ND/0 <0.2-<0.4
3BF	6	18	64/9 <2-200	ND/0 <10-<100	ND/0 <2-<500	ND/0 <3-<100	3,000/17 62-6,800	9,000/14 8-31,000	ND/0 <0.01	0.3/2 <0.2-0.3
4BF	2	3	ND/0 <2	ND/0 <10-<100	4/1 4-<100	ND/0 <3-<30	58/3 38-90	3/1 3-<100	ND/0 <0.01	0.5/2 0.3-0.7
5BF	4	15	21/5 <2-40	ND/0 <10-<100	4/1 4/<500	ND/0 <30-<100	1,750/15 1,500-2,900	1,210/9 130-3,700	ND/0 <0.01	0.4/2 <0.2-0.5
6BF	3	8	143/5 <2-280	ND/0 <10-<100	ND/0 <2-<100	ND/0 <3-<30	2,470/8 210-4,700	10,700/7 61-18,000	ND/0 <0.01	0.4/1 <0.2-0.4
7BF	3	9	ND/0 <2	ND/0 <10-<100	ND/0 <2-<100	31/1 <3-31	1,710/7 4-5,000	62/2 <2-120	ND/0 <0.01	0.3/6 0.2-0.5
8BF	3	9	ND/0 <2	ND/0 <10-<100	ND/0 <20-<100	ND/0 <10-<30	2,460/9 320-8,500	26/2 <20-<100	ND/0 <0.01	0.3/6 <0.2-0.5
9BF	3	5	ND/0 <2	ND/0 <10-<100	ND/0 <2-<100	ND/0 <3-<30	515/4 5-1,000	4/1 4-<100	ND/0 <0.01	0.5/1 <0.2-0.5
10C	3	9	ND/0 <2	ND/0 <10-<100	ND/0 <2-<50	ND/0 <3-<30	400/8 3-1,500	150/3 <2-<360	ND/0 <0.01	0.3/6 <0.2-0.4
11C	3	9	4/4 <2-6	ND/0 <10-<100	47/1 <2-<500	ND/0 <3-<10	2,770/9 1,500-5,000	1,000/8 500-1,700	ND/0 <0.01	0.4/4 <0.2-0.7
12C	3	9	6/3 <2-7	ND/0 <10-<100	38/1 <2-<50	4/1 <3-<10	2,140/9 920-3,900	430/9 240-600	ND/0 <0.01	0.4/4 <0.2-0.5
13C	2	3	6/1 <2-6	ND/0 <10	3/1 <2-<50	ND/0 <3-<10	3,670/3 3,600-3,800	90/3 84-100	ND/0 <0.01	0.4/2 <0.2-0.4

1/ Refers to well-group number shown in figure 20 and listed in table 12.

mercury concentration in ground water measured during the study was 0.7 µg/L and most concentrations were less, ranging from 0.2 to 0.4 µg/L. Mercury in ground water does not correlate with the locations of contaminated-sediment deposits and samples with large concentrations of arsenic, iron, and manganese usually do not contain detectable concentrations of mercury.

Hydrogeochemical Processes

At the outset of this investigation it was hypothesized that oxidization of sulfide minerals known to be present in the contaminated sediments would release arsenic, iron, and other constituents into the ground water. The monitoring wells that were drilled and sampled were designed and located to determine if ground-water contamination was occurring. The thrust was to determine the presence, magnitude, and areal extent of any contamination; not to define the geochemical processes controlling the chemistry at any particular site. Therefore, detailed site-specific data, such as hydraulic conductivity, sulfide concentrations with depth, oxygen concentrations with depth, were not determined or collected. However, by consideration of the processes known to be involved with oxidation/reduction and sorption/desorption, and review of the chemical data available from the well sampling, inferences about the process controlling the release and transport of constituents in the alluvial ground-water system can be made. A much more detailed discussion of ground-water geochemistry in the contaminated-sediment deposits along Whitewood Creek is presented by Cherry and others (1986).

Contamination of the alluvial aquifers underlying large deposits of contaminated sediment is not as widespread a problem as was anticipated at the outset of the investigation. Almost all the wells drilled along Whitewood Creek and the Belle Fourche River penetrated layers of contaminated sediments from less than 1 to as much as 9.4 ft thick. Weathering of the contaminated sediments was expected to produce acid and release arsenic and metals. Measurements of pH made during the collection of ground-water samples indicated that the pH of most of the ground water was about 7.0. The pH ranged from 6.1 to 7.8 with most wells yielding slightly alkaline water. Without exception, ground water with a pH of less than 7.0 contained substantial concentrations of dissolved arsenic, iron, and manganese but only four wells yielded such water.

Sulfide minerals are a major constituent of the mined ore but, as was previously discussed, were not commonly present in the near-surface, contaminated-sediment samples analyzed during this study. The sulfide minerals originally present in the ore may have been oxidized during the milling process, during transport downstream along the study reach, and during the intervening years since deposition. Visual inspection of large deposits of contaminated sediments and well cores indicates unoxidized sediment comprises less than 25 percent of the sediment at most locations and commonly is not present. However, sediments that appear to be completely oxidized may only appear so due to iron-oxide grain coatings and may still contain large proportions of sulfide minerals.

Dissolved-oxygen concentration and Eh measurements made during ground-water sample collection indicate that reducing conditions exist in the aquifers at the sampling sites. Dissolved-oxygen concentrations usually ranged from 0.0 to 0.2 mg/L. The lack of available oxygen was confirmed by the rapid precipitation (1 to 2 hours) of ferric hydroxide in unacidified water samples. The dissolved iron, consisting of from 90 to 98 percent Fe^{+2}, is a sink for any available oxygen. Laboratory experiments reported by Cherry and others (1986) determined that oxygen was rapidly (1 to

20 hours) depleted in stoppered laboratory vessels containing mixtures of contaminated sediment and water. Eh measurements commonly ranged from 0 to -250 mV (millivolts) for samples containing large concentrations of dissolved iron and zero dissolved oxygen. With a relatively neutral pH and an Eh of about -200 mV, pyrite would be stable and could exist unaltered for long periods (Hem, 1970). Iron oxides and hydroxides would be unstable under these reducing conditions.

The rarity of acidic ground water in areas containing at least some oxidizable sulfide minerals may be the result of carbonate buffering and reduction of iron hydroxides. Several wells located along the downstream reach of Whitewood Creek (well group 2W) and the Belle Fourche River (well group 3BF) yielded slightly acidic ground water. Water from these wells also contains large concentrations of dissolved iron, possibly indicating the decomposition of pyrite by sulfuric acid. Water from other wells along the Belle Fourche River also contains large concentrations of dissolved iron, but the water is neutral or slightly basic. The cause of this inconsistency may be the result of neutralization of the sulfuric acid by carbonate minerals present in the contaminated sediments and alluvium. The occurrence of carbonate minerals in the ore was previously described. Other sources of carbonate minerals in the Cheyenne River basin are the major limestone formations that outcrop around the Black Hills. In areas of thin, discontinuous, contaminated-sediment deposits, the buffering capacity is sufficient to maintain a neutral or basic water even in the presence of oxidizing sulfide minerals. The neutral water containing large dissolved-iron concentrations also could be explained by the instability of iron hydroxides under the reducing conditions present in the alluvial aquifer. Under reducing conditions, iron hydroxides would dissolve, releasing iron while also buffering acidity.

The concentration of dissolved arsenic that could be maintained at the values of Eh and pH present in the ground water, considering only the solubility of the arsenates, is much larger than the concentrations measured during this study. The solubility of metal arsenates increases with increasing pH (Hem, 1970). At a pH of about 7.0, the solubility of calcium arsenates and magnesium arsenates is such that as much as 10,000 µg/L arsenic could be maintained in solution. Dissolved-copper concentrations of about 50 µg/L could limit the solubility of arsenic to 100 to 300 µg/L (Hem, 1970). However, dissolved-copper concentrations usually were not more than the detection limit of 2 µg/L in any of the samples.

It is plausible that the less than expected dissolved-arsenic concentrations in the ground water are the result of sorption/desorption of arsenic on active surfaces, particularly metallic hydroxides. A number of investigators have reported that arsenic adsorption on or coprecipitation with hydrous iron oxide appear to be major factors that can maintain small concentrations of arsenic in water (Hem, 1970). Recent experiments by a graduate student at the South Dakota School of Mines and Technology (R. Wuolo, oral commun., 1986) determined that contaminated sediments have an enormous capacity for arsenic removal. In these experiments, water containing as much as 5,000 µg/L dissolved arsenic was passed through columns containing contaminated sediment collected from the flood plain along Whitewood Creek. The resultant eluant contained less than 20 µg/L dissolved arsenic, a decrease of more than 99 percent.

SUMMARY AND CONCLUSIONS

For about 100 years, huge volumes of mining and milling wastes were discharged into Whitewood Creek and its tributaries at Lead and Deadwood, South Dakota. Sediments derived from or contaminated by these wastes were deposited along Whitewood Creek and the Belle Fourche and Cheyenne Rivers. The contaminated sediment is largely derived from mill wastes that originally contained 7 to 8 percent iron-sulfide minerals, including the mineral arsenopyrite ($FeAsS$), as well as traces of cyanide and mercury derived from the milling process.

The gross contamination of Whitewood Creek and the downstream rivers was alleviated by the discontinuance of milling-wastes discharge in 1977. However, the huge deposits of contaminated sediments that still exist along these streams is continuing to degrade surface and ground waters in the basin. Because the contaminated sediments were deposited by natural surface flow, they are subject to resuspension and downstream movement, particularly during periods of high discharge. Physical and chemical weathering of the sulfide minerals or metallic hydroxides present in the contaminated sediments has the potential to release arsenic and other constituents into the alluvial aquifers underlying the sediments.

The potential hazard of the contaminated sediments to the environment caused the U.S. Environmental Protection Agency to list an 18-mi reach of Whitewood Creek and the adjacent flood plain as an Interim Priority Site, under the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA).

The composition of the wastes discharged to Whitewood Creek was similar to the iron-magnesium-silicate and carbonate-mineral composition of the ore bodies. Most of the ore bodies are chloritized sideropleisite [$(Fe, Mg)\ CO_3$] or cummingtonite [$(MgFe)_7Si_8O_{22}(OH)_2$] schists. Quartz masses and veins are abundant and the iron sulfides, pyrrhotite (Fe_xS), pyrite (Fe_2S) and arsenopyrite ($AsFeS$) comprise 7 to 8 percent of the ore. The carbonate minerals ankerite [$Ca(Mg, Fe)(CO_3)_2$] and dolomite [$CaMg(CO_3)_2$] are sometimes substantial constituents of the ore.

Mineral-composition analyses of 46 contaminated-sediment samples collected from the flood plains along Whitewood Creek and the Belle Fourche River indicate that about 97 percent by weight of the contaminated sediments consists of silicate minerals and clay. Only a small proportion, less than 3 percent, consists of reactive iron-sulfide and carbonate minerals. It seems likely that a substantial proportion of the sulfide minerals originally present have been weathered and now exist as secondary oxides and hydroxides. Carbonate minerals have been removed by solution, a process accelerated by the sulfuric acid produced during sulfide-mineral oxidation.

Almost all the wastes discharged to Whitewood Creek at Lead/Deadwood consisted of rock particles crushed to sand size or smaller by various milling methods. Prior to about 1920, the ore was crushed by stamp mills; since then, modern rod and ball mills were used resulting in a larger proportion of finely ground rock materials. During the period of waste discharge, the percentage of fines in the discharged wastes increased substantially and most of the discharge during the last 50 years consisted of material smaller than 0.045 mm. Particle-size analysis of 17 samples of contaminated sediments indicate the sediments generally are well sorted, fine to very fine sand-size and silt-size particles.

The concentrations of arsenic and several other trace constituents are from several orders of magnitude to several times larger in contaminated sediments than in uncontaminated sediments. Arsenic, cadmium, copper, and silver are trace constituents known to be associated with minerals present in the ore, and have mean concentrations from 200 times (arsenic), to 4 times (copper) larger in the contaminated sediments than in the uncontaminated sediments. Arsenic is by far the most anomalous trace constituent with a mean concentration of 9.2 µg/g in uncontaminated sediments and a mean concentration of 1,920 µg/g in contaminated sediments. Iron and manganese are also constituents known to be associated with the ore minerals, but iron and manganese also are common constituents in the natural environment, and the mean concentrations in contaminated sediments are only about two to three times that in uncontaminated sediments. Chromium, lead, nickel, selenium, and zinc are not associated with the ore and there are no substantial differences between the concentrations of these constituents in the uncontaminated sediments and the contaminated sediments. Cyanide and mercury are constituents contributed largely by ore processing and were detected in many of the contaminated-sediment samples but were never more than the detection limit in uncontaminated sediments.

Results of a stratified, random, sediment-sampling program indicate that most of the near-surface sediments on the flood plains along Whitewood Creek and the Belle Fourche River are contaminated by arsenic. On the flood plain along Whitewood Creek downstream from the junction with Gold Run, 82 percent of the sediment samples contained anomalously large concentrations of arsenic; the mean arsenic concentration was 1,400 µg/g and the maximum concentration was 11,000 µg/g. Mean arsenic concentrations gradually decreased downstream along the Belle Fourche River from about 1,300 µg/g just downstream from the junction with Whitewood Creek to about 400 µg/g near the mouth. There was less arsenic contamination of the Cheyenne River flood plain where arsenic in near-surface sediment samples averaged about 70 µg/g.

In the study area, the major-ion chemistry of the surface water changes downstream due to the effects of underlying rock formations. Whitewood Creek originates as ground-water discharge from the Deadwood Formation and the Madison Limestone and the water in the upstream reaches of Whitewood Creek is a calcium bicarbonate type. As Whitewood Creek flows out of the Black Hills, water quality is first affected by the Spearfish Formation, a unit that contains considerable gypsum, and then by the Cretaceous marine shale that underlies the downstream reaches of Whitewood Creek and the Belle Fourche and Cheyenne Rivers. Weathering of these units adds some calcium and sodium and considerable sulfate to the surface streams and the water in the Cheyenne River is a sodium sulfate type. Dissolved-sulfate concentrations increase downstream along Whitewood Creek from about 7 mg/L in the headwaters to about 360 mg/L near the mouth, and increase to 1,000 mg/L or more in the Belle Fourche and Cheyenne Rivers.

Delineation of the extent and magnitude of surface-water contamination caused by the contaminated sediments is complicated by the other sources of contamination present in the study area. The most important of these is the Homestake Mining Co. effluent discharge to Gold Run, a tributary of Whitewood Creek. The effluent contains arsenic, heavy metals, and cyanide. In the case of copper and cyanide, the proportion contributed to Whitewood Creek by the effluent is a large proportion of the constituent load transported by the stream. The municipal sewage lagoon at the city of Whitewood also contributes arsenic and metals to Whitewood Creek although the effects of these constituents are not considered important due to the small volume of effluent being discharged to Whitewood Creek.

Appreciable surface-water contamination caused by the deposits of contaminated sediment is confined to Whitewood Creek and a reach of the Belle Fourche River downstream from the mouth of Whitewood Creek. The downstream reaches of the Belle Fourche River, and reach of the Cheyenne River downstream from the mouth of the Belle Fourche River are not seriously affected. Arsenic, cadmium, silver, total-recoverable iron, and manganese generally increase in concentration downstream along Whitewood Creek, then decrease in concentration downstream along the Belle Fourche River. These constituents primarily are derived from the contaminated-sediment deposits that add leachate and solids to the stream as it flows through the Whitewood Creek valley. Copper, dissolved iron, cyanide, and mercury generally decrease in concentration downstream from Lead and Deadwood along Whitewood Creek. The only source of cyanide is the Homestake Mining Co. effluent discharge and substantial dissolved copper and iron are complexed with the cyanide.

The most important surface-water contaminant derived from the contaminated sediments is arsenic. The dissolved-phase concentrations in Whitewood Creek vary between about 20 and 80 µg/L during the year in response to variations in ground-water inflow and dilution. The suspended-phase concentrations in Whitewood Creek vary between about 20 and 8,000 µg/L during short periods in response to rapid changes in suspended-sediment concentration. The relations among discharge, suspended-sediment concentration, and total-recoverable-arsenic concentrations indicate that total-recoverable-arsenic concentrations exceed the criteria of 200 mg/L recommended by the U.S. Environmental Protection Agency for livestock water about 32 percent of the time in the downstream reach of Whitewood Creek.

Arsenic, cadmium, mercury, and silver are all primarily contributed to Whitewood Creek and the Belle Fourche River by contaminated sediments along these streams, and all sometimes have concentrations that exceed standards for drinking water or criteria for agricultural use or protection of aquatic life. For these constituents, the occurrence and magnitude of surface-water contamination is controlled by natural processes acting on the contaminated sediments, and so, even though the contamination is the result of human activities, continued contamination of the surface streams can not be easily mitigated. However, detectable concentrations of copper and cyanide are the direct result of effluent discharge into Whitewood Creek. Although these constituents sometimes have concentrations that exceed criteria for the protection of aquatic life, continued efforts to decrease cyanide concentrations in the Homestake Mining Co. mill effluent should decrease the problem considerably. Iron and manganese are the least problematic of the constituents attributed to the contaminated sediments. Neither are particularly harmful to the environment, and although both have concentrations more than the secondary standards for drinking water, neither occurs without accompanying constituents considerably more toxic.

The major-ion composition of the water in the alluvial aquifers results from the cumulative effects of the underlying shale units. Constituents characteristically derived from shale, particularly sulfate, attain large concentrations throughout the study area. Calcium and sodium are the predominant cations, and sulfate is the predominant anion. Sulfate concentrations exceed the secondary drinking-water standard of 250 mg/L at all sampling sites, and range from about 1,000 to more than 6,000 mg/L.

Arsenic is the only constituent directly attributable to the contaminated sediments that exceeds a primary drinking-water standard in ground water. Dissolved arsenic was detected in samples from 16 of 36 wells, but exceeded the drinking-water standard of 50 µg/L in only four samples. Arsenic contamination apparently is not widespread but rather limited to areas in the vicinity of large deposits of contaminated sediment.

Dissolved iron and manganese were present in the alluvial aquifer at concentrations many times their respective secondary standards for drinking water, 300 and 50 µg/L. Water from wells completed in or near large deposits of contaminated sediment usually contained iron concentrations ranging from 1,000 to 10,000 µg/L with a maximum concentration of 150,000 µg/L, whereas manganese concentrations ranged from 500 to 5,000 µg/L with a maximum concentration of 35,000 µg/L.

Other constituents associated with the contaminated sediments, cadmium, copper, silver, and cyanide, were not usually present in the ground water in concentrations more than the detection limit. Concentrations of mercury commonly were more than the detection limit of 0.2 µg/L, but all concentrations were small, and generally ranged from 0.2 to 0.4 µg/L; concentrations never exceeded 0.7 µg/L. The presence of mercury in the ground water does not correlate with the locations of contaminated-sediment deposits, and ground-water samples with large concentrations of arsenic, iron, and manganese usually did not contain detectable concentrations of mercury.

Contamination of the alluvial aquifers along Whitewood Creek and the Belle Fourche River is limited to areas in direct contact with thick deposits of contaminated sediments. Although there is insufficient information to absolutely define the geochemistry of the ground-water system, available evidence indicates that: (1) Sulfide minerals present in the sediments are being oxidized at a slow rate due to the lack of oxygen at the mineral surfaces, (2) pH is buffered by carbonate minerals and ferric-hydroxide dissolution, and (3) arsenic concentrations are limited by adsorption on or coprecipitation with hydrous iron oxides.

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