HYDROGEOLOGY, WATER CHEMISTRY, AND SUBSIDENCE OF UNDERGROUND COAL MINES AT HUNTSVILLE, MISSOURI--JULY 1987 TO DECEMBER 1988

By Dale W. Blevins and Andrew C. Ziegler

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CONVERSION FACTORS

Multiply	By	To obtain
cubic foot	0.02832	cubic meter
cubic foot per second	0.02832	cubic meter per second
foot	0.3048	meter
inch	25.4	millimeter
mile	1.609	kilometer
square foot	0.09294	square meter
foot squared per day	0.09290	meter squared per day
square mile	2.590	square kilometer
gallon per minute	0.06308	liter per second

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

°F = 9/5 °C + 32.

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

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ABSTRACT

Abandoned underground coal mines at Huntsville, Missouri, are the source of acidic mine water containing large concentrations of iron and sulfate and are the cause of land subsidence in some areas. The decomposition of pyrite in these abandoned mines has resulted in dissolved iron concentrations of 16 to 620 milligrams per liter in underground-mine water. Oxidation of soluble ferrous iron in flooded mines is inhibited by the lack of oxygen, but some unflooded cavities along the flow path allow oxygen to contact underground-mine water and increase the extent of oxidation and acidification. At three wells in up dip parts of the mines, the pH of water ranged from 6.2 to 6.5. Underground-mine water has not contaminated a nearby aquifer because the aquifer is isolated from the coal seam by stream-valley erosion and the dip of the coal seam is away from the aquifer. The total volume of mine drainage per year was equivalent to 0.43 inch of water over the area of mines, or less than 2 percent of the average annual precipitation.

Eighty percent of the mine discharge emerged at two springs where the pH ranged from 4.7 to 5.9 and total iron concentrations ranged from 265 to 620 milligrams per liter. Oxidation and hydrolysis of the iron acidified two ephemeral streams downstream from the mine springs to pH values less than 3. Sewage effluent entering one of the receiving streams just downstream from Huntsville often neutralized the acidity caused by mine drainage.

Subsidence has occurred in areas where overburden is less than 30 feet thick, usually over drift entries and at shafts. Subsidence has been limited to areas where the overburden did not include a massive sandstone that halted the upward migration of overburden collapse. Collapsed shaft entries have been filled and were not observed in this study. However, improperly filled shafts have the potential to recollapse.

INTRODUCTION

Underground coal mining in and near Huntsville, in Randolph County in north-central Missouri, (1980 population 1,650; U.S. Department of Commerce, 1983; fig. 1), began soon after 1831 (Gentile, 1967). Mining in the Huntsville area was at its peak during 1903 and continued until 1966 when the last underground mine was closed (data on file at the Missouri Department of Natural Resources, Land Reclamation Commission, Jefferson City), and the economically recoverable coals under Huntsville had been mostly, if not completely, removed. The now abandoned mines are of concern to the public and to various State and Federal agencies for two reasons: (1) mine drainage acidifies streams and leaves large, soft, dangerous deposits of iron oxyhydroxides at mine springs and on streambeds (data on file at the Missouri Department of Natural Resources, Land Reclamation Commission), and (2) collapse of mine cavities sometimes causes surface subsidence resulting in property damage or personal injury. To address these concerns, the U.S. Geological Survey, in cooperation with the Missouri Department of Natural Resources, in 1987 initiated a study to:

1. Determine the location of mine springs, the seasonal variation of stream-water chemistry, and the effects of underground-mine water on flow and water quality of nearby ground water and receiving streams, and
2. Identify areas susceptible to surface subsidence because of mine collapse.

The purpose of this report is to present the findings and data collected for this study.

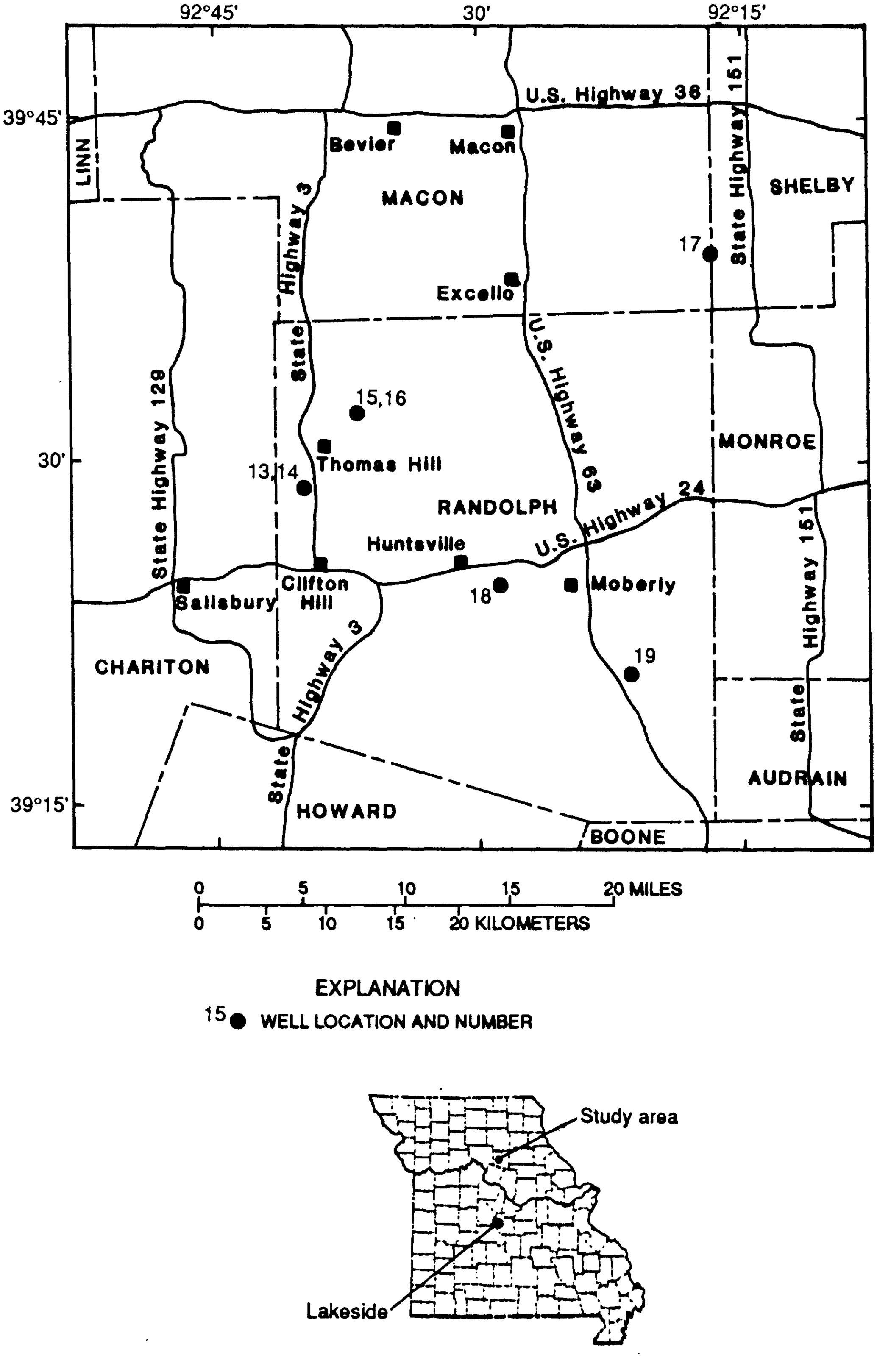

Figure 1.--Location of study area, selected wells, and Lakeside pan evaporation site.

Acknowledgments

Much information about location of mine entries, mine seeps, and subsidence features, as well as resident interviews and data from unpublished geologic maps was obtained from Mimi Garstang and others at the Missouri Division of Geology and Land Survey. City officials from Huntsville also were helpful in providing information. The authors are grateful for their assistance. Support of this study by the U.S. Department of the Interior, Office of Surface Mining Reclamation and Enforcement also is acknowledged; however, the contents of this publication do not necessarily reflect the views and policies of the Office of Surface Mining Reclamation and Enforcement.

Study Methods

Geologic and mining data were collected for the entire study area to locate collapse features and determine the slope of the mines. Rock outcrops, seeps and springs, drift entries, and subsidence features were located onsite and altitudes were determined from the U.S. Geological Survey topographic quadrangle map. Drift entries are defined in this report as the horizontal to slightly inclined tunnels into the side of a hill that serve as entrances to some of the underground mines.

Hydrologic and water-quality data were collected at more than 60 sites to determine effects of mine drainage on ground and surface water. Water levels in the mines were measured periodically with a steel tape at four wells along U.S. Highway 24. Well reference-point altitudes were determined by surveying from Missouri Highway and Transportation Department bench marks. Sulpho Rhodamine B (Acid Red 52) dye was injected into a well February 24, 1988, and dye concentrations in nearby wells and surface-water sites were periodically measured with a fluorometer calibrated from 0.1 to 1,000 μg/L (micrograms per liter), compensating for natural fluorescence of the water. A continuously recording flow gage with a 60 degree V-notch weir control was installed at the largest mine spring. Surface-water sites were selected where changes in water quality were known or expected, such as downstream from mine seeps, tributaries, and sewage effluent discharges.

Discharge, specific conductance, pH, Eh (oxidation-reduction potential), water temperature, dissolved oxygen, and total iron (Fe) were measured periodically at selected stream sites. Discharge was measured volumetrically and with pygmy current meters. Specific conductance was measured onsite with a portable meter with manual temperature compensation. The meter was calibrated in a range bracketing the specific conductance of the water sampled. Values of pH were measured with a portable pH meter calibrated in a range bracketing the pH of the water sample with a set of standard buffers. The Eh was measured with a platinum-silver silver-chloride electrode and reported relative to the standard hydrogen electrode. Between each measurement the electrode was cleaned and checked against standard Zobell solution with a potential of 0.43 volts. Temperature was measured with a mercury thermometer and reported to the nearest 0.5 °C (degree Celsius). Dissolved oxygen was measured with a portable dissolved-oxygen meter calibrated in an air chamber saturated with water and checked in a solution of sodium thiosulfate containing less than 0.1 mg/L (milligram per liter) dissolved oxygen.

One set of water samples was collected synoptically at 3 wells and 17 surface-water sites for analysis of selected properties and dissolved constituents. Specific conductance, pH, Eh, temperature, and dissolved oxygen were measured in-situ at all surface-water sites. In ground water, these properties and constituents were measured in a flow-through chamber supplied by a 3-in. (inch) submersible pump. Surface-water samples were collected from the midpoint of the stream cross section in polyethylene bottles.

Dissolved Fe was determined at the time of sample collection and by laboratory analysis. Onsite, concentrations of Fe were measured colorimetrically with a spectrophotometer set at a wavelength of 510 nanometers. Methods were adapted from those described by HACH[1] (Hach Company, 1987), with HACH reagents containing 1,10 phenanthroline and hydroxylamine hydrochloric acid.

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

Laboratory analyses of water samples were made by the U.S. Geological Survey in accordance with procedures described by Fishman and Friedman (1985). Dissolved constituents were determined from water samples that were filtered in the field through a 0.45 μm (micrometer) filter in a polyvinyl chloride chamber using a peristaltic pump as the pressure source. Samples analyzed for anions (except dissolved nitrogen (N) species) were filtered but otherwise unpreserved. Samples analyzed for dissolved N species were preserved with 1 mL (milliliter) of mercuric chloride, chilled, and maintained near 4 °C until analysis. Samples to be analyzed for metals were filtered and then acidified in the field with double-distilled, laboratory-grade nitric acid to a pH of less than 2.0. Samples analyzed for total organic carbon were collected directly from the stream or from the pump outflow in a glass bottle and chilled and maintained near 4 °C until analysis.

Acidity is defined in this report as the capacity of a solution to react with hydroxyl ions (OH^-) and was determined by endpoint titration with sodium hydroxide to a pH value of 8.3 (Brown and others, 1970). Alkalinity is similarly defined as the capacity of a solution to react with hydrogen ions (H^+). Alkalinity and bicarbonate (HCO_3) concentrations were determined at the time of sample collection by incremental electrometric titration with 0.16 normal sulfuric acid to the inflection point of the titration curve at a pH value of about 4.5, where nearly all carbon dioxide (CO_2) species are in the form of carbonic acid (H_2CO_3).

Computations of saturation indices were made using chemical equations and equilibrium constants in a computer algorithm called WATEQF (Plummer and others, 1976). A modification of WATEQF that considers several minerals commonly associated with mine drainage (WATEQ4F) by Ball and others (1987) was used for this study.

Four unnamed tributaries in the study area were designated west, north, east, and south creeks for ease of identification. Sampling sites along these streams have been designated by two letters and a number. The first letter indicates the sources of the water and is either M for mine spring or S for surface water. The second letter indicates the location--W, west creek, N, north creek, E, east creek, and S, south creek. The number was assigned for identification purposes only and is unique to this report. SA1 is the designation for a site where dye concentrations were measured.

HYDROGEOLOGY

Bedrock near the surface in the vicinity of Huntsville consists of rocks of Pennsylvanian age assigned to the Cherokee[2], Marmaton, and Pleasanton Groups. These rocks commonly are covered by unconsolidated deposits of Pleistocene glacial drift, and Quaternary alluvium (Work and others, 1982). Of particular importance are the Bevier-Wheeler coals and the Pennsylvanian rocks just above and below them (fig. 2). The coal seams are separated by 1 to 2 in. of shale or clay and were mined as a single unit. The Bevier-Wheeler coals averaged about 48 in. thick and were the primary coal source in and around Huntsville for more than 100 years. The room and pillar method of coal removal was dominant (Weigel, 1921). The Bevier-Wheeler coals [altitude 690 to 760 ft (feet) above sea level] lie above the flood plains of the two largest streams in the area, the East Fork Little Chariton River and Collier Branch. Consequently, water from the mines drains onto the land surface along outcrop lines. Tributary streams have eroded much of the coal seam, isolating "lobes" of mine workings (fig. 3). Although no mine maps are available, all areas of Huntsville where coal was present were undermined (Weigel, 1921).

Most of the Pennsylvanian rocks above the Bevier-Wheeler coals are unsaturated. However, small quantities of water move downward and become perched in thin layers on top of the least permeable rocks. The combination of low-permeability rocks and thin saturated layers causes Pennsylvanian rocks to have small values of transmissivity (table 1). The underclay immediately beneath the Bevier-Wheeler coals is about 3-ft thick and small quantities of water commonly are perched on the underclay. The water perched on the underclay often appears as seeps on hillsides and in creek beds. The intersection of a creek bottom and the coal-underclay layers often can be located by the presence of small quantities of reddish water with an iridescent scum (typical of underground-mine water) in an otherwise dry creek.

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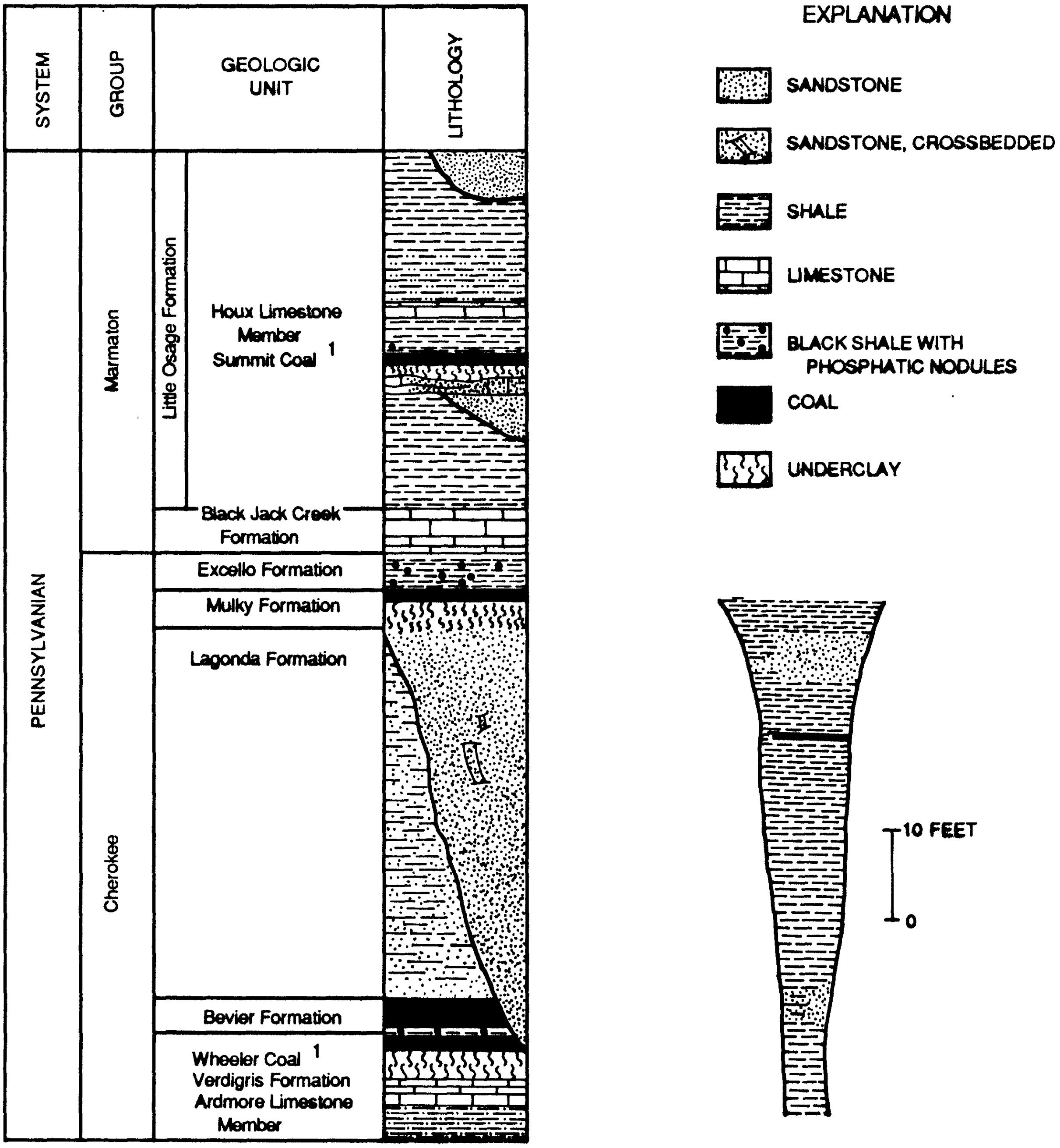
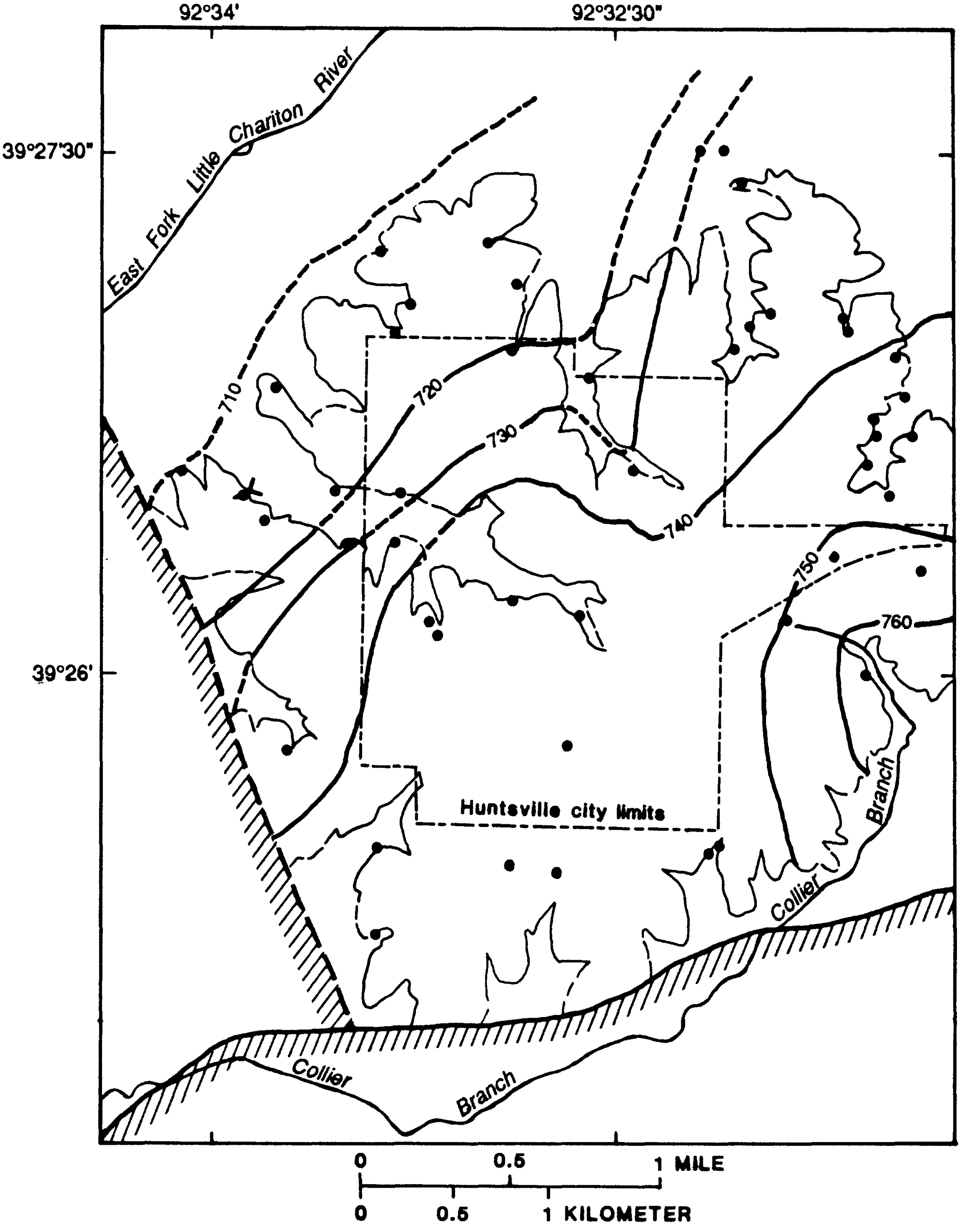
[2] Unit follows the usage of Missouri Division of Geology and Land Survey.



[1] Nomenclature follows the usage of Missouri Division of Geology and Land Survey

MOBERLY CHANNEL FILL--Composed predominately of shale and sandstone; can replace the section of Pennsylvanian rocks as shown in this figure; thought to be late Pleasanton (modified from Gentile, 1967)

Figure 2.--Generalized stratigraphy of the Huntsville area.



EXPLANATION

APPROXIMATE CONTACT OF COAL WITH CHANNEL-FILL SANDSTONE

APPROXIMATE CONTACT OF COAL WITH THE MOBERLY CHANNEL FILL (modified from Gentile, 1967)

TOP OF THE BEVIER-WHEELER COALS OUTCROP--Dashed where approximately located

—740 – – ALTITUDE OF THE TOP OF THE BEVIER-WHEELER COALS--Dashed where eroded. Contour interval 10 feet. Datum is sea level

OPEN DRIFT

● CONTROL POINT

Figure 3.--Location and altitude of the top of the Bevier-Wheeler coals and their relation to the Moberly channel fill.

Table 1.--*Reported transmissivity of Pennsylvanian rocks in Macon and Randolph Counties, Missouri*

[--, unknown; data from Hall and Davis, 1986]

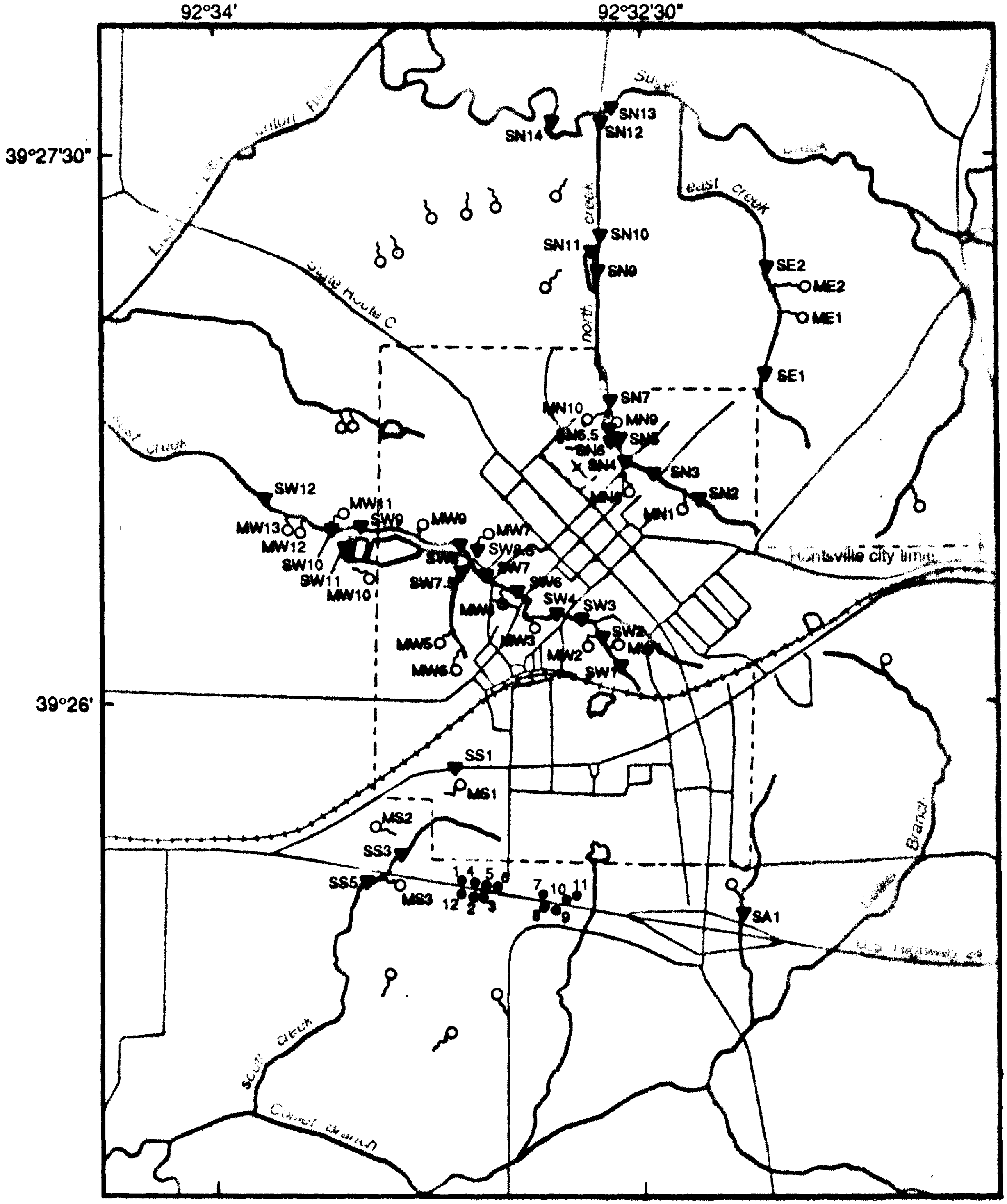
Source	Aquifer[a]	Location	Number of sites	Transmissivity, in foot squared per day
Haliburton Associates (1981)	--	near Excello	2	0.08 - 1.0
Horner and Shifrin, Inc. (1981)	above Bevier-Wheeler coals	near Thomas Hill	5	.007 - 1.0
Horner and Shifrin, Inc. (1981)	below Bevier-Wheeler coals	near Thomas Hill	4	.003 - .016

[a] Aquifer thicknesses not reported.

The underclay below the Bevier-Wheeler coals is firm when dry, but becomes moist and soft when exposed to air (Weigel, 1921). Softened clay allows the weight of the overburden to press supporting pillars in coal mines down into the underclay, thus narrowing the cavity several inches. The clay often was removed from mine entries and from under supporting timbers, and perhaps a few other locations. The clay rests on about 3 ft of the upper Ardmore Limestone member of the Verdigris Formation (fig. 2), which made a firm floor and foundation for mining operations. Weigel (1921, p.75), reporting on the underground coal mines in and around Huntsville, wrote:

> "The drainage question does not affect the operation of the mines to any more than a very slight extent. Many of them are absolutely dry, except for the surface water which runs in at the shaft. A few have local wet spots, where passage is made through ground immediately below creeks. Even this is small and is entirely local in the mine. The Macon, Randolph, and Adair county mines are almost entirely dry. *** The mines at Huntsville are outcrop mines and work under very shallow cover, and hence are bothered with considerable surface water, especially near the outcrop.
>
> The large shipping mine recently opened at Huntsville by the Powhatan Coal Company has had especial difficulties with water. This mine is opened on the outcrop through a slope. As the coal lies rather high above stream level the line of outcrop is extensive. All along this for fifty years or more there have been opened from time to time many small country banks and a few larger wagon mines. These have been worked to a varying extent, but all are alike in that they have not been mapped and that no records have been kept of them. Many have even been lost track of altogether. These have become filled with water and constitute natural reservoirs in the coal horizon. Owing to the lack of definite information a new company can never tell when it is likely to get near one of these abandoned mines. Usually the first warning is the appearance of large quantities of muddy water seeping through."

From this eyewitness account one can reason that most recharge to the mines must come from seepage through mined outcrops or, perhaps, surface-water impoundments above mine cavities because streams above the coal seam generally flow only during runoff from intensive rainfall. Most recharge probably originated from southern and eastern outcrops because of the northwesterly dip of the coal seam and mine cavities. The small quantity of discharge emanating from the mines compared to their large areal extent is additional evidence that limited quantities of water seep into the mines. Data from several sets of synoptic stream discharge measurements (table 2, at the back of this report) indicate discharge from two mine drainage sites, MW1 and MN9 (fig. 4), constitutes about 80 percent of the mine drainage in the study area. Data in table 2 are presented by date to indicate effects of mine drainage on receiving streams during different flow regimes. The combined flow from these two sites averaged 0.11 ft^3/s (cubic foot per second) during this study (fig. 5). Increasing the quantity of discharge from MW1 and MN9 by 20 percent to account



NOTE: Four unnamed tributaries in this figure are referred to as west creek, north creek, east creek, and south creek

EXPLANATION

1 ●	OBSERVATION WELL DATA-COLLECTION SITE AND NUMBER
MW6 ○	MINE SPRING DATA-COLLECTION SITE AND NUMBER
SW12 ▼	SURFACE-WATER DATA-COLLECTION SITE AND NUMBER

Figure 4.--Location of observation wells, mine springs, and surface-water sites.

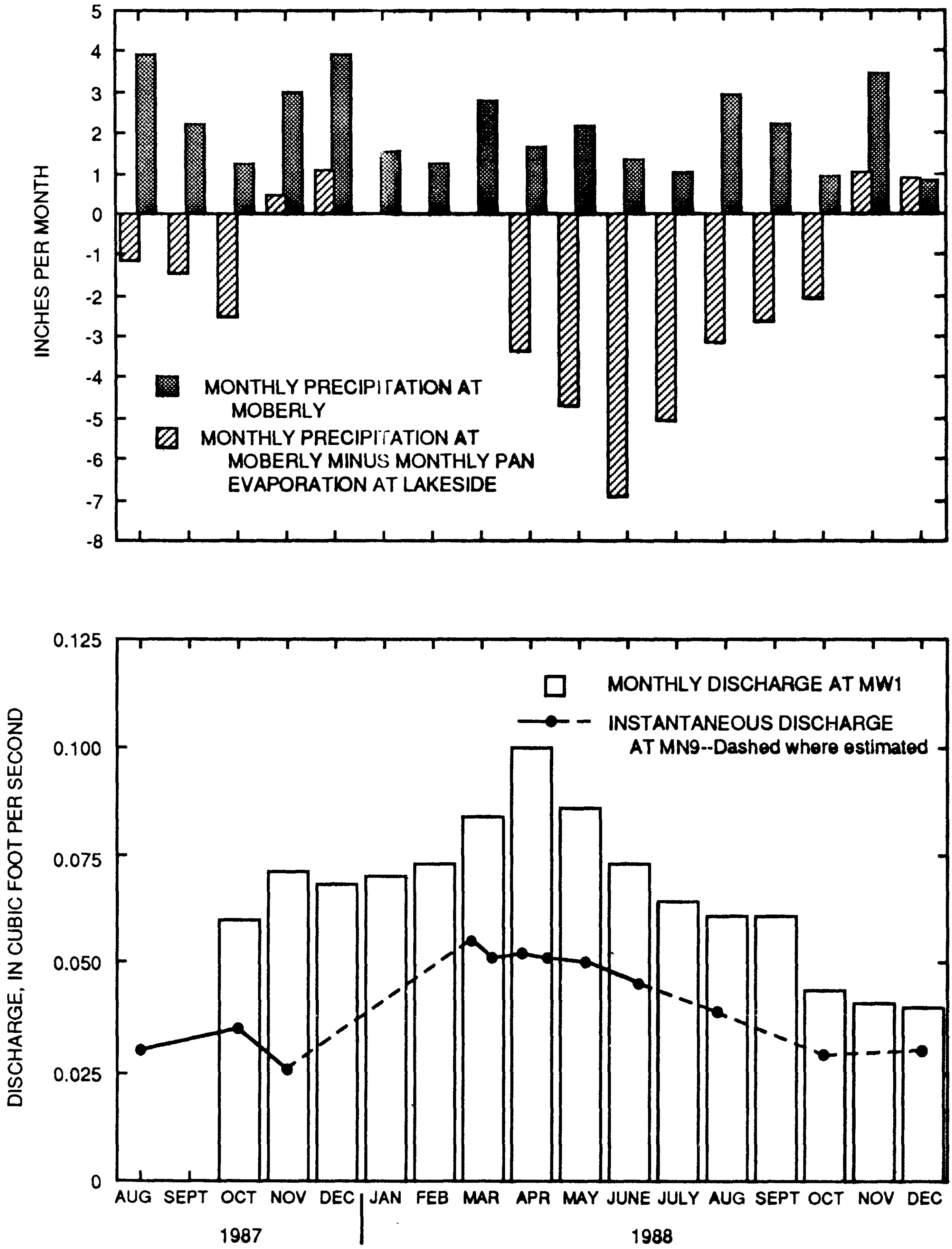


Figure 5.--Precipitation, precipitation minus pan evaporation, and discharge at two mine springs (precipitation and pan evaporation data from National Oceanic and Atmospheric Administration, 1987-88).

for all other mine seeps, and assuming the 4.3 mi^2 (square miles) of coal in the study area are completely mined out, the average recharge to the mines is 0.43 in. per year, or less than 2 percent of the precipitation for the year (National Oceanic and Atmospheric Administration, 1987-88) over the 4.3 mi^2 recharge area. These calculations assume negligible quantities of water flow downward through the underclay below the Bevier-Wheeler coals. Maximum and minimum discharges from MW1 and MN9 lagged maximum and minimum recharge periods by 3 to 5 months (fig. 5).

Immediately above the Bevier-Wheeler coals is the Lagonda Formation, which in the study area is a variable mix of shale and sandstone. Characteristically, the shale is gray-green, silty to sandy, and micaceous with concretions, horizontal bands, and vertical veins of Fe minerals, such as pyrite and siderite. Where shale is the prevalent lithology, the Lagonda Formation is about 20 ft thick, but increases to more than 40 ft where the sandstone thickens. Sandstone normally is present at the top of the formation and sometimes cuts through both the shale and Bevier-Wheeler coals below. The replacement of the coal by channel sandstone was observed in the open drift shown in figure 3. The sandstone is resistant to erosion and forms steep valley walls in the northern part of the study area. However, in the southern part of the study area along U.S. Highway 24, there are only 1- to 2-in. thick bands of sandstone interbedded with the shale. Nearly all Lagonda Formation rock types weather to an orange-tan color indicating oxidation of Fe minerals.

As a roof rock, the shale in the Lagonda Formation "*** gives fair satisfaction if carefully watched. In places, however, sandstone comes down next to the coal, making a strong roof, but one with an uneven under surface that causes irregularity in the thickness of the coal***. About 50 percent of the entries were timbered" (Weigel, 1921). The room roofs were heavily propped with 4- to 5-in.-diameter posts spaced 3 to 5 ft apart. However, the large number of injuries and accidents reported in the mines testifies to the unpredictability of failure of the Lagonda Formation (Gentile, 1967). Room props often were removed allowing rooms to collapse. Even when the untreated props and timbers were retained, they usually failed within 2 to 5 years (Weigel, 1921).

The Missouri Highway and Transportation Department (1981) drilled twelve 6-in.-diameter wells into mine cavities along the shoulder of U.S. Highway 24 (shown as observation wells in figure 4). Photographs taken with a downhole camera are used to monitor collapse underneath the highway where the cavities are not flooded. These photographs show large slabs of the roof have fallen (fig. 6), but the cavities have remained open with a porous rubble zone at the bottom. Even where major collapse has occurred, large void spaces in the rubble would allow unimpeded water movement. The wells penetrated cavities ranging from 10 to 40 ft in diameter (Missouri Highway and Transportation Department, 1981). Only 7 of the 12 wells penetrated cavities that were flooded. Water levels were measured in the seven flooded cavities while three wells were pumped at 3 to 9 gal/min (gallons per minute) for a maximum of 2 hours (figs. 7 to 9) during sample collection on September 3, 1987. Withdrawals were small compared to mine-cavity volumes and only one well had a total drawdown greater than 0.1 ft. These small drawdowns would be expected if open cavities larger than 700 ft^2 (square feet) were being dewatered.

A dye trace indicated little hydraulic connection between observation well 11 (fig. 4) and any other nearby observation wells. Sulpho Rhodamine B was selected as a tracer dye because it had been used successfully to trace ground-water flow through underground coal mines in England (Aldous and Smart, 1988). This success was attributed to low sorption on coal and stability under acidic conditions. Thirty pounds of dye were injected into well 11 on February 24, 1988. Well 10, 50 ft from well 11, was continuously pumped for 2.5 hours at 9 gal/min and samples were analyzed for dye concentrations. The dye concentration in well 10 after pumping was 120 μg/L. The small dye concentration indicates minimal hydraulic connection between wells 10 and 11. Subsequent sampling of wells 4, 7, 10, and 11 indicated the dye concentration in well 11 remained large (greater than could be read with the fluorometer) more than 10 months after dye injection. The small dye concentrations in well 10 decreased in subsequent days and months, but remained slightly greater than the near-zero concentrations measured in wells 4 and 7. The continued large dye concentration in well 11 indicates little water movement through the flooded cavity. Consequently, most dye movement was probably by diffusion. Even so, much larger dye concentrations would be expected in well 10 if well 11 penetrated the same cavity or if flow paths were interconnected. Certain areas of the mines are preferred flow paths, but the small discharge from mine springs compared to the total volume of water in the mines indicates slow movement and average residence times as long as tens of years for water in the mines. Dye concentrations also were monitored at MW1, SW8, SN7, MS1, MS2, SS5, and SA1 (fig. 4), but no dye was detected at any of these sites during 10 months of monitoring.

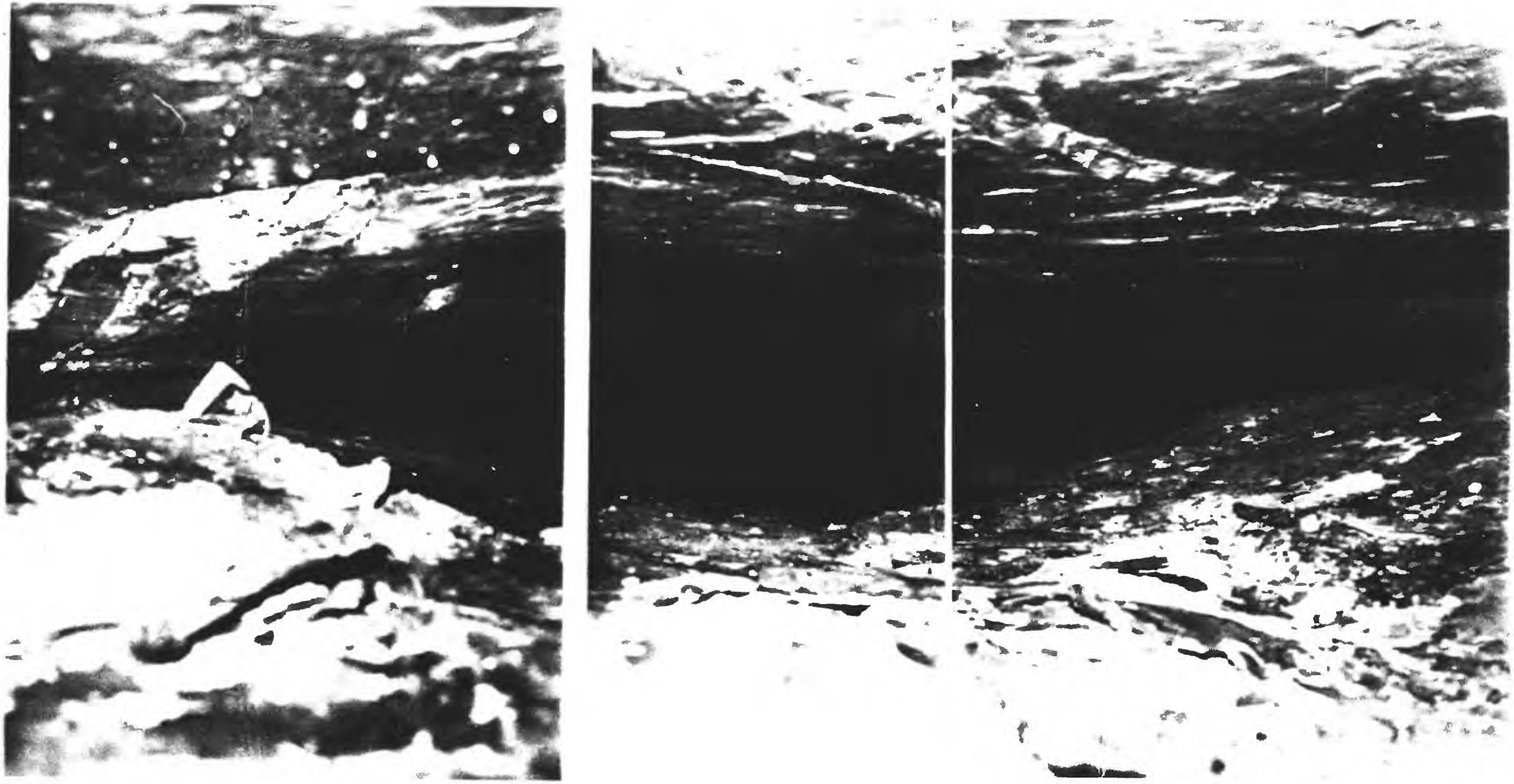


Figure 6.--Mine cavity north of U.S. Highway 24 at observation well 5 (photographs by the Missouri Highway and Transportation Department).

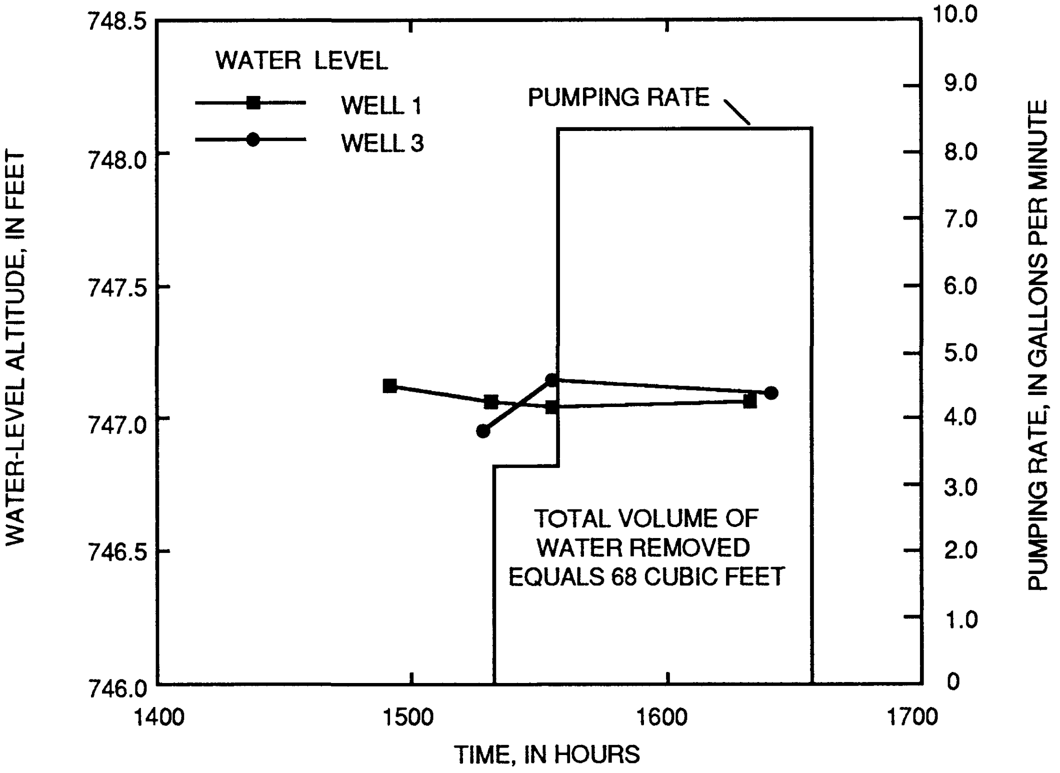


Figure 7.--Water levels and pumping rate in mine cavities at well 1 and pumped well 3, September 3, 1987.

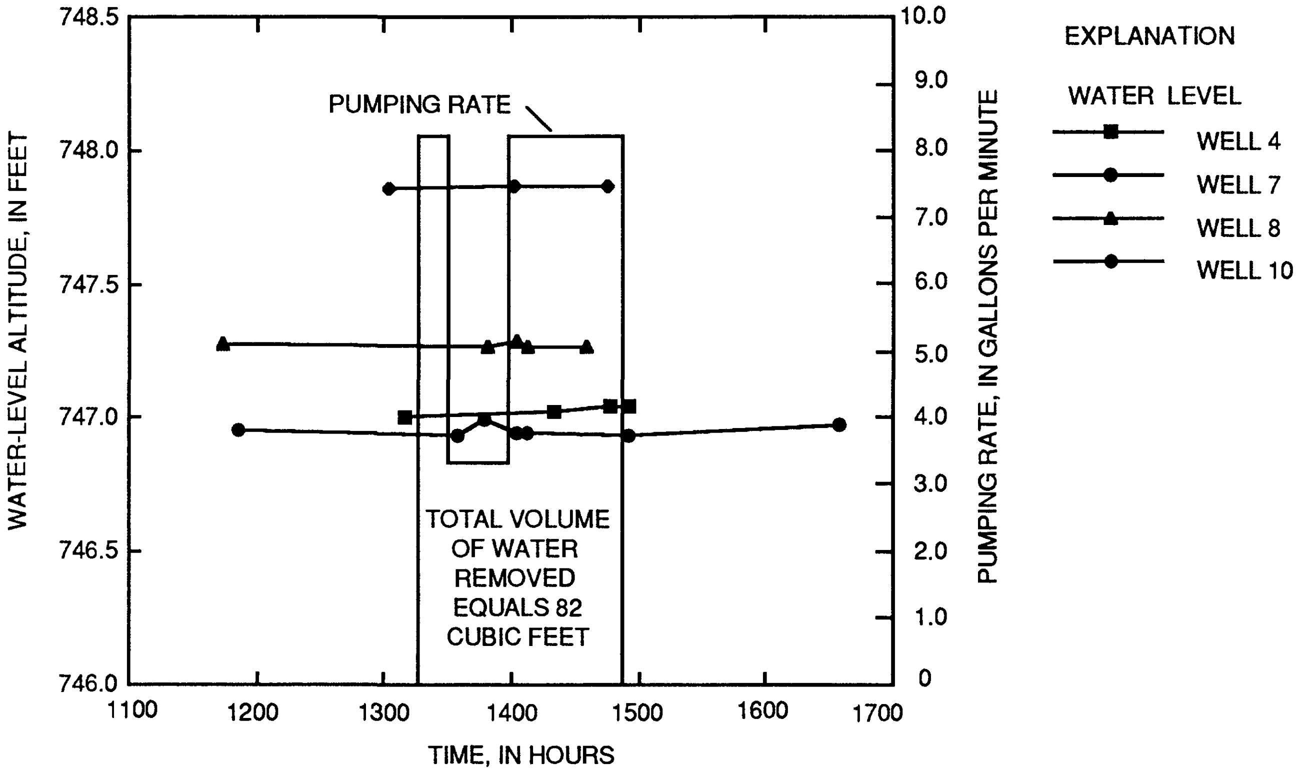


Figure 8.--Water levels and pumping rate in mine cavities at wells 4, 8, and 10 and pumped well 7, September 3, 1987.

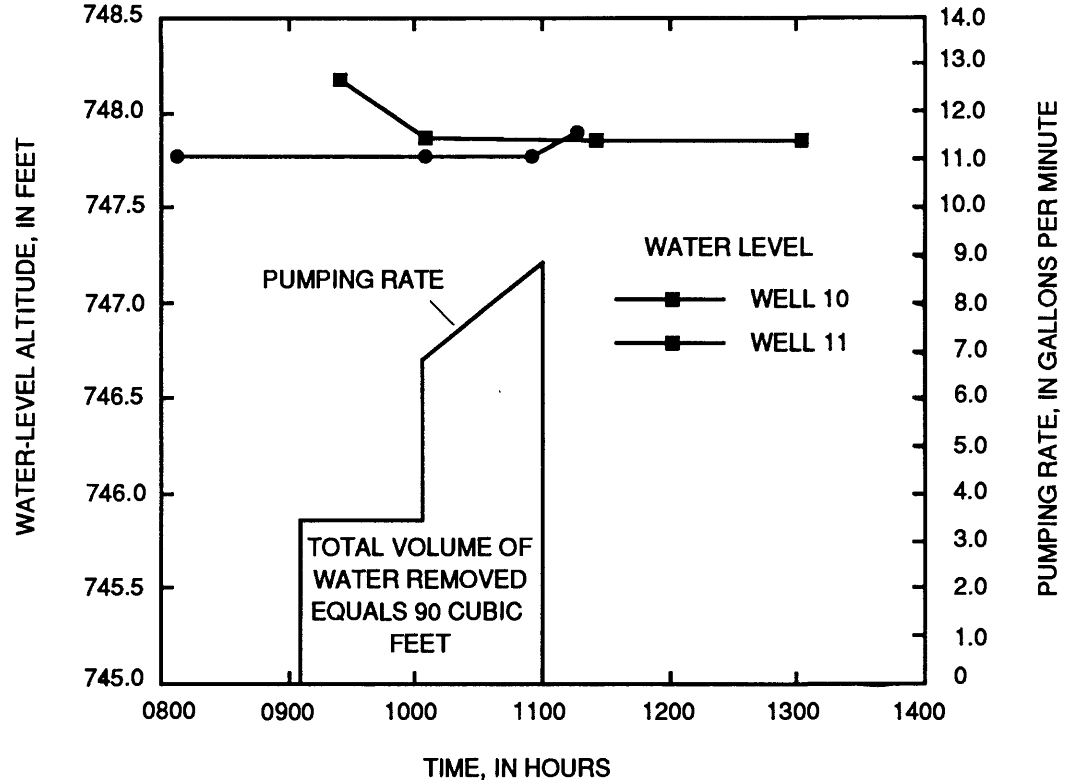


Figure 9.--Water levels and pumping rate in mine cavities at well 10 and pumped well 11, September 3, 1987.

The Moberly channel fill (fig. 2) is a sandstone and shale sequence of Pennsylvanian rocks younger than the Lagonda Formation, probably of late Pleasanton age, that truncates the Bevier-Wheeler coals along the southern edges of the study area (Gentile, 1967; fig. 3). Sandstone is the only rock cropping out in the western part of the study area. An indefinite boundary was established in the western part of the study area (fig. 3) because of the difficulty of distinguishing between the sandstone of the Lagonda Formation and sandstone in the Moberly channel fill. The Moberly channel fill is an aquifer that occasionally is used as a drinking-water source because its permeability is slightly larger than that of surrounding Pennsylvanian rocks. Although the unit supplies only moderate quantities of ground water (Gentile, 1967), it is the only significant water-bearing rock in the area. Therefore, there was some concern that underground-mine water could contaminate the Moberly aquifer. However, the mines do not recharge the Moberly aquifer. If areas of contact between the mines and the Moberly channel fill exist, they are limited to small areas in the southern and possibly western parts of the study area. The Bevier-Wheeler coals dip about 50 ft in the 2.0 mi (miles) across the study area from southeast to northwest (fig. 3). This dip indicates that the overall direction of ground-water flow in the mines would be to the northwest, as evidenced by the two large springs MW1 and MN9 at down-dip locations. This northwesterly ground-water flow direction is away from the Moberly channel fill. Conversely, the small discharge from the mines indicates little, if any, recharge from the Moberly channel fill to the mines.

WATER CHEMISTRY

Underground-Mine Water

The formation of sulfuric acid (H_2SO_4) in underground-mine water is caused by the oxidation of iron disulfide (FeS_2) minerals, primarily pyrite, by either oxygen (O_2) or ferric iron (Fe^{+3}). According to Sato (1960) and Nordstrom (1982), the initial oxidation of pyrite by O_2 is described by the following reaction:

$$FeS_2 + O_2 + 2H^+ \text{-->} Fe^{+2} + S_2^0 + H_2O_2. \qquad (1)$$

Hydrogen peroxide (H_2O_2) rapidly decomposes to water (H_2O) and O_2 under most conditions. Aqueous, elemental sulfur (S_2^0) also is unstable and quickly oxidizes to sulfate (SO_4) according to:

$$S_2^0 + 3O_2 + 2H_2O \text{-->} 2SO_4^{-2} + 4H^+. \qquad (2)$$

Six electrons are transferred per sulfur atom in reaction 2, indicating that this reaction is a summation of several intermediate steps. Reaction 2 can be written with Fe^{+3} as the electron acceptor (reaction 3), but at the near-neutral pH values detected in the underground mines, Fe^{+3} tends to hydrolyze and precipitate (Langmuir and Whittemore, 1971), thus Fe^{+3} cannot be present in sufficient quantities (Langmuir and Whittemore, 1971) to oxidize S_2.

$$S_2 + 12Fe^{+3} + 8H_2O \text{-->} 2SO_4^{-2} + 16H^+ + 12Fe^{+2} \qquad (3)$$

Reaction 2 is much slower kinetically than reaction 3 (Nordstrom, 1982), especially in underground mines where dissolved-oxygen concentrations are low. Also, oxidation by O_2 (reaction 2) produces much less H^+ than oxidation by Fe^{+3} (reaction 3). Therefore, the underground-mine water is not strongly acidified, but large quantities of SO_4 are produced. In the presence of O_2, ferrous iron (Fe^{+2}) oxidizes, and then the hydrolysis of Fe^{+3} acidifies water (reaction 4), but these processes cannot occur at a fast rate in the underground mines due to the limited supply of O_2.

$$Fe^{+2} + 5/2H_2O + 1/4O_2 \text{-->} Fe(OH)_3 + 2H^+ \qquad (4)$$

The precipitation of siderite ($FeCO_3$) also can lower the pH value according to:

$$Fe^{+2} + HCO_3^- \text{-->} FeCO_3 + H^+. \qquad (5)$$

This reaction becomes insignificant below pH values of 5.5 as siderite becomes more soluble.

On September 3, 1987, three flooded cavities were sampled for 38 properties and constituents (table 3) at observation wells 4, 7, and 11 (fig. 4). These wells are located in the up dip parts of the mines and therefore, represent underground-mine water near the beginning of a geochemical flow path. The chemical analyses were used for ion-speciation and mineral-equilibria calculations done by the computer algorithm WATEQ4F (Ball and others, 1987). Saturation indices [log (activity product/equilibrium constant)] for selected minerals in underground-mine water are listed in table 4. Mine springs also were sampled at several locations (table 5, at the back of this report).

The water chemistry of mine discharge at sites MW1 and MN9 was considered representative of underground-mine water because the mine discharge could be sampled immediately after it reached the ground surface. The springs at sites MW1 and MN9 discharge down-dip underground-mine water at the end of geochemical flow paths. Therefore, saturation indices for water from sites MW1 and MN9 were used in the mineral-equilibrium calculations (table 4). At other mine seeps, the discharge was too small to prevent large quantities of O_2 from dissolving into the water at sampling sites and affecting concentrations of H^+, Fe species, and CO_2 species. Analyses of water from these seeps are included with analyses of surface-water samples in table 5.

Table 3.--*Properties and constituents in underground-mine water, September 3, 1987*

[Concentrations are dissolved; ft, feet; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; ROE, residue on evaporation; µg/L, micrograms per liter; --, no data; <, less than]

Well or mine spring (fig. 4)	Well depth (ft)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)	Total acidity as $CaCO_3$ (mg/L)
4	38	2,080	6.2	0.21	14.0	0.1	80
7	42	1,960	6.5	.19	14.5	--	50
11	26	2,200	6.2	.23	15.5	< .1	5
MW1	--	2,800	5.7	.24	14.5	.4	320
MN9	--	5,600	5.3	.32	15.0	.4	1,100

Well or mine spring (fig. 4)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Bicarbonate (mg/L)	Total alkalinity as $CaCO_3$ (mg/L)	Sulfate (mg/L)	Chloride (mg/L)
4	250	120	44	12	250	210	1,100	18
7	260	97	42	10	340	280	830	17
11	270	110	34	9.5	270	220	1,100	5.4
MW1	370	180	87	21	190	153	1,900	18
MN9	440	310	210	32	52	43	3,600	9.6

Table 3.--*Properties and constituents in underground-mine water, September 3, 1987*--Continued

Well or mine spring (fig. 4)	Fluoride (mg/L)	Silica as SiO_2 (mg/L)	Dissolved solids (ROE)	Iron (mg/L)	Manganese (mg/L)	Nitrite plus nitrate as nitrogen (mg/L)	Orthophosphate as phosphorous (mg/L)	Aluminum (µg/L)
4	0.6	12	1,770	66	2.4	<0.5	0.06	50
7	.4	13	1,590	16	.43	<.5	.18	10
11	.4	19	1,750	34	2.3	<.5	.06	50
MW1	.2	27	3,040	238	4.6	<.5	.09	90
MN9	.6	49	5,460	620	13	<.5	.15	340

Well or mine spring (fig. 4)	Barium (µg/L)	Beryllium (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)	Copper (µg/L)	Lead (µg/L)	Lithium (µg/L)
4	120	<5	2	5	<3	10	20	97
7	68	<5	<1	<5	<3	<10	<10	51
11	32	6	2	<5	<3	<10	10	260
MW1	130	<2	9	<20	<9	<30	30	190
MN9	61	2	23	<20	<3	<30	10	340

Well or mine spring (fig. 4)	Molybdenum (µg/L)	Nickel (µg/L)	Silver (µg/L)	Strontium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)	Total organic carbon (mg/L)	Total inorganic carbon (mg/L)
4	<10	30	<1	1,800	<9	86	1.4	50
7	<10	<10	<1	2,100	<6	120	1.0	64
11	<10	90	2	1,100	<6	100	.4	65
MW1	<10	<30	<3	1,500	33	77	.5	73
MN9	<30	<30	10	880	88	79	.2	71

Table 4.--*Saturation indices calculated by the computer program WATEQ4F for selected minerals dissolved in underground-mine water during dry weather, August 31 through September 3, 1987*

		Saturation indices for water from indicated well or spring (fig. 4)				
Mineral	Chemical formula	Well 4	Well 7	Well 11	Spring MW1	Spring MN9
Calcite	$CaCO_3$	-0.98	-0.44	-0.85	-1.4	-2.5
Gypsum	$CaSO_4 \cdot 2H_2O$	-.42	-.48	-.39	-.18	-.01
Nesquehonite	$MgCO_3 \cdot 3H_2O$	-4.0	-3.6	-3.6	-4.4	-5.3
Silica (amorphous)	SiO_2 (a)	-.55	-.52	-.57	-.31	.06
Siderite	$FeCO_3$	.29	.20	.12	.29	-.46
Melanterite	$FeSO_4 \cdot 7H_2O$	-3.2	-3.9	-3.5	-2.6	-2.0
Ferrihydrite	$Fe(OH)_3$	1.1	1.4	1.2	.58	.92
Potassium jarosite	$KFe_3(OH)_6(SO_4)_2$	5.1	4.8	5.1	5.2	8.2
Gibbsite	$Al(OH)_3$	-.11	-.04	.32	.10	.51
Alunite	$KAl_3(OH)_6(SO_4)_2$	1.0	-.14	2.0	3.2	6.5
Unnamed mineral	$Al_4(OH)_{10}SO_4$	.22	-.84	1.1	1.4	4.1
Kaolinite	$Al_4(Si_4O_{10})(OH)_8$	1.0	1.2	1.9	2.2	3.5
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	-1.6	-.97	-.61	-.06	1.4
Rhodochrosite	$MnCO_3$	-1.2	-.44	-1.1	-1.5	-2.2
Barite	$BaSO_4$	1.1	.80	.51	1.2	.90
Strontianite	$SrCO_3$	-2.6	-1.9	-2.6	-3.1	-4.4
Unnamed mineral	$ZnCO_3 \cdot H_2O$	-2.9	-2.3	-2.8	-3.5	-4.7
Goslarite	$ZnSO_4 \cdot 7H_2O$	-6.8	-6.7	-6.7	-6.7	-6.6
Franklinite	$ZnFe_2O_4$	9.5	11	10	7.7	7.4

Dissolved solids concentration in underground-mine water ranged from 1,590 to 5,460 mg/L (table 3) with the larger concentrations occurring at the down-dip springs MW1 and MN9. These dissolved solids concentrations were substantially larger than concentrations in nearby shallow ground water (table 6). The large concentrations of dissolved solids primarily were because of large concentrations of sulfate in mine water.

The ionic composition of underground-mine water also differed from that of ground water in the region. Major ions in underground-mine water were calcium and sulfate, whereas ground water in the region was a calcium or sodium bicarbonate water. Concentrations of Fe, manganese (Mn), nickel (Ni), strontium (Sr), and zinc (Zn) also were substantially larger in underground-mine water than nearby ground water (tables 6 and 7). Large differences in concentrations of other common cations and anions between mine water and ground water unaffected by mining were not detected. Concentrations of SO_4 and Fe in underground-mine water exceeded Missouri drinking water standards for ground water (250 mg/L for SO_4 and 0.3 mg/L for Fe; Missouri Department of Natural Resources, 1987). Individual discussions of sources and chemical pathways of several ions in underground-mine water follow.

The pH of underground-mine water in observation wells 4, 7, and 11 (table 3) and at mine springs MW1 and MN9 (tables 3 and 5) ranged from 5.3 to 6.5 during sampling and was less than the range of pH (6.5 to 10.3) in ground water from undisturbed Pennsylvanian rocks in the region [tables 6 (well locations are shown in fig. 1) and 7]. The smaller pH values probably were caused by the oxidation of pyrite (reaction 2). The pH values were smaller and acidities were larger at mine springs (table 5) than at wells 4, 7, and 11 (table 3) because of further pyrite oxidation and subsequent carbonate dissolution along the geochemical flow path.

Calcium (Ca) generally was the most abundant cation in underground-mine water (table 3). Concentrations of Ca in underground-mine water were two to three times larger than the average Ca concentration in water from Pennsylvanian rocks in the region (tables 6 and 7). Appreciable quantities of CO_2 species in underground-mine water indicated most of the Ca is derived from dissolution of calcite, although some could be derived from dissolution of gypsum or clay minerals. The slightly acidic underground-mine water would dissolve more calcite than the slightly alkaline ground water in most nearby Pennsylvanian rocks. Calcite and gypsum are common minerals in Pennsylvanian rocks of Missouri. Draney (1982) reports that calcite and dolomite each constitute 2 to 10 percent of the glacial drift and non-limestone rocks above the Bevier-Wheeler coals in the study area. Usually, the only limestone present above the Bevier-Wheeler coals is that of the Blackjack Creek Formation (fig. 2).

Magnesium (Mg) usually was the second most abundant cation in underground-mine water and was dissolved primarily from dolomite and calcite where it commonly substitutes for Ca, and secondarily from clay minerals such as illite. The Mg concentrations in underground-mine water were several times larger than Mg concentrations in water from Pennsylvanian rocks in the region (tables 6 and 7), probably because underground-mine water is more acidic. Ca and especially Mg concentrations were substantially larger in water from spring MN9 than in water from spring MW1, probably because more carbonate rocks and clay minerals were dissolved by the more acidic water in the vicinity of MN9. Two samples from nearby locations in the Moberly channel fill (table 6) had concentrations of Ca and Mg substantially smaller than those from the underground mines and the mean concentrations for the region. The Ca to Mg mole ratio for up dip wells 4, 7, and 11 ranged from 1.28 to 1.62 (table 3), which is typical of water in Pennsylvanian rocks in Missouri, but smaller than the ratios of 2.0 and 2.3 in two samples from nearby wells in the Moberly channel fill. The Ca to Mg ratio of the mine spring at MN9 was only 0.87. This smaller value probably was because Ca concentrations were limited or decreased by gypsum saturation.

Sodium (Na) concentrations were small (less than 35 mg/L) in underground-mine water compared to a mean concentration of 574 mg/L in ground water from Pennsylvanian rocks in the region (table 7). Concentrations probably were smaller in underground-mine water because underground-mine water is nearer the surface than water in many of the wells listed in table 7. Brackish water was encountered during drilling of a gas test well 965 ft deep 5 mi west of Huntsville. The brackish water was under artesian pressure and flowed at 26 gal/min from this well. The Na concentration of this water was 1,600 mg/L and the chloride (Cl) concentration was 3,300 mg/L (Gentile, 1967). This brackish water leaks upward from the Ordovician and Mississippian carbonate rocks and mixes with water in overlying Pennsylvanian rocks. Consequently, the mean concentration of Na in deeper Pennsylvanian ground water is larger than that in ground water from rocks near the surface. The concentrations of Na in underground-mine water were

Table 6.--*Properties and constituents of ground water from unmined Pennsylvanian rocks near Huntsville*

[Results in milligrams per liter except as indicated; constituents are dissolved except as indicated; ft, feet; gal/min, gallons per minute; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; µg/L, micrograms per liter; --, no data; <, less than]

Well number (fig. 1)	Date	Well depth (ft)	Water source	Screened interval (ft)	Well yield (gal/min)	Specific conductance (µS/cm)	pH (standard units)	Temperature (°C)
[a]13	4-09-81	138	above Bevier-Wheeler coals	109 - 138	--	--	7.8	14.2
[a]14	4-09-81	160	below Bevier-Wheeler coals	140 - 160	--	--	9.8	15.3
[a]15	9-15-81	125	above Bevier-Wheeler coals	71 - 125	--	1,370	8.1	14.0
[a]16	9-15-81	151	below Bevier-Wheeler coals	125 - 151	--	1,540	10.3	14.0
[b]17	3-16-66	70	Moberly channel fill	--	10	--	7.2	--
[b]18	3-16-66	140	Moberly channel fill	--	6	--	7.6	--
[c]19	10-06-70	85	--	--	30	--	6.9	--

Well number (fig. 1)	Dissolved oxygen (mg/L)	Hardness as $CaCO_3$ (mg/L)	Noncarbonate hardness as $CaCO_3$ (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)
13	--	--	--	76	16	49	1.8
14	--	--	--	8.8	9.7	80	120
15	0.5	62	6	13	7.0	300	10
16	.0	13	330	3.7	.8	320	20
17	--	410	0	114	30	[d]36	[d]36
18	--	300	0	79	24	[d]55	[d]55
19	--	390	0	105	30	53	3.7

Table 6.--*Properties and constituents of ground water from unmined Pennsylvanian rocks near Huntsville*--Continued

Well number (fig. 1)	Bicarbonate (mg/L)	Carbonate (mg/L)	Alkalinity as $CaCO_3$ (mg/L)	Carbon dioxide (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Fluoride (mg/L)
13	269	--	--	--	125	6.8	<0.1
14	336	--	--	--	102	7.9	<.1
15	550	6	460	6.9	270	6.6	.6
16	500	330	960	.0	<5	19	2.1
17	500	0	410	--	26	18	.2
18	398	8.4	340	--	35	4.0	.3
19	475	0	--	--	49	4.0	.5

Well number (fig. 1)	Silica as SiO_2 (mg/L)	Dissolved solids (mg/L)	Total iron (mg/L)	Iron (mg/L)	Total manganese (mg/L)	Manganese (mg/L)	Nitrate as nitrogen (mg/L)
13	28	580	--	.02	.10	--	7.1
14	23	720	--	.05	.01	--	32
15	12	883	--	.020	.10	.1	.62
16	9.4	831	--	.022	.007	.1	1.7
17	16	504	.73	--	.00	--	7.3
18	17	418	1.09	--	.19	--	.0
19	--	541	3.20	--	.12	--	1.2

Table 6.--*Properties and constituents of ground water from unmined Pennsylvanian rocks near Huntsville*--Continued

Well number (fig. 1)	Nitrite as nitrogen (mg/L)	Ammonia as nitrogen (mg/L)	Orthophosphate as phosphorous (mg/L)	Aluminum (µg/L)	Arsenic (µg/L)	Barium (µg/L)	Cadmium (µg/L)
13	--	--	--	10	<100	65	<10
14	--	--	--	30	<100	21	<10
15	0.03	1.4	0.00	10	1	--	<1
16	.07	4.0	.03	30	2	--	<1
17	--	--	--	--	--	--	--
18	--	--	--	--	--	--	--
19	--	--	--	50	--	--	--

Well number (fig. 1)	Chromium (µg/L)	Copper (µg/L)	Lead (µg/L)	Mercury (µg/L)	Nickel (µg/L)	Selenium (µg/L)	Strontium (µg/L)	Zinc (µg/L)
13	20	20	<50	--	<100	<100	280	20
14	<10	10	<50	--	<100	<100	210	<10
15	0	16	2	7	0	0	400	29
16	0	16	4	130	0	0	61	24
17	--	--	--	--	--	--	--	--
18	--	--	--	--	--	--	--	--
19	--	--	--	--	--	--	--	--

[a] All dissolved samples were filtered through 0.45 micrometer filters (Hall and Davis, 1986).

[b] Filtering procedures not reported (Gentile, 1967).

[c] Analysis on file at the Missouri Division of Geology and Land Survey, Rolla, Missouri.

[d] Reported as sodium plus potassium as sodium.

Table 7.--*Summary of ground-water-quality data from Pennsylvanian rocks in northern Missouri and southern Iowa*

[Concentrations in milligrams per liter unless otherwise specified; <, less than; data from Detroy and others, 1983]

Constituent	Range	Mean	Number of samples
Specific conductance (microsiemens per centimeter at 25 degrees Celsius)	350 - 7,700	3,075	75
pH (standard units)	6.5 - 8.3	7.5 (median)	95
Hardness ($CaCO_3$)	29 - 2,000	528	96
Calcium (Ca)	2.4 - 460	133	97
Magnesium (Mg)	1.5 - 394	48	97
Sodium (Na)	5.5 - 2,400	574	96
Potassium (K)	.9 - 38	8.5	84
Bicarbonate (HCO_3)	120 - 1,240	437	94
Alkalinity ($CaCO_3$)	98 - 1,080	360	98
Sulfate (SO_4)	1 - 4,000	1,046	97
Chloride (Cl)	.5 - 3,060	222	98
Dissolved solids	250 - 6,790	2,339	98
Iron (Fe)	.01 - 22	2.5	96
Manganese (Mn)	.01 - 2.3	.16	95
Nitrate (NO_3)	<.1 - 200	4.3	97

similar to concentrations of Na in the two Moberly channel fill samples (table 6). Possible sources of Na are from the slow dissolution of aluminosilicate minerals, such as feldspar and clay minerals, or cation exchange. No plausible solubility control was determined for Na, although sodium jarosite was substantially oversaturated (however, thermodynamic data for sodium jarosite are not well established).

Concentrations of potassium (K) in underground-mine water were similar to those detected in other Pennsylvanian rocks (tables 6 and 7), including the Moberly channel fill. Every sample of underground-mine water was oversaturated with respect to potassium jarosite (table 4). The larger concentrations of K at mine springs MW1 and MN9 may result from greater dissolution of aluminosilicate minerals and because of the increased solubility of jarosite at smaller pH values.

Concentrations of HCO_3 in water from the mines were smaller than average concentrations in Pennsylvanian rocks of the region (table 7). However, the total concentration of all CO_2 species in underground-mine water was as large or larger than concentrations in water from most Pennsylvanian rocks. WATEQ4F speciation calculated 41 to 91 percent of the CO_2 species in the samples in table 3 was aqueous H_2CO_3, whereas only about 10 percent of the CO_2 species was H_2CO_3 at a pH of 7.5 (fig. 10), a pH value typical of water in Pennsylvanian rocks in the region. The most abundant source of carbonate in Pennsylvanian rocks is calcite. The large concentrations of CO_2 species in underground-mine water caused large values of acidity in surface streams as HCO_3 became fully protonated during hydrolysis of Fe^{+3}. The HCO_3 and H_2CO_3 ions tended to buffer pH values between 5.8 and 7.1 in the mines (fig. 10). At pH values less than 5.8, the buffering capacity was greatly diminished and rapid decreases in pH could occur. The pH of underground-mine water was near the lower limit of carbonate buffering action. The only carbonate mineral for which water from the mines was above saturation was siderite, and the siderite saturation indices of water from wells 4, 7, and 11 were between 0.1 and 0.3 (table 4), indicating siderite precipitation may limit concentrations of both Fe^{+2} and CO_2 species in underground-mine water. Siderite was undersaturated at MN9 because of the smaller pH value. Several chemical reactions are indicated by the undersaturation of calcite and the oversaturation of siderite. Oxygenated water dissolves pyrite and calcite, becomes oversaturated with siderite, and then siderite may be precipitated from solution. The precipitation of siderite (reaction 5) and partial oxidation of pyrite (reactions 1 and 2) tend to decrease the pH value, which, in turn, causes more calcite to dissolve. Conversely, the dissolution of calcite increases the pH value. These reactions can explain some of the common properties and characteristics of underground-mine water.

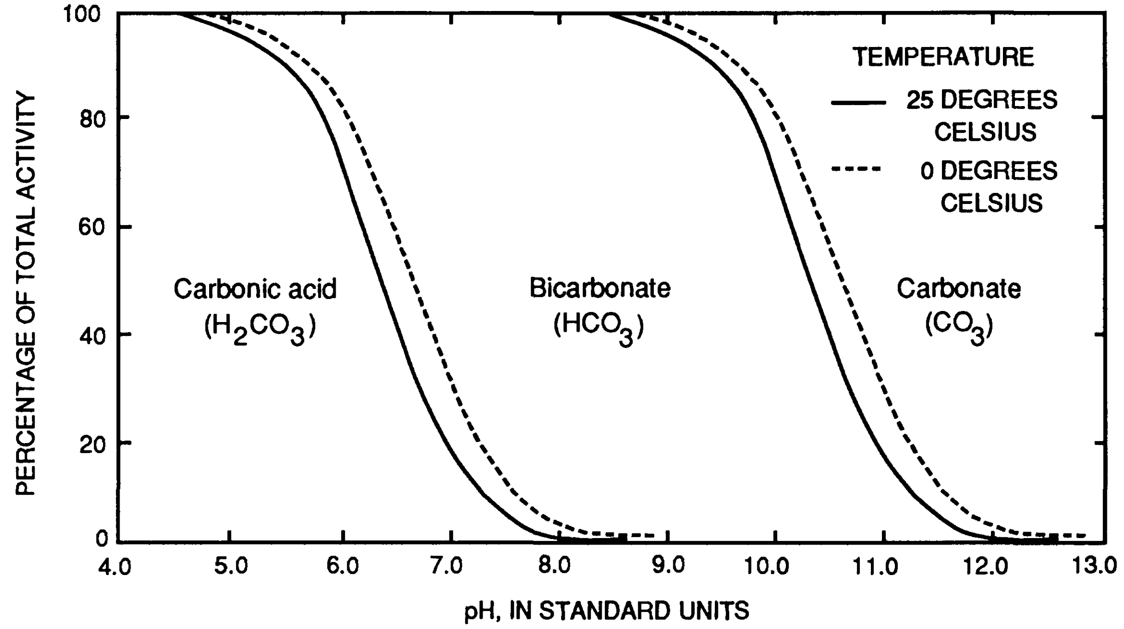


Figure 10.--Percentages of dissolved carbon dioxide species activities at 1 atmosphere pressure and two temperatures as a function of pH (modified from Hem, 1985).

Concentrations of SO_4 ranged from 830 to 3,600 mg/L and were larger than any other ion in underground-mine water (table 3). Concentrations of SO_4 in underground-mine water were several times larger than drinking water standards in Missouri (250 mg/L; Missouri Department of Natural Resources, 1987) and nearby concentrations of SO_4 in shallow ground water (table 6). However, SO_4 concentrations in underground-mine water were within the typical range of SO_4 concentrations detected in Pennsylvanian rocks of the region (table 7). The sulfate concentrations listed in table 7 were larger than those listed in table 6 probably because many of the analytical results in table 7 were for water from deeper wells. The two most abundant sulfur-bearing minerals in Pennsylvanian rocks are pyrite and gypsum, which are probable sources of SO_4 in underground-mine water. Pyrite oxidation, not gypsum, was the primary source of dissolved SO_4 in water draining a surface mine in west-central Missouri (Blevins and Chafin, 1988). Concentrations of SO_4 were substantially larger at mine springs MW1 and MN9 than in wells 4, 7, and 11, indicating pyrite oxidation occurs along the flow path. Water from mine spring MW1 was slightly under saturation and water from mine spring MN9 was near saturation with respect to gypsum (table 4). Gypsum solubility may limit the concentrations of Ca or SO_4, or both.

Sulfate readily forms aqueous complexes with many cations, especially divalent cations. Therefore, larger concentrations of Fe^{+2} and Mg can cause larger concentrations of SO_4 when the solution is saturated with gypsum. Aqueous Fe and Mg sulfates accounted for 10 to 23 percent of the dissolved SO_4 in underground-mine water, according to WATEQ4F speciations. Therefore, concentrations of SO_4 were larger at MN9 probably because of the larger concentrations of Fe and Mg.

Concentrations of Cl were substantially smaller than Na concentrations in underground-mine water, but were similar to Cl concentrations in ground water from other Pennsylvanian rocks in northern Missouri (table 7). The Cl concentrations in ground water may be limited by small concentrations in source rocks. Generally, Cl content in shales (Krauskopf, 1967) and Missouri coals (Wedge and Hatch, 1980) are 10 to 40 times less than Na concentrations. Dissolution of aluminosilicate minerals and impure carbonate rocks would be sources of Na but not Cl. Also, transport of Cl in Pennsylvanian rocks may be limited. "Because the chloride ion is physically large compared with many of the other major ions in water, it could be expected to be held back in interstitial or pore water in clay and shale while water (and smaller ions) was transmitted" (Hem, 1985, p. 120). The Pennsylvanian rocks above the mines primarily are shales and clays and may limit the movement of Cl into the underground mines.

Fluoride (F) concentrations in the underground-mine water were similar to F concentrations in other ground water from Pennsylvanian rocks in north central Missouri. Fluoride minerals, such as apatite, are resistant to acid decay, and though F minerals are likely to exist, they are not likely to dissolve. No F minerals were near or above saturation.

Concentrations of silica (SiO_2) in underground-mine water were similar to those in ground water from nearby Pennsylvanian rocks (table 6). Clay and other silicate minerals in Pennsylvanian rocks provide an abundant source for SiO_2. Saturation indices for amorphous SiO_2 in underground-mine water ranged from -0.57 to 0.06, with the largest values at MW1 and MN9. Kaolinite was oversaturated in all underground-mine water. Quartz, kaolinite, and other possible solubility controls of SiO_2 are discussed by Hem (1985).

Large quantities of SO_4 and Fe^{+2} indicate oxygenated water has decomposed pyrite (by reactions 1 and 2) wherein sulfur is oxidized, but most of the dissolved Fe has not been oxidized, hydrolyzed, or precipitated. This partial oxidation of pyrite produces only 2 net moles of H^+ for each mole of pyrite, whereas complete oxidation and hydrolysis of the Fe produces 4 net moles (reactions 1, 2, and 4). Thus, the availability and solubility of O_2 probably are limiting and help prevent underground-mine water from becoming strongly acidic. Five of the 12 mine cavities penetrated by observation wells were dry, indicating that some areas of the mines are not flooded. Unflooded cavities probably permit some exposure to atmospheric oxygen that would allow more extensive pyrite oxidation. Increased quantities of Fe^{+2} would oxidize and subsequently hydrolyze, lowering the pH value at some places in the mines. Subsequent dissolution of calcium carbonate would increase acidities and the pH of water emerging from mine springs (table 3). The Eh values of water from the MW1 and MN9 mine springs (table 3) were slightly larger than Eh values for water from the wells, also reflecting some possible contacts with O_2 along the flow path. There probably was some contact with the atmosphere near the discharge points because both springs had detectable concentrations of dissolved O_2. Also at MW1, the slow rise in water level behind a dam blocking the flow from the spring indicated about 2,000 ft^3 (cubic feet) of a cavity was filled during a 0.26-ft increase in water level behind the dam (equivalent to a square room 87.5 ft on a side).

The Fe concentrations were larger in underground-mine water (16 to 620 mg/L, table 3) than in ground water from other Pennsylvanian rocks in the region (tables 6 and 7). Small concentrations of Fe^{+3} were detected in water having near-neutral values of pH because of the tendency for precipitation of insoluble Fe^{+3} minerals, such as ferrihydrite and potassium jarosite. These two minerals were oversaturated in all five mine-water samples (table 4). Partially flooded cavities in the mines allow atmospheric O_2 to contact underground-mine water in some locations. Consequently, oxidation of Fe^{+2} and the subsequent hydrolysis and precipitation of ferrihydrite could remove or limit Fe in solution. However, near-neutral pH values and large concentrations of Fe^{+2} indicate overall rates of ferrihydrite precipitation may be low in the mines. The Fe^{+2} minerals generally are more soluble than Fe^{+3} minerals. Therefore, at the Eh values measured in underground-mine water, the large supply of Fe^{+2} from the partial oxidation of pyrite is stable and causes Fe concentrations to be much larger in underground-mine water than in ground water from other Pennsylvanian rocks. Larger concentrations of Fe^{+2} are possible in underground-mine water when SO_4 concentrations are large because of the tendency of SO_4 to form complexes with divalent cations. The WATEQ4F calculations indicated 19 to 33 percent of dissolved Fe^{+2} in underground-mine water was in the form of aqueous $FeSO_4$. These larger concentrations of Fe^{+2} are then available for oxidation and hydrolysis reactions in receiving streams. Siderite was slightly oversaturated (as computed by WATEQ4F) in four of five underground-mine water samples (table 4) and siderite may be a sink for dissolved Fe where pH values are greater than 5.5 (table 3). Therefore, as pyrite is oxidized, siderite may be precipitating and accumulating in the mines. The importance of siderite solubility on Fe concentrations is indicated at MN9 where the pH value was 5.3 and siderite was undersaturated, despite having a dissolved Fe concentration of 620 mg/L.

The Mn concentrations were larger in underground-mine water than in water from other Pennsylvanian rocks in the region (tables 6 and 7). Manganese is widely disseminated in sedimentary rocks as oxides and carbonates in shales and limestones, where concentrations average about 1 part per thousand (Krauskopf, 1967). Oxides and carbonates of Mn are more soluble in acidic waters. Concentrations of Mn in underground-mine water were larger at the down dip mine springs (where the pH value was lower) than at the up dip wells. No plausible sink for Mn was indicated from speciation calculations with WATEQ4F, but Mn is commonly absorbed by ferrihydrite.

Concentrations of nitrite plus nitrate (NO_3 + NO_2) were less than 0.5 mg/L as N in mine-water samples, and concentrations probably are limited because of small concentrations in surrounding rocks. No nitrate minerals were above saturation. Small concentrations of NO_3 + NO_2 and total organic carbon in underground-mine water (table 3) indicate little or no effects from sewage reportedly dumped directly into the mines (resident interviews on file at the Missouri Department of Natural Resources, Land Reclamation Commission, Jefferson City).

Orthophosphate (PO_4) concentrations were small in underground-mine water (table 3) and apatite and vivianite were undersaturated despite substantial quantities of phosphate nodules in Pennsylvanian rocks. Concentrations of dissolved PO_4 can be limited to a few hundredths of a milligram per liter by adsorption onto Fe and Mn oxyhydroxides (Hem, 1985). Large concentrations of Fe and Mn were present in underground-mine waters and deposits of Fe oxyhydroxides have probably accumulated in oxygenated parts of the mines, leading to depletion of dissolved PO_4 in the underground-mine water.

Aluminum (Al) concentrations in underground-mine water and ground water from other Pennsylvanian rocks were small (less than or equal to 50 µg/L) because of the decreased solubility of Al hydroxides at near-neutral values of pH. At the more acidic pH values in the mine springs, Al concentrations were slightly larger (table 3), probably from limited dissolution (hydrolysis) of aluminosilicate minerals.

The concentrations of barium (Ba) in underground-mine water and ground water from other Pennsylvanian rocks in the area were small (less than 130 µg/L). The large concentrations of SO_4 in underground-mine water prevent large concentrations of Ba in solution because the solubility of barite is extremely small. All underground-mine water was oversaturated with barite (table 4). Even the smaller concentrations of SO_4 in ground water unaffected by mining are large enough to limit Ba concentrations.

Most trace-element concentrations, including beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), Ni, molybdenum (Mo), and silver (Ag), were near or less than detection limits in underground-mine water and other Pennsylvanian rocks in the area. Concentrations of Cd and Pb were near detection limits of 10 µg/L in the observation wells, but were slightly larger in the mine springs where more acidic pH values existed. Concentrations of lithium (Li) in underground-mine water ranged from 0.05 to 0.34 mg/L (table 3). These concentrations have been reported to be toxic to some plants (Bradford and Iwatsubo, 1978). Concentrations of Ag usually were less than detection limits, and always less than drinking water standards for Missouri of 0.05 mg/L (Missouri Department of Natural Resources, 1987). Strontium concentrations in underground-mine water were larger than concentrations detected in water from other Pennsylvanian rocks in the area (tables 3 and 6), but no Sr mineral was at or above saturation. Strontium commonly substitutes for Ca as a trace constituent in calcite, gypsum, and other minerals. Concentrations of Sr average about 0.3 part per thousand in shales and 0.6 part per thousand in carbonate rocks (Krauskopf, 1967), which probably are the source of Sr in the mines. Zinc concentrations were somewhat larger in underground-mine water than in other ground water from Pennsylvanian rocks in the area. Zinc minerals were likely to be dissolved, because the water was undersaturated with respect to Zn-bearing minerals. Vanadium (V) concentrations were substantially larger in the down dip mine springs than the up dip wells. Hem (1985) suggested a mechanism involving ferrous vanadate that could control V concentrations in ground water.

Effects of Mine Drainage on Receiving Streams

The oxidation and hydrolysis of Fe acidifies streams receiving underground-mine drainage in Huntsville. Streamflow was composed entirely of mine drainage except during wet weather. The availability of Fe disulfides is limited in these streams, but abundant O_2 is available to oxidize the Fe^{+2} emerging at the mine springs. At pH values greater than about 4.0, Fe^{+2} oxidizes and precipitates as amorphous ferrihydrite (reaction 4). The precipitation of ferrihydrite limits Fe^{+3} in near-neutral water to small concentrations (Langmuir and Whittemore, 1971). The precipitation of jarosite can decrease the pH to about 2.0, as illustrated in the reaction:

$$X^+ + 3Fe^{+3} + 2SO_4^{-2} + 6H_2O \text{ --> } XFe_3(SO_4)_2(OH)_6 + 6H^+, \qquad (6)$$

where X is a monovalent cation, usually Na, K, or H^+. Miller (1979) has suggested that where ferrihydrite (dissolving) and jarosite (precipitating) are both present, the pH of mine drainage is buffered between 3.0 and 3.4. This is comparable to the pH values in the receiving streams at Huntsville.

Buffering of the receiving waters by HCO_3 slows the acidification because HCO_3 combines with some of the newly formed H^+ to form H_2CO_3. However, the buffering effect is not effective below a pH of 4.5 where HCO_3 is fully protonated (fig. 10). Therefore, the mole ratio of Fe^{+2} to HCO_3 effectively determines the potential of mine drainage to become acidic after reaching a stream. If this ratio is greater than 0.5, then the mine drainage has the potential to acidify (reaction 4). None of the Fe^{+2} to HCO_3 ratios in up dip wells 4, 7, and 11 exceeded 0.5. However, at mine springs MW1 and MN9 (representing more than 80 percent of the mine discharge in the study area) the water had Fe^{+2} to HCO_3 ratios of 1.4 and 13. Consequently, the mine drainage acidified a short distance downstream from the mine springs. Dissolution of carbonate minerals on the streambed could increase the HCO_3 in solution. However, limited contact time and armoring of carbonate minerals in the streambed by precipitation of Fe oxyhydroxides drastically decreases their capacity to neutralize the pH value of the streams.

Several streams received drainage from underground mines in the study area (fig. 4). However, two streams, west and north creeks, received more than 90 percent of the mine drainage in the study area (table 2 and fig. 4) and were chosen for detailed analyses. The west and north creeks would be ephemeral were it not for mine drainage. Effects of mine drainage on the pH value of the east and south creeks were minimal (table 8 and fig. 4). However, specific conductance values indicate slightly increased SO_4 concentrations probably were present in the east and south creeks.

Table 8.--*Results of synoptic measurements of selected properties in water from mine springs and surface-water sites in the east and south creeks*

[ft^3/s, cubic foot per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; --, no data; <, less than; e, estimated]

Site number (fig. 4)	Date	Instantaneous discharge (ft^3/s)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)
			east creek			
SE1	2-23-88	[a]0.094	990	7.3	0.43	5.5
ME1	2-23-88	[a].0013	4,500	4.3	.44	8.0
ME2	2-23-88	[a].0056	--	5.6	.30	--
SE2	2-23-88	.12	1,400	6.6	.19	6.0
			south creek			
MS1	2-24-88	<.005e	3,800	6.8	.16	--
MS2	2-24-88	[a].012	1,850	5.8	.21	13.0
SS3	2-24-88	.11	1,180	7.1	.17	3.0
SS5	2-24-88	.12	1,150	7.1	.11	2.5
MS1	5-18-88	<.001e	3,950	6.9	.28	--
MS2	5-18-88	[a].0061	2,050	5.9	.22	--
MS3	5-18-88	<.001e	3,600	6.1	.26	--
SS5	5-18-88	[a].0045	2,230	6.8	.24	--
MS1	4-13-88	<.001e	--	7.0	--	--
SS5	4-13-88	--	--	7.0	--	--
MS1	4-28-88	<.001e	--	6.9	--	--
SS5	4-28-88	--	--	6.9	--	--
MS1	6-23-88	[b]0	--	--	--	--
MS2	6-23-88	[a].0015	--	5.9	--	--
SS5	6-23-88	--	--	7.3	--	--
MS1	8-04-88	[b]0	--	--	--	--
MS2	8-04-88	[b]0	--	--	--	--
MS1	10-19-88	[b]0	--	--	--	--
MS2	10-19-88	[b]0	--	--	--	--
MS1	12-21-88	[b]0	--	--	--	--
MS2	12-21-88	<.001e	--	--	--	--

[a] Instantaneous discharge was measured volumetrically.

[b] No discharge on this day.

West Creek

Synoptic measurements of instantaneous discharge, specific conductance, pH, Eh, and water temperature in west creek (table 2) were made during base-flow conditions on several occasions during 1987 and 1988, and water samples were collected during base-flow conditions on August 31 and September 1, 1987, for detailed chemical analyses. Streamflow data and physical and chemical data for west creek are presented in table 5 and illustrated in figures 11 and 12. Concentrations in figure 12 are plotted in millimoles to allow comparisons between ions.

Mine spring MW1 discharged more than 90 percent of the mine drainage received by the west creek, which usually was characterized by a dry streambed upstream from MW1. Base flow consisting entirely of mine drainage was sampled on September 1, 1987, and October 19, 1988 (fig. 11 and table 2). However, on February 24, 1988, base flow from non-mine sources was more than one-half of the flow just downstream from MW1 (fig. 11). Discharge from MW1 and effluent from the sewage lagoons at SW11 comprised more than 80 percent of flow at the downstream site, SW10, during most periods of base flow. Sewage effluent approximately doubled the flow at SW10 during most periods of base flow.

Generally, flow in the west creek began at MW1 and the water had chemical characteristics of underground-mine water as described previously. Consequently, concentrations of SO_4 (1,200 to 2,300 mg/L), Fe (3.1 to 238 mg/L), and Mn (4.1 to 7.0 mg/L) in the west creek (table 5) were much larger than concentrations of these constituents detected in streams upstream from mining activity. An average concentration of SO_4 in 189 streamflow samples upstream from mining in northern Missouri and southern Iowa was 88 mg/L (Detroy and others, 1983). The regional median concentration was 0.07 mg/L for Fe and 0.24 mg/L for Mn. Dissolved solids concentrations in the west creek upstream from the inflow of sewage treatment effluent at SW10 ranged from 2,710 to 3,410 mg/L and primarily reflected changes in SO_4 concentrations that constitute from 62 to 75 percent of the dissolved solids concentrations. The pH values were less than, and Fe and Zn concentrations were greater than, Missouri water-quality standards (Missouri Department of Natural Resources, 1987) for protection of aquatic life at most places in the creek.

The largest decrease in pH values in the west creek usually occurred between 1,000 and 2,000 ft downstream from MW1 (between SW4 and SW6) where acidification from oxidation and hydrolysis of Fe^{+2} (reaction 4) exceeded the buffering capacity of HCO_3 alkalinity. Water samples from the mine spring at MW1 had pH values that ranged from 5.4 to 5.9 (tables 2 and 5), HCO_3 concentrations of about 190 mg/L, and dissolved Fe concentrations of 240 mg/L. Nearly all Fe was in the ferrous form. As the underground-mine water became oxygenated, Fe^{+2} began to oxidize and hydrolyze (reaction 4) and a large deposit of Fe oxyhydroxides formed around the spring and on the streambank at MW1. The hydrolysis of Fe^{+3} also decreased the pH value to as low as 2.7 at site SW8. During most base-flow periods, the west creek usually had pH values less than 4.0 upstream from the point where it was neutralized by sewage effluent (5,700 ft downstream from MW1). However, short periods of increased base flow kept the pH of the west creek near neutral over its entire length. Near-neutral pH values were measured at all sites on February 24, 1988 (table 2 and fig. 11).

Thornstenson (1984) concluded that unique Eh values do not exist in natural water and attempts to measure Eh of an aquatic environment would fail. However, he also suggested that analysis of individual oxidation-reduction couples is valid. In contrast, data collected by Nordstrom and others (1979) indicate that in water where Fe dominates the multivalent elements and the pH is less than 4.5, Eh measurements reflect the electromotive potential of Fe species. These conditions are met in acidic water downstream from SW4. The downstream increase in values of Eh in the west creek in September 1987 and October 1988 (fig. 11) generally reflect the increasing percentage of Fe^{+3} downstream to the junction with sewage effluent. However, the Eh measurements of near-neutral pH water on February 24, 1988, violate the conditions stipulated by Nordstrom and others (1979) and may have little meaning. Sewage effluent caused a substantial decrease in Eh at SW10, as might be expected from the large quantities of reduced organic constituents and ammonia generally present in sewage effluent. On September 1, 1987, dissolved oxygen concentrations increased to near saturation at SW4, the first sampling site downstream from MW1, and was near or greater than saturation throughout the entire reach from SW4 to SW9 (fig. 12). After mixing with sewage effluent, dissolved oxygen concentrations at SW10 generally decreased because O_2 was consumed during oxidation of reduced species in the sewage effluent.

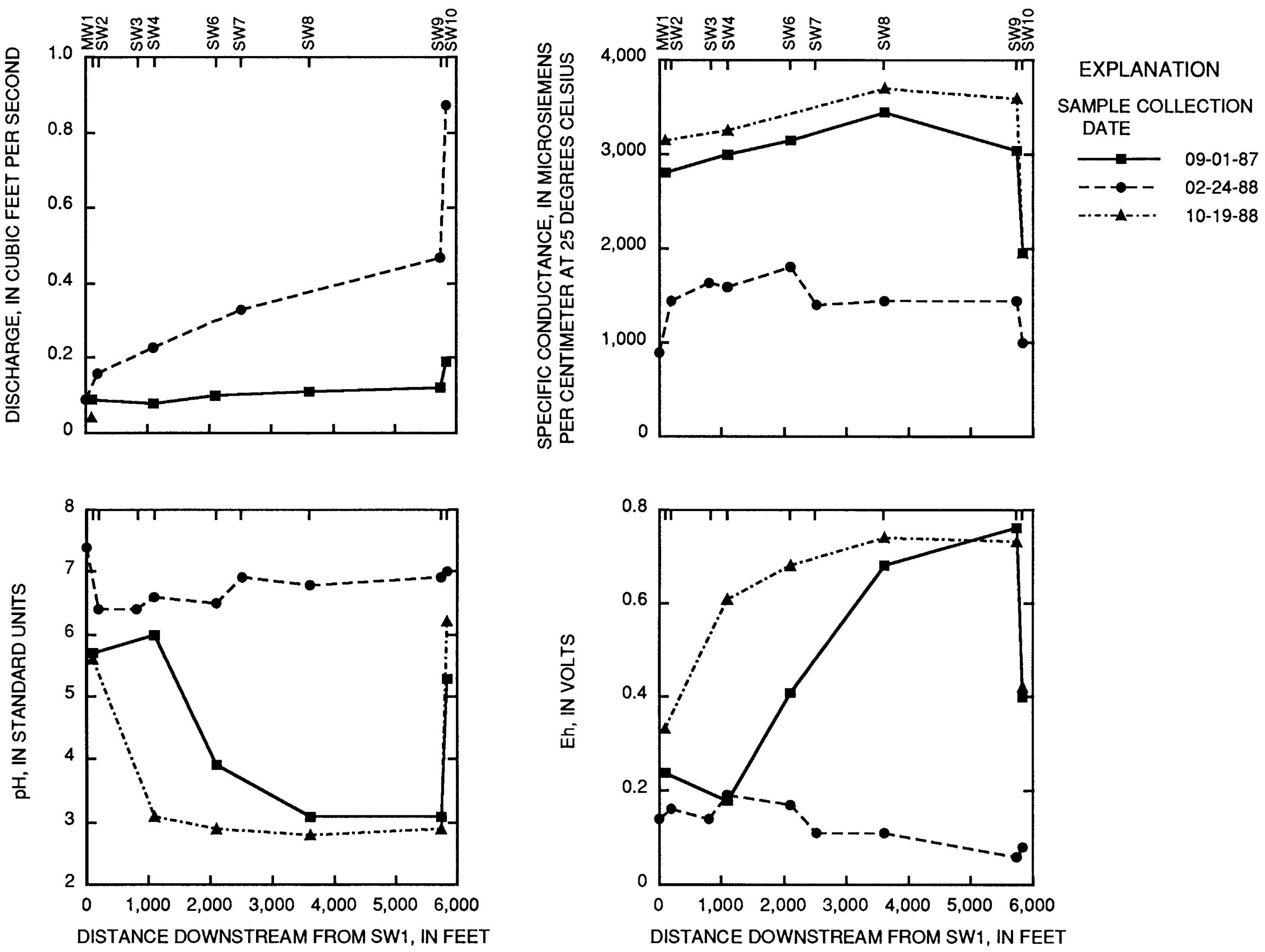


Figure 11.--Downstream changes in selected physical properties in the west creek (see figure 4 for location of SW1).

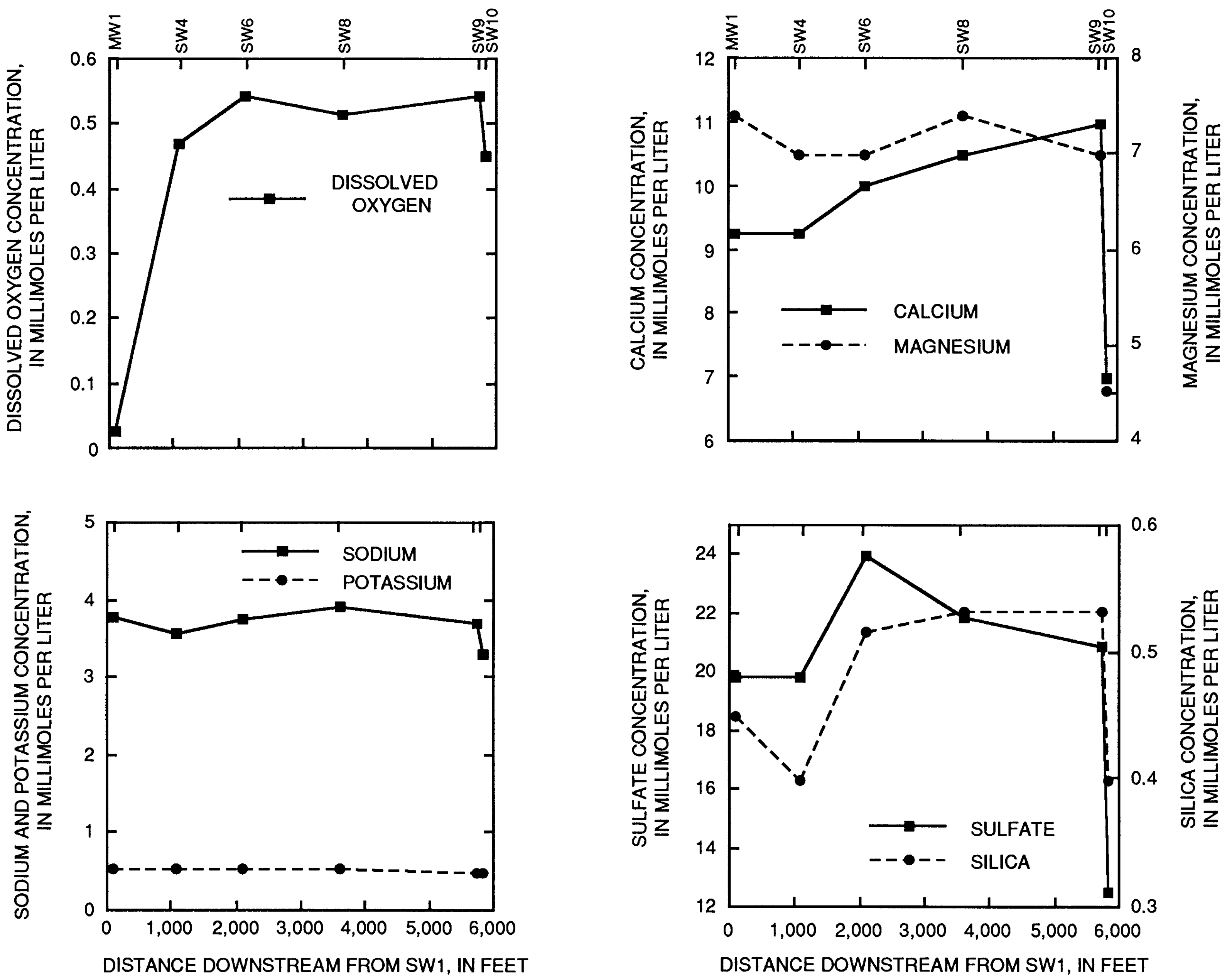


Figure 12.--Downstream changes in selected constituents in the west creek during base-flow conditions, September 1, 1987 (see figure 4 for location of SW1).

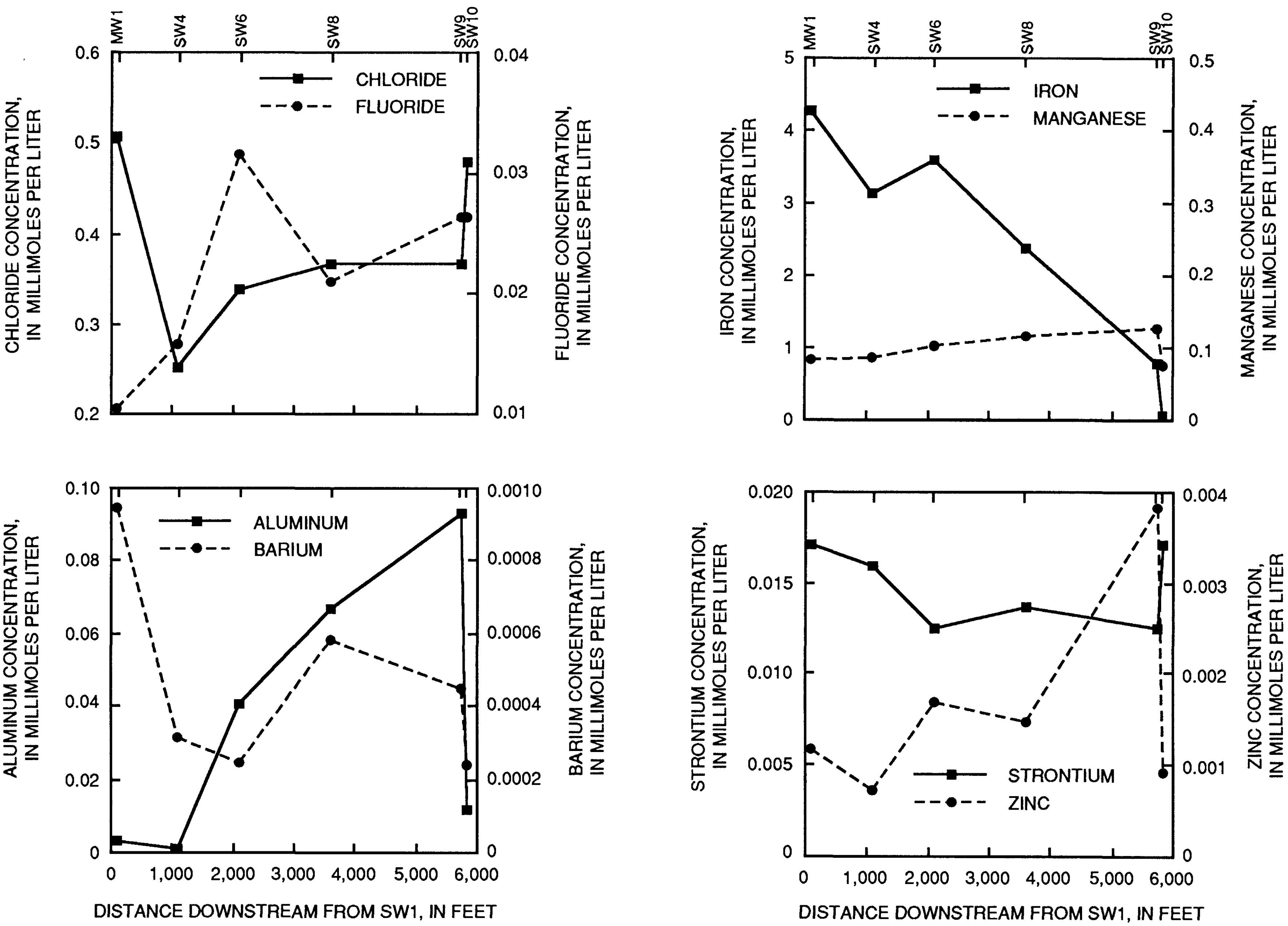


Figure 12.--Downstream changes in selected constituents in the west creek during base-flow conditions, September 1, 1987 (see figure 4 for location of SW1)--Continued.

Variations in the concentrations of the major cations and silica with distance downstream from SW1 were not consistent. Concentrations of Ca increased slightly downstream, probably from dissolution of limestone rocks on the streambed by the acidic water. Concentrations of Mg were nearly unchanged throughout the reach. Concentrations of Ca and Mg were substantially diluted by sewage effluent at SW10 (fig. 12). Concentrations of Na and K also were nearly unchanged from MW1 to SW10. Concentrations of SiO_2 increased slightly between SW4 and SW9 and corresponded with the decrease in pH values.

The major anion in water from the west creek was SO_4, which ranged from 1,900 to 2,300 mg/L until dilution at the sewage treatment outflow. Concentrations of SO_4 increased 21 percent between SW4 and SW6. The source of this increase probably was the small mine seep at MW3 emanating from the west streambank. The small discharge at MW3 must have had a SO_4 concentration of about 3,900 mg/L before mixing with the receiving stream water to cause the measured increase in SO_4 between SW4 and SW6. The saturation index for gypsum at SW6 was near zero and SO_4 concentrations decreased downstream from SW6. This downstream decrease in SO_4 may have been related to the increase in Ca concentration and subsequent precipitation of gypsum. Further downstream at SW10 sewage effluent substantially diluted SO_4 concentrations.

Concentrations of Fe generally decreased downstream from MW1 because of oxidation and precipitation of Fe as ferrihydrite (reaction 4). Unidentified Fe deposits covered the streambed of the west creek. A slight increase in Fe concentrations between SW4 and SW6 may have been caused by mine seepage from MW3. The small but visible quantity of seepage that was emanating from a diffuse area on the streambank was impossible to measure or sample. The diffuse mine seepage from MW3 would have to have had a discharge of about 0.02 ft^3/s and an Fe concentration of about 300 mg/L to account for changes between SW4 and SW6. At SW6 the saturation index for ferrihydrite was -2.1, but for potassium jarosite it was +2.8. Therefore, the acidification downstream (pH less than 3.9) probably was from jarosite precipitation rather than ferrihydrite precipitation.

Concentrations of Al and, to a lesser extent, Mn and Zn increased downstream as pH decreased. Dissolution of streambed minerals is a likely source as many minerals in near-surface rocks contain these metals.

North Creek

Mine spring MN9 contributed more than 70 percent of the streamflow in the north creek, except during short periods of runoff and high-base flow (table 2). During periods of low-base flow, the balance of the flow came from several smaller mine springs and sewage effluent. Occasionally, however, non-underground-mine water made up most of the flow. On February 23, 1988, onsite measurements of several water-quality properties were made during these high-base-flow conditions (table 2). At that time, base flow from sources other than mine springs was about 78 percent of the streamflow at SN10. The non-underground-mine water kept the pH values of the north creek greater than 6.0 and specific conductance values less than 1,500 µS/cm (microsiemens per centimeter at 25 °C) except for a short distance downstream from MN9.

On September 2, 1987, the common base-flow condition where the source of most of the flow was mine springs was sampled. At the time of sampling, mine spring MN9 contributed more than 80 percent of the flow in the north creek, and little or no ground water, other than mine discharge, was entering the creek. On this day, the sewage settling ponds were being dredged and no effluent was discharged. The chemistry of the north creek was dominated by mine spring MN9 and pH values were less than 4.0 at all locations, except immediately downstream from MN9. Results of analyses of samples collected from the north creek (tables 2 and 5) are plotted as a function of distance downstream from SN2 in figures 13 and 14. Several mine-drainage sources upstream from SN3, including MN1, combined to contribute about 0.01 ft^3/s to streamflow on September 2, 1987. The pH value of the combined flow from these small springs was always less than 4.0.

On September 2, 1987, the pH of north creek ranged from 3.0 to 3.3, except in a short reach near SN6, because all the water in the creek was from mine drainage that had already acidified before entering north creek. Concentrations of SO_4, Fe, and Mn were much larger than concentrations of these constituents in streams upstream from mining and were even larger than concentrations in west creek. Concentrations of SO_4 in north creek ranged from 2,400 to 3,200 mg/L, as compared with an average of 88 mg/L for streams upstream from mining activity reported

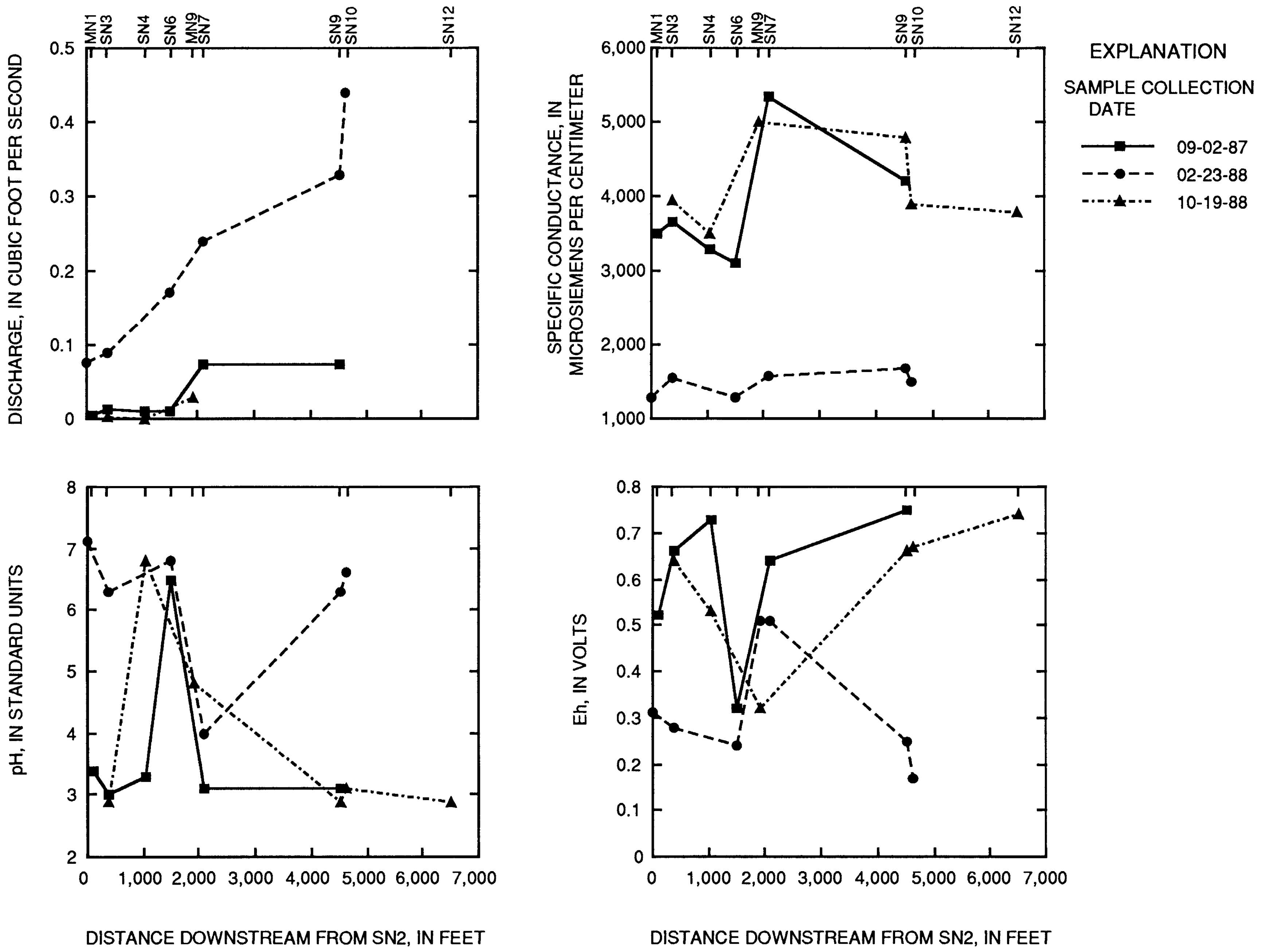


Figure 13.--Downstream changes in selected physical properties in the north creek (see figure 4 for location of SN2).

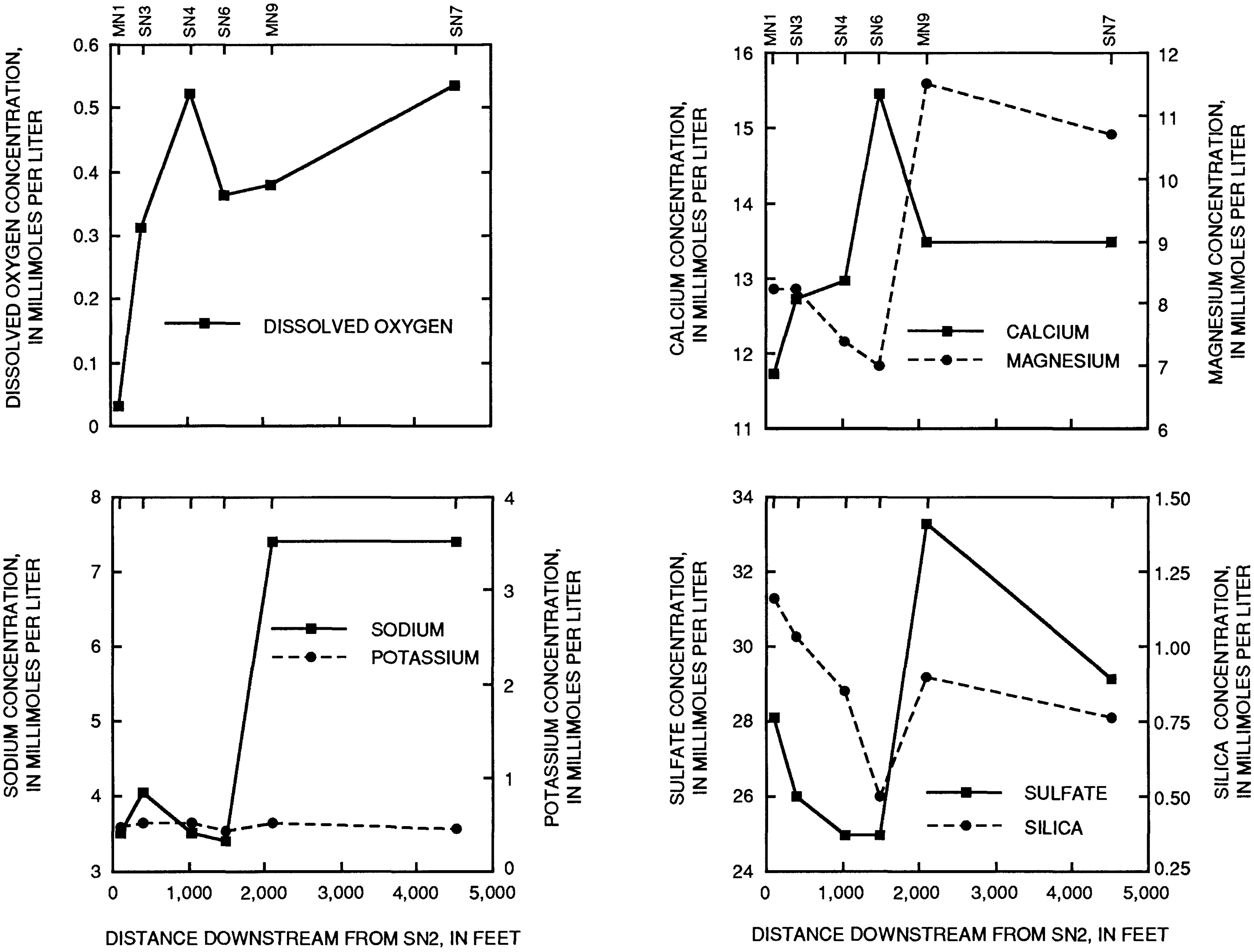


Figure 14.--Downstream changes in selected constituents in the north creek during base-flow conditions, September 2, 1987 (see figure 4 for location of SN2).

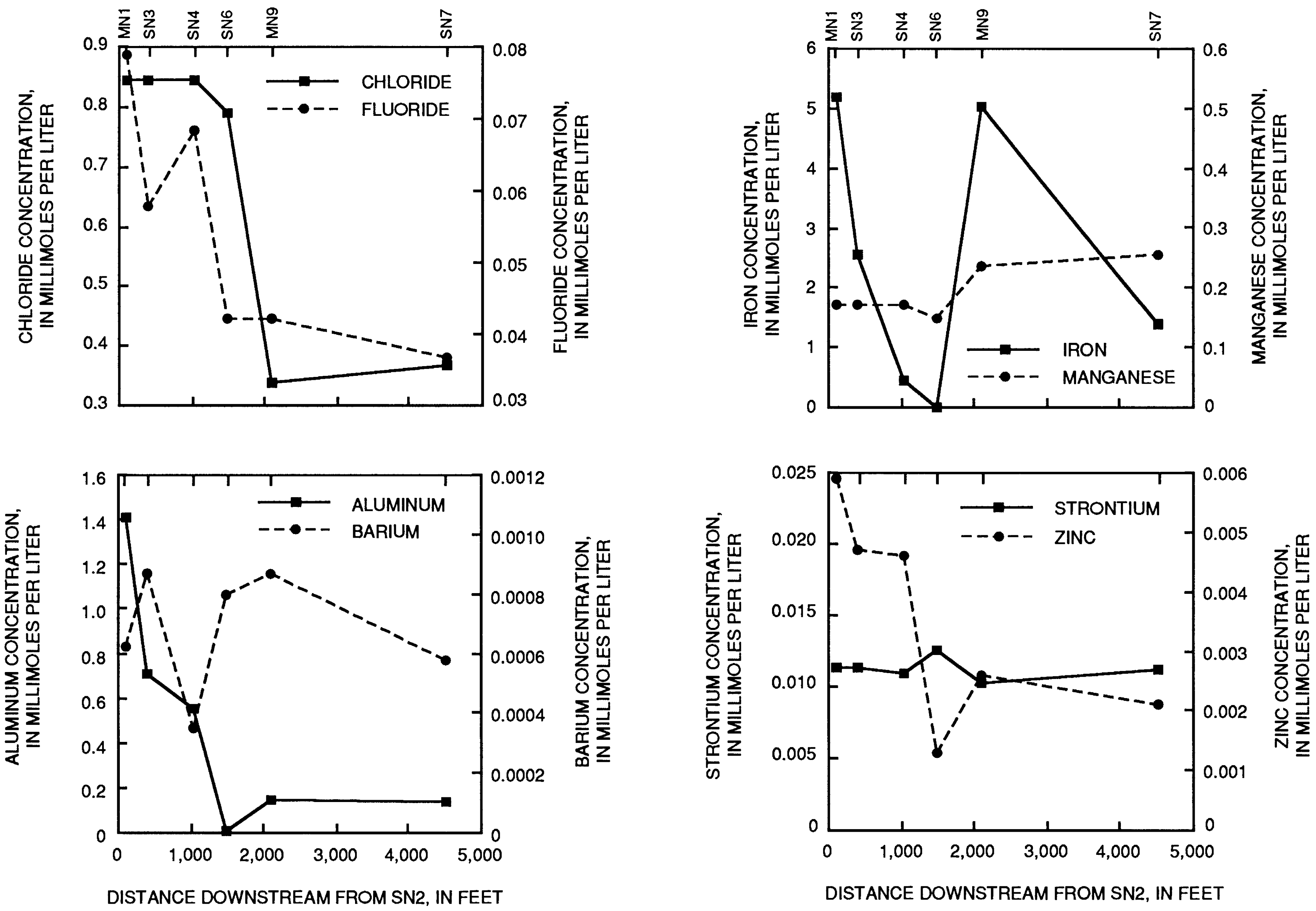


Figure 14.--Downstream changes in selected constituents in the north creek during base-flow conditions, September 2, 1987 (see figure 4 for location of SN2)--Continued.

reported by Detroy and others (1983). Iron concentrations ranged from 26 to 483 mg/L and Mn concentrations ranged from 9.5 to 14 mg/L in north creek except for the short reach near SN6 as compared with a median Fe concentration of 0.07 mg/L and a median Mn concentration of 0.24 mg/L in other streams in northern Missouri and southern Iowa. Dissolved solids concentrations in north creek ranged from 3,450 to 5,500 mg/L. Changes in dissolved solids concentrations primarily were reflecting changes in SO_4 concentrations, which constituted 54 to 72 percent of the dissolved solids concentrations, and at several places in north creek concentrations of Fe, Ni, and Zn were greater than, and the pH values were less than, Missouri water-quality standards (Missouri Department of Natural Resources, 1987) for the protection of aquatic life in unclassified streams.

Dissolved O_2 was detected and the pH was less than 4.0 in the small quantity of water emerging at MN1. Apparently, mine springs with small discharges acidify quicker upon contact with atmospheric oxygen than do mine springs with larger discharges. Water from MN1 probably acidified after contact with O_2 just below land surface near the spring. An increase in pH value of two to four units consistently occurred between SN4 and SN6 during most of the flow conditions (fig. 13 and table 2). This part of north creek flows in a side ditch along the west side of a limestone-gravel road and had numerous limestone rocks in the streambed. The dissolution of carbonate rocks in the gravel and dust from this road probably accounts for the increase in pH value. Drainage from MN9 entered the north creek immediately downstream from SN6, and the pH decreased from about 6.5 to between 3.0 and 4.0 at SN7, except during short periods of runoff and high-base flow (table 2). The small quantities of sewage effluent from SN11 generally increased pH values only 0.1 to 0.4 pH unit (table 2). Acidic drainage from the north creek flows into Sugar Creek upstream from SN14. Water in Sugar Creek often was acidic at SN14 and was slightly acidic at SN13 upstream from the junction of the north creek because of oxidation of mine tailings in the creek bed.

The major cations in water in the north creek were Ca and Mg. Concentrations of Ca in the north creek increased 110 mg/L through the neutralizing reach between sites SN3 and SN6 (table 5), as would be expected from limestone dissolution. However, the saturation index for gypsum was 0.02 at SN4 and 0.07 at SN6, indicating that as limestone dissolved gypsum precipitated. The 100 mg/L decrease in SO_4 concentrations between SN3 and SN6 is slightly less than might be expected from a 110 mg/L increase in Ca concentration. This probably is because of the differences in precision of the analytical methods for Ca and SO_4 at the concentrations reported. A milky-white precipitate resembling gypsum commonly was observed in this reach. The decrease in Ca concentrations between sites SN6 and SN7 was caused by dilution with spring discharge from site MN9. The Mg concentration, on the other hand, increased from 170 mg/L at SN6 to 280 mg/L at SN7 downstream from MN9.

The variations in concentrations of Na and K with distance on the north creek differed. Concentrations of Na in the north creek increased 2.5 times as a result of mixing with water from MN9. However, K concentrations were nearly constant throughout the reach (fig. 14).

Concentrations of SO_4 in the north creek decreased slightly between SN3 and SN6, probably because of gypsum precipitation. Drainage from MN9 had large concentrations of SO_4 and substantially increased concentrations downstream in the creek. The decrease in SO_4 concentration downstream from MN9 indicates precipitation of gypsum or jarosite, or both.

The concentration of Fe rapidly decreased from 290 to 26 mg/L between MN1 and SN4 by precipitation of ferrihydrite and perhaps jarosite. The streambed in this reach was covered with bright orange precipitates. The small concentration of Fe in the reach between SN4 and SN6 allowed a substantial increase in pH between those sites. However, discharge from MN9 resupplied large Fe^{+2} concentrations to the creek. Oxidation and hydrolysis of the Fe reacidified the creek downstream from MN9.

Other metals of interest in the north creek include Mn, Al, Ba, and Zn. Except where the north creek received drainage from MN9, Mn concentrations varied little in the creek because Mn is slow to oxidize and is soluble in acidic water. The largest concentrations of Al and Zn corresponded with acidic values of pH because the solubilities of minerals containing these elements generally are dependent on the pH value. Concentrations of Ba were small in the north creek because of the large concentration of SO_4 and the low solubility of barite.

SUBSIDENCE

Subsidence from mine collapse has occurred most often at drift entries and mine shafts. Several historical occurrences of subsidence were recorded from interviews of local residents by the Missouri Division of Geology and Land Survey (records on file at the Missouri Department of Natural Resources, Land Reclamation Commission, Jefferson City). Many other areas of subsidence were located during this investigation and are plotted in figure 15.

Most instances of documented subsidence occurred near coal outcrops where the overburden is thin (less than 30 ft) and does not include the massive sandstone in the upper Lagonda Formation (fig. 2). Evidently, collapse can migrate upward through the shales of the lower Lagonda Formation but generally does not progress beyond the massive sandstone of the upper part of the formation, if the sandstone is present. Weigel (1921) noted that where mine roofs were sandstone, mine collapse was a minimal hazard. Most of the documented mine collapses probably occurred upon removal or failure of supporting timbers and props from rooms and entries. Timbers were used in about one-half of the entries where the roof was most unstable. Most rooms were propped. Upward movement of collapse in the subsurface along U.S. Highway 24 (fig. 6) was documented by the Missouri Highway and Transportation Department (1981) with downhole photography showing slabs of rock that have fallen from the roof. Drill logs from these holes indicate some of the voids had migrated upward as much as 15 ft (data on file at the Missouri Highway and Transportation Department, Jefferson City). The Lagonda Formation in Macon and Randolph Counties normally contains about 10 ft of sandy shale overlain by 4 to 5 ft of sandstone (Gentile, 1967). Along U.S. Highway 24, the Lagonda Formation is about 30 ft thick and has almost no sandstone. The lack of sandstone may partly account for collapses encountered during construction of U.S. Highway 24 during 1978 (Randolph County Herald-Times, written commun., 1977). However, the sandstone is substantially thicker to the north (along State Route C) and west and even replaces the Bevier-Wheeler coals in an open drift shown in figure 3. All areas with less than 30 ft of overburden are identified as areas of potential subsidence in figure 15.

Subsidence near mine shafts seems to be a function of how well the shafts were backfilled. Although numerous cases of shaft subsidence have been reported by local residents, no subsidence at mine shafts was noted during this investigation. Subsidences at shafts usually have been quickly filled. However, improperly filled shafts have the potential to recollapse. Shaft collapse seems to occur most frequently after intense rainfall. Reported shaft collapses and all known shaft locations are plotted in figure 15 (Missouri Department of Natural Resources, Land Reclamation Commission, written commun., 1986-87).

SUMMARY

Bevier-Wheeler coals underneath the city of Huntsville, Missouri, were mined extensively during the late 1800's and early 1900's. By 1966 most of the coal had been removed and the mines were abandoned. These abandoned mines are of concern for two reasons: (1) mine drainage affects the water quality, appearance, and safety of streams and nearby ground water; and (2) collapse of mine cavities sometimes causes surface subsidence resulting in property damage or personal injury.

The coal seams were above the altitude of the larger streams in the area and the coals and associated mines were, therefore, areally limited by stream-valley erosion. Many of the mine cavities are not flooded and calculations indicate that the mines received and discharged only about 0.43 in. of water per year averaged over the areal extent of the mines during this study. The coal seams and their cavities dipped to the northwest about 50 ft in 2 mi. Contamination of the Moberly channel fill aquifer by mine drainage has not occurred because of the isolation of the coal seams by erosion and the dip of the seams away from the aquifer.

Water in up dip parts of the mines had pH values ranging from 6.2 to 6.5, Fe concentrations from 16 to 66 mg/L, SO_4 concentrations from 830 to 1,100 mg/L, and HCO_3 concentrations from 250 to 340 mg/L. These concentrations, as well as concentrations of Mn, Ni, and Zn, were much larger than concentrations of these constituents detected in nearby ground water unaffected by mining. The primary source of Fe^{+2} and SO_4 in underground-mine water probably was pyrite. High concentrations of SO_4 and Fe^{+2} indicate that the sulfur in pyrite was oxidized to SO_4, but oxygen in

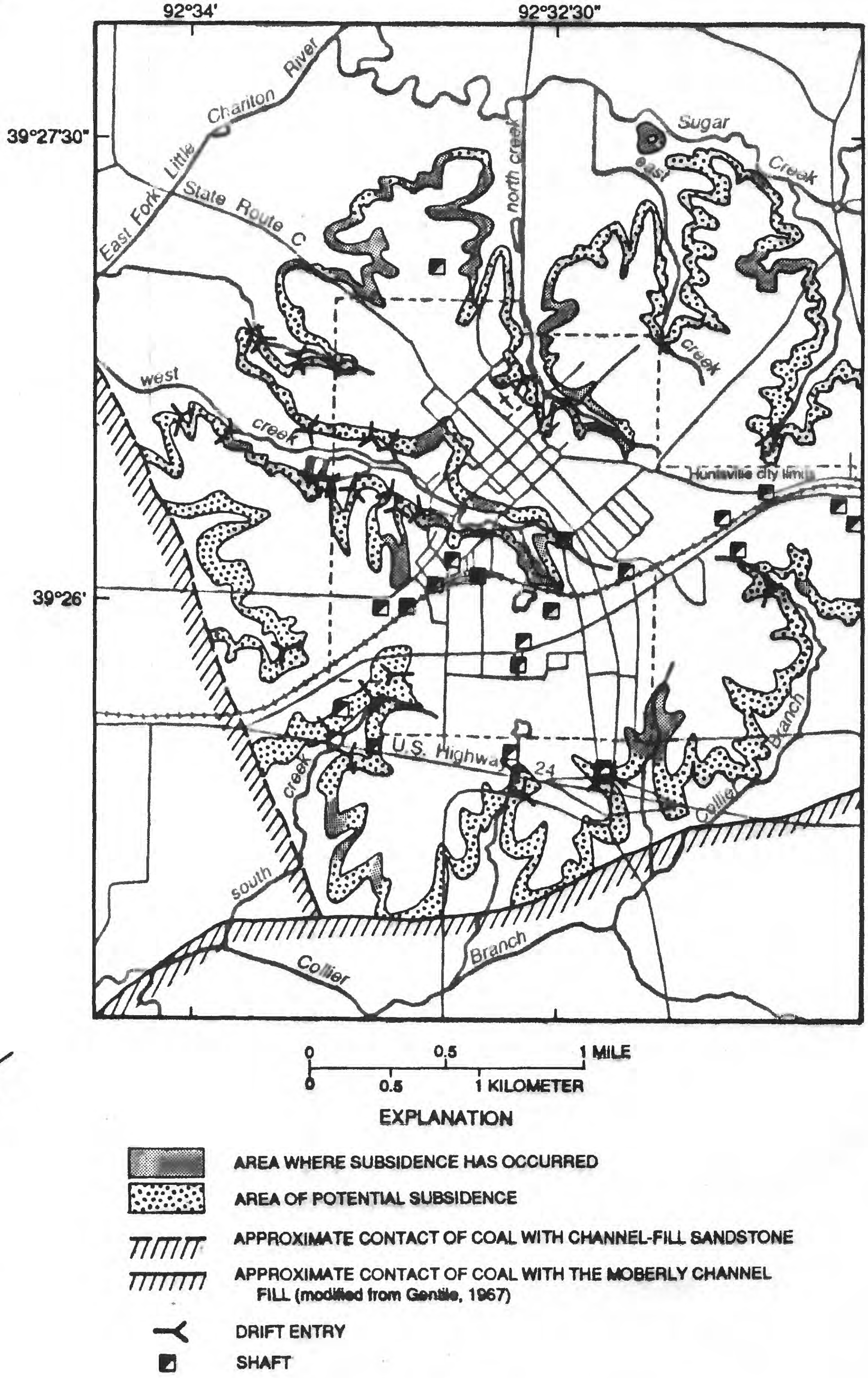


Figure 15.--Areas of subsidence and potential subsidence.

the mine water was insufficient to oxidize all the Fe^{+2}. Thus, limited availability of dissolved O_2 inhibits further acidification by the oxidation and subsequent hydrolysis of Fe in underground-mine water. Most of the mine-water samples were oversaturated with siderite, which may limit concentrations of CO_2 species and Fe^{+2}. As pyrite oxidizes and calcite dissolves, siderite may precipitate in the mines.

Unflooded parts of the mines increase the availability of atmospheric oxygen to underground-mine water and allow increased rates of oxidation of pyrite or Fe^{+2}, or both. Compared to water samples collected from up-dip wells, water from mine springs had more acidic pH values (4.7 to 5.9), larger Eh values (0.24 to 0.32 volts), larger Fe^{+2} concentrations (238 to 620 mg/L), detectable concentrations of dissolved O_2, and increased SO_4 concentrations (1,900 to 3,600 mg/L), indicating some exposure to O_2 in unflooded cavities along the flow path. Small concentrations of N species and total organic carbon indicate few, if any, effects from domestic sewage that may have been dumped in some part of the mines.

The oxidation and subsequent hydrolysis of Fe^{+2} in mine drainage caused the acidification of two streams just downstream from mine springs MW1 and MN9. These two streams have no flow other than mine drainage during most base-flow conditions and the combined flow of MW1 and MN9 accounted for about 80 percent of the mine drainage in the study area. Consequently, the pH values were much lower and concentrations of SO_4, Fe, and Mn were much larger in these two streams than in most other streams unaffected by mining. During August 31 through September 3, 1987, pH ranged from 3.0 to 6.5, concentrations of SO_4 ranged from 1,900 to 3,600 mg/L (not including the sewage effluent at SW10), Fe ranged from 0.41 to 620 mg/L, and Mn ranged from 3.8 to 14 mg/L in the two streams most affected by mining. The median pH value was 7.7 for streams upstream from mining in northern Missouri and southern Iowa, the average SO_4 concentration was 88 mg/L, the median Fe concentration was 0.07 mg/L, and the median Mn concentration was 0.24 mg/L. At several locations, the pH value was less than and concentrations of Fe, Ni, and Zn were larger than Missouri water-quality standards for the protection of aquatic life.

Fe concentrations decreased downstream from MW1 and MN9 because ferrihydrite and probably jarosite were precipitated on the streambed, as indicated by bright orange deposits. The acidic water also dissolved limestone and the increased concentrations of Ca caused gypsum to precipitate on the streambed. Sewage effluent neutralized the pH values of mine drainage downstream from Huntsville when the effluent had a large flow.

Subsidence from mine collapse occurs above drift entries and at shafts. Subsidence not associated with shafts was limited to areas where the overburden is less than 30 ft thick and did not include the massive sandstone in the upper Lagonda Formation. The sandstone halted the upward migration of overburden collapse. In this report, areas with less than 30 ft of overburden are identified as areas of potential subsidence. All areas of existing subsidence occurred in this zone, usually above drift entries.

Historically, shaft subsidence has been documented with recorded interviews of local residents. However, no shaft subsidence was detected in this study. Open shafts generally have been promptly filled. However, unless proper techniques are used to fill open shafts, they are prone to recollapse, especially after intense rains.

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SUPPLEMENTAL DATA

Table 2.--*Results of synoptic measurements of selected properties and constituents in water from mine springs and surface-water sites in the west and north creeks*

[ft^3/s, cubic foot per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; --, no data; <, less than; e, estimated]

Site number (fig. 4)	Date	Instantaneous discharge (ft^3/s)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)	Total iron (mg/L)
				west creek				
MW1	7-14-87	--	3,250	5.4	--	16.5	--	--
SW6	7-14-87	--	1,180	6.3	--	22.5	--	--
MW7	7-14-87	<0.001e	2,950	2.9	--	23.0	--	--
SW7.5	7-14-87	--	980	6.1	--	25.0	--	--
SW8	7-14-87	--	1,180	5.9	--	23.0	--	--
SW8.5	7-14-87	--	1,200	6.8	--	20.0	--	--
MW9	7-14-87	--	3,480	2.8	--	23.5	--	--
MW10	7-14-87	<.001e	1,330	5.1	--	25.0	--	--
MW11	7-14-87	--	2,850	3.2	--	19.5	--	--
MW1	8-11-87	[a].076	3,300	5.6	--	13.5	--	--
MW2	8-11-87	[a].0001	1,700	6.3	--	--	--	--
SW2	8-11-87	--	3,250	5.7	--	--	--	--
SW3	8-11-87	--	3,050	6.0	--	--	--	--
SW4	8-11-87	[a].084	3,050	6.0	--	17.0	--	--
SW6	8-11-87	.12	3,500	3.3	--	18.0	--	--
MW4	8-11-87	[a].001	3,500	2.6	--	22.0	--	--
SW7	8-11-87	.12	3,500	3.3	--	20.0	--	--
SW8	8-10-87	.10	3,900	2.7	--	--	--	--
SW8.5	8-10-87	[a].0009	1,650	6.9	--	--	--	--
MW9	8-10-87	[a].0100	3,500	4.1	--	--	--	--
SW9	8-10-87	.14	3,650	2.8	--	--	--	--
SW10	8-10-87	.24	2,450	5.4	--	--	--	--
MW11	8-10-87	[a].0016	3,250	3.0	--	--	--	--
MW1	8-31-87	[a].086	2,800	5.7	0.2	14.5	0.4	270
SW4	8-31-87	[a].078	3,000	6.0	.2	19.0	7.5	180
SW6	9-01-87	[a].098	3,150	3.9	.4	13.0	8.7	230
MW5	9-01-87	[a].0026	3,150	3.1	.7	18.5	3.3	92
SW8	9-01-87	.11	3,450	3.2	.7	14.0	8.2	140
MW9	9-01-87	[a].002	2,930	3.4	--	21.5	--	--
SW9	9-01-87	.12	3,050	3.1	.8	16.5	8.7	45
SW10	9-01-87	.19	1,950	5.3	.3	18.0	7.2	3.1

Table 2.--*Results of synoptic measurements of selected properties and constituents in water from mine springs and surface-water sites in the west and north creeks*--Continued

Site number (fig. 4)	Date	Instantaneous discharge (ft^3/s)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)	Total iron (mg/L)
MW1	10-09-87	[a] 0.062	3,100	5.6	0.2	13.5	--	--
SW4	10-09-87	--	3,000	6.1	.2	14.0	--	--
SW6	10-09-87	--	3,550	3.5	.6	11.5	--	--
SW8	10-09-87	--	3,550	3.1	.7	11.5	--	--
SW9	10-09-87	[a] .096	3,600	3.2	.7	11.5	--	--
SW10	10-09-87	.16	2,200	4.8	.4	12.5	--	--
MW1	11-13-87	[a] .070	3,000	5.9	.2	13.5	--	--
SW4	11-13-87	--	3,050	6.3	.2	11.5	--	--
SW6	11-13-87	--	3,400	3.9	.5	8.0	--	--
SW7	11-13-87	[a] .094	--	--	--	--	--	--
SW7.5	11-13-87	--	2,450	5.8	.4	5.0	--	--
SW8	11-13-87	--	3,400	3.1	.7	7.0	--	--
SW9	11-13-87	[a] .092	3,200	3.2	.7	5.0	--	--
SW11	11-13-87	--	850	8.0	.4	8.5	--	--
SW10	11-13-87	.22	1,980	6.0	.4	5.0	--	--
SW1	2-24-88	.093	890	7.4	.1	4.5	--	--
MW1	2-24-88	.067	2,850	5.6	.2	13.5	--	--
SW2	2-24-88	.16	1,450	6.4	.2	--	--	--
SW3	2-24-88	--	1,630	6.4	.1	3.5	--	--
SW4	2-24-88	.23	1,600	6.6	.2	6.0	--	--
SW6	2-24-88	--	1,800	6.5	.2	2.0	--	--
SW7	2-24-88	.33	1,400	6.9	.1	2.5	--	--
SW7.5	2-24-88	.046	925	6.7	.2	1.5	--	--
SW8	2-24-88	--	1,450	6.8	.1	2.0	--	--
SW9	2-24-88	.47	1,450	6.9	.1	--	--	--
SW11	2-24-88	.40	850	7.3	.1	5.5	--	--
SW10	2-24-88	.87	1,000	7.0	.1	--	--	--
MW1	4-13-88	--	--	5.6	--	--	--	--
SW8	4-13-88	--	--	6.6	--	--	--	--
MW1	4-28-88	--	--	5.5	--	--	--	--
SW8	4-28-88	--	--	5.0	--	--	--	--

Table 2.--*Results of synoptic measurements of selected properties and constituents in water from mine springs and surface-water sites in the west and north creeks*--Continued

Site number (fig. 4)	Date	Instantaneous discharge (ft^3/s)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)	Total iron (mg/L)
MW1	5-18-88	0.082	2,850	5.4	0.2	13.5	--	--
SW4	5-18-88	--	2,850	6.1	.6	--	--	--
SW6	5-18-88	--	2,980	3.6	.4	--	--	--
SW8	5-18-88	--	3,100	3.0	.6	--	--	--
SW9	5-18-88	.092	2,800	3.0	.7	--	--	--
SW11	5-18-88	.056	1,150	7.9	.4	--	--	--
SW10	5-18-88	.15	2,350	3.6	.6	--	--	--
MW1	6-23-88	--	--	5.6	--	--	--	--
SW8	6-23-88	--	--	2.7	--	--	--	--
SW9	6-22-88	.07	3,400	2.9	.7	23.5	7.5	23
SW11	6-22-88	.036	1,080	7.4	.2	26.5	3.8	.07
SW10	6-22-88	.11	2,310	5.6	.3	24.5	4.1	2.3
SW12	6-22-88	--	2,230	5.6	.3	25.7	5.6	2.3
MW1	8-03-88	.059	2,900	5.6	.3	13.5	--	--
MW1	8-04-88	.069	3,400	5.6	.2	13.5	--	--
SW4	8-04-88	--	3,000	5.7	.2	20.5	--	--
SW6	8-04-88	.057	3,400	2.9	.6	23.0	--	--
SW8	8-04-88	--	3,500	2.7	.7	24.0	--	--
SW9	8-04-88	.048	3,200	2.9	.7	24.5	--	--
SW11	8-04-88	.032	1,050	7.3	.1	25.0	--	--
SW10	8-04-88	.08	2,500	5.0	.4	24.5	--	--
SW12	8-04-88	--	2,150	6.5	.2	24.5	--	--
MW1	10-19-88	.044	3,150	5.6	.3	13.5	--	265
SW4	10-19-88	--	3,200	3.1	.6	--	--	--
SW6	10-19-88	--	3,500	2.9	.7	--	--	--
SW8	10-19-88	--	3,700	2.8	.7	--	--	--
SW9	10-19-88	--	3,600	2.9	.7	--	--	--
SW11	10-19-88	.007	950	7.2	.4	--	--	--
SW10	10-19-88	--	1,950	6.2	.4	--	--	--

Table 2.--*Results of synoptic measurements of selected properties and constituents in water from mine springs and surface-water sites in the west and north creeks*--Continued

Site number (fig. 4)	Date	Instantaneous discharge (ft^3/s)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)	Total iron (mg/L)
MW1	12-21-88	0.04	3,100	5.8	0.3	13.5	--	--
MW2	12-21-88	.000	1,800	7.0	.2	8.0	--	--
SW4	12-21-88	--	3,100	3.9	.3	6.0	--	--
SW6	12-21-88	--	3,600	3.2	.6	3.0	--	--
SW7	12-21-88	.048	--	--	--	--	--	--
SW7.5	12-21-88	<.001e	2,550	6.0	.6	.5	--	--
SW8	12-21-88	--	3,400	3.1	.7	.0	--	--
SW9	12-21-88	.04	2,950	3.3	.7	.5	--	--
SW11	12-21-88	.11	710	8.5	.4	5.5	--	--
SW10	12-21-88	.15	1,400	7.2	.4	2.5	--	--
MW11	12-21-88	<.001e	--	--	--	--	--	--
				<u>north creek</u>				
SN6.5	7-14-87	--	4,000	4.7	--	15.5	--	--
SN9	7-14-87	--	2,175	6.1	--	21.0	--	--
SN10	7-14-87	--	1,720	6.1	--	21.5	--	--
SN2	8-10-87	[a].006	--	--	--	--	--	--
MN1	8-10-87	[a].0012	4,400	3.7	--	--	--	--
SN3	8-10-87	[a].0082	4,050	3.0	--	23.0	--	--
SN4	8-10-87	[a].0062	3,950	3.2	--	25.0	--	--
MN8	8-10-87	[a].0031	3,300	4.0	--	15.0	--	--
SN6	8-11-87	--	3,400	6.6	--	--	--	--
MN9	8-11-87	[a].031	5,500	4.9	--	15.5	--	--
SN6.5	8-11-87	[a].030	5,600	2.8	--	28.0	--	--
MN10	8-10-87	[a].0016	3,700	3.3	--	--	--	--
SN7	8-11-87	[a].094	5,000	3.0	--	23.5	--	--
MN1	9-01-87	[a].0046	3,500	3.4	.5	14.5	0.5	350
SN3	9-01-87	[a].013	3,650	3.0	.7	20.0	5.0	130
SN4	9-02-87	[a].011	3,300	3.3	.7	16.0	8.4	33
MN8	9-01-87	[a].0022	2,850	4.1	.5	13.5	.8	120
SN6	9-02-87	[a].011	3,100	6.5	.3	16.0	5.8	.43
MN9	9-02-87	[a].060	5,600	5.3	.3	15.0	.4	620
SN6.5	9-02-87	[a].016	6,800	3.0	.6	24.5	2.4	--
MN10	9-02-87	[a].0058	3,750	3.2	.7	17.0	6.8	92
SN7	9-02-87	[a].075	4,590	3.1	.6	17.0	6.1	290
SN9	9-02-87	[a].073	4,200	3.1	.8	17.0	8.6	96

Table 2.--*Results of synoptic measurements of selected properties and constituents in water from mine springs and surface-water sites in the west and north creeks*--Continued

Site number (fig. 4)	Date	Instantaneous discharge (ft^3/s)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)	Total iron (mg/L)
SN4	10-09-87	[a]0.010	3,400	3.1	0.7	9.5	--	--
SN6	10-09-87	--	3,350	5.7	.5	9.0	--	--
MN9	10-09-87	[a].035	5,400	4.8	.3	14.0	--	--
SN6.5	10-09-87	[a].035	5,500	3.0	.6	9.0	--	--
SN7	10-09-87	[a].035	5,000	3.0	.6	10.5	--	--
SN4	11-12-87	[a].015	3,500	3.3	.7	8.0	--	--
SN5	11-12-87	--	2,950	5.7	--	14.0	--	--
SN6	11-12-87	--	3,050	5.4	.4	8.5	--	--
MN9	11-12-87	[a].026	5,050	5.0	.3	14.0	--	--
SN6.5	11-12-87	[a].026	5,200	2.9	.6	10.0	--	--
SN7	11-12-87	[a].055	4,450	3.0	.7	10.0	--	--
SN9	11-12-87	[a].059	4,100	3.0	.8	9.0	--	--
SN11	11-12-87	[a].024	1,050	7.8	.5	9.0	--	--
SN10	11-12-87	[a].084	3,400	3.3	.7	10.0	--	--
SN12	11-12-87	--	3,450	3.2	--	9.0	--	--
SN14	11-12-87	--	2,200	3.8	--	7.0	--	--
SN2	2-23-88	[a].076	1,275	7.1	.3	--	--	--
MN1	2-23-88	--	3,100	3.3	.6	--	--	--
SN3	2-23-88	[a].089	1,550	6.3	.3	--	--	--
MN8	2-23-88	[a].0084	2,350	4.7	.4	12.0	--	--
SN6	2-23-88	.17	1,300	6.8	.2	3.0	--	--
MN9	2-23-88	[a].070	4,650	4.7	.3	13.5	--	--
MN10	2-23-88	[a].0068	2,200	3.5	.6	--	--	--
SN7	2-23-88	.24	1,580	4.0	.5	3.5	--	--
SN9	2-23-88	.33	1,680	6.3	.2	5.0	--	--
SN11	2-23-88	.11	900	6.9	.2	6.5	--	--
SN10	2-23-88	.44	1,500	6.6	.2	--	--	--
SN13	2-23-88	--	560	6.8	.2	--	--	--
MN9	3-10-88	[a].055	--	--	--	--	--	--

Table 2.--*Results of synoptic measurements of selected properties and constituents in water from mine springs and surface-water sites in the west and north creeks*--Continued

Site number (fig. 4)	Date	Instantaneous discharge (ft^3/s)	Specific conductance (μS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)	Total iron (mg/L)
MN9	3-30-88	0.051	4,500	4.7	0.3	14.0	--	--
MN9	4-13-88	.052	3,400	4.8	.3	13.5	--	--
SN7	4-13-88	--	--	5.9	--	--	--	--
MN9	4-28-88	.051	4,800	4.7	.1	13.5	--	--
SN7	4-28-88	--	--	5.2	--	--	--	--
SN3	5-18-88	.013	3,190	2.9	.6	--	--	--
SN6	5-18-88	--	2,900	5.4	.4	--	--	--
MN9	5-18-88	.050	4,600	4.8	.3	13.5	--	--
SN7	5-18-88	.078	3,950	3.8	.5	--	--	--
SN9	5-18-88	.078	3,850	2.9	.6	--	--	--
SN11	5-18-88	.018	1,570	7.5	.1	--	--	--
SN10	5-18-88	.096	3,460	3.2	.6	--	--	--
SN12	5-18-88	--	3,050	2.9	--	--	--	--
SN13	5-18-88	--	1,300	6.2	--	--	--	--
SN14	5-18-88	--	1,770	3.7	--	--	--	--
MN9	6-23-88	[a].045	--	4.8	--	--	--	--
SN7	6-23-88	--	--	3.7	--	--	--	--
SN9	6-23-88	--	--	2.8	--	--	--	--
SN11	6-23-88	[a].0060	--	7.4	--	--	--	--
SN10	6-23-88	--	--	2.8	--	--	--	--
MN1	8-03-88	--	3,800	3.7	.4	14.5	--	--
SN3	8-03-88	[a].0035	4,000	2.9	.6	26.0	--	--
SN4	8-03-88	[a]<.0001	3,480	3.3	.6	28.0	--	--
SN6	8-03-88	[a].0000	--	--	--	--	--	--
MN9	8-03-88	[a].039	5,000	4.7	.3	14.0	--	--
SN7	8-03-88	.04	4,600	3.2	.6	20.0	--	--
SN11	8-03-88	[a].0038	1,070	7.5	.3	27.5	--	--
SN12	8-03-88	[a].021	3,900	2.9	.7	27.0	--	--

Table 2.--*Results of synoptic measurements of selected properties and constituents in water from mine springs and surface-water sites in the west and north creeks*--Continued

Site number (fig. 4)	Date	Instantaneous discharge (ft^3/s)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)	Total iron (mg/L)
SN3	10-19-88	[a] 0.0031	3,950	2.9	0.6	--	--	--
SN4	10-19-88	[a] .001	3,500	6.8	.5	--	--	--
MN9	10-19-88	[a] .029	5,000	4.8	.3	13.5	--	--
SN9	10-19-88	--	4,800	2.9	.7	12.5	--	--
SN11	10-19-88	[a] .011	980	7.4	--	14.0	--	--
SN10	10-19-88	--	3,900	3.1	.7	11.5	--	--
SN12	10-19-88	--	3,800	2.9	.7	--	--	--
SN13	10-19-88	[a] .0000	--	--	--	--	--	--
MN1	12-22-88	[a] .0022	3,950	3.7	.5	--	--	--
SN3	12-22-88	[a] .008	3,500	4.0	.5	2.0	--	--
SN4	12-22-88	--	3,400	3.5	.7	--	--	--
SN6	12-22-88	--	3,000	6.6	.5	--	--	--
MN9	12-22-88	[a] .030	5,050	5.0	.4	14.0	--	--
SN7	12-22-88	--	4,450	3.3	.6	--	--	--
SN9	12-22-88	[a] .059	4,000	3.2	.6	--	--	--
SN11	12-22-88	[a] .028	940	8.4	.4	--	--	--
SN10	12-22-88	--	3,000	3.4	.6	--	--	--
SN12	12-22-88	--	2,900	3.3	.6	--	--	--

[a] Instantaneous discharge was measured volumetrically.

Table 5.--*Properties and constituents of water from selected mine springs and surface-water sites in the west and north creeks, August 31 through September 3, 1987*

[Constituents are dissolved except as indicated; ft^3/s, cubic foot per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; $CaCO_3$, calcium carbonate; µg/L, micrograms per liter; --, no data; <, less than]

Site number (fig. 4)	Instantaneous discharge (ft^3/s)	Specific conductance (µS/cm)	pH (standard units)	Eh (volt)	Temperature (°C)	Dissolved oxygen (mg/L)
			west creek			
MW1	[a] 0.090	2,800	5.7	0.2	14.5	0.4
SW4	.08	3,000	6.0	.2	19.0	7.5
SW6	.10	3,150	3.9	.4	13.0	8.7
MW5	[a] .0026	3,150	3.1	.7	18.5	3.3
SW8	.11	3,450	3.1	.7	14.0	8.2
SW9	.12	3,050	3.1	.8	16.5	8.7
SW10	.19	1,950	5.3	.4	18.0	7.2
			north creek			
MN1	[a] .0046	3,500	3.4	.5	14.5	.5
SN3	[a] .013	3,650	3.0	.7	20.0	5.0
MN8	[a] .0022	2,850	4.1	.5	13.5	.8
SN4	[a] .011	3,300	3.3	.7	16.0	8.4
SN6	[a] .011	3,100	6.5	.3	16.0	5.8
MN9	[a] .060	5,600	5.3	.3	15.0	.4
SN6.5	--	5,350	3.0	.7	24.5	2.4
MN10	[a] .0058	3,200	3.2	.7	17.0	6.8
SN7	[a] .075	5,350	3.1	.6	17.0	6.1
SN9	[a] .073	4,200	3.1	.8	17.0	8.6

Table 5.--*Properties and constituents of water from selected mine springs and surface-water sites in the west and north creeks, August 31 through September 3, 1987*--Continued

Site number (fig. 4)	Total acidity as $CaCO_3$ (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Bicarbonate (mg/L)
			west creek			
MW1	320	370	180	87	21	190
SW4	235	370	170	82	21	78
SW6	370	400	170	86	21	0
MW5	355	470	170	65	18	0
SW8	290	420	180	90	21	0
SW9	190	440	170	85	19	0
SW10	25	280	110	76	19	--
			north creek			
MN1	550	470	200	81	19	0
SN3	475	510	200	93	20	0
MN8	235	490	150	82	14	0
SN4	205	520	180	81	20	0
SN6	5	620	170	78	17	64
MN9	1,100	440	310	210	32	52
SN6.5	1,150	470	300	220	28	0
MN10	230	510	140	64	11	0
SN7	--	540	280	170	20	0
SN9	300	540	260	170	18	0

Table 5.--*Properties and constituents of water from selected mine springs and surface-water sites in the west and north creeks, August 31 through September 3, 1987*--Continued

Site number (fig. 4)	Total alkalinity as $CaCO_3$ (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Fluoride (mg/L)	Silica as SiO_2 (mg/L)	Dissolved solids (residue at 180 °C) (mg/L)
			west creek			
MW1	153	1,900	18	0.2	27	2,710
SW4	64	1,900	8.9	.3	24	3,040
SW6	0	2,300	12	.6	31	3,410
MW5	0	2,300	29	1.0	56	3,080
SW8	0	2,100	13	.4	32	3,030
SW9	0	2,000	13	.5	32	2,960
SW10	--	1,200	17	.5	24	1,860
			north creek			
MN1	0	2,700	30	1.5	70	3,980
SN3	0	2,500	30	1.1	62	3,450
MN8	0	2,100	42	.4	55	3,110
SN4	0	2,400	30	1.3	51	3,460
SN6	64	2,400	28	.8	30	3,240
MN9	43	3,600	9.6	.6	49	5,460
SN6.5	0	3,000	9.9	.7	46	5,500
MN10	0	1,900	14	.8	50	2,870
SN7	0	3,200	12	.8	54	4,820
SN9	0	2,800	13	.7	46	4,300

Table 5.--*Properties and constituents of water from selected mine springs and surface-water sites in the west and north creeks, August 31 through September 3, 1987*--Continued

Site number (fig. 4)	Iron (mg/L)	Manganese (mg/L)	Nitrite plus nitrate as nitrogen (mg/L)	Orthophosphate as phosphorous (mg/L)	Aluminum (µg/L)	Barium (µg/L)
			west creek			
MW1	238	4.6	<0.1	0.03	90	130
SW4	175	4.8	--	--	30	43
SW6	201	5.6	--	--	110	34
MW5	85	4.3	<.1	.05	15,000	71
SW8	133	6.4	--	--	1,800	80
SW9	44	7.0	<.1	.041	2,500	62
SW10	3.1	4.1	<.1	<.01	310	33
			north creek			
MN1	290	9.4	<.1	.12	38,000	86
SN3	143	9.5	<.1	.42	19,000	120
MN8	120	3.8	<.1	.041	4,200	92
SN4	26	9.5	--	--	15,000	49
SN6	.41	8.2	--	--	120	110
MN9	620	13	<.1	.05	1,600	61
SN6.5	483	13	--	--	1,700	140
MN10	70	4.1	<.1	.090	6,900	78
SN7	280	13	--	--	3,900	12
SN9	78	14	<.1	.070	3,700	81

Table 5.--*Properties and constituents of water from selected mine springs and surface-water sites in the west and north creeks, August 31 through September 3, 1987*--Continued

Site number (fig. 4)	Beryllium (µg/L)	Cadmium (µg/L)	Chromium (µg/L)	Cobalt (µg/L)	Copper (µg/L)	Lead (µg/L)	Lithium (µg/L)
			west creek				
MW1	<2	9	<20	<9	<30	30	190
SW4	3	12	<20	<9	<30	60	200
SW6	<2	8	<20	<9	<30	40	210
MW5	4	4	<20	<9	<30	<30	240
SW8	2	4	<20	<9	<30	<30	200
SW9	2	5	<20	<9	<30	50	190
SW10	<2	4	<20	<9	<30	<30	110
			north creek				
MN1	11	7	20	<9	<30	<30	350
SN3	4	<3	<20	50	<30	<30	250
MN8	<2	4	<20	<9	<30	<30	110
SN4	3	<3	<20	40	<30	<30	240
SN6	<2	<3	<20	20	<30	<30	160
MN9	2	23	<20	<3	<30	100	340
SN6.5	4	20	<20	280	<30	80	350
MN10	4	<3	<20	<9	<30	<30	130
SN7	3	10	<20	<9	<30	40	300
SN9	<2	<3	<20	<9	<30	<30	270

Table 5.--*Properties and constituents of water from selected mine springs and surface-water sites in the west and north creeks, August 31 through September 3, 1987*--Continued

Site number (fig. 4)	Molybdenum (μg/L)	Nickel (μg/L)	Silver (μg/L)	Strontium (μg/L)	Vanadium (μg/L)	Zinc (μg/L)	Total organic carbon (mg/L)
				west creek			
MW1	<30	<30	<3	1,500	33	77	0.5
SW4	<30	30	5	1,400	23	48	--
SW6	<30	<30	6	1,100	28	110	--
MW5	<30	140	5	640	<18	300	--
SW8	<30	<30	39	1,200	18	96	--
SW9	<30	<30	6	1,100	<18	250	--
SW10	<30	<30	<3	1,500	<18	60	--
				north creek			
MN1	<30	490	<3	1,000	44	390	--
SN3	<30	270	<3	990	<18	310	--
MN8	<30	<30	<3	770	<18	93	--
SN4	<30	260	3	970	<18	30	--
SN6	<30	80	<3	1,100	<18	86	--
MN9	<30	<30	10	880	88	79	.2
SN6.5	<30	<30	10	890	70	150	--
MN10	<30	90	<3	650	<18	140	--
SN7	<30	50	4	900	38	170	--
SN9	<30	70	<3	980	18	140	--

[a] Instantaneous discharge was measured volumetrically.