U.S. GEOLOGICAL SURVEY TOXIC SUBSTANCES HYDROLOGY PROGRAM--SURFACE-WATER CONTAMINATION: PROCEEDINGS OF THE TECHNICAL MEETING, DENVER, COLORADO, FEBRUARY 2-4, 1987

By Gail E. Mallard, editor

U.S. GEOLOGICAL SURVEY

Open-File Report 87-764

Reston, Virginia

1988

DEPARTMENT OF THE INTERIOR

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FOREWORD

The U.S. Geological Survey Toxic Substances Hydrology, Surface-Water Contamination Program is designed to provide the earth-science information needed to understand the movement and fate of hazardous substances in the Nation's surface waters. A key element of this program is intensive interdisciplinary investigations of the occurrence and movement of hazardous substances within specific hydrologic systems. This report documents the results of research conducted at three river basins that are currently (1987) under study and that were discussed, in part, at a technical meeting held in Denver in February 1987.

The three study sites, selected because they are known to be contaminated, provide field laboratories for basic and applied research into the physical, chemical, and biological processes that affect the movement and fate of major types of organic and inorganic contaminants. The water-quality problem being investigated in the Whitewood Creek, Belle Fourche River, and Cheyenne River system in South Dakota is the result of many years of discharge of mine wastes containing high concentrations of arsenic. The Calcasieu River in Louisiana receives industrial effluent from the petrochemical industry and is contaminated by organic chemicals. In Colorado, the headwaters of the Arkansas River receive water from mine drains and abandoned tailings that contains high concentrations of metals. At the time of the technical meeting, February 1987, the studies in Louisiana and South Dakota had been underway for about 1 and 1/2 years; the investigations of the Arkansas River in Colorado had been underway for 1 year. Thus, the results presented in this report are preliminary and represent a relatively early stage of research at these sites. As research continues, results may be reported in professional journals, in Geological Survey publications, and in the proceedings of future technical meetings as information becomes available.

This report is organized into three chapters that focus on the results of work at the three sites. A fourth chapter contains two papers that are not tied to study of a specific river system but that describe sediment sampling strategies and sediment movement in more general terms. The first paper in each of the chapters devoted to a river basin contains an overview of the hydrologic setting and describes the nature and history of the contamination problem under investigation. Subsequent papers report the results of a specific research problem. Collectively, the papers document our understanding of the river basins under study and demonstrate the extent of knowledge that can be gained in a relatively brief period of time as a result of intensive interdisciplinary study.

Gail E. Mallard, Coordinator
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Surface-Water Contamination Program

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Chapter A

GOLD-MILL-TAILINGS CONTAMINATION OF THE CHEYENNE RIVER SYSTEM, WESTERN SOUTH DAKOTA

By Kimball E. Goddard[1]

INTRODUCTION

For about 100 years, from the original discovery of gold at Deadwood, S. Dak., in 1875 until the late 1970's, large volumes of gold-mill tailings were discharged into Whitewood Creek and its tributaries at Lead and Deadwood, S. Dak. Substantial quantities of these tailings, perhaps the majority, have been intermixed with sediments and deposited along Whitewood Creek and the Belle Fourche and Cheyenne Rivers (fig. A-1). This paper describes the history of contamination in the area and summarizes information on ground-water and surface-water hydrology.

To comply with environmental laws enacted in the early 1970's, including the U.S. Environmental Protection Agency's Ore Mining and Dressing Effluent Guidelines, the current mining operator implemented the Grizzly Gulch Tailings Disposal Project. A 70-m- (meter) high earth and rockfill dam was constructed across a steep, narrow canyon (Grizzly Gulch), about 5 km (kilometers) south of the mine and mill area to create an impoundment area for tailings storage. The tailing disposal system became operational on December 1, 1977, and no discharge of tailings has occurred since that time.

The gross contamination of Whitewood Creek and the downstream rivers was alleviated by the discontinuance of tailings discharge in 1977. However, there is concern that the large deposits of contaminated sediments present along these streams are continuing to degrade surface and ground water in the Cheyenne River 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 when sediments could enter the flow 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 tailings discharge continue to have unusually large concentrations of total arsenic, iron, and manganese. An additional concern is the possible contamination of the alluvial aquifers along Whitewood Creek and the Belle Fourche and Cheyenne Rivers. A study by Stach and others (1978) determined that dissolved-arsenic concentrations ranged from 2.5 to 1,530 μg/L (micrograms per liter) in water from wells near large deposits of contaminated sediment. This evidence indicated a possible environmental hazard along Whitewood Creek. Because the areal extent of the possible environmental hazard was not well defined, the U.S. Environmental Protection Agency listed a reach of Whitewood Creek and the Belle Fourche River that is about 30 river km long as an Interim Priority Site under the Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA). The listing took place in October 1981.

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[1] U.S. Geological Survey, Rapid City, South Dakota

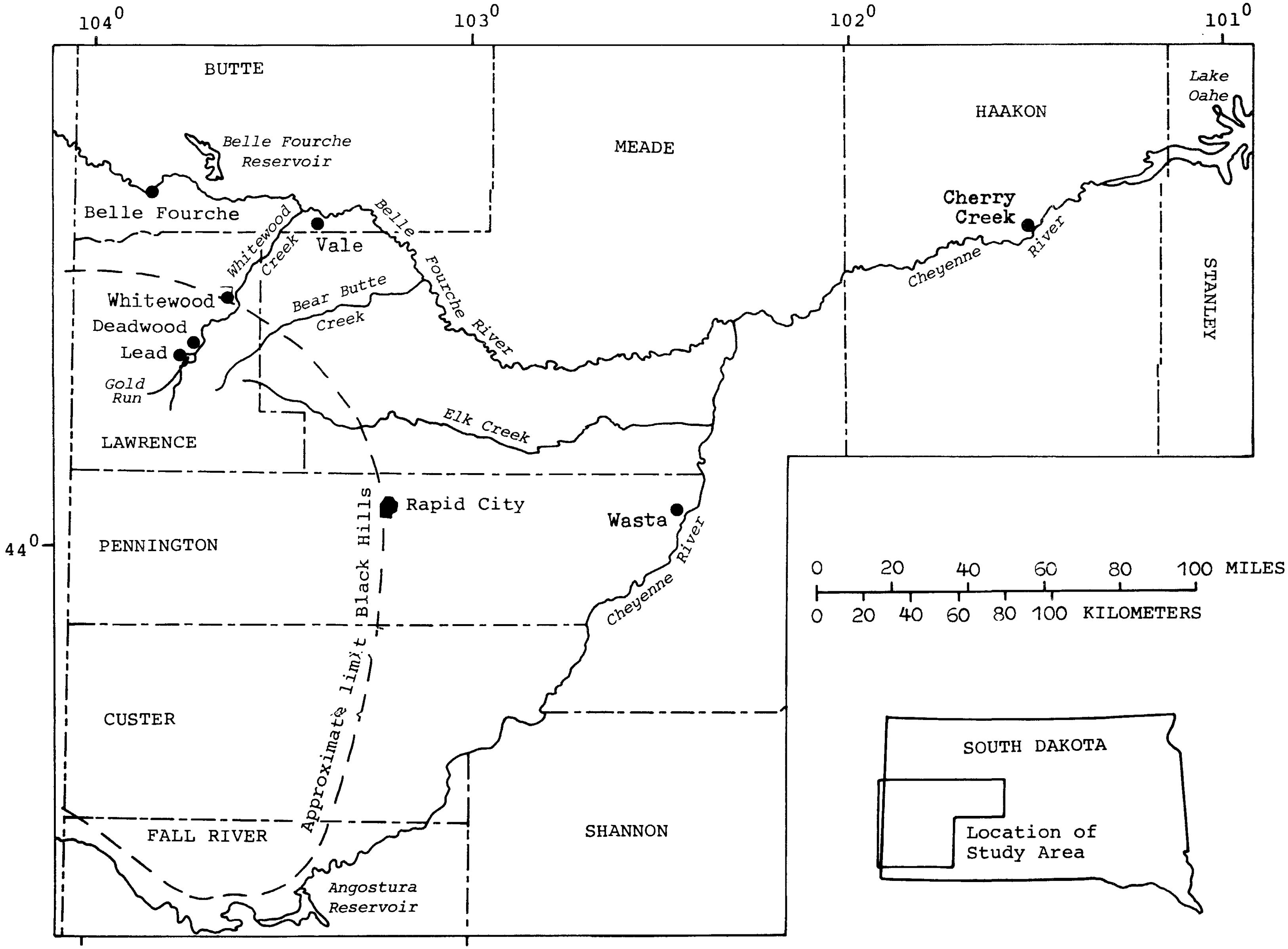

Figure A-1.--Location of study area in South Dakota.

Before an accurate evaluation to the potential hazard can be made, it was necessary that systematic investigations of the hydrologic effects of the contaminated sediments be conducted. Therefore, in the fall of 1982, the U.S. Geological Survey, in cooperation with the South Dakota Department of Water and Natural Resources, conducted a 2-year, basinwide study of the potential problem. Detailed results of this investigation are presented by Goddard (in press).

Simultaneously with the U.S. Geological Survey's investigation, a separate but related study was conducted that focused on the alluvial aquifers along Whitewood Creek and the Belle Fourche River. Clusters of vacuum lysimeters, piezometers, and wells were drilled and sampled at three sites along Whitewood Creek and one site along the Belle Fourche River. Results of this investigation are reported in a series of unpublished reports prepared by Fox Consultants, Inc., Denver, Colo. (written commun., 1984). The Phase I report includes field procedures, data, data-analysis-control procedures, and a general overview of the study area. The Phase II report is an interpretation of the data in the Phase I report as well as a literature review pertaining to topics of concern. Additional interpretations of the data collected by Fox Consultants, Inc., are presented by Cherry and others (1986).

In April 1985, the Whitewood Creek-Belle Fourche River-Cheyenne River-Lake Oahe system was selected for study as part of the U.S. Geological Survey's Toxic Substances Hydrology Program--Surface Water Contamination. The goals of the Surface Water Toxics Program are to improve the understanding of how toxic substances enter, are transported by, and are removed from surface-water systems.

NATURE AND EXTENT OF TAILINGS CONTAMINATION

Almost all of the mining wastes discharged to Whitewood Creek consisted of rock particles crushed to sand size or smaller by various milling methods used during processing. These tailings have intermixed to varying degrees with natural sediments and have been deposited along Whitewood Creek and the Belle Fourche River in deposits that can be identified visually by color, texture, and stratigraphic position. No contaminated-sediment deposits that can be identified by these characteristics have been found along the Cheyenne River. The deposits normally consist of well-sorted, fine-grained sediment with laminar or small-angle cross bedding. Deposits are present in three different lithologies. The first, limited in extent to the more steeply sloping reaches between and near Lead and Deadwood, is a reddish-brown, cemented, conglomerate-type sediment. The second is a brown to red, fine-grained silty sand. The third, nearly identical in appearance to tailings now produced by the mill at Lead, is a medium to dark gray, fine-grained silty sand. The texture is similar to that of the second lithology. The reddish-brown and medium to dark gray sediments are commonly found alternating in complex patterns within a deposit. Color banding commonly is seen along the edges of the medium to dark gray materials and in concentric rings around tree roots or worm holes. The color change indicates that oxidation of sulfide minerals present in the contaminated sediments is occurring with the consequent formation of iron oxides and hydroxides.

X-ray diffraction analysis of 46 contaminated-sediment samples indicates that the material is comprised largely of silicate minerals derived from the chloritized schists of the gold-bearing Precambrian Homestake Formation as used by Noble (1950). Quartz, feldspar, chlorite, and amphibole comprise about 75 percent by weight of the sediment. Some of the quartz is likely to be the result of intermixing with natural alluvial sediments, which are largely sand and silt-sized quartz grains. Nearly all of the remaining material, 22 percent by weight of the samples, consists of clay minerals derived from weathering of the ore-body silicate minerals or introduced from the shale of the northern Great Plains. Pyrite was detected in only 5 of the 46 samples and never in a proportion greater than 1 percent by weight (Goddard, in press). This lack of sulfide minerals contrasts with the 7 to 8 percent by weight of iron-sulfide minerals (phyrrhotite, pyrite, and arsenopyrite) reported in the ore by Noble (1950). Apparently, the majority of the sulfide minerals originally present in the mill tailings have been weathered to secondary oxides and hydroxides. The 46 samples described above were treated with oxalic acid to remove amorphous oxides; however, several additional samples of reddish-brown contaminated sediments, which were not treated with oxalic acid and which were specifically analyzed for oxide composition, contained between 16 and 22 percent by weight of amorphous iron oxide (Wuolo, 1986).

The concentrations of arsenic and several other trace elements are from several times to several orders of magnitude larger in contaminated sediments along Whitewood Creek and the Belle Fourche River than in uncontaminated sediments collected from the Belle Fourche River flood plain upstream from the mouth of Whitewood Creek. Arsenic is by far the most anomalous trace constituent; 95 samples collected from contaminated-sediment deposits in 1984 and 1985 had a mean arsenic concentration of 1,920 $\mu g/g$ (microgram per gram) and a maximum concentration of 11,000 $\mu g/g$ (Goddard, in press). In contrast, concentrations of arsenic in uncontaminated sediments within the Cheyenne River basin are typical of concentrations measured in the Cretaceous Pierre Shale, which averaged about 10 $\mu g/g$ for 202 samples (Schultz and others, 1980). Thirteen samples of sediment collected from an uncontaminated part of the Belle Fourche River flood plain in 1984 had a mean arsenic concentration of 9.2 $\mu g/g$. Antimony, cadmium, copper, iron, manganese, and silver are associated with the ore minerals and have anomalous concentrations in the contaminated sediments. Cyanide and mercury are constituents contributed largely from ore processing and commonly are detected in contaminated sediments. Analysis for chromium, lead, nickel, selenium, and zinc also was conducted, but these constituents are not associated either with the ore or ore processing and so are not associated with the tailings contamination.

Random sampling of flood-plain sediments in 1984 indicated anomalous concentrations of arsenic occur throughout the Cheyenne River basin. As would be expected, the largest concentration of arsenic occurs in sediments along Whitewood Creek, and arsenic concentrations measured in 42 randomly collected flood-plain sediment samples from Whitewood Creek averaged 1,400 $\mu g/g$. Concentrations measured in sediments from the Belle Fourche River flood plain decrease gradually in a downstream direction from about 1,300 $\mu g/g$ just downstream from the mouth of Whitewood Creek to about 400 $\mu g/g$ at the mouth of the river. Arsenic contamination of the Cheyenne River flood plain is much less and concentrations in 312 randomly collected flood-plain sediment samples averaged about 70 $\mu g/g$ (Goddard, in press). Throughout the contaminated reach, flood-plain sediments contain between 150 and 500 percent larger concentrations of arsenic than do active-channel sediments.

SURFACE-WATER HYDROLOGY

Whitewood Creek is a small, perennial tributary of the Belle Fourche River. The drainage basin of 270 km^2 (square kilometers) is divided about equally between the rugged topography of the northern Black Hills and the gently rolling grass-covered hills of the northern Great Plains prairie. Whitewood Creek originates as ground-water discharge from the Mississippian Madison Limestone and Cambrian and Ordovician Deadwood Formation and then flows across a complex of Precambrian metamorphic and Tertiary intrusive rocks in which the mining area is located. Downstream from Lead and Deadwood, the Whitewood Creek basin is underlain by progressively younger limestone and shale as the stream flows away from the Black Hills onto northern Great Plains prairie.

In the upstream reach located within the Black Hills, Whitewood Creek occupies a deep, narrow canyon with minimal flood plain, has a gradient of about 50 m/km (meters per kilometer), and flows over channel material consisting of gravel, cobbles, and bedrock outcrops. In the downstream reach located within the Great Plains, Whitewood Creek occupies a much wider channel with a substantial flood plain and has a gradient of about 20 m/km. The most important geomorphological characteristic of the downstream reach of Whitewood Creek is the large deposits of contaminated sediments that completely cover the flood plain. The channel material in the downstream reach still is comprised largely of gravel and cobbles although outcrops of Cretaceous Carlile Shale are present along the 3 river km just upstream from the mouth.

The discharge of Whitewood Creek increases downstream in response to surface-water tributary inflow, ground-water inflow, and waste-effluent discharge. Upstream from Lead, Whitewood Creek is small and has a mean annual discharge of about 0.15 m^3/s (cubic meter per second). Just downstream from Lead at the U.S. Geological Survey's streamflow-gaging station, Whitewood Creek at Deadwood, the mean annual discharge increases to about 1.1 m^3/s because of the inflow of several tributaries and effluent discharge from current mining operations. The only perennial inflow downstream from this station is effluent from the municipal sewage-treatment plant that serves Lead and Deadwood. The mean annual discharge at the mouth is about 1.4 m^3/s. Continuous discharge data currently (1987) are being obtained at four streamflow-gaging stations on Whitewood Creek; the oldest of these stations was established in 1981.

The Belle Fourche River is the largest tributary of the Cheyenne River; together they receive all the runoff from the Black Hills. The Belle Fourche River originates in the Powder River structural basin of eastern Wyoming and flows first northeast and then southeast around the northern Black Hills, while the Cheyenne River, which also originates in eastern Wyoming, flows first southeast and then northeast around the southern Black Hills. The Cheyenne River has a somewhat larger drainage basin upstream from its junction with the Belle Fourche River, about 34,500 km^2 compared to the Belle Fourche River drainage basin of about 20,500 km^2. However, both rivers have mean annual flows that are nearly identical and both have average flows of about 10 m^3/s based on a period of record of about 50 years. Continuous discharge data are available at two stations along the contaminated reach of the Belle Fourche River and at two stations along the Cheyenne River downstream from the mouth of the Belle Fourche River.

Within the study area, the Belle Fourche and Cheyenne Rivers occupy flat-floored valleys underlain by Pierre Shale. The boundaries between the surrounding hills and the valley floors generally are marked by abrupt breaks in slope. A continuous alluvial deposit between 3 and 10 m thick occupies the valleys. Channel slopes are considerably flatter than that along Whitewood Creek and are between 2 and 5 m/km. Both rivers have active point bars and moderate meanders. Channel material consists of cobbles, gravel, and some sand and silt.

The major-ion chemistry of Whitewood Creek and the Belle Fourche and Cheyenne Rivers is controlled by the underlying geologic formations. The source area for Whitewood Creek is located at the outcrop of the Madison Limestone and the water in the upstream reach of Whitewood Creek is a calcium bicarbonate type that is typical of water in contact with carbonate rocks. As Whitewood Creek flows from the Black Hills, major-ion chemistry is first affected by the Permian and Triassic Spearfish Formation, a unit that contains gypsum, and then by the shale that underlies the downstream reach of Whitewood Creek and the Belle Fourche and Cheyenne Rivers. These rocks yield sulfate and sodium to the surface streams. Sulfate concentrations increase from about 10 mg/L (milligrams per liter) near the headwaters of Whitewood Creek to about 360 mg/L near the mouth; sulfate concentrations in excess of 1,000 mg/L occur in the Belle Fourche and Cheyenne Rivers (Goddard, in press).

Surface-water contamination resulting from previous discharge of mill tailings to Whitewood Creek is most evident in Whitewood Creek and a reach of the Belle Fourche River immediately downstream from the mouth of Whitewood Creek. Arsenic, cadmium, and silver primarily derived from contaminated-sediment deposits increase in concentration downstream along Whitewood Creek as large deposits along the stream contribute leachate and solids to the flow. Copper, cyanide, and mercury are derived primarily from effluent discharges in the Lead and Deadwood area and decrease in concentration downstream along Whitewood Creek due to dilution, sorption on bottom sediments, or biodegradation.

The most important contaminant is arsenic. Undetected, or rarely present in measurable concentrations at uncontaminated sites in the Cheyenne River basin, dissolved arsenic has a mean concentration of about 35 μg/L in the downstream reach of Whitewood Creek. Dissolved-arsenic concentrations vary seasonally with maximum yearly concentrations of about 70 μg/L occurring in July or August. The maximum measured dissolved-arsenic concentration between April 1983 and October 1986 was 130 μg/L on August 7, 1985, when discharge was 0.065 m^3/s at the streamflow-gaging station, Whitewood Creek above Vale, which is about 4 river km upstream from the mouth. Large concentrations of solid-phase arsenic occur in bed and suspended sediments throughout the study reach. Typical concentrations of solid-phase arsenic in bed sediments decrease from about 1,000 μg/g in Whitewood Creek to about 300 μg/g in the Belle Fourche River and to about 30 μg/g on the Cheyenne River. In the suspended-sediment samples collected in 1986, typical solid-phase arsenic concentrations decreased from about 1,000 μg/g in Whitewood Creek to about 100 μg/g in the Belle Fourche River and to about 30 μg/g on the Cheyenne River. These concentrations contrast with the mean concentration of 9.2 μg/g measured in uncontaminated sediments.

Prior to the discontinuance of tailings discharge in 1977, Whitewood Creek was devoid of aquatic organisms downstream from the wastewater discharge at Lead. The tailings prevented the existence of any substrate suitable for attached plants and concentrations of cyanide and metals complexed with the cyanide were toxic to aquatic insects and fish. However, in the 10 years since the tailings discharge was stopped, most of the tailings material has been flushed from the active channel and the resulting substrate of gravel and cobbles is suitable for an aquatic ecosystem to develop. Since December 1984, cyanide concentrations have been controlled by an advanced wastewater treatment system and are less than concentrations toxic to species as sensitive as rainbow trout according to recent bioassay work (F.M. Fox, Homestake Mining Co., oral commun., 1985). Subsequently, a complex aquatic community has developed in Whitewood Creek.

Large populations of attached algae are found in Whitewood Creek downstream from Lead and Deadwood because of nutrient enrichment of the stream by discharge effluent from the municipal sewage-treatment plant. During sampling in 1981–82, Herricks (1982) found periphytic algae in all 12 sites he visited; the algae community was dominated by Achnanthese minutissima and Nitzschia paleacea, algae commonly occurring in western streams. On the basis of hierarchical cluster analysis, Herricks (1982) concluded that natural seasonal factors such as discharge and water temperature were more significant in controlling periphyton distribution and abundance than the toxic effects of the then-current (1981) point or nonpoint source contamination.

Benthic macroinvertebrates also were common in Whitewood Creek during 1981–82. Sampling by Herricks (1982) in 1981–82 identified 262 macroinvertebrate taxa. The most diverse order was true flies (Diptera) with 93 taxa, while beetles (Coleoptera) were represented by 45 taxa. All major orders of aquatic insects were found including stoneflies, mayflies, and caddisflies. After analysis of the data, Herricks (1982) concluded that changes in macroinvertebrate groups between sites along Whitewood Creek were due to natural factors such as water temperature as well as to wastewater from current mining operation and effluent from the municipal sewage-treatment plant. Arsenic, mercury, cadmium, and copper were determined to be accumulating in or on benthic organisms collected from the contaminated reach of Whitewood Creek. Invertebrates from the contaminated reach had arsenic concentrations more than 50 times those measured in organisms from uncontaminated sites. Mercury was about five times more concentrated and cadmium and copper were about four times more concentrated in the Whitewood Creek organisms. A mean arsenic concentration of 60.5 μg/g was determined for benthic organisms from the contaminated reach of Whitewood Creek, a value larger than reported in most literature for organisms from other arsenic contaminated sites (Herricks, 1982).

Also during 1981–82, the fisheries population of Whitewood Creek was significantly affected by both point and nonpoint contamination. Downstream from Lead and Deadwood, no fish were found during four separate electrofishing collections at five different sites along Whitewood Creek; however, upstream from Lead, significant numbers of small (<200 mm (millimeters)) brook trout were collected (Herricks, 1982). Brook trout commonly are stocked in Black Hills streams and the population present in the upstream reach of Whitewood Creek probably is a result of this stocking. Probably because of recent (1984) improvements in the quality of wastewater discharge, fish now (1987) are established in the downstream reach of Whitewood Creek. High water temperature during the summer will preclude cold-water fish, but catfish, carp, and other warm-water fish now are able to survive as noted by sightings during the past several years.

GROUND-WATER HYDROLOGY

Most of the Whitewood Creek Valley and all of the Belle Fourche and Cheyenne River Valleys 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 characteristic of the upstream reach of Whitewood Creek; the alluvium generally increases in thickness and lateral extent downstream. The alluvium generally is less than 10 m thick throughout most of the study area although it is as much as 25 m thick along the Cheyenne River. An alluvial-fan deposit at the mouth of the Whitewood Creek Canyon, near the town of Whitewood, is more than 15 m thick, but is of limited areal extent. Saturated thickness of the alluvium ranges from about 3 m along Whitewood Creek and the Belle Fourche River to almost 20 m along the Cheyenne River (Goddard, in press).

The major-ion composition of water in the alluvium results from the cumulative effects of underlying shale units. Solutes 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 is present in concentrations of about 1,000 to 6,000 mg/L in water from the alluvium.

Ground-water contamination along Whitewood Creek and the Belle Fourche River is limited to alluvial aquifers in direct contact with large deposits of contaminated sediments. The magnitude of contamination also is less than might be expected considering the quantity of arsenic-sulfide minerals present in the tailings discharge. Although the geochemistry of the ground-water system is not yet completely understood, several factors affecting ground-water quality have been determined. First, most of the sulfide minerals originally present in the tailings have been oxidized. The remaining sulfide minerals are in deposits that have minimal permeability, which decreases the availability of oxygen. Dissolved-oxygen concentrations of 0.0 mg/L and Eh values ranging from 0 to -100 mV (millivolts) have been measured in contaminated water from the alluvial aquifer (Goddard, in press; Wuolo, 1986). Second, the pH of the system is buffered by natural and introduced carbonate. Large outcrops of limestone bedrock are present along the upstream reach of Whitewood Creek and limestone cobbles, pebbles, and gravel are common in the alluvial materials. Carbonate minerals are present in the ore body (Noble, 1950) and so were present in the tailings discharge. In addition, lime was added to the milled ore before cyanide leaching as a part of the processing (F.M. Fox, Homestake Mining Co., oral commun., 1986). Measurements of pH in contaminated water from the alluvial aquifers range from 6.1 to 7.6 (Goddard, in press). Finally, arsenic concentrations are attenuated by adsorption onto the large quantities of ferric oxides and hydroxides present in the contaminated sediments and aquifer materials. Laboratory experiments on the adsorption-desorption characteristics of contaminated sediments indicated that oxidized sediments readily adsorb arsenic and the maximum adsorption occurs at near-neutral pH (Wuolo, 1986).

Although catastrophic ground-water contamination currently (1987) is not occurring within the study area, arsenic, iron, and manganese are being released from contaminated sediment and large concentrations of these constituents are present in some water from the alluvial aquifers. Dissolved-arsenic concentrations between 50 and 500 μg/L were measured in water from seeps and wells along Whitewood Creek (Goddard, in press).

Dissolved-iron and dissolved-manganese concentrations are much larger in samples from wells yielding water from large deposits of contaminated sediments. Dissolved-iron concentrations commonly ranged from 1,000 to 10,000 μg/L and dissolved-manganese concentrations commonly ranged from 500 to 5,000 μg/L (Goddard, in press). It is not known if the arsenic, iron, and manganese are being released by oxidation of sulfide minerals or by dissolution of ferric and manganese hydroxides under reducing conditions.

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TRANSPORT AND FLOOD-PLAIN STORAGE OF METALS ASSOCIATED WITH SEDIMENT DOWNSTREAM FROM LEAD, SOUTH DAKOTA

By Donna C. Marron[1]

Between 1880 and 1977, about 90 million metric tons of finely milled mine tailings containing arsenopyrite and other metallic sulfides were discharged into Whitewood Creek near Lead, S. Dak. Overbank deposition and meander migration have caused much of the sediment to be stored in the flood plain and on terraces along Whitewood Creek and downstream along the Belle Fourche River. This stored sediment contains greater than background concentrations of a variety of metals, particularly arsenic.

The metal-contaminated sediments in the flood plains of Whitewood Creek and the Belle Fourche River contain as much as 0.6 percent arsenic; the arsenic concentrations of these sediments are not characterized by a statistically significant decrease with increasing distance downstream from Lead. This lack of pattern apparently is caused by the overwhelming quantity of mine tailings that were discharged into the stream system yearly in relation to the quantity of "clean" sediment that was available in the stream system to dilute the contaminated sediments. In contrast, arsenic concentrations of streambed sediments collected in 1985 in Whitewood Creek and the Belle Fourche River, 8 years after the cessation of mine-tailings discharge, decrease systematically with increasing distance downstream from Lead (K.E. Goddard, U.S. Geological Survey, written commun., 1986).

Metals analyses of different size fractions of contaminated flood-plain sediments indicate greater concentrations of metals in the finer size fractions. In two samples from the flood plain of Whitewood Creek and two samples from the flood plain of the Belle Fourche River, arsenic concentrations in the greater than 64-μm (micrometer) fraction range from 60 to 95 percent of the arsenic concentrations of the 16- to 64-μm fraction, and from 17 to 41 percent of the arsenic concentrations of the less than 4-μm fraction. Arsenic concentrations obtained by a partial-digestion procedure that is not effective for sulfide minerals were more than 70 percent of the arsenic concentrations obtained by using a total digestion procedure for 13 flood-plain sediment samples for which both types of data were obtained. This result indicates that much of the arsenic that is presently (1986) in the contaminated flood-plain sediments no longer occurs in association with the primary sulfide minerals that were the original source of the arsenic.

Metal-contaminated sediment is stored in the flood plains of Whitewood Creek and the Belle Fourche River as point-bar deposits, overbank deposits, and deposits filling abandoned channels. Preliminary calculations of the quantity of metal-contaminated sediment stored on flood plains indicate that at least one-third of the mine tailings discharged into the river system presently (1986) are stored along about 120 km (kilometers) of the Belle Fourche River flood plain downstream of Lead. Measurements of meander-migration rates of channels in contaminated flood-plain areas indicate that the metal-contaminated flood-plain deposits will continue to be a source of metals to adjacent streams for centuries.

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(p. 13 follows)

DISTRIBUTION OF SOLID-PHASE ARSENIC AND TRACE ELEMENTS IN BOTTOM AND SUSPENDED SEDIMENTS, WHITEWOOD CREEK AND THE BELLE FOURCHE AND CHEYENNE RIVERS, WESTERN SOUTH DAKOTA

By Kimball E. Goddard[1], Arthur J. Horowitz[2], and Charles K. Shearer[3]

About 100 million metric tons of finely ground gold-mill tailings were discharged into Whitewood Creek near Lead, S. Dak., between 1876 and 1977. The tailings contained substantial concentrations of arsenic, mercury, and other trace elements resulting in widespread contamination of the alluvial sediments along Whitewood Creek and the Belle Fourche and Cheyenne Rivers. The primary contaminant is arsenic derived from, or still present as, the sulfide mineral arsenopyrite (FeAsS), a gangue mineral common to the gold-bearing deposits at Lead. The trace elements antimony, cadmium, copper, iron, manganese, mercury, and silver also are associated with the mill tailings and are present in the contaminated alluvial sediments.

The areal distribution of arsenic and selected trace elements in bottom sediments was determined by collecting samples of bottom sediments from 15 sites along Whitewood Creek and the Belle Fourche and Cheyenne Rivers (fig. A-2) in August 1985. Samples were collected by hand and wet sieved in the field to less than 64 μm (micrometers) using plastic implements and sieves. The remaining water-sediment slurry was further concentrated by centrifugation and freeze-dried for storage until analysis. The areal and temporal distribution of arsenic and selected trace elements in suspended sediments was determined by collecting large-volume suspended-sediment samples at four primary and several secondary sites between,February and October 1986. Sample collection followed standard U.S. Geological Survey procedures for the collection of discharge-weighted suspended sediment as presented in Guy and Norman (1970). Total digestion procedures followed those of Elrick and Horowitz (1985; 1987). Analysis was by atomic-absorption spectrometry. A completed description of the sample collection and analysis procedures, and of the analytical results is presented by Goddard (in press).

Arsenic and the trace elements copper, antimony, and mercury occur in large concentrations in bottom sediments downstream from Lead (fig. A-2). Although the concentration of trace elements in bottom sediments vary, the pattern of concentration change downstream is similar. Concentrations of other trace elements known to be associated with the mill tailings do not have such distinct patterns of change downstream. Iron and manganese are present in substantial concentrations in uncontaminated sediments, and the contrast between these trace-element concentrations in contaminated and uncontaminated sediments is small. Cadmium and silver have small concentrations in the mill tailings; the concentrations of these trace elements in many contaminated-sediment samples were less than the analytical detection limits. Differences in the patterns of concentration change downstream for arsenic, copper, antimony, and mercury can be attributed to: (1) the current (1986) primary source of the element, (2) geochemical reactions of the element, and (3) concentration contrast between contaminated and uncontaminated sediments.

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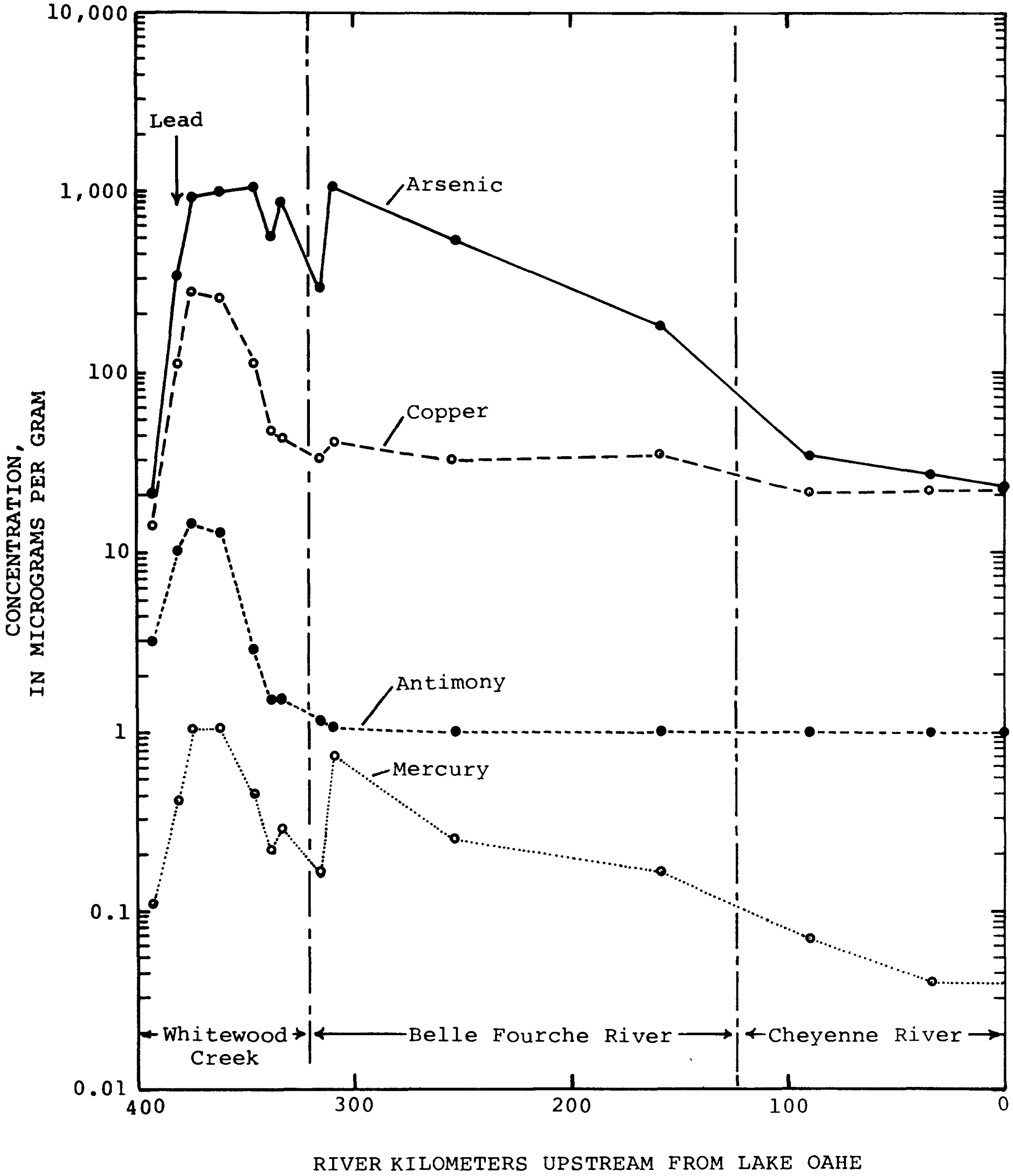

Figure A-2.—Arsenic, copper, antimony, and mercury concentrations measured in bottom sediments collected in August 1985.

Substantial concentrations of arsenic and mercury occur in bottom sediments for more than 150 river km (kilometers) downstream from the original tailings discharge point at Lead, and the patterns of concentration change are similar. Because there currently (1986) is no significant point-source discharge of these elements to Whitewood Creek at Lead, the large concentrations present in the bottom sediments downstream from Lead are the result of input from the large deposits of contaminated sediments present along these reaches. The dual mechanisms of this input are the addition of solid-phase components by bank collapse and the adsorption of dissolved-phase components present in ground-water inflow.

Evidence for bank collapse is apparent as indicated by visible erosion of contaminated-sediment deposits that occurs during periods of high discharge. In addition, well-crystallized arsenopyrite has been identified in both Cheyenne River suspended sediment and Lake Oahe bottom sediments by A.J. Horowitz (written commun., 1986). He concluded that the material was derived from the banks or flood plains of the Whitewood Creek-Belle Fourche River system.

Evidence for the adsorption of dissolved-phase components comes from the comparison of arsenic concentrations in bottom sediments with those in suspended sediments (fig. A-3). At the sites along Whitewood Creek and the Cheyenne River for which both types of data are available, there is similarity between bottom- and suspended-sediment arsenic concentrations. This similarity is expected because bottom and suspended sediments freely interchange. However, arsenic concentrations in bottom sediments at the sites along the Belle Fourche River are substantially greater than arsenic concentrations in the suspended sediments collected at these sites. This apparent anomaly is caused, at least partially, by the large inflow of water and sediment from Horse Creek, an uncontaminated tributary that enters Belle Fourche River at river km 296. Arsenic concentrations in suspended sediment increased downstream along the Belle Fourche River from 51 μg/g (micrograms per gram) at river km 288 to 140 μg/g at river km 158 during the March 5-6, 1986, high-discharge period, as contaminated bottom and bank sediments contributed arsenic to the uncontaminated sediment from the Horse Creek basin. Horse Creek has a much larger drainage basin than Whitewood Creek and may dominate the sediment contribution to the Belle Fourche River. Arsenic enrichment of these bottom sediments may be explained if dissolved arsenic is absorbed from the water column. Dissolved arsenic is contributed to the Belle Fourche River by Whitewood Creek and inflow from the alluvial aquifer.

Comparison between mercury concentrations measured in bottom and suspended sediments (fig. A-3) is inconclusive. Mercury concentrations in suspended sediments generally decrease downstream, but there is little correlation between mercury concentrations in bottom and suspended sediments possibly because of problems in sample preparation and laboratory analysis resulting from mercury's tendency to volatilize and the small concentrations being measured. Like arsenic, mercury concentrations appear enriched in the bottom sediment at almost all sites. It cannot be determined, with the available data, if mercury is being concentrated in bottom sediments due to adsorption from the water column. However, a pattern of downstream concentration change nearly identical to that for arsenic and the small mercury concentrations measured in suspended-sediment samples measured in 1986 indicate a similar enrichment process is possible.

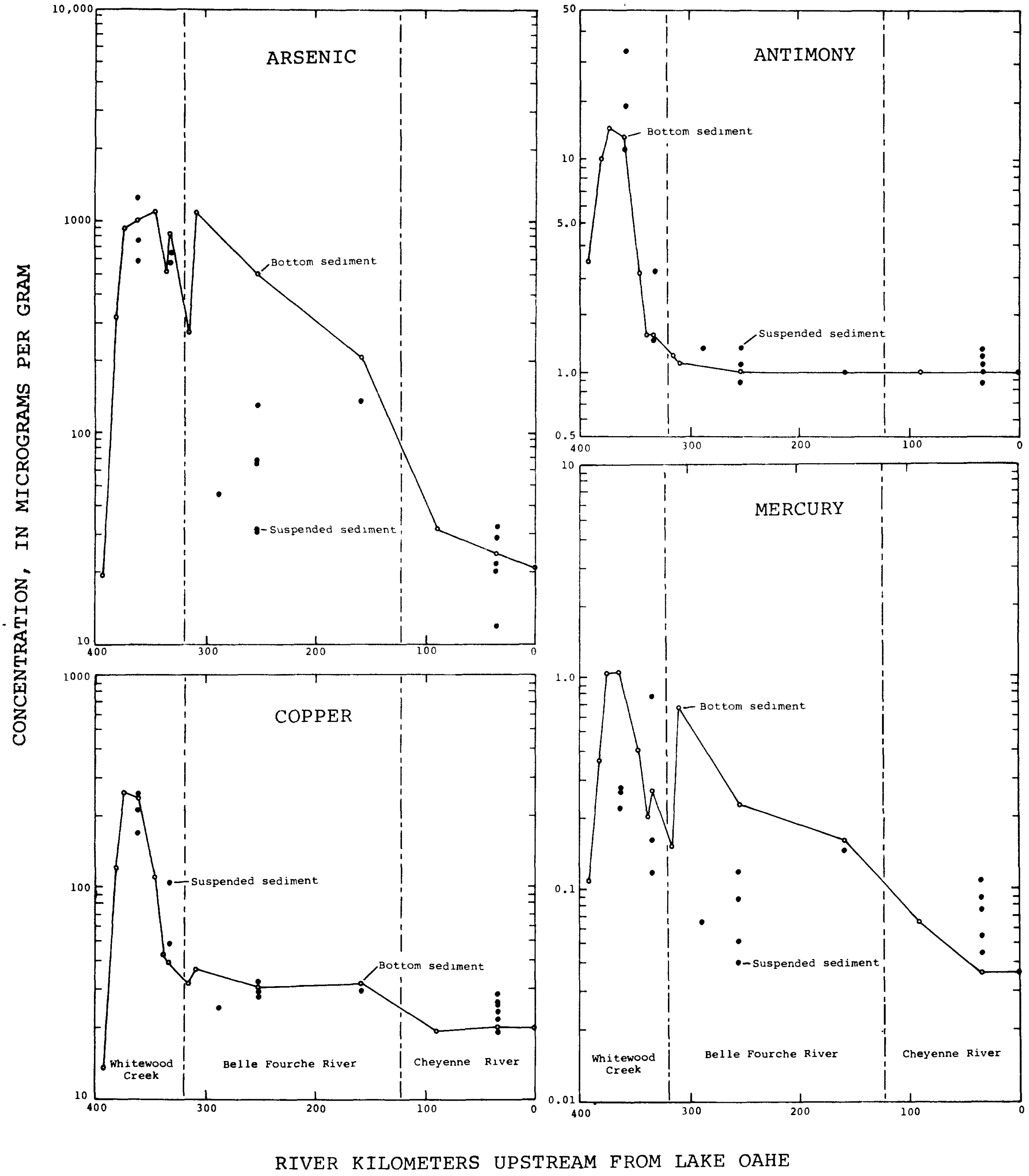

Figure A-3.--Selected element concentrations measured in bottom and suspended sediments.

The large concentrations of copper in bottom sediments downstream from Lead and Deadwood is not caused by contaminated sediment entering the stream channel but by precipitation or adsorption of dissolved-phase copper present in the water column. Unlike arsenic, the dissolved copper is not contributed by inflow of contaminated surface or ground water but rather by the effluent discharged by a mining company at Lead. Dissolved copper is a known component of the effluent being discharged and concentrations as large as 300 μg/L (micrograms per liter) have been reported in Whitewood Creek downstream from Lead (Goddard, in press). Hem (1970) reported the solubility of copper in aerated water at a pH of 8.0 (typical of Whitewood Creek) to be about 6.4 μg/L. Hem (1985) also suggested that adsorption or coprecipitation with ferric hydroxide can cause even smaller solubility limits. The accumulation of copper in bottom sediments results in concentrations of as much as 280 μg/g, which is several times larger than the concentrations of 50 to 100 μg/g measured in tailings or contaminated sediments. Because little or no antimony data are available for streamflow, it is impossible to determine if a similar process is responsible for the substantial concentrations of antimony in bottom sediments downstream from Lead and Deadwood. However, dissolved antimony was detected (3 μg/L) in a sample of effluent collected in March 1986, and a pattern of change in bottom-sediment concentrations downstream nearly identical to that of copper would make such an explanation plausible.

Unlike arsenic and mercury, copper and antimony concentrations in bottom and suspended sediments are similar (fig. A-3). Concentrations of copper and antimony in bottom sediments have decreased to near background concentrations at the mouth of Whitewood Creek. Downstream from this point, little contrast between concentrations in bottom and suspended sediments occur.

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PARTITIONING OF ARSENIC BY IRON OXIDES IN WHITEWOOD CREEK, SOUTH DAKOTA

By Christopher C. Fuller[1], James A. Davis[1], and Regina G. Claypool-Frey[1]

This paper describes research on the role of iron oxyhydroxides in controlling the concentration of dissolved arsenate by sorption processes and the transport of arsenic in association with disaggregated colloidal iron that were studied in Whitewood Creek, a small perennial tributary of the Belle Fourche River, in South Dakota. This stream and the Belle Fourche River downstream of its confluence with Whitewood Creek have been heavily contaminated by the discharge of processed tailings and debris from large-scale gold-mining operations. An estimated 75 to $100x10^6$ tons of ground tailings have been discharged to the watershed; the tailings consist primarily of unoxidized sulfide minerals including a large amount of arsenopyrite (FeAsS). This large input of fine-grain material has changed the stream morphology, resulting in extensive overbank deposits of unoxidized tailings. Subsequent oxidation of this material, either in the stream or in the bank deposits, has resulted in the formation of iron oxyhydroxide which has deposited as coatings on the coarser alluvium along the stream (Goddard, in press). These coatings have high arsenic concentrations resulting from adsorption and coprecipitation with iron oxyhydroxides.

Ground waters from within the tailings deposits have high dissolved iron (Fe) (to 0.2 mM (millimolar)), arsenic (As) (to 10 μM (micromolar)), and sulfate (SO_4) (to 12 mM) and are relatively reducing $Fe^{2+}/Fe_T=0.9$ and $As(III)/As_T=0.4$ to 0.8), probably as a result of <u>in-situ</u> oxidation of the sulfides. However, the pH values of the ground waters are generally neutral (7–8), due to buffering by carbonates. Ground waters in the alluvial deposits also have high As, Fe, and SO_4, possibly derived from reductive dissolution of iron oxides following infiltration from shale aquifers or streamwater, or from infiltration of ground water from adjacent tailings deposits (Cherry and others, in press). The shallow ground water systems are perched on Pierre shale and are recharged partially from the stream during high flows in the spring. Subsequent discharge of the high Fe and As ground water into the stream occurs throughout the spring and summer; some of the discharge is visible as seeps at or above stream level. Formation of iron oxyhydroxide occurs upon contact of the ground water with the atmosphere or the stream. Sorption of As onto the ferric oxyhydroxide removed some of the dissolved As.

To evaluate the role of iron oxides in controlling the partitioning of arsenic by sorption-desorption equilibrium and to determine if there is significant transport of As associated with disaggregated colloidal iron, samples of streamwater, bed sediments, and iron oxide precipitates were collected in August 1986. Total iron and arsenic were determined in filtrates of streamwater from 0.4, 0.1, and 0.01 μm (micrometer) membrane filters at seven sites. In addition, filtrates at two of the sites which had active seeps were analyzed for arsenate and arsenite following separation in the field by an anion exchange technique. Samples of the iron oxyhydroxide precipitate were collected by syringe just below seep outlets. These samples were analyzed for total arsenic and iron following dissolution

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in concentrated nitric acid. Bed sediments were collected and separated into coarse (>60 µm) and fine (<60 µm) size fractions. These samples were analyzed for Fe and As after concentrated nitric-acid digest. Iron concentrations were determined by the ferrozine colorimetric technique (Stookey, 1970) and arsenic by graphite furnace AA for filtrate samples and hydride generation for solid leachates.

Dissolved As concentrations in stream samples were greater than 90 percent arsenate and ranged from 0.2 to 0.9 µM, with the higher concentrations observed at sites with seeps. Negligible differences in arsenic concentrations were observed in filtrates passing through 0.4, 0.1, and 0.01 µm filters. Iron concentrations ranged from 0.13 to 0.48 µM in 0.4 µm filtrates with higher values again observed at sites near active seeps. In contrast to arsenic, up to a threefold decrease was observed in iron concentration between filtrates from 0.4 and 0.1 µm filters.

Iron oxide precipitates (20–30 percent Fe by weight) had total arsenic concentrations ranging from 0.03 to 0.1 mmole/g (millimole per gram) (1,800–8,200 mg/L (milligrams per liter)). The molar ratios of As to Fe in these precipitates ranged from 0.010 to 0.026. The sand fraction of the bed sediments yielded As concentrations of 0.0021 to 0.016 mmole/g (160–1,200 mg/L) and total Fe concentrations of 0.12 to 0.70 mmole/g (6,700–39,000 mg/L). Despite variation of nearly an order of magnitude in both As and Fe concentrations, the As:Fe ratio ranged only from 0.017 to 0.025 (mean: 0.0219±0.0033). The corresponding fine-grain fraction yielded As concentrations of 0.01 to 0.02 mmole/g (600–1,400 mg/L) and Fe concentrations of 0.44 to 0.64 mmole/g (29,000–36,000 mg/L). These values correspond to As:Fe molar ratios of 0.013 to 0.032 (mean: 0.022±0.006). Thus, for the three types of sediment examined, relatively constant As:Fe ratios were observed. This result indicates that the arsenic measured in the sand and fine-grain sediments is probably associated with iron oxides despite the nonselective dissolution technique used. Selective extraction techniques have been found unsuitable for arsenic (Gruebel and others, 1986).

The attenuation of a significant fraction of the 0.4 µm filtrate iron by the 0.1 µm filters indicates a disaggregated colloidal-iron phase. Transport of iron and phosphate as colloidal particles (0.01–1 µm) has been observed in a shallow ground-water system (Gschwend and Reynolds, 1986). Owing to the similarities in the sorption characteristics of arsenate and phosphate (Goldberg, 1986), transport of arsenic in association with iron as colloidal particles might be expected in this system. To determine if there is significant transport of As in association with the colloidal iron (0.1–0.4 µm) analysis of this particle-size fraction is required. Although insufficient particulate material was collected for a quantitative analysis, the constancy of dissolved As concentrations over the range of filter-pore sizes employed indicates that only a small fraction of the total dissolved As was associated with colloidal iron particles in the 0.1 to 0.4 µm size range. This result is also evident by assuming that the colloidal phase had a similar As:Fe ratio as that measured in the iron oxyhydroxide precipitates collected in the stream (0.01–0.03). Therefore, during the low-flow period at the time of sampling, the <0.4 µm filtrate As is transported primarily as dissolved arsenate. During high-flow periods, however, disaggregation induced by turbulence may result in large increases in the number of colloidal iron particles less than 0.4 μm, and thereby increases As transport by this mechanism.

In determining the role of As sorption-desorption equilibria with iron oxyhydroxide surfaces in controlling the dissolved arsenate concentration in the stream, comparison of the observed arsenic partitioning with laboratory sorption data can be made. For example, the equilibrium arsenate concentration, C_{eq}, can be estimated from sorption isotherms for arsenate uptake by amorphous iron oxide (Pierce and Moore, 1982) by equating the measured As:Fe ratio of the solid phases analyzed with sorption density. A precipitation experiment was conducted in the field with seep water that was collected before contact with the atmosphere and allowed to precipitate in the absence of other solids. A final arsenate concentration of 0.7 μM and a solid phase As:Fe ratio of 0.013 were measured with 80 percent of the total arsenic associated with the solid phase. From the sorption isotherm (Pierce and Moore, 1982), a C_{eq} of 0.5 μM is predicted for the measured As:Fe ratio of the iron precipitate. A range of C_{eq} values of 0.6 to 10 μM are predicted at pH 8 (stream pH 7.9–8.7) for the range of As:Fe (0.01–0.03) observed in the solid phases collected in the field. These values are generally higher than the corresponding streamwater concentrations (0.2–0.9 μM), indicating that As desorption may be slow or that aging of the precipitate leads to greater As uptake. The hypothesis of slow desorption kinetics is supported in part by the results of desorption studies conducted with the iron oxyhydroxide precipitate collected at the seep areas. In these experiments, release of 0.03 to 0.3 μM As into an artificial streamwater at pH 8 was observed during a 1-week reaction time. Desorption to a dissolved concentration of 0.05 μM As was observed 3 weeks after precipitate formation from the collected seep water; this indicates that subsequent reactions and aging of the solid may render As less available for desorption. A laboratory study of the mechanisms of As uptake by amorphous iron oxyhydroxide as a function of the As:Fe ratio and the rates of desorption are currently being conducted.

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PROCESSES CONTROLLING THE CONCENTRATION OF DISSOLVED ARSENIC IN WHITEWOOD CREEK, SOUTH DAKOTA

By Kimball E. Goddard[1] and Ray W. Wuolo[2]

Between 1876 and 1977, about 100 million metric tons of finely ground mill tailings that contained arsenopyrite (FeAsS) and other metallic sulfide minerals were discharged to Whitewood Creek at Lead and Deadwood, S. Dak. Sediments present on the Whitewood Creek flood plain have become contaminated by the mill tailings and some flood-plain deposits consist of nearly 100 percent mill tailings. Because of the substantial concentration of arsenopyrite present in the mill tailings, sediments along Whitewood Creek contain large concentrations of arsenic, as much as 11,000 μg/g (micrograms per gram) (Goddard, in press). Although the entire arsenic mass originally was present in the sulfide mineral arsenopyrite, field observations and mineralogic data indicate that a substantial proportion of the arsenic now exists absorbed by or coprecipitated with iron and other metallic oxides (Cherry and others, in press; Goddard, in press). The solid-phase arsenic mass present in the Whitewood Creek flood plain is slowly releasing dissolved arsenic to Whitewood Creek. This paper examines some of the processes controlling the concentration of dissolved arsenic in Whitewood Creek.

The magnitude and variation of dissolved-arsenic concentrations in water from Whitewood Creek and the underlying alluvial aquifers was determined by collecting water samples from monitoring sites on Whitewood Creek and from wells and seeps along Whitewood Creek. Surface- and ground-water samples were collected by using standard U.S. Geological Survey procedures for the collection of water samples. Surface-water samples generally were discharge integrated, although several samples were collected by the use of automatic point samplers. Ground-water samples were collected by using portable peristaltic or submersible pumps. Water samples for dissolved-arsenic analysis were filtered immediately through a 0.45 μm (micrometer), cellulose-nitrate, membrane filter and preserved with ultrapure nitric acid. Colloidal material smaller than 0.45 μm is included in the dissolved analysis. The water samples were analyzed for arsenic by the U.S. Geological Survey laboratory in Arvada, Colo., by using procedures presented by Skougstad and others (1979). Descriptions of sampling laboratory procedures and summaries of the analytical data are presented by Wuolo (1986) and Goddard (in press).

Dissolved-arsenic concentrations in Whitewood Creek fluctuate seasonally (fig. A-4) as a result of variation in ground-water inflow that contains dissolved arsenic. Water in the alluvial aquifer along Whitewood Creek contains between 50 and 500 μg/L (micrograms per liter) dissolved arsenic (Goddard, in press). The rate of ground-water inflow to Whitewood Creek varies as the areally limited alluvial aquifer responds to precipitation, recharge, and bank storage. Substantial recharge usually occurs each spring due to snowmelt, increased rainfall, and high stages in Whitewood Creek. Maximum ground-water inflow to Whitewood Creek occurs in late spring or early summer. Maximum dissolved-arsenic concentrations occur in Whitewood Creek in July and August when ground-water inflow is still substantial, but dilution by streamflow is less than that earlier in the

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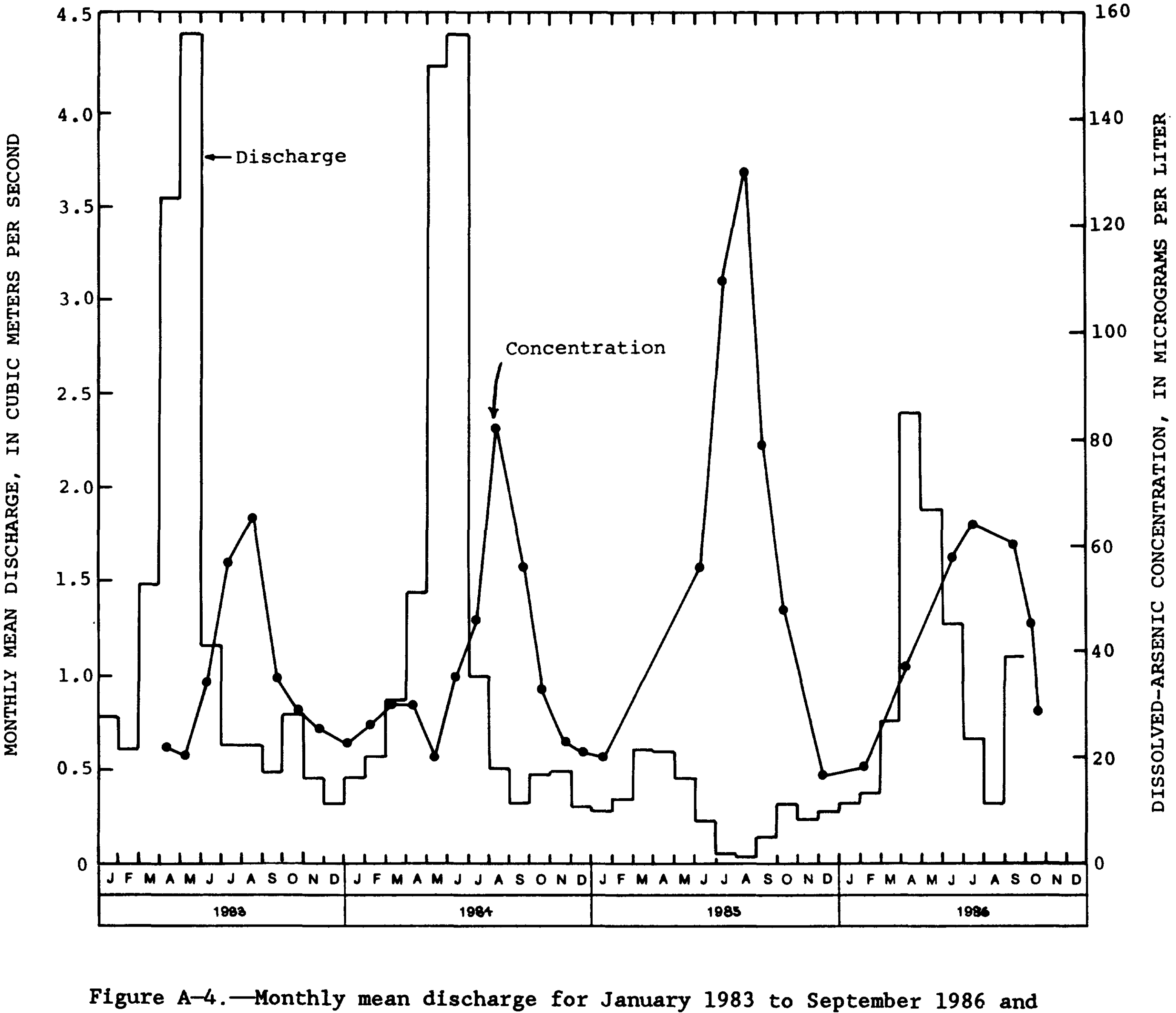

Figure A-4.—Monthly mean discharge for January 1983 to September 1986 and measured dissolved-arsenic concentrations for March 1983 to October 1986 at Whitewood Creek above Vale.

year. Dilution of ground-water inflow results in a negative correlation between discharge and arsenic concentration in Whitewood Creek during the summer (fig. A-5).

Although maximum instream dissolved-arsenic concentrations are the result of ground-water inflow, minimum concentrations are the result of desorption of arsenic from flood-plain sediments. Water samples collected periodically, during 4 years at Whitewood Creek above Vale, have a minimum dissolved-arsenic concentration of slightly less than 20 µg/L (fig. A-5). Samples collected at the site within a short period usually have similar dissolved-arsenic concentrations even though discharge may vary greatly. A sample collected at Whitewood Creek above Vale at 2130 on June 9, 1985, at a discharge of 5.07 m^3/s (cubic meters per second) had a dissolved-arsenic concentration of 18 µg/L. A second sample collected 5 hours later at a discharge of 28.0 m^3/s also contained 18 µg/L dissolved arsenic. The dissolved-arsenic load indicated by the second sample was more than five times larger than indicated by the first sample. The short time between collection of these samples indicates the increase in dissolved-arsenic load was the result of release of arsenic from entrained sediment rather than by changes in the quantity of ground-water inflow.

Solution-chemistry experiments using mixtures of water and flood-plain sediments conducted in a laboratory also provide evidence of the rapid release of arsenic. The adsorption/desorption process as defined by these experiments was determined to be mostly dependent on the pH of the mixtures (fig. A-6). Maximum adsorption and minimum desorption is predicted to occur at a pH of 6.5; at this pH, only about 2 µg/L of dissolved arsenic is predicted to remain in the dissolved phase. However, at a pH of 8.5, not unusual for Whitewood Creek (Goddard, in press), the predicted dissolved-arsenic concentration is about 12 µg/L. This concentration is somewhat smaller but comparable to concentrations measured in Whitewood Creek. Additional sample and laboratory data are required before it can be determined if instream pH variations are a significant factor in controlling dissolved-arsenic concentrations.

Data collected between 1983 and 1986 indicate that the concentration of dissolved arsenic in Whitewood Creek will continue to fluctuate between 20 and 150 µg/L into the foreseeable future. Mass-balance calculations, comparing the measured dissolved-arsenic load transported by Whitewood Creek with the estimated solid-phase arsenic mass stored in the flood-plain sediments along Whitewood Creek, indicate that if the current (1986) release rate continues, it will take hundreds of years before the solid-phase mass is depleted.

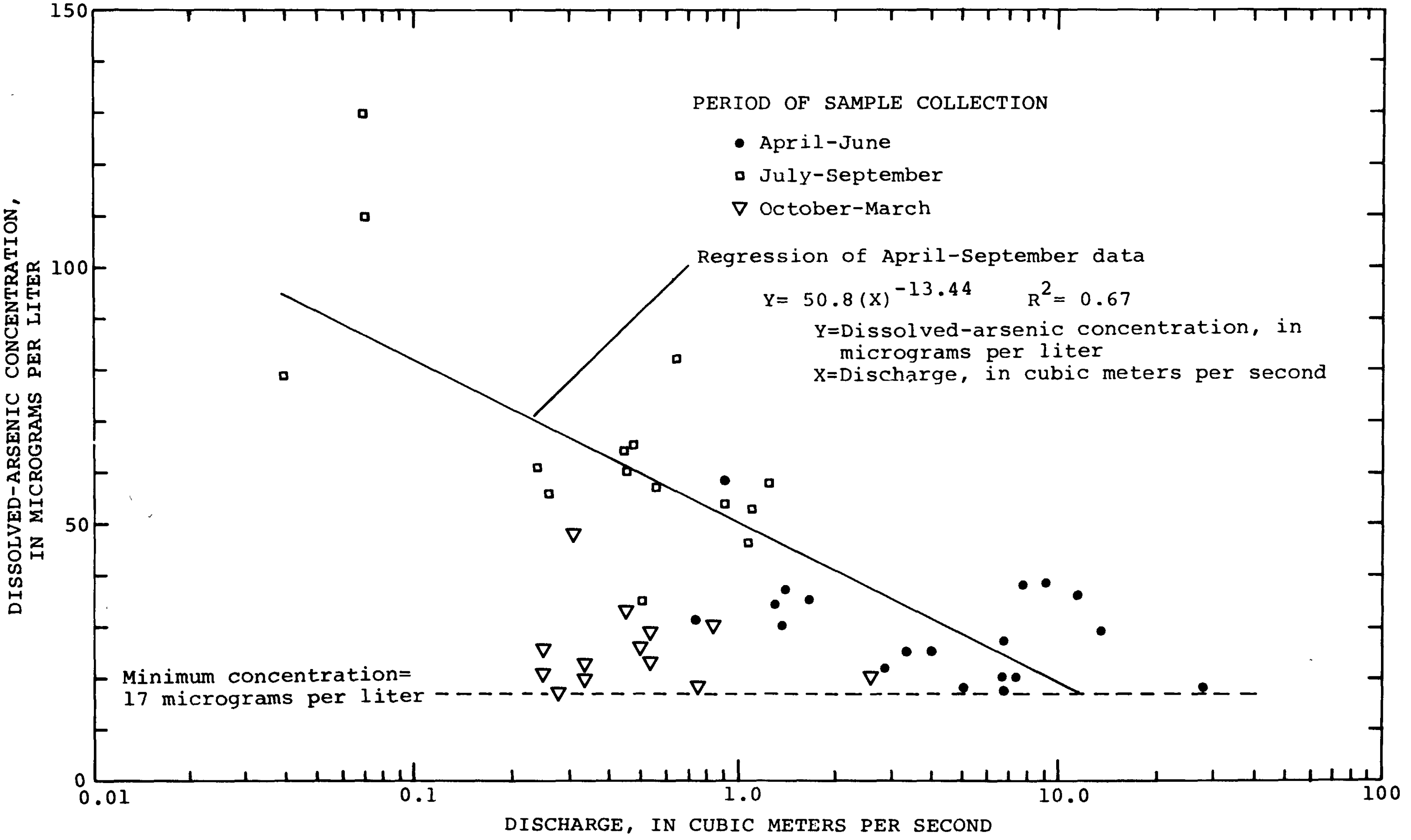

Figure A-5.--Relation between discharge and dissolved-arsenic concentrations measured at Whitewood Creek above Vale between March 1983 and October 1986.

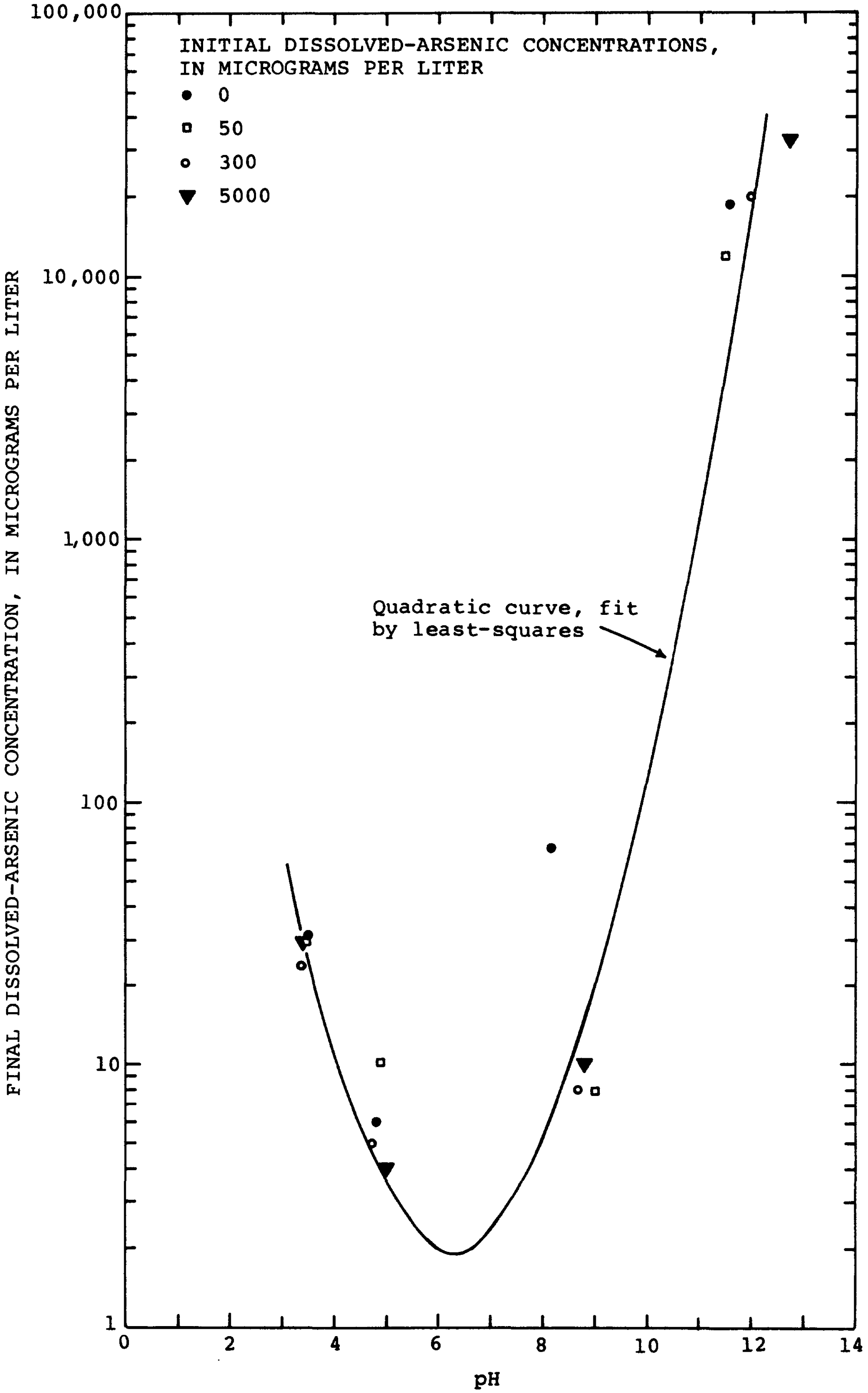

Figure A-6.--Dissolved-arsenic concentrations measured in laboratory mixtures of water and sediment prepared to determine the effect of pH variation on the sorptive characteristics of flood-plain sediment.

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IDENTIFICATION OF COLLOIDS PRESENT AT SHEELER SEEPS, WHITEWOOD CREEK, SOUTH DAKOTA

By Terry F. Rees[1] and James F. Ranville[1]

There is increasing evidence that a variety of organic pollutants, heavy metals, and radioactive materials can be transported through the geosphere in association with suspended colloidal materials. A colloid is a finely dispersed phase with at least one dimension in the range 1 to 1,000 nm (nanometers), which is dispersed in a second continuous phase such as water. As pollutants become associated with suspended colloids, their transport is increasingly controlled by that of the colloids. Unfortunately, very little is known about the relative importance of colloids and the mechanisms of their transport through the geosphere. The first step in gaining a better understanding of colloidal transport of pollutants is to identify and characterize systems in which colloids are present. This paper presents information about the physical and chemical characteristics of colloids present in water from the Sheeler Seeps which are adjacent to Whitewood Creek, S. Dak.

The Sheeler Seeps are adjacent to Whitewood Creek approximately 1 km (kilometer) from its confluence with the Belle Fourche River near Newell. The seeps are a result of downcutting through a historic meander of Whitewood Creek that was filled with tailings washed down from a mine near Lead. After the meander filled, Whitewood Creek changed course, eroded through the meander sediments and into the underlying shale bedrock. Ground water percolates through the tailings until it encounters the relatively impermeable bedrock. Further flow is then directed laterally across the surface of the shale, until the water discharges at the land surface near the creek. Emergent ground water then flows over the shale into small, quiescent pools prior to mixing with the streamwater.

Samples for this study were collected from Whitewood Creek immediately upstream and downstream from the seeps, from a quiescent pool, from water flowing over the face of the outcrop, and from several inches into the outcrop. Analyses were performed for various chemical components on filtered (400-, 100-, and 50-nm Nucleopore[2] filters) and unfiltered fractions. The presence of suspended colloids was determined by using photon correlation spectrometry (PCS). Samples for PCS analysis were collected and sealed in ampules under nitrogen (N_2) atmosphere to minimize oxidation. Finally, the materials retained on the filters were examined by using scanning electron microscope (SEM)/X-ray analysis.

Analytical data for the filtrates are given in table A-1. Because of a malfunction of the field pH meter, no pH values are available. Iron (Fe) and manganese (Mn) concentrations are approximately 10 times greater in the seep than in the stream. Concentrations of several other species—arsenic (As), calcium (Ca), nickel (Ni), silicon (Si), strontium (Sr), and sulfate (SO_4)—were 2 to 3 times greater in the seeps than in the stream. Filtration resulted in decreases in Fe and As concentrations; this indicates that these elements may be associated with particulate or colloidal materials.

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[2] Use of brand names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table A-1.—Concentrations of selected chemical species in unfiltered and filtered waters collected from the Sheeler Seeps, Whitewood Creek, South Dakota

[µm, micrometer; µM/L, micromole per liter; mM/L, millimole per liter; -, not analyzed]

Sample	Unfiltered	Filter size, in µm			Unfiltered	Filter size, in µm		
		0.4	0.1	0.05		0.4	0.1	0.05
	Iron (Fe), in µM/L				Calcium (Ca), in mM/L			
Downstream	16.4	1.3	0.8	—	3.35	3.41	3.34	—
Seep	145.0	144.9	148.0	—	7.75	7.74	7.96	—
Surface flow	—	22.7	29.1	21.6	—	7.77	7.89	7.83
Pool	17.8	10.0	—	6.2	7.92	7.73	—	7.75
Upstream	—	8.9	—	.8	—	3.45	—	3.41
	Manganese (Mn), in µM/L				Magnesium (Mg), in mM/L			
Downstream	1.9	1.4	1.4	—	3.58	3.65	3.56	—
Seep	18.2	18.3	18.7	—	4.49	4.48	4.51	—
Surface flow	—	8.8	9.0	8.9	—	4.52	4.52	4.52
Pool	8.6	8.2	—	8.3	4.52	4.53	—	4.53
Upstream	—	1.3	—	1.1	—	3.78	—	3.70
	Arsenic (As), in µM/L				Strontium (Sr), in µM/L			
Downstream	1.05	0.44	0.40	—	11.0	11.2	11.0	—
Seep	3.12	3.78	3.42	—	25.4	25.3	25.6	—
Surface flow	—	.66	.46	0.48	—	25.1	25.4	25.2
Pool	.50	.36	—	.32	25.5	24.9	—	24.9
Upstream	—	.89	—	.50	—	11.3	—	11.4
	Nickel (Ni), in µM/L)				Barium (Ba), in µM/L			
Downstream	1.6	1.3	0.92	—	0.28	0.25	0.24	—
Seep	3.2	2.3	2.9	—	.11	.11	.11	—
Surface flow	—	2.7	2.7	2.1	—	.11	.13	0.12
Pool	3.0	2.7	—	2.7	.12	.11	—	.12
Upstream	—	1.4	—	.7	—	.28	—	.24
	Silicon (Si), in mM/L				Sulfate (SO_4), in mM/L			
Downstream	0.30	0.27	0.27	—	6.15	—	—	—
Seep	.52	.50	.50	—	—	10.9	—	—
Surface flow	—	.50	.50	0.53	11.0	10.9	11.4	—
Pool	.46	.46	—	.46	10.6	—	—	—
Upstream	—	.32	—	.28	—	5.74	—	—

To ascertain the presence of colloids, samples were analyzed 2 to 4 hours after collection by use of PCS. This technique is described in detail by Rees (1987), and provides information about particle-size distributions and particle concentrations. Results of these analyses are given in table A-2. In all samples, the scattering intensity decreased with decreasing pore size of the filter. This is strong evidence for removal of colloids by filtration. The translational diffusion coefficient (D_t) which is inversely related to particle size also shows the expected trend, that is--D_t increases as the pore size decreases. These data indicate median particle diameters in the filtrates that are too large to have passed through the filters used. If the assumption of particle sphericity is reasonable, then the data are consistent with two alternative explanations. First, that small particles that passed through the filters aggregated prior to PCS analysis; or second, that despite the precautions taken, some iron oxidation and precipitation of ferric hydroxide ($Fe(OH)_3$) occurred between the time samples were collected and PCS analysis. The presence of the larger particles indicate the importance of measuring colloids quickly after collection to preclude temporal changes in size and surface distributions.

Table A-2.—Photon correlation spectroscopy results for samples collected at the Sheeler Seep site, Whitewood Creek, South Dakota

[The translational diffusion coefficient (D_t) is obtained from the temporal variation in scattering intensity (I). The mass median spherical diameter (d) is obtained from D_t assuming a spherical shape. Polydispersivity is a measure of the narrowness of the particle-size distribution]

[Counts/μs, counts per microsecond; cm^2/s, square centimeter per second; μm, micrometer; —, sample not analyzed; <, less than detection limit]

Sample	Filtrate[1]	Intensity (I), in counts/μs	Diffusion coefficient (D_t), in cm^2/s (x10^8)	Diameter (d), in μm	Polydispersivity
Downstream	0.40	0.141	1.01	0.100	0.466
	.10	<	<	<	<
	.05	—	—	—	—
Upstream	.40	.191	.558	.158	.465
	.10	.144	.665	.158	.505
	.05	<	<	<	<
Surface flow	.40	1.93	.053	.901	1.09
	.10	1.80	.103	4.45	.005
	.05	1.10	.245	.222	.552
Pool	.40	.45	.282	1.67	.005
	.10	.25	.255	.50	.380
	.50	.10	.278	1.85	.005

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[1] Filtrate = material which passed through indicated porosity filter (in micrometers)

The most interesting results were from the SEM/X-ray analyses. Samples collected from the creek contained mostly clay with little iron. After filtration through 400-nm filters, virtually no particles were retained on the 100-nm filter and those that were present were calcite and some amorphous iron oxides.

Particles with a dimension larger than 400-nm collected from the quiescent pool included several noncrystalline calcium-potassium aluminosilicates with Si:Al ratios of approximately 5:1. Large particles (1x4 μm (micrometers)) of well crystalized gypsum also were present. Polyframboidal iron pyrite approximately 5 μm in diameter and large (5x7 μm) magnesium-calcite crystals were identified, as well as a particle high in titanium with associated calcium and phosphorous. This latter particle may be rutile, brooksite, or aratase. Amorphous-iron masses were observed with either adsorbed calcium or perhaps calcite nuclei. Potassium silicates were observed that had no iron coatings.

The 100-nm filter used for the pool sample retained individual pyrite framboids that had diameters of 400 to 500 nm. Trace quantities of arsenic were associated with these framboids. Iron sulfide also was present as an amorphous phase which also contained arsenic. The diameters of individual particles of this amorphous phase were less than 100 nm. Numerous calcite and silica particles were retained. Frequently, the calcite had sulfur associated with it; this indicates formation of surface coatings of gypsum. Many small particles that should have passed through the 100-nm filter were retained, and at least one particle impacted the filter and was pushed toward a pore, as indicated by a scratch on the filter. These observations indicate that the filtration process might promote coagulation of small particles into larger aggregates that would then be retained by the filter.

Particles collected from the seep consisted of spheroids of amorphous iron oxides and hydroxides, crystalline silica with no iron coatings, and platy calcium silicates with iron coatings. Individual particle dimensions ranged from 200 to about 1,000 nm. A large gypsum crystal with a maximum dimension of about 700 nm was also identified. In general, particles with dimensions that range from 100 to 400 nm are much more abundant in seeps and pool than in the creek, a trend that also is indicated in the chemical data presented in table A-1.

This preliminary study determined that particles of colloidal dimension are present in water from the Sheeler Seeps. An association of arsenic with iron-sulfide phases also was determined. Future work at the site will attempt to shorten the time required for analyses of particle size, shape, and surface charge using in-situ PCS analysis, and will include a systematic approach to establish if arsenic at the site is moving in association with colloidal particles.

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EFFECTS OF ALGAL GROWTH ON ARSENIC TRANSPORT IN WHITEWOOD CREEK, SOUTH DAKOTA: PRELIMINARY RESULTS

By James S. Kuwabara[1], Cecily C.Y. Chang[1], and Sofie P. Pasilis[1]

Arsenate inhibits the growth of certain algal species at submicromolar concentrations, presumably due to an interference with phosphate metabolism (Button and others, 1973; Sanders, 1979). Conversely, primary producers may alter arsenic speciation in natural waters by releasing methylated arsenic (As) metabolites (Andreae, 1977). Increased abundance of algae in Whitewood Creek, S. Dak., during the summer months suggests that this interaction between toxic substances and biota may significantly affect As transport and distribution.

This paper describes the results of a study to determine the effects of algal growth on transport and speciation of As in Whitewood Creek. The study involves determining As transport parameters for algae (fig. A-7) collected in the creek from upstream of discharge from a mine to a site above the confluence of Whitewood Creek and the Belle Fourche River (K.E. Goddard, U.S. Geological Survey, written commun., 1986). These transport parameters--algal standing crop (ρ_b), sorption and release rate constants (λ_{bf} and λ_{br}, respectively), and the accumulation factor (biological partitioning coefficient, K_{db})--may be used in a biological submodel that is a component of a comprehensive transport model describing other hydrologic, chemical and biological processes (fig. A-7). Modeling the periphyton component for As is complicated by: (1) effects of arsenic speciation on rate and partitioning parameters, (2) interactive effects with phosphate from sewage and agricultural inputs along the reach, and (3) variability in algal abundance, presumably due to factors in addition to arsenate and phosphate concentrations (for example, physical substrate type, temperature, and light intensity).

Rates of uptake and release by algae for inorganic and methylated forms of As are currently being studied as a function of added concentrations of dissolved arsenate and orthophosphate. Unialgal cultures of the chlorophyte <u>Stichococcus</u> spp Nageli collected along the study reach (see fig. A-1) are being used to determine rate parameters (for example, the submodel λ_b values). After isolation, algal stocks are maintained in a chemically defined growth medium (Kuwabara and others, 1985) with added arsenate and orthophosphate concentrations similar to ambient levels at the sampling sites. A method for As speciation analysis by high performance liquid chromatography coupled with hydride generation atomic absorption spectroscopy is currently being developed. We observed arsenate and phosphate uptake in ^{73}As and ^{32}P-labelled experiments using living cells and cells heat killed as described by Fisher and others (1984). Arsenic and phosphate uptake was similar for living and dead cells over the first 24 hours with slightly greater P uptake by living cells at 48 hours (fig. A-8). This indicates that active uptake of both As and P was not significant over the first 24 hours. Uptake for both As and P were similar for algae collected from different sites and preconditioned at different dissolved arsenate concentrations. If As uptake is initially a passive cell surface process, then the lack of a difference was similar for these isolates. The most dramatic difference was that observed between As and P uptake. All three algal isolates appeared to have some exclusion mechanism by which they either selectively took up PO_4 more efficiently than AsO_4 or released

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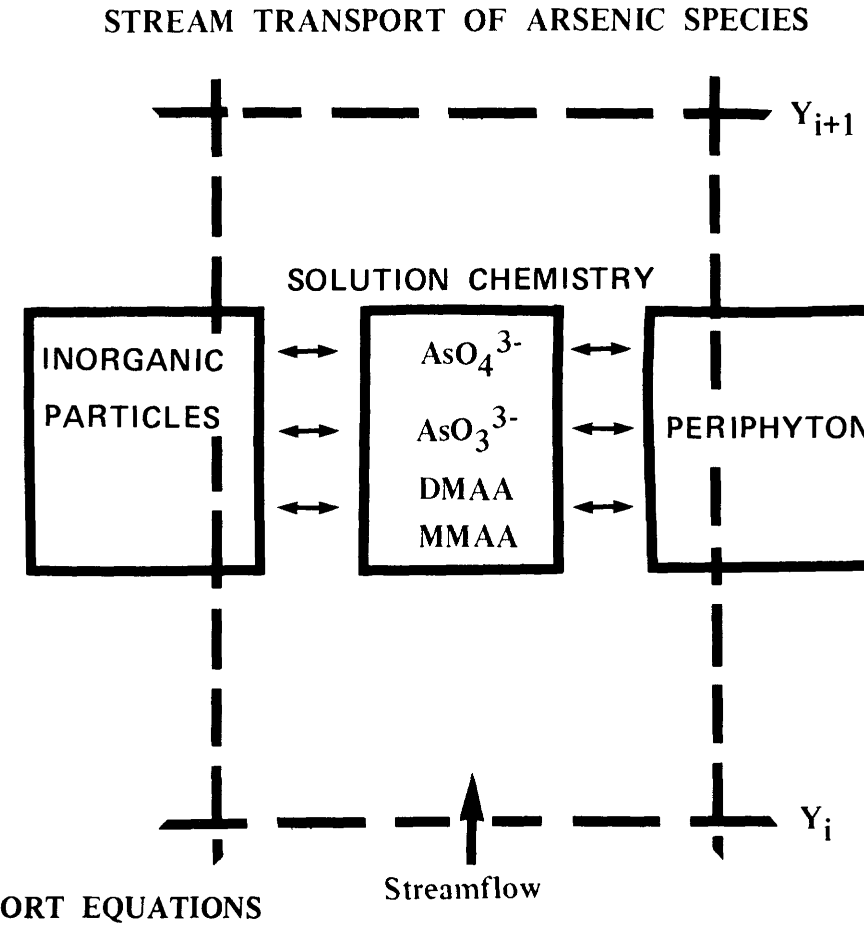
[1] U.S. Geological Survey, Menlo Park, California



TRANSPORT EQUATIONS

$$\frac{\partial C_j}{\partial t} = \text{Physical Terms}_j + \text{Chemical Terms}_j + \text{Biological Terms}_j$$

$$\text{Biological Terms}_j = \rho_{bj} R_{bj} = -\rho_{bj}\frac{\partial C_{bj}}{\partial t} = \lambda_{bj_{f,r}} (C_{bj} - K_{d_{bj}} C_j)$$

$$\lambda_{bj_{f,r}} = f(\Delta t, [PO_4^{3-}], [AsO_4^{3-}], [AsO_3^{3-}], \text{DMAA}, \text{MMAA}, ...)$$

$$K_{d_{bj}} = f(\Delta t, [PO_4^{3-}], [AsO_4^{3-}], [AsO_3^{3-}], \text{DMAA}, \text{MMAA}, ...)$$

Figure A—7.—Conceptual model used to help formulate the experimental design for this study. Figure illustrates potentially important periphyton processes affecting arsenic transport and distribution in a stream interval Y_i to Y_{i+1}. The biological submodel is represented as a first order rate equation for chemical species j. Parameters in the submodel have been previously defined in the text. Inorganic and organic As species, such as arsenate, arsenite, monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA), are being considered.

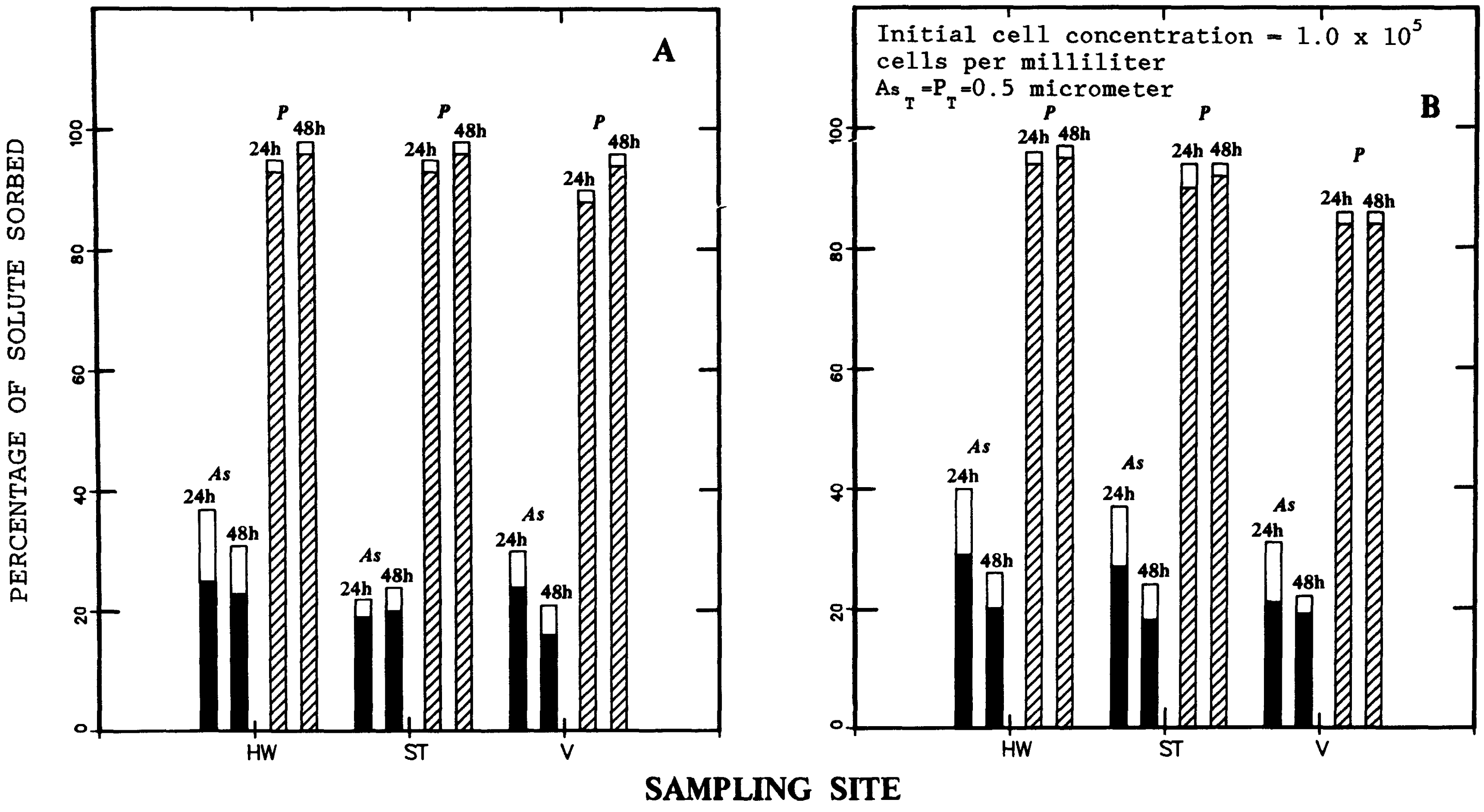


Figure A-8.--Algal uptake at 24 and 48 hours of arsenic (solid bars) and orthophosphate (dashed bars) using three isolates from Whitewood Creek: Headwater site (HW) (8km upstream of Gold Run), Sewage Treatment Plant discharge site (ST) (at Deadwood), and the above Vale site (V) (Goddard, in press). The calculated 95 percent CI/2 (half confidence interval) is shown as an unshaded bar above the mean value (n=3). Culturing media additions of total As and total P at 0.5 µM were used. A. Sorption by living cells normalized to initial cell concentrations. B. Sorption by heat-killed cells.

excessive intracellular As. Morris and McCartney (1984) found that certain diatoms (namely Thalassiosira spp., Chaetoceras spp., and Skeletonema costatum) are also capable of discriminating between PO_4 and AsO_4. Button and others (1973) found that the yeast Rhodotorula rubra did not have this selective P uptake or As excretion process. Although the exclusion mechanism for this alga has not been identified, it does not appear to be acquired by prolonged As exposure.

Standing crop was estimated by chlorophyll-a analysis of periphyton attached to cobble (table A-3). Results indicate an increased algal abundance moving downstream from the Headwater site (HW) to the above Vale site (V) then decreasing abruptly farthest downstream at the Sheeler site (SC) (approximately 2 km above the mouth of Whitewood Creek). Temperature effects on algal growth rates may explain the downstream increase in algal abundance. At the Sheeler site, decreased abundance may be due to a scarcity of firm substrate to establish a massive algal community. There was a patchy nature to periphyton growth within the channel at the two most downstream sampling sites. Increased sample sizes at these stations would provide much improved estimates of average standing crop as well as a measure of variability. The autotrophic index (mass ratio of periphyton to chlorophyll-a) ranged from 120 at the Headwater site to 210 downstream of the sewage treatment plant discharge (ST). The HW and V sites (Goddard, in press) displayed typical autotrophic indices, while elevated values at the ST and SC sites indicate higher concentrations of senescent algal cell or increased heterotrophic growth associated with environmentally stressed conditions (Leland and Carter, 1985). Uptake and standing crop data can be used to calculate a crude estimate of periphyton-associated As per volume of stream channel. Using a conservative estimate of cell As concentration from uptake experiments (0.1 μM (micromole) per 10^8 cells), standing crop of 50 g/m^2 (grams per square meter), average stream channel depth of 0.3 m (meter), and average cell weight of 10 pg/cell, a concentration of about 17 μM As (1.2 mg/L (milligrams per liter)) results. This concentration is an order of magnitude higher than measured total arsenic concentrations in the reach (Goddard, in press) and, therefore, represents a significant As pool interacting with the water column. A quantitative description of these biological interactions for various As species continues to be the focus of this study.

Table A-3.—Estimated periphyton standing crop (ρ_b) in g/m^2 (grams per square meter) for four sampling sites along Whitewood Creek: Headwater site (HW), Sewage Treatment Plant site (ST), above Vale site (V), and Sheeler site (SC)

[The mass ratio of periphyton to chlorophyll-a (autotrophic index) has been used as an indicator of environmental stress with increasing values indicating greater abundance of senescent algal cells or increased heterotrophic growth (Weber, 1973)]

Site	Temperature, in °C	Autotrophic index	ρ_b, in g/m^2
HW	13.2	120	21 ± 14
ST	17.5	210	34 ± 13
V	19.0	140	77 ± 27
SC	24.2	190	25 ± 11

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(p. 39 follows)

ARSENIC GEOCHEMISTRY OF SEDIMENT CORES FROM THE CHEYENNE RIVER ARM OF LAKE OAHE, SOUTH DAKOTA—1985 RESULTS

By Arthur J. Horowitz[1] and Kent A. Elrick[1]

Six bed sediment cores, ranging in length from 1 to 2 meters, were collected in the Cheyenne River arm of Lake Oahe, S. Dak.(see fig. A-1), to investigate potential effects from gold-mining operations around Lead, S. Dak. Sedimentation rates in the river arm seem to be event-dominated and rapid, on the order of 6 to 7 centimeters per year. Except for arsenic, all the trace element concentrations in the core samples fall within the broad ranges previously reported for the Pierre Shale, a major component of the local geology, and are similar to those found in bed sediments in the Cheyenne River, in the Cheyenne River arm of Lake Oahe, and Lake Oahe.

On the basis of the downcore distribution of manganese, it appears that reducing conditions exist in the sediment column of the river arm below 2 to 3 centimeters. The level of reduction does not seem to be severe enough to produce the differentiation of iron and manganese as reported in the literature, but it is sufficient to produce at least partial dissolution of iron and manganese oxides and some remobilization. Cross-correlations of high element concentration-bearing strata within the sediment column can be made for several strata and for several cores; however, cross-correlations for all the high element concentration-bearing strata are not feasible at this time.

Arsenic is the only element that seems to be elevated in the core samples compared with concentrations previously reported in surface sediment. Examination of two elevated arsenic-bearing strata indicates that the highest arsenic concentrations are associated with the 8 to 32 micrometer size fractions. These fractions contain well crystallized arsenopyrite, which on thermodynamic grounds, is unlikely to be authigenic and probably is detrital. The arsenopyrite has remained stable in the sediment column because of the reducing conditions. Some arsenic also may be associated with authigenic sulfides that formed after the deposition and subsequent remobilization of arsenic associated with iron and manganese oxides. However, the highest major arsenic concentrations in the cores seem to be associated with arsenopyrite. Whether associated with detrital arsenopyrite, or authigenic sulfides, the arsenic seems to be relatively immobile in the sediment column.

Suspended-sediment samples collected from the Cheyenne River at Cherry Creek (see fig. A-1), about 10 land miles from the mouth of the river arm, had arsenic concentrations that ranged from 12 to 36 mg/kg (milligrams per kilogram). The sample with the highest arsenic concentration, 36 mg/kg, was collected during high flow. It was size fractioned in the same manner as the core samples. The highest arsenic concentration, 50 mg/kg, occurred in the 8- to 32-micrometer size fractions, the same size-fraction range found for the core samples. These fractions contained both arsenopyrite and octahedral pyrite. In addition, significantly smaller but detectable concentrations of arsenic were found associated with iron and manganese

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oxide coatings. The differences in arsenic concentration between the arsenopyrite and the coatings indicate that most of the arsenic in the sample probably was from the arsenopyrite. The arsenopyrite and octahedral pyrite probably originated in the hydrothermal ore deposits near Lead and subsequently were stored and preserved in pockets displaying reducing conditions in the banks and flood plains of Whitewood Creek or the Belle Fourche River. The octahedral pyrite displayed relatively sharp cleavage planes and exhibited little evidence of dissolution; this indicates that it was transported rapidly from its point of origin.

Additional suspended-sediment samples collected from the Cheyenne River at Wasta (see fig. A-1), above the confluence of the Belle Fourche River, contained between 8.5 and 10 mg/kg arsenic. Arsenic concentrations in the suspended sediment from the Belle Fourche ranged from 100 to 140 mg/kg during high flow. It is estimated that during high flow, suspended sediment from the Belle Fourche accounts for about 25 percent of the suspended-sediment load in the Cheyenne River. If correct, the Belle Fourche would contribute between 25 to 35 mg/kg arsenic and the Cheyenne would contribute between 6 and 8 mg/kg arsenic for a total calculated arsenic concentration of between 31 and 43 mg/kg. This compares favorably with the 36 mg/kg arsenic concentration determined for the Cherry Creek sample. Thus, most of the arsenic in suspended sediments collected, during high flow above the Cheyenne River arm of Lake Oahe seem to come from the Whitewood Creek-Belle Fourche River system. In addition, a major contributor to this arsenic concentration probably is arsenopyrite that previously was deposited and stored in the banks and flood plains of the Whitewood Creek-Belle Fourche-Cheyenne River system.

REMOBILIZATION OF ARSENIC IN SEDIMENTS FROM THE CHEYENNE RIVER ARM OF LAKE OAHE, SOUTH DAKOTA

By Edward Callender[1] and Walter H. Ficklin[2]

INTRODUCTION

The Cheyenne River arm of Lake Oahe constitutes the receiving water for mine-tailing wastes that were discharged by a large gold-mining activity some 500 km (kilometers) to the west in the Black Hills of South Dakota. Presently, these arsenic-rich wastes reside in flood-plain and overbank deposits along the Belle Fourche and Cheyenne Rivers.

Episodic sediment inputs from the Cheyenne River and more constant input of local Pierre Shale via bluff erosion constitute the major sources of reservoir sediment in the Cheyenne River arm of Lake Oahe. This paper describes the distribution of arsenic and other metals in sediment cores taken from the Cheyenne River arm of Lake Oahe and discusses the potential contribution of these metals to the overlying water as a result of sedimentary diagenetic remobilization processes.

METHODS

Two sets of gravity cores (1985, 1986) were obtained from eight sites along the Cheyenne River arm of the Oahe Reservoir (fig. A-9) in south-central South Dakota. Interstitial water was extracted under a nitrogen-gas atmosphere from several intervals (6 to 12) in each sediment core and analyzed for nutrient species, arsenic (As), iron (Fe), and manganese (Mn). In 1985 and 1986, sediment samples were digested by using a combination of nitric, hydrofluoric, and perchloric acids; the extracts were analyzed for major elements (aluminum (Al), Fe, and titanium (Ti)) and minor/trace elements (As, cobalt (Co), chromium (Cr), copper (Cu), lead (Pb), Mn, nickel (Ni), and zinc (Zn)).

RESULTS

Interstitial-water profiles of alkalinity; ammonium; reactive phosphate; dissolved As, Mn, and Fe; and solid-phase profiles of As, Mn, and Fe for cores collected at site 2/2' in the upper Cheyenne River arm and site 6 in the lower arm are presented in figures A-10 and A-11. At site 2/2', there are large differences in the concentrations of interstitial-water constituents between the 2 years. In cores from 1985, only a thin layer of surficial sediment (0-1 cm (centimeter)) was oxidizing and the underlying sediment was reducing. This is corroborated by the interstitial Fe, Mn, and reactive phosphate profiles that show peak concentrations at 1- and 2-cm depths. On the other hand, the surficial sediment column in 1986 was strongly oxidizing (very positive redox potential) to depths of 7 cm, and consequently the interstitial-water concentrations of iron and manganese are very low over this depth interval.

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[1] U.S. Geological Survey, Reston, Virginia

[2] U.S. Geological Survey, Denver, Colorado

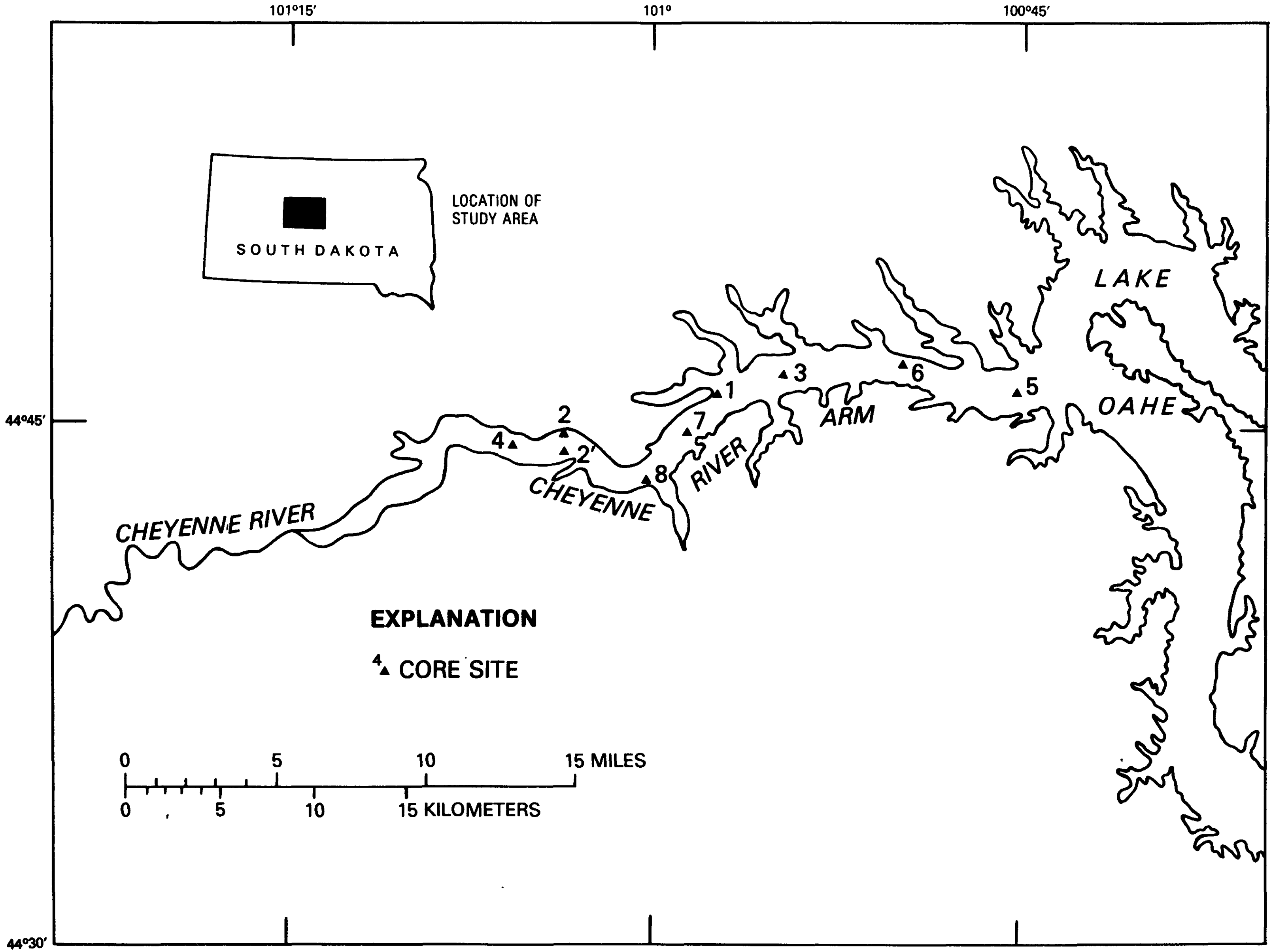

Figure A-9.--Location of sediment cores taken from the Cheyenne River arm, Lake Oahe, South Dakota.

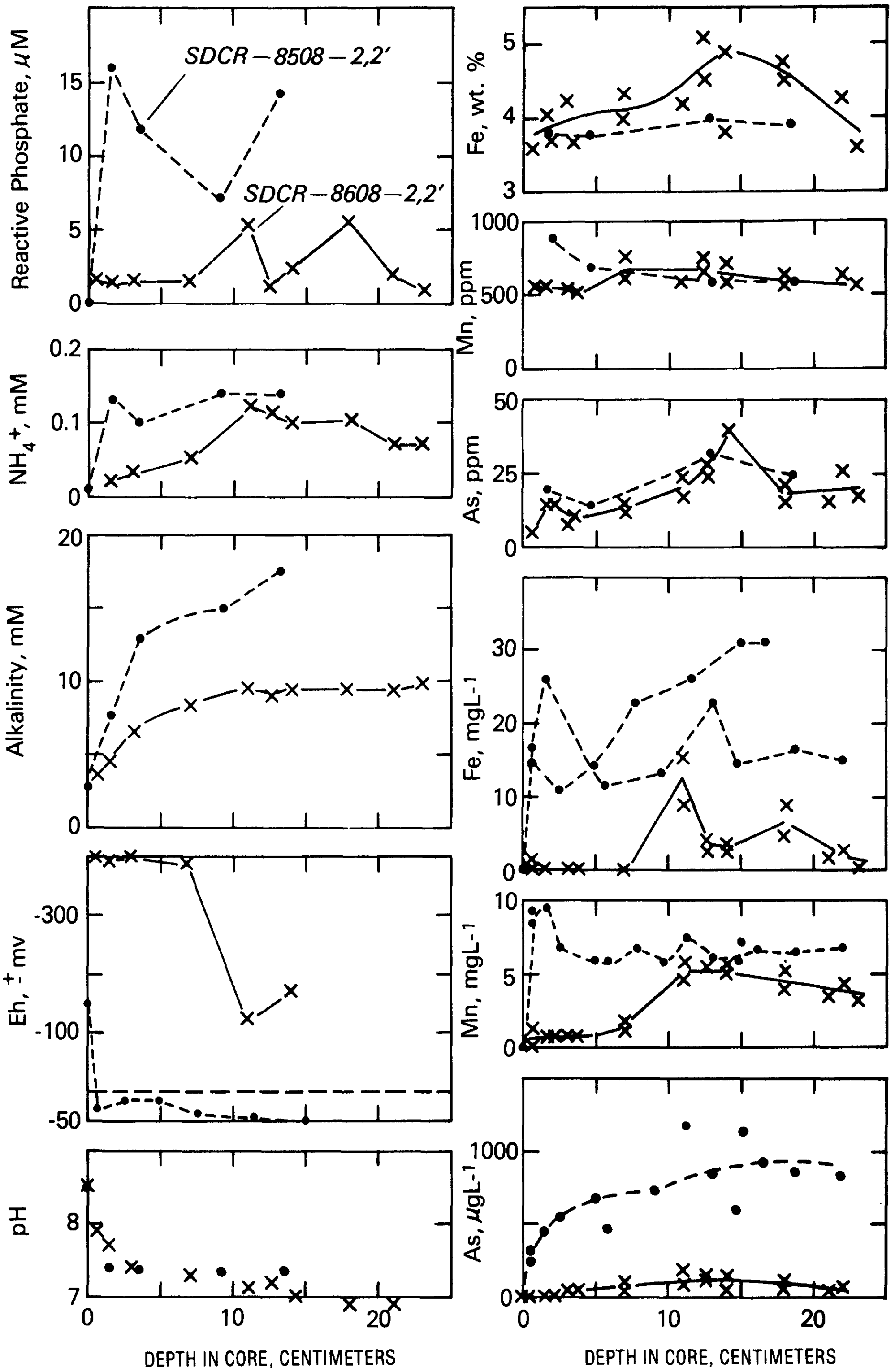

Figure A–10.—Interstitial water and sediment chemistry of cores (sites 2/2′) from the western part of the Cheyenne River arm, Lake Oahe, South Dakota. Interstitial water concentrations are given in µM, mM, µg/L, and mg/L; and sediment concentration units are ppm (parts per million) and weight percent.

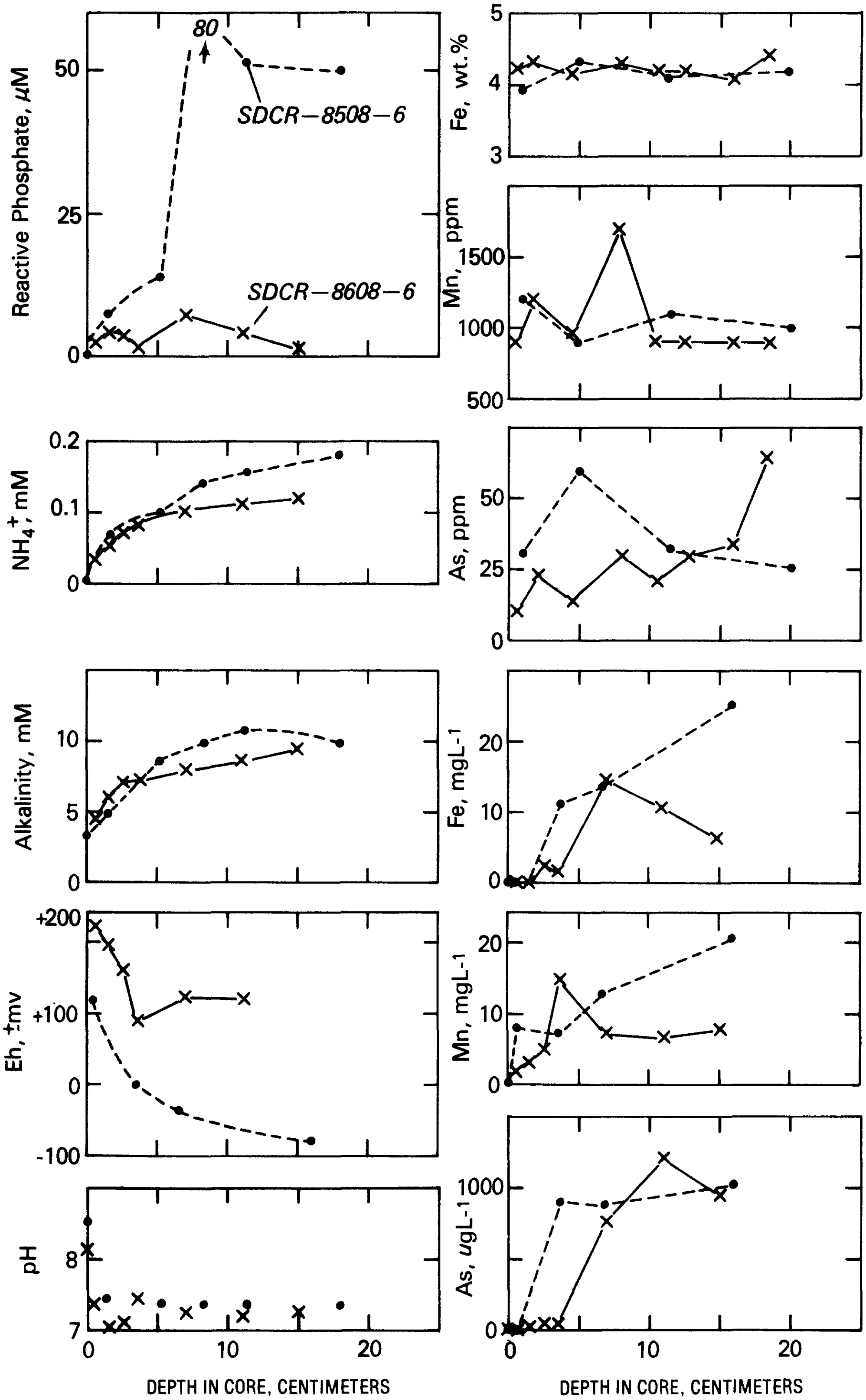

Figure A-11.—Interstitial water and sediment chemistry of cores (site 6) from the eastern part of the Cheyenne River arm, Lake Oahe, South Dakota. Interstitial water concentrations are given in μM, mM, μg/L, mg/L; and sediment concentration units are ppm (parts per million) and weight percent.

It is interesting to note that the interstitial phosphate, Mn, and Fe profiles show a repetitive pattern that is offset by a depth of 12 cm. Using data from the U.S. Army Corps of Engineers aggradation surveys of the Cheyenne River arm (1959 to 1976), the sedimentation rate for site 2/2' is estimated to be 13 cm/yr (centimeters per year). Thus, the possibility exists that the sedimentary record has preserved the interstitial-water chemistry of redox-sensitive species in accumulated sediment. Little precipitation fell in the Cheyenne and Belle Fourche River basins of western South Dakota in 1985. In contrast, 1986 was a wet year in this area, so it seems plausible that there were periods of small sediment input at this site during 1985, and that there was time for diagenetic remobilization of sedimentary ferromanganese oxhydroxides. This process results in sharp gradients, such as illustrated in figure A–10. Even the solid-phase Mn profile for the 1985 core indicates that there has been diagenetic remobilization, diffusional transport toward the sediment surface, and reprecipitation of oxides in surficial sediment. During 1986, there appears to have been large sediment inputs to this area.

Large sedimentation rates would entrain dissolved oxygen and nitrate in surficial sediment layers, and dilute the concentration of degradable organic matter with inorganic particles. This generally creates a geochemical environment that would not be conducive to diagenetic remobilization of Fe and Mn oxyhydroxides and associated arsenic and phosphorus.

The interstitial-water data for the 1985 and 1986 cores from site 6 (fig. A–11) are not as divergent as those for site 2/2'. Sediment redox potentials are more oxidizing in the 1986 cores than in the 1985 cores. The more oxidizing conditions are reflected in the interstitial reactive phosphate, As, Mn, and Fe data. The profiles of these constituents for the 2 years are offset by a vertical distance of 5 cm. A core from this site has been analyzed for ^{137}Cs and the 1963 peak was found at a depth of 131 cm. Thus, the sedimentation rate for this site is calculated to be 5.7 cm/yr. Although site 6 is much farther (40 km) away from the Cheyenne River delta than site 2/2' (10 km), high sediment discharges in the Cheyenne River during 1986 have resulted in transport of this particulate material to site 6. The buff-brown color of the surficial sediment at this site indicates that most of the sediment originated from the Cheyenne River. The solid-phase As and Mn profiles are somewhat different for the 2 years, and they do not appear to exhibit a repetitive pattern. Although the two cores were taken from the same transect, they are located approximately 2 km apart. Proximity to local sediment sources and the erratic nature of sediment inputs and redistribution may explain the divergent data. Also, the sampling interval for the 1985 core is much coarser (4 points) than the 1986 core (8 points).

DIAGENETIC REMOBILIZATION

In general, there is a peak in the interstitial manganese concentration at a shallower sediment depth than the peaks of interstitial phosphate, arsenic, and iron (figs. A–10 and A–11). The lack of coincidence between interstitial Mn and total As peak concentrations suggests that the release of solid-phase As to interstitial water is not simply the result of Mn solid-phase dissolution. There is a good correlation between the interstitial-water maxima of reactive phosphate, ferrous Fe, and total dissolved As for all cores sampled during this study. It is well known that Fe oxyhydroxides sorb phosphate and arsenate in freshwater and marine sedimentary systems. When these Fe oxyhydroxides are reduced during the microbial degradation of sedimentary organic matter, As and phosphorus (P) are released to the interstitial water.

Depositional Arsenic Fluxes

Generally, the contemporary flux of an element that is being incorporated into a sediment column usually cannot be calculated by just multiplying the sediment accumulation rate times the surface sediment concentration of the element. Mixing and diagenetic processes within surficial sediment can substantially alter the surface sediment concentration from that of particles arriving at the sediment-water interface. However, examination of the solid-phase data (figs. A–10 and A–11) indicates that there has not been substantial remobilization and reprecipitation of As associated with ferromanganese oxyhydroxides. For the 1986 core from site 6, a comparison was made between the total As inventory (depositional flux) in the upper 20 cm of the sediment column and the As accumulation rate calculated by the first method stated above (As accumulation rate). The depositional As flux was calculated to be 35 ($\mu g/cm^2$)/yr (micrograms per square centimeter per year), whereas the As accumulation rate was calculated to be 39 ($\mu g/cm^2$)/yr. Because the data for calculating depositional As fluxes are not available for all cores, the As accumulation rate was calculated. Table A–4 gives the As accumulation rates for each of three regions in the Cheyenne River arm of Lake Oahe. Each region contains at least two core locations, and the data are averaged. It is apparent from table A–4 that sedimentary As accumulates (and deposits) at a much faster rate in the upper Cheyenne River arm. This is understandable because these stations are located within 1 to 10 km of the Cheyenne River delta.

Table A–4.—Estimated arsenic fluxes for the Cheyenne River arm, Lake Oahe, South Dakota

[J, diffusional As flux; A, As accumulation flux]

Site	Fluxes, in micrograms per square centimeter per year		
	J	A	J/A
Upper Cheyenne River arm (sites 4, 2/2', 8, and 7)	4	171	0.02
Middle Cheyenne River arm (sites 1 and 3)	6	40	.15
Lower Cheyenne River arm (sites 5 and 6)	18	54	.33

The solid-phase As, Mn, and Fe data (normalized to Ti) for the 1986 cores at site 2/2' show a general depletion relative to the normalized ratios in Cheyenne River suspended sediment. These suspended-sediment samples were collected from the river between the confluence with the Belle Fourche River and the delta. All of the As-contaminated sediment in the Cheyenne River comes from the Belle Fourche River. It is likely that the depletion of As, Mn, and Fe in the upper part of the sediment cores from site 2/2' is due to the incorporation of As/Mn/Fe-poor sediment that originates from the White River Formation in the South Dakota Badlands. Sediment erosion must have been at a maximum during the prolonged high-flow events of 1986.

Diffusive Arsenic Fluxes

Molecular diffusion is a potential mechanism for the transport of dissolved constituents in sedimentary deposits. In addition, diagenesis of ferromanganese oxyhydroxides and adsorbed/coprecipitated As and P may be responsible for solid-phase Mn-As-P maxima due to upward diffusion of dissolved species and reprecipitation of oxyhydroxide phases in surficial oxidizing sediments.

The vertical diffusional As flux (J) along concentration gradients away from the dissolved As maxima may be calculated from interstitial As concentration gradients (dc/dz) and Fick's first law in one dimension:

$$J = (\emptyset)(D_s)(dc/dz),$$

where

$\emptyset$ is the porosity;
D_s is the bulk sediment diffusion coefficient, in square centimeter per year; and
dc/dz is the interstitial As concentration gradient, in micrograms per cubic centimeter per centimeter.

It was assumed that the As concentration gradients are linear. Examination of the interstitial As data collected from the 1986 cores indicates that, whereas nearly linear gradients prevail for cores from the upper arm, concave upward gradients prevail for cores from sites on the middle and lower arm of the river. The interstitial As gradients for 1985 cores tend to be more nearly linear and steeper near the sediment-water interface. Potential diffusional fluxes of As have been calculated for all cores taken during 1985 and 1986. These have been averaged for each of the three sections of the Cheyenne River arm and are presented in table A-4. Diffusional As fluxes in sediments from the upper and middle arm are one-third the rate of fluxes in lower-arm sediments.

A comparison between J and the accumulation of sedimentary As (A) is presented in table A-4. The ratio (J/A) for upper-arm sediments is very low (0.02). This indicates that 98 percent of the As deposited in these rapidly accumulating sediments remains in the sediment column and is not transferred to the water column.

Considering sediments from the middle section of the Cheyenne River arm, the ratio increases to 0.15, indicating that more of the As that is deposited in these sediments may be recycled to the water column. The flux ratio for lower-arm sediments is 0.33. By assuming that there is no consumption of dissolved As near the sediment-water interface, 30 percent of the solid-phase As is being recycled to the water column. Solid-phase As data from both 1985 and 1986 cores exhibit a general decrease in the upper 5 cm of the sediment column relative to underlying sediment. This indicates that no consumption of dissolved As is occurring in these surficial sediments.

CONCLUSIONS

Sediments from the upper part of the Cheyenne River arm of Lake Oahe are accumulating at a rate of between 12 and 23 cm/yr. Middle-arm sediments are accumulating at rates of from 6 to 10 cm/yr; lower-arm rates approximate 5 cm/yr. These extremely rapid sediment-accumulation rates serve to preserve, at diminished concentrations, the original interstitial-water chemistry profiles. This is in contrast to the usual situation where there is sufficient time for molecular diffusion to "smooth out" the original interstitial-water chemistry profiles. For the 2 years studied (1985 and 1986), the profiles are offset vertically by approximately 12 cm in upper-arm sediments and 5 cm in lower-arm sediments. Solid-phase constituents do not show a discernible repetitive pattern due to the extreme heterogeneity of the sedimentary system. In addition, a decrease in sedimentary As of 1 μg/gm (micrograms per gram) would result in an interstitial As increase of 300 micrograms per liter.

Calculated upward-diffusion/sediment-accumulation ratios (J/A) for As indicate that little sedimentary As is being recycled to the water column from rapidly accumulating sediments in the upper Cheyenne River arm. On the contrary, as much as 30 percent of the sedimentary As may be recycled to bottom water in the lower Cheyenne River arm. During warm summer months the deep (30 to 40 m (meters)) water column stratifies and the thermocline is located near the bottom because of high, prevalent winds. The environmental effect of the potentially large As transport (flux) from surficial sediment to this bottom water needs to be evaluated.

SPECIATION OF ARSENIC IN SEDIMENTS AND INTERSTITIAL WATER FROM THE CHEYENNE RIVER ARM OF LAKE OAHE, SOUTH DAKOTA

By Walter H. Ficklin[1] and Edward Callender[2]

Arsenic occurs in sufficient abundance in interstitial water and solid-phase material from sediments of the Cheyenne River arm of Lake Oahe in South Dakota, to allow its separation into discrete chemical species. Eighty-seven samples of sediment and associated interstitial water were examined for total arsenic content to determine the abundance and distribution of discrete arsenic species; the concentrations of these species provide some of the information necessary to determine the chemical environment that controls the solubility of arsenic. As(V) (arsenate) and As(III) (arsenite) are the anticipated species in interstitial water, and these constituents should occur in extracts of sediments as well. As expected, the sediment contains four normal hydrochloric acid- (4N-HCl) soluble arsenic, separable into As(V) and As(III), but the arsenic concentration of the extract is commonly less than the total arsenic content. The arsenic resistant to 4N HCl is thought to be associated with a solid-sulfide phase.

The samples used for this study were collected from gravity cores of bottom sediment which were extruded in 1- or 2-cm (centimeter) intervals under a nitrogen atmosphere according to the method of Goodwin and others (1984). The location of the sample sites is shown in figure A-12. The interstitial water was separated from the sediment by centrifugation, and part of the water was acidified with HCl so that the acid concentration was 0.12 N. Arsenic in the interstitial water was separated into As(V) and As(III) by the ion-exchange method of Ficklin (1983), and the concentration of each was determined by graphite-furnace atomic absorption spectrophotometry. The sediment samples were kept frozen until chemical extraction and separation of the arsenic were started. The arsenic was extracted as quickly as possible by using boiling 4N HCl. The extract was cooled, the volume was adjusted to compensate for evaporation, and the arsenic was separated into As(V) and As(III) by using a modification of the Ficklin (1983) method. Arsenic not affected by the 4N HCl was extracted from the sediment with a predetermined amount of potassium chlorate ($KClO_3$) and concentrated HCl (Olade and Fletcher, 1974; Chao and Sanzolone, 1977).

Three phases of arsenic were found using the 4N-HCl extraction and the sequential sulfide extraction. One phase is As(V), defined as that part of the HCl-extracted arsenic that eluted from the ion-exchange column in the same fraction of eluent as the As(V) in a known solution of As(V) and As(III). Likewise As(III) is defined as the arsenic that eluted in the same fraction that contained As(III) in the known solution. Finally, the third phase is the arsenic, As(sulf) that was solubilized by the sulfide extraction. It was not separated into As(V) and As(III) because of the strong oxidizing reagent used. Generally, the total aqueous arsenic concentration was accounted for by the concentrations of As(V) and As(III) in the interstitial water. In the solid phase, the total arsenic concentration, determined by the digestion method of Elrick and Horowitz (1985), approximated the sum of the concentrations of As(V), As(III), and As(sulf).

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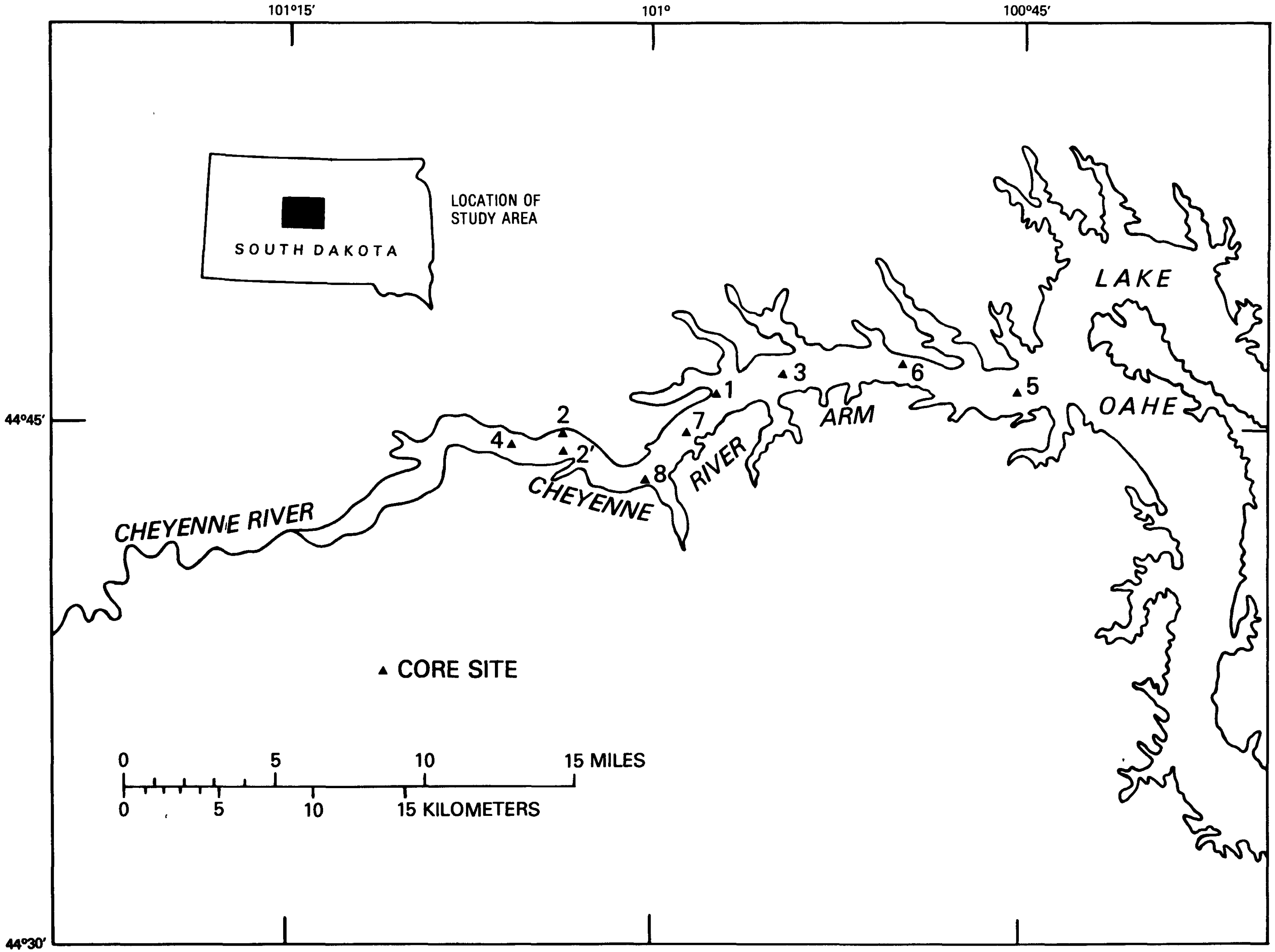


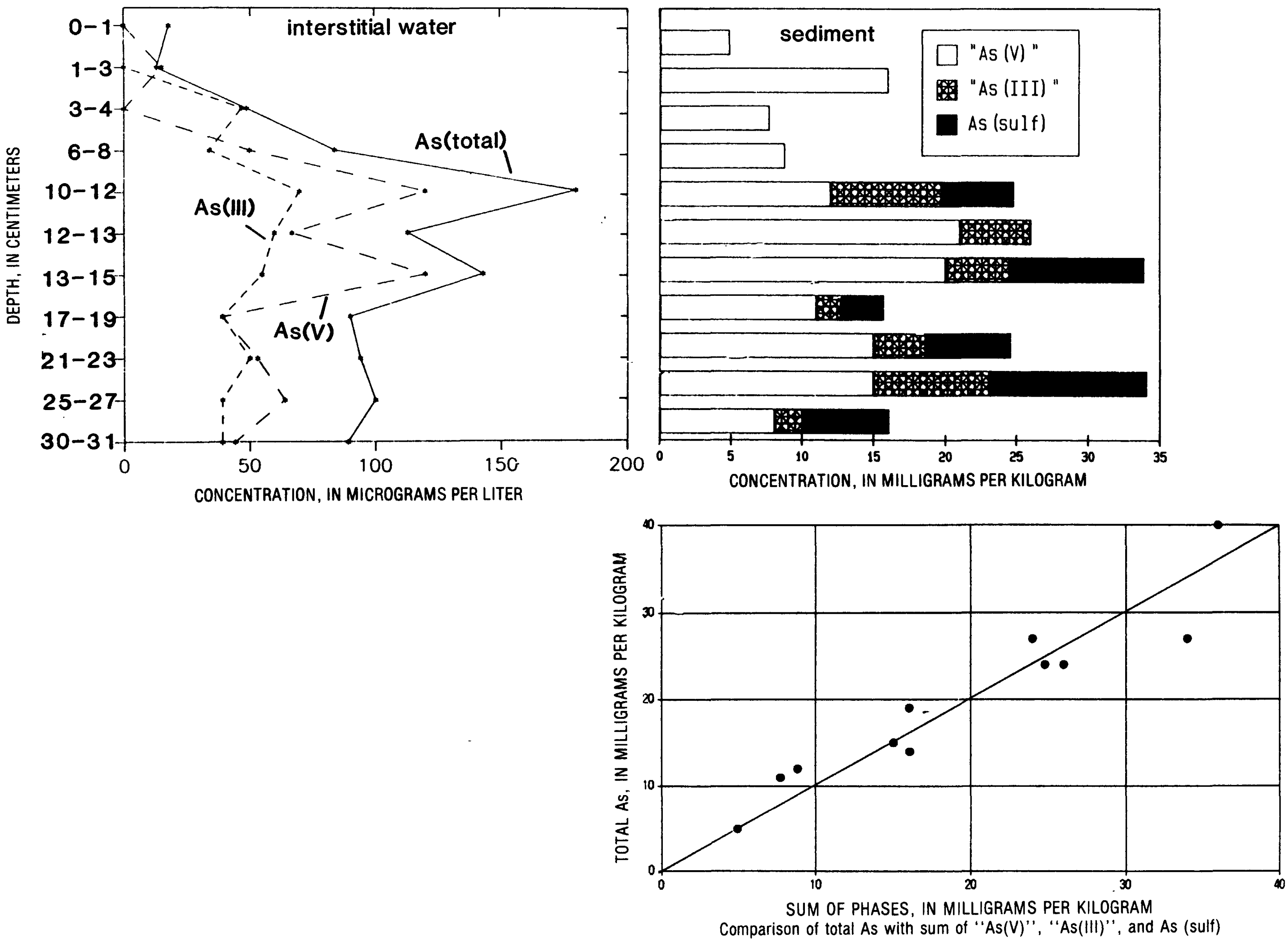
Figure A-12.--Location of sample sites for gravity cores of bottom sediment.

The distribution of arsenic was not uniform throughout the cores. Figure A-13 shows the distribution of arsenic in the interstitial water and in the sediment at the westernmost sample site (2-5). From depths of 0 to 8 cm, the total arsenic occurred as extractable As(V). From 10 to 31 cm, the arsenic was distributed among the three phases with As(V) the most abundant. The greatest total arsenic concentration in the sediment was 34 mg/kg (milligrams per kilogram) at 13 to 15 cm and at 25 to 27 cm, with 15 mg/kg As(V), 8.1 mg/kg As(III), and 11 mg/kg As(sulf) for 25 to 27-cm interval. The concentration of arsenic in the interstitial water increased steadily from 18 μg/L (micrograms per liter) at 0 to 1 cm to 180 μg/L at 10 to 12 cm. At the 10 to 12-cm depth, the aqueous As(V) was 120 μg/L and the As(III) was 70 μg/L. For the remaining samples in the core, except at 13 to 15 cm, the total aqueous arsenic concentration was approximately 100 μg/L with nearly equal distribution between As(V) and As(III).

In contrast, the results for the easternmost core (5-6) are considerably different (fig. A-14). The acid-extractable arsenic occurred exclusively as As(V) only in the upper 4 cm (9-23 mg/kg). In the depth intervals from 5 to 17 cm, all three arsenic phases were identified in the sediment with the greatest concentrations in this section of core occurring at 11 to 13 cm, where the As(V) concentration (15 mg/kg) was less than the As(III) concentration (28 mg/kg). In this same interval, the As(sulf) content was 10 mg/kg and the total As was 56 mg/kg. The concentration of arsenic in the interstitial water was less than 5 μg/L in the surficial sediment (0-7 cm) but increased to 520 μg/L at 5 to 7 cm and about 1,000 μg/L at 7 to 17 cm.

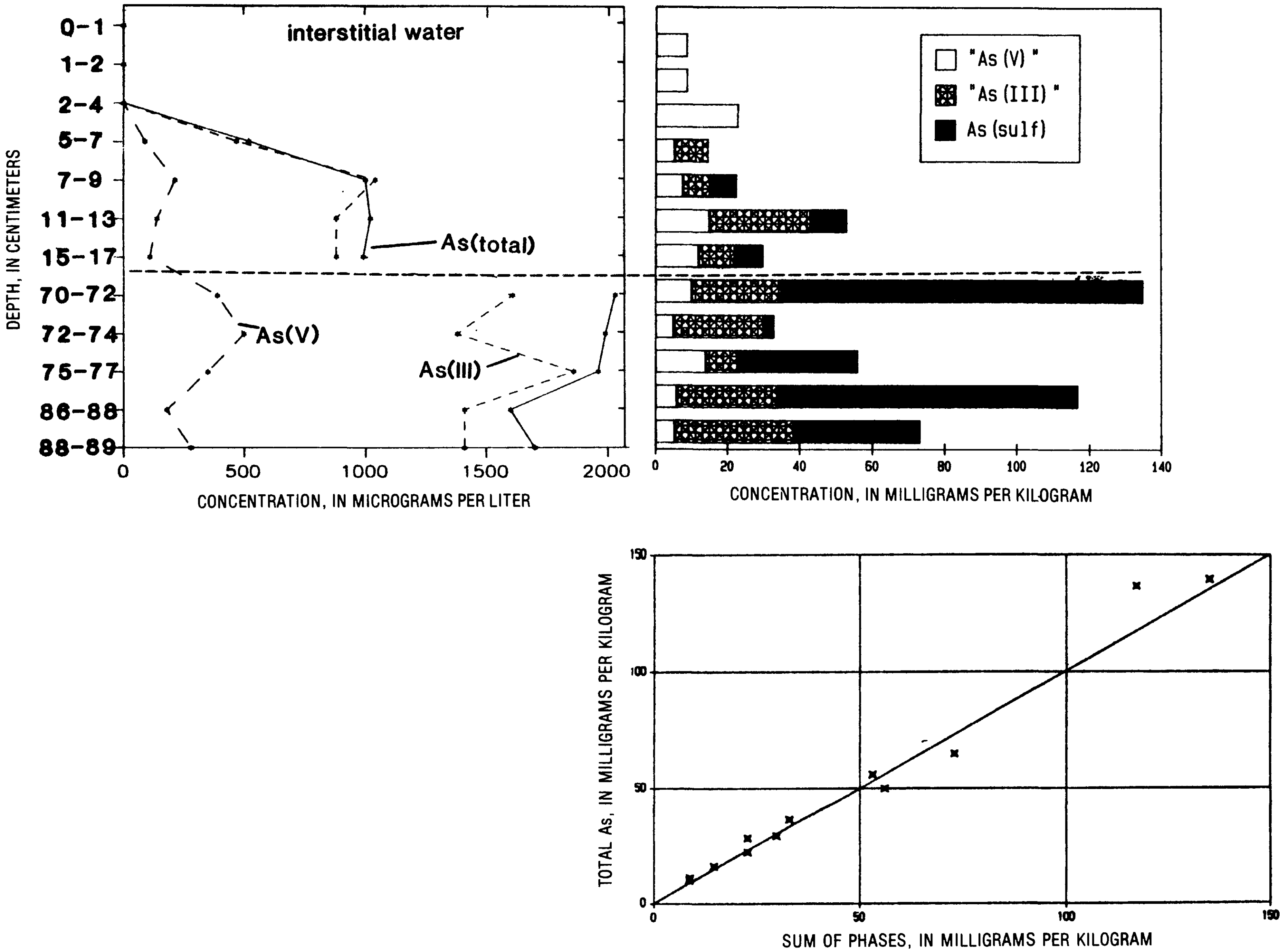
Some of the cores were sampled at much greater depth to determine the distribution of arsenic in the deeply buried sediment. Core 5-6 (fig. A-14) was sampled at depths of 70 to 72 cm, 72 to 74 cm, 86 to 88 cm, and 88 to 89 cm. The total arsenic concentration in the sediment for the 70 to 72-cm interval was 140 mg/kg, the greatest arsenic concentration found in any of the samples. In that sample, As(sulf) was 100 mg/kg, As(III) was 25 mg/kg, and As(V) was 10 mg/kg. The large As(sulf) concentration is an indication of the reducing conditions that prevail at greater depths in these sediments. The greatest concentration of arsenic in the interstitial water also occurred in this sample (2,030 μg/L total, 1,610 μg/L As(III), and 390 μg/L As(V)).

In shallow sediments, the predominance of solid-phase As(V) and the low concentration of total aqueous arsenic in associated interstitial water suggest that arsenic geochemistry is controlled by oxidizing conditions (sediment redox potentials greater than 200 mV (millivolts)) and iron oxyhydroxide chemistry. In deeper sediments, the predominance of As(III) in the interstitial water and reduced arsenic in the associated solid phase suggests that arsenic geochemistry is controlled by reducing conditions (sediment redox potential less than 50 mV) and sulfide chemistry.



Comparison of total As with sum of ''As(V)'', ''As(III)'', and As (sulf)

Figure A-13.--Distribution of arsenic in the interstitial water and in the sediment at the westernmost sample site (2-5).



Comparison of total As with sum of "As(V)", "As(III)", and As (sulf)

Figure A-14.--Distribution of arsenic in the interstitial water and in the sediment at the easternmost sample site (5-6).

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ARSENIC CONCENTRATIONS OF SELECTED BENTHIC INSECTS IN WHITEWOOD CREEK AND THE BELLE FOURCHE RIVER, SOUTH DAKOTA

By Daniel J. Cain[1], Steven V. Fend[1], and James L. Carter[1]

The tendency of organisms to concentrate trace contaminants makes them potentially useful in defining spatial and temporal trends in environmental contamination. Ideally, a bioindicator should meet several criteria. It should: (1) be an efficient accumulator for the contaminant, (2) be easy to collect in sufficient quantities to facilitate analytical and statistical analysis, (3) inhabit the area from minimum through maximum contamination, (4) have limited migration, (5) accumulate the contaminant as a function of exposure so that contaminant levels of the bioindicator reflect the environmental levels, and (6) be available throughout the period of study. This concept of bioindicator is different from the use of relative abundance of indicator organisms as a method of delineating areas of contaminant impact (Warren, 1971).

Bioindicators have been used most extensively in marine ecosystems where physical conditions are relatively stable and many organisms have cosmopolitan distributions (Goldberg and others, 1978). Bioindicators have been used on a more limited scale in freshwater lotic ecosystems. Physical gradients that occur from low to high order streams affect species distributions (Vannote, 1980). Thus, a single species may not be present throughout a river system. However, organisms differ less among closely related taxa than among major taxonomic groups in their abilities to accumulate contaminants (Bryan and Gibbs, 1983). Compositing samples of closely related and ecologically similar species may be a practical method of evaluating the spatial distribution of contaminants in rivers.

In this study, benthic insects were sampled in Whitewood Creek and the Belle Fourche River (site abbreviations defined in table A-5; see fig.1 for locations) to evaluate their potential as bioindicators of arsenic (As) contamination. Benthic insects were chosen as potential bioindicators because they are relatively easy to collect and have limited mobility. Criteria examined were spatial and temporal variation in abundance and the ability to concentrate As in proportion to environmental levels.

Benthic insects were collected with kick nets at 10 locations in Whitewood Creek and the Belle Fourche River. Two stations, HW and BFAWW, were located outside the contaminated area. Samples representing 3 to 5 minutes of kick sampling effort were taken for analysis of species abundance. Additional insects collected for elemental analysis were separated by taxon in the field. The insects were kept in cooled streamwater for at least 6 hours to clear their digestive tracts and were then frozen using dry ice. In the laboratory, the samples were thawed, thoroughly rinsed with de-ionized water, and sorted further by taxonomic grouping and individual size. Individuals were pooled to attain enough biomass (about 100 mg (milligrams) dry weight) for elemental analysis. Samples were homogenized, freeze dried, ashed, and analyzed for As by hydride generation atomic absorption spectroscopy (AAS). Subsamples of the ashed material were also acidified with 50 percent hydrochloric acid (HCl) and analyzed for iron (Fe) by flame AAS.

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Table A-5.—Relative abundance in 3- to 5- minute kick samples of selected benthic insects in Whitewood Creek, Belle Fourche River, and the Cheyenne River

HW = Whitewood Creek, upstream of Lead
BGR = Whitewood Creek, downstream of the confluence with Gold Run
STP = Whitewood Creek, Deadwood sewage treatment plant
CERCLA = Whitewood Creek, CERCLA station (Whitewood Creek at Whitewood)
BERGER = Whitewood Creek, near Berger ranch (approximately 20 kilometers downstream of Whitewood)
SHEELER = Whitewood Creek, Sheeler site at mouth of Whitewood Creek
BFAWW = Belle Fourche River, upstream of the confluence of Whitewood Creek
BFBWW = Belle Fourche River, 100 meters downstream of Vale Bridge
BFIS = Belle Fourche River, upstream of Interstate Bridge about 32 kilometers east of Sturgis
CH = Cheyenne River, downstream confluence of Belle Fourche River

Abundance	0–5	5–10	10–20	20–50	50–100	>100
Categories	1	2	3	4	5	6

Taxa	Site									
	HW	BGR	STP	CER-CLA	BER-GER	SHEE-LER	BFA-WW	BFB-WW	BFIS	CH
Relative abundance of selected taxa, June 1986										
Baetid mayflies										
Baetis tricaudatus	6	6			6	4				
Baetis brunneicolor	4		3	5	1					
Baetis flavigistra			2	6	2		1			
Baetis nr. *pygmaeus*								2	1	1
Baetis sp.								1	1	
Dactylobaetis sp.							1	3	4	
Paracloeodes minutus							1	2	4	
Pseudocloeon sp.			1	1	5	6		3	2	1
Miscellaneous taxa										
Ephemerella inermis	4	4	1	2						
Choroterpes sp.					3	4	1	4	3	
Tricorythodes sp.					4	3	1	1	1	
Leucrocuta sp.					1	2	2	5	1	
Hesperoperla pacifica	2									
Rhyacophila sp.	2									
Limnephilus sp.			1	1						
Hydropsychid caddisflies										
Hydropsyche oslari ?	2									
Hydropsyche slossonae	1		1							
Hydropsyche bronta ?				1		1	4	1		
Cheumatopsyche sp. 1							1	1		
Cheumatopsyche sp. 2				1			4			

Table A-5.—*Relative abundance in 3 to 5 minute kick samples of selected benthic insects in Whitewood Creek, Belle Fourche River, and the Cheyenne River*—Continued

Taxa	Site HW	STP	BERGER	SHEELER	BFBWW	BFIS
Relative abundance of selected taxa, August 1986						
Baetid mayflies						
Baetis tricaudatus	4	6				
Baetis brunneicolor ?	3		4	3	5	4
Baetis flavigistra					4	
Dactylobaetis sp.			1	4	4	3
Paracloeodes minutus						1
Pseudocloeon sp.		1	3	5	5	1
Miscellaneous taxa						
Choroterpes sp.			5	4	5	5
Tricorythodes sp.			5	4	4	1
Isonychia sp.				1	3	1
Ephoron album			5	2	1	2
Limnephilus sp.	1	1				
Hydropsychid caddisflies						
Hydropsyche slossonae	1	6				
Hydropsyche bronta ?		4	4	5	6	1
Cheumatopsyche sp. 1				4	6	3
Cheumatopsyche sp. 2			3	3	6	1

Samples collected in June 1986 showed considerable among-site variation in species composition (table A-5). Upstream parts of Whitewood Creek were dominated by cold-water species (such as *Rhyacophila* sp., *Hesperoperla pacifica*, and *Ephemerella inermis*) whereas downstream areas were dominated by warm-water or silt-tolerant species (such as *Choroterpes* sp., *Tricorythodes* sp., and *Dactylobaetis* sp.). Although no single species was abundant at all sites, baetid mayflies and hydropsychid caddisflies occurred at most sites. Each of these taxa were composed of several morphologically and ecologically similar species. Other ephemeropterans and the trichopteran, *Limnephilus* sp., also appeared useful for intersite comparison over a limited range. Several potentially useful taxa (notable Baetidae and other mayflies) were not collected for As analysis.

Comparison of June with August samples (table A-5) indicates that seasonal variation in species abundance need to be considered when planning a sampling program. Some taxa abundant in June at HW (including *E. inermis*) were absent in August, and individual sizes of other taxa (notably baetid mayflies) were smaller than in June (data not shown). However, at downstream sites at least two mayflies (*Ephoron album* and *Isonychia* sp.) were larger and more abundant. Life history patterns restrict the availability of some taxa to certain times of the year. During these times, short-lived taxa may better represent the concentration of a contaminant than long-lived taxa.

Hydropsychid caddisflies were the most consistently abundant organisms among sites. Arsenic concentrations in these benthic insects increased as As levels in sediments increased (table A-6) (Goddard and others, this report). One hundred meters downstream from the confluence of Gold Run with Whitewood Creek, the point of historic discharge of mining wastes, As concentrations in hydropsychids and E. inermis were 5 to 6 times higher than at the HW site. The highest hydropsychid As levels were observed at the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) site on Whitewood Creek and were approximately 15 times higher than at the HW site. This was also the area of highest sediment As concentrations (Goddard and others, this report). Arsenic concentrations in hydropsychids declined below CERCLA but remained 6 to 8 times higher at the Vale bridge on the Belle Fourche River than at HW and BFAWW, two uncontaminated sites. Thus, concentration of As in insects 72.9 kilometers from the original source of mine-wastes discharge into Whitewood Creek were similar to concentrations just below the mine.

Fuller and others (this report) observed that As was associated with Fe under the conditions found in Whitewood Creek. Iron concentrations in benthic insects generally followed trends observed for As. Molar ratios of As to Fe in benthic insects (0.01-0.03) from impacted sites were within the range of As:Fe found in the flocculent material associated with ground-water seeps and surface coatings of the stream sediments. This indicates that a portion of the As and Fe accumulated by the insects was from this source. This accumulation may be associated with the exoskeleton and/or from the ingestion of particulate material.

Two lines of evidence indicate that deposition/sorption to the exoskeleton was a major mechanism of As uptake (Smock, 1983a). Both As and Fe were negatively correlated with the dry weight of hydropsychids within a site. Because small individuals have high surface-to-mass ratios, one would expect high concentrations of As to be associated with small individuals if As was surface related. Second, different life stages of the caddisfly Limnephilus sp. had consistently different As concentrations (table A-6). In June, some individuals of this species existed as larvae and some as pupae, both living in sealed cases. Prior to the case being sealed, the larval exoskeleton is in direct contact with the aquatic environment, including suspended Fe-As flocs. When the insect pupates (changes from a larva to a pupa), it sheds its larval exoskeleton while still in the sealed case and, consequently, the pupal exoskeleton is not directly exposed to the aquatic environment. Larvae at two sites had much higher As levels than pupae and As:Fe ratios in the larvae were within the range observed for the Fe-As floc, whereas As:Fe ratios in the pupae were below levels observed in the floc. The simplest explanation for the difference in As concentration between larva and pupa is that most of the As in the larva was associated with the exoskeleton which was shed during pupation.

Table A-6.—Concentrations of arsenic in benthic insects in Whitewood Creek and Belle Fourche River, June 1986

[Stations: HW = Whitewood Creek, upstream of Lead; BGR = Whitewood Creek, downstream of the confluence with Gold Run; STP = Whitewood Creek, Deadwood sewage treatment plant; CERCLA = Whitewood Creek, CERCLA station; BFAWW = Belle Fourche River, upstream of the confluence of Whitewood Creek; and BFBWW = Belle Fourche River, 100 meters downstream of Vale Bridge]

[Values are mean ±1 standard error (micrograms per gram dry weight). Sample size, n, given in parenthesis. nd = not determined]

Station	*E. infrequens*	Hydropsychids	*H. pacifica*	*Rhyacophila* sp.	*Limnephilus* sp.
HW	11.3±0.5 (2)	3.1 (1)	0.8±0.05 (2)	0.2 (1)	nd
BGR	65.3±8.1 (3)	22.4 (1)	nd	nd	nd
STP	nd	nd	nd	nd	[1]3.6 (1) [2]19.5 (1)
CERCLA	nd	46.4±3.9 (2)	nd	nd	[1]2.0±0.02 (2) [2]12.4±1.8 (2)
BFBWW	nd	26.3±6.4 (3)	nd	nd	nd
BFAWW	nd	1.7±0.3 (4)	nd	nd	

[1] Pupa of *Limnephilus* sp.

[2] Larva of *Limnephilus* sp.

Arsenic concentrations varied widely among species within a site (table A-6). Concentrations found at HW on Whitewood Creek were lowest (0.02–0.08 μg As/g (microgram of arsenic per gram) dry weight) in the predators, *Rhyacophila* sp. and *Hesperoperla pacifica*; moderate (3.1 μg As/g dry weight) in the filtering omnivore, *Hydropsyche* spp.; and highest (11.3 μg As/g dry weight) in the bottom-feeding herbivore, *Ephemerella inermis*. This suggests that differences in trophic preference may affect accumulation of As, with herbivores concentrating more As than predators (Giesy and others, 1979; Smock, 1983b).

In summary, benthic insects appear to be suitable organisms for use as bioindicators on the basis of their ability to concentrate As in relation to environmental levels. Problems encountered relate to the limited geographic distribution of individual species and large interspecific variation in As concentration. To increase the usefulness of benthic insects as bioindicators, it will be necessary to: (1) identify the effects of grouping organisms at higher taxonomic levels than species; (2) show the relation between trophic level and the ability to concentrate trace elements; and (3) determine the contribution of different routes of uptake, such as, surface sorption/deposition, ingestion, and diffusion.

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Chapter B

OBJECTIVES AND PRELIMINARY RESULTS OF RECONNAISSANCE SAMPLING FOR SELECTED HAZARDOUS SUBSTANCES IN THE LOWER CALCASIEU RIVER, LOUISIANA

By Charles R. Demas[1]

The presence and effect of hazardous substances in the aquatic environment have been documented nationwide in recent years. These hazardous substances enter the environment from sources such as industry, agriculture, urban runoff, and atmospheric fallout. Industry and agriculture will continue to use chemicals in their activities and will create the potential for release of hazardous substances into the environment. The Calcasieu River in southwestern Louisiana (fig. B-1) is a prime example of an area that may be threatened by the release of hazardous substances. The purpose of this paper is to document the objectives and preliminary results of reconnaissance sampling for selected hazardous substances in the lower Calcasieu River.

The Calcasieu River is a tidally affected stream that lies within the Coastal Plain. The upper Calcasieu River basin is characterized by hardwood forests, cypress, and related vegetation. Rice and soybeans are the principal crops grown in the upper and middle basin, including the upper part of the study area.

Long-term water-quality data (1968–present) collected at the Kinder site (fig. B–1) indicate that the upper reach of the Calcasieu River is a dilute, colored-water stream. Specific conductance concentrations range from 13 to 187 μS/cm (microsiemens per centimeter) at 25 °C. Dissolved organic carbon (DOC) concentrations range from 5 to 6 mg/L (milligrams per liter) in this reach. Discharges at Kinder range from less than 200 to 182,000 ft^3/s (cubic feet per second) and average 2,500 ft^3/s for the period of October 1938 to the present. Agricultural input of chemicals into the river appears to be minor; however, some chlordane, diazinon, and aldrin have been detected in water at the Kinder and Oberlin sites.

The middle and lower reaches of the Calcasieu River basin are bordered by swamp and marshland. The middle reach of the Calcasieu River basin is bordered upstream by a saltwater barrier and downstream by the Intracoastal Waterway. The Lake Charles urban and industrial complex dominates land use in this part of the study area. The specific conductance of water ranges from 200 to 33,000 μS/cm at 25 °C in the middle reach of the river. The DOC ranges from 3 to 4 mg/L in the middle reach of the river. Decrease in the hydrophobic fraction of the DOC is responsible for the lower DOC in the middle reach compared to the upper reach. Petrochemical and agricultural-chemical plants use the Calcasieu River for water supply, navigation, and effluent discharge. Byproducts such as oil and grease, phenols, and metals are discharged into the river by petrochemical industries. Metals, sulfates, and nutrients also are discharged into the river by agricultural-chemical industries in the area. The lower reach of the Calcasieu River extends from the Intracoastal Waterway to the Gulf of Mexico. Commercial and sport fishing, and facilities that support oil drilling also are major industries in the area.

[1] U.S. Geological Survey, Baton Rouge, Louisiana

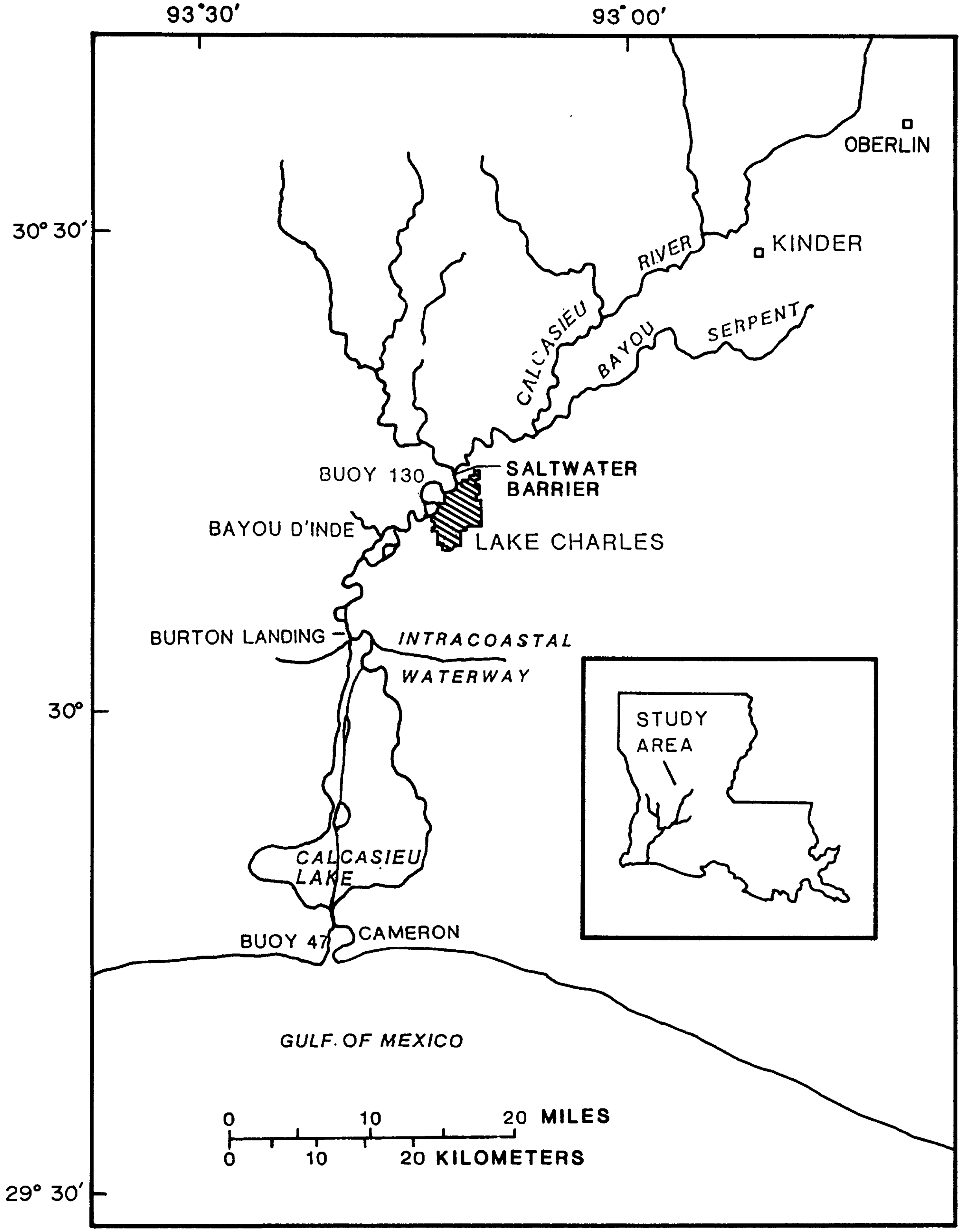

Figure B-1.--Calcasieu River surface-water toxics study area.

Past studies link the occurrence of hazardous substances in the water, bottom material, and aquatic organisms of the lower Calcasieu River to the industries in the basin. These industries in the Lake Charles area are expected to continue production at their current levels. The lower Calcasieu River estuary will continue to be exposed to industrial wastes. Therefore, processes that act on these industrial wastes are important to the overall health of this ecosystem.

Although several Federal, State, and local agencies have collected large amounts of data that describe the sources and occurrence of toxic substances in the lower Calcasieu River, the relation between the hydraulics of this tidal stream and the processes that control the movement and fate of these potentially hazardous substances are poorly understood. To determine these processes in the river, the U.S. Geological Survey is conducting a detailed study with the following objectives: (1) Determine the biological and chemical fates of selected organic compounds, nutrients, and metals in the industrial reach of the river and in the transition zones between brackish and freshwater areas, and the processes involved in the breakdown of these products in the water, suspended sediment, and bottom material of the Calcasieu River; (2) Define: (a) the flow and sediment characteristics in the lower Calcasieu River, including rate and direction of movement of water, sediment, and contaminants, (b) flow routing and solute transport through the system, and (c) circulation patterns within the areas bordering the main channel; and (3) Identify the physical and chemical characteristics such as specific conductance, temperature, oxidation-reduction potential, pH, and dissolved-oxygen concentrations that affect the chemical and biological fates of hazardous substances in the lower Calcasieu River.

Organic compounds, metals, and nutrients in water, bottom material, and biota (table B-1) selected for study are based on the results of intensive reconnaissance sampling. The study area of major interest was selected on the basis of reconnaissance results and extends from the saltwater barrier north of Lake Charles to Burton Landing immediately upstream of the Intracoastal Waterway, a distance of 14 miles. Areas near Cameron and between Kinder and the saltwater barrier will also be studied to gain a better understanding of inputs and outflows of selected hazardous substances from the main study area.

Table B-1.—Substances selected for intensive study in the lower Calcasieu River

Nutrients	Metals	Volatiles	Acid and base-neutral extractables
Ammonium (NH_4)	Iron (Fe)	Bromoform	Benzopyrene
Nitrite (NO_2)	Mercury (Hg)	Chloroform	Benzoperylene
Nitrate (NO_3)	Chromium (Cr)	1,2 Dichloroethane	Hexachlorobenzene
			Napthalene
			Hexachlorobutadiene
			Octachloronapthalene

Flow will be defined using unsteady-state flow modeling techniques. Transport will be defined by dye studies and Lagrangian modeling techniques. Data necessary for input into and calibration of the models will be collected by Geological Survey personnel as part of this study and other ongoing investigations. Flow and routing information will be vital in monitoring movement of hazardous substances in the lower Calcasieu River.

Reconnaissance and preliminary intensive sampling results indicated that volatile organic compounds in variable concentrations within the water column are dependent on wind conditions and sampling schemes used. Mechanisms for transport of volatiles in unaffected areas were determined on the basis of results of dye and density studies. Acid and base-neutral extractable organic compounds (table B-1) were found in low concentrations in water (0.008 μg/L, hexachlorobenzene), in slightly higher concentrations, 34 μg/g (micrograms per gram), in suspended sediment, and in highest concentrations, 7,544 μg/g, in bottom material. Movement into the bottom material appears to be caused by a "salting out" process in which organic compounds such as the haloarenes in the water column flocculate out in saltwater. High concentrations of these same compounds were found in whole organism samples collected concurrently with water and bottom material samples. Nutrients (table B-1) were also found in high concentrations at two sampling sites, but data indicate that high biological activity (phytoplankton blooms) and environmental conditions (wind) effectively and quickly reduce these levels to near background levels downstream. Metals selected for study (table B-1) were found to be associated with naturally occurring organic compounds (humic and fulvic acids); mechanisms for their movement are being studied.

Future studies planned include: (1) determination of means of remobilization of organic compounds from bottom material, (2) movement of volatile organic compounds under different wind conditions and density of volatile compounds, (3) dispersion studies, and (4) in situ uptake studies of organic compounds by mollusks indigenous to the area to determine equilibrium constants for these compounds in aquatic biota.

AUTOMATED INSTRUMENTATION USED FOR THE LOWER CALCASIEU RIVER STUDY

By Dennis K. Demcheck[1]

An objective of the lower Calcasieu River surface-water toxics study is to define flow characteristics of the river, using a two-dimensional laterally-averaged flow model. This is difficult to accomplish because of tidal and wind effects on streamflow in this low-slope estuarine system. To develop a data base of stage, directional velocity, specific conductance, and temperature information, instrumentation has been placed at the upstream boundary (Interstate 10 Bridge at Lake Charles) and downstream boundary (Burton Landing) of the intensive study area (fig. B-2). The data are recorded hourly and, in conjunction with monthly instantaneous discharge measurements, used as input to and verification of the model.

Instrumentation at the upstream boundary monitors directional velocity, specific conductance, and temperature at two depths, 0.2 and 0.8 of the average depth. These depths were chosen as a result of preliminary multiple-point (0.2, 0.4, 0.6, and 0.8 of the average depth) discharge measurements. Stage is also monitored. Stream velocity is sensed with a Marsh-McBirney Model 201 flowmeter[2], modified for sensing upstream-downstream flow. Specific conductance and temperature are measured with a U.S. Geological Survey water-quality minimonitor. Specific conductance and temperature data are necessary for defining layers of differing density, which can affect water movement, routing, and dispersion properties. Stage and directional-velocity data are stored on Stevens paper-tape recorders, but can be displayed at the Geological Survey office in Baton Rouge through the use of a Handar-GOES (Geostationary Operational Environmental Satellite) data acquisition system.

Instrumentation at the downstream boundary consists of two minimonitors. One minimonitor senses stage, wind direction, and wind velocity. These data are necessary for the investigation of tidal movement, reaeration, and volatilization of organic compounds. The second minimonitor senses specific conductance and temperature at 0.9 of the average depth. All data are stored on Stevens paper-tape recorders.

[1] U.S. Geological Survey, Baton Rouge, Louisiana

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

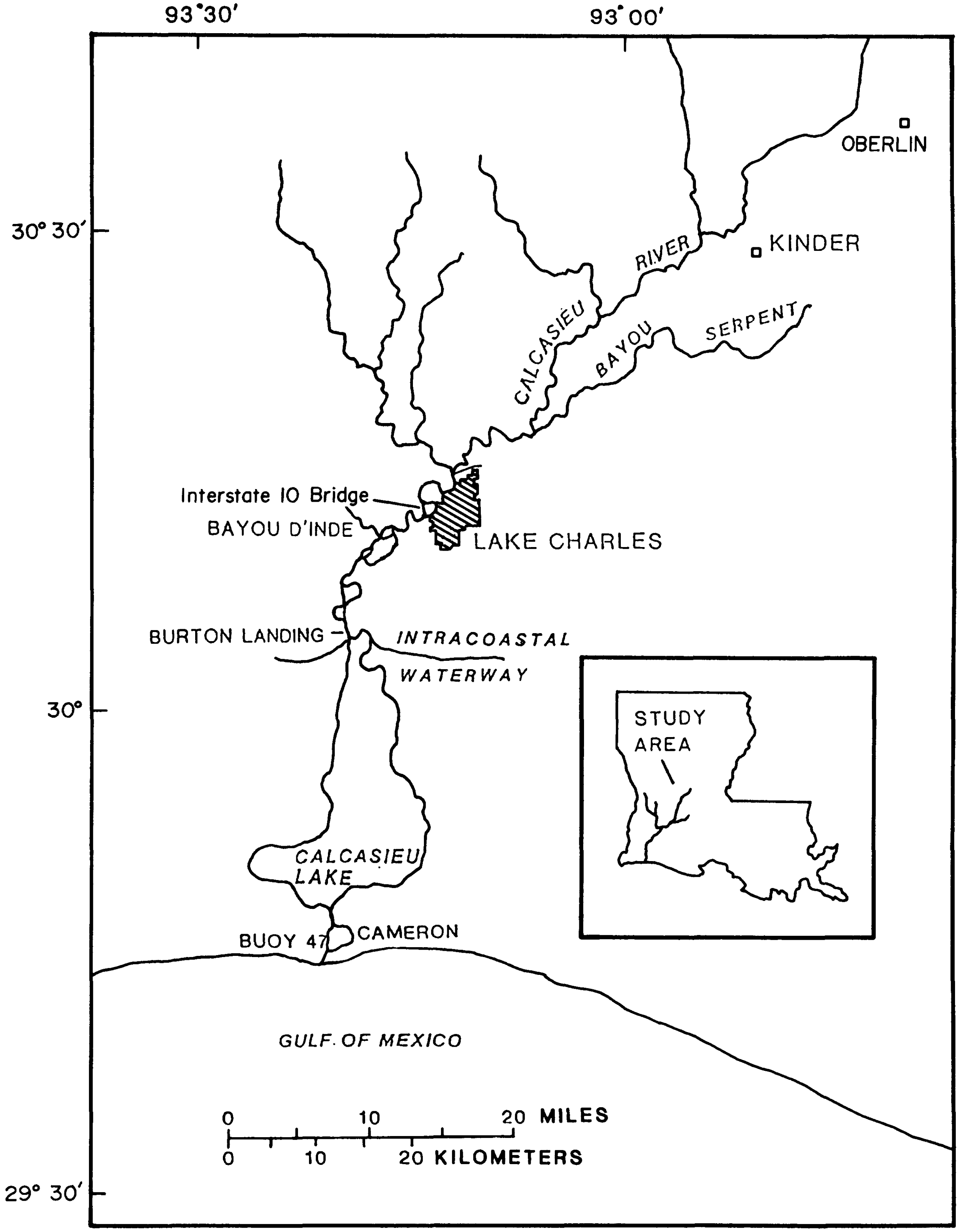

Figure B-2.--Calcasieu River surface-water toxics study area.

USE OF DYE-TRACING TECHNIQUES TO DETERMINE MIXING AND CIRCULATION IN THE LOOPS AND LAKES OF THE LOWER CALCASIEU RIVER

By Philip B. Curwick[1]

The use of fluorescent dyes and dye-tracing techniques provides a means for observing the mixing and circulation patterns of the lower Calcasieu River. Data collected from two dye-tracing studies in May and October 1978 were compiled and interpreted for use in an ongoing study of the occurrence, transport, and fate of selected hazardous substances in the lower Calcasieu River.

At 9:00 a.m. on May 16, 1978, rhodamine WT, a fluorescent dye, was injected into the lower Calcasieu River about 2 miles downstream from the outlet of Lake Charles (fig. B–3). The freshwater inflow of the lower Calcasieu River into Lake Charles was extremely low (near zero), based on estimates from the streamflow gaging station at Kinder, La., and water-use data from the major industries in the area. Mixing and circulation patterns observed in the river were the result of tidal and meteorological conditions. Semidiurnal tides were observed at the beginning of the study with a range of approximately 1 foot. Mixed tides were experienced at the end of the study and ranged approximately 2 feet between the highest high water and lowest low water. In-situ measurements of specific conductance showed the river was partially mixed. No marked interface between freshwater and saltwater was observed, but the specific conductance increased from the surface to the bottom along the entire study reach. The incomplete vertical mixing was the result of extremely low velocities experienced at the extreme low flows. The extent of the dye cloud after three tidal cycles is shown in figure B–3. The dye cloud dispersed around the Coon Island loop and throughout Prien Lake. Rapid dispersion of the dye cloud around Coon Island resulted from the withdrawal of river water by industries located on the north end of the loop.

On October 2, 1978, rhodamine WT dye was injected at three locations into the Calcasieu River: (1) 1 mile upstream from the inlet of Lake Charles at 11:00 a.m., (2) ½-half mile downstream from the outlet of Lake Charles at 2:00 p.m., and (3) at a point at the junction of Bayou d'Inde at 3:00 p.m. The dye was traced for 3 days. Hydrologic, meteorologic, and freshwater inflow conditions were similar to those of the May 1978 study. Tidal conditions were also similar. The extent of the dye cloud after three tidal cycles is shown in figure B–4.

Analysis of data from the two dye-tracing studies showed that longitudinal, near-surface mixing in the lakes and loops of the study reach is complete in approximately three tidal cycles. Residence time for dye near the surface in these areas is approximately six tidal cycles or slightly more than 6 days. Vertical mixing throughout the entire water column was considerably longer than longitudinal mixing. Dye injected in the Calcasieu River at the junction of Bayou d'Inde quickly disperses into Prien Lake under tidally-dominated conditions.

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[1] U.S. Geological Survey, Baton Rouge, La.

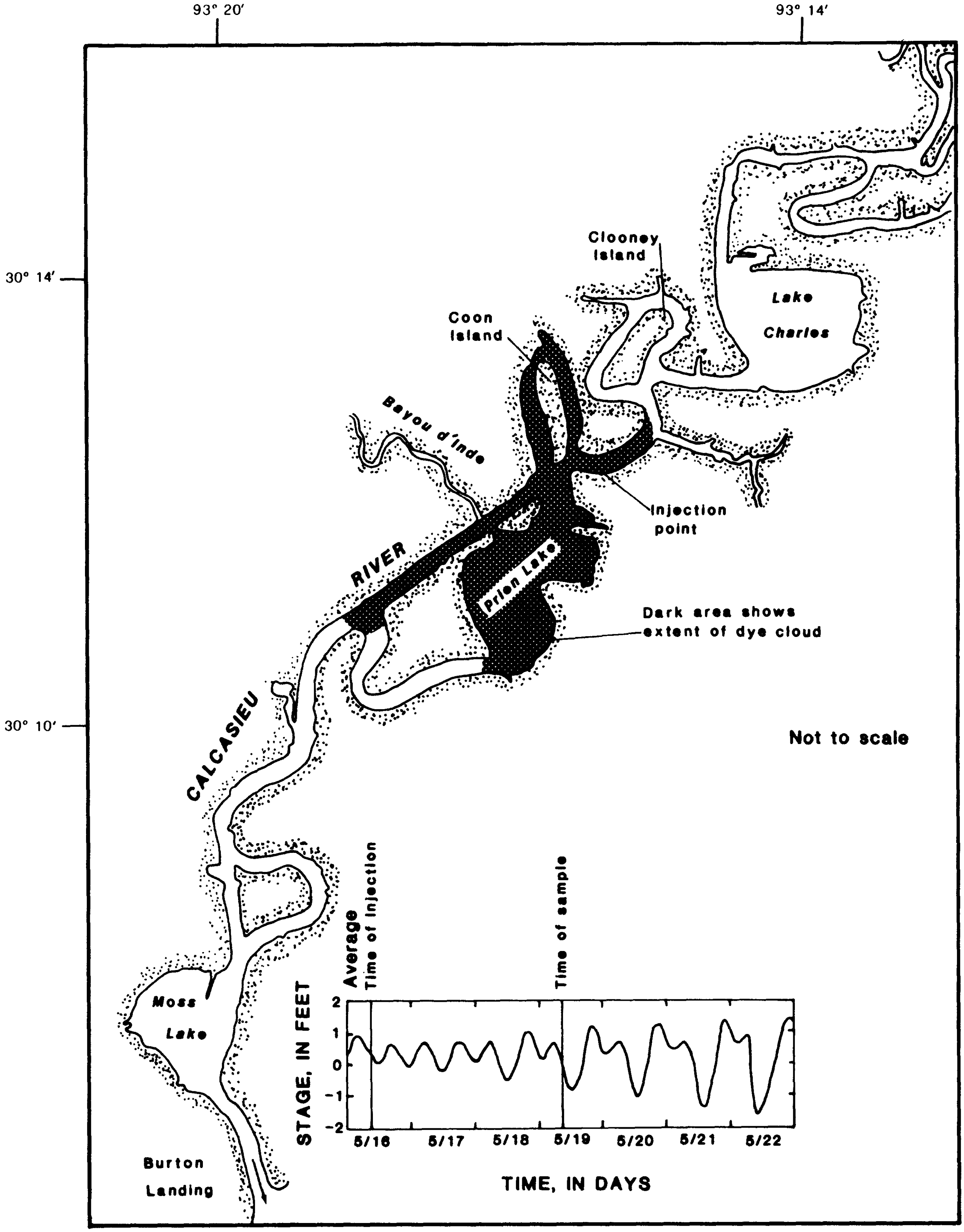

Figure B-3.--Extent of dye cloud approximately three tidal cycles after injection on May 16, 1978.

FIELD EQUIPMENT AND TECHNIQUES FOR SAMPLING METALS AND ORGANIC COMPOUNDS IN THE LOWER CALCASIEU RIVER

By Dennis K. Demcheck[1]

An objective of the lower Calcasieu River surface-water toxics study is to determine the distribution of selected hazardous substances in water and sediments and their chemical and biological fates. This requires the use of a wide variety of field techniques and samplers.

Physical characteristics of the lower Calcasieu River determine the types of samplers used. The river is tidally affected, and although velocities can exceed 2 ft/s (feet per second), sampling equipment and techniques are usually determined by low velocity (less than 1 ft/s) conditions. The distribution of salinity, dissolved oxygen, and pH throughout the water column are highly variable in this estuarine system. These physical and chemical properties are measured immediately before sampling by use of a Marsh-McBirney directional-velocity flowmeter[2] and a Hydrolab _in situ_ water-quality monitor.

Metals in the water column are sampled using either a depth-integrating sampler or point sampler. At velocities greater than 1 ft/s, the integrating sampler (D–77) or point sampler (P–61) is used. At velocities less than 1 ft/s, the wire-basket sampler, fitted with a narrow-mouthed glass bottle or a metals-approved Van Dorn sampler, is used for sample collection. Similarly, organic compounds in the water column can be sampled with either depth-integrating or point samplers. These include the point sampler (P–61), wire-basket, and sewage sampler. All samples are collected in glassware that has been heated to 325 °C for 8 hours.

The low suspended-sediment concentrations in the lower Calcasieu River require a means of concentrating enough sediment for analysis. A Pellicon tangential flow system is effective in processing the large volumes of water (100–200 gallons) required for sample collection. This system can be used in conjunction with a Johnson-Keck pump with Teflon tubing for sampling large quantities of water at a particular depth.

Bed sediments can be sampled for metals and organics with stainless-steel or Teflon-coated Ponar grab samplers. Corers, either handheld or gravity driven, are equipped with stainless-steel liners for organics work or with plastic liners for metals studies.

Techniques and samplers for gathering biota must be tailored to the species desired. Monofilament gill nets, oyster dredges, crab traps, and hook and line are used for sampling. A scientific collector's permit, issued by the appropriate State agency, may be required.

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[1] U.S. Geological Survey, Baton Rouge, Louisiana

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

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THE EFFECT OF DIFFERENT METHODS FOR REMOVAL OF ORGANIC MATTER ON HYDROCHLORIC ACID EXTRACTION OF METALS FROM SEDIMENT—CALCASIEU RIVER, LOUISIANA

By Nancy S. Simon[1]

BACKGROUND

Analyses of sediment samples collected during a 1985 reconnaissance of the lower Calcasieu River indicated that sediment concentrations of chromium (Cr) and iron (Fe) are greater than background concentrations of these metals. Cr is on the U.S. Environmental Protection Agency's list of toxic materials.

OBJECTIVE

This paper describes the results of a study to determine the phase partitioning of Cr in the sediment. Determination of metal partitioning in the sediment would lead to an understanding of the cycling of metals between the sediment and the water column.

APPROACH

Sediment cores and surface sediment samples were collected at four locations. Cores were prepared in a nitrogen atmosphere where interstitial waters were separated from solids. Interstitial water and solids from cores and whole sediment samples taken from the sediment surface were analyzed for metals including Cr and Fe. Extraction techniques were used to identify the sediment components with which the metals were associated.

METHODS

Sediment cores were collected at Buoy-130 (B–130), Bayou d'Inde (BDI), Citgo, and Burton Landing (fig. B–5) in May 1986. Concentration depth profiles were determined for interstitial water collected from these cores. Total metal concentrations for selected sediment intervals are currently (1987) being determined at the U.S. Geological Survey, Geologic Division, laboratories. Surface grab samples were collected in July 1986 at B–130, a site considered unaffected by petrochemical pollution, and BDI, a site affected by petrochemical plants. This material was used to determine the techniques needed to identify sediment components containing Cr, to provide sufficient data for a statistical comparison of the methods, and to compare the 1985 reconnaissance data with the 1986 data. National Bureau of Standards (NBS) Estuarine Sediment 1646 that was collected from the lower Chesapeake Bay was included in the analytical scheme as a control. Figure B–6 is a flow chart of sample treatments.

Two drying techniques were used. One set of samples was air-dried as suggested in Geological Survey standard sediment techniques (Skougstad and others, 1979). Another set of samples was freeze-dried for comparison because freeze-drying has proved useful with Calcasieu River sediment in which petrochemical contamination complicates the extraction of organic material (W.E. Pereira, U.S. Geological Survey, oral commun., 1986).

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[1] U.S. Geological Survey, Reston, Virginia

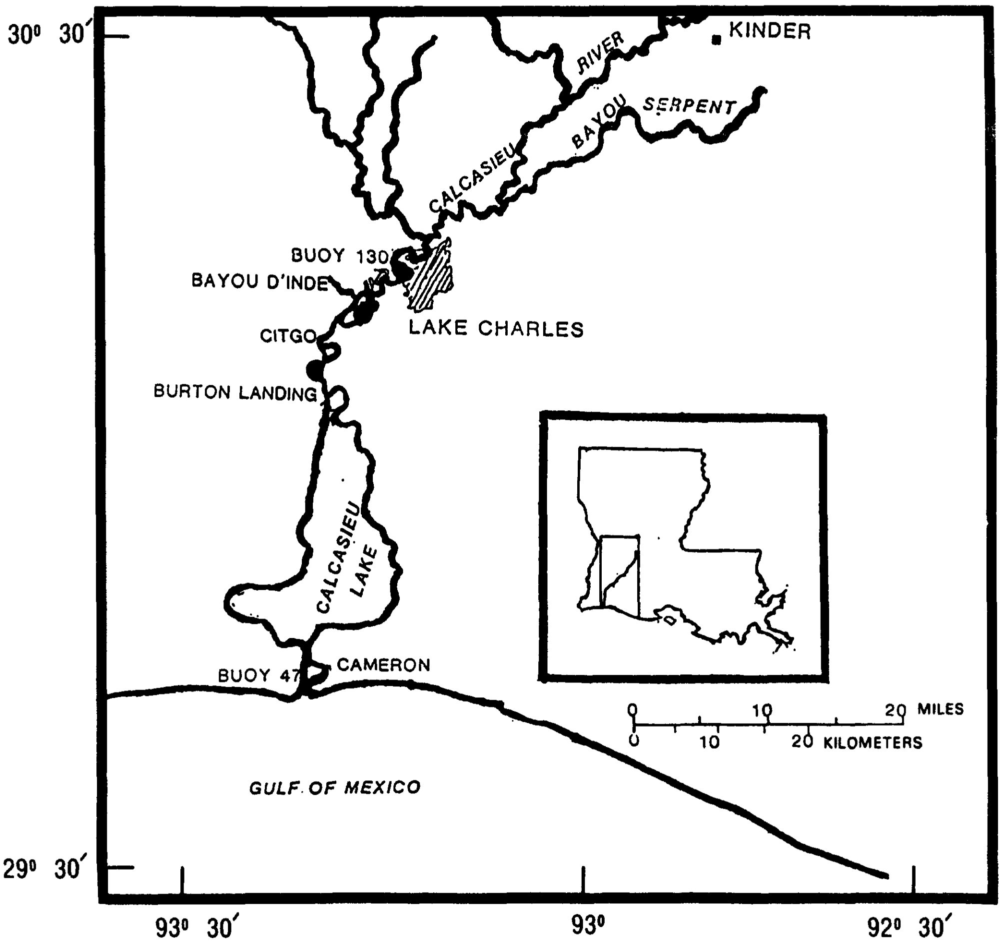

Figure B-5.--Calcasieu River surface-water toxics study area.

Three methods for the oxidation of organic matter were used. The Survey method (Skougstad and others, 1979) for determining total recoverable metals requires the oxidation of organic matter with 30 percent hydrogen peroxide (H_2O_2). Fe oxidized in this procedure can precipitate on the solids blocking complete H_2O_2 oxidation of surficial organic matter (Sequi and Aringhieri, 1977), and the pH of the solution during H_2O_2 oxidation is uncontrolled and can become acidic. Therefore, in the second method 0.25 mmol (millimoles) of sodium pyrophosphate ($Na_4P_2O_7$) (Sequi and Aringhieri, 1977) was added per 0.2 g (gram) dry weight of sediment. The addition of $Na_4P_2O_7$ was expected to complex iron in the solution (Sequi and Aringhieri, 1977), to buffer the solution pH at about 7 (which approximates environmental values, avoids the dissolution of silicates, and permits more

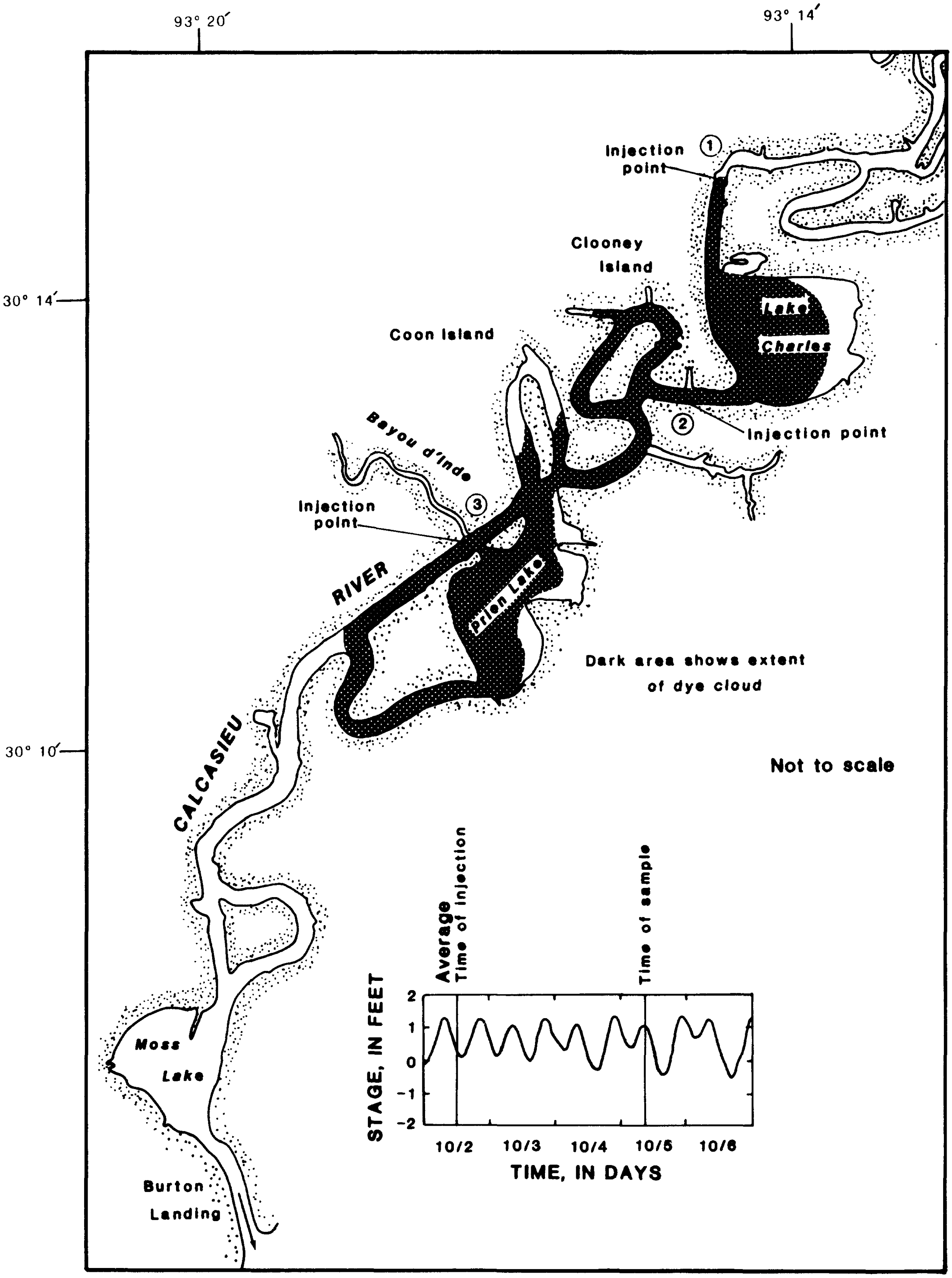

Figure B-4.--Extent of dye cloud approximately three tidal cycles after injection on October 2, 1978.

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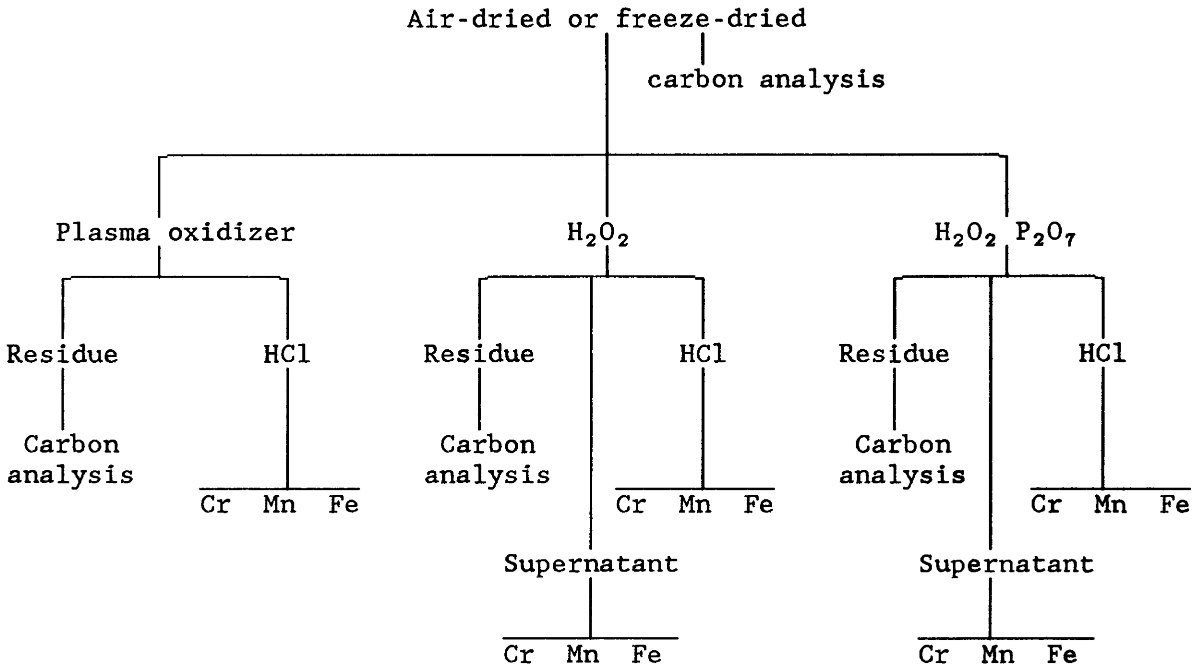
Calcasieu River, Louisiana
B–130 and Bayou d'Inde



National Bureau of Standards Estuarine Sediment 1646

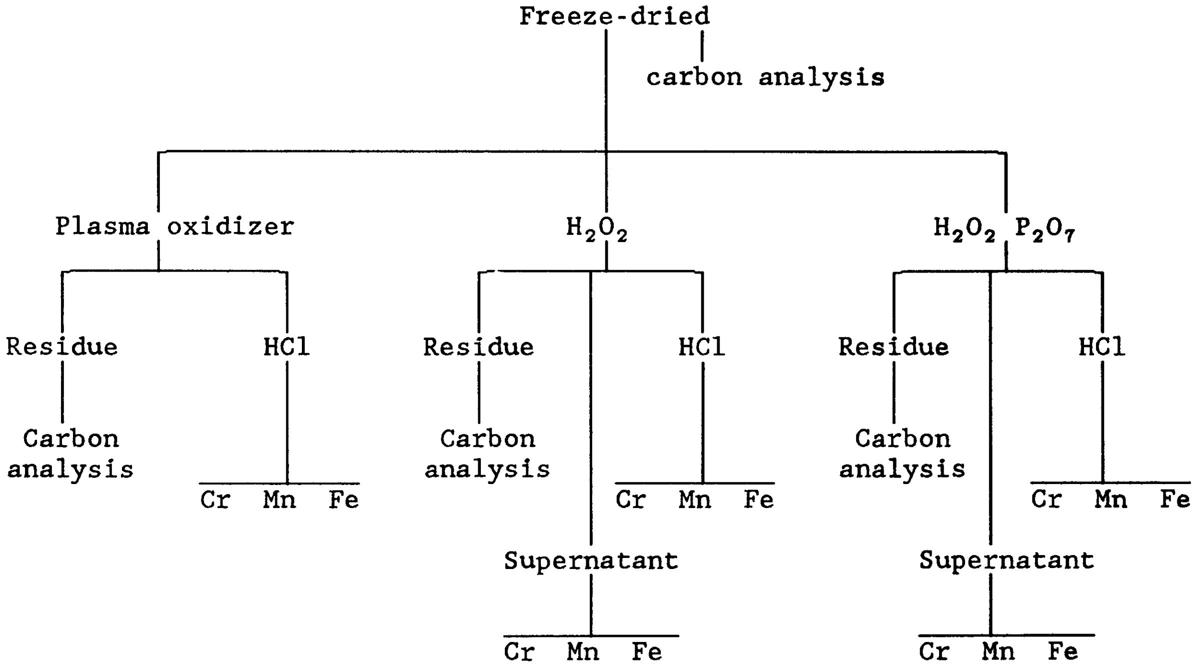


Figure B–6.—Flow chart of sediment analyses.

complete oxidation of organic matter), and to solubilize amorphous Fe oxides and organically bound metals (Bascomb, 1968; Sequi and Aringhieri, 1977). One half of the samples treated with either H_2O_2 or H_2O_2 + $Na_4P_2O_7$ was centrifuged. The supernatant was analyzed for Cr, manganese (Mn), and Fe concentrations. The residue was analyzed for organic carbon. Plasma oxidation, a low temperature ashing procedure, was the third technique used for organic-matter oxidation. Organic carbon was determined in samples before and after the ashing procedure. One-half of all the samples treated by each of the techniques for removal of organic carbon was treated to extract metals (Skougstad and others, 1979) with 1 N (normal) isothermally distilled HCl (hydrochloric acid) at a solution concentration of 0.5 N. Suspensions were filtered and the filtrate analyzed for Cr, Mn, and Fe. Each analytical step included five replicate samples.

RESULTS AND DISCUSSION

Analytical results are given in table B–2 for sediment Fe concentrations and in table B–3 for sediment Cr concentrations. The data are preliminary and will be updated when all analyses are completed. There is no apparent statistical difference between the data obtained using the two drying techniques for sample preparation.

Table B–2.—Sediment analyses for iron with concentrations expressed as micrograms per gram dry weight of the sediment

Sediment analyses	National Bureau of Standards Estuarine Sediment 1646	Calcasieu River B–130		Calcasieu River BDI	
	Freeze-dried	Freeze-dried	Air-dried	Freeze-dried	Air-dried
1985–86 recoverable			3,500/2,500		2,500/5,100
1986 total	33,500	15,000	--	29,000	--
H_2O_2	1,800 ±600	500 ±600	1,600 ±800	1,400 ±1,100	1,200 ±300
H_2O_2+$Na_4P_2O_7$	3,200 ±1,800	4,600 ±1,500	2,300 ±550	2,100 ±500	700 ±300
H_2O_2/HCl	8,300 ±2,100	3,100 ±600	-- --	600 ±300	-- --
H_2O_2+$Na_4P_2O_7$/HCl	6,800 ±550	4,400 ±500	-- --	1,100 ±300	-- --
Plasma oxidized/HCl	6,000 ±2,000	1,200 ±1,000	-- --	1,200 ±1,000	-- --

Table B-3.—Sediment analyses for chromium with concentrations expressed as micrograms per gram dry weight of the sediment

Sediment analyses	National Bureau of Standards Estuarine Sediment 1646	Calcasieu River B-130		Calcasieu River BDI	
	Freeze-dried	Freeze-dried	Air-dried	Freeze-dried	Air-dried
1985-86 recoverable			100/50		450,220/80
1986 total	72	30		100	
H_2O_2	3.3 ±0.9	1.1 ±0.5	1.3 ±0.4	2.5 ±1.1	2.8 ±1.8
$H_2O_2+Na_4P_2O_7$	11.3 ±1.4	15.4 ±6.1	8.4 ±1.3	7.2 ±2.1	4.0 ±0.5
H_2O_2/HCl	36.6 ±4.8	7.8 ±3.1	5.7 ±0.7	5.7 ±0.8	7.7 ±0.3
$H_2O_2+Na_4P_2O_7/HCl$	29.0 ±2.8	7.8 ±1.2	4.7 ±0.3	6.3 ±1.2	7.5 ±0.6
Plasma oxidized/HCl	24.8 ±8.5	11.0 ±7.8	-- --	9.0 ±1.5	-- --

Extraction with H_2O_2 + $Na_4P_2O_7$ and HCl resulted in removal of approximately 20 percent of the total Fe concentration from the NBS standard sediment sample. Extraction with H_2O_2 + $Na_4P_2O_7$ without HCl resulted in the removal of approximately 20 percent of the total Fe content of sediment from B-130. Approximately 30 percent of the total concentration of Fe in the B-130 sediment was extracted with H_2O_2 + $Na_4P_2O_7$. Results of extraction techniques were variable with BDI sediment but the most efficient extracting solution was H_2O_2 + $Na_4P_2O_7$.

The Geological Survey's Water Resources Division Central Laboratory in Denver, Colo., reported extractable Cr concentrations that are approximately equal to or greater than the total concentrations determined by the Survey's Geologic Division Analytical Laboratories. Cr extraction in our project's laboratory was most efficient with H_2O_2 + $Na_4P_2O_7$. Extraction efficiency decreased with the addition of HCl.

Extraction of plasma-oxidized sediment with HCl gave occasionally equal, but more often lower, concentrations of extractable Fe and Cr compared with concentrations obtained with HCl extraction after wet oxidation.

Profiles of sediment interstitial-water sulfate concentration suggest that sulfate reduction is occurring in the upper few centimeters of sediment at B–130 and BDI. Interstitial-water concentration profiles of Fe and Mn show no change in concentration to a depth of 10 cm (centimeters) at B–130. Fe and Mn interstitial-water concentrations are elevated (greater than 6.5 mg/L^{-1}) at a depth of approximately 3 cm in BDI sediment. To a depth of 10 cm, Mn interstital-water concentrations continue to increase but Fe interstitial-water concentrations decrease.

Cr interstitial-water concentrations are variable (table B–4). The best correlation for Cr interstitial-water concentrations in both B–130 and BDI sediments is with sediment adsorbed ammonium concentrations (fig. B–7). This correlation could reflect changes in surface properties.

Table B–4.—Interstitial-water chromium concentrations in Calcasieu River sediment samples

[Results are expressed in micrograms per liter]

Depth in sediment, centimeters	Buoy–130	Bayou d'Inde	Citgo	Burton Landing
0–2	5.2	5.5	3.4	5.2
2–4	17.2	11.6	2.6	4.5
4–6	8.7	8.3	3.2	4.2
6–8	8.0	11.2	2.7	3.0
8–10	8.3	15.6	1.8	2.4
~20	22.3	10.8	1.2	2.2
~30	--		1.4	
~40	15.7	14.2	1.6	2.5
~50	--	--	--	--
~60	--	14.4	--	--
~70	--	--	--	--
~80	--	9.3	--	--

A similar relation was found in Potomac River Estuary sediments (Simon and Kennedy, 1987). In those sediments there was a correlation (R^2 of greater than or equal to 0.9) between interstitial water dissolved Fe concentrations and adsorbed ammonium concentrations. The data collected in the Potomac River study suggested that methanogenic oxidation of sediment organic matter created conditions favorable for the reduction of Fe^{3+} to Fe^{2+}. The higher solubility of Fe^{2+} resulted in the elevated interstitial-water Fe concentrations, and the dissolution of sediment coatings increased the cation-adsorption capacity of the sediment.

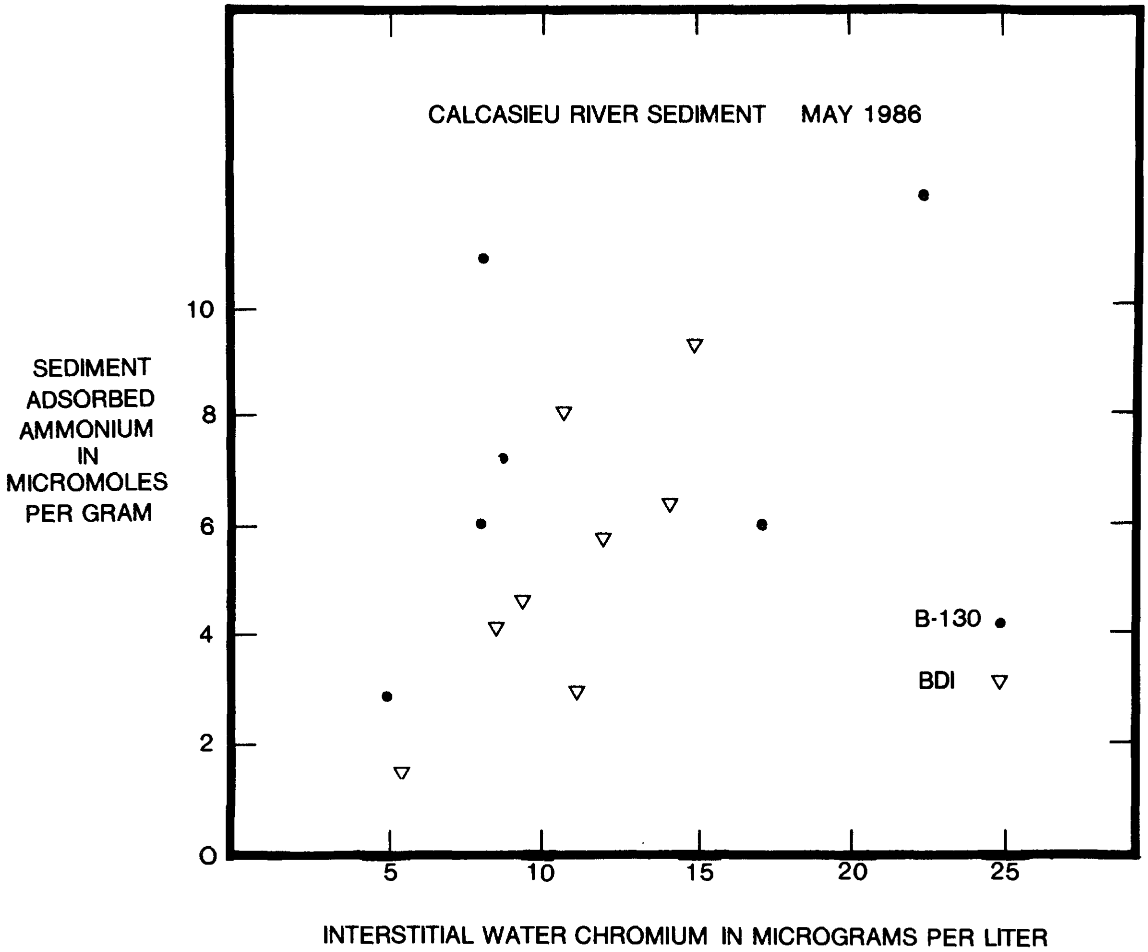


Figure B–7.--Comparison of sediment adsorbed ammonium to interstitial-water chromium.

Because sulfide produced during the microbial oxidation of organic matter by sulfate reduction would precipitate FeS, interstitial water in sulfate-reducing sediment would not be expected to have elevated Fe concentrations. However, the interstitial water concentrations of those metals that do not readily precipitate as sulfides could increase. Cr is not readily precipitated by sulfide; therefore, elevated interstitial water concentrations of Cr would not necessarily correlate with interstitial-water concentrations of Fe. Interstitial water in Calcasieu River sediments from B-130 and BDI, where sulfate reduction appears to occur, do not increase in dissolved Fe concentrations with depth in the sediment. Interstitial-water concentrations of Cr do tend to increase with depth in the sediment. Cr added to interstitial water from these sediment solids could have been coprecipitated with amorphorous Fe oxides or have been organically bound. At the same intervals where interstitial-water concentrations of Cr are elevated, sediment adsorbed ammonium concentrations are also elevated.

PRELIMINARY CONCLUSIONS

1. On the basis of preliminary data, it was concluded that air-dried and freeze-dried sediment can be used in metal extraction procedures with results that are statistically the same.

2. Data collected during the reconnaissance study may overestimate the Cr concentrations in Calcasieu River sediment.

3. Elevated sediment adsorbed ammonium concentrations may be an indicator of elevated interstitial-water trace-metal concentrations.

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PROPERTIES OF CALCASIEU RIVER AND SUWANNEE RIVER HUMIC SUBSTANCES THAT AFFECT CONTAMINANT SOLUBILITY ENHANCEMENT

By Cary T. Chiou[1] and Jerry A. Leenheer[1]

One important consequence of dissolved organic matter in natural waters is that this organic matter can markedly enhance the apparent water solubility of some otherwise extremely insoluble organic contaminants. These solubility enhancements thus affect the mobility and behavior of these contaminants in the aquatic environment. From a practical standpoint, it is of interest to elucidate the mechanism causing this effect and the magnitude of this effect in relation to the molecular properties of the dissolved organic matter and contaminants.

In an earlier study, we determined the solubility enchancement effect of organic solutes by dissolved humic substances of soil and aquatic origins. The enhancement effect was effectively explained in terms of a partition-like interaction of solutes with dissolved humic substances. The solubility enhancement of a solute by dissolved organic matter (DOM), or dissolved organic carbon (DOC), can be expressed as:

$$S_w^* = S_w\,(1 + XK_{dom}) \tag{1}$$

or

$$S_w^* = S_w\,(1 + XK_{doc})\ , \tag{2}$$

where

S_w^* = apparent water solubility of the solute in the organic-matter solution;
S_w = solubility of the solute in "pure water;"
X = concentration of DOM or DOC, in grams per milliliter of water
K_{dom} = partition coefficient of the solute between DOM and water; and
K_{doc} = partition coefficient of the solute between DOC and water.

Dissolved humic substances in the earlier study consisted of humic and fulvic acids isolated from a sample of Sanhedron soil collected from northern California and humic and fulvic acids extracted from a sample collected from the Suwannee River near Fargo, Ga. Because of the sensitivity of their solubility to dissolved humic substances, p,p-DDT, 2,4,5,2'5'-PCB, and 2,4,4'-PCB were selected as test solutes (contaminants).

In general, the magnitude of solubility enhancement (S_w^*/S_w) for various solutes by a given dissolved humic substance at a given DOM concentration is inversely related to solute solubility in pure water (S_w). The difference in K_{dom} (or K_{doc}) for a solute is related to the molecular size and abundance of nonpolar organic moiety of the dissolved humic substance. For ordinary humic substances of relatively large molecular weights, the enhancement effects are largely related to their polarities (as approximated by their oxygen-to-carbon ratios).

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[1] U.S. Geological Survey, Denver, Colorado

Because the molecular composition and configuration of dissolved humic substances is expected to vary with their source, we have extended our investigation on the solubility enhancement effect with a humic extract isolated from a sample from the Calcasieu River near Oberlin, La., and compared the results with earlier data. The Calcasieu River humic extract (humic and fulvic acids) has a higher carbon-to-oxygen content relative to that for the Suwannee River humic (or fulvic) acid used earlier. The elemental data of the Calcasieu River humic extract, Sanhedron soil humic acid, and Suwannee River humic and fulvic acids are listed in table B-5. The observed solubility enhancement effects (log K_{doc} values) for p,p'-DDT, 2,4,5,2',5'-PCB, and 2,4,4'-PCB with these humic samples are listed in table B-6.

Table B-5.—Ash-free elemental contents of Sanhedron soil humic acid, Calcasieu River humic extract, and Suwannee River humic and fulvic acids

Sample	Percentage on moisture-free basis							
	C	H	O	N	S	P	Total	Ash
Sanhedron soil humic acid	58.03	3.64	33.59	3.26	0.47	0.10	99.09	1.19
Calcasieu River humic extract	56.68	4.69	35.72	1.14	.64	—	98.87	3.63
Suwannee River humic acid	54.22	4.14	39.00	1.21	.82	.01	99.40	3.18
Suwannee River fulvic acid	53.78	4.24	40.28	.65	.60	.01	99.56	.68

The results in table B-6 indicate that the Calcasieu River humic extract is about as effective as the Sanhedron soil humic acid and about five times as effective as the Suwannee River humic-fulvic acids. The difference in log K_{doc} values among the humic substances is consistent with the polarity effect as postulated. The relative inability of a more polar humic substance (such as the Suwannee River humic-fulvic acids) in solubility enhancement may be attributed to its lack of sizeable regions of intense nonpolar molecular moiety (such as aromatic or branched aliphatic groups) for promoting a partitionlike interaction with relatively nonpolar organic solutes. The following analysis provides some information on the likely molecular environment (structure) for the Calcasieu River humic extract and Suwannee River fulvic acid.

Table B-6.—Comparison of log K_{doc} values of p,p'-DDT; 2,4,5,2',5'-PCB; and 2,4,4'-PCB for sources of dissolved organic carbon

Source of dissolved organic carbon	log K_{doc}		
	p,p'-DDT	2,4,5,2',5'-PCB	2,4,4'-PCB
Calcasieu River humic extract	4.93	4.81	4.24
Sanhedron soil humic acid	5.06	4.87	4.40
Suwannee River humic acid	4.39	4.07	3.54
Suwannee River fulvic acid	4.40	4.10	3.57

The Calcasieu River humic extract has a lower number-average molecular weight (600 daltons) than the Suwannee River fulvic acid (750 daltons). The carboxyl-group content of the Calcasieu River humic extract is 5.1 meq/g (milliequivalents per gram) compared to 6.2 meq/g for the Suwannee River fulvic acid. About three-fourths of the difference in oxygen contents of the Calcasieu and Suwannee River samples in table B-5 can be attributed to difference in carboxyl-group content. The fraction aromatic carbon (fa), which has been assumed to be a factor affecting the contaminant partitioning, is only slightly greater for the Calcasieu River humic extract (fa=35 percent C) than for the Suwannee River fulvic acid (fa=32 percent C).

The fivefold increase in the K_{doc} value for the Calcasieu River humic extract compared to that for the Suwannee River fulvic acid cannot be explained based solely on molecular weight or fraction aromaticity differences. It is also unlikely that a 4.56 percent difference in oxygen content (table B-5) or a 18 percent difference in carboxyl-group content can completely explain the much greater K_{doc} value for the Calcasieu River humic extract that has a smaller average molecular size if oxygen is uniformly distributed throughout the molecular network.

Proton nuclear magnetic resonance spectra show significant differences in molecular configuration between the Calcasieu River humic extract and the Suwannee River fulvic acid. About 30 to 50 percent of the carboxyl groups in the Suwannee River fulvic acid terminate with straight-chain, aliphatic hydrocarbon structures, whereas the carboxyl groups in the Calcasieu River humic extract are attached to branched aliphatic, alicyclic, or aromatic hydrocarbon structures. Therefore, a significant factor that may affect the K_{doc} values may be the adjacent intense nonpolar-environment to the carboxyl group as well as the absolute quantity of carboxyl groups.

A preliminary study of the water solubility enhancement of DDT by some well-defined dissolved organic substances provides additional support for the kind of molecular environment in DOM that is important for promoting partition interactions with organic solutes. In an aqueous solution containing 100 mg/L (milligrams per liter) of sodium dodecylsulfate, a straight-chain hydrocarbon, no significant enhancement was detected for the solubility of DDT. This finding is in contrast to a large (about fivefold) solubility enhancement of DDT that was detected in an aqueous solution containing 100 mg/L of Triton X-100[2], a surfactant with a branched octyl group attached to a benzene ring in one end and ethylene oxide groups in the other, which contains sizeable regions of nonpolar organic environment.

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

DETERMINATION OF HALOGENATED ORGANIC COMPOUNDS IN ESTUARINE BIOTA AND SEDIMENTS BY CHEMICAL IONIZATION TANDEM MASS SPECTROMETRY

By Colleen E. Rostad[1] and Wilfred E. Pereira[1]

Biota and sediment samples from near a contaminated industrial site were initially analyzed by capillary gas chromatography/electron impact mass spectrometry (GC/EIMS). The samples contained fatty acids, aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, and sterols that interfered with determination of the halogenated compounds of interest (halogenated benzenes, styrenes, and polycyclic aromatics). Rather than do further laborious sample cleanup, the mode of ionization in the mass spectrometer was changed to more halogen-specific conditions. Halogenated standards were analyzed under positive and negative ion chemical ionization (CI) by using methane as reagent gas, and conditions were optimized for maximum production of molecular ions. For some of the less halogenated compounds, positive ion CI produces a more intense signal than negative ion CI; however, positive ion CI is less specific for halogenated compounds, and interferences from the sample matrix are probable. Negative ion CI, on the other hand, involves ion formation by electron capture, a process specific to halogenated compounds. Analysis of crab tissue taken near the industrial outfall by GC/negative ion CI mass spectrometry revealed highly halogenated biphenyls and biphenyl ethers not previously seen by GC/EIMS. The molecular ions produced were then subjected to collision activated decomposition (CAD) using argon for the collision gas. After ionization in the ion source, the first quadrupole allowed only molecular ions through to the collision cell, where the CAD occurred, and the ions produced by this fragmentation then were analyzed by scanning the third quadrupole. By use of the GC for separation, only the molecular ions for the entire selected halogenated series were passed through the first quadrupole. Daughters of the positive ion CI-generated molecular ions were analyzed in the third quadrupole. Interference from the fatty acids, aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, and sterols present in the samples were eliminated. The technique was applied to the biota and sediment samples. By scanning for the characteristic neutral loss of the fragment, COCl, by polychlorinated dibenzo-p-dioxins, the bottom sediment from the industrial outfall was screened for tetra-, hexa-, hepta-, and octachlorodibenzo-p-dioxins. Analysis by solid probe of an octachlorodibenzo-p-dioxin (OCDD) standard, sediment sample, and an OCDD-spiked sediment sample verified the technique. The dioxins were not present in the bottom sediment.

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[1] U.S. Geological Survey, Denver, Colorado

(p. 87 follows)

CONTAMINATION OF ESTUARINE SEDIMENTS, WATER, AND BIOTA BY HALOGENATED ORGANIC COMPOUNDS, CALCASIEU RIVER ESTUARY, LOUISIANA

By Wilfred E. Pereira[1], Colleen E. Rostad[1], and Cary T. Chiou[1]

Preliminary studies conducted in the vicinity of an industrial outfall in the Calcasieu River Estuary, La., indicated that bottom and suspended sediments, water, and biota were contaminated by halogenated organic compounds (HOC) derived from the manufacture of trichloroethylene and tetrachloroethylene. These compounds included chlorinated benzenes, naphthalenes, styrenes, and butadienes (Demas and others, in press). Because of the tendency of these compounds to partition into organic matter associated with sediments and bioconcentrate in lipid tissue of aquatic organisms, a field study was designed to investigate the distribution of these compounds in different compartments of this estuarine system such as bottom and suspended sediments, the water column, and biota. This report presents the results of this field study and discusses the possible effects of estuarine dynamics on the distributions of HOC among these compartments.

Sampling locations for this study are shown in figure B-8. Biota species investigated are shown in table B-7. Bottom sediments were collected with a petite Ponar[2] grab sampler, and suspended sediments were collected by dewatering a large volume of river water using a Pellicon tangential-flow filtration system. Methodology was developed for extraction, concentration, isolation, identification, quantitation, and confirmation of HOC in bottom and suspended sediments, the water column, and biota. Determination of analytes of interest was accomplished by gas chromatography/mass spectrometry (GC/MS). To compare uptakes of HOC by sediments and biota, concentrations were normalized to organic carbon content in the case of sediments, and to lipid content for biota.

The effects of salinity on the distribution and concentations of HOC was studied by determining their octanol/water (K_{ow}) and octanol/Bayou d'Inde water (K_{ow*}) partition coefficients. These results are shown in table B-8. Data in table B-8 indicate that, in general, K_{ow*} values are about 20 percent greater than K_{ow} values, indicating that the solubility of these compounds in saline water is decreased as a result of a "salting-out" effect; consequently, sediments and lipid tissue of biota probably are major sinks for these compounds, affecting their transport and fate in the Calcasieu River Estuary.

Concentrations of HOC in sediments and water collected near the industrial outfall are shown in table B-9. Concentrations in suspended sediment were greater than concentrations in the water column, but substantially less than concentrations in bottom sediments; hexachloro-1,3-butadiene (HCBD), pentachlorobenzene (5 Cl), and hexachlorobenzene (6 Cl) were the major HOC identified.

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[1] U.S. Geological Survey, Denver, Colorado

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

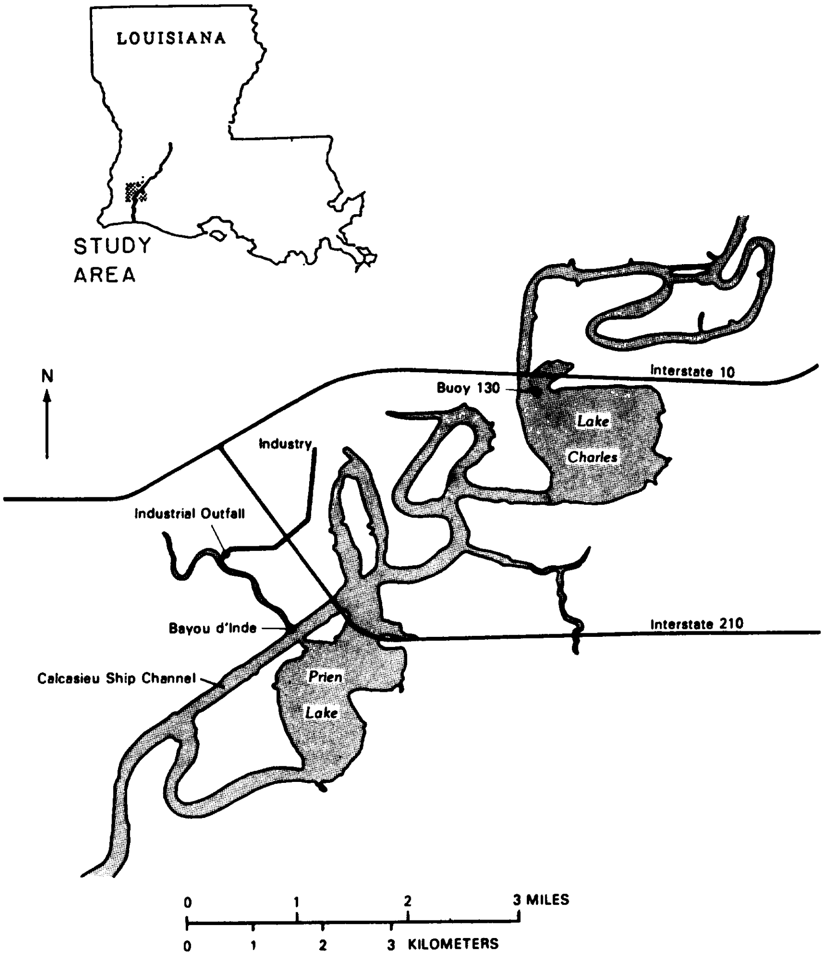


Figure B-8.--Location of lower Calcasieu River sampling sites.

Table B-7.—Biota species selected for field study

Common name	Genus and species	Number of individuals for analysis	Lipid content (percent)
Atlantic croakers	*Micropogonias undulatus*	6	2.2
Blue crabs	*Callinectes sapidus*	6	.49
Spotted sea trout	*Cynoscion nebulosis*	4	2.3
Blue catfish	*Ichtalurus furcatus*	6	3.3

Table B-8.—Partition coefficients of selected halogenated organic compounds

[K_{ow} = octanol/distilled water partition coefficient;
K_{ow*} = octanol/Bayou d'Inde water partition coefficient]

Compound	Log K_{ow}	Log K_{ow*}	$\frac{Kow*}{Kow}$
Chlorobenzene	2.84	2.92	1.20
1,3-dichlorobenzene	3.50	3.85	1.20
1,4-dichlorobenzene	3.47	3.56	1.23
1,2-dichlorobenzene	3.49	3.56	1.17
1,3,5-trichlorobenzene	4.31	4.40	1.23
1,2,4-trichlorobenzene	4.02	4.09	1.18
1,2,3-trichlorobenzene	4.14	4.20	1.15
1,2,3,5-tetrachlorobenzene	4.59	4.67	1.20
1,2,4,5-tetrachlorobenzene	4.70	4.71	1.02
1,2,3,4-tetrachlorobenzene	4.60	4.67	1.18
Pentachlorobenzene	5.20	5.27	1.18
Hexachlorobenzene	5.50	5.59	1.23
Hexachloro-1,3-butadiene	4.90	5.17	1.86

Table B-9—Concentrations of halogenated organic compounds in sediments and water in Bayou d'Inde near the industrial outfall

[Nd, not detected]

Compound	Bottom sediments[1] (microgram per gram organic carbon)	Suspended sediments (microgram per gram organic carbon)	Water (nanogram per liter)
Chlorobenzene	1.5	0.22	18.0
1,3-dichlorobenzene	101.0	.98	48.0
1,4-dichlorobenzene	82.0	1.2	74.0
1,2-dichlorobenzene	7.1	Nd	9.0
1,3,5-trichlorobenzene	83.0	0.96	Nd
1,2,4-trichlorobenzene	306.0	4.9	40.0
1,2,3-trichlorobenzene	9.6	0.49	12.0
1,2,3,5-tetrachlorobenzene 1,2,4,5-tetrachlorobenzene	102.0	4.85	42.0
1,2,3,4-tetrachlorobenzene	48.0	2.5	9.0
Pentachlorobenzene	1,110.0	16.4	32.0
Hexachlorobenzene	7,544.0	33.7	8.0
Hexachloro-1,3-butadiene	1,148.0	23.5	1,298.0
Octachlorostyrene[2]	56.0	5.6	Nd
Octachloronaphthalene[2]	12.0	.81	Nd

[1] Values reported are for combined sand and fine fractions.

[2] Values determined by positive ion, methane chemical ionization.

Concentrations of HOC in blue catfish collected at the three sampling sites are shown in table B-10. Concentrations in blue catfish collected at the junction of Bayou d'Inde and the Calcasieu River were greater than concentrations collected at buoy 130 in Lake Charles, but less than concentrations collected near the industrial outfall, indicating greater exposure levels to blue catfish near the industrial outfall. Data in tables B-9 and B-10 indicate that HOC signatures (compositions) in sediments, water, and blue catfish were different, indicating different rates of uptake and elimination of individual isomers as affected by the hydrodynamics of the system or temporal and spatial variations of concentrations of HOC in the water column.

Table B-10.—Concentrations of halogenated organic compounds in catfish

[Microgram per gram lipid, Nd, not detected]

Compound	Sampling site		
	Lake Charles (buoy 130)	Junction of Calcasieu River and Bayou d'Inde	Bayou d'Inde (near industrial outfall)
Chlorobenzene	Nd	0.05	Nd
1,3-dichlorobenzene	0.03	.12	.19
1,4-dichlorobenzene	.17	.24	.47
1,2-dichlorobenzene	Nd	.06	.11
1,3,5-trichlorobenzene	Nd	.25	.48
1,2,4-trichlorobenzene	Nd	1.9	3.9
1,2,3-trichlorobenzene	Nd	.37	.77
1,2,3,5-tetrachlorobenzene 1,2,4,5-tetrachlorobenzene	0.7	3.4	7.2
1,2,3,4-tetrachlorobenzene	.03	1.9	3.8
Pentachlorobenzene	.41	12.0	36.0
Hexachlorobenzene	.61	7.7	27.0
Hexachloro-1,3-butadiene	1.0	46.0	120.0
Octachlorostyrene	Nd	.30	2.1
Octachloronaphthalene	Nd	Nd	Nd

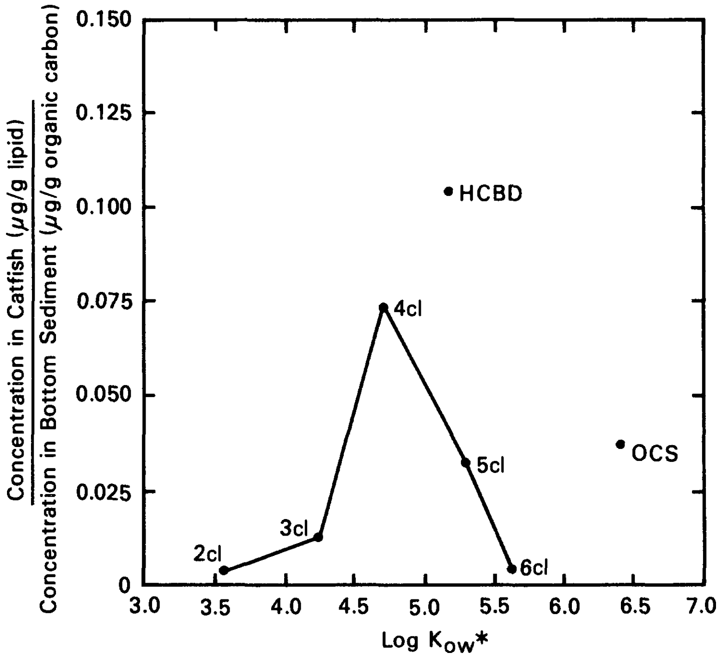
Concentrations of HOC in four different biotic species are shown in table B-11. Data in table B-11 indicate considerable species variability resulting from biouptake, bioelimination, and probably exposure time and concentrations of HOC. HOC concentrations in these biotic species are orders of magnitude greater than corresponding concentrations in the water column, indicating that these species bioconcentrate HOC; therefore, they influence the transport of HOC in the Calcasieu River.

Table B-11.—Concentrations of halogenated organic compounds in biota from the Calcasieu River at the junction with Bayou d'Inde

[Microgram per gram lipid, Nd, not detected]

Compound	Atlantic croakers	Blue crabs	Spotted sea trout	Blue catfish
Chlorobenzene	0.10	0.41	0.18	0.05
1,3-dichlorobenzene	.19	.35	.09	.12
1,4-dichlorobenzene	.60	2.5	.90	.24
1,2-dichlorobenzene	.08	.26	.06	.06
1,3,5-trichlorobenzene	.38	.42	.05	.25
1,2,4-trichlorobenzene	2.3	3.2	.14	1.9
1,2,3-trichlorobenzene	.42	.71	.02	.37
1,2,3,5-tetrachlorobenzene 1,2,4,5-tetrachlorobenzene	4.7	7.5	.79	3.4
1,2,3,4-tetrachlorobenzene	2.6	4.5	.43	1.9
Pentachlorobenzene	27.0	42.0	2.9	12.0
Hexachlorobenzene	21.0	41.0	7.3	7.7
Hexachloro-1,3-butadiene	41.0	12.0	15.0	46.0
Octachlorostyrene	Nd	1.0	.16	.30
Octachloronaphthalene	Nd	Nd	Nd	Nd

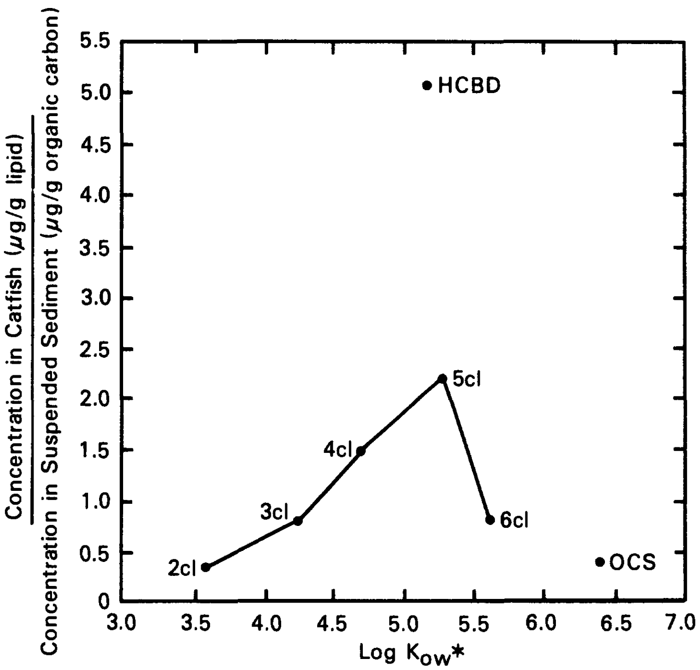
Relative concentration factors of HOC in blue catfish collected near the industrial outfall (ratio of the concentration in blue catfish to the concentration in bottom sediment) as a function of log K_{ow*}, are shown in figure B-9. In the chlorobenzene series, a slight linear increase in relative concentration factors is observed with dichlorobenzenes and trichlorobenzenes, followed by a marked increase for tetrachlorobenzenes, and a subsequent rapid decrease for pentachlorobenzene and hexachlorobenzene. Data for HCBD and octachlorostyrene (OCS) are included for comparison. These results indicate that compounds with log K_{ow*} values less than 5.2 show a greater tendency toward equilibrium with respect to lipid tissue of blue catfish. In comparison, compounds with log K_{ow*} values greater than 5.2 probably are associated more with bottom sediments; therefore, they are desorbed more slowly into the water column; hence, they are less bioavailable to blue catfish, that is, they are subject to more kinetic limitations in attaining equilibrium with biota. Because relative concentration factors based on laboratory equilibrium studies are likely to be in the range of 3 to 6 (Chiou, 1985; Oliver, 1984), the small values observed (<1) in this study indicate that HOC concentrations in blue catfish are less than concentrations to be expected under equilibrium conditions.



2Cl, dichlorobenzenes;
3 Cl, trichlorobenzenes
4 Cl, tetrachlorobenzenes
5 Cl, pentachlorobenzene
6 Cl, hexachlorobenzene
HCBD, hexachloro-1,3-butadiene
OCS, octachlorostyrene.

Figure B-9.—Relative concentration factors of halogenated organic compounds in blue catfish (blue catfish/bottom sediment) collected near the industrial outfall as a function of log K_{ow*}.

Relative concentration factors of HOC between blue catfish and suspended sediments collected near the industrial outfall as a function of log K_{ow*} are shown in figure B–10. A linear increase in relative concentration factors is indicated for the chlorobenzenes, with a maximum for pentachlorobenzene followed by a marked decrease for hexachlorobenzene. Data for HCBD and OCS are included for comparison. In contrast to the results for the blue-catifish/bottom-sediment system, relative concentration factors for the blue-catfish/suspended-sediment system are much greater in magnitude, and they are reasonably close to equilibrium values. The fact that HOC concentrations in suspended sediment and blue catfish are much closer to equilibrium concentrations appears to result from a more rapid exchange of HOC between suspended sediment, the water column, and lipid tissue of fish. Hence, HOC associated with suspended sediment are more available to blue catfish and probably other aquatic species as well.



2Cl, dichlorobenzenes;
3 Cl, trichlorobenzenes
4 Cl, tetrachlorobenzenes
5 Cl, pentachlorobenzene
6 Cl, hexachlorobenzene
HCBD, hexachloro-1,3-butadiene
OCS, octachlorostyrene.

Figure B–10.—Relative concentration factors of halogenated organic compounds in blue catfish (blue catfish/suspended sediment) collected near the industrial outfall as a function of log K_{ow*}.

Bioconcentration factors (ratio of concentrations of HOC isomers in four species of biota (micrograms per kilogram lipid) compared to their concentration in Bayou d'Inde water (micrograms per liter)) are shown in table B-12. Considering the dynamics of the estuarine system and errors associated with sampling, bioconcentration factors reported are in reasonable agreement with those reported in the literature. Variability in bioconcentrtion factors for individual isomers with the same degree of chlorination, as well as for the same compound in different species, indicates nonuniformity of HOC concentrations in the water column with time and possibly differences in the rate of uptake or elimination by the organisms.

Table B-12.—Bioconcentration factors of halogenated organic compounds in four different biota species

Compound	Lipid-based log bioconcentration factors				
	Atlantic croakers	Blue crabs	Spotted sea trout	Blue catfish	Rainbow trout[1]
1,3-dichlorobenzene	3.60	3.86	3.25	3.40	3.70-4.02
1,4-dichlorobenzene	3.91	4.53	4.09	3.51	3.64-3.96
1,2-dichlorobenzene	3.94	4.46	3.79	3.82	3.51-3.80
1,3,5-trichlorobenzene	4.40	4.45	3.51	4.22	4.34-4.67
1,2,4-trichlorobenzene	4.76	4.90	3.54	4.68	4.19-4.56
1,2,3-trichlorobenzene	4.54	4.77	3.13	4.49	4.15-4.47
1,2,3,5-tetrachlorobenzene	5.05	5.20	4.27	4.90	[2]4.86
1,2,4,5-tetrachlorobenzene					4.80-5.17
1,2,3,4-tetrachlorobenzene	5.46	5.70	4.68	5.30	4.80-5.13
Pentachlorobenzene	5.93	6.12	4.96	5.57	5.19-5.36
Hexachlorobenzene	6.42	6.71	5.96	5.98	5.16-5.37
Hexachloro-1,3-butadiene	4.50	3.97	4.06	4.55	4.84-5.29

[1] Data from Oliver and Niimi (1983).

[2] Data (in guppies) from Konemann and van Leeuwen (1980).

Because of the recognized importance of lipids in aquatic bioconcentration of pollutants, the relation between log bioconcentration factors (BCF) and log K_{t-w} (triolein-water partition coefficients) was examined for HOC in four biotic species. Triolin has been determined to be a good model surrogate lipid in bioconcentration of lipophilic compounds. A plot of log BCF (on a lipid basis) for the four species of biota against log K_{t-w} for compounds listed in table B-7 is shown in figure B-11. There is reasonable linear correlation between log BCF and log K_{t-w} (r^2=0.57; n=44), indicating that the lipid tissue of biota is the major component for bioconcentration. Although the data in figure B-11 have some degree of scattering that reflects the dynamic nature of the system, most data points are reasonably close to the equilibrium correlation line, assuming BCF=K_{t-w}. The scattering of data points appears to be random, indicating no apparent relation to the biotic species. Results in figure B-11 also indicate that the lipid tissue of biota probably equilibrates more rapidly with the water column than with bottom or suspended sediments. Therefore, reasonable estimates of field BCF values can be made on the basis of concentrations in water, the lipid content in biota, and the equilibrium K_{t-w} values. Equilibrium-distribution patterns provide a useful basis for assessing the effects of system dynamics on the fate and transport of HOC in estuarine systems.

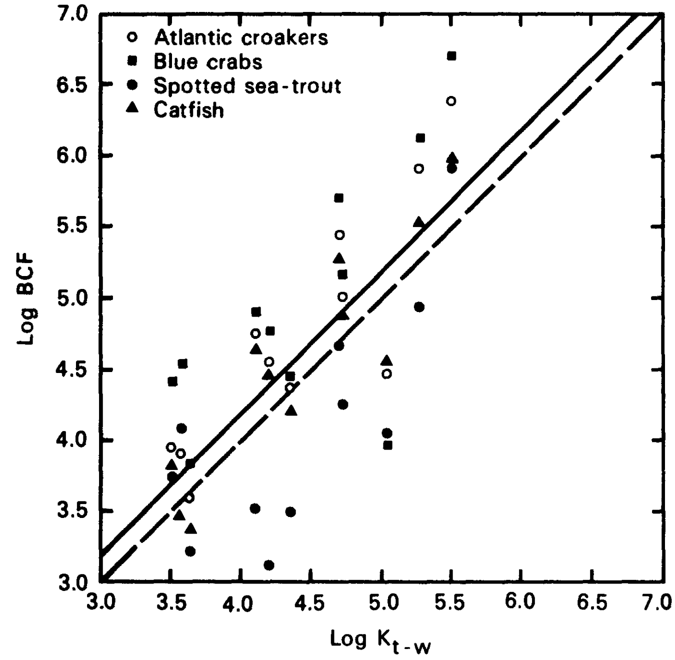


Figure B-11.—Correlation of log BCF (on a lipid basis) with log K_{t-w} in four different species of biota. The dashed line is the equilibrium correlation line, assuming BCF = K_{t-w}.

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OCCURRENCE AND FATE OF VOLATILE ORGANIC COMPOUNDS UNDER DIFFERENT WIND AND SAMPLING CONDITIONS IN THE LOWER CALCASIEU RIVER, LOUISIANA

By Charles R. Demas[1], Dennis K. Demcheck[1], and Philip B. Curwick[1]

Volatile organic compounds in water were sampled under different wind and sampling conditions on three occasions to determine the distribution of and possible modes of transport and fates of these compounds in the lower Calcasieu River, La. This paper describes the results of the sampling surveys.

Water samples were collected during moderate (15.3 miles per hour) and low (7.5 miles per hour) wind conditions in May and August 1985 from a reach of the lower Calcasieu River that extends from Lake Charles to Burton Landing (fig. B-12). Samples were depth integrated and collected under similar temperature and specific conductance profiles in the water column. Results indicated that only four volatile organic compounds were detected at two sites during moderate wind conditions compared to six compounds detected at four sites during low wind conditions. Also, volatile organic compounds such as bromoform (fig. B-13), chloroform, 1,2 dichloroethane, and chlorodibromomethane were found in concentrations as much as five times greater during the low wind conditions as compared to moderate wind conditions. These results indicate the importance of wind intensity in determining the presence or absence of volatile organic compounds in the aquatic environment.

Water samples also were collected at different depths in the water column from the same reach to determine the effects of different densities of organic compounds and specific conductance profiles on the distribution of volatile organic compounds in the lower Calcasieu River. Samples were collected in May 1986 during low wind conditions (6.9 miles per hour). Results (fig. B-14) indicated that the different densities of organic compounds investigated had little effect on the vertical distribution of these volatiles in the water column. Concentrations of volatile organic compounds at different depths were similar at all sites (fig. B-14) except the site at buoy 130, independent of the density of the volatile organic compound. For example, bromoform, which has a density of 2.9, had a similar vertical distribution to 1,2 dichloroethane (density 1.3) and trichloroethylene (density 1.5) and occurred in similar concentrations at all three depths sampled.

Vertical differences in concentrations were observed at the upstream site, Lake Charles (buoy 130), only and can be explained by the results of dye and specific conductance profile studies as compared to differences in compound densities. Dye studies completed in 1979 and 1987 indicate slow vertical mixing in the water column when differences exist between surface and bottom specific conductance values. These differences in specific conductance profiles were most pronounced at the Lake Charles site where the bottom sample, which had the highest concentration of volatile organic

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[1] U.S. Geological Survey, Baton Rouge, La.

compounds, occurred in a part of the water column which had a similar specific conductance value to downstream sites. In contrast, surface waters at the Lake Charles site had lower concentrations of volatile organic compounds than deeper water at this site. Surface water at the Lake Charles site was lower in specific conductance than water at downstream sites. This indicates that movement upstream of volatile organic compounds occurs along the bottom when salinity gradients exist in the lower Calcasieu River.

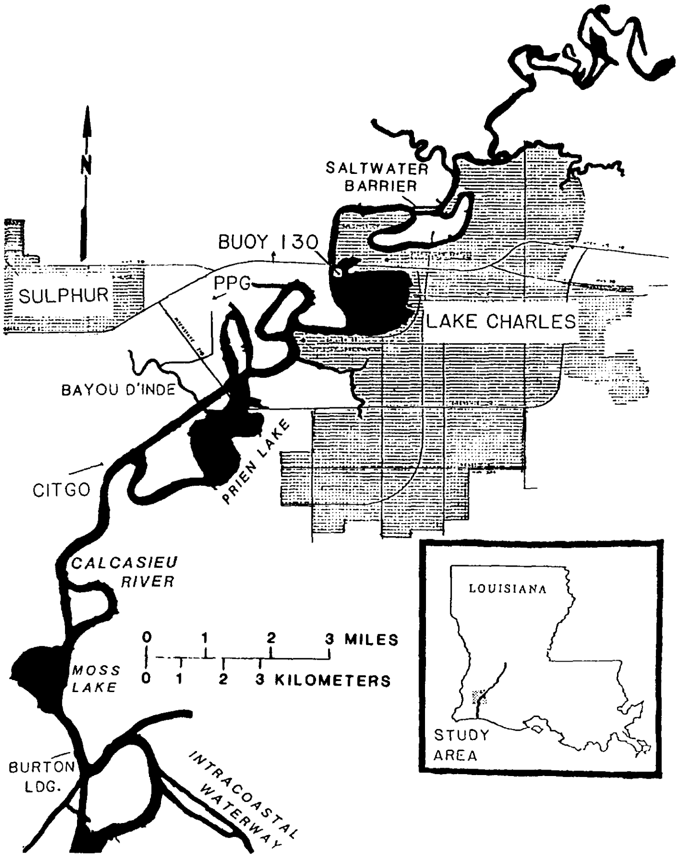

Figure B-12.—Calcasieu River intensive study area, extending from saltwater barrier to Burton Landing.

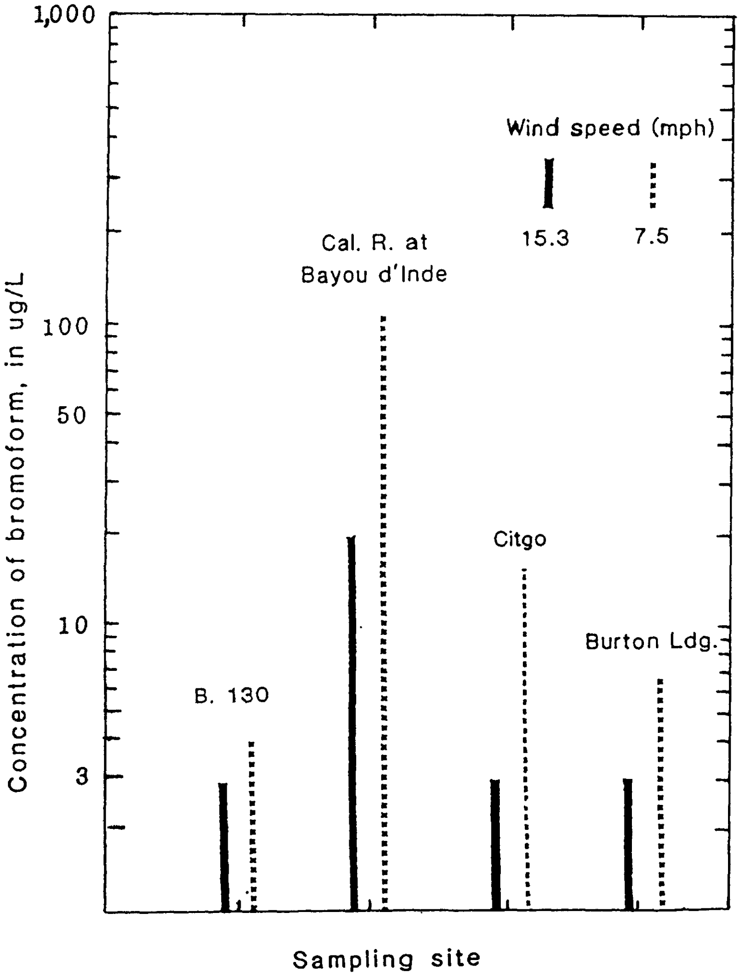

Figure B-13.—Occurrence of bromoform in the lower Calcasieu River under different wind conditions.

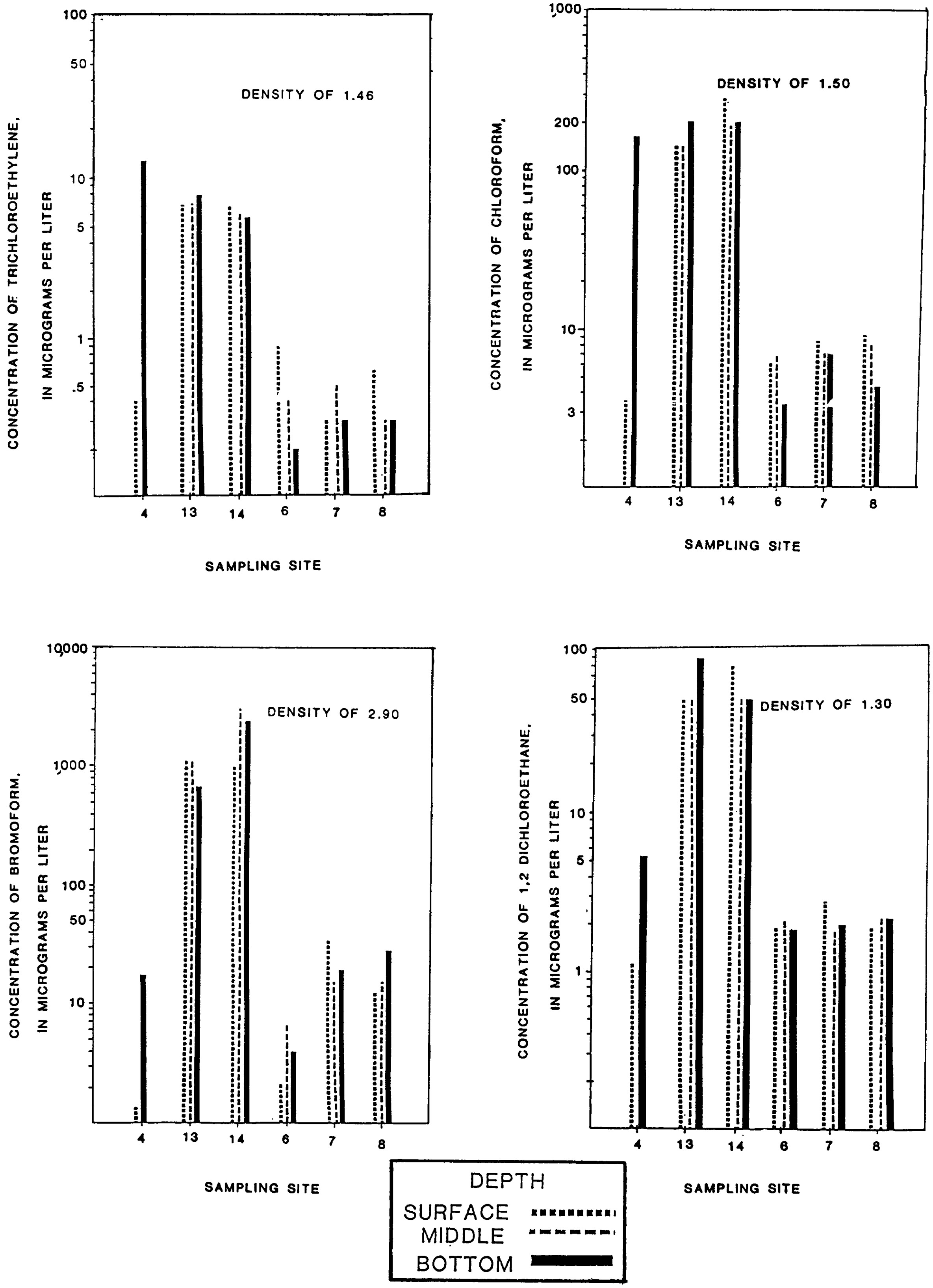

Figure B-14.—Distribution of different density volatile organic compounds in the lower Calcasieu River, May 1986.

Chapter C

OVERVIEW OF THE UPPER ARKANSAS RIVER SURFACE-WATER TOXICS STUDY NEAR LEADVILLE, COLORADO

By Briant A. Kimball[1]

INTRODUCTION

Mining of sulfide-ore deposits near Leadville, Colo., has yielded profitable quantities of gold, silver, copper, lead, zinc, iron, and bismuth (Tweto, 1968). Water flowing through abandoned mines and tailings contributes large concentrations of cadmium, copper, iron, manganese, and zinc to the Arkansas River (Moran and Wentz, 1974; Wentz, 1974). These conditions provide an opportunity to study metal-sediment interactions in a natural setting. The various metals have different reactive mechanisms as they move from the acid mine drainages to the neutral Arkansas River. Some metal concentrations, notably manganese concentrations, remain large downstream from the primary drainage sources; most other trace metals are removed from solution in the Arkansas River. The metal sources in the Leadville area are well documented (Moran and Wentz, 1974); however, the reactive solute-transport processes occurring in stream channels are not well quantified.

An interdisciplinary study of geochemical controls on metal concentrations in streams of the Leadville area will provide a better understanding of the reactive mechanisms that affect metal concentrations during transport in mountain streams that are affected by mine drainage. The study will integrate research on the hydrology, geology, biology, and chemistry of the streams. Investigating the natural processes is necessary to develop effective treatment of acid mine drainage. An interdisciplinary study of geochemical controls on metal concentrations in streams of the Leadville area was begun in April 1986. The objectives of the Upper Arkansas Surface-Water Toxics study are to:

1. Characterize the chemical processes that control the transport and distribution of metals in streams of the Leadville area.
2. Characterize the chemistry of sediment that controls the dissolved concentrations of metals.
3. Quantify the rates of chemical and hydrologic processes that affect the metals and the stream distance in which they occur. This will help determine the extent to which chemical equilibrium has been obtained.
4. Quantify the effects of metals on biota and the effects of biota in controlling metal concentrations.

The purpose of this paper is to provide background information on the processes that may affect contaminant behavior in the headwaters of the Arkansas River and to provide an overview of the research currently underway in this study.

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[1] U.S. Geological Survey, Denver, Colorado

DESCRIPTION OF STUDY AREA

The headwaters of the Arkansas River, which comprise the study area (fig. C-1), drain about 590 km^2 (square kilometers). Elevations range from about 2,700 to 4,200 m (meters) above sea level. Streamflow in the Arkansas River is sustained principally by snowmelt and ranges from about 3 to 57 m^3 (cubic meters) per second. Streamflow in the Arkansas River approximately triples in the reach of the Arkansas River shown in figure C-1. Most of the base flow is sustained by shallow ground-water systems; a small part of the base flow is thought to originate from deeper crystaline-rock formations. From 10 to 40 years of streamflow data are available for two mainstem and two tributary locations. Stream-channel slopes generally are steep to moderate and bed material consists of cobbles and gravel. Suspended-sediment concentrations are small, generally less than 10 mg/L (milligrams per liter) even during high runoff. Few sediment data are available.

WATER QUALITY

Natural water quality in the area generally is suitable for all uses; however, conditions in mine-affected areas are characterized by large concentrations of metals, such as cadmium, copper, iron, manganese, and zinc, which at times exceeded drinking-water standards in Califronia Gulch (Moran and Wentz, 1974). Specific conductance is relatively small except in mine-affected areas where values may exceed 1,500 microsiemens per centimeter at 25° Celsius. There are three main sources of acid water to streams in the area: the Yak Tunnel, which discharges to California Gulch; the Leadville Drain, which discharges to the East Fork Arkansas River; and St. Kevin Gulch, which receives acid water from tailings piles in the drainage basin (fig. C-1). Values of pH can be as small as 2.9 in mine-affected areas.

The major chemical processes in these streams probably are: (1) Acid-base reactions, which control pH and, therefore, affect the solubility of trace metals; (2) precipitaton and dissolution reactions; and (3) oxidation and reduction reactions (McKnight and others, 1984). These processes can cause amorphous iron oxides to be formed on stream sediments. Other processes, which also may affect metal transport, become important when these coatings are formed. These processes include adsorption on oxide surfaces and ion-exchange reactions.

DATA COLLECTION

A network of data-collection sites has been chosen to define the transition from water that is naturally mineralized to water that is affected by acid mine drainage. Continuous streamflow data will be obtained at three gaging stations. At each of the three main inflows of acid mine drainage and at several of the major confluences, a cluster of three sampling sites provides data about the loads of metals in or entering the Arkansas River (fig. C-1). Data collection at each site will include streamflow measurements and collection of water-quality and sediment samples. In order to document changes with time, the network includes some sites that were previously sampled by Moran and Wentz (1974).

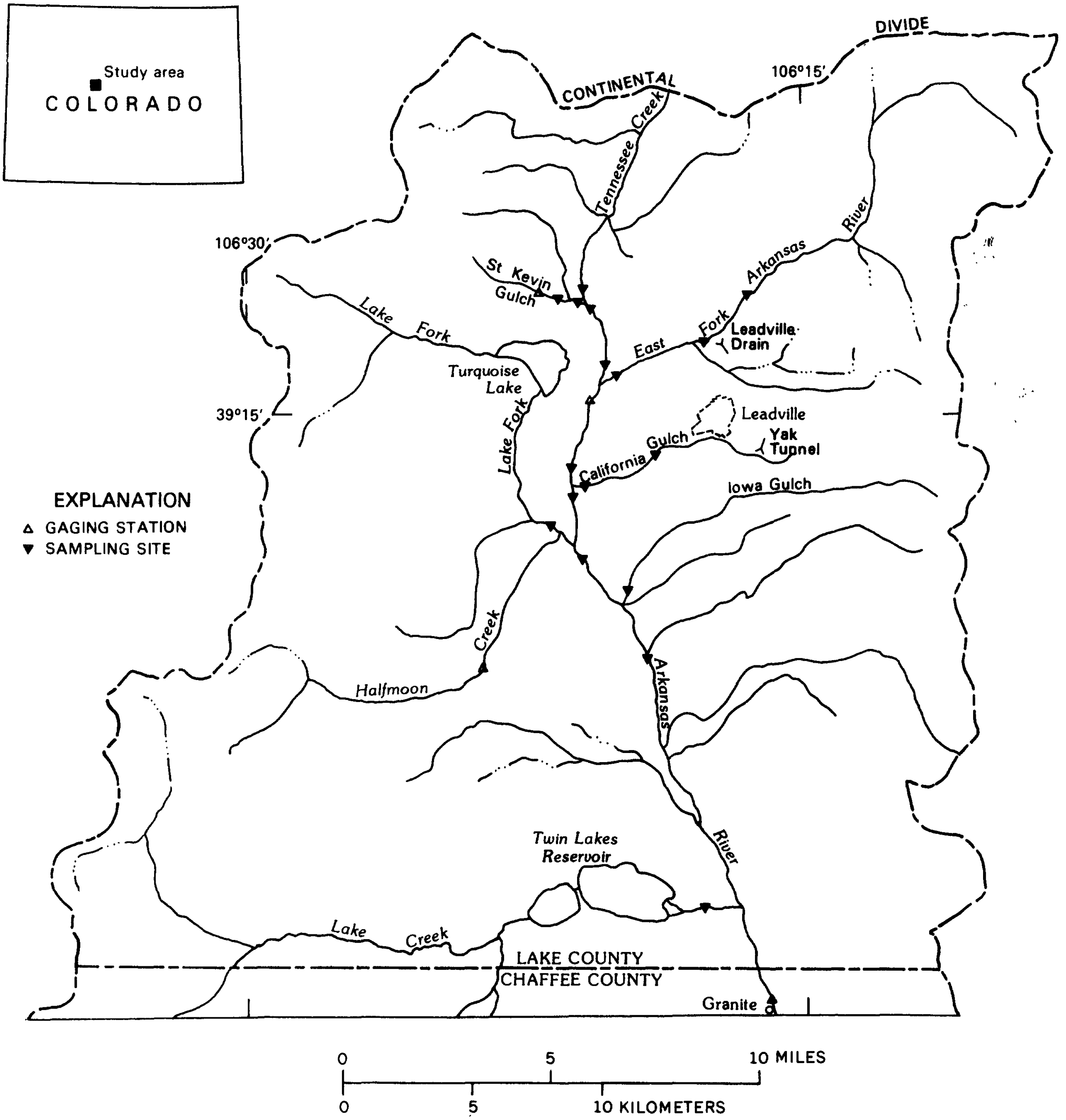

Figure C-1.—Location of study area, gaging stations, and sampling sites.

Samples of suspended sediment and bed material will be collected for determinations of suspended-sediment concentration, mineralogy, and particle-size distribution. Suspended-sediment concentrations are small, generally less than 10 mg/L. This has necessitated a technique for dewatering large volumes of sample to obtain a sufficient weight of sediment for chemical and mineralogical characterization. Bed-material samples and some suspended-sediment samples will be separated into clay, silt, and sand fractions. Organic and metallic coatings on the sediment will be analyzed by extraction procedures to determine their chemistry (Kimball, 1981). Combined with X-ray diffraction and scanning electron microscopy, the chemical analyses will be used to determine the mineral and organic phases that might control heavy-metal concentrations in the dissolved phase.

METHODS OF DATA ANALYSIS

Changes in the mineral form of coatings on bed material and suspended sediment may affect partitioning of metals between water and the bed material and suspended sediment; such changes also may affect transport rates of metals. Especially important are changes in amorphous-iron phases that occur where acid-mine drainage discharges to the Arkansas River and its tributaries. At these points of discharge, a rapid change in physical and chemical conditions causes changes in the surface chemistry of the sediment. The water chemistry at these sites will be evaluated by chemical-equilibrium models to determine if chemical equilibria control the metal concentrations (Ball and others, 1980; Parkhurst and others, 1980). Hypotheses that result from such analysis will be tested by instream-transport experiments.

In St. Kevin Gulch, an acid headwater stream, an instream-transport experiment was done in August 1986 (fig. C–2). Lithium chloride and sodium bromide were injected into the stream, as conservative tracers, to characterize baseline solute transport variables such as travel time, discharge, and dispersion through the study reach. Synoptic and diurnal sampling was done during this period of known baseline conditions. An unshaded reach of stream was used to study the photoreduction of iron (see McKnight and others, this report). During daylight hours, ferrous-iron mass flow increased throughout the reach. At night, the pattern reversed and ferric-iron mass flow increased throughout the reach. During the synoptic sampling, aluminum, cadmium, copper, manganese, and zinc generally were transported conservatively, that is, there was no loss of metal mass during transport. Iron transport was nonconservative with an exponential-type loss of iron mass downstream from the tailings inflows (see Kimball and others, this report).

A second instream-transport experiment in St. Kevin Gulch will use reactive and nonreactive solutes to analyze response of the stream system to transient perturbations in chemistry. Laboratory studies to characterize the amorphous iron hydroxides in the stream will precede this second instream-transport experiment to develop an appropriate experimental design. Results of this experiment will test chemical and hydrologic interactions, particularly with respect to the adsorption of metals on the iron-hydroxide floc. The experiment will be simulated using a stream solute-transport model (Bencala, 1984; Bencala and others, 1984).

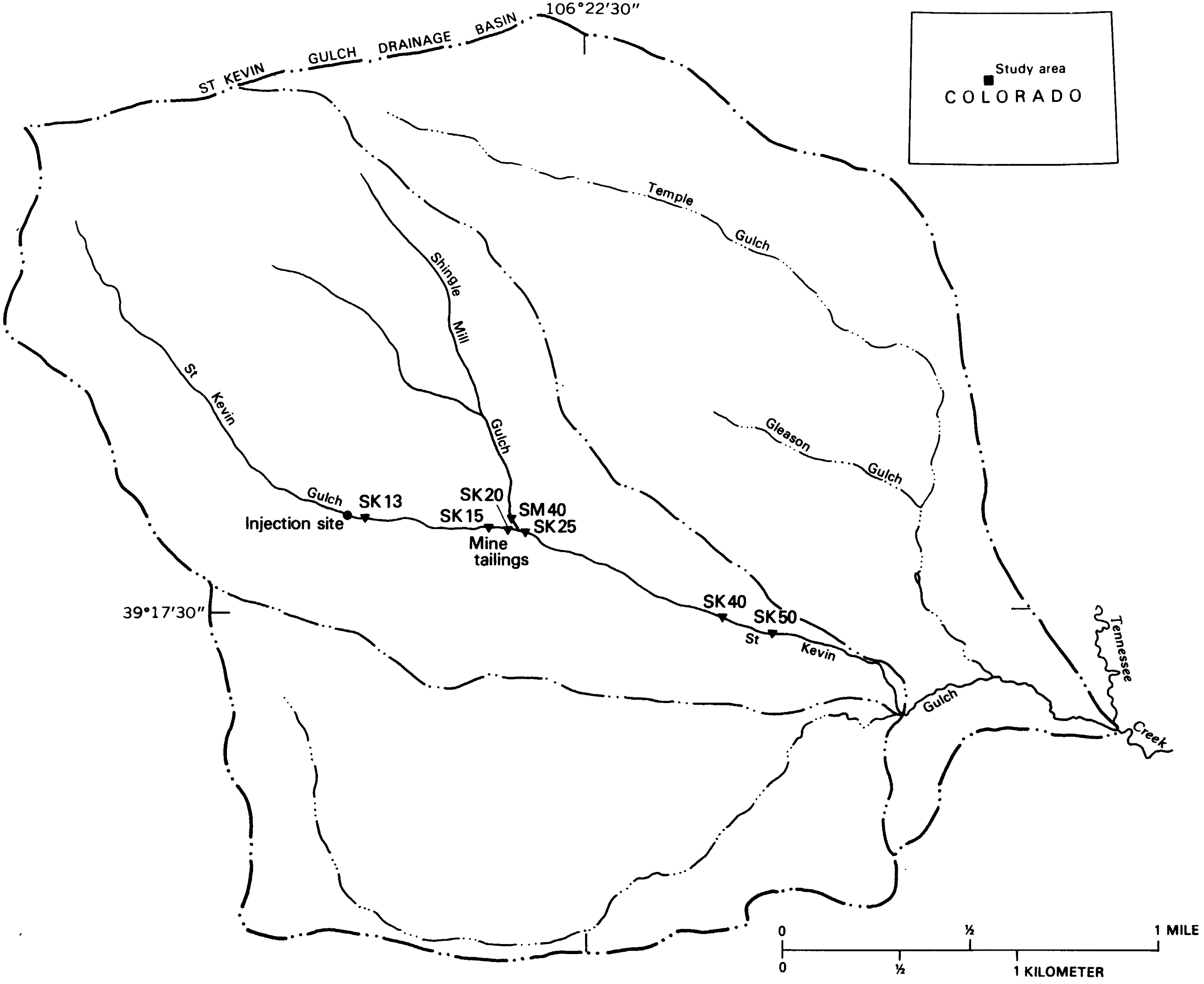

Figure C-2.--Location of instream-transport experiment in the St. Kevin Gulch drainage basin.

NEED FOR FUTURE STUDY

Future research, in addition to the second instream-transport experiment in St. Kevin Gulch, will include monthly synoptic sampling of the Arkansas River and tributaries near Leadville, downstream synoptic sampling of the Arkansas river from Leadville to Pueblo Reservoir near Pueblo, Colo., (not shown in fig. C-1), synoptic sampling of California Gulch, and studies of the effects of metals on biota. Results of this research will provide information to scientists and officials about the fate of heavy metals in streams. Effects of remedial actions, planned by the U.S. Environmental Protection Agency in California Gulch, will be evaluated if they begin during this study.

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(p. 111 follows)

MICROBIOLOGY OF THE ARKANSAS RIVER NEAR LEADVILLE, COLORADO: PRELIMINARY STUDY, 1986

By Christine L. Miller[1]

Microbiological studies were undertaken to determine the effect of the metal-rich Leadville Drain waters on the planktonic bacterial population of the Arkansas River near Leadville, Colo. On April 30, 1986, water samples were collected upstream (site EF–20) and downstream (site EF–30) from the Leadville Drain in the East Fork Arkansas River and assayed for the following: ^{3}H-glucose uptake (5 h (hours) at stream temperature), adenosine triphosphate (ATP) extraction (of 500 mL (milliliters) sample), and aerobic heterotroph plate counts (colony forming units (CFU) on nutrient agar).

The ^{3}H-glucose turnover time results shown in table C–1 correspond to uptake of 64 nCi glucose L^{-1} h^{-1} and 58.3 nCi glucose L^{-1} h^{-1} (sites EF–20 and EF–30, respectively) from samples spiked to 14,910 nCi glucose L^{-1}. The turnover time is the time required for the microbial populations to process the glucose present in the stream. The glucose concentration will be determined for the streamwater once an enzyme technique for analyzing trace levels of glucose is developed.

Table C–1.—Results of microbiological assays

	Arkansas River		Deer Creek
	4/30/86 EF–20	4/30/86 EF–30	4/30/85
Heterotrophic activity; ^{3}H-glucose uptake, turnover time (hrs.)	233	256	153
ATP (ng/L)	23.3	55.3	22.6
(M)	4.2×10^{-11}	1×10^{-10}	4.1×10^{-11}
Aerobic heterotrophs per mL (CFU on nutrient agar)	387	393	760

The plate counts were determined from serial dilutions of the sample in filter-sterilized Deer Creek water (similar to the Arkansas River in conductivity and pH, but lower in metal concentration). Deer Creek assay results for the same date 1 year previously, are provided for purposes of comparison. An important aspect of these data is that spring is a period of high fluctuation in environmental conditions and 1 day in either direction can make a large difference in the heterotrophic status.

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[1] U.S. Geological Survey, Denver, Colorado

The heterotrophic activity results indicate a slight depression in ^{3}H-glucose uptake between sites EF–20 and EF–30 (longer turnover time at site EF–30). This could be a result of an increase in metal concentration at site EF–30 or a result of an increase in the pool size of glucose in the sample at site EF–30. The Leadville Drain is a rich source of green-algae (probably Ulothrix, similar to St. Kevin Gulch) and the downstream rocks in the Arkansas River are slippery, periphyton coated. The algae could contribute glucose and other nutrients (note that dissolved organic carbon (DOC) is higher downstream, table C–2) and are probably responsible for the statistically significant higher ATP content of the downstream waters, inasmuch as the slight increase in aerobic heterotrophs (CFU on nutrient agar) is not a statistically significant increase.

Table C–2.—Physical and chemical parameters determined for the samples

	EF–20	EF–30
Time of day	10:30–11:00 a.m.	9:30–10:00 a.m.
Licor light meter reading (microeinsteins per m^2 per sec.)	1,600–1,800	1,200–1,500
Conductance (μS/cm^{-1})	125	200
Temperature (stream)	5 °C	4.5 °C
pH	7.75	7.93
Dissolved organic carbon (mg/L)	1.55	1.75
Suspended organic carbon (mg/L)	.15	.10

Of possible relevance is the observation that the ATP assay was more inhibited by streamwater at site EF–30 than by streamwater at site EF–20 (0.88 and 0.96 of the theoretical value, respectively). Because metals are known to inhibit enzymatic assays, the observed inhibition of the ATP assay may reflect the concentration of metals.

Future microbiological activity studies will need to take into account the possible difference in glucose pool size between the upstream and downstream sites, since any negative effect of the metal input might be masked by input of glucose. Also, it will be important to monitor the light intensity during sampling periods because of the pronounced effect that light is known to have on microbiological activity in Deer Creek and the Snake River, two Rocky Mountain streams at a similar altitude.

METAL-TOLERANT ALGAE IN ST. KEVIN GULCH, COLORADO

By Diane M. McKnight[1]

INTRODUCTION

Algal-species composition in aquatic environments generally is related to the chemistry of the particular stream or lake. This relation is especially common for streams contaminated by acid mine drainage where the acid conditions and high concentrations of dissolved trace metals comprise an environmental extreme that only some algal species can tolerate. On July 14, 1986, samples of periphytic algae were collected from two sites in St. Kevin Gulch, a small stream in the Rocky Mountains of Colorado contaminated with acid mine drainage (Kimball and others, this report) as part of a comprehensive study of trace metal geochemistry of St. Kevin Gulch (fig. C-3). In this report, the results from the identification and enumeration of these periphytic algae are described and the influence of acid mine drainage on these results are discussed.

STREAM SAMPLING AND SAMPLE PREPARATION

One sampling site was one of several small seeps that flow through a tailings pile at the abandoned mine. At this site, the periphyton were abundant on the rocks. The mine seepage was acidic and had high concentrations of dissolved trace metals (table C-3). The stream sampling site was in St. Kevin Gulch (sample site SK50, fig. C-3), about 2 river km (kilometers) downstream from the mine discharge, where periphytic "streamers" were abundant in the shallow stream. These streamers extended for 250 m (meters) upstream from sampling site SK50, where the stream flows through a more open area with a lesser gradient than the area near the mine discharge. At this downstream site, there is also abundant iron-hydroxide floc and the concentration of dissolved trace metals is much less than in the mine seepage (table C-3).

The water samples for chemical analysis were filtered onsite through 0.2-μm (micrometers) Nuclepore[2] filters using an Antilla hand pump. Samples were acidified with 1 mL (milliliter) Ultrex nitric acid added to 100 mL of a sample and analyzed for concentrations of cations and trace metals using a Jarrel-Ash inductively coupled plasma spectrophotometer. The pH was measured onsite using a Beckman hand-held pH meter. The periphyton samples were preserved with formaldehyde and counted and identified by Chadwick and Associates, Littleton, Colo. Light intensity was measured using a Licor quantum meter with a probe detecting photosynthetically active radiation (PAR) placed 3 cm (centimeters) below the water surface.

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[1] U.S. Geological Survey, Denver, Colorado

[2] Use of brand names or trade names in this report are for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

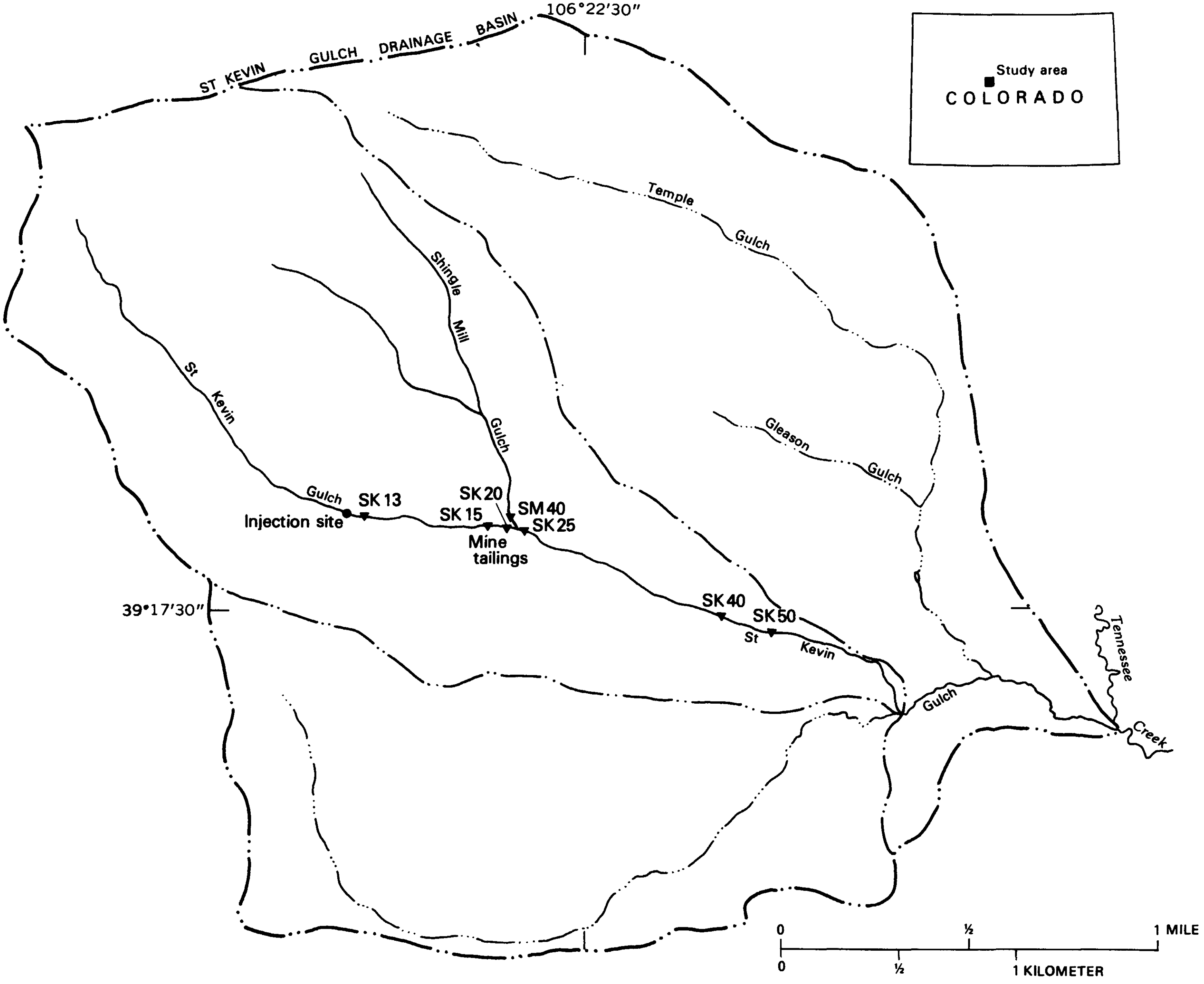

Figure C-3.--Location of mine seeps and stream sampling sites.

Table C—3.—Chemical composition of mine seepage and streamwater, July 14, 1986

[$\mu Em^{-2} s^{-1}$, microeinsteins per square meter par second; mg/L, milligrams per liter; —, no data; ND, not determined due to interferences; <, less than]

	Mine site				Stream site SK50			
	Stream[1]	Seep 1	Seep 2	Seep 3				
Time (p.m.)		2:30 to 4:30			1:30	2:30	4:30	5:35
Light intensity ($\mu Em^{-2} s^{-1}$)	-	-	-	-	2,000	600	200	175
pH	3.55	2.80	2.69	2.72	4.52	4.45	3.99	4.18
Cations (mg/L)								
Ca	11.1	—	71.1	89.6	7.04	7.24	7.35	8.42
Mg	3.78	—	22.7	31.6	2.22	2.28	2.29	2.44
Na	1.48	—	3.06	4.12	1.33	1.34	1.44	1.39
Metals (mg/L)								
Al	1.88	—	17.8	12.0	0.88	1.00	0.96	1.2
Ba	.011	—	.002	.004	.011	.010	.010	.013
Cd	.06	—	.69	.55	.027	.027	.028	.028
Co	.018	—	.32	.32	.003	.003	.004	.006
Cu	.11	—	.61	.405	.049	.048	.052	.054
Fe	3.40	—	85.6	82.4	.53	.57	.43	.67
[2]Fe_T	5.37	—	ND	ND	.70	.76	.63	1.0
[2]Fe(II)	.63	—	ND	ND	.54	.58	.35	.40
Mn	4.42	—	39.7	44.7	1.73	1.81	1.83	2.04
Ni	.024	—	.079	.084	.009	<.001	.004	.009
Pb	<.001	—	.001	<.001	<.001	<.001	<.001	<.001
Sr	.027	—	.067	.078	.022	.022	.022	.024
Zn	9.34	—	92.6	106.2	3.96	4.19	4.31	4.74

[1] Sampled at site SK20 downstream from inflow of mine seeps.

[2] Concentrations determined onsite using a 2,2-bipyridine colorimetric procedure.

RESULTS AND DISCUSSION

Algal growth was apparent in mine seep 1, but there was no algae apparent in mine seeps 2 or 3. Mine seep 3 was sampled for chemical analysis at the top of the tailings pile where a dark red precipitate was observed. The algal species distribution data for mine seep 1 (table C—4) indicate that two species of diatoms comprise 30 percent of the total algal abundance, and one green algal species comprises 70 percent of the total algal abundance. Such a minimal diversity of algal species is typical of metal-stressed aquatic environments. These three dominant species commonly are present in streams contaminated by acid mine drainage in the Rocky Mountains of Colorado (Steven Canton, Chadwick and Associates, written commun., 1986). For example, the diatom Eunotia exigua is also dominant in the Snake River, an acidic metal-enriched stream in the Rocky Mountains in Summit County, Colo., north of St. Kevin Gulch (McKnight and Feder, 1984).

Table C-4.—Species and relative abundance of periphyton taxa collected at mine seep 1 and stream site SK50 on July 14, 1986

[<, less than; —, not found]

Taxa	Relative abundance (percentage composition)	
	Mine seep 1	Stream site SK50
Bacillariophyta (diatoms)	(30 of total)	(<1 of total)
Cyclotella sp.	—	11
Eunotia exigua	71	24
Navicula accomoda	—	65
Nitzschia paleacea?	<1	—
Pinnularia hilseana	29	—
Chlorophyta (green algae)	(70 of total)	(99+ of total)
Ulothrix (prob. *subtilissima*)	99	99
Stigeoclonium sp.	<1	<1
Cyanophyta (blue-green algae)	—	(<1 of total)
Oscillatoria sp.	—	5
Phormidium sp.	—	95
Number of species	5	7

At stream site SK50, *Ulothrix subtilissima* comprised 99 percent of the total algal abundance, with only trace numbers of diatoms and blue-green algae associated with the streamers. The genus *Ulothrix* commonly forms streaming clumps in flowing streams as are found in this downstream reach of St. Kevin Gulch (Prescott, 1970). Similar algal streamers are observed in other tributaries in the upper Arkansas River system, also in association with iron-hydroxide floc. It may be that the algal streamers affect the retention of iron and other trace metals in these streams.

Another contrast between the two sites is that two species of filamentous blue-green algae are present at stream site SK50, but not at mine seep 1. The presence of these algae can be explained by the lesser tolerance of blue-green algae for acidic environments (Brock, 1973). The pH of about 4.0 to 4.5 at stream site SK50 is within the pH range of 4.0 to 5.0 that is thought to be the lower limit of acid tolerance of blue-green algae.

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MONITORING ACIDIC STREAMS FOR TRANSPORT STUDIES

By Kenneth E. Bencala[1], Diane M. McKnight[2]
Gary W. Zellweger[1], and Briant A. Kimball[2]

INTRODUCTION

Acidic streams are generally characterized by high concentrations of trace metals and the presence of hydrous metal oxides on the streambed. High potential exists for instream chemical processes to alter solute concentrations. For such streams the design of monitoring schemes to study reactive solute transport need to take into account the scales of spatial and temporal variation of both physical and chemical processes within the stream. The design of a monitoring study in St. Kevin Gulch (Leadville, Colo.) was based on previous extensive studies of the naturally acidic Snake River (Montezuma, Colo.) and the affected Leviathan Mine drainage (Alpine County, Calif.). St. Kevin Gulch is a small, affected stream in the Upper Arkansas River drainage (see fig. C-1). This paper reports the results of a study designed as a preliminary investigation of the reactivity and variation within the stream.

SNAKE RIVER—SAMPLING DURING NATURAL AND CONTROLLED CONDITIONS

Geochemical aspects of the Snake River drainage have been studied by several investigators. The data in figure C-4 show the ranges of iron concentration and pH observed in the Snake River and two tributaries, Deer Creek and Peru Creek. Deer Creek is characterized as a "pristine Rocky Mountain Stream"; however, Peru Creek is directly affected by acid mine effluent. The Snake River is acidic, even in reaches upstream of the confluence with Peru Creek. Included in figure C-4 are data from samples of small surface-water inflows to the main channels. Within the Snake River drainage, iron concentrations spanned three orders of magnitude from approximately 0.01 mg/L (milligrams per liter) to over 10.0 mg/L. The span for pH was over 5 units ($3.0 < pH < 8.1$). Although there is a general trend of increasing iron concentration with decreasing pH, additional factors clearly control iron chemistry in this system.

Solute transport studies include monitoring during experimentally controlled conditions. Work of this type has been part of ongoing studies in the Snake River. A controlled injection of H_2SO_4 was used to induce a change in pH, with a resulting change in iron concentration, along the already naturally acidic and metal enriched reaches of the Snake River. The ranges of sulfate and iron concentrations observed during the controlled period were similar to the ranges observed at various conditions and locations throughout the Snake River drainage. Shown in figure C-5 are dissolved iron concentration profiles along the Snake River during background and experimental conditions. All samples were obtained by filtering through 0.2 μm (micrometer) membranes. During the experiment, iron concentrations were increased by tenths of a milligram per liter. In the context of monitoring design, these increases are an indication of potential variations in situations of rapidly changing pH.

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[1] U.S. Geological Survey, Menlo Park, California

[2] U.S. Geological Survey, Denver, Colorado

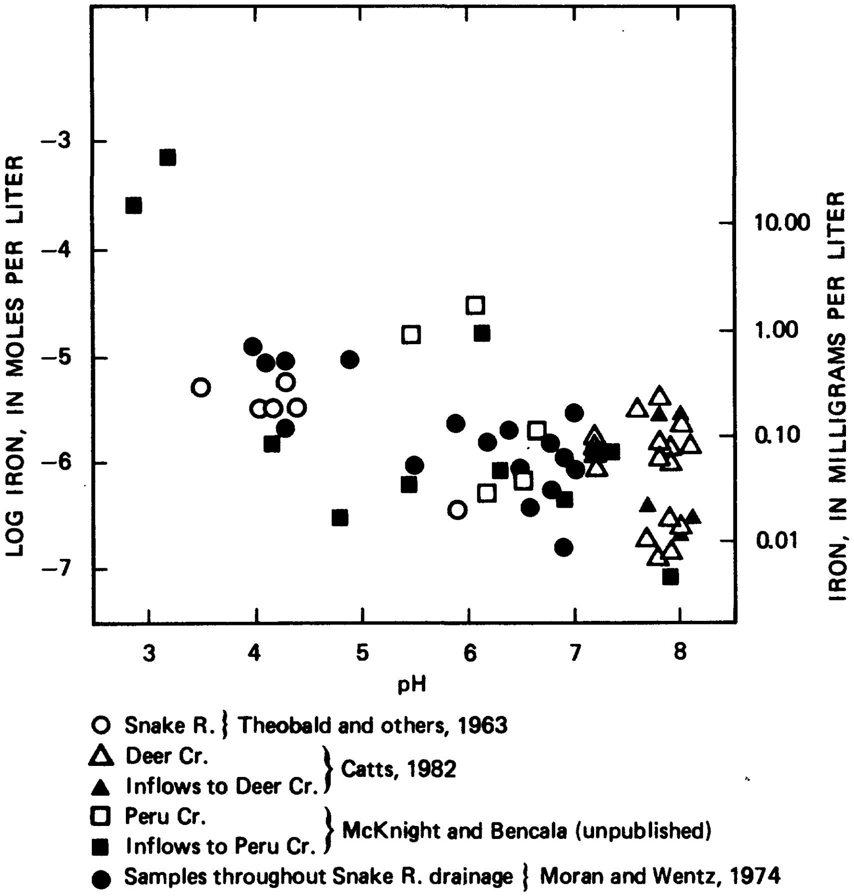

Figure C-4.—Ranges of iron concentrations and pH observed throughout the Snake River drainage.

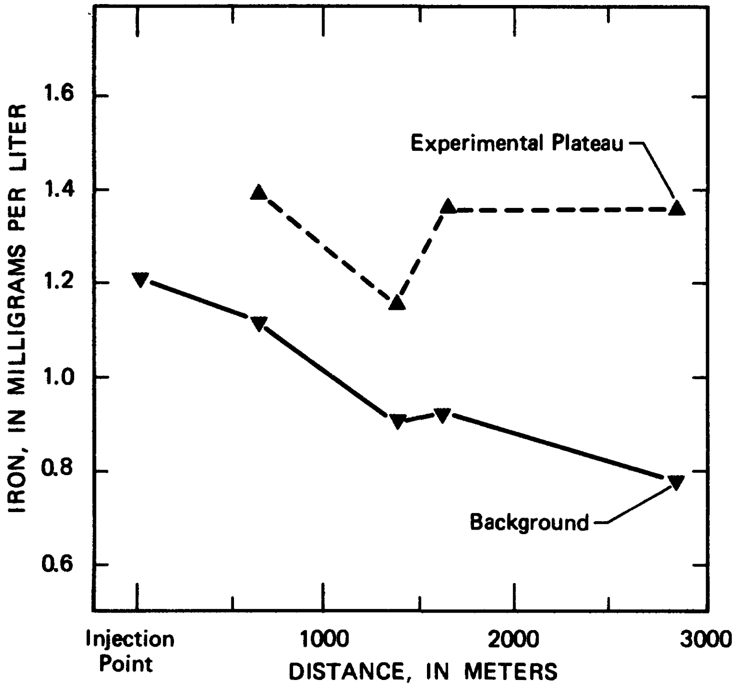

Figure C-5.—Iron concentration profile along the Snake River.

SPATIAL SCALE OF VARIATION

Figure C-6 shows observed variation of iron concentration along one intensively studied reach of the Snake River. Samples were obtained at locations approximately 600 to 1,600 m (meters) below the point of the previously discussed experimental injection. Iron concentrations of streamwater varied by 0.5 mg/L. Samples also were obtained from eight inflows to the stream, consisting of visible ground-water seeps and trickles of surface water. Iron concentrations varied by an order of magnitude between the various inflow samples. The spatial scale of variation within the Snake River was as short as tenths of a kilometer.

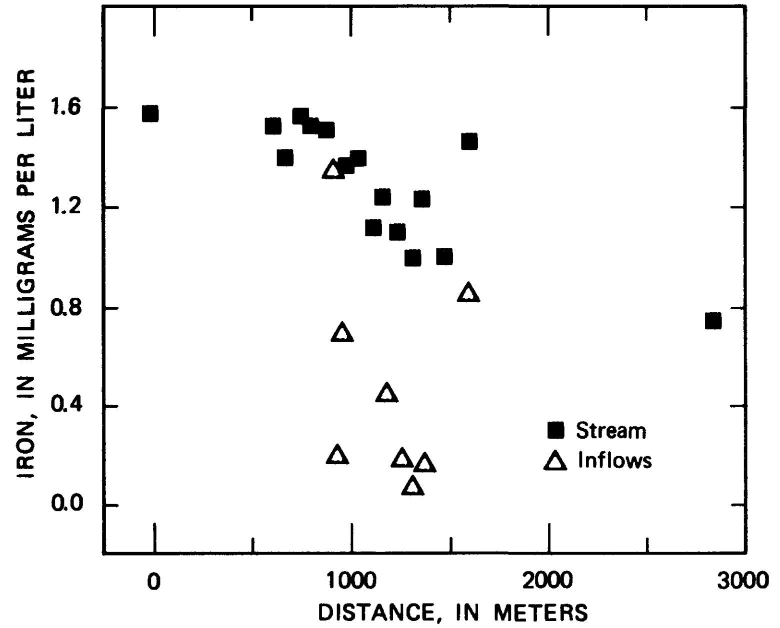

Figure C-6.—Detailed iron concentration profile along the Snake River and concentrations in eight inflows to the stream. ("Distance Along Stream" is measured relative the Injection Point of the experiment discussed above.)

Monitoring studies designed for process-oriented research in systems similar to the Snake River need at least to characterize, if not quantify, the range of solute variation. In the Snake River, it is clear that isolated sampling within the main channel would be only an initial step for interpretation of chemical processes.

DISCHARGE VARIATION

Field investigations of the Leviathan Mine drainage have been undertaken in collaborative work by the Nevada District Office of the U.S. Geological Survey (Hammermeister and Walmsley, 1985) and National Research Program projects studying geochemistry (Ball and Nordstrom, 1985) and solute transport (Flint and others, 1985). During the experimental study of solute transport, a pronounced variation of sulfate concentration was observed in the vicinity of inflows from Leviathan Mine (fig. C-7). The range of the observed dissolved sulfate concentrations during a 35-hour monitoring period was from 1.6 to 2.6 g/L (grams per liter). Concurrent with the solute monitoring, discharge was recorded in Leviathan Creek at a site upstream of the inflows from the mine. Discharge at this site ranged from approximately 3 to 5 L/s (liters per second). As shown in figure C-7, an apparent inverse relation existed between sulfate concentration in the stream reaches affected by mine effluent and discharge in the pristine upper reaches of Leviathan Creek. Sulfate concentration in Leviathan Creek varied by 1 g/L in response to discharge variation during 35 hours. This variation is an example of the extent and the fine time scale of chemical variation present in streams receiving acid mine effluent.

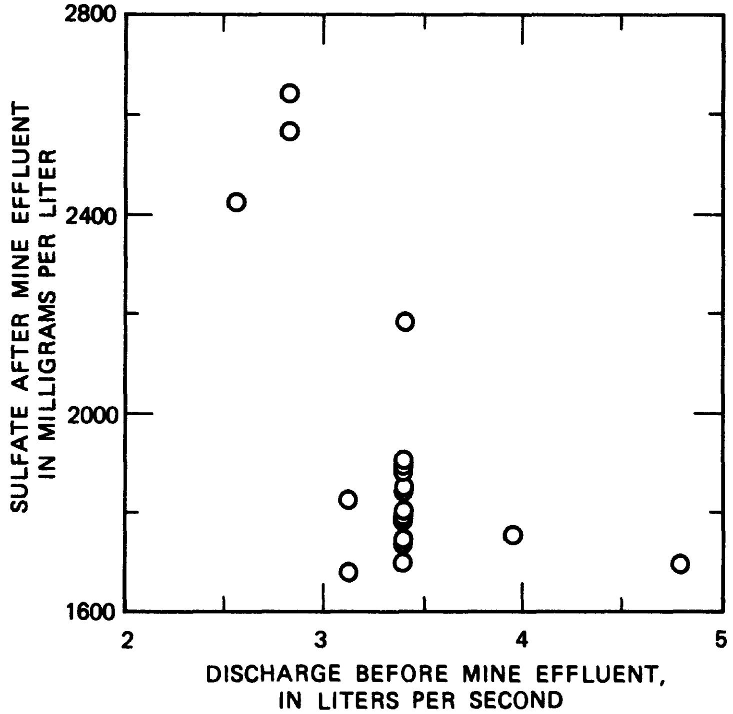

Figure C-7.—Variation of sulfate concentration in Leviathan Creek during a 35-hour period (October 7, 1982, and October 8, 1982) illustrated as a function of discharge. Sulfate concentrations were measured for a site in the vicinity of inflows from Leviathan Mine. Discharge was recorded at a site upstream of the inflows from the mine.

DESIGN OF ST. KEVIN GULCH MONITORING

For the transport study in St. Kevin Gulch the monitoring program was designed according to expectations of process scales on the order of 1 hour and 10 to 100 m. Concentrations were expected to vary at these scales, on the basis of data in the Snake River and Leviathan Creek. Controlled injections of expected conservative tracers, LiCl and NaBr, were used to provide discharge and solute residence-time information. The injection and sampling schedule is shown in figure C-8. LiCl was continuously injected at the top of the study reach from midday on day 1 until midday on day 3. NaBr was continuously injected at the bottom of the study reach for a somewhat shorter period. Sampling was done in three phases: First, sampling of the LiCl arrival and trailing edges was done to determine solute residence time; second, hourly samples were obtained at seven monitoring sites to determine discharge and chemical variations; and finally, discrete samples were taken at many locations of suspected inflows.

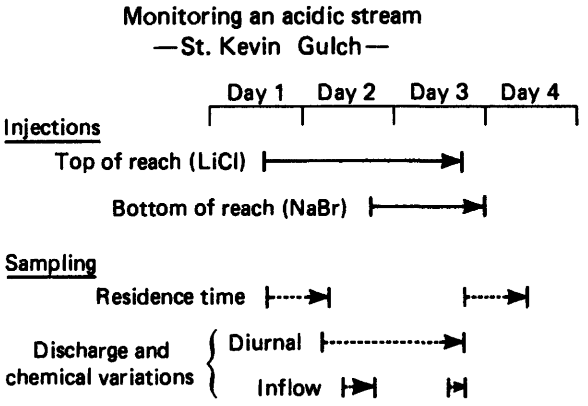

Figure C-8.—Illustration of injection and sampling schedule (August 18, 1986, through August 21, 1986) in St. Kevin Gulch.

There is no *a priori* solution to the problem of knowing how many monitoring sites to establish and how frequently to sample within a given drainage area. The concept of the St. Kevin Gulch study was based on several years of prior detailed field research with mountain streams.

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PRACTICAL ASPECTS OF TRACER EXPERIMENTS IN ACIDIC, METAL ENRICHED STREAMS

By Gary W. Zellweger[1], Kenneth E. Bencala[1], Diane M. McKnight[2],
Robert M. Hirsch[3], and Briant A. Kimball[2]

Tracer injections into streams have been used to determine a variety of hydrologic characteristics (Hubbard and others, 1982, and Kilpatrick and Cobb, 1984). In small streams, the use of conservative ions as tracers has been extended to experimental investigations of reactive solute transport (Kennedy and others, 1984/1985).

The possibility of chemical interactions of the tracer is a consideration in planning studies of acidic, metal enriched streams. Lithium, sodium, chloride, and bromide, and the fluorescent dye rhodamine WT have been used experimentally as tracers in such streams. In this paper, two aspects of experimental design are presented: (1) continuous injection of ionic tracer, and (2) use of rhodamine WT for preexperiment injections to aid in planning continuous ion injections.

CONTINUOUS IONIC TRACER INJECTION

For studies of reactive solute transport, continuous tracer injection provides a means of determining hydrologic transport parameters. A detailed analysis involves simulation of the convective-dispersive equations of transport (Jackman and others, 1984/1985) and may involve sophisticated parameter estimation algorithms (Wagner and Gorelick, 1986).

The basic conceptual characteristics are shown in figure C-9. The concentration-time response curve for a conservative tracer is used to determine plateau concentration (C_p), time (T_{50}) to 50 percent of plateau (C_{50}), and duration of spreading, a characteristic of dispersion. From these determinations, the hydrologic properties of discharge, velocity, and a measure of dispersion may be calculated. There are several important criteria in selecting ions for a tracer; for example, background concentration, measurability, solubility, and cost.

The Snake River, Summit County, Colo., is a naturally acidic mountain stream. In August 1983, a multiple-injection transport study was done to investigate the behavior of the stream solutes. LiCl and NaBr were chosen as the injection salts because background concentrations in the study reach were low for all four ions and all could be easily measured.

It is essential to a continuous tracer injection that the injection rate remain constant. Two battery-operated metering pumps capable of delivering from 5 to 48 mL/min (milliliters per minute) ± 1 percent were plumbed in parallel to inject 87 mL/min of LiCl (~447 g/L (grams per liter) LiCl) solution into the stream. The solution was stored in a plastic trash can. Simultaneously, another injection was made into Deer Creek, a major tributary of the Snake River. One pump was used to inject NaBr (~287 g/L NaBr) delivered at 21.6 mL/min into the tributary. Chloride and bromide were measured by ion chromatography and lithium and sodium by atomic adsorption spectroscopy. Stream concentrations downstream of the injection points were increased for chloride from background concentration of 0.17 to

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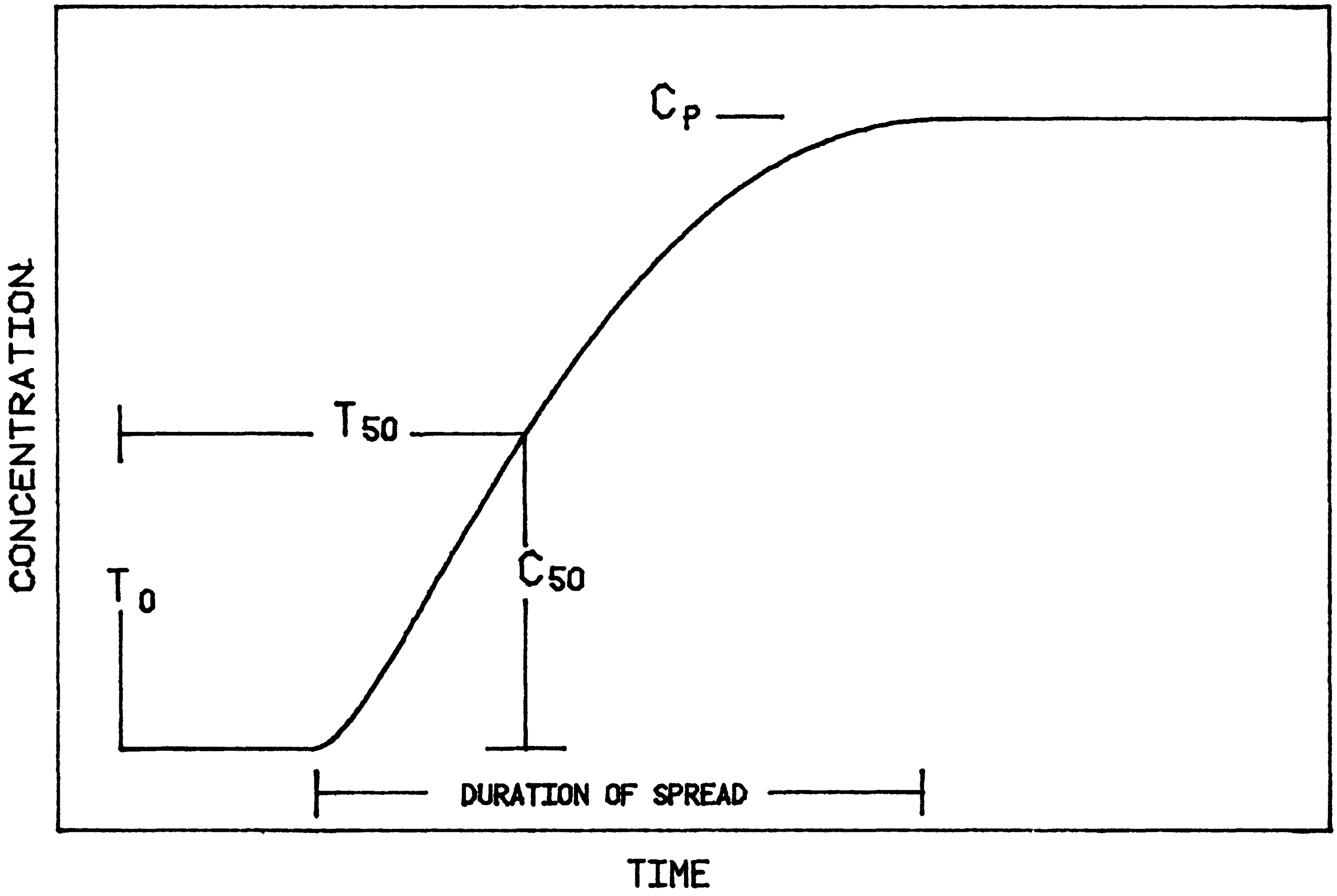

Figure C-9.--An idealized concentration curve showing the arrival of a solute at a downstream site. T_{50} is the time to reach C_{50}, the concentration halfway between background and C_p, the "plateau" concentration.

2.55 mg/L (milligrams per liter), for bromide from 0.02 to 1.48 mg/L, for lithium from 0.00 to 0.47 mg/L, and for sodium from 1.10 to 1.55 mg/L. Preliminary comparisons of tracer data confirm that the tracers were approximately conservative within the study reach.

In August 1984 in Lake County, Colo., a similar experiment using LiCl and NaBr was conducted in a study of St. Kevin Gulch, which received mine effluent and in which the stream pH varied between 3.4 and 4.1. Iron concentrations as high as 13 mg/L were measured.

PREEXPERIMENTS USING RHODAMINE WT

To aid in planning a sampling schedule during a tracer injection it is helpful to estimate arrival time of the injection pulse at each sampling station. In the Snake River a preexperiment was conducted by using a 5-minute pulse of rhodamine WT dye and a battery operated fluorometer to estimate arrival times. Although rhodamine WT fluorescence is known to be attenuated within acidic streams (Bencala and others, in press), figure C-10 shows that the first arrival time of rhodamine WT was an accurate estimate of the first arrival time of chloride.

In St. Kevin Gulch, a preexperiment with rhodamine WT was also made. A fluorometer was set up for real-time analysis 489 meters downstream of the dye injection. A few samples were collected by dipping the fluorometer cuvette directly into the stream. The fluorescence of these samples was determined immediately upon collection. Additional samples, collected in plastic bottles, were measured approximately 30 minutes after the detection of fluorescence in the cuvette samples. Fluorescence in the bottle samples was about 10 percent of that of the cuvette samples collected at about the same time. The fluorescence in the bottle samples decreased so rapidly that estimates of arrival times could not be made.

To verify the loss of fluorescence in the bottle samples, a field test was made. Rhodamine WT was mixed with water from St. Kevin Gulch. This mixture was poured into two plastic and two glass bottles of which one each was kept in sunlight and one in darkness except during removal for measurements. Fluorescence was measured about 11 times during 2½ hours. Figure C-11 is a plot of the fluorescence against elapsed time. Fluorescence decreased in all four bottles; however, the rate of loss was much greater for the samples exposed continuously to light. There was also a greater loss in plastic than in glass bottles; however, from this data it cannot be determined if surface effects or transparency was the important factor. Presumably, the loss of fluorescence was caused by a combination of chemical and photo-induced reactions with the rhodamine WT. Additional experiments controlling light, pH, surfaces, and bacteria would be needed to ascertain the causes of rhodamine WT decay.

The high sensitivity of portable field fluorometers makes fluorescent dyes leading candidates for water tracing. It may be possible, using multiple fluorometers, operating in real time, to design procedures for using rhodamine WT for preexperiments in acidic streams. However, the rapid decrease of fluorescence observed with water from St. Kevin Gulch indicates that a decrease of fluorescence in the stream would probably occur on a time scale comparative to that of solute transport.

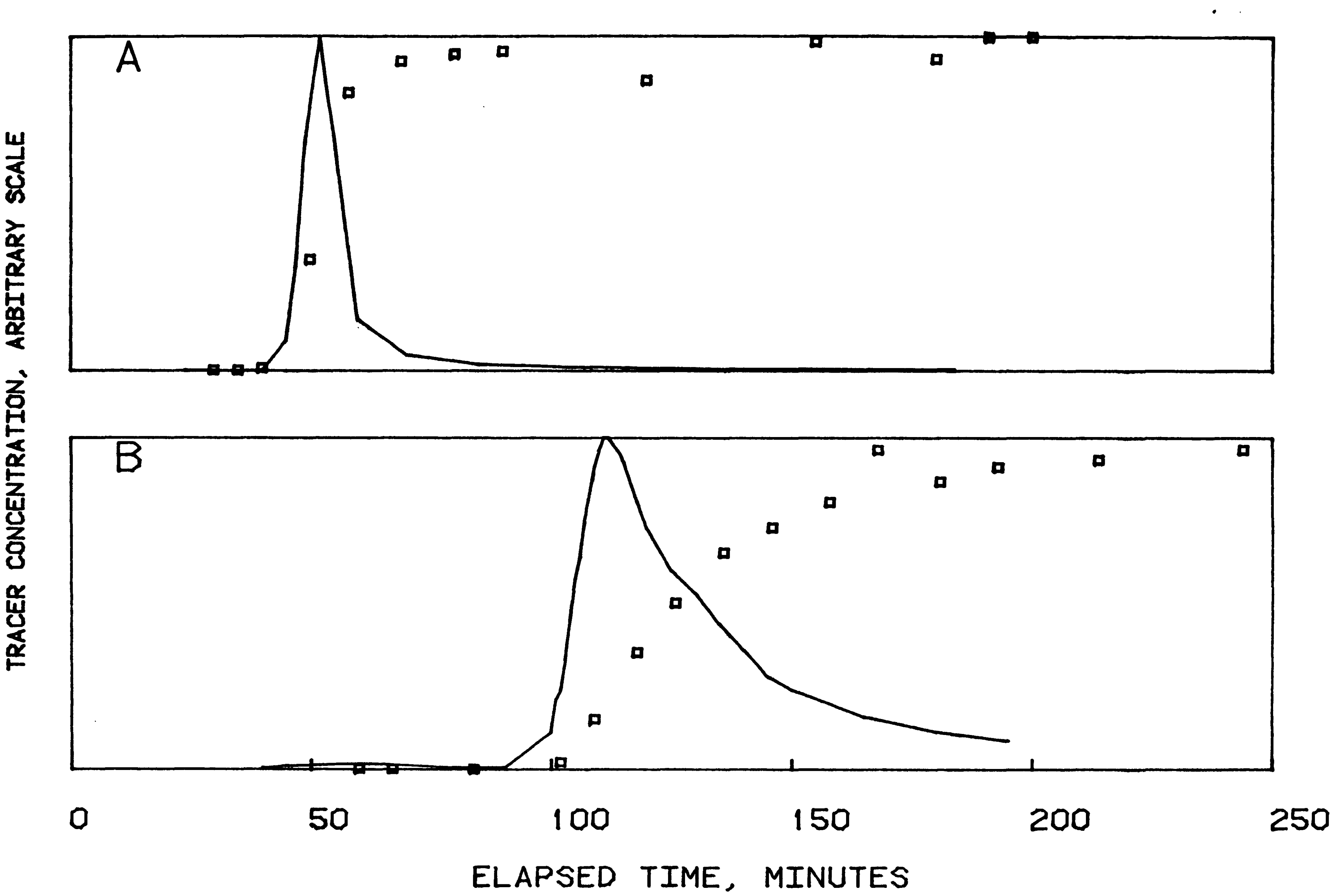

Figure C-10.--Rhodamine WT data from a preexperiment in Snake River, Colorado, superimposed on chloride data from the main experiment showing the close agreement of arrival times at sites: (A) 1,365 meters, and (B) 2,845 meters below injection. Open squares: Chloride, solid line: Rhodamine WT.

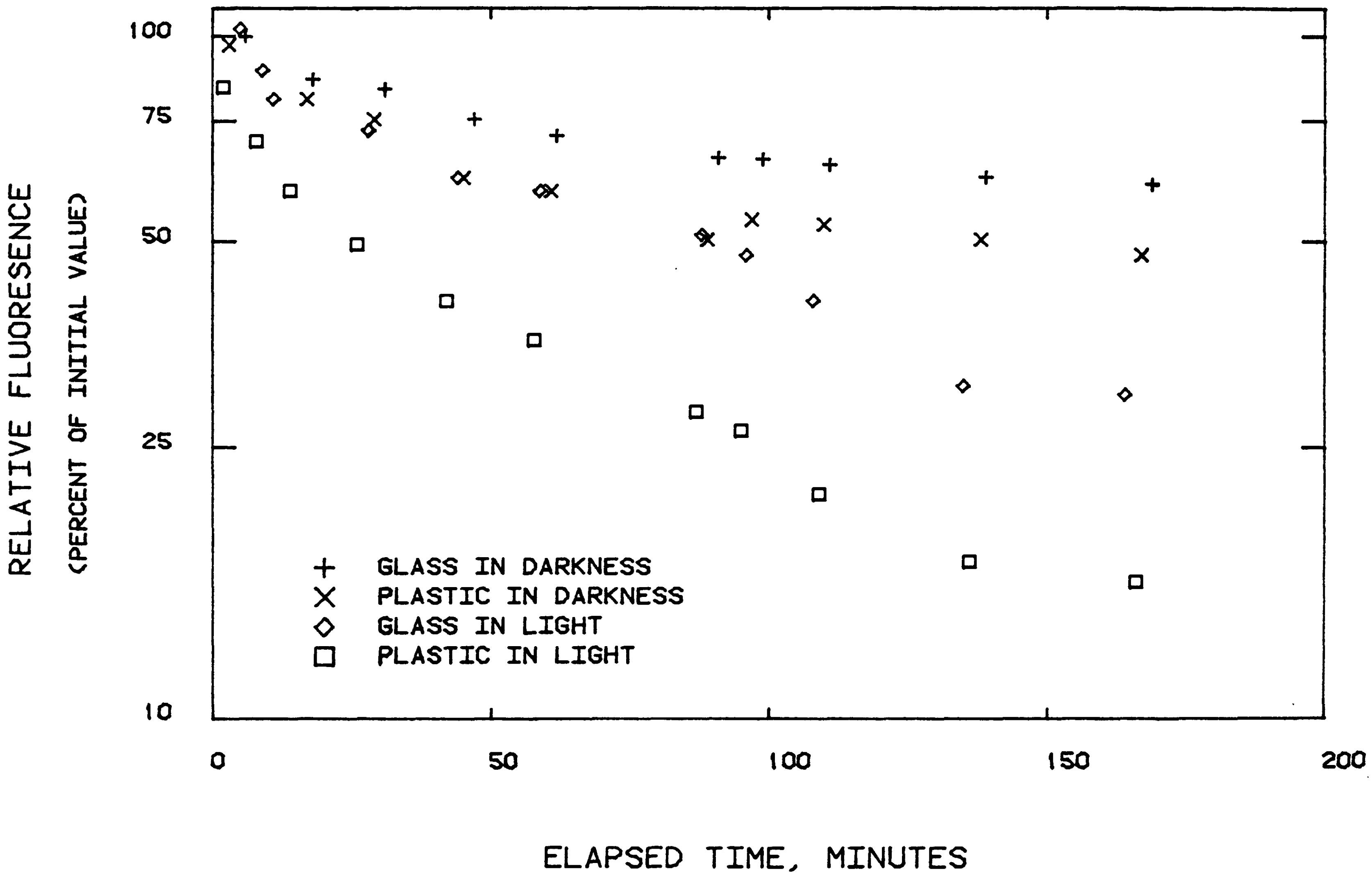

Figure C-11.--A plot of fluorescence, scaled as percent of initial fluorescence versus elapsed time in minutes, for samples of rhodamine WT mixed with water from St. Kevin Gulch. Loss from bottles exposed to sunlight was greater than loss from bottles stored in the dark, and greater from plastic bottles than from glass bottles.

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PHOTOREDUCTION OF HYDROUS IRON OXIDES IN ACIDIC MOUNTAIN STREAMS IN COLORADO

By Diane M. McKnight[1], Briant A. Kimball[2], and Kenneth E. Bencala[2]

INTRODUCTION

The presence of hydrous iron oxides on streambed surfaces and in suspension is a common feature of acidic, metal-enriched mountain streams and indicates that within-stream precipitation of hydrous iron oxides is occurring. Other processes also may be important in controlling stream iron chemistry; these processes include: (1) biotic or abiotic oxidation of dissolved ferrous iron to ferric iron, (2) oxidation of pyrite by ferric iron; and (3) photoreduction of dissolved ferric iron or ferric hydroxides suspended in the stream or deposited on the streambed. At any point in time and location along a stream, the iron chemistry will be determined by the rate of iron inflow and the rates of these and other chemical processes. Because of low pH, which limits the rate of ferrous oxidation, and their high elevation, with a greater flux of ultraviolet radiation, acidic streams in the Rocky Mountains in Colorado are primary environments for photoreduction to be a dominant process. This paper presents results which document the occurrence of photoreduction in two acid mountain streams.

Photoreduction of ferric iron is induced by radiation in the near ultraviolet (250-425 nanometers) part of the solar spectrum. The photoreduction reaction is represented by reaction 1 for a hydrated hydroxide species:

$$\mathrm{FeOH}^{2+} \xrightarrow{h\nu} \mathrm{Fe}^{2+} + \mathrm{OH} \qquad (1)$$

Similar reactions can occur involving hydrous ferric oxide releasing ferrous iron and hydroxyl radicals to solution (Waite and Morel 1984a, b; Cunningham and others, 1985; K.M. Cunningham, M.C. Goldberg, and E.R. Weiner, U.S. Geological Survey, written commun., 1987). The quantum yield for the solution-phase reaction is about 10^{-2}; for the ferric oxides, quantum yields for the most amorphous forms are about 10^{-3} and decrease with increasing crystalinity to 10^{-5} to 10^{-6}. Organic species may enhance the production of ferrous iron by scavenging the hydroxyl radicals and decreasing the rate of reoxidation of ferrous iron. Organic species sorbed on the surface of ferric oxides may enhance the production of ferrous iron by more readily donating an electron to photolytically excited Fe(III) than a hydroxyl species.

RESULTS AND DISCUSSION

In the Snake River, a small, naturally acidic (pH=4) mountain stream near Montezuma, Colo., rapid changes in iron chemistry were observed in response to changes in light intensity (fig. C-12; table C-5) (McKnight and Bencala, in press). Significant increases occurred at midday in both total dissolved iron and in ferrous iron. Similar changes were observed during two other diel studies. These results indicate that photoreduction of iron oxides on the streambed releases dissolved ferrous iron to the stream during

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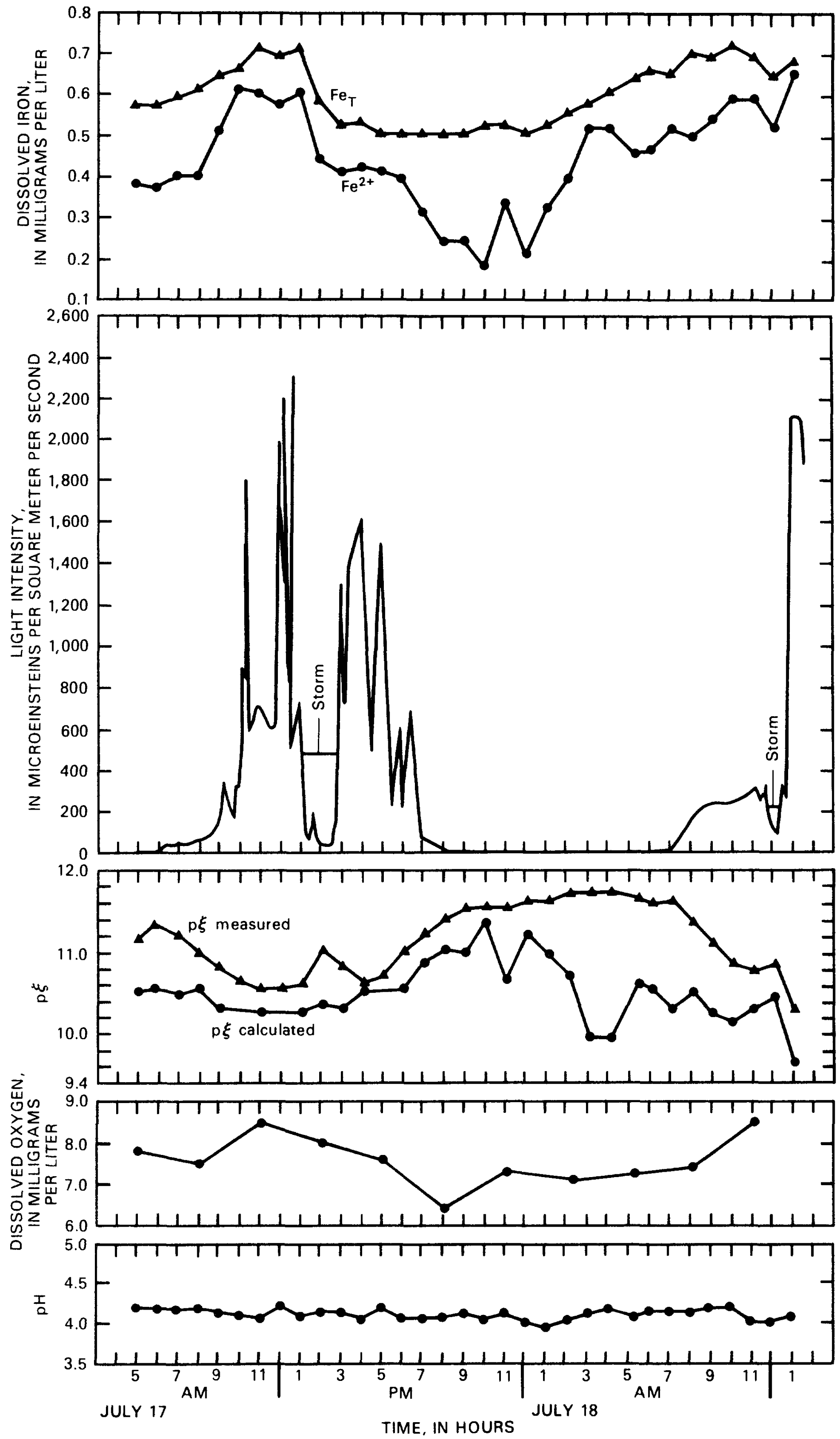

Figure C-12.—Temporal changes in iron chemistry and related characteristics in the Snake River at a site above the confluence with Deer Creek in Colorado on July 17–18, 1985.

Table C-5.—Concentration of major ions and trace metals in filtered water samples from the Snake River, July 17-18, 1985, and St. Kevin Gulch, August 18-19, 1986, in Colorado

[—, no data]

Characteristic[1]	Snake River[2]	St. Kevin Gulch[3]
pH	4.13 ± 0.07	3.78 ± 0.05
	Major ions (milligrams per liter)	
Na^+	1.77 ± 0.10	2.4 ± 0.1
Ca^{2+}	7.20 ± 0.09	13.0 ± 0.3
Mg^{2+}	2.69 ± 0.03	4.3 ± 0.2
Sr^{2+}	0.045± 0.0008	.03 ± 0.008
Ba^{2+}	0.028± 0.0015	.02 ± 0.002
SO_4^{2-}	46.4 ± 0.6	—
Cl^-	0.13 ± 0.02	—
F^-	0.15 ± 0.008	—
SiO_2	12.45 ± 0.35	16.3 ± 0.3
	Trace metals (milligrams per liter)	
Al	1.75 ± 0.04	2.0 ± 0.2
Mn	0.445± 0.006	4.2 ± 0.1
Zn	0.294± 0.006	8.6 ± 0.3
Fe	0.57 ± 0.06	1.6 ± 0.1
Fe_T	0.60 ± 0.07	1.1 ± 0.1
Pb	<0.001	.023± 0.056
Cu	0.018± 0.004	.088± 0.003
Cd	0.0016± 0.0014	.050± 0.004
Ni	0.031± 0.011	.013± 0.013

[1] Major cations and trace metals (including Fe) were analyzed by ICP (inductively coupled plasma spectroscopy); major anions were analyzed by IC (ion chromotography); Fe_T (total dissolved iron) was analyzed by the 2, 2-bipyridine method.

[2] Data from analysis of water samples that were collected at Snake River site above confluence with Deer Creek: all 33 samples were analyzed for pH and Fe_T; first 21 samples were analyzed for cations and trace metals and every third sample in time series were analyzed for anions (McKnight and Bencala, in press).

[3] Data from analysis of 40 water samples that were collected at hourly intervals at site SK40 at St. Kevin Gulch (Kimball and others, this report).

periods of full sunlight. In situ batch experiments using streamwater and rocks from the streambed of the Snake River reproduced the daytime changes in iron chemistry observed in the stream. An apparent quantum yield of 3×10^{-3} was calculated; this value is consistent with laboratory experiments of photoreduction of amorphous iron oxides.

Another aspect of the results in figure C–12 is that changes in iron chemistry also occurred during the night. The dissolved ferrous iron concentration decreased between sunset and midnight, which indicates oxidation of ferrous iron, and then increased between midnight and 3 a.m., which may indicate microbial iron reduction associated with increased microbial activity during the night (McKnight and Bencala, in press).

Diel changes in iron chemistry also were observed in St. Kevin Gulch, a small tributary in the Arkansas River system near Leadville, Colo., (fig. C–13; table C–5). In contrast to the Snake River, St. Kevin Gulch receives drainage from an abandoned mine, resulting in large concentrations of several potentially toxic trace metals, such as zinc and aluminum (table C-5). The results presented in figure C-13 were obtained at two

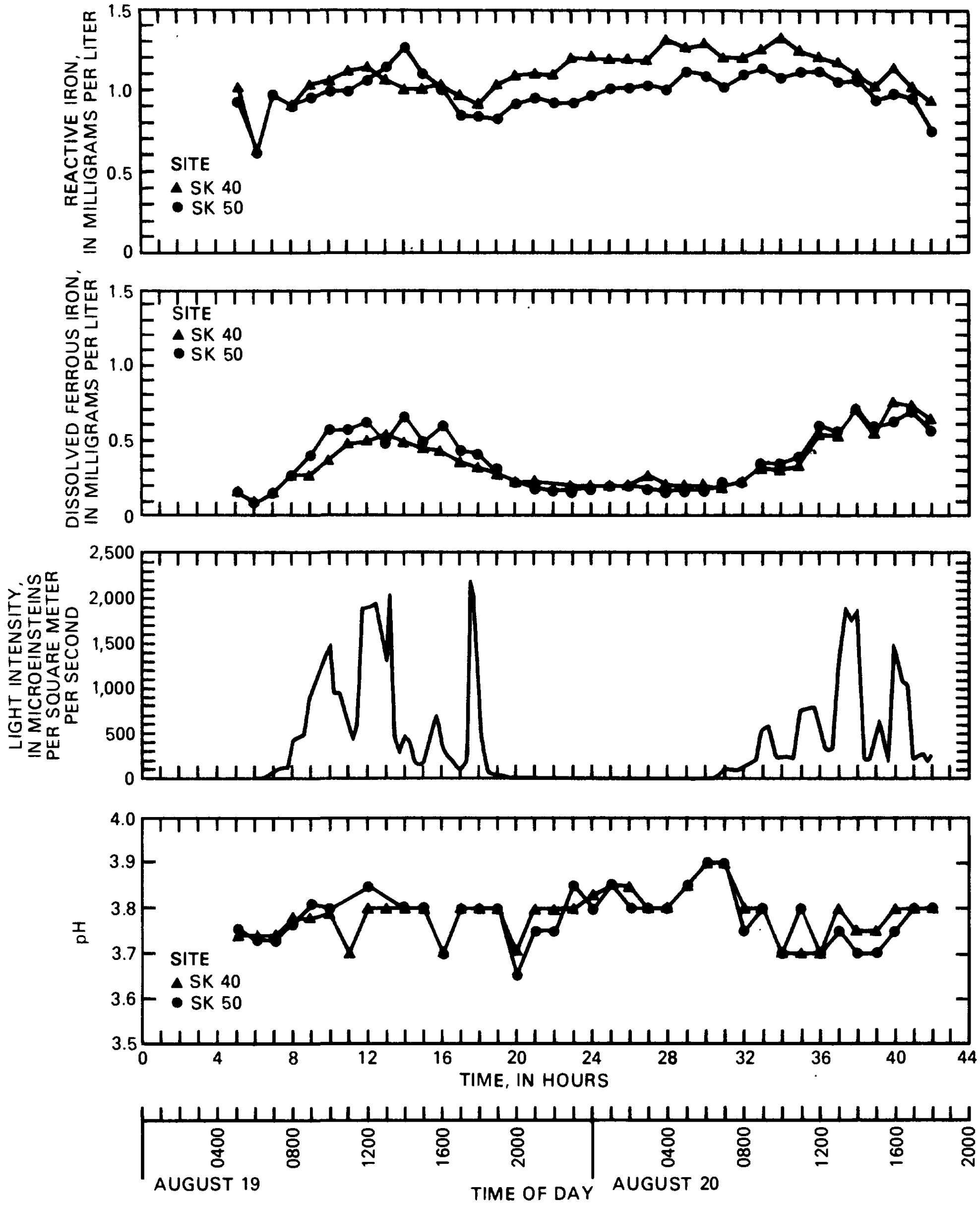

Figure C–13.—Temporal changes in iron chemistry and related characteristics in St. Kevin Gulch at two sites about 2 kilometers downstream from an abandoned mine.

sites 2 kilometers downstream from the inflow of the mine drainage in a reach characterized by precipitation of hydrous iron oxides (Kimball and others, this report). These results show the same increase in dissolved ferrous iron during the day that was observed in the Snake River and was attributed to photoreduction. However, a distinct simultaneous increase in total dissolved iron did not occur; this indicates that the main photoreductive process involved reaction of the ultraviolet radiation with dissolved ferric iron or colloidal hydrous ferric oxides in the streamwater, rather than with hydrous iron oxides on the streambed. The concentration of colloidal hydrous ferric oxides is much greater in St. Kevin Gulch than in the Snake River.

Another difference between the diel variations in iron chemistry in St. Kevin Gulch and the Snake River is that, during the night, the dissolved ferrous iron concentration was virtually constant in St. Kevin Gulch, but varied significantly in the Snake River. We hypothesize that the greater concentrations of Cd, Pb, and other toxic trace metals in St. Kevin Gulch were responsible for this difference between the two streams. These greater metal concentrations may inhibit the activity of microorganisms involved in iron cycling. Another possibility is that these elevated metal concentrations may catalyze abiotic ferrous oxidation and accelerate the decrease in ferrous concentration following sunset. This more rapid oxidation also may limit the release to the stream of dissolved ferrous iron produced by nocturnal microbial processes.

These results indicate that photoreduction is a dominant process controlling iron speciation in acidic mountain streams. These results have consequences for understanding the geochemistry of acid streams. For example, the dependence of iron speciation on light intensity explains the lack of correlation between changes in discharge and dissolved-iron concentration in the Snake River. In the Arkansas River monitoring study, light intensity and iron speciation measurements have been included. The daily dissolution and reprecipitation of hydrous iron oxides also provide an explanation for the abundance of amorphous iron oxides compared to more crystalline forms in such streams and these processes may enhance the transport of other metals that are sorbed by the iron oxides.

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GEOCHEMISTRY OF DISSOLVED METALS IN ST. KEVIN GULCH, AN ACIDIC MOUNTAIN STREAM NEAR LEADVILLE, COLORADO

By Briant A. Kimball[1], Kenneth E. Bencala[2], Diane M. McKnight[1], and Wendy S. Maura[1]

INTRODUCTION

A small mountain stream, St. Kevin Gulch near Leadville, Colo., that receives acid drainage from abandoned mines and tailings piles was sampled to determine the variations in mass flow of dissolved metals. The tailings piles resulted from mining of silver sulfide ores that are present in veins within a quartz biotite feldspar schist and gneiss bedrock (Tweto, 1956). Weathering of these silver sulfide ores and of the tailings piles releases metals to surface and ground waters. Metals having the largest concentrations in St. Kevin Gulch include aluminum, cadmium, copper, iron, manganese, and zinc. This paper presents preliminary ideas about the processes that affect metals concentrations in water downstream from tailings piles in St. Kevin Gulch.

FIELD AND LABORATORY PROCEDURES

Samples were filtered at the sampling sites using 0.1-μm (micrometer) pore-size membranes; temperature, specific conductance, and pH were measured at the sampling sites. Filtered samples for determining dissolved metal concentrations were acidified with nitric acid to a pH less than 1.5. Ferrous iron, in filtered samples, was fixed with a 2,2-bypiridine solution at the sampling sites. All the dissolved iron was reduced to ferrous iron in a second sample with hydroxylamine hydrochloride to give the "total" dissolved iron in the samples. Dissolved-ferrous and dissolved-total iron concentrations were determined colorimetrically within a few days after sample collection. Other dissolved-metal concentrations were determined by inductively coupled argon plasma spectrometry. Unacidified samples were used for anion determinations by ion chromatography.

Streamflow was determined by dilution of lithium chloride, which was injected upstream from the tailings piles. Discharges of inflows from the tailings and tributaries were determined by the difference in streamflow upstream and downstream from each inflow. Streamflow increases gradually downstream, except at the entry point of the largest tributary, 504 m (meters) downstream from the injection point, where the total streamflow doubles (fig. C-14). At least-square line was fit to the values of streamflow for the reach downstream from the tributary inflow, and the calculated streamflow was used to determine mass flow of the metals. Mass flow, in milligrams per second, was used to indicate changes because it indicates the actual gain or loss of a metal from the stream. The smaller inflows downstream from the large tributary are chemically important, even though they have little effect on the increase of streamflow (fig. C-14). At the present time, values of streamflow that have been calculated from lithium concentrations have not been verified by the values of discharge that will be calculated from chloride concentrations.

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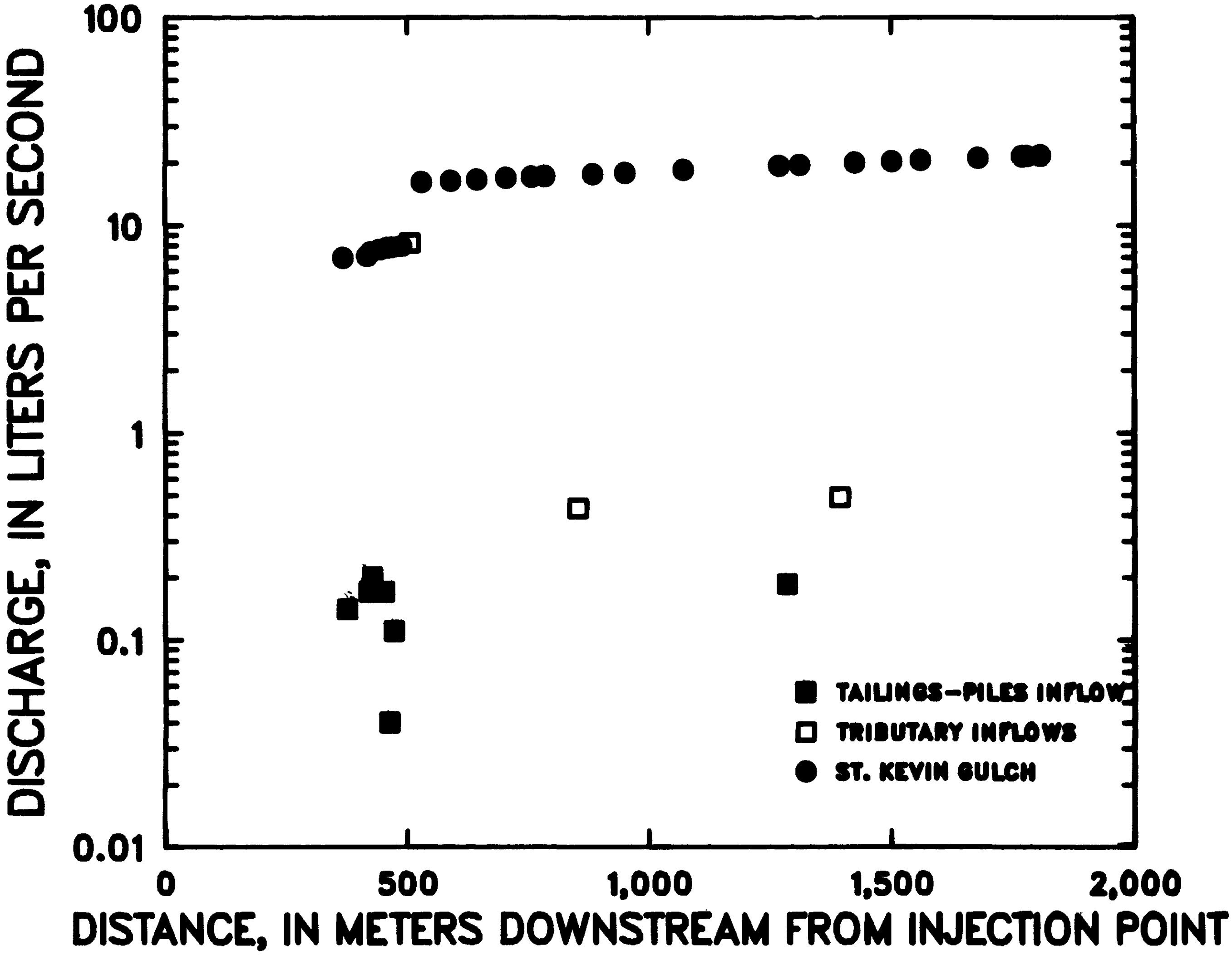

Figure C-14.—Downstream variations in streamflow and inflow discharge.

RESULTS AND DISCUSSION

Downstream variations in pH are shown in figure C-15. Inflows from the tailings piles resulted in a decrease of instream pH to less than 3.50 within about 30 m downstream. However, the tributary inflow just downstream from the tailings piles had a pH of 6.50, and the instream pH increased to 4.00 downstream from that inflow. Additional changes in pH occurred 854 m downstream from the injection point, due to an inflow that had a pH of 5.98. Otherwise, there generally was a gradual decrease of instream pH downstream.

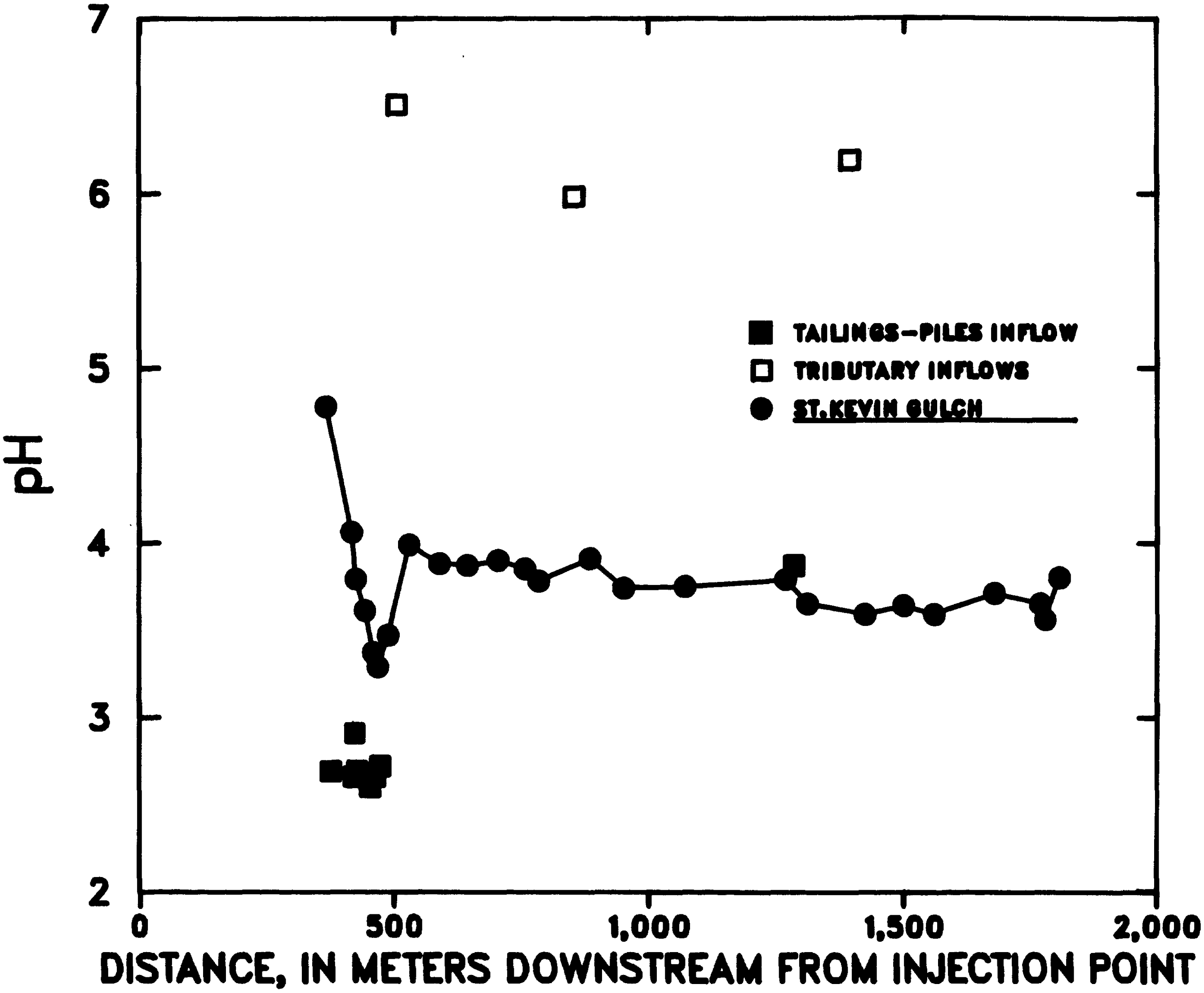

Figure C–15.—Downstream variations in pH and inflow pH.

Large concentrations of dissolved metals were added to the stream from tailings piles along the stream. The largest inflow concentrations of dissolved metals, in milligrams per liter, were aluminum, 17; cadmium, 0.5; copper, 0.5; iron (ferric plus ferrous species), 125; manganese, 56; and zinc, 100. The mass flow of each dissolved metal greatly increased downstream from the tailings. A typical increase for most of the metals is shown for the mass flow of manganese and zinc in figure C–16. Once the metals were in solution, there were generally two different patterns; there was either a large, continuous loss of the metal from the stream (dissolved iron) or else a nearly conservative transport, with only small losses (aluminum, manganese, and zinc). When pH increased at the tributary inflows (figs. C–15 and C–16), a decrease in each of the mass-flow values occurred. This may be caused either by the formulation of a hydrous metal oxide that was large enough to be removed by a 0.1-μm membrane filter, by incorporation within a hydrous iron-oxide floc, or by precipitation to the streambed.

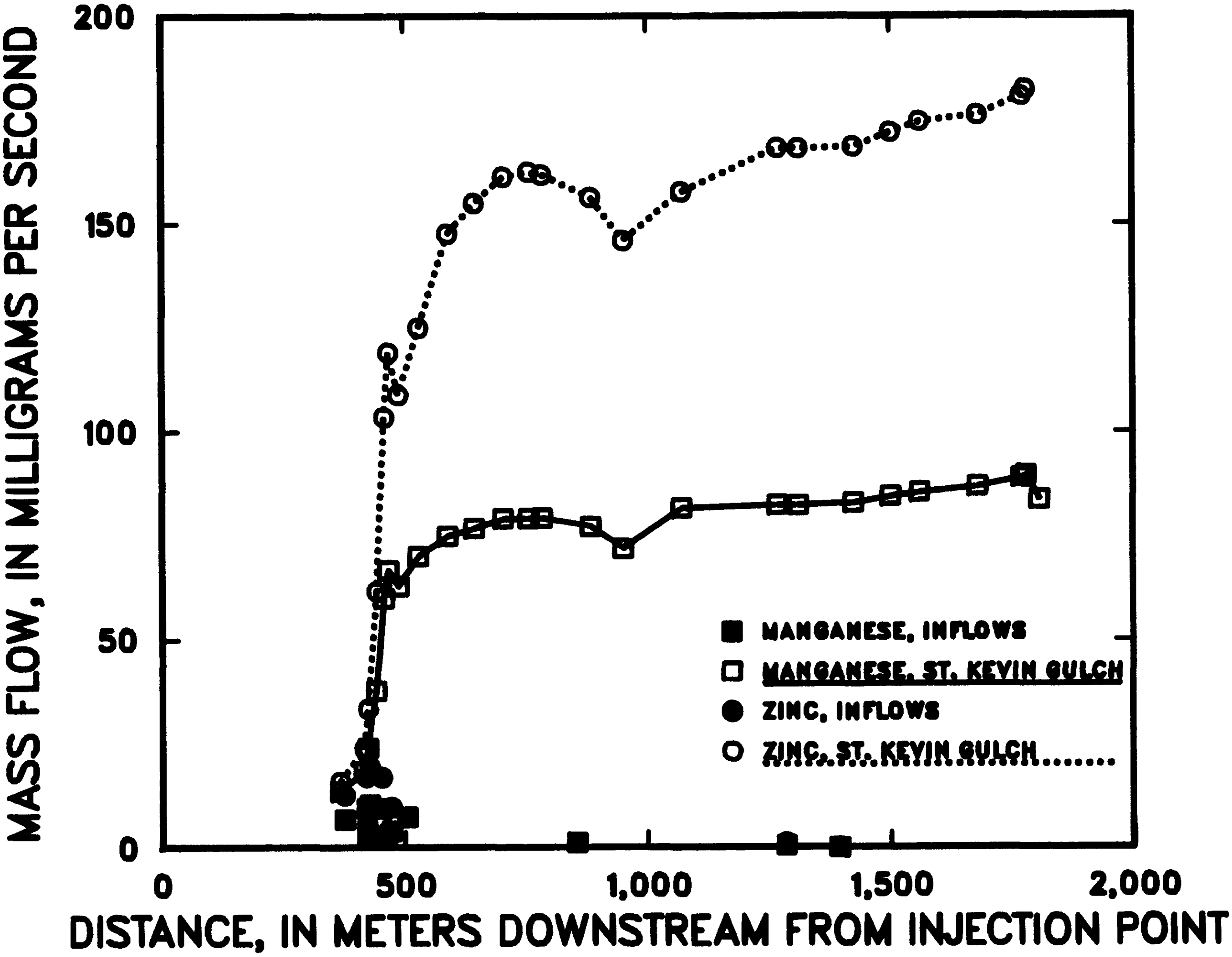

Figure C-16.—Downstream variations in mass flow of manganese and zinc.

After the decrease of mass flow of each dissolved metal, there was an increase downstream over a short distance as pH decreased. This was not caused by any visible inflow, although there could be an inflow of ground water not evident at the land surface. Otherwise, the decrease in pH may result from an acid buffering. The result of the pH decrease was an increase in metal mass flow. The increase could come from dissolution of the suspended floc, or dissolution of the bed material that included large quantities of floc; both processes would increase the mass flow of dissolved metals. These variations, however, are clearly related to fluctuations in pH.

Speciation calculations by Nordstrom and Ball (1986) have shown that dissolved aluminum in samples from a drainage basin containing acid mine waters may exhibit both conservative and nonconservative geochemical behavior. The pattern of aluminum mass flow (fig. C-17) also indicates both types of transport. At the two locations, immediately downstream from inflows with a pH near 6.0, the mass flow of dissolved aluminum decreases; this indicates nonconservative transport at higher pH. The first decrease 951 m downstream from the injection point, was larger than the second, 1,424 m downstream from the injection point. However, after each decrease, the aluminum mass flow again increased. Beyond the last point, aluminum concentration remained almost constant at 2.0 mg/L (milligrams per liter). This may indicate that an aluminum floc is formed with the increase in pH, and then dissolves downstream, maintaining a nearly constant concentration of aluminum.

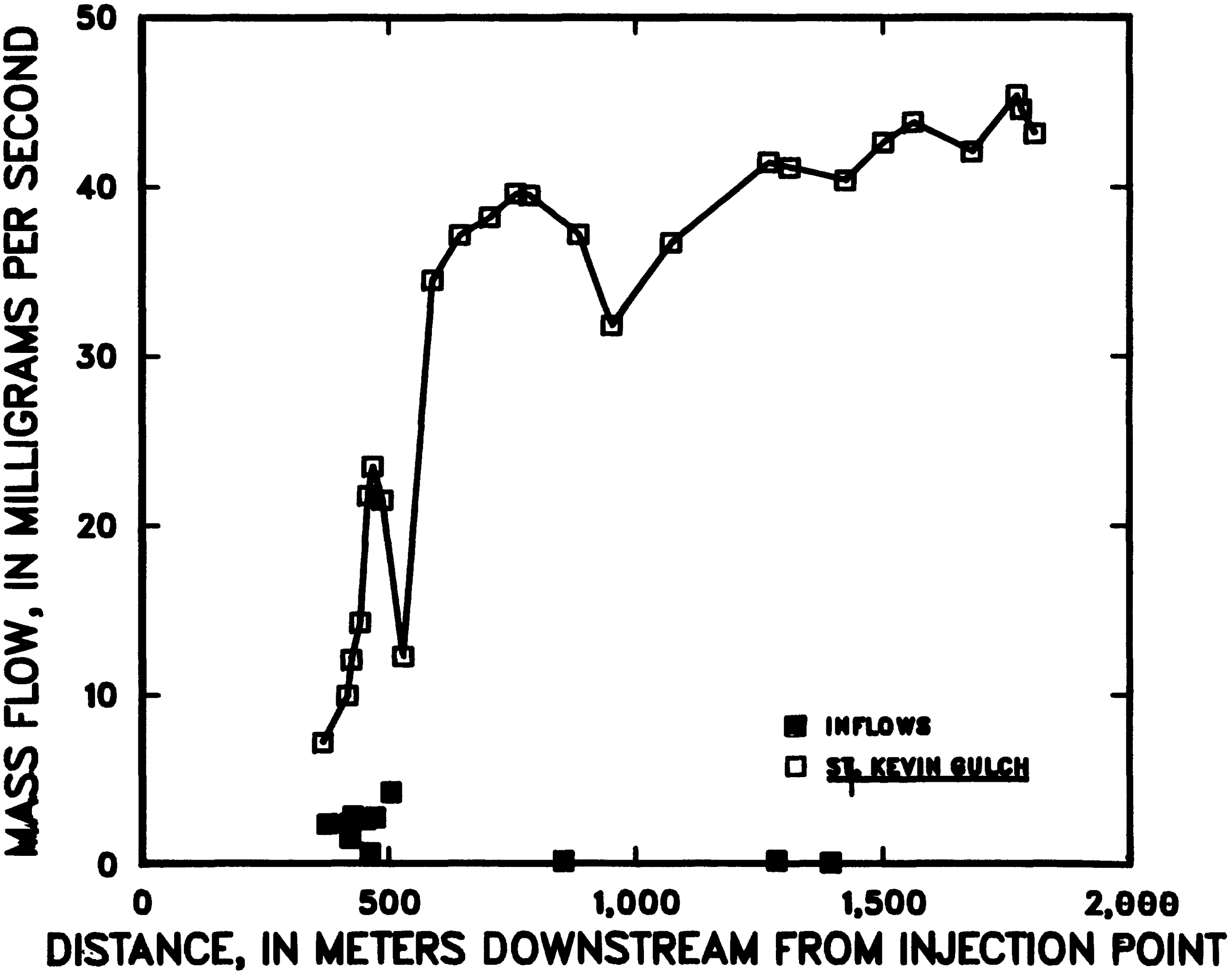

Figure C-17.—Downstream variations in mass flow of aluminum.

Dissolved iron increased immediately downstream from the tailings piles (fig. C-18). At the tributary inflow it decreased, and then continued to decrease, nearly exponentially downstream, opposite to the pattern for the other dissolved metals. The initial increase of dissolved iron at the

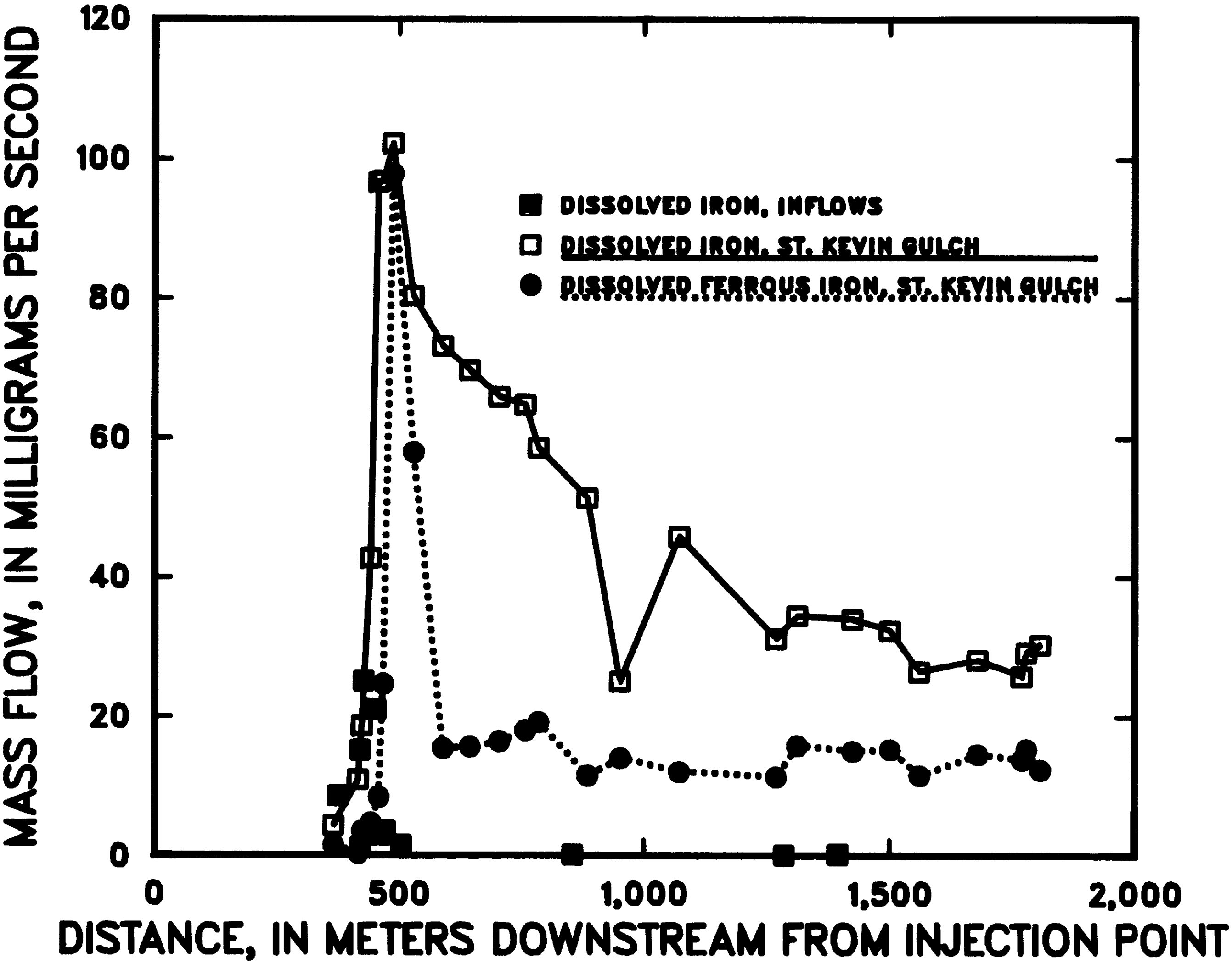

Figure C-18.—Downstream variations in mass flow of dissolved iron and dissolved ferrous iron.

tailings had a ferrous-iron to dissolved-iron ratio of about 0.2 (fig. C–19). The ratio rapidly increased to a maximum of 0.96 about 30 m downstream from the tailings piles. Further downstream, the ratio decreased to 0.72 and then decreased to about 0.2. The initial increase in the ratio could have been caused by photoreduction of the iron because the inflows from the tailings piles enter the stream in an area open to sunlight.

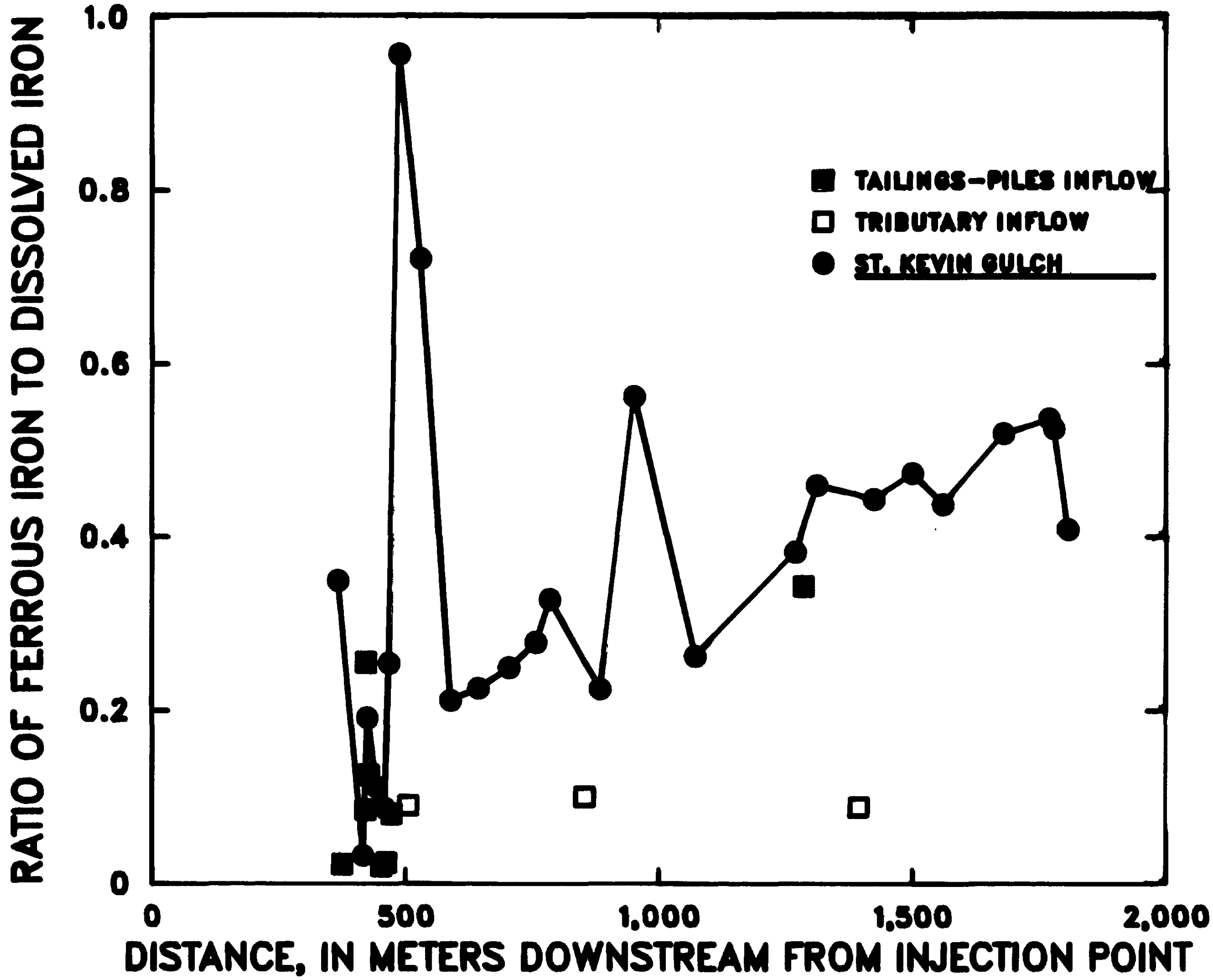

Figure C–19.—Downstream variations in the ratio of dissolved ferrous iron to dissolved iron.

Photoreduction of iron has been documented in other acidic mountain streams (D.M. McKnight and K.E. Bencala, U.S. Geological Survey, written commun., 1978), and also was studied during this experiment (see D.M. McKnight, this report). The gradual increase in the ratio from 0.2 to about 0.55 is from the loss of ferric-iron species while ferrous iron remains virtually constant.

The decrease in the ferrous-iron to dissolved-iron ratio indicated a rapid oxidation of the ferrous iron. When iron is present in the stream as ferric iron, it is lost from the stream through the formation of hydrous ferric oxide(s) that either are deposited on the stream bottom or transported as colloidal floc in the stream. The pattern of generally decreasing dissolved-iron mass flow indicated a net rate for the removal of the ferric part of the dissolved iron from the stream. The distance downstream and the stream velocity can be combined to determine a rate for this removal; however, the stream velocity has not yet been determined. Dissolved-iron mass flow decreased at the inflows with values of pH near 6.0 along with the other dissolved metals, but then showed an overall decreasing pattern downstream from the inflows.

The oxidation and reduction reaction and the variable, pH-dependent mass flows of other dissolved metals indicates the dynamic nature of geochemical reactions in the acid stream environment. Future studies as part of this project will evaluate the solid-phase composition of the floc, the rates at which the oxidation-reduction reactions occur, and the controls of equilibrium chemistry of the solid-solution reactions.

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Chapter D

SOME OBSERVATIONS ON THE INTERACTION OF FINE SEDIMENT WITH ALLUVIAL STREAMBEDS

Harvey E. Jobson[1] and William P. Carey[2]

LIST OF SYMBOLS

A - a proportionality constant between the mean concentration of sediment in the vertical and the concentration at the boundary between the flow and the bed

C - the mean concentration (weight/unit volume) in the flow at time T

C_o - the mean concentration in the flow at time zero ($T=0$)

d - depth of flow

D_{15} - size of sediment for which 15 percent is finer

D_{50} - size of sediment for which 50 percent is finer

D_{85} - size of sediment for which 85 percent is finer

n - porosity of the bed

s - specific gravity of solids

T - time

v - the settling velocity of the sediment particles

V - volume of solids in the active bed per unit length

W_s - weight of sediment in active bed per unit length

W_f - weight of fine sediment in active bed per unit length

γ - unit weight of water

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ABSTRACT

More knowledge is needed about the physical processes that control the transport of fine sediment moving over an alluvial bed. This knowledge is needed to design a rational sampling program that assesses the transport and fate of toxic substances in the Nation's surface waters because toxic substances are commonly associated with fine sediment. This paper reviews some of the past research in areas that may contribute to an increased understanding of the processes involved. An alluvial bed can have a large capacity to store fine sediments that are extracted from the flow when instream concentrations are high, and it can gradually release fine sediment to the flow when the instream concentrations are low. Several types of storage mechanisms are available, depending on the relative size distribution of the suspended load and bed material, as well as the flow hydraulics. Alluvial flow tends to segregate the deposited material according to size and density. Some of the storage locations are temporary, but some can store the fine sediment for very long periods of time.

INTRODUCTION

In recent years, increasing attention has been focused on the transport and fate of toxic materials in our Nation's surface waters. The U.S. Geological Survey is currently expanding its efforts in this area and is attempting to better understand the processes involved in order to design rational sampling and monitoring programs. Toxic substances in surface waters tend to be associated with silt and clay size particles ($<62\mu m$ (micrometer)), and therefore the transport mechanisms of this fine material is commonly a major factor in determining the dispersion of contaminants throughout a drainage basin. A considerable amount of work has been done concerning the transport of sand-sized sediment (62 to 2,000 μm), but relatively little is known about the transport processes important for transporting fine particles (<62 μm).

The purpose of this paper is to review some of the past research that may contribute to an increased understanding of the transport and fate of fine sediment and to draw as many inferences from that research as possible. A review of several research reports that are not directly related to studying the transport mechanics of fine particles will be given, and the results will be drawn together in an attempt to describe some of the important processes relative to the transport and fate of fine sediment.

Conceptual Framework

A common assumption in the study of erosion and transport of fine material is that once the material is set in motion, and particularly once it enters the channel system, it remains in suspension as long as the streamflow is not impeded. This assumption has fostered the concept of "washload" which is defined as that part of the total sediment load consisting of particles whose sizes are finer than those present in significant quantities in the bed material (U.S. Geological Survey, 1977). Normally, the discharge of washload is considered to be determined by the supply rate, which is considerably less than the transport capacity of the stream. Although this definition does not specify a size boundary for washload, the usual assumption is that a freely flowing stream is capable of transporting all of the material finer than 62 μm that is supplied to it.

The concept of washload forms an integral part of mass-balance modeling where fine material is treated as a conservative substance, and only additions to the amount in transport are allowed. There is usually no provision for loss or exchange of fine material in mass-balance sediment transport models. In reality, however, the paths of individual sediment particles through a drainage basin consist of a sequence of transport and storage periods. Every particle that is eroded from an upland area is not conveyed to a drainage channel, and every particle that enters a drainage channel is not transported to the basin outlet. There is a constant interchange between particles in transport and particles in storage in upland slopes, channel boundaries, and flood plains.

In the study of contaminants associated with fine material, the concept of washload and the mass-balance approach based on this concept are inappropriate. In order to quantify the movement of contaminated sediment through a drainage basin, the pathways of contaminated material and the interactions along these pathways must be understood. Inasmuch as the channel network of a basin is probably the most important pathway for the movement of fine material, the emphasis of this paper will be on interactions between suspended fine material and alluvial channel beds.

INTERACTION OF FINE MATERIAL AND ALLUVIAL CHANNEL BEDS

Rivers generally flow through a valley that has been at least partly filled with alluvial material. A conceptual cross section of a river valley is illustrated in figure D-1. The active bed is mobilized by frequent events and contains the lowest percentage of fine material. The semiactive bed is only mobilized during infrequent or extreme events and contains more fine material than the active bed but less fine material than the underlying valley alluvium. The soil below the water table is saturated and the pore water is in motion. The pore-water velocity vector probably has a major component parallel to the river and some component perpendicular to the river. In addition to the general components of pore-water velocity mentioned above, there are local components caused by local variations in pressure. Typical flowlines for the region near a dune (Thibodeaux and Boyle, 1987) are shown in figure D-2. Flowlines similar to those shown in figure D-2 would be caused by any pervious obstruction to the flow such as a riffle.

The exchange of water between the river and the pore-water system is apparently very efficient. For example, Bencala (1984) found that shallow wells located several meters from the edge of an alluvial channel responded quickly to changes in streamflow conditions. Increasing the chloride concentration of the flow appeared as increased chloride concentrations in the wells. Likewise, Simons and others (1963, p. G42) noted that very fine sediment added to the flow in a flume rapidly increased the fine-sediment concentration of the interstitial water until it was equal to that in the flow. Thibodeaux and Boyle (1987) concluded from experimental observations of dye traces that significant in-bed convection currents can be generated by water flowing over small obstructions on the surface of a porous bed.

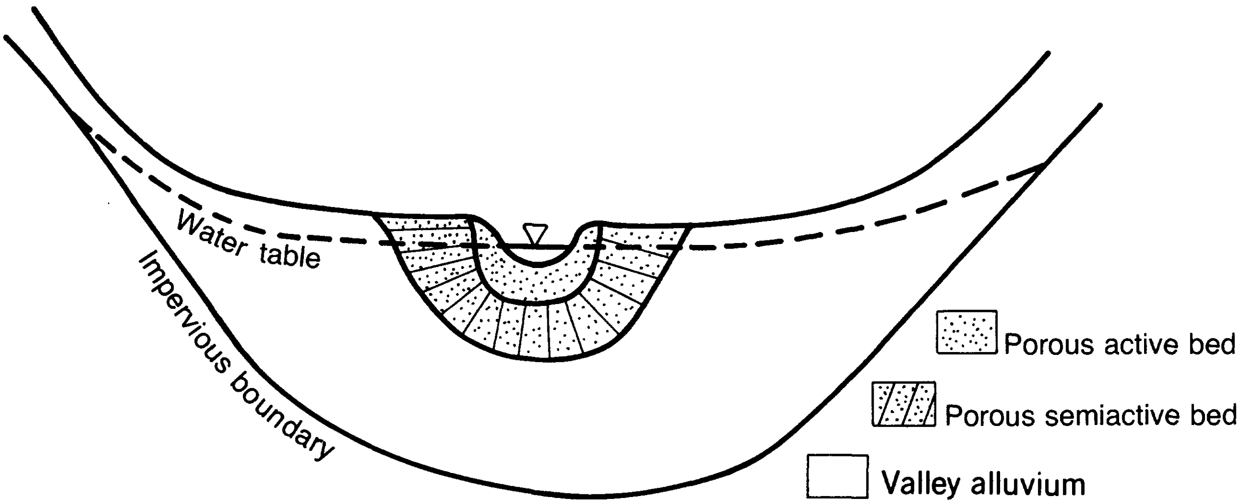

Figure D-1.—Conceptual cross section of a river valley.

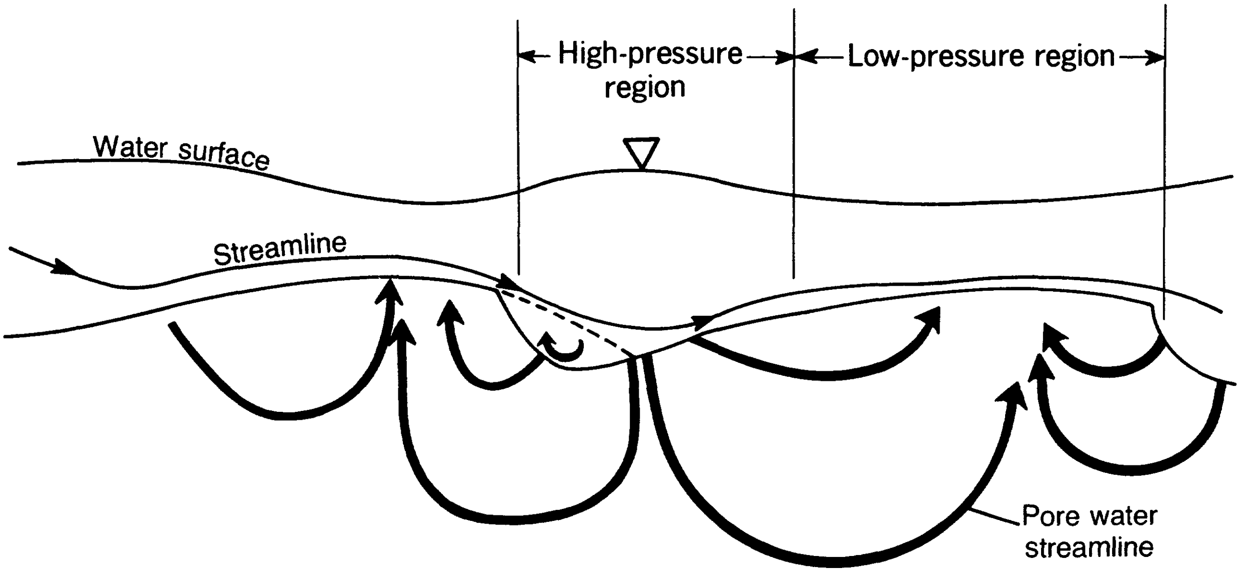

Figure D-2.—Typical flowlines of pore water in a dune bed.

Because there appears to be significant exchange flow between the stream and the pore-water system, it would appear that the bed material may act as a storage area for fine particles carried by the flow. McDowell-Boyer and others (1986) have identified three mechanisms of interaction for fine particles attempting to move through a porous material: particle straining, the formation of a surface cake, and physical-chemical interactions. In this paper, the physical mechanisms of particle-porous media interaction will be emphasized.

Particle Straining

Particle straining refers to the process where fine particles move into the porous media until they encounter pore spaces that are too small to let them pass. The potential for particle penetration into a porous media is known to be a function of the size distribution of the particles and the effective pore diameter of the media. In soil engineering, a good filter material is defined as one that allows for free drainage but prevents movement of soil particles through the filter. To prevent soil particles from moving through the filter, the effective pore diameter of the filter must be smaller than the D_{85} of the soil; and to allow for free drainage, the effective pore diameter must be larger than the D_{15} of the soil (Sowers and Sowers, 1970). The D_{85} is defined as the particle diameter for which 85 percent of the material is finer. The effective pore diameter of a filter is about $(D_{15})/5$; therefore, a good filter is one in which

$$D_{15}(\text{soil}) < D_{15}(\text{filter})/5 < D_{85}(\text{soil}). \qquad (1)$$

Similarly, in a study of sand and gravel filters, Sherard and others (1984) found that finer sand (fs) could not penetrate coarser sand (cs) if

$$D_{15}(\text{cs}) < (9)D_{85}(\text{fs}). \qquad (2)$$

Simons and others (1963) conducted experiments in a flume that recirculates all of the sediment and water so that the total amount of material (both sediment and water) in the system remains constant. The basic procedure was to establish steady uniform flow with a sandbed (D_{15}=300 μm), usually with dune bed forms. A large amount of clay (D_{85}=10 μm) was then added to the flow, and the transport rate measured as a function of time. They found the concentration of clay decreased with time and that the clay was deposited at the floor of the flume even though the dune troughs never scoured to the floor. Immediately after adding the clay, when the transport concentrations were quite high, the clay was deposited in the bottomset beds. As the concentration decreased, because of the loss of material to the bed, these bottomset beds would disappear. Notice that the effective pore diameter of the bed material ($D_{15}/5$=60 μm) is larger than the D85 of the fine material (10 μm). According to equation 1, the fine material in these experiments would be expected to penetrate the bed.

These results compare favorably with a similar laboratory study performed by Einstein (1968). Einstein looked at the interactions of silt-size particles in the range 3.5 to 30 μm flowing over a gravel bed. He also found that the fine particles worked their way down to the flume floor and that the flow concentration decreased exponentially with time according to

$$C = (C_o)\mathrm{EXP}(-vT/Ad) \tag{3}$$

where C = the mean concentration (weight/unit volume) in the flow at time T,

C_o = the mean concentration in the flow at time zero (T=0),
v = the settling velocity of the sediment particles,
d = the depth of flow, and
A = a proportionality constant between C and the concentration at the boundary between the flow and the bed. If there is no concentration gradient, which is commonly the case for silt and clay, then A=1.

In these laboratory experiments, net flow into and out of the bed was virtually zero and the fine material penetrated the bed below the zone of bed movement. Presumably, the material was carried into the bed with the pore water and settled in regions of very low pore-water velocity. This stored material could not be remobilized even if the concentration of fines in the flow was reduced to zero.

When flow into the bed occurs, fine particles can be transported deep into the bed with the flow. Pilgrim and Huff (1983) found suspended-sediment concentrations greater than 1,000 milligrams per liter in subsurface flow through soil macropores. The ability of flow into the bed to transport fine particles is an important factor in determining the vertical distribution of fine material below the active bed. Changes in flow rate and direction in porous media have been found to remobilize fine particles stored in the pore spaces in some cases (Muecke, 1979). Thus, it is possible that fine material may go into storage below the active bed (fig. D-1) during influent conditions and be remobilized during effluent conditions. However, if effluent flow is absent or weak, then the fine material will remain in storage until the bed is disturbed.

Surface Caking

Einstein and Chien (1953) performed an experiment similar to that of Simons and others (1963), but their purpose was to study the sediment transport of a well-graded material. In the one series of experiments, the D_{15} of the bed material was 150 μm and the D_{85} of the fine material was 400 μm. Applying these numbers in equation 1 indicates that the fine material will be prevented from being transported into the bed. Einstein and Chien (1953) observed that the fine material accumulated on the surface of the bed following the injection of a large concentration, and then the material was selectively removed as the supply was decreased. They did state that the slow filtration of water through the bed carried some fine particles into the bed and left them behind in the voids. Thus, if the effective pore diameter of the bed material is too small, fine material will be prevented from penetrating much below the active bed layer. When bed movement ceases, the fine material trapped in the active bed layer will probably be retained even if effluent flow is present.

Size Sorting by Bed Forms

Brady and Jobson (1973) studied the segregation of heavy minerals by using a large recirculating flume. The experiment did not contain a large amount of very fine material but the bed material was well graded with D_{15}=190, D_{50}=290, D_{85}=500 μm, and significant sorting according to size and density occurred in the bedding structure. A summary of selected observations will contribute to the understanding of how bed material can be sorted by size and concentrated at certain locations in the bed.

The bedding structure observed in all dune-bed runs is illustrated in figure D–3. The topset and bottomset beds tend to be composed of the finest component of the bed material. For example, the size distribution, expressed in terms of D_{15}–D_{50}–D_{85} sizes of the quartz grains in the topset beds for run 2 were 136–187–254 μm whereas the size distribution of the material in the foreset beds was 150–212–281 μm, and the size distribution of the material in transport was 124–183–269 μm. The bedding structure was flow dependent however. At low values of boundary shear, the topset and bottomset beds were generally missing, but the topset beds became more extensive with increasing values of shear.

When the topset beds are absent, the selective deposition zone (B-C of fig. D–3) is missing and all material eroded from the upstream side of the dune reaches the brink and is either suspended or avalanches down the dune face. With well-defined topset beds, the fine material is selectively deposited in the deposition zone B-C before reaching the dune face.

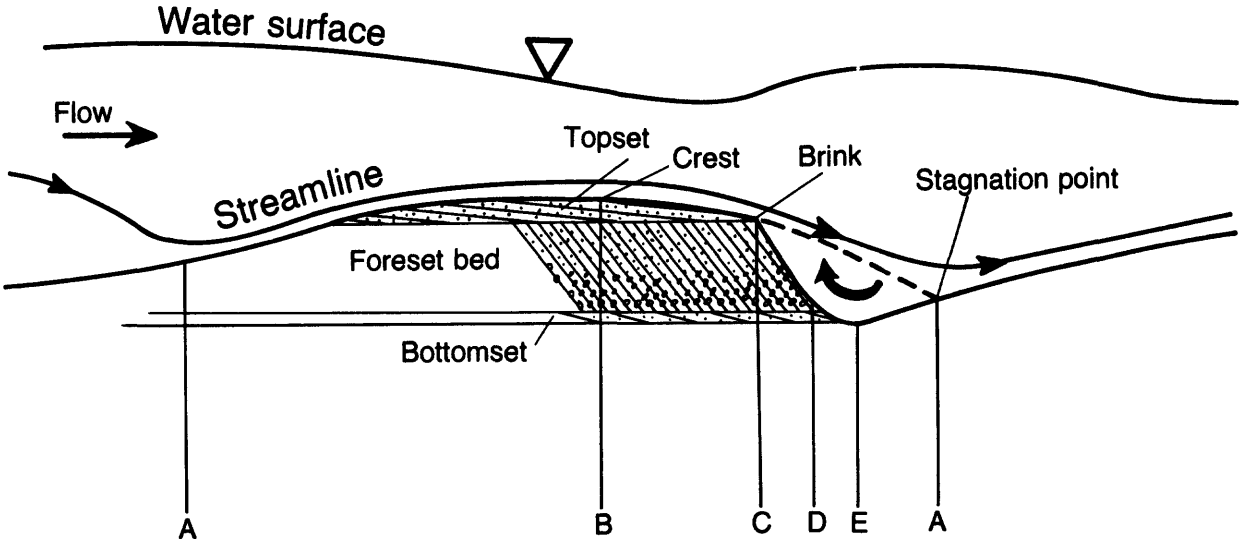

Figure D–3.—Typical bedding structure for a dune bed.

Although the finer material tended to be selectively transported and deposited in the topset and bottomset beds, the vast majority of the finer particles were always trapped in the foreset beds. To illustrate, the mass of material smaller than 100 μm suspended in the water, tied up in the topset beds and tied up in the foreset beds, was computed from the concentration, size distribution, and volume of the water above an average dune, and the size distribution and volumes of material deposited in the topset and foreset beds of the average dune. For run 2, in which the average dune was 724 cm (centimeters) long and 30 cm high, the volume of topset material in the average dune was only 180 cm^3 (cubic centimeters) per centimeter width and only 1.4 percent of the material finer than 100 μm was deposited in the topset beds of the average dune whereas only 0.07 percent of the material finer than 100 μm was suspended in the flow. In other words, 98.53 percent of the fine material in the flume system was trapped in the foreset beds. Actually this estimate is low because the volume of foreset beds should be computed as the volume of material above the deepest dune trough rather than the volume of material in the average dune.

Local Interactions of Fine Sediment with Individual Dunes

Dunes move downstream as material is eroded from the upstream side and deposited on the downstream side. Although their speed, size, and shape do not remain constant, these factors change rather slowly so that a specific bed-surface profile pattern is usually recognizable after the dunes have moved downstream for a distance of several dune lengths. Assuming dunes translate downstream without any change in size or shape, the following observations can be made.

Net erosion occurs at all points where the dune-surface slope is positive and net deposition occurs at all points where the slope is negative. The dune surface can be divided into five zones (see fig. D-3), each controlled by different processes. In zones A-B and E-A, erosion is the dominant process, and all particles eroded from the surface are likely to be transported out of the zones. The end of zone E-A and beginning of zone A represent the location of the highest water pressure (the stagnation point) and the point B (the crest), represents the region of lowest water pressure. Pore water enters the bed in the high-pressure region and leaves the bed in the low-pressure region (fig. D–2). Very fine particles trapped in the bed near the high-pressure region may be carried deeper into the bed by the pore water. If these very fine particles are not filtered out as the water passes through the foreset beds, they may be trapped at the interface of the topset or bottomset beds as the pore water moves through these zones of finer material. Large amounts of fine material on or in the moving bed layer may inhibit the exchange of water between the stream and the pore-water system, thus contributing to anoxic conditions within the bed. Unless a particle is carried into the bed by the pore water, it will be eroded by the flow and transported out of zone A-B.

The sediment transport rate is larger at the crest (point B) than at any other point along the dune, because every moving particle must pass this point. Downstream of the crest, selective deposition of the topset bed occurs in zone B-C. Smaller particles are deposited in this region of tractive deposition, perhaps because they do not protrude above the boundary layer and so are protected from the higher velocities. Most of the moving particles, however, reach the brink, (point C), where the flow separates from the bed.

At the brink, all material is either suspended or avalanches down the dune face. Zone C-D is a region of massive deposition of the foreset beds by the avalanche process. The avalanche process naturally segregates the material to some extent, leaving the finer material near the top. Material tends to accumulate at the brink, and when too much has been accumulated, it breaks loose and avalanches down the face. This process leaves a bedding structure which shows up as layers.

A characteristic of dunes is the softness, or lack of compaction of the bed material. It is possible that the large effluent velocity of the pore water in the deposition zones partly supports the grains and contributes to the looseness of the bed.

Zone D-E is the area where bottomset beds are deposited. The reverse flow in the trough brings material, eroded from zone E-A, upstream. In zone D-E, the material is selectively deposited by tractive deposition much like that occurring in zone B-C. The bottomset beds look almost identical to the topset beds but the material has been transported upstream instead of downstream. The bottomset beds create a relatively tight region of the bed which may trap fine particles carried by the influent pore water.

Storage and Remobilization of Fine Material

During runoff events, the highest concentrations of fine material usually are delivered to the channel system early in the event when erosion of available material is high and the channel system is receiving direct overland runoff. As the supply of fine material is depleted, sediment concentration in the stream reaches a peak and begins to recede even though streamflow may still be increasing. During the rising part of the hydrograph, the concentration of fine material in the flow is usually high and more fine material is likely to be deposited in zones B-C and C-D than is eroded from zones A-B and E-A. Flow is induced within the bed forms (fig. D-2) and the increasing water depth may induce flow into the bed and banks. Fine material in the flow will be stored in the moving part of the bed and some fine material may be carried into storage with the pore water moving into the banks and the region below the active bed. On the receding limb of the hydrograph, overland-flow contributions cease and the recession curve is governed in part by effluent flow through the channel boundary. The onset of effluent conditions begins to return fine material from storage in the bed to the streamflow, and the rate of return of this material may strongly influence the rate of recession of the concentration curve. The duration of effluent conditions and the character and rate of movement of the bed forms will determine how much of and the rate at which the stored material is returned to the streamflow.

There is little field information available on storage and remobilization of fine material in alluvial beds. Jobson (1985), in analyzing data from a regulated river, concluded that fine particles of biochemical oxygen demand (BOD) were being deposited in the bed during low-flow conditions when bed movement was minimal and then reentrained when increased flow caused more rapid bed movement or agitation. At steady low-flow conditions, the BOD decreased more rapidly than could be explained by oxygen consumption, then the BOD suddenly increased as the increase in flow occurred.

Storage Capacity of Alluvial Beds

In the definition of washload, the term "significant quantities" is commonly taken to mean the coarsest 95 percent of the bed material. In order to understand what this means in terms of storage of fine material, consider a channel reach 5,280 feet long with an alluvial bed 100 feet wide and 1 foot deep, having a volume of 528,000 ft^3 (cubic feet) of active bed material per mile. Typical values of porosity (n) for an alluvial sand range from 0.33 to 0.52 (Davis and DiWiest, 1966) so the actual volume of solids (V) in the active bed is given by

$$V = (1-n)(528{,}000) \tag{4}$$

and ranges from 253,440 to 353,760 ft^3/mi (cubic feet per mile). Assuming the specific gravity of the sediments (s) to be 2.65 and the unit weight of water (γ) to be 62.4 lb/ft^3 (pounds per cubic foot), the actual weight (w) of the active bed material is given by:

$$W_s = (V)(\gamma)(s) \tag{5}$$

and ranges from 20,954 to 29,249 ton/mi (tons per mile).

Assume the range of W_s is indicative of bed conditions before fine material is introduced. Now if a runoff event deposits fine material in the bed such that the percent of fine material in the bed material is increased by 1 percent (much less than a "significant quantity"), the weight of fine material stored in the bed (W_f) is given by:

$$W_f = (1/99)W_s \tag{6}$$

and ranges from 212 to 295 ton/mi. If the runoff event occurs for one day, the riverbed is capable of storing enough fine material to decrease the load in the downstream direction by between 212 and 295 ton/d/mi (tons per day per mile). The material stored in the active and semiactive bed is, of course, available for reentrainment at a later time.

IMPLICATIONS FOR SAMPLING ALLUVIAL BEDS

The problem of quantifying the distribution of sediment-associated containments in an alluvial bed can be appreciated by considering that the volume of the sample chamber on commonly used bed-material grab samplers is about 0.0055 ft^3. Using the range of W_f given above, the expected weight of fine material in any one sample ranges from 0.0044 to 0.0061 lb (pound); or if W_f accounts for 5 percent of the bed material, the expected weight of fine material in any one sample ranges from 0.022 to 0.031 lb. Because the fine material and associated contaminants in a reach tend to segregate within bed forms (fig. D-3), any one sample or any set of several samples may have only a small chance of encountering the contaminated fine material. Another complication is that sampling schemes using grab samplers are virtually two dimensional because the sample chamber only penetrates 2 inches into the bed. In order to adequately sample the assumed reach, a grid would have to be established and cores taken at each node on the grid. A 2-inch diameter core 1 foot in length has a volume of 0.022 ft^3 which, assuming W_f accounts for 5 percent of the bed material, would yield from 0.087 to 0.121 lb of fine material per core.

SUMMARY

The alluvial bed material of a river provides a potentially huge storage reservoir for fine sediment. Physical interactions between the fine material and the bed material are primarily controlled by the size distribution of the fine material and the effective pore diameter of the bed material. If the relation between these two factors is such that fine material is prevented from penetrating the bed material, then interactions will be limited to the depth of bed movement. If dunes are present, most of the finer material will be trapped in the foreset beds. Removal of fine material on the bed surface will be rapid when the stream concentration falls, but material trapped in the bed will likely remain if the bed is immobile or will be released slowly if the bed is mobile.

If conditions are favorable for fine material to penetrate the bed with the pore water, then large amounts of fine material may be stored in the bed when stream concentrations are high or when flow into the bed is occurring. If effluent flow occurs, as stream stage and concentration decrease, the inactive bed may contribute substantial quantities of fine material to the stream. This return of stored sediment from the bed may be a primary factor controlling the concentration recession following a runoff event.

The distribution of fine material and associated contaminants cannot be assumed to be uniform throughout the bed material. Physical and hydrologic conditions may be different along the channel; channel geometry, obstructions, and bed forms may cause selective sorting, and variations in the quantity of fine sediment with depth may be strongly influenced by the recent event history. In addition, the distribution of contaminants may be a function of the distance from the source. Bed-material sampling programs need to be designed with these factors in mind. If the objective of sampling is simply to determine the widespread presence or absence of a contaminant, then sampling design may not be critical. However, if the objective is to determine the spatial or temporal distribution of contaminants, then the three-dimensional characteristics of alluvial beds and antecedent hydrologic conditions need to be accounted for.

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DEVELOPMENT OF A HOLLOW-FIBER TANGENTIAL-FLOW FILTRATION SYSTEM FOR CONCENTRATION OF SUSPENDED SEDIMENT SAMPLES FROM NATURAL WATERS

By James S. Kuwabara[1] and James R. Robinson[2]

Biological availability of various inorganic and organic solutes is significantly affected by partitioning of those solutes between solid and solution phases (Stumm and Leckie, 1971; Grobler and Davies, 1979; Kuwabara and others, 1986). Researchers interested in quantifying concentrations of particulate-bound toxic substances and nutrients face the formidable problem of collecting a sufficient mass of suspended sediment when particulate mass concentrations in natural waters are on the order of 10 mg/L (milligrams per liter). Therefore, hundreds of liters of sample need to be processed in order to produce gram quantities of suspended sediment required for various chemical analytical sequences. The two currently (1987) available methods that appear to have the greatest potential for large volume particle separation at the submicron level are continuous-flow centrifugation and tangential-flow filtration (TFF). Continuous-flow centrifugation has distinct logistical, performance and maintenance-related disadvantages. To conduct high-speed (greater than 40,000 × gravitational acceleration) or approximately 18,000—20,000 rpm (revolutions per minute) continuous-flow centrifugation for suspended sediment collection, large sample volumes had to be brought from the field to a high-speed centrifuge. At such speeds, maintenance of the rotor distributor and continuous monitoring of the centrifuge during operation was imperative. The high capacity TZ28000 rotor (Sorval[3], Claremont, Calif.) produces a supernatant discharge of approximately 1 liter per minute. Efficient removal of submicron particles with high organic content at 20,000 rpm is not always achieved (Ronald Harvey, U.S. Geological Survey, oral commun.).

A hollow-fiber TFF system, fabricated by SETEC (Livermore, Calif.), allows on-site operation with minimal hardware maintenance and monitoring during operation. TFF operates on the principle that sample, flowing at low pressure (less than 25 pounds per square inch) perpendicular to filtrate flux rather than in the same direction, provides a scouring effect that mitigates clogging problems and thus yields higher overall filtrate flux per unit membrane area than conventional dead-ended filtration. The linear flow path of hollow-fiber TFF, in comparison to the rectangular serpentine sample flow path of plate and frame TFF, has the added advantage of minimal "dead" zones in the cartridge where particulates may accumulate, and the capability of periodic resuspension of particulates through membrane backwashing. The initial sample, in a reservoir, is continually pumped though the filter cartridge composed of many porous tubules (hollow fibers). As sample passes through these tubules, filtrate "weeps" perpendicularly through the pores. The dewatered sample (retentate) returns to the reservoir for further cycling through the cartridge until the desired retentate volume is achieved. A smaller volume filtration or freeze-drying device may be used for further dewatering. Our system is composed of a pump and filtration module (fig. D—4). The pump module contains a centrifugal pump with a polypropylene head that can be run dry for up to 10 hours, allowing the operator to leave the sampling site during sample processing. The module also has a compressor, connected to a 2-liter filtrate reservoir, for

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[3] Use of brand, firm, or product names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

SCHEMATIC DIAGRAM OF THE HOLLOW FIBER DEWATERING DEVICE

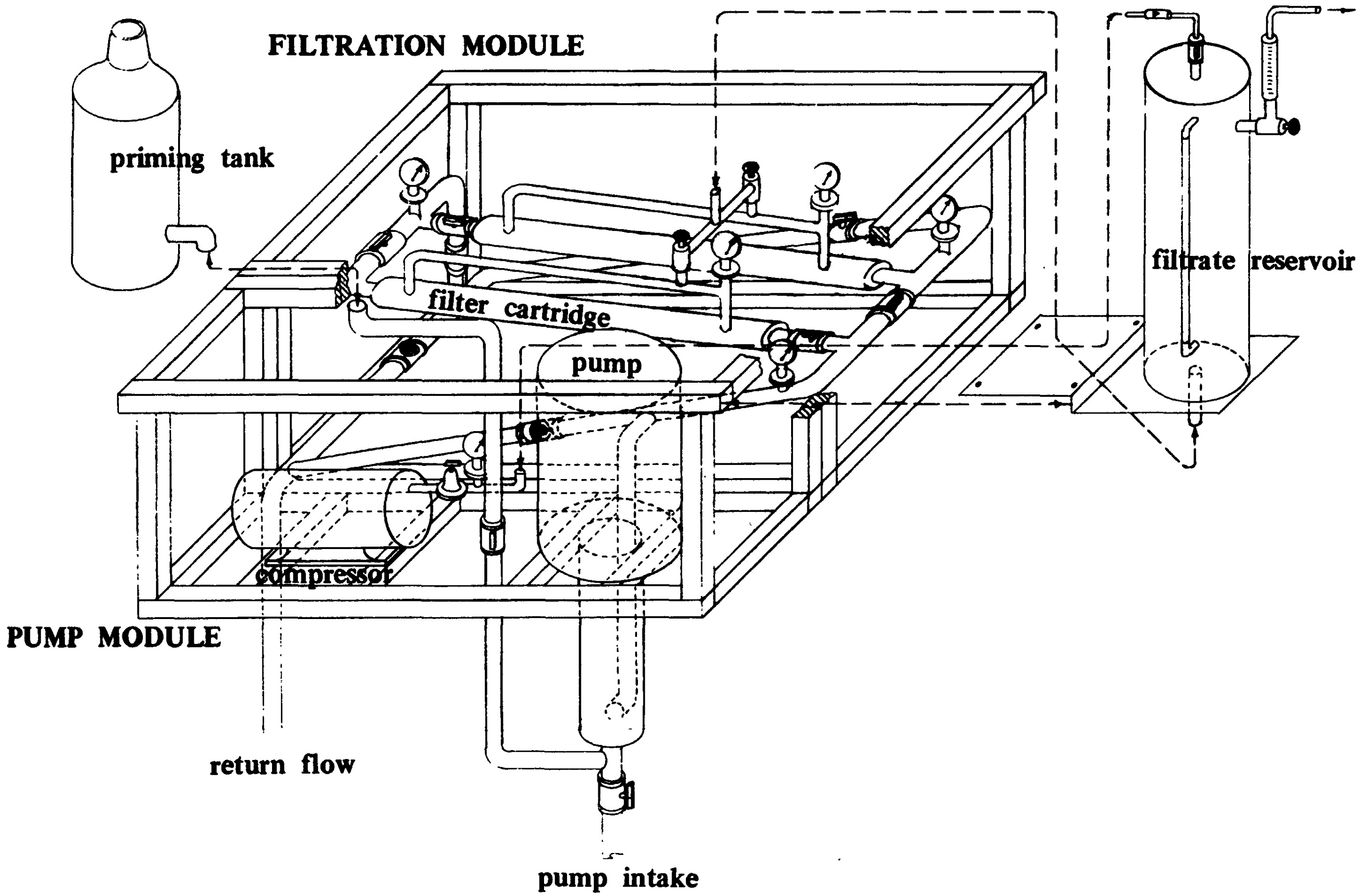

Figure D--4.--Schematic diagram of the hollow-fiber tangential-flow filtration device showing two all polypropylene filter cartridges within the filtration module. (Compressed air generates pressure against filtrate flow to allow membrane backwashing during operation.)

periodic backwashing of the filter cartridges. The filtration module contains two linear, all polypropylene TFF cartridges (0.2-μm (micrometer) pore size), each capable of approximately 4 liter-per-minute filtrate flux, depending on the turbidity of the sample and the physical character of the suspended particles. The two cartridges can be operated independently, in series or in parallel, in order to adapt to between-sample variations in filtrate flux. Plumbing of the filtration module has been done with polypropylene parts so that the entire module can be placed in an autoclave for sterilization or acid washed after pressure gages are removed. Both modules fit within a linear polyethylene reservoir for system transport and processing of 400 liter samples.

Initial tests of this system by microbial counts indicate highly efficient particle separation (table D-1). Microbial recovery for South San Francisco Bay samples were approximately 88 percent with periodic membrane backwashing. The effect of using these dewatering devices on particle size distribution poses some fundamental performance questions:

1. How efficiently are particles removed around the specified membrane pore size?
2. How does this efficiency change as the particle suspension concentrates?
3. How is the particle size distribution of the retentate altered by compacting and scouring of particles during the concentration procedure?
4. What are the carryover effects of replicate sampling with the same set of filter cartridges?

Table D-1.—Initial performance tests by microbial counts (10^6 cells/mL ± 95 percent (CI) for the hollow-fiber tangential-flow filtration system

[Counts, performed by L. George, U.S. Geological Survey, National Research Program, Menlo Park, Calif., reflect bacterial abundance in the initial 390 liter sample (raw), cartridge filtrate, and final 12 liter retentate volume]

Sample	Raw sample	Filtrate	Retentate	Recovery (percent)
South San Francisco Bay sample, Redwood Creek, 11/20/86 (no backwashing)	8.19±0.92	0.19 ±0.06	48.43±17.12	19±8
San Fransisco Bay sample, Station 27, 12/15/86 (with backwashing)	3.89±0.76	0.003±0.001	114.72±18.25	88±15

The answers to the above questions directly affect the experimental protocol at our five study sites (Whitewood Creek, South Dakota; South San Francisco Bay, Calif.; and three tributaries in the Lake Tahoe basin, Calif./Nev.). To begin addressing the above questions, we will collect replicate samples from two sites along Whitewood Creek by using the SETEC system. The raw sample, filtrate and retentate, collected during sample processing, will be analyzed by Coulter Counter for particle size distribution above 2 microns and by laser light scattering spectroscopy for submicron particles. If filter separation significantly alters the particle-size distribution of the retentate, it will then be important to standardize techniques to minimize or possibly quantify these effects.

Further comparisons between dewatering systems are ultimately needed to establish procedures for other research applications. However, performance of this hollow-fiber filtration device in terms of filtrate flux, particle separation, and convenience of operation has thus far shown it to be an attractive alternative to other currently available methods.

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☆U.S. GOVERNMENT PRINTING OFFICE: 1988-530-101/60019