HYDROLOGY AND WATER CHEMISTRY OF AN ABANDONED SURFACE COAL MINE, SOUTHWESTERN HENRY COUNTY, MISSOURI--1984-86

By Dale W. Blevins

U.S. GEOLOGICAL SURVEY

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CONVERSION FACTORS AND VERTICAL DATUM

Multiply	By	To obtain
acre	0.4047	hectare
acre-foot	0.001233	cubic hectometer
cubic foot per second per square mile	0.01093	cubic meter per second per square kilometer
cubic foot per second	0.02832	cubic meter per second
foot	0.3048	meter
inch	25.4	millimeter
mile	1.609	kilometer
square mile	2.590	square kilometer
gallon per minute	0.06308	liter per second
foot per day	0.3048	meter 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

The 2,400 acres of abandoned surface-mined land northwest of Montrose, Missouri, contained more than 100 lakes and 1,200 acres of barren, acidic spoil. More than one-half of the lakes had pH values less than 4.0. Seventy-seven percent of the Horn Branch basin has been mined and drains most of the acidic spoil.

Ground water in the spoil had a water-table surface and was bounded on the bottom and sides by Pennsylvanian rocks of low permeability. The sides of the spoil aquifer usually were marked by linear, last-cut lakes that fully penetrated the aquifer and received ground-water discharge. The spoil aquifer averaged 30 feet thick. The direction of flow was controlled by the location and altitude of lakes that discharged to or received recharge from ground water.

Overland runoff from bare mine spoil and fly ash had pH values between 2.9 and 3.5. Small values of pH were caused by flushing of the products of pyrite oxidation that occurs between storms. Two samples of runoff from revegetated mine spoil had pH values 2 to 3 units higher than runoff from bare spoil. Calcium and sulfate concentrations in runoff usually totaled a few hundred milligrams per liter, indicating gypsum quickly dissolved in runoff. The pH value of streamflow leaving the mine indicated only minimal effects from acidic overland runoff because the large quantity of near-neutral lake water from deep lakes moderated fluctuations in water chemistry. Also, large areas of internal drainage prevented much acidic runoff from entering streams.

Acidic ground-water recharge near the spoil surface became depleted in oxygen and dissolved calcite at depth. The lack of oxygen to drive pyrite oxidation and the bonding of hydrogen ions to carbonate anions increased the pH. The pH of ground water was between 5.7 and 6.8 except in fly ash and near some acidic recharge lakes where the pH decreased to less than 4.0 during wet weather. Reducing conditions in the spoil caused iron concentrations to average 93 milligrams per liter in sampled wells. Computer models calculating ionic speciation and mineral equilibria were used with data from water analyses to indicate probable chemical reactions occurring in the spoil. Gypsum, ferrihydrite, and potassium jarosite were usually near or above saturation in ground water. Calcite and rhodochrosite were near or above saturation when the pH was greater than 6.4.

Lakes with insignificant dry-weather inflows and with average depths less than 8 feet had pH values between 2.8 and 4.3. The pH of lakes averaging more than 9 feet deep was greater than 6.0. Shallow lakes usually were perched above the water table between ridges of spoil. However, a few shallow lakes intercepted the water table and received ground-water discharge with high iron concentrations. Water in these lakes became acidified to a pH between 2.7 and 3.4 upon exposure to the atmosphere and produced sustained base flows that decreased pH values downstream. The pH of acidic water was seldom less than 3.0 because of stability of ferrous iron in solution and the buffering capacity of sulfate-rich water at low pH values. The deeper lakes were near neutral because of substantial quantities of near-neutral surface runoff from unmined or topsoiled areas and because of ground-water contributions with lower iron to bicarbonate ratios. The pH value of base flow in Horn Branch, where it left the mine, was decreased to 3.5 during the dry summer months by sustained outflow from the shallow, ground-water-supplied lakes. During the rest of the year, outflows from near-neutral lakes were large enough to dominate the water chemistry in the downstream reaches of Horn Branch.

A substantial part of the mined area had internal drainage (20 percent of the Horn Branch basin) caused by spoil ridges that blocked drainage paths. Consequently, unit peak discharges were about 40 percent less and total surface-outflow volumes were about 15 percent less from the Horn Branch basin than from two larger unmined

basins. Forty-seven percent of the runoff was caused by precipitation directly falling on lakes having outflow. Lakes receiving runoff in areas of internal drainage supplied most of the recharge to ground water and increased base-flow volumes.

INTRODUCTION

Surface coal mining in the area around Montrose, Missouri, has supplied fuel for the Montrose Power Plant since 1956 (Kansas City Power and Light, written commun., 1954). Major reclamation of surface mines began about 1972, but by 1987 most of the mined lands northwest of Montrose remained unreclaimed. The mined area contained more than 1,200 acres of barren spoil, 100 lakes, and several streams, many of which are acidic. Prereclamation data and understanding of water chemistry were needed to determine the effects of reclamation activities on water quality in the mine. This study, conducted in cooperation with the Missouri Department of Natural Resources, Land Reclamation Commission, was intended to provide the data necessary for reclamation activities in the study area.

Purpose and Scope

The purpose of this report is to present the results of a hydrologic and water-quality study made in west-central Missouri at an abandoned surface coal mine from June 1984 to September 1986. Objectives of the study included quantifying the volume of water in, on, and moving through the spoil and determining the chemical characteristics of and major chemical reactions occurring in water affected by the mine.

Description of Study Area

The study area consists of about 3,000 acres in west-central Missouri (fig. 1), underlain by Pennsylvanian shale, sandstone, limestone, and coal of the Cherokee Group[1] (fig. 2). From 1956 to 1973, 2,400 acres of the study area were surface mined. In most places, two coal seams, one in the Weir Formation[1] (Weir-Pittsburg coal member) and a coal seam on the Tebo Formation[1], were mined, but coal seams in the Fleming and Croweburg Formations[1] also were removed where they had not been eroded and were thick enough to be economically mined. (Peabody Coal Company maps of Power Mine, Montrose, Missouri). Thirty-three percent of the mined area had been regraded and revegetated as of 1987. Reclaimed areas have smooth topography and usually are covered with grass, whereas the rough unreclaimed areas usually are either barren or forested. Topsoil has been applied to about 20 percent of the regraded areas. About 40 acres between lakes LM and LEE were covered with fly ash from the power plant and have been regraded. This area has no vegetation (fig. 1). Both reclaimed and unreclaimed areas have numerous lakes larger than 2 acres caused by last-cut and haul-road excavations that have filled with water. In addition to these lakes, the unreclaimed areas contain countless smaller bodies of water trapped between ridges of spoil.

The western 1,200 acres of the study area are drained by Horn Branch, and the eastern part of the study area is drained by six smaller streams (fig. 1). However, a large part of the mined area has internal drainage because of ridges of spoil and deep depressions that trap runoff.

Methodology

Data were collected at several sites to determine the hydrology of the study area. Streamflow was continuously monitored at the two largest outflow sites (sites G1 and G3, fig. 1) and at one large tributary (site G2). Weirs, rated with discharge measurements, were used as controls at lake outlets at all three gaging stations. Rainfall was continuously monitored at one site in the study area (site RG, fig. 1). Daily precipitation data from Peabody Coal Company, Montrose (collected 2 mi (miles) from the study area) and from the National Weather Service station near Appleton City (7 mi from the study area; fig. 1) were used during periods of missing record. The water level of one lake (L17) with no surface outflow was continuously monitored to measure evaporation, seepage losses, and runoff into the lake (site G4). The water levels of several lakes were monitored weekly to obtain estimates of these processes. Synoptic discharge measurements were made during dry periods to locate the larger springs and ground-water outflows. Although 33 wells were drilled into spoil, only 25 of the wells penetrated the water table. These wells were used to determine hydraulic heads, and water samples for chemical

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

analysis were collected from 11 of the wells. The wells were cased with 3-in. (inch) diameter plastic pipe, slotted in the bottom 5 ft (feet). Water levels in wells were measured at 1 to 3 week intervals in 18 of the wells, using a steel tape. Altitudes were determined by land survey from benchmarks set by a contractor for the Missouri Land Reclamation Commission during reclamation work.

The depths of 28 lakes were measured with a depth finder during bathometric surveys done between September 17 and October 4, 1984. Surface areas were measured with a planimeter and combined with the depth data to approximate the volume of each lake. Profiles of pH and specific conductance with depth were determined at one to five locations in each lake, depending on the size and shape of the lake. Measurements were made at 3 ft below the surface, 1 to 3 ft above the bottom, and at intermediate depths if the maximum depth of the lake was more than 10 ft.

Surface- and ground-water samples were collected to identify hydrochemical processes and establish baseline water-quality characteristics before reclamation. Temperature, specific conductance, and pH were continuously monitored at sites Q1, Q2, and Q3 to determine fluctuations of these properties with flow and season. Two sets of water samples were collected synoptically at 25 surface-water sites during high- and low-base flows and 11 wells. Runoff and lake outflows were sampled at 24 sites during one storm on May 13, 1985. Stream samples were collected from the midpoint of the stream cross section in polyethylene bottles. Ground water from wells that would not sustain pumpage of about 0.5 gal/min (gallon per minute) was sampled several minutes after all water from the well bore was removed by pumping. Larger yielding wells were sampled several minutes after the temperature and specific conductance of the pumped water became constant. Ground-water samples were collected in a plastic churn splitter and sent to the laboratory in polyethylene bottles.

Laboratory analyses of water samples were by the U.S. Geological Survey Laboratory in Arvada, Colorado, in accordance with procedures outlined by Skougstad and others (1979). All analyzed constituents were in the dissolved phase and were determined from water samples that were filtered at the time of sampling through a 0.10 µm (micrometer) filter in a polyvinyl chloride chamber using a peristaltic pump as the pressure source. Water samples analyzed for metals were acidified in the field with double-distilled, laboratory-grade nitric acid to a pH value of less than 3.0. Specific-conductance values were measured using a portable conductivity meter with temperature compensation designed to express readings in microsiemens per centimeter at 25 °Celsius. The electrometric method was used to measure pH values and titrate alkalinity in the field.

Acidity is defined in this report as the capacity of a solution to react with hydroxyl ions and was determined by endpoint titration to a pH of 8.3. Alkalinity is similarly defined as the capacity of a solution to react with hydrogen ions and was determined by incremental titrations made to the inflection point of the titration curve at a pH of about 4.5, where nearly all the carbonate is in the form of carbonic acid (H_2CO_3).

Computations of saturation indices were done using the 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 Nordstrom (1987) was used for this study.

Acknowledgments

HYDROLOGY

Surface-Water Movement

Surface-water drainage in the mined areas is primarily from lake to lake by connecting streams (fig. 1). A significant part of the mined area (20 percent of the Horn Branch basin, fig. 3) did not contribute runoff to streams leaving the study area. Ridges of spoil blocked surface drainage and impounded water in the low places between
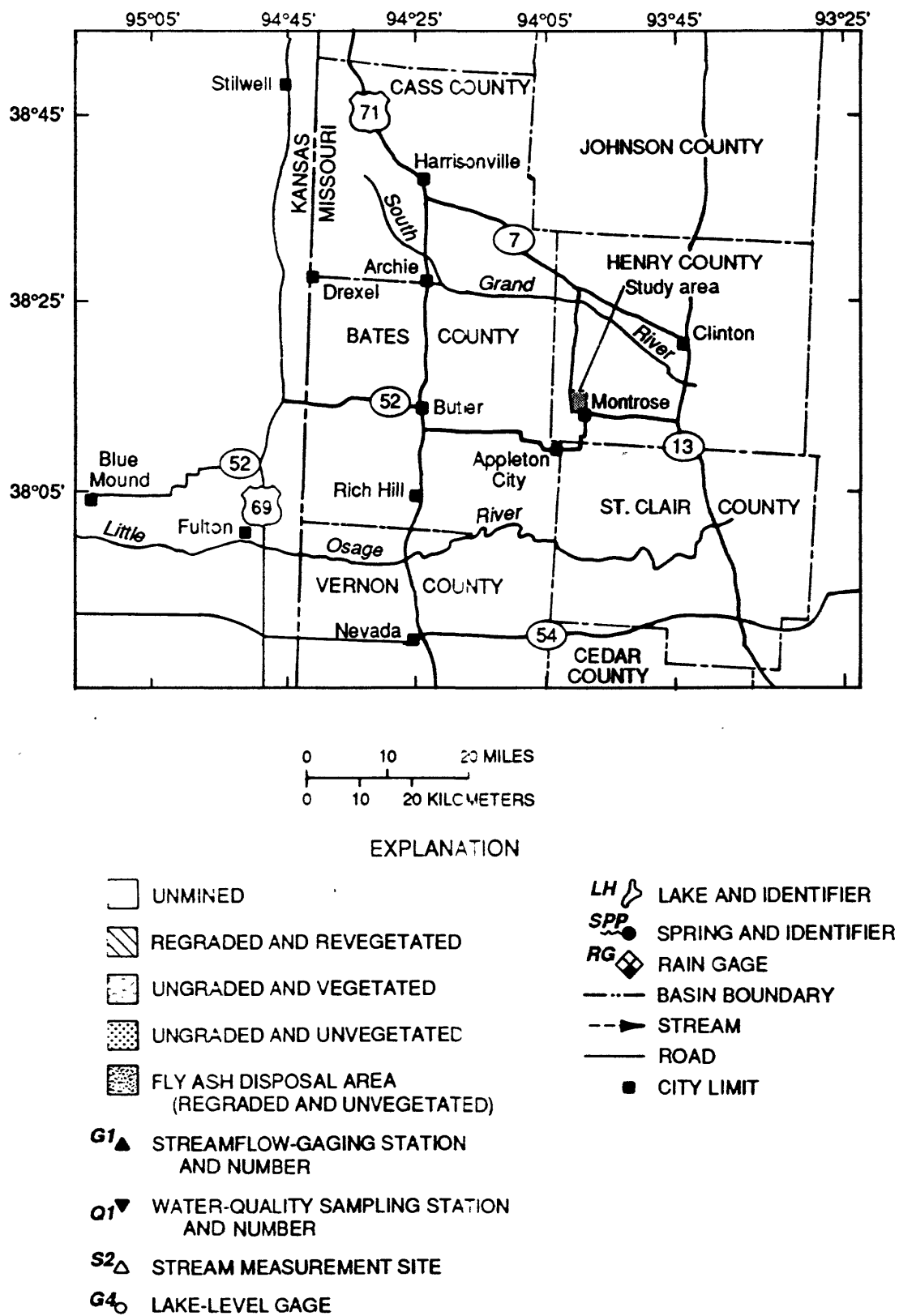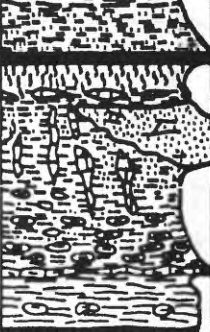
Figure 1.--Location of study area, surface features, and surface-water-data-collection sites.

Figure 1.--Location of study area, surface features, and surface-water-data collection sites--Continued.

EXPLANATION

▦	LIMESTONE
▦	FOSSILIFEROUS LIMESTONE
▦	NODULAR LIMESTONE
▦	SANDSTONE
▦	CROSS-BEDDED SANDSTONE
▦	SHALE
▦	BLACK SHALE WITH PHOSPHATE NODULES
▦	SILT STONE
▦	UNDERCLAY
▦	CHANNEL LAG DEPOSIT
■	COAL

SYSTEM	SERIES	GROUP	FORMATION	LITHOLOGY	THICKNESS, IN FEET
PENNSYLVANIAN	Desmoinesian	Marmaton	Undifferentiated		greater than 5
			Verdigris[1] (Wheeler Coal member)[1]		3 - 15
		Cherokee[1]	Croweburg[1]		20 - 35
			Fleming[1] and Robinson Branch[1] (undifferentiated)		5 - 15
			Mineral[1]		5 - 10
			Scammon[1] (Tiawah Limestone Member)[1]		10 - 25
			Tebo[1]		5 - 10
			Weir[1] (Weir-Pittsburg Coal member)		5 - 10
			Seville[1]		0 - 5
			Blue Jacket[1] (aquifer)		30 - 70
			Rowe[1] and Drywood[1] (undifferentiated)		10 - 55
			Warner[1] (primary aquifer)		20 - 50

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

Figure 2.--Generalized stratigraphy of the study area (nomemclature modified from Koenig, 1961).

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EXPLANATION

☐	MINED AREA
▨	UNMINED AREA
◈	AREA WITH INTERNAL DRAINAGE
◈	AREA WITH INFREQUENT OUTFLOW
◇	LAKE
—·—·—	BASIN BOUNDARY
----→	STREAM--Arrow indicates direction of flow

94°

38°17'

38°16'

STATE ROAD K

STATE ROAD K

Horn Branch

0   1 MILE

0   1 KILOMETER
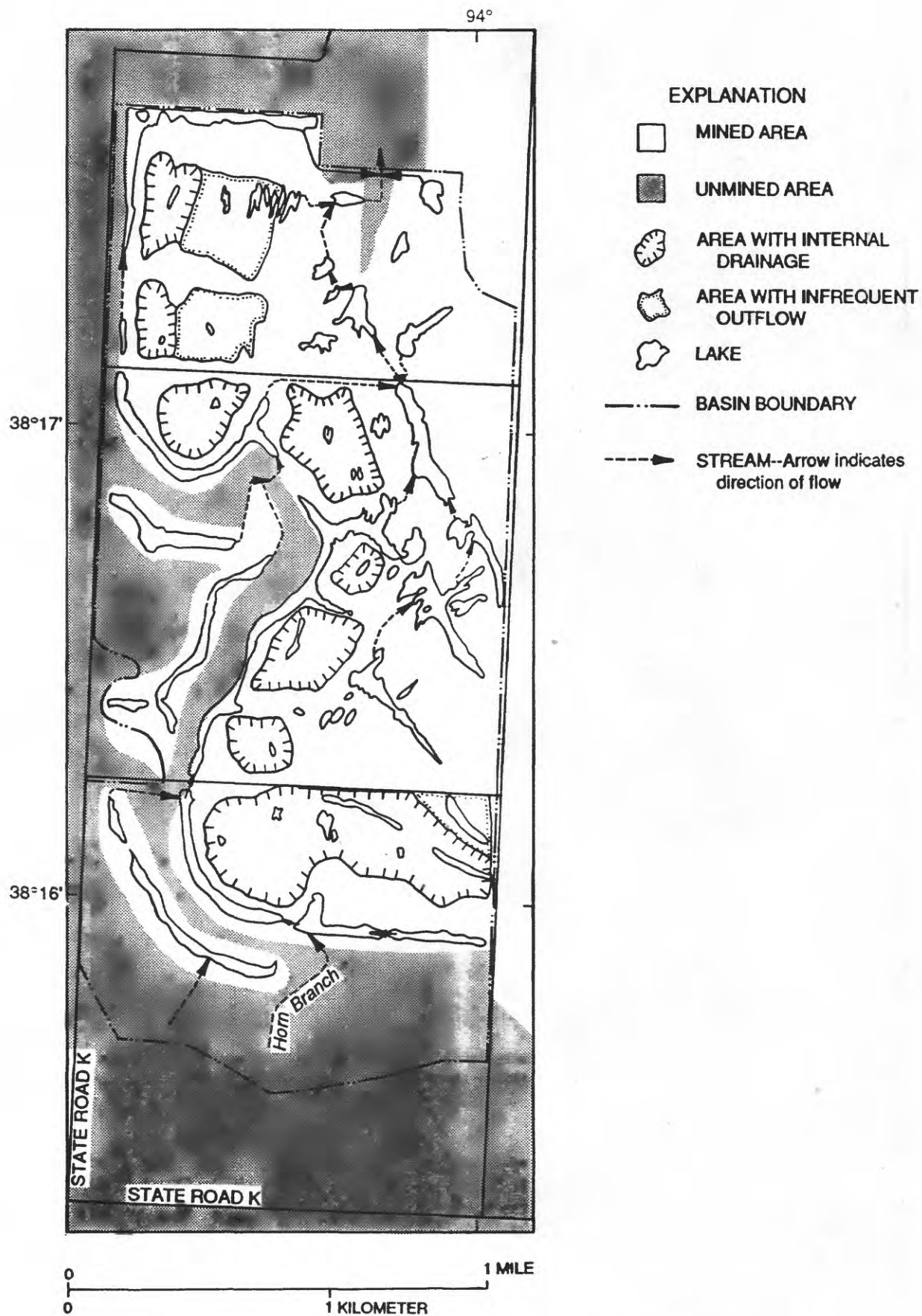
Figure 3.--Areas of internal drainage and infrequent outflow in the Horn Branch basin.

Table 1.—Comparison of peak discharges from a mined basin and two unmined basins in west-central Missouri and east-central Kansas

[Units of rainfall are in inches; discharge in cubic feet per second; unit peak discharge in discharge per square mile per inch of rainfall; e, estimated; --, no data available]

Storm date	Horn Branch near Montrose, Mo. (fig. 1) Mined[a]			South Grand River at Archie, Mo. (fig. 1) Unmined[b]			Little Osage River at Fulton, Kans. (fig. 1) Unmined[c]		
	Storm rainfall	Peak discharge per square mile	Unit peak discharge	Storm rainfall[d]	Peak discharge per square mile	Unit peak discharge	Storm rainfall[f]	Peak discharge per square mile	Unit peak discharge
10-15 through 18-1984	3.5	12	3.5	3.0	9.4	3.1	2.6	1.9	0.72
11-1-1984	3.0	50e	17	1.9	32	17	1.5	3.9	2.6
12-29 and 30-1984	2.4	20e	8.3	2.5	42	17	1.6	17	10
5-27-1985	1.5	4.5	3.0	1.6	31	19	1.1	3.7	3.3
6-4 through 7-1985	3.8	38	10	3.8	48	13	3.0	22	7.4
6-15 through 17-1985	3.3	22	6.6	1.4	29	20	.8	4.3	5.3
6-24-1985	1.5	5.3	3.5	1.0	.40	.40	.7	.58	.83
8-21 through 23-1985	3.2	15	4.7	4.2	36	8.7	2.9	25	8.6
9-29-1985	1.0	2.7	2.7	2.4	31	13	1.7	12	6.9
10-12 and 13-1985	.8	1.4	1.7	3.2	19	6.0	1.6	4.5	2.8
10-18-1985	1.2	3.9	3.2	.8	11	14	.8	8.8	11
11-15 and 16-1985	4.9	40	8.3	3.6	59	16	4.7	40	8.5
11-19-1985	1.8	1	5.6	.8	14	18	.6	12	21
11-12-1985	1.2	6.4	5.3	1.0	13	13	.6	11	19
2-3 and 4-1986	2.3	7.5	3.3	0.7	5.9	8.4	1.3	12	9.2
4-4 and 5-1986	2.0	6.4	3.2	1.4	8.2	5.9	1.8	7.8	4.4
5-13 through 15-1986	1.2	5e	4.2	1.7	26	15	1.7	18	11
5-17-1986	2.8	21	7.5	1.6	26	16	2.4	8.2	7.6
7-1 and 2-1986	1.6	2.1	1.3	2.1	3.1	1.5	1.8	12	6.4
7-11 and 12-1986	1.1	.80	.73	2.2	12	5.3	3.4	9.9	2.9
9-18-1986	1.9	9.6	5.1	3.7	11	2.9	.6	.76	1.3
Mean	2.2	14	5.2	2.1	22	11	1.7	11	7.2

[a]Drainage area is 1.88 square miles.
[b]Drainage area is 356 square miles.
[c]Drainage area is 295 square miles.
[d]Data collected at Drexel, Mo. and Stanley, Kans. (National Oceanic and Atmospheric Administration, 1984-86b).
[f]Data collected at Blue Mound, Kans. (National Oceanic and Atmospheric Administration, 1984-86b).
Note: According to Clement (1987), the 2-year peak discharge for the Horn Branch basin before mining was about 300 cubic feet per second per square mile, and according to Hauth (1974) it was about 160 cubic feet per second per square mile.

ridges. This internal drainage caused areas of unreclaimed spoil to have smaller peak discharges and runoff volumes than unmined areas. Unit peak discharges (discharge per drainage area per inch of rainfall) from the Horn Branch basin (60 percent unreclaimed, 23 percent unmined, and 17 percent regraded) averaged 53 and 28 percent less than the unit peak discharges from two larger unmined basins in the same physiographic region during 1984-86 (table 1). If the total volumes of surface runoff are examined on a per-area basis, the percentage of rainfall leaving the Horn Branch basin as surface outflow was 22 percent less than the South Grand basin and 11 percent less than the Little Osage basin (table 2).

Table 2.--*Volume of surface outflow and rainfall on a mined basin and two unmined basins having surficial Pennsylvanian rock in west-central Missouri and east-central Kansas from September 7, 1984, through September 6, 1986*

Gaging station	Rainfall[a] (inches)	Surface outflow		Approximate percentage lost to evapotrans- piration[b]	Drainage area (square miles)
		Inches[a]	Percentage of rainfall		
Horn Branch near Montrose, Mo. (fig. 1, site G1)	99	32	32	68	1.88
South Grand River at Archie, Mo.	[c]100	41	41	59	365
Little Osage River at Fulton, Kans.	[d]91	33	36	64	295

[a]Volume expressed as equivalent depth over the entire basin.
[b]Assuming negligible gains or losses to regional ground-water system and to ground-water storage.
[c]Data collected at Drexel, Mo. and Stilwell, Kans. (National Oceanic and Atmospheric Administration, 1984-86a).
[d]Data collected at Blue Mound, Kans. (National Oceanic and Atmospheric Administration 1984-86a).

Lakes receiving runoff from areas of internal drainage were filling with sediment during this study, especially where spoil was unvegetated and erosion was rapid. Some areas of infrequent outflow contributed runoff only after a large storage capacity was filled. These areas generally are only temporary features because erosion tends to quickly cut through barren spoil ridges when they are overtopped by streamflow. At the end of the study (September 1986), an extremely rare rainfall occurred in which 17 in. of rain fell in 5 days. This event occurred after 6 in. of rain in the preceding week had saturated the soil. The large volume of runoff generated by this rain completely filled many between-spoil-pile lakes, and they overflowed into outside drainages for the first time since mining ended. The erosion and sedimentation caused by this flood decreased the capacity of the area to retain runoff and hastened the time when many lakes will no longer be able to retain runoff. In fact, 60 acres that had internal drainage in the Horn Branch basin at the beginning of this study presently (1987) retain little, if any, runoff. Water trapped behind spoil ridges either evaporated or seeped through lake bottoms into ground-water storage and eventually increased base flow.

Ground-Water Movement

The rocks near Montrose predominately are shales (fig. 2) of low permeability. More permeable soil and weathered rock less than 20 ft from the surface lie atop the shales and constitute a small, but historically significant, aquifer in the area. During a survey of 16 private wells within 1 mi of the study area, it was discovered that most farms had used large diameter wells less than 25 ft deep in the past, although nearly all farms and the city of Montrose presently (1987) use sandstone aquifers between 200 and 350 ft deep for their supplies. Observation of active, nearby mine pits indicated that nearly all of the rocks between the two aquifers were unsaturated. Water levels in 5 shallow wells ranged from 2.0 to 11.8 ft below the land surface on April 17-18, 1985. The remaining 11 wells were drilled into what probably are the Bluejacket and Warner Sandstones (fig. 2). The water levels in these deeper wells ranged from 84.5 to 148.8 ft below the land surface (average depth to water was 108 ft), indicating artesian pressure in these aquifers. The difference in water levels in the shallow and deep wells indicate an overall downward vertical gradient through the unsaturated zone. The steepness of this gradient and the presence of unsaturated rocks between the near-surface and sandstone aquifers are caused by the low

permeability of undisturbed rock in this area. However, surface mining generally increases the permeability of the rocks by at least two orders of magnitude (Weiss and Razem, 1984). This relative difference in permeability between spoil and undisturbed rock allows the spoil to be considered a water-table aquifer bounded on the sides and bottom by undisturbed and unsaturated rocks of low permeability that allow only insignificant quantities of leakage.

Lakes were the primary control of water levels in the spoil. They supplied recharge in the topographically high areas and collected ground-water discharge in the low areas (fig. 4). Data from 55 lakes during base-flow conditions are summarized in table 3. Lakes were identified as having net ground-water discharge if they had dry-weather outflow, were supplied by springs in the littoral (near-shore) zone, or had water levels consistently lower than water levels in nearby wells. Lakes identified as having net recharge are those having no or infrequent surface outflow and drainage areas at least twice as large as the lake surface areas or water levels consistently higher than water levels in adjacent wells. Several lakes could not be identified as having net discharge or recharge because of missing outflow and ground-water data. The range of pH and specific conductance data in table 3 is the range of values measured during a bathometric survey and one to three surface measurements made at various times during the study, except as noted.

The water levels in wells in spoil ridges on opposite sides of 5 shallow lakes (lakes L9, L12, L15, L18, and L19) averaged 11 ft below the bottom of the associated lake. Ground-water levels in wells near another shallow lake (lake L10) were at an altitude similar to that of the lake bottom. These data indicate that most of the shallow lakes between spoil ridges were not in saturated contact with the ground-water system. However, these lakes supplied recharge through the unsaturated zone.

Water-level data from 19 wells and more than 30 lakes in contact with the saturated spoil were used to prepare a water-table map (fig. 5). Ground-water mounds typically represent areas of recharge. Generally, ground-water mounds also were over ridges and domes of undisturbed rock below the spoil (figs. 4-6). The contours of undisturbed rock in figure 6 were based on hundreds of drill logs from Peabody Coal Company (drill logs and mining maps on file at the Power Mine, Montrose). Ground-water mounds typically were below or intersected by topographically high lakes that collected runoff from areas of internal drainage and leaked some of the runoff to the ground-water system. The spoil water flowed toward, and was received by, fully penetrating lakes at the edges of the spoil aquifer. A comparison of 48 grid points evenly spaced over the entire spoil area in figures 5 and 6 indicates the spoil aquifer averaged 30 ft thick with a standard deviation of 9 ft. The range of water levels in the wells averaged 3.3 ft or about 11 percent of the aquifer thickness during the 14-month period of monitoring. Fluctuations in water levels closely followed monthly precipitation with lagtimes of 1 to 2 weeks.

Data from three large and two small sets of synoptic discharge measurements made during base flow are displayed in figures 7 to 11. The largest sources of ground-water discharge to the surface-water system at the time of these measurements were lakes LK, LM, LN, LO, LX, LII, and LLL. For example, in figure 7 the inflow to lake LN was 0.17 ft^3/s (cubic foot per second) and the outflow was nearly twice as much (0.32 ft^3/s), indicating lake LN was a significant source of ground water to Horn Branch in April 1985. Lakes provided base flow to receiving streams if the outflow point and thus the water level of the lake was lower than the water table around the lake. Springs and seeps occurred in littoral zones of some lakes (spring SPP), gullies in spoil (spring SPC), and along haul roads incised below the water table in the surrounding spoil (springs SPB and SPD, fig. 1). Also, where data exist, stream discharges are expressed in figures 7 to 11 as percentages of discharge of the stream to which they contribute flow where that stream leaves the study area (lakes LF and LHH).

Water Budget and Surface-Ground Water Exchange

A 2-year period beginning September 7, 1984, was used to estimate selected components of the water budget in the Horn Branch basin because of similar base flow conditions at the beginning and end of the period. On September 7, 1984, outflow from the basin measured 0.10 ft^3/s and 2.09 in. of rain had fallen in the previous 28 days. On September 6, 1986, outflow from the basin measured 0.19 ft^3/s, and 3.19 in. of rain had fallen in the preceding 28 days. Therefore, the ground-water storage volumes should be similar at the beginning and at the end of the period. This assumption could not be verified with water levels because observation wells were not drilled until 1985. Any small difference in storage volumes is assumed to be negligible compared to the total, 2-year volume of outflow from Horn Branch. The total volume of precipitation in the Horn Branch basin during the 2-year period measured 99 in. or 9,900 acre-feet and the total volume of outflow at site G1 was 32 in. or 3,200 acre-feet (fig. 12). Assuming the net loss or gain from the regional ground-water system and the change in storage of
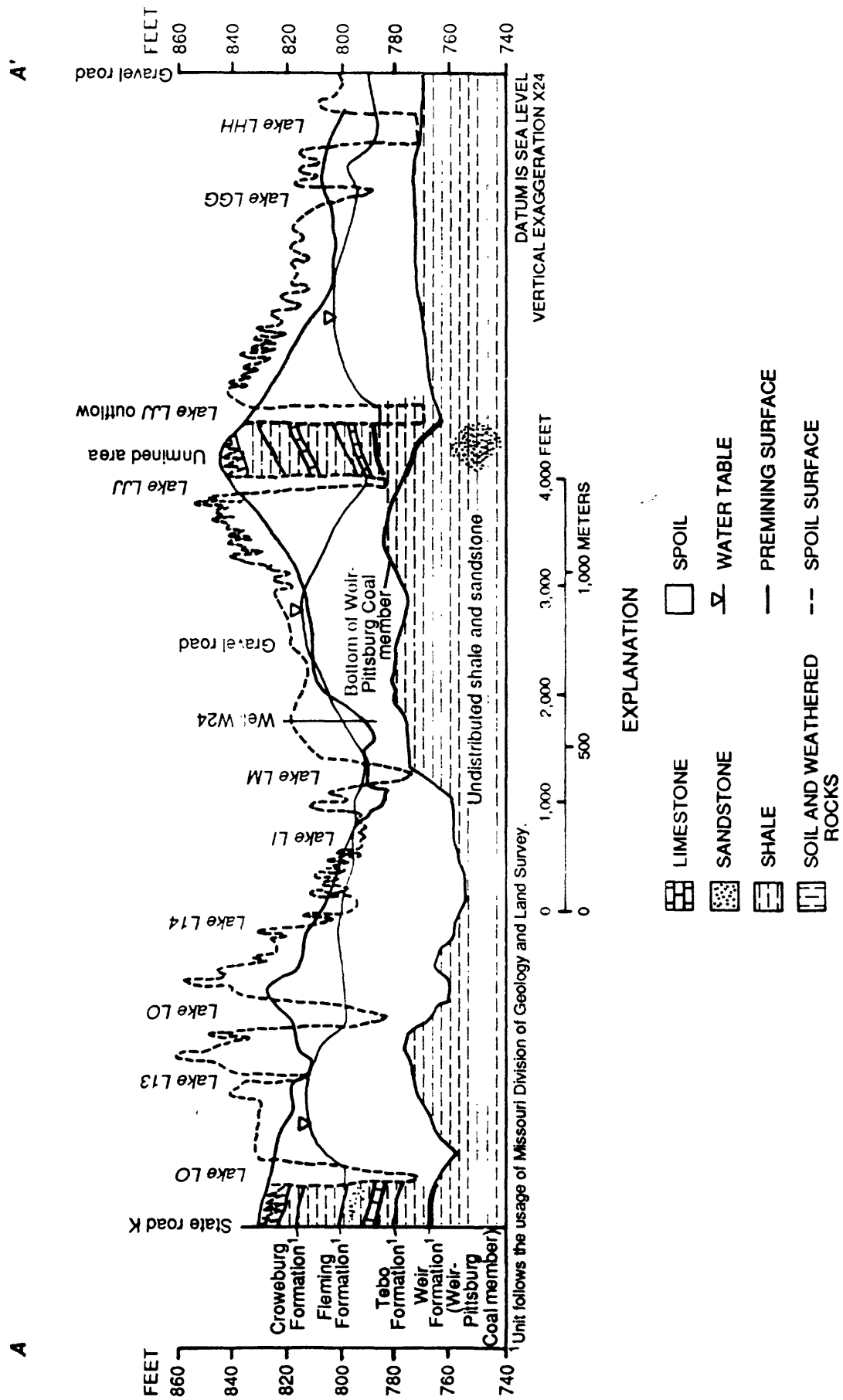
Figure 4.--Generalized hydrogeologic section A-A' (location of section shown on fig. 5).

EXPLANATION

LIMESTONE	SPOIL
SANDSTONE	▽ WATER TABLE
SHALE	— PREMINING SURFACE
SOIL AND WEATHERED ROCKS	-- SPOIL SURFACE

DATUM IS SEA LEVEL
VERTICAL EXAGGERATION X24

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

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Table 3.--*Physical characteristics of selected lakes in spoil areas during base-flow conditions*

[R, lake is a net recharger to the ground-water system; D, lake is a net discharger from the ground-water system; --, no data available; <, less than; µS/cm, microsiemens per centimeter at 25 °Celsius]

Lake (fig. 1)	Relation to ground water	Maximum depth (feet)	Approximate average depth (feet)	Surface area (acres)	Approximate volume (acre-feet)	pH[ab]	Specific conductance (µS/cm)[b]
L9	R	--	<8	--	--	acidic[c]	--
L10	R	--	<8	--	--	acidic[c]	[c]790-1,680
L11	R	--	<8	--	--	acidic[c]	--
L12	R	--	<8	--	--	acidic	[c]40
L13	R	--	<8	--	--	acidic[c]	--
L14	R	--	<8	--	--	acidic[c]	--
L15	R	--	<8	--	--	acidic[c]	[c]930
L16	R	--	<8	1.5	--	--	--
L17	R	--	<8	--	--	extremely acidic to acidic[c]	[c]1,750
L18	R	--	<8	--	--	acidic[c]	--
L19	R	--	<8	--	--	acidic[c]	[c]875-1,100
L20	R	--	<8	--	--	acidic[c]	--
LA	D	13.4	8	12.3	98	acidic	2,400-3,600
LB	R	--	<8	--	--	acidic[c]	--
LE	--	--	--	--	--	acidic to neutral[c]	[c]3,350
LF	D	5.8	4	1.3	5	acidic to neutral[d]	[d]2,000-4,100
LG	--	--	<8	1.8	--	acidic[c]	--
LH	--	--	<8	.8	--	acidic[c]	--
LI	R	--	<8	--	--	acidic[c]	[c]1,900
LJ	D	5.5	3	6.5	20	acidic to neutral	2,400-3,800
LK	D	--	--	1.5	--	neutral[c]	--
LL	D	16.0	7	3.3	23	neutral	3,800-4,200
LM	D	19.3	10	7.8	78	acidic to neutral	2,500-3,000
LN	D	35	16	19.8	320	neutral	1,800-4,000
LO	D	29.3	17	9.5	60	neutral	1,750-3,100

Table 3.--Physical characteristics of selected lakes in spoil areas during base-flow conditions--Continued

Lake (fig. 1)	Relation to ground water	Maximum depth (feet)	Approximate average depth (feet)	Surface area (acres)	Approximate volume (acre-feet)	pH[ab]	Specific conductance (µS/cm)[b]
LP	D	28.2	7	4.9	30	acidic[d]	[d]3,200-3,900
LQ	D	30.9	22	6.3	140	neutral	315-1,760
LR	D	--	--	6.8	--	neutral[c]	[c]1,760
LS	D	19.2	11	10.7	120	slightly acidic	2,000-3,500
LT	D	8.0	4	8.4	30	acidic to extremely acidic	2,800-4,000
LU	D	15.5	10	5.8	58	neutral	450-520
LV	R	--	<8	1.5	--	acidic[c]	--
LW	R	--	--	1.6	--	slightly acidic[c]	--
LX	D	25.9	24	6.5	160	neutral	975-1,190
LY	D	32.4	22	5.6	123	neutral	480-1,200
LZ	D	15.7	10	2.7	27	neutral	760-775
LAA	D	13.4	7	2.0	10	extremely acidic	2,800-3,300
LBB	--	--	<8	6.2	--	extremely acidic to acidic[c]	[c]2,250-3,250
LCC	D	21.5	11	9.0	100	slightly acidic to neutral	2,750-3,250
LDD	--	8.0	5	2.8	10	neutral[c]	[c]4,000
LEE	R	21.9	19	5.7	100	neutral	3,000-3,200
LFF	--	--	<8	1.5	--	acidic[c]	[c]3,800
LGG	D	--	<5	2.5	--	extremely acidic[c]	[c]5,000-6,200
LHH	D	16.0	9	5.1	50	neutral[d]	[d]2,800-6,000
LII	D	15.0	12	3	36	neutral	3,500-3,800
LJJ	D	7.7	5	2.1	10	neutral	3,000-3,750
LKK	D	8.3	7	2.8	20	neutral	2,950-3,250
LLL	D	22.7	16	4.8	77	neutral	2,850-3,500
LMM	R	30.8	17	3.1	53	neutral	1,500-1,560
LNN	--	33.3	20	7.6	150	neutral	1,940-2,200
LOO	--	--	--	5.6	--	neutral[c]	[c]2,050

Table 3.--*Physical characteristics of selected lakes in spoil areas during base-flow conditions*--Continued

Lake (fig. 1)	Relation to ground water	Maximum depth (feet)	Approximate average depth (feet)	Surface area (acres)	Approximate volume (acre-feet)	pH[ab]	Specific conductance (µS/cm)[b]
LPP	--	31.9	18	15.8	280	neutral	950-1,200
LQQ	D	--	<8	1.2	--	slightly acidic to neutral[c]	[c]3,400
LRR	R	--	<8	--	--	acidic[c]	[c]1,300-1,500
LRV	R	--	<8	--	--	acidic to slightly acidic[c]	c415-440

[a]Neutral-pH between 6.0 and 8.5, slightly acidic-pH between 4.0 and 6.0, acidic-pH between 3.0 and 4.0, extremely acidic-pH between 2.5 and 3.0.

[b]Values based on at least one set of measurements with depth and one to three instantaneous measurements of the lake surface, unless otherwise noted.

[c]Values based on surface measurements only.

[d]Values based on continuous records.

14
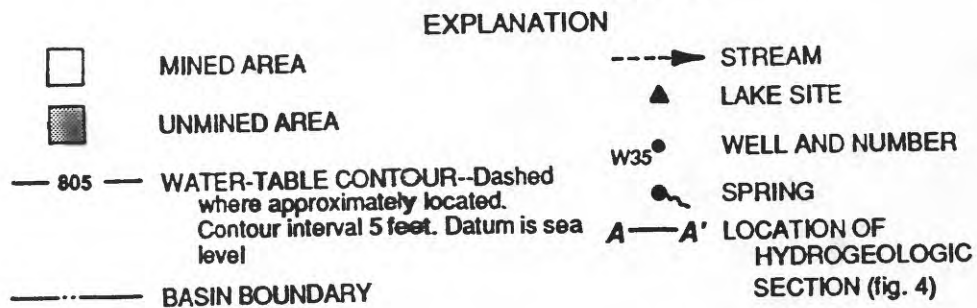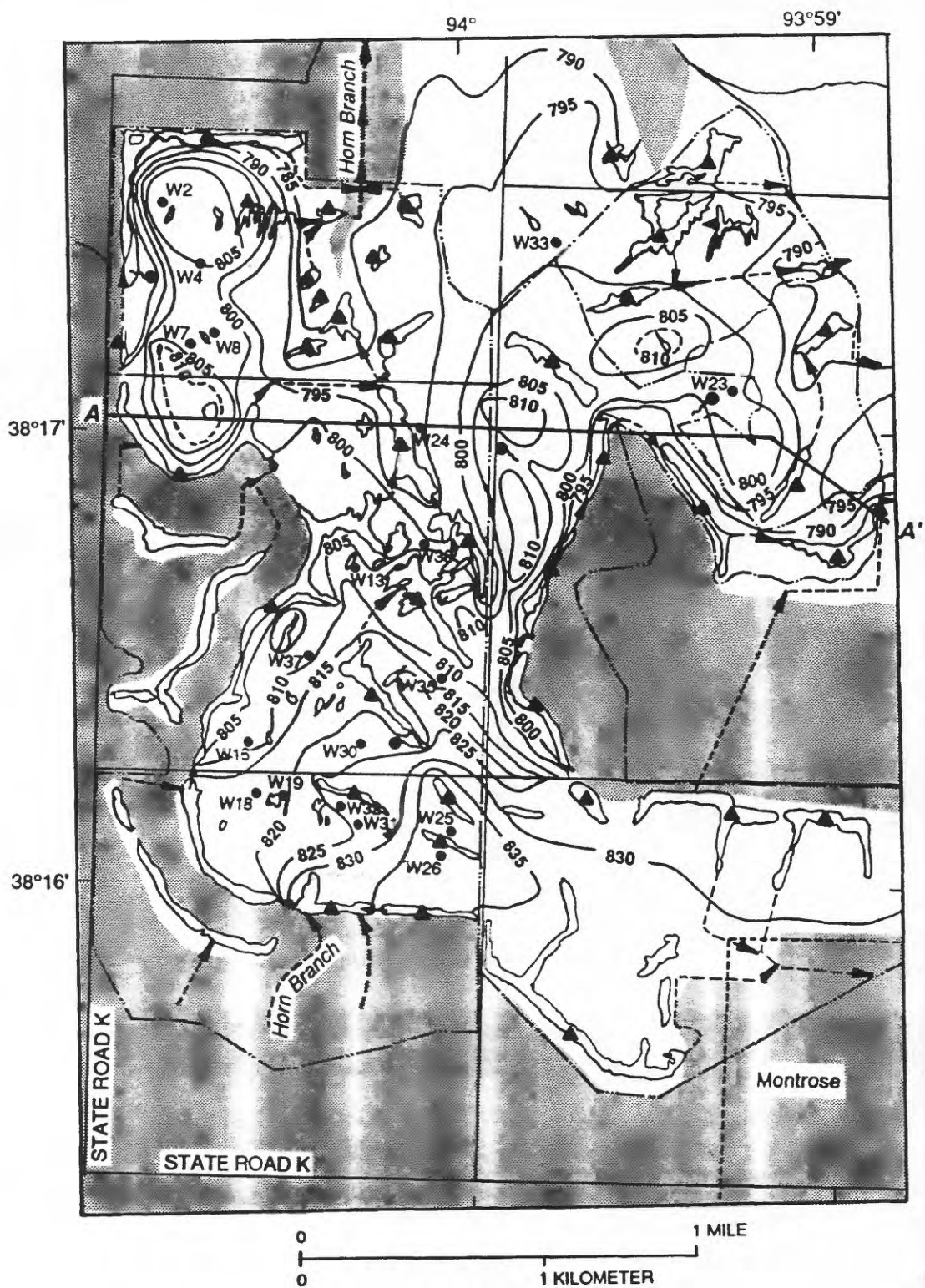
Figure 5.--Altitude of the water table in spoil.

15

Figure 6.--Altitude of the undisturbed rock below spoil.

LA

0.16
3.3
3,000
F 8.1

1.97
6.8
2,700
F 100

LE

G1
Q1 1.83
6.8
2,400
F 93

0.04
6.0
3,400
F 2

LF

0.19
6.5
2,200
F 10

LJ

0.09
3.4
3,800
F 5

LK   LL

LO

0.32
7.5
2,000
F 16

0.98e
3.4
2,500
F 50e

LM

0.02

LQ

--
--
F 1

G2   0.17
3.6
3,200
Q2   F 8.6

LP

0.13
4.1
2,000
F 7

LS

0.05
3.2
2,800
F 3

LR

LN

LT

0.03
8.6
500
F 2

0.17
8.3
LX   980
F 8.6

0.02e
7.9
780
F 1e

LY   LZ

<0.01e
8.2
1,100

0.01e   1,100
7.6   --
1,000
F 1e

LU

0.01e
7.9
480
F 1e

LAA   0.09
2.9
2,800
--

LCC   LRR

LDD   LQQ

0.34
7.2
3,400
--

0.35
7.0
3,500
HH 39

0.11
3.2
3,800
--

LFF

0.11
3.5
5,000
--

LJJ   SPB

LII   LGG   G3
Q3

LHH

0.9e
7.5
3,600
HH 100

--
8.1
3,200
--

0.02
6.7
5,000
HH 2

SPE

LKK

0.81
7.7
3,400
HH 90

0.22
8.7
1,600
HH 24

LLL

0.04
7.9
1,900
--

LMM   LNN   LOO

0.01
8.7
1,600
--

LPP

0.10
8.0
2,000
--

0.02
7.6
960
--

EXPLANATION

⬭ LAKE AND IDENTIFIER
LF

0.19   LOCATION OF DISCHARGE, pH, AND SPECIFIC CONDUCTANCE MEASUREMENT--Top
6.5   number is discharge, in cubic feet per second; middle number is pH value; bottom number
2,200   is specific conductance, in microsiemens per centimeter at 25 degrees Celsius; e Indicates
F 10   an estimated value; - - indicates no data; numbers following F and HH indicate outflow as
        percentage of outflow from lakes LF or LHH

SPE
●↘ SPRING AND IDENTIFIER

⟶ STREAM SEGMENT

▲G1 STREAMFLOW-GAGING STATION AND NUMBER

▼Q1 WATER-QUALITY MONITOR AND NUMBER

Figure 7.--Discharge, pH, and specific conductance measurements made April 17-19, 1985.

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EXPLANATION

⬭ LF LAKE AND IDENTIFIER

0.06   LOCATION OF DISCHARGE, pH, AND SPECIFIC CONDUCTANCE MEASUREMENT--Top
7.6   number is discharge, in cubic feet per second; middle number is pH value; bottom number
1,750 is specific conductance, in microsiemens per centimeter at 25 degrees Celsius; e indicates
F 15   an estimated value; - - indicates no data; numbers following F and HH indicate outflow as
       percentage of outflow from lakes LF or LHH

SPE
●↖ SPRING AND IDENTIFIER

⟶ STREAM SEGMENT

▲G1 STREAMFLOW-GAGING STATION AND NUMBER

▼Q1 WATER-QUALITY MONITOR AND NUMBER

Figure 8.--Discharge, pH, and specific conductance measurements made September 10-13, 1985.

18

Figure with discharge, pH, and specific conductance measurements (diagram with lakes and stream segments):

LA

0.024 / 0.53
3.0 / 7.0
3,250 / 3,200
F 5 / F 100

LE G1 Q1

0.0 LF 0.0
--   --
--   --
LJ --

SPD less than 0.01 F 0.0   F 0.0 LL
8.4
5,200
--
LK
6.8
2,600

LO

0.12 LM
6.8
2,500   0.12
F 23   3.3
        3,400
0.0   F 23
--   G2
LQ --   Q2
    F 0.0
        0.08
        7.3
        2,300
        F 15   LP

LR   LS

        0.01
        3.2
        3,250
        F 2

LN   LT

0.0   0.01
--   7.2
-- LX 1,200
F 0.0   F 2
                0.0
                --
        LY F 0.0 LZ
                --
0.0   0.0   0.0
--   --   --
LU   --   --   --
  F 0.0   F 0.0 F 0.0

0.0 LAA
--
--

F 0.0 LRR
LCC   LQQ 0.08
                     6.8
0.1e   3,400
6.2 LDD   --
3,250
--

0.21 0.10   LFF
7.1   6.6
3,600 4,250   0.01
HH 54 HH 26   2.7
LJJ   SPB   5,400
    LII   --
                LGG   G3
LKK   Q3
            LHH
SPE   0.39
                7.3
                4,000
                HH 100

LLL

LMM   LNN   LOO
  0.0   0.0
  --   --   0.0
  --   --   --
  --   --   --
LPP   --
        0.0
        --
        --
        --

EXPLANATION

LF LAKE AND IDENTIFIER

0.10   LOCATION OF DISCHARGE, pH, AND SPECIFIC CONDUCTANCE MEASUREMENT--Top
6.6   number is discharge, in cubic feet per second; middle number is pH value; bottom number
4,250   is specific conductance, in microsiemens per centimeter at 25 degrees Celsius; e indicates
F 15   an estimated value; - - indicates no data; numbers following F and HH indicate outflow as
        percentage of outflow from lakes LF or LHH

SPE SPRING AND IDENTIFIER

STREAM SEGMENT

G1 STREAMFLOW-GAGING STATION AND NUMBER

Q1 WATER-QUALITY MONITOR AND NUMBER

Figure 9.--Discharge, pH, and specific conductance measurements made April 21-25, 1986.

EXPLANATION

LF LAKE AND IDENTIFIER

0.45
3.45
3,210
F 100
LOCATION OF DISCHARGE, pH, AND SPECIFIC CONDUCTANCE MEASUREMENT--Top number is discharge, in cubic feet per second; middle number is pH value; bottom number is specific conductance, in microsiemens per centimeter at 25 degrees Celsius; e indicates an estimated value; - - indicates no data; numbers following F indicate outflow as percentage of outflow from lake LF

SPE
● SPRING AND IDENTIFIER

→ STREAM SEGMENT

▲G1 STREAMFLOW-GAGING STATION AND NUMBER

▼Q1 WATER-QUALITY MONITOR AND NUMBER

Figure 10.--Discharge, pH, and specific conductance measurements made July 9, 1986.

20

LA

LE

G1
Q1

0.076
3.3
3,800
F 100

0.064
- -
0.00
- -
F 84
- -
- -
F 0.0

LF

LJ

LK

LL

LO

LQ

0.0021
- -
- -
- -
F 3

LM
0.015
- -
- -
F 20

G2
Q2

LP

LR

LS

LN

LT

LX

LU

LY

LZ

LAA

LCC

LRR

LDD

LQQ

LFF

LJJ

SPB

LI

LGG

G3
Q3

LKK

LHH

SPE

LLL

LMM

LNN

LOO

LPP

EXPLANATION

LF   LAKE AND IDENTIFIER

0.076   LOCATION OF DISCHARGE, pH, AND SPECIFIC CONDUCTANCE MEASUREMENT--Top
3.3   number is discharge, in cubic feet per second; middle number is pH value; bottom number
3,800   is specific conductance, in microsiemens per centimeter at 25 degrees Celsius; ● indicates
F 84   an estimated value; - - indicates no data; numbers following F indicate outflow as
           percentage of outflow from lake LF

SPE
 ●   SPRING AND IDENTIFIER

──→   STREAM SEGMENT

▲G1   STREAMFLOW-GAGING STATION AND NUMBER

▼Q1   WATER-QUALITY MONITOR AND NUMBER

Figure 11.--Discharge, pH, and specific conductance measurements made July 31, 1986.

21

BASIN INPUT

```
          ┌─────────────┐
          │ Precipation │
          │  99 inches  │
          └─────────────┘
                 │
          ┌──────┴──────────────┐
          │                     │
    ┌──────────┐    ┌─────────────────────────────────┐
    │  Total   │    │ Infiltration, interception, and runoff │
    │  runoff  │    │ trapped by lakes without outflows │
    │ 19 inches│    │           80 inches              │
    └──────────┘    └─────────────────────────────────┘
        │                           │
    ┌───┴────┐        BASIN OUTFLOW  ┌──────┴──────┐
```

BASIN OUTFLOW

┌──────────┐	┌──────────┐	┌──────────┐	┌──────────────────────────┐
│ 10 │	│ 9 │	│ 13 │	│ Lake evaporation and │
│ inches │	│ inches │	│ inches │	│ spoil evapotranspiration │
└──────────┘	└──────────┘	└──────────┘	│ 67 inches │
			└──────────────────────────┘

Overland	Runoff from	Ground-water
runoff	precipitation	contribution to
	on lakes with	base flow
	outflows	

Surface outflow
32 inches

Total evapotranspiration
67 inches

Figure 12.--Two-year water budget for the Horn Branch basin.

22

spoil water was negligible compared to the total quantity of discharge, 68 percent of precipitation was lost to evapotranspiration from lakes, streams, and spoil (table 2). This percentage is 6 to 15 percent more than the percentages in the larger unmined basins of the South Grand and Little Osage Rivers (table 2), even though the Horn Branch basin has sparse vegetation. This small quantity of increased evapotranspiration may have been caused by the large number of lakes in the Horn Branch basin.

The hydrograph from site G1 was separated into contributions from overland runoff and from ground water using a technique described by Linsley and others (1975). Streamflow recession curves from site G1, plotted on semilogarithmic paper, indicated that the slope of the recessions beginning the day after rainfall ended became flatter with time and had two characteristic slopes (fig. 13). The initial steeper recession slope averaged 17 days per log cycle of discharge, and the subsequent slope averaged 46 days per log cycle until the next rise. In a small mined basin such as Horn Branch basin, virtually all overland runoff reached a stream or lake within a few hours after rainfall ended, but the lakes stored runoff and released it much slower than from an unmined basin. The release of this stored water accounted for the initial steep slope of the recession curve. The subsequent flatter slope of the recession curve was assumed to be ground-water discharge alone. Ground-water discharge then was separated from overland runoff by extending the ground-water slope back under the steeper slopes of the hydrograph. All discharge above the ground-water hydrograph was considered overland runoff. These two hydrographs were integrated over a 2-year period, and 19 in. of overland runoff and 13 in. of ground-water discharge were calculated for the basin. Therefore, about 40 percent of the outflow from Horn Branch was ground water that had passed through the spoil. Using an aquifer volume of 36,000 acre-feet (computed from figs. 5 and 6), an estimated effective porosity of 25 percent, and ground-water discharge of 6.5 in. per year, the average residence time of ground water in the spoil was about 14 years. Of the 19 in. of runoff, 9 in. was precipitation falling directly on 110 acres of lakes that have surface outflows most of the time. The remaining 10 in. were from overland runoff that represented only 11 percent of the precipitation on 1,090 acres of nonlake surface in the Horn Branch basin.

A primary reason for small volumes of overland runoff was the large areas of internal drainage that route runoff into shallow (less than 8 ft deep) recharge lakes. These lakes supplied much larger quantities of recharge to ground water than did the noninundated spoil surfaces. Water levels of 10 shallow recharge lakes were recorded from staff gages at intervals ranging from 1 to 15 days from May to November 1985 and March to September 1986. Continuous water-level data were collected from another shallow recharge lake (lake L17) during these same periods. The rate of daily water-level decline was computed for nonrunoff periods from 2 to 15 days in length. These rates of decline were averaged for each lake, then the 11 averages were averaged to determine a mean daily rate of decline for the study area (table 4). The mean decline was 0.066 ft/d (feet per day, table 4), which is more than four times the May through October average for lake evaporation (0.014 ft/d) in the region (U.S. Weather Bureau, 1959). Pan evaporation at both Weather Bureau measuring sites within 75 mi of the study area (Lakeside and Mount Vernon, Missouri, fig. 1) was within 5 percent of the long-term average during 1985 and 1986 (National Oceanic and Atmospheric Administration, 1984-86a), indicating lake evaporation was at near normal rates during data collection. The exact quantity of lake-bottom recharge to ground water is unknown. However, if even only 75 percent of the difference between average daily lake decline and average daily lake evaporation recharged ground water and 40 acres of the area 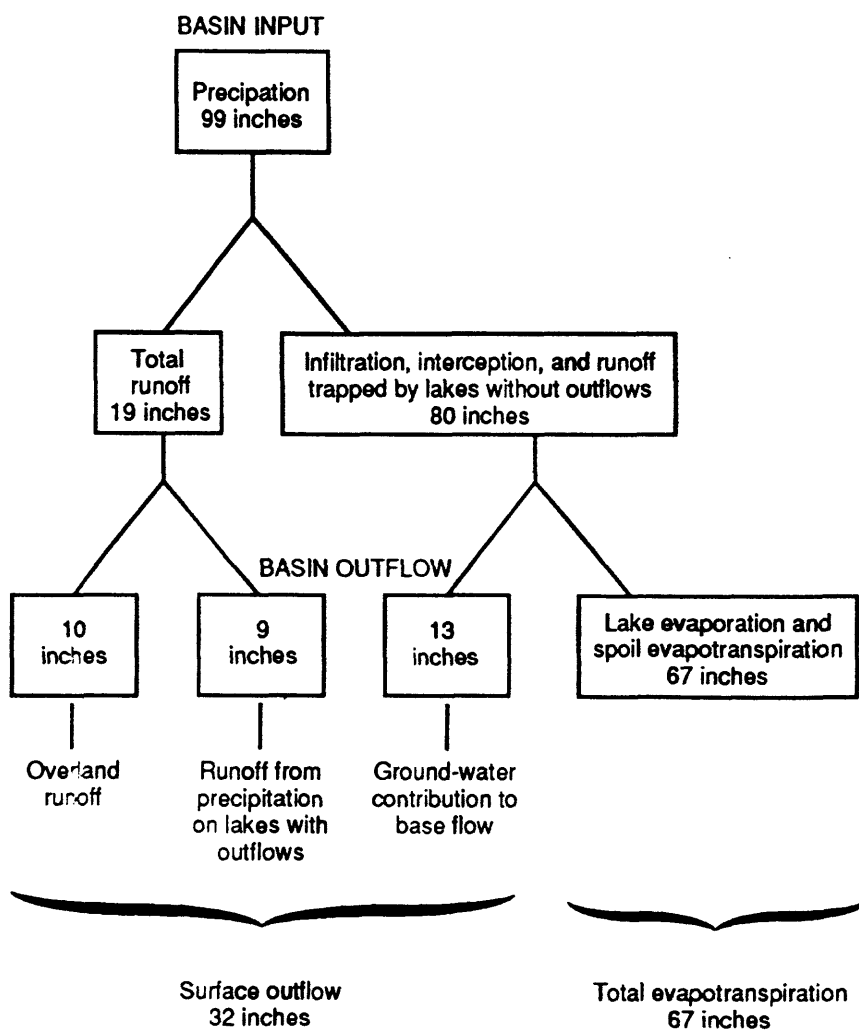were covered by recharge lakes, then more than 85 percent of the estimated 13 in. of ground-water recharge is accounted for. Therefore, as these lakes disappear because of erosion, the ground-water recharge, ground-water levels, and base flows will decrease.

WATER CHEMISTRY

The chemical reactions that produce acidic mine drainage have been described by many authors. Therefore, the details of this process are not reiterated in this report. However, a short summary of the process emphasizing selected reactions is presented to explain certain aspects of mine-water chemistry described later in this report.

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

$$FeS_2 \longrightarrow Fe^{+2} + S_2^0 + 2e^-. \tag{1}$$
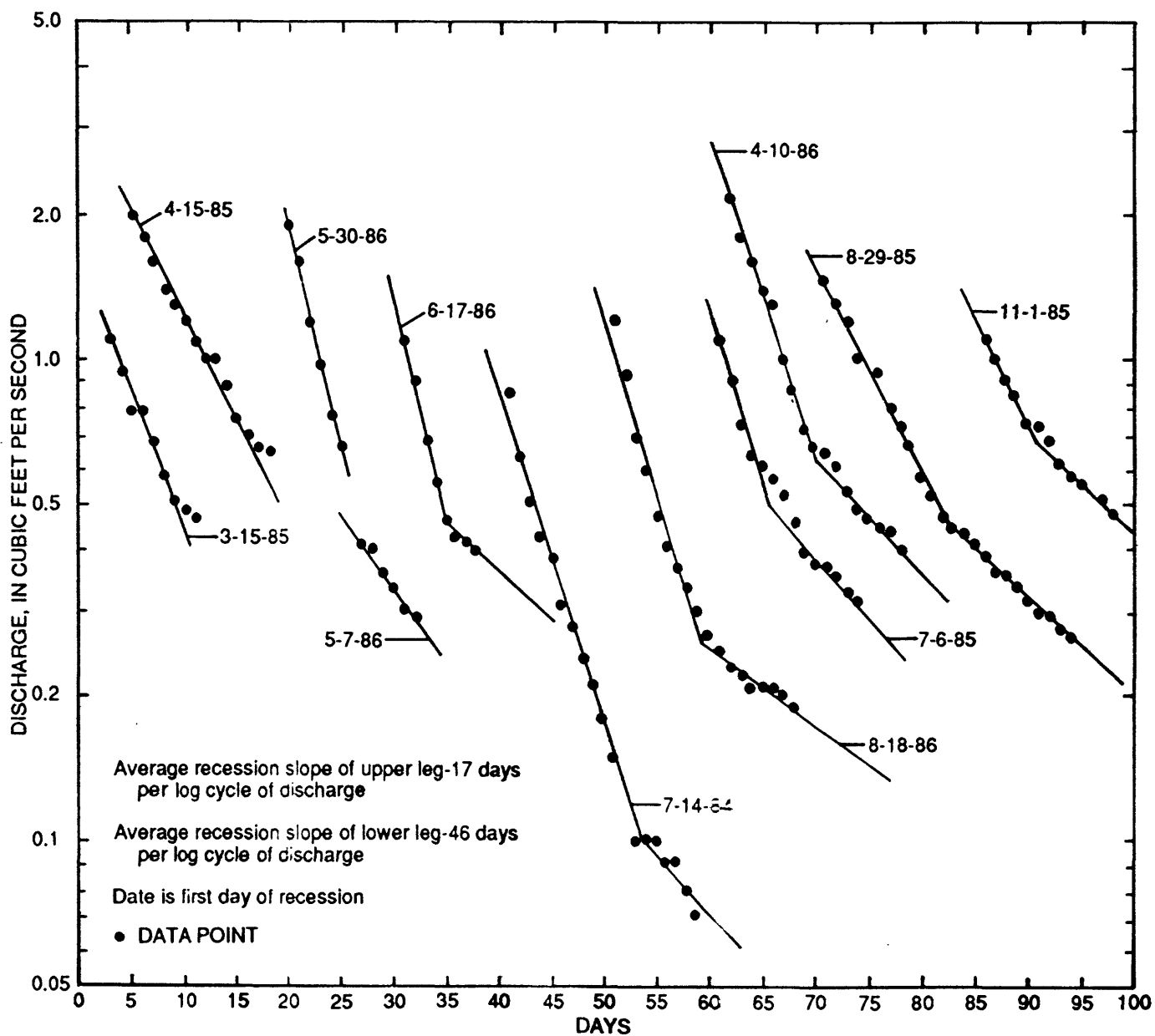
Figure 13.--Recession of streamflow in the Horn Branch basin from June 29, 1984, to September 22, 1986.

Table 4.--*Average daily declines of water levels in recharge lakes during nonrunoff periods 2 to 15 days between May and November 1985 and between March and September 1986*

[--, not relevant]

Lake	Number of nonrunoff periods	Average daily decline (feet)
L9	9	0.061
L10	6	.065
L11	15	.065
L12	9	.068
L13	19	.080
L14	11	.061
L15	17	.055
L17	38	.040
L18	11	.089
L19	18	.065
L20	8	.072
Mean	15	.066
Standard deviation	--	.013

The electron acceptor for this half-cell reaction can be either O_2 or Fe^{+3}. Aqueous elemental sulfur (S_2^0) is unstable and quickly oxidizes according to:

$$S_2^0 + 12Fe^{+3} + 8H_2O \longrightarrow 2SO_4^{-2} + 12Fe^{+2} + 16H^{+1} \tag{2}$$

or

$$S_2^0 + 3O_2 + 2H_2O \longrightarrow 2SO4^{-2} + 4H^{+1}. \tag{3}$$

Six electrons are transferred per sulfur atom in both reaction 2 and reaction 3, indicating that these reactions are summations of several intermediate steps. Reaction 2 is dominate at pH values less than about 4.5 where large quantities of dissolved Fe^{+3} can be available for an oxidant. At larger pH values, O_2 is the primary electron acceptor (reaction 3), but this reaction is much slower than reaction 2. Blevins and Chafin (1988) have shown with oxygen isotopes that reaction 2 produces most of the dissolved sulfate (SO_4^{-2}) draining from the spoil. Therefore, it appears that Fe^{+3} is the primary oxidant. However, large quantities of Fe^{+3} are required for reactions 1 and 2 and are produced according to:

$$Fe^{+2} \longrightarrow Fe^{+3} + e^-. \tag{4}$$

The electron acceptor for this half-cell reaction, and thus, the driving oxidant for the whole chemical breakdown of pyrite, is O_2, perhaps through the intermediate hydrogen peroxide (H_2O_2). Reaction 4 proceeds slowly unless catalyzed by aerobic, thiobacillus bacteria. Singer and Stumm (1970) concluded that reaction 4 is the rate-limiting step in the production of acidic mine drainage.

Hydrolysis occurring during the precipitation of Fe^{+3} minerals also acidifies water in coal mines. This process can acidify streams and lakes where the availability of pyrite to water is limited. At pH values greater than about 4.0, Fe^{+3} precipitates as amorphous ferrihydrite [$Fe(OH)_3$]:

$$Fe^{+3} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^{+1}. \tag{5}$$

At pH values greater than 4.5, this reaction limits dissolved Fe^{+3} to small concentrations. The precipitation of jarosite [$XFe_3 (SO_4)_2 (OH)_6$] can lower the pH to about 2.0 according to:

$$X^{+1} + 3Fe^{+3} + 2SO_4^{-2} + 6H_2O \longrightarrow XFe_3(SO_4)_2 (OH)_6 + 6H^{+1}, \tag{6}$$

where X is a singly charged cation, usually potassium (K^{+1}), sodium (Na^{+1}), or hydrogen (H^{+1}).

Siderite ($FeCO_3$) is a common mineralogic form of iron in unmined rock. The oxidation of siderite and hydrolysis of the resultant Fe^{+3} at pH values greater than 4.5 produces H^{+1} according to:

$$FeCO_3 + 3H_2O \rightarrow Fe(OH)_3 + HCO_3^{-1} + 2H^{+1} + e^-. \tag{7}$$
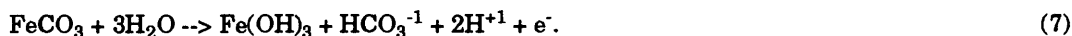
In acidic water, one more of the H^{+1} may be removed by the bicarbonate ion (HCO_3^{-1}) to form carbonic acid (H_2CO_3).

Chemistry of Surface Runoff

Analyses of 10 samples of surface runoff collected during a 2.86-in. rain on May 13, 1985, are listed in table 5. The pH of runoff was between 3.2 and 3.5 over the areas of barren, unreclaimed spoil and is consistent with laboratory data that indicated almost immediate acidification of neutral water after addition of only small quantities of spoil collected from the land surface (fig. 14). Less than 25 ml (milliliter) of surface spoil acidified more than 200 ml of near neutral lake water [alkalinity as calcium carbonate ($CaCO_3$), about 100 mg/L (milligrams per liter)] to a pH less than 4.0. The changes in pH occurred in a matter of seconds. The effect of surface spoil on rainwater would be even more pronounced because of the low alkalinity and slightly lower pH of rainwater. The rapid acidification of rainwater probably was because of dissolution of ferric sulfates such as coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$; Nordstrom, 1982) and bisulfate (HSO_4^{-1}) salts formed near the spoil surface between rains as depicted in reactions 8 and 9,

$$Fe_2(SO_4)_3 \cdot 9H_2O \rightarrow 2Fe(OH)_3 + 6H^{+1} + 3SO_4^{-2} + 3H_2O. \tag{8}$$

$$XHSO_4 \rightarrow X^{+1} + H^{+1} + SO_4^{-2}. \tag{9}$$
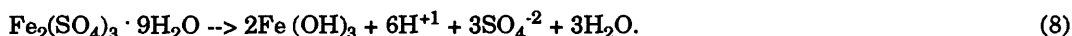
Ferric sulfates and HSO_4^{-1} salts form from iron disulfide-oxidation products only as near-surface spoil water evaporates between storms and cause H^{+1}, SO_4^{-2}, and Fe^{+3} to reach large concentrations. The large concentrations also cause the rapid oxidation of pyrite according to reactions 1, 2, and 4. Also, Miller (1979) has suggested that when jarosite and ferrihydrite are present, acidic spoil water is buffered at pH values between 3.0 and 3.4, which is about the same range in pH detected in surface runoff from unvegetated spoil.

Samples collected near lakes LDD and LQQ (table 5) were collected from ungraded, but revegetated spoil in the eastern part of the study area. The pH values at these sites were about 2 to 3 units larger than those in the unvegetated areas, which would indicate that successful revegetation of spoil substantially decreases the acidity of runoff. The specific conductance of runoff from revegetated spoil also was less than the unreclaimed areas, indicating less dissolution in general in the vegetated areas. Decreased exposure of unoxidized pyrite by slowing erosion and the presence of organic material in revegetated spoil are likely causes of increased pH values of runoff. However, the pH values of runoff from the revegetated and reclaimed areas were 1 to 2 units less than runoff from the unmined area at site S2.

Samples collected immediately after the May 13, 1985, storm from small perched lakes with no surface outflow (table 6) had pH values similar to those of direct runoff from bare spoil. Although activities (chemically effective concentrations) of calcium (Ca^{+2}) and SO_4^{-2}, as calculated by WATEQ4F, were well below saturation, they were large enough to indicate that substantial quantities of calcite, coquimbite, HSO_4^{-1} salts, or gypsum dissolve in the first few minutes of contact with the spoil surface. Dissolved SO_4^{-2} begins to form HSO_4^{-1} in substantial quantities at pH values less than 3.5, and thus, may help keep the pH of runoff from being much less than 3.0.

The pH values of samples collected from surface outflows of larger lakes immediately after the May 13, 1985, rain (table 7) were not appreciably different from base-flow pH values (figs. 15-17). This was because of the relatively large volumes of water stored in the lakes.

Continuous discharge, specific conductance, and pH data were collected at sites Q1, Q2, and Q3 and continuous rainfall data were collected at site RG (fig. 1). Horn Branch at site Q1 drained a mixture of acidic and near-neutral lakes and a land surface of mostly unreclaimed and unvegetated spoil. Water draining from lake LN was always neutral, but water draining from lake LP (site Q2) always was acidic. The pH value at site Q1 was determined in large part by which of these two tributaries contributed the majority of flow. If the pH at site Q1 was more than 5.0 just before rainfall, runoff temporarily tended to decrease the pH value (figs. 15-17). However, if the pH was less than 5.0 just before rainfall, runoff tended to increase the pH value. Increases of pH value were

Table 5.--Analyses of samples collected from surface runoff on spoil, May 13, 1985

[Results in milligrams per liter, except as indicated; μS/cm, microsiemens per centimeter at 25 °Celsius; CaCO₃, calcium carbonate; <, less than]

Location or site number (fig. 1)	Land-surface condition	Specific conductance (μS/cm)	pH (units)	Total acidity as CaCO$_3$	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Total bicarbonate
S2	Unmined	1,200	7.1	5	170	50	44	9.8	124
Near lake LPP	Reclaimed	1,200	6.0	5	250	31	1.1	4.7	33
Near lake LDD	Revegetated	60	6.0	<5	7.2	1.2	.6	3.7	23
Near lake LQQ	Revegetated	70	5.4	5	8.4	1.3	1.3	1.5	1
Near lake LM	Unreclaimed fly ash and spoil	2,150	2.9	600	260	48	<10	.4	0
Near lake LX	Unreclaimed	810	3.2	30	92	8.0	1.0	4.9	0
Near lake LS	Unreclaimed	160	3.4	10	15	1.2	.5	3.4	0
Near lake LM	Unreclaimed	540	3.5	25	83	6.6	.8	3.3	0
Near lake LO	Unreclaimed	1,400	3.2	170	270	34	1.4	2.9	0
Near lake LA	Unreclaimed	840	3.5	35	150	11	.4	3.4	0

Location or site number (fig. 1)	Total alkalinity as CaCO$_3$	Dissolved sulfate	Dissolved chloride	Dissolved fluoride	Dissolved silica	Dissolved solids	Dissolved aluminum	Dissolved iron	Dissolved manganese	Dissolved strontium
S2	126	570	0.5	0.2	3.4	1,010	<0.1	0.14	1.3	0.65
Near lake LPP	29	700	3.7	.4	3.4	1,100	<.1	.004	4.2	.18
Near lake LDD	17	19	1.0	<.1	2.8	61	<.1	.061	.009	.022
Near lake LQQ	3	23	.9	.2	9.1	52	.2	1.3	.078	.031
Near lake LM	0	1,400	1.3	1.2	4.6	2,100	82	25	8.6	.28
Near lake LX	0	270	1.1	.5	8.2	388	2.7	.25	1.3	.11
Near lake LS	0	49	.6	.1	4.5	72	.2	.023	.23	.039
Near lake LM	0	230	.7	.4	5.1	330	2.3	.20	.87	.85
Near lake LO	0	830	.6	1.0	5.5	1,260	3.8	.58	2.7	.29
Near lake LA	0	400	.4	.6	5.6	610	2.8	.21	1.3	.18

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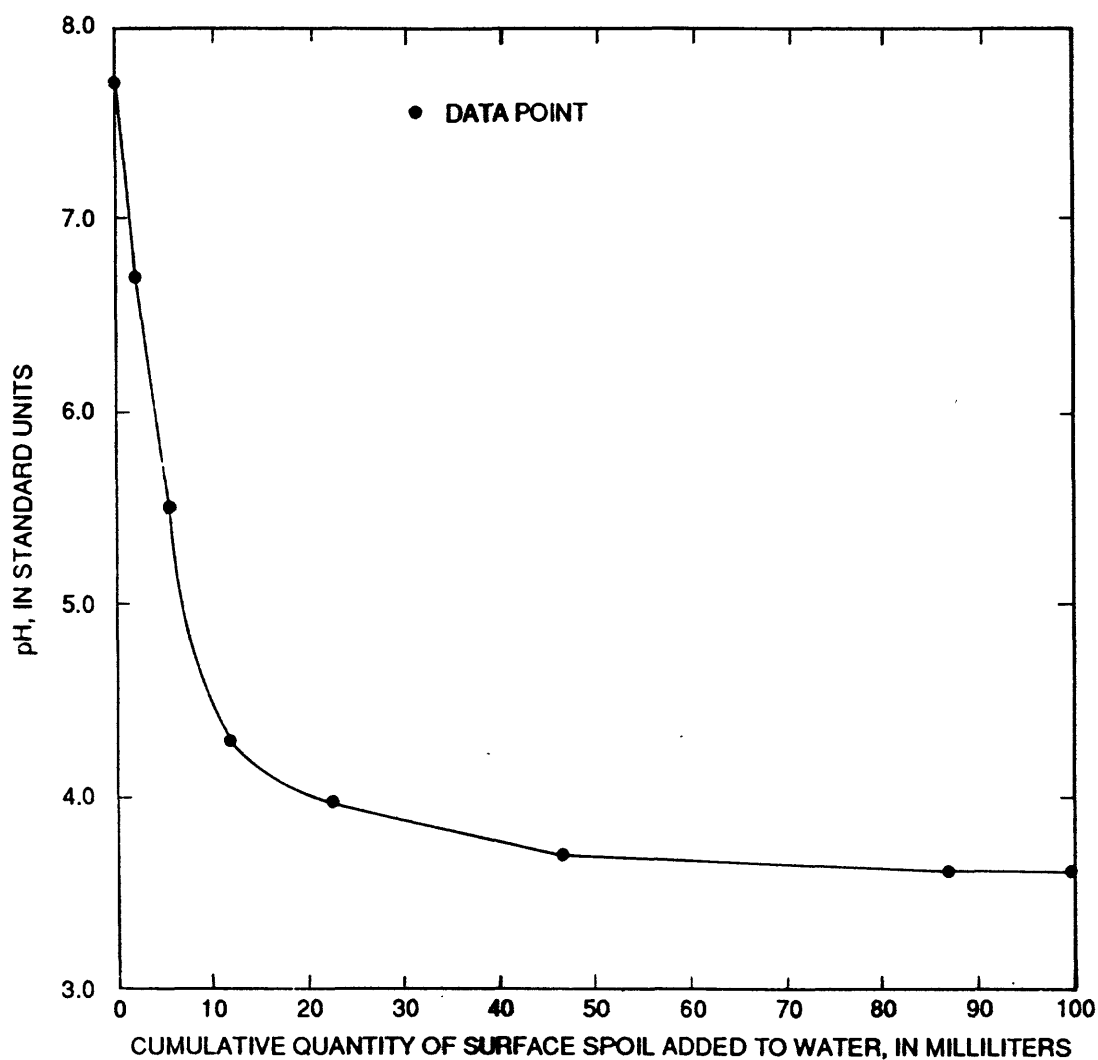
Figure 14.--Decrease in pH value of 213 milliliters of water from lake LN with the addition of surface spoil.

Table 6.--Analyses of samples collected from perched recharge lakes on spoil with no surface outflow immediately after 2.86 inches of rain, May 13, 1985

[Results in milligrams per liter, except as indicated; µS/cm, microsiemens per centimeter at 25 °Celsius; CaCO₃, calcium carbonate; --, not relevant]

Lake (fig. 1)	Specific conductance (µS/cm)	pH (units)	Acidity as CaCO₃	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Total bicarbonate	Total alkalinity as CaCO₃
L12	710	3.8	30	110	10	0.5	2.8	0	0
L13	1,290	3.3	130	190	19	.8	2.5	0	0
L17	1,200	3.2	180	130	17	1.8	2.5	0	0
L18	385	4.3	10	59	4.2	.7	3.3	0	0
Mean	900	--	90	120	13	1.0	2.8	0	0

Lake (fig. 1)	Dissolved sulfate	Dissolved chloride	Dissolved fluoride	Dissolved silica	Dissolved solids	Dissolved aluminum	Dissolved iron	Dissolved manganese	Dissolved strontium
L12	310	0.4	0.4	4.2	470	2.4	1.6	1.0	0.13
L13	650	.5	.8	4.3	955	16	2.2	2.2	.16
L17	560	.6	.6	4.4	790	19	7.3	2.4	.22
L18	160	.3	.3	2.4	240	.7	.08	.47	.06
Mean	420	.4	.5	3.8	615	9.5	2.8	1.5	.14

Table 7.--*Analyses of samples collected from surface outflows of larger spoil lakes and outflows leaving the study area immediately after 2.86 inches of rain, May 13, 1985*

[Results in milligrams per liter, except as indicated; µS/cm, microsiemens per centimeter at 25 °Celsius; CaCO$_3$, calcium carbonate; <, less than]

Lake (fig. 1)	Specific conductance (µS/cm)	pH (units)	Acidity as CaCO$_3$	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Total bicarbonate	Total alkalinity as CaCO$_3$
LA	2,150	3.4	110	320	160	120	11	0	0
LF[a]	2,600	6.2	<5	310	130	130	11	8	19
LM	2,600	5.0	<5	300	140	110	21	2	10
LN	2,020	7.3	<5	240	110	110	11	111	106
LP	3,000	3.2	120	360	180	98	22	0	0
LT	3,200	3.3	210	370	190	90	12	0	0
LX	880	7.1	<5	110	30	34	7.5	57	55
LFF[a]	3,100	3.0	310	270	140	94	7.6	0	0
LHH[a]	3,500	7.2	<5	360	200	200	19	170	184
LJJ	2,700	7.2	5	310	150	100	17	188	188

Lake (fig. 1)	Dissolved sulfate	Dissolved chloride	Dissolved fluoride	Dissolved silica	Dissolved solids	Dissolved aluminum	Dissolved iron	Dissolved manganese	Dissolved strontium
LA	1,900	3.2	1.2	11	2,800	8.1	6.1	12	2.0
LF	1,600	3.2	.5	3.5	2,330	<.1	1.3	5.5	2.5
LM	1,500	3.0	.5	3.4	2,330	.2	1	5.6	3.0
LN	1,100	3.8	.4	<1.0	1,770	<.1	.02	.10	2.8
LP	2,000	2.2	.7	9.1	3,020	12	4.4	12	3.2
LT	2,100	2.2	.8	16	3,030	19	8.4	13	3.0
LX	410	3.4	.3	b	676	<.1	.01	.78	.72
LFF	1,800	1.7	1.5	19	2,610	19	35	18	.98
LHH	2,000	3.4	.6	2.4	2,690	<.1	.04	1.0	4.2
LJJ	1,600	3.9	.5	2.6	2,440	<.1	.16	1.5	4.2

[a]Outflow leaving the study area.
[b]Possible lab error in value.
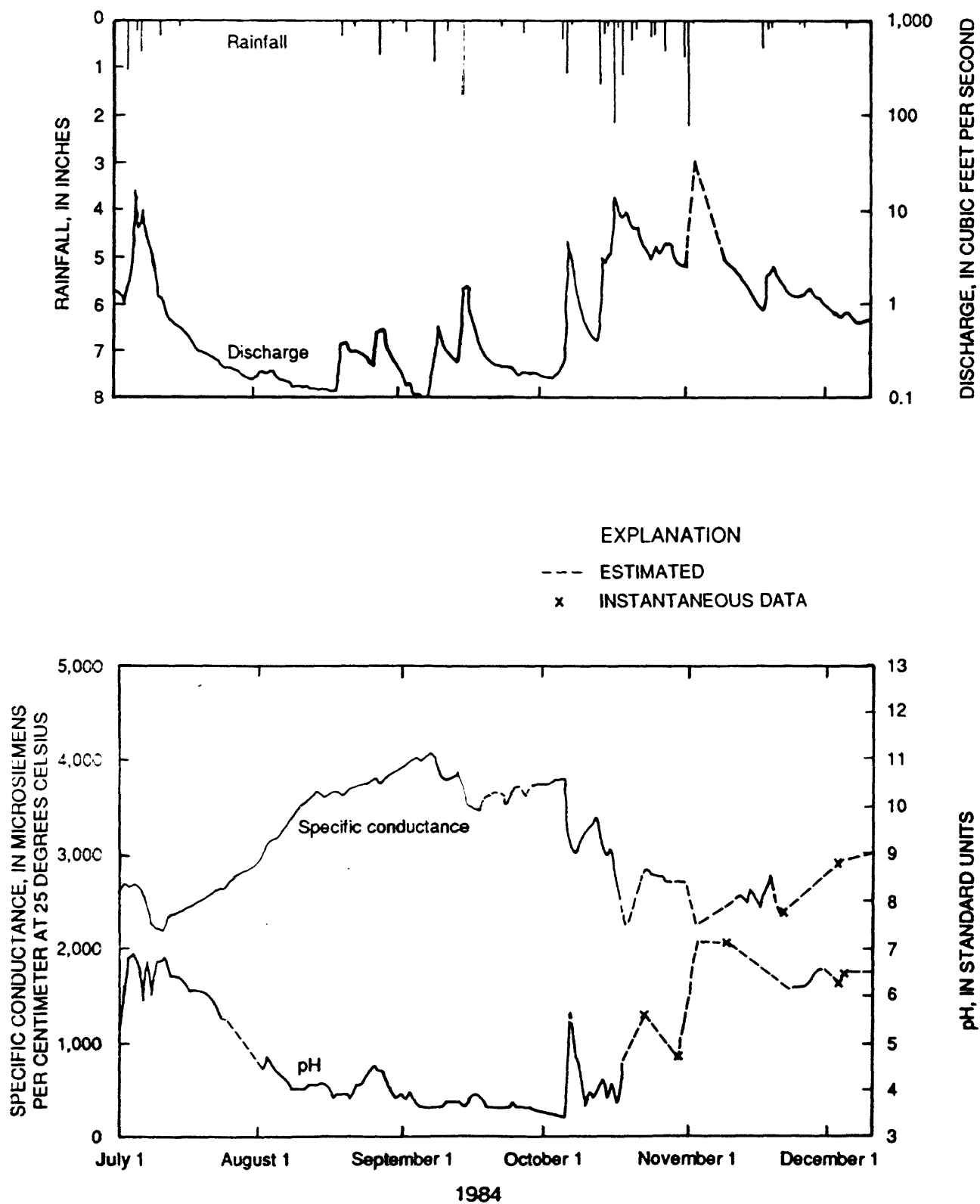
Figure 15.--Daily rainfall and daily mean discharge, specific conductance, and pH
at site Q1, July 1 through December 15, 1984.
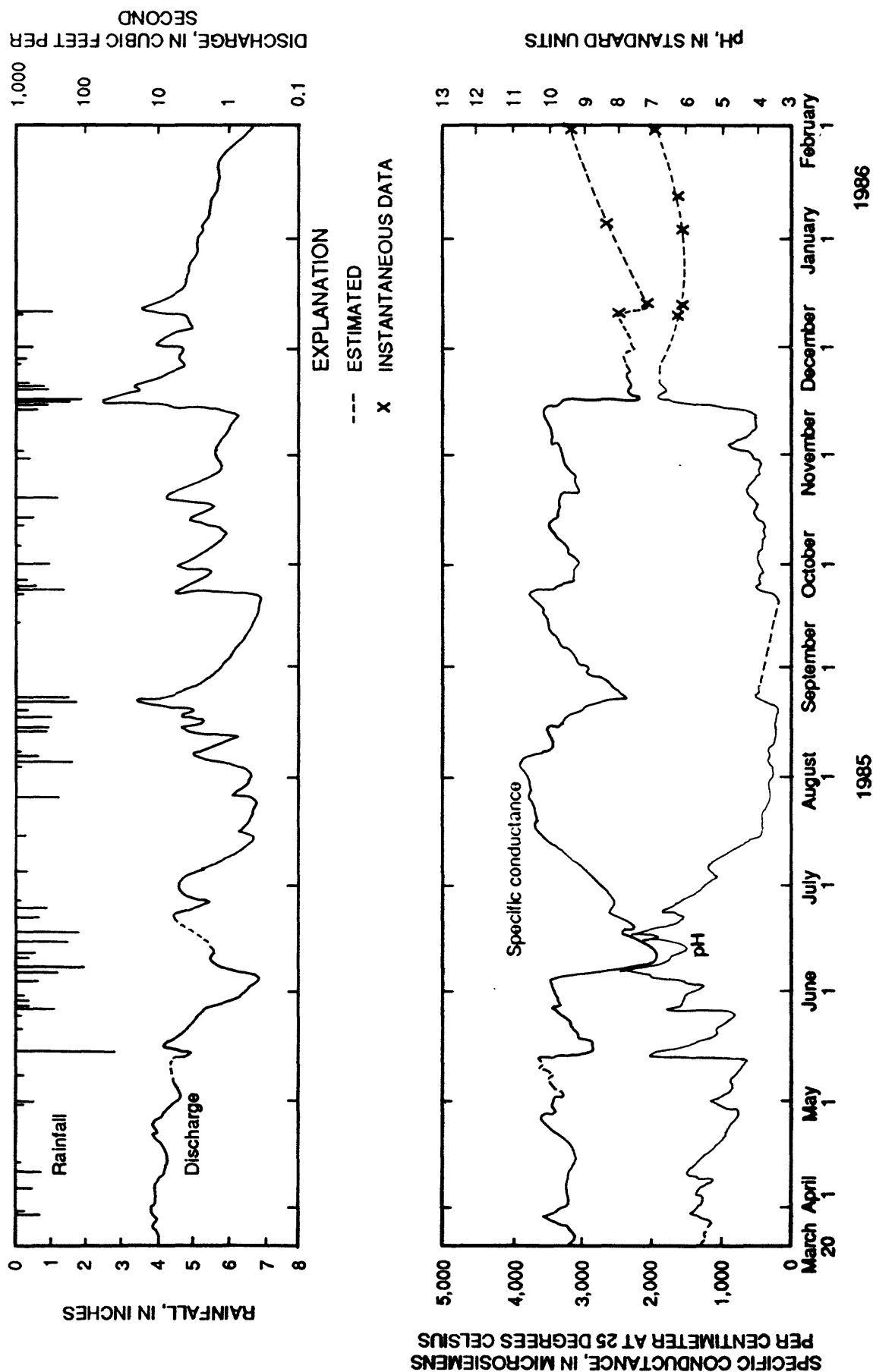
Figure 16.--Daily rainfall and daily mean discharge, specific conductance, and pH at site Q1, March 20, 1985, through February 1, 1986.

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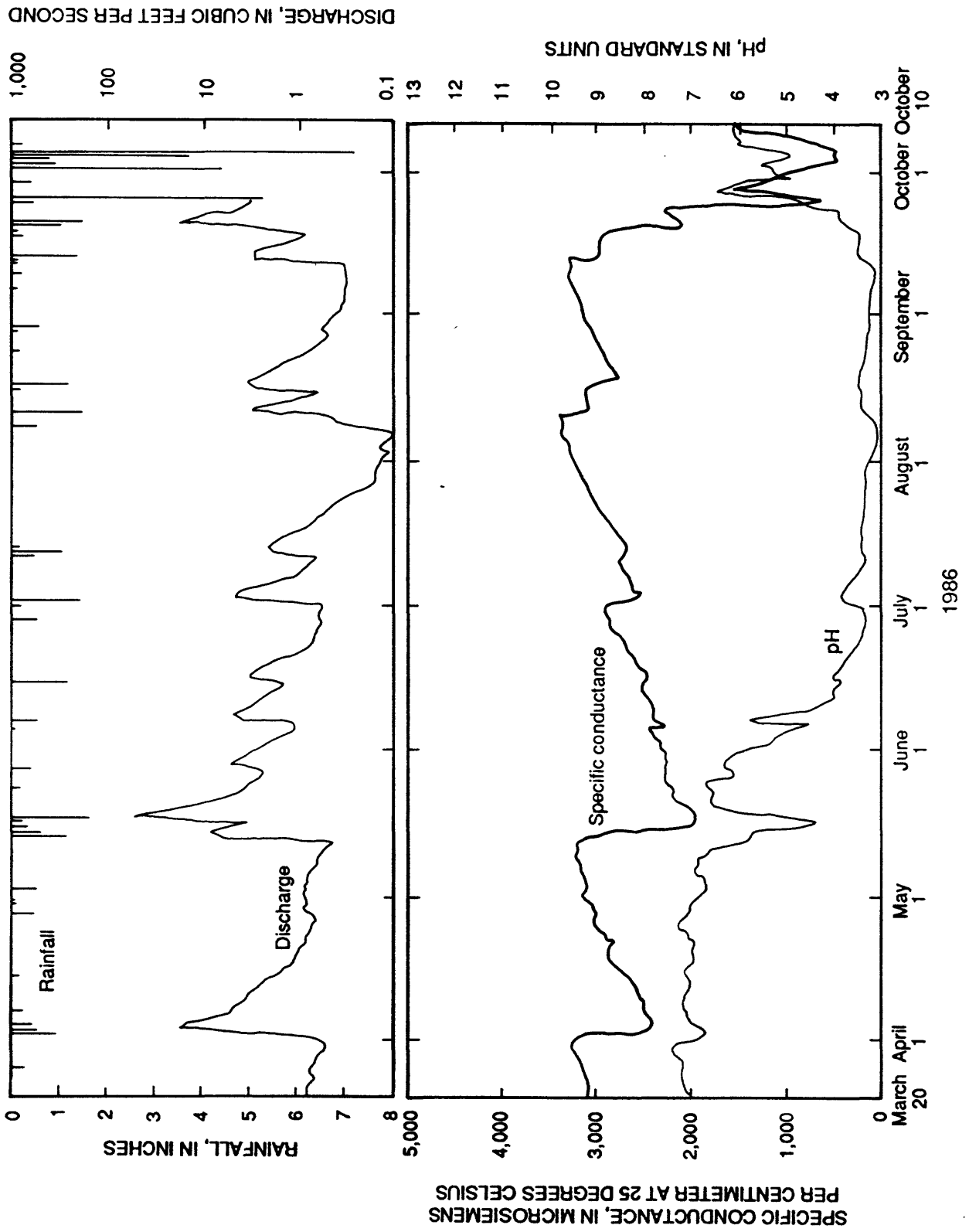
Figure 17.--Daily rainfall and daily mean discharge, specific conductance, and pH at site Q1, March 20 through October 10, 1986.

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caused by flushing of neutral lake water and decreases were caused by acidic runoff. The pH values of runoff in Horn Branch were probably larger than they would have been if the areas of internal drainage had not held much of the acidic runoff.

At site Q2 between June 30 and December 3, 1985, daily values of pH ranged from 2.9 to 3.4, with only the largest flows causing a slight increase in pH. Specific conductance ranged from 2,300 (peak flow) to 3,700 (low flow) μS/cm (microsiemens per centimeter at 25 degrees Celsius). The area drained by this site was unreclaimed and unvegetated. Much of the base flow was from two shallow lakes that effectively acidified all ground water entering them. Therefore, acidic runoff did not substantially change the already low pH value of water leaving the drainage area.

At site Q3 from June 29 to December 14, 1984, and March 20 to July 1, 1985, the pH ranged from 6.5 to 8.2, and the specific conductance ranged from 2,000 (peak flow) to 4,000 (low flow) μS/cm. This stream site received water from ungraded but mostly vegetated spoil in the eastern part of the study area with only small areas contributing overland runoff.

Ground-Water Chemistry

A summary of selected characteristics of the major dissolved constituents in water samples from wells completed in spoil is given in table 8. Some information in this table was determined by speciating dissolved ions from 17 analyses of water from 11 wells and determining saturation indices for various minerals from WATEQ4F. Saturation indices [log (activity product/equilibrium constant)] for selected minerals were calculated by WATEQ4F (table 9) based on data from water analyses and temperatures measured onsite. Eh values were required to speciate iron and manganese ions that have more than one valence. Values of Eh in ground water were estimated using pH and dissolved-iron concentrations (Barnes and Clark, 1964). These values were generally near 0.25 volt and close to a value of 0.23 volt measured in well W30 1 year after this study on September 25, 1987. The dissolved oxygen concentration in this well was below the detection limit of 0.1 mg/L and no hydrogen sulfide (H_2S) odor was detected. To determine the sensitivity of model results to errors in estimates of the Eh value, the models were run at Eh values 0.1 volt greater than and less than the estimate. There was little change in dominant aqueous species or saturation indices of manganese minerals. However, saturation indices of Fe^{+3} minerals, such as ferrihydrite and jarosite, were sensitive to even 0.05-volt changes in Eh.

Table 8.--*Characteristics of major dissolved constituents in water samples from wells completed in spoil*

Constituent	Probable major sources	Probable controls	Dominant species
H^{+1}	Oxidation of iron disulfides and Fe^{+2}	Dissolved-oxygen concentration	H^{+1}, HCO_3^{-1}
Ca^{+2}	Calcite and gypsum	Solubility of gypsum and calcite	Ca^{+2}, $CaSO_4^{0}$
Mg^{+2}	Limestone (substitution for Ca^{+2}), dolomite, and clays	Limited by source rock	Mg^{+2}, $MgSO_4^{0}$
Na^{+1}	Silicate minerals, impurities in cementing agents, cation exchange from clays	Limited by source rock	Na^{+1}
Fe^{+2}	Pyrite and siderite	pH, solubility of siderite	$FeSO_4^{0}$, $FeOH^{-1}$
Fe^{+3}	Oxidation of ferrous iron	Solubility of iron oxyhydroxides and jarosite	$Fe(OH)_2^{-1}$
Mn^{+2}	Limestone (substitution for Ca^{+2}) and clays	pH, solubility of rhodochrosite	Mn^{+2}
Al^{+3}	Clay and silicate minerals	pH, solubility of aluminum hydroxides	AlF_2^{+1} $Al(OH)_2^{+1}$
SO_4^{-2}	Pyrite, gypsum	Solubility of gypsum and jarosite	SO_4^{-2}, $CaSO_4^{0}$ $MgSO_4^{0}$
CO_3^{-2}	Calcite	pH, solubility of calcite	HCO_3^{-1}

Table 9.--pH values and saturation indices of ground-water samples

[Saturation index is log (activity product/equilibrium constant); saturation indices were calculated by WATEQ4F (Ball and Nordstrum, 1987)]

Well number (fig. 5)	Base-flow regime	pH	Saturation index									
			Gypsum	Calcite	Rhodochrosite	Siderite	Ferri-hydrite	Potassium jarosite	Alunite	$Al_4(OH)_{10}SO_4$	Crystalline gibbsite	Kaolinite
W2	low	6.7	0.02	0.20	0.07	0.24	1.90	6.30	0.35	0.50	0.08	1.40
W4	low	6.7	.01	.27	.05	-1.20	.37	1.80	[a].41	[a]-.48	[a].10	[a]1.50
W4	high	6.2	0	-.19	-.02	-1.50	-.94	-.59	.50	-1.60	-.31	.79
W7	low	6.6	.07	.23	.30	-.39	1.10	4.20	[a].69	[a]-.47	[a].12	[a]1.40
W7	high	6.3	0	-.22	-.09	-2.00	-1.10	-1.50	1.38	.25	.02	1.40
[b]W18	low	5.9	-.02	-1.60	-1.20	.25	1.20	7.70	3.80	.84	.30	[c]
[b]W18	high	5.3	-.04	-2.30	-2.00	-.61	-.67	3.30	3.40	.07	-.40	.27
W23	low	6.4	.02	-.02	.26	.62	1.70	6.80	.60	-1.30	[a]-.01	[a]1.30
W23	high	5.8	-.01	-.70	-.39	.09	.06	3.30	.57	-1.90	-.62	-.16
[d]W24	low	5.3	0	-2.50	-1.90	-.80	-.72	3.30	6.20	3.70	.48	2.50
[d]W24	high	5.2	0	-2.20	-1.70	-.68	-1.10	2.50	3.40	-.65	-.46	.06
[e]W26	low	6.6	.40	-.38	-.38	-.03	1.80	6.20	[a].60	[a]-.62	[a]-.11	[a]1.20
[e]W26	high	6.1	-.52	-.94	-.92	-.71	.10	2.50	.11	-2.00	-.50	-.04
W30	high	5.7	.02	-1.30	-1.10	.16	.61	6.00	3.20	.71	-.13	.13
W31	high	6.1	.00	-.64	-.31	.72	1.30	7.70	1.40	-2.30	-.34	-.38
W34	high	6.8	.00	.26	.10	-1.60	.27	2.00	2.00	.48	.61	2.20
W37	high	6.0	-.05	-.85	-.80	.03	.63	5.30	2.90	.43	.10	.93

[a]Aluminum concentrations for these analyses were less than the detection limit of 0.1 mg/L.
[b]Well affected by adjacent acidic recharge lake L19.
[c]The saturation index for kaolinite was not calculated because of no available concentration for dissolved silica.
[d]Well completed in fly ash.
[e]Well affected by adjacent neutral recharge lake LW.

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The pH of ground-water samples from all wells and springs except W18 and W24 ranged from 5.7 to 7.0 (tables 10 and 11). Well W18 was near lake L19, which was an acidic recharge lake in the southern part of the study area (fig. 1). Water in well W18 had pH values less than 4.0 after intense rains, but increased to values about 6.0 during dry weather. Water in well W24 (pH 5.2-5.3) probably was affected by fly ash from the power plant. Apparently, acid production in the ground-water system was limited by low dissolved-oxygen concentrations that slowed the rates of reactions 1, 2, 3, and 4. Dissolved-oxygen concentrations measured in water in observation wells during low base flow were at or below the detection limit of 0.1 mg/L. VomDemfange (1974) determined that pyritic sulfur was substantially depleted in only the top 2 ft of spoil at two sites in and one site near the study area. He also concluded that pyrite oxidation was limited by oxygen depletion at depth. HCO_3^{-1} concentrations of 265 to 800 mg/L in ground-water samples from wells not adjacent to acidic lakes or completed in fly ash indicate substantial quantities of carbonate minerals remained in the spoil and neutralized acidic recharge after a short time. Sources of CO_3^{-2} in the spoil are the Tiawah Limestone Member[1] in the Scammon Formation[1], numerous thin layers of limestone above the Tiawah[1], numerous vertical stringers of limestone that penetrate several of the shales, and siderite (fig. 2).

Calcite and gypsum are common constituents of rocks in the area (drillers' logs for water-supply wells in Montrose, Missouri, on file at Missouri Division of Geology and Land Survey, office in Rolla, Missouri), and consequently Ca^{+2} usually was measured in larger concentrations than any other cation in spoil water. At the low pH values detected near the spoil surface, calcite dissolves more rapidly than gypsum. Therefore, calcite is probably the major source of Ca^{+2} in ground water. Also, Blevins and Chafin (1988) used oxygen isotopes to show that most SO_4^{-2} dissolved in mine water was from pyrite oxidation and not from dissolution of premining gypsum. Ground water was saturated with calcite only in wells where pH values were greater than 6.4 (table 9), but gypsum was near saturation in all wells not near recharge lakes. In wells where calcite was undersaturated and gypsum was saturated, the dissolution of calcite could cause the precipitation of gypsum. At pH values greater than 6.4 and under the slow rate of pyrite oxidation at depth, calcite and gypsum approach saturated equilibrium with Ca^{+2} concentrations between 520 and 680 mg/L (table 10, wells 2, 4, 7, and 34).

The second largest cation concentration in ground water was usually magnesium (Mg^{+2}; tables 10 and 11). The mole ratio of Ca^{+2} to Mg^{+2} in ground-water samples averaged 1.6. This small ratio is evidence that Ca^{+2} was taken out of solution at a faster rate than Mg^{+2}. No plausible Mg^{+2} mineral was near saturation in spoil water. However, both calcite and gypsum were commonly near or above saturation, and this fact probably limited concentrations of Ca^{+2}. WATEQ4F speciation calculated 40 percent of dissolved Ca^{+2} and Mg^{+2} was in the form of aqueous sulfates. The propensity of SO_4^{-2} to form complexes permits larger concentrations of dissolved Ca^{+2} and Mg^{+2}.

Na^{+1} concentrations were nearly as large as Mg^{+2} concentrations in spoil water (tables 10 and 11). The concentrations probably originated from silicate minerals, impurities in cementing agents (Hem, 1985), and the abundant clay in spoil, where the large concentrations of Ca^{+2} may have forced Na^{+1} from cation-exchange sites. Also, 10 samples of ground water from undisturbed Pennsylvanian rocks in adjacent Bates County had Na^{+1} and chloride (Cl^{-1}) concentrations ranging between about 500 and 4,000 mg/L (Kleeschulte and others, 1985). The last traces of sodium chloride (NaCl) may persist for long periods where circulation of water is impaired (Hem, 1985) and may account for the Na^{+1} detected in spoil water. However, the small concentrations of Cl^{-1} in ground water (averaging less than 5 mg/L) indicated NaCl was not a large source of Na^{+1}. However, Hem (1985) also suggested that the large diameter of the chloride ion causes it to be retained in molecular layers of clay and shale, which are the most abundant constituents of mine spoil. Concentrations of Na^{+1} and Cl^{-1} were limited by source material rather than the solubility product of a salt in spoil water.

The largest concentration of any ion in spoil water was SO_4^{-2} (tables 10 and 11). Blevins and Chafin (1988) stated the largest source for SO_4^{-2} was oxidation of iron disulfides. This oxidation primarily occurs near the spoil surface where pH values are small and oxygen is available. The tendency of SO_4^{-2} to form strong ion pairs with divalent cations (such as aqueous calcium, magnesium, and iron sulfates) allows SO_4^{-2} concentrations in minewater to substantially exceed saturated SO_4^{-2} concentrations in a single cation system. The contributions of these ion pairs to SO_4^{-2} concentrations must be computed with speciation models before saturation indices for gypsum are computed. The saturation indices for gypsum in 15 of 17 samples were between -0.05 and +0.07 (table 9), indicating gypsum was near saturation in most ground water. The two samples significantly below saturation

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

Table 10.--*Analyses of samples collected from wells completed in spoil*

[Results in milligrams per liter, except as indicated; µS/cm, microsiemens per centimeter at 25 °Celsius; CaCO$_3$, calcium carbonate; --, no data available; <, less than; low base-flow samples were collected September 10-13, 1985, and high base-flow samples were collected April 21-25, 1986]

Well number (fig. 5)	Depth of well (feet)	Surrounding spoil character	Base-flow regime	Specific conductance (µS/cm)	pH (units)	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Total acidity as CaCO$_3$	Total bicarbonate
W2	25.7	ungraded unvegetated	low	4,400	6.7	530	190	320	11	--	740
W4	38.0	ungraded unvegetated	low	4,000	6.7	560	230	190	14	--	800
			high	4,000	6.2	580	290	180	13	65	780
W7	18.4	ungraded unvegetated	low	4,000	6.6	680	300	180	15	--	730
			high	3,900	6.3	550	280	180	13	70	670
[a]W18	22.9	ungraded unvegetated	low	3,400	5.9	460	170	8	40	640	76
			high	3,200	5.3	480	170	10	35	600	56
W23	19.0	ungraded	low	3,400	6.4	610	140	100	11	40	600
		vegetated	high	3,200	5.8	590	140	95	9.7	160	530
W24	37.6	graded	low	3,400	5.3	460	140	43	33	700	41
		fly ash	high	3,250	5.2	520	140	43	28	420	74
[b]W26	19.0	graded	low	1,990	6.6	280	110	39	32	20	300
		vegetated	high	1,750	6.1	230	88	27	27	45	290
W30	17.0	ungraded unvegetated	high	4,500	5.7	490	280	230	30	300	265
W31	20.0	ungraded unvegetated	high	5,350	6.1	470	380	440	47	120	460
W34	19.0	ungraded	high	3,000	6.8	520	260	320	37	45	620
		vegetated									
W37	26.0	ungraded unvegetated	high	3,500	6.0	480	210	170	48	60	310
Mean[c]	--	--	--	3,500	--	500	220	184	28	210	440

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Table 10.--Analyses of samples collected from wells completed in spoil--Continued

Well number (fig. 5)	Dissolved sulfate	Dissolved chloride	Dissolved fluoride	Dissolved silica	Dissolved solids, residue at 100 °Celsius	Dissolved aluminum	Dissolved iron	Dissolved manganese	Dissolved strontium	Mole ratio of iron to bicarbonate (dimensionless)
W2	2,500	5.0	0.5	12	4,160	<0.1	7.9	6.3	2	0.012
W4	2,300	10	.4	13	3,990	<.1	.23	15	3	.00031
W7	2,300	11	.4	15	3,980	.01	.33	14	4.1	.00046
	2,400	4.8	.4	11	3,990	<.1	2.2	13	1.4	.0033
[a]W18	2,300	4.3	.4	13	3,910	.02	.13	12	3.1	.0021
	2,800	2.5	6.6	--	4,330	3.0	380	16	2.1	5.4
W23	2,200	1.3	1.7	10	3,890	1.3	310	14	2.8	6.0
	2,000	4.2	.5	14	3,340	<.1	33	19	1.0	.060
W24	1,800	4.4	.2	7.2	3,210	.02	49	20	1.2	.10
	2,700	3.2	2.0	17	4,070	2.7	300	29	1.5	8.0
[b]W26	2,300	2.6	.4	9.5	3,610	.41	220	25	2.2	3.2
	1,000	2.1	.3	9.3	1,710	<.1	8.7	4.5	5.1	.032
	810	2.0	.3	8.8	1,440	.01	5.4	4.0	4.0	.020
W30	--	--	--	--	--	--	--	--	--	--
W31	3,000	3.6	.3	4.4	4,580	.13	190	12	7.1	.78
W34	3,600	5.6	.6	4.5	5,540	.02	130	16	8.0	.31
W37	2,600	7.4	.5	9.4	4,290	.02	.09	5.7	8.0	.00016
	2,200	1.6	.1	6.9	3,600	.02	48	8.7	10	.17
Mean[c]	2,400	4.5	.8	9.7	3,900	<.4	94	13	4.6	1.3

[a]Samples from well W18 were affected by water from an adjacent acidic lake L19.
[b]Samples from well W26 were affected by water from an adjacent near-neutral lake LW.
[c]Mean calculated using equal weight for each well. Where both high and low base-flow analyses were available, an average of the two values for the well was used for the overall mean.

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Table 11.--Analyses of samples collected from springs discharging from spoil

[Results in milligrams per liter, except as indicated; µS/cm, microsiemens per centimeter at 25 °Celsius; <, less than; $CaCO_3$, calcium carbonate; --, no data available; e, estimated; low base-flow samples were collected September 10-13, 1985, and high-base flow samples were collected April 21-25, 1986]

Spring number (fig. 1)	Base-flow regime	Discharge (cubic feet per second)	Specific conductance (µS/cm)	pH (units)	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Total acidity as $CaCO_3$	Total bicarbonate
SPB	low	0.02	4,600	7.0	560	380	230	34	40	350
	high	.10	4,250	6.6	520	350	190	28	25	280
SPC	low	<.01	3,800	6.6	520	270	300	32	40	580
SPD	low	.01e	5,500	6.7	520	480	370	27	30	300
	high	.01e	5,200	6.4	480	510	320	23	50	290
SPP	low	<.02	3,700	6.6	530	210	130	30	40	520
Mean[a]	--	--	4,300	--	520	340	250	30	38	430

Spring number (fig. 1)	Dissolved sulfate	Dissolved chloride	Dissolved fluoride	Dissolved silica	Dissolved solids, residue at 180 °Celsius	Dissolved aluminum	Dissolved iron	Dissolved manganese	Dissolved strontium
SPB	2,900	3.7	1.8	11	4,780	<0.1	0.09	15	3.7
	2,800	3.0	1.3	9.9	4,320	.02	.11	3.1	4.7
SPC	2,600	19	1.5	11	--	<.1	51	16	4.8
SPD	3,700	4.5	1.9	10	5,300	<.1	18	17	3.1
	3,700	3.6	1.3	5.8	5,570	.01	28	16	4.6
SPP	2,200	4.9	.8	9.8	3,630	<.1	29	9.7	4.9
Mean[a]	2,800	7.8	1.4	9.8	4,800	<.1	26	13	4.4

[a]Mean calculated with equal weight for each spring. Where two analyses exist for a spring, an average of the two values was used to calculate the overall mean.

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were from a well (W26) within 30 ft of a recharge lake. As previously mentioned, when the pH is greater than 6.4, ground water also is saturated with calcite. Combining the solubility equilibria for dissolution of calcite and gypsum leads to the expression

$$\frac{[SO_4^{-2}][H^{+1}]}{[HCO_3^{-1}]} = 10^{-6.5}$$

where the brackets denote activities (Hem, 1985). This expression can be useful for predicting changes in ground-water chemistry if changes or amendments are made that change one of these three constituents, or for predicting whether more gypsum or calcite will dissolve before equilibrium is reached.

Aluminum (Al^{+3}) concentrations often were below or near the detection limits (tables 10 and 11) probably because of minimal solubility of Al^{+3} at pH values near 6.0 with respect to gibbsite $Al(OH)_3$ (Hem, 1985), although several sulfates and silicates of Al^{+3} also were near or above saturation (table 9). Larger concentrations of Al^{+3} occurred in water from wells completed in fly ash and near acidic recharge lakes where pH values were lower (5.2-5.9) and F^{-1} (fluoride) concentrations were higher (0.4-6.6 mg/L) than in water from other wells. AlF^{-1} complexes are strong and can cause higher concentrations of dissolved Al^{+3} (Hem, 1985).

Fe concentrations ranged from 0.09 to 380 mg/L. Larger concentrations were detected in samples with pH values between 5.3 and 6.1 and lower concentrations in samples with pH values between 6.2 and 6.8 (tables 10 and 11). It is not likely that the larger concentrations of Fe come from pyrite oxidation below the water table. Large quantities of Fe^{+3} are required for the bacterially catalyzed reaction path (reactions 1 and 2) and O_2 is required for the much slower abiotic path (reactions 1 and 3). Only minute quantities of Fe^{+3} can be available at the typical pH (5.2-6.8) of ground water in the spoil (reaction 5) and dissolved oxygen usually was less than the detection limit of 0.1 mg/L. Pyrite oxidation does occur near the acidic spoil surface where both Fe^{+3} and O_2 are available. Even at near-surface potentials as high as 0.7 volt, a substantial part of the dissolved Fe is Fe^{+2} at low pH values. Blevins and Chafin (1988) showed that most SO_4^{-2} in ground water is from pyrite oxidation, and because most of this oxidation occurs near the surface, it is likely that some Fe^{+2} also is leached to the water table where lower potentials would stabilize Fe^{+2} even at the larger pH values.

Another large source of Fe in ground water is the abundant siderite in nodules and disseminated throughout limestones, sandstones, and shales in the area. Fe also may have been removed by precipitation of siderite in some cases. Eight of 17 ground-water samples were determined to be near or above saturation with siderite (table 9). No other plausible Fe^{+2} minerals were determined to be near saturation. Mn was similar to Fe in that rhodochrosite ($MnCO_3$) was near or above saturation in 7 of 17 samples.

Although strongly affected by small changes in Eh, ferrihydrite and potassium jarosite were usually near or above saturation at an Eh of 0.25. Also, most cuttings from wells drilled in spoil below the water table were colored with iron hydroxides, indicating ferrihydrite or jarosite, or both, were usually saturated in the ground water and limited concentrations of Fe^{+3}.

Lake and Base-Flow Chemistry

Shallow perched lakes (averaging less than 8 ft deep) on spoil usually had a pH values less than 4.0 (tables 6 and 12 and fig. 18). These lakes received little or no ground water to neutralize acidic runoff or produce sustained outflow. Although acidic, these lakes had low concentrations of Ca^{+2}, Mg^{+2}, Na^{+1}, SO_4^{-2}, and Fe because their only source of water, acidic runoff, also had low concentrations of these constituents. The perched lakes usually were clear with no visible Fe precipitates.

However, several shallow lakes, including lakes LA, LP, LT, and LGG, received substantial quantities of ground water with large Fe concentrations and also were acidic (table 13). These ground-water-supplied lakes were the primary sources of acidic base flow in the study area. The acidification occurring in these shallow lakes primarily was from oxidation of large concentrations of Fe^{+2} (reaction 5) in the ground water that supplies them. Also, acidic runoff and some iron disulfides from bare spoil were received by these lakes during rain storms. However, little change in pH value of lake LP occurred regardless of wet or dry weather, which indicates that the oxidation of Fe^{+2} from the steady supply of ground water was the primary source of H^{+1}.

Table 12.--Analyses of samples from selected shallow lakes perched on spoil during dry periods

[Results in milligrams per liter, except as indicated; μS/cm, microsiemens per centimeter at 25 °Celsius; CaCO₃, calcium carbonate; --, no data available; <, less than; low base-flow samples were collected September 10-13, 1985, and high base-flow samples were collected April 21-25, 1986]

Lake	Base-flow regime	Specific conductance (μS/cm)	pH (units)	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Total acidity as CaCO₃	Total alkalinity as CaCO₃
L10	low	790	3.5	87	9.5	2.1	7.7	40	0
	high	1,680	3.0	240	31	6.8	18	160	0
L14	low	1,400	3.2	190	17	8.1	16	140	0
L17	low	1,750	3.0	190	29	2.8	2.4	370	0
	high	1,750	2.8	150	25	3.3	1.4	320	0
L19	low	1,100	3.3	180	14	2.4	8.6	90	0
	high	875	3.4	120	10	2.8	6.8	50	0
LRR	low	1,500	3.4	190	40	11	20	40	0
	high	1,300	3.2	170	40	10	18	45	0
LRV	low	415	3.5	28	2.2	7.2	21	30	0
	high	440	4.0	57	--	4.3	5.2	10	0
Mean[a]	--	1,200	--	160	16	5.7	12	120	0

Lake number	Base-flow regime	Dissolved sulfate	Dissolved chloride	Dissolved fluoride	Dissolved silica	Dissolved solids, residue at 100°Celsius	Dissolved aluminum	Dissolved iron	Dissolved manganese	Dissolved strontium
L10	low	320	0.6	0.8	3.3	473	3.3	0.24	1.6	0.12
	high	840	1.4	1.7	11	1,300	<.1	<.1	4.6	.47
L14	low	680	.7	1.1	31	1,030	16	.73	2.8	.29
L17	low	880	.4	1.0	13	1,320	45	5.7	4.8	.26
	high	750	.7	.7	7.4	1,080	37	12	3.6	.24
L19	low	570	.8	1.0	14	836	8.4	1.6	2.9	.16
	high	390	.7	.7	12	574	5.3	.28	1.9	.11
LRR	low	730	1.7	.8	1.4	1,090	2.5	1.4	4.0	.35
	high	630	1.2	.5	6.2	949	2.6	1.7	3.8	.32
LRV	low	140	.5	.2	1.8	187	.50	.50	.89	.17
	high	200	.4	.4	17	296	.96	.19	3.6	.11
Mean[a]	--	570	.8	.8	12	850	11	2.1	3.1	.24

[a]Mean calculated with equal weight for each lake. Where two analyses exist for one lake, an average of the two values was used to calculate the overall mean.
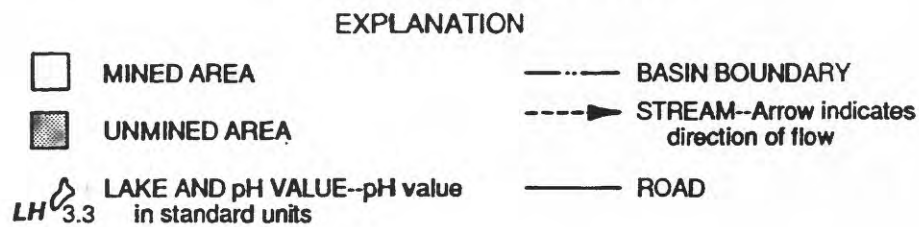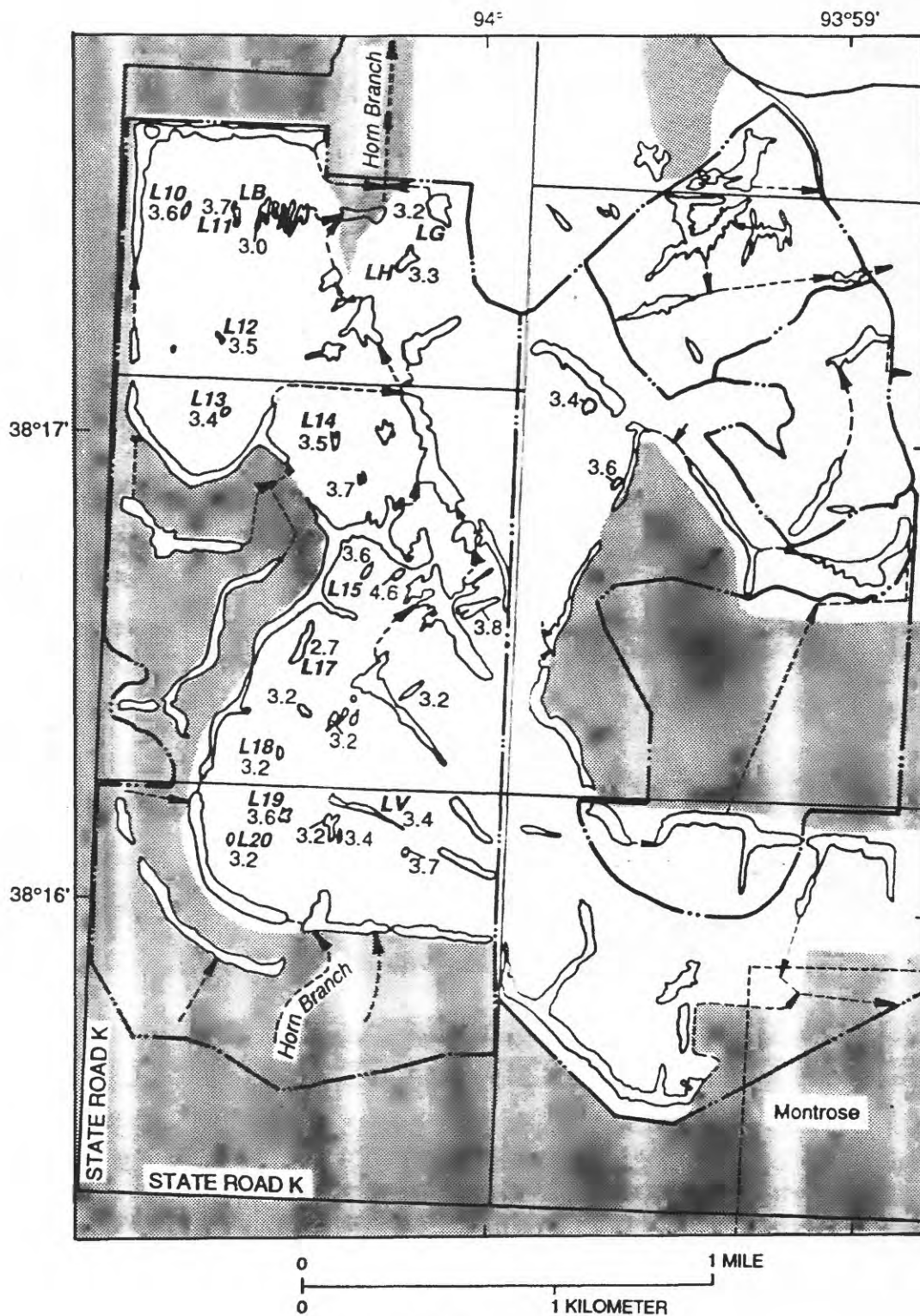
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Figure 18.--pH value of selected shallow lakes in mined areas.

Table 13.--Analyses of samples collected from lakes in saturated contact with the ground-water system in the spoil

[Results in milligrams per liter, except as indicated; μS/cm, microsiemens per centimeter at 25 °Celsius; CaCO₃, calcium carbonate; <, less than; --, no data available; e, estimated; low base-flow samples were collected September 10-13, 1985, and high base-flow samples were collected April 21-25, 1986]

Lake number	Approximate average depth (feet)	Base-flow regime	Discharge (cubic feet per second)	Specific conductance (μS/cm)	pH (units)	Dissolved calcium	Dissolved magnesium	Dissolved sodium	Dissolved potassium	Total acidity as CaCO₃	Total alkalinity as CaCO₃
LA	8	low	0.00	3,050	3.1	350	160	120	2.3	140	0
		high	.024	3,250	3.0	350	170	120	18	115	0
LF	4	low	.39	3,200	3.8	400	180	190	30	50	0
		high	.53	3,200	7.0	350	170	160	23	5	32
LM	10	low	.24	2,700	3.7	320	160	130	25	110	0
		high	--	2,600	6.8	320	170	120	20	5	25
LN	16	low	.07	2,100	7.5	200	100	110	24	5	76
		high	.08	2,300	7.3	260	130	130	18	10	120
LO	17	low	.06	1,750	7.6	200	100	120	21	5	110
		high	.12	2,500	6.8	270	140	140	17	5	150
L	7	low	.073	3,300	3.3	410	200	110	27	200	0
		high	.11	3,400	3.3	380	210	130	27	94	0
LT	4	low	.00	3,300	3.1	390	170	86	24	280	0
		high	.01	3,250	3.2	370	180	100	20	160	0
LW	--	low	.00	415	6.0	53	10	1.7	9.1	<5	2
		high	.00	390	5.6	46	9.6	1.7	6.9	5	.3
LX	24	low	.02	1,100	7.8	140	38	49	10	<5	50
		high	.01	1,200	7.2	140	41	50	9.4	5	74
LCC	11	low	--	3,050	8.6	390	200	150	22	<5	32
		high	.02e	3,400	6.7	460	210	160	29	10	85
LCC	11	low	.1	3,250	6.2	400	220	160	21	20	82
LGG	<5	low	<.01	6,200	2.9	560	470	340	8.7	600	0
		high	.013	5,400	2.7	200	390	300	9.4	470	0
LHH	9	low	.29	3,250	7.5	350	200	200	25	10	120
		high	.39	4,000	7.3	400	240	250	29	10	210
LJ	5	low	.26	3,500	7.1	400	210	210	27	5	150
		high	.21	3,600	7.1	400	220	190	31	30	220
LQQ	<8	low	<.01	3,400	7.4	460	230	150	24	5	43
		high	.076	3,400	6.8	420	220	150	22	5	48

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Table 13.--Analyses of samples collected from lakes in saturated contact with the ground-water system in the spoil--Continued

Lake number	Base-flow regime	Dissolved sulfate	Dissolved chloride	Dissolved fluoride	Dissolved silica	Dissolved solids, residue at 180°Celsius	Dissolved aluminum	Dissolved iron	Dissolved manganese	Dissolved strontium
LA	low	1,700	2.0	1.3	10	2,690	7.8	8.2	12.0	1.5
LF	low	2,100	3.1	.9	5.9	3,020	3.8	.99	9.3	2.4
LM	high	1,900	3.8	.7	1.6	2,960	.02	.06	5.5	2.8
	low	1,800	3.0	.8	5.7	2,620	11	18	8.6	2.2
LN	high	1,600	3.4	.5	3.5	2,450	.02	.26	5.4	3.1
	low	1,200	4.4	.5	1.2	1,830	<.1	.04	.28	2.1
LO	high	1,300	7.8	.5	.8	2,010	--	.03	.40	2.5
	low	1,200	5.0	.5	2.7	1,890	<.1	.04	.71	1.7
LP	high	1,300	3.4	.5	2.9	2,130	--	.02	1.8	2.6
	low	1,800	1.6	1.0	7.3	--	20	6.7	13	2.7
LT	high	2,100	4.4	.6	11	3,320	6.7	3.5	11	3.1
	low	2,000	2.1	.9	11	2,910	24	14	12	2.2
LW	high	2,000	2.4	.5	19	3,020	13	13	11	2.5
	low	180	1.3	.3	2.4	264	<.1	<.003	1.1	.15
LX	high	160	1.4	.2	1.8	232	.02	.012	19	.13
	low	540	3.5	.4	1.1	866	<.1	<.003	.22	.97
LCC	high	550	4.0	.3	3.2	923	.01	.039	1.0	1.0
	ow	2,000	3.3	1.3	1.0	2,970	<.1	.07	.04	2.5
LCC	low	2,300	5.1	1.9	6.2	3,240	<.1	3.1	13	2.7
	high	2,200	3.8	1.3	4.8	3,230	.05	4.1	3.9	3.4
LGG	low	3,700	3.4	1.5	27	6,140	28	58	25	1.9
	high	3,500	2.3	.9	2.9	5,110	20	63	22	2.3
LHH	low	2,000	2.9	.8	2.6	2,910	<.1	.16	.13	2.9
	high	2,600	5.3	.6	1.6	3,830	.02	.02	2.4	1.6
LJ	low	2,000	3.8	.7	4.9	3,260	<.1	.18	1.1	3.5
	high	2,200	4.9	.4	1.1	3,430	.01	.03	1.0	4.3
LQQ	low	2,100	6.1	1.7	1.1	3,340	<.1	.06	.83	2.6
	high	2,300	4.3	1.5	3.4	3,250	.04	.06	.45	3.2

The Eh of outflow from the shallow, acidic lake LP on September 24, 1987, measured 0.71 volt. This Eh matched the value calculated using the Fe^{+3} to Fe^{+2} ratio in the Nernst equation, which supports the contention of Nordstrom and others (1979) that Eh measurements in acidic streams with large Fe concentrations are reliable if done correctly. At this Eh, most of the dissolved Fe was Fe^{+3} and although concentrations of ferrihydrite were less than saturation because of low pH values, jarosite was oversaturated. Acidic lakes receiving ground water were a dark, but transparent, red color from relatively high concentrations of Fe compared with the clear perched lakes. The transparency may have been caused by the undersaturation of ferrihydrite. Concentrations of Fe in the acidic lakes receiving ground water, while higher than perched lakes, were substantially lower than ground-water concentrations, reflecting the precipitation of Fe required to acidify the lakes. These lakes retained other chemical characteristics of ground water, such as high concentrations of Ca^{+2}, Mg^{+2}, Na^{+1}, and SO_4^{-2}. Large concentrations of SO_4^{-2} in ground-water-supplied lakes had a buffering effect when the pH was less than about 3.5. According to WATEQ4F calculations, at a pH of 3.0, the large quantities of SO_4^{-2} in lake LA caused the quantity of H^{+1} in the form of HSO_4^{-1} to be 40 percent of the quantity of free H^{+1}. Dissolved Al^{+3} concentrations primarily were a function of pH value with concentrations as large as 45 mg/L in acidic lakes (lake L17, table 12) but less than 0.1 mg/L in neutral lakes (tables 12 and 13).

Most deep lakes (average depth greater than 9 ft) had near-neutral pH values and dissolved concentrations of Fe less than 0.25 mg/L (depth and pH value in table 3 and fig. 19; Fe concentration in tables 7 and 13). Even at these low concentrations, WATEQ4F calculated saturation indices for ferrihydrite and potassium jarosite greater than 1.0 with arbitrary Eh values as low as 0.30. Evidently, most Fe entering the deep lakes with ground water was oxidized by atmospheric oxygen and precipitated at near neutral pH. The transparency of these lakes was usually less than the shallow lakes and some of the neutral, ground-water-supplied lakes were occasionally an opaque, bright orange from suspended iron hydroxides. The chemical character of deep lakes that received ground water, such as lakes LN, LO, LX, and LHH was similar to ground water except the lake water was somewhat diluted from rainfall and surface runoff. These characteristics included near-neutral pH values and large concentrations of Ca^{+2}, Mg^{+2}, Na^{+1}, and SO_4^{-2}. The pH value of these lakes is somewhat surprising because shallow lakes receiving ground water are acidified by Fe oxidation. Two factors, in varying degrees, may account for the near-neutral pH values. Most of the deeper lakes, such as lakes LN, LO, LQ, LU, LX, LY, LZ, LHH, LKK, LLL, LMM, LNN, LOO, and LPP, receive substantial quantities of near-neutral runoff from unmined or topsoiled drainage areas. Also, large variability existed in the Fe concentrations of ground water (table 10). If the mole ratio of Fe^{+2} to HCO_3^{-1} in near-neutral ground water was less than 0.5, then, theoretically, acidification below a pH of about 5 could not occur according to:

$$Fe^{+2} + 5/2H_2O + 1/4O_2 + 2HCO_3^{-1} \rightarrow Fe(OH)_3 + 2H_2CO_3.$$

Therefore, some of the deeper lakes may not acidify because the Fe to HCO_3^{-1} ratio in most ground-water samples was less than 0.5 (table 10). Exceptions were wells W18 (affected by an adjacent acidic recharge lake), W24 (affected by fly ash), W30, and W31. Wells W30 and W31 are upgradient from two shallow acidic ground-water-supplied lakes LT and LV. It is doubtful that the depth of the lake is a direct factor in keeping lake water near neutral, except for the tendency of deep lakes to receive a larger and more integrated quantity of ground water than shallow lakes. Stratification and low concentrations of dissolved oxygen at depth could decrease Fe oxidation and consequent acidification. However, only small concentrations of Fe were detected in outflows from deep, neutral lakes. Larger concentrations would be expected if Fe oxidation was limited and Fe remained as Fe^{+2}.

Horn Branch forked into two primary tributaries that had substantial effects on the water chemistry downstream during base flow. Outflows from lakes LN and LX (fig. 19) had near neutral pH values and formed the western tributary. Outflows from lakes LP, LS, and LT at site Q2 always were acidic and formed the eastern tributary. The two tributaries flowed into lake LM where mixing occurred. Continuous pH data (figs. 15-17) collected at site G1 and data collected during synoptic sampling (table 13) indicate that during high base flow, neutral water from lake LN dominated the water chemistry downstream and during low base flow acidic water from lake LP dominated water chemistry downstream. Although lake LN released more base flow than lake LP, base flow from lake LN ceased sooner than from lake LP during dry late-summer periods, possibly because of larger evaporation losses from lakes LN, LU, LX, LY, and LZ. Also, onsite experiments confirmed that the pH value of an equal mixture of lake LN and lake LP outflow was closer to the pH value of lake LP than lake LN because pH is a logarithmic measure of the H^{+1} concentration. Consequently, the pH at site Q1 usually was between 3.0 and 4.0 for a few months in the summer and between 5.5 and 7.0 for the rest of the year.
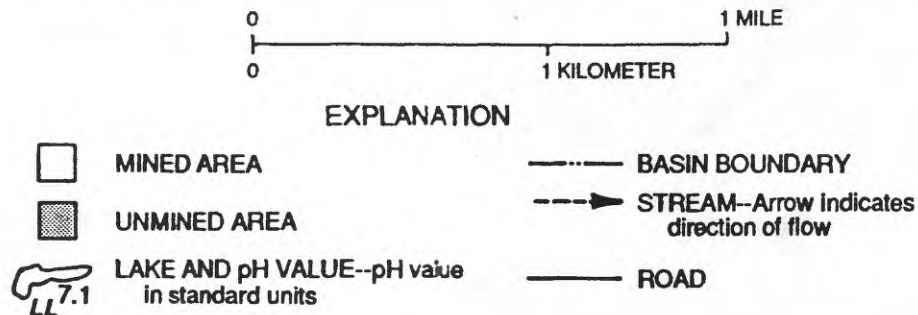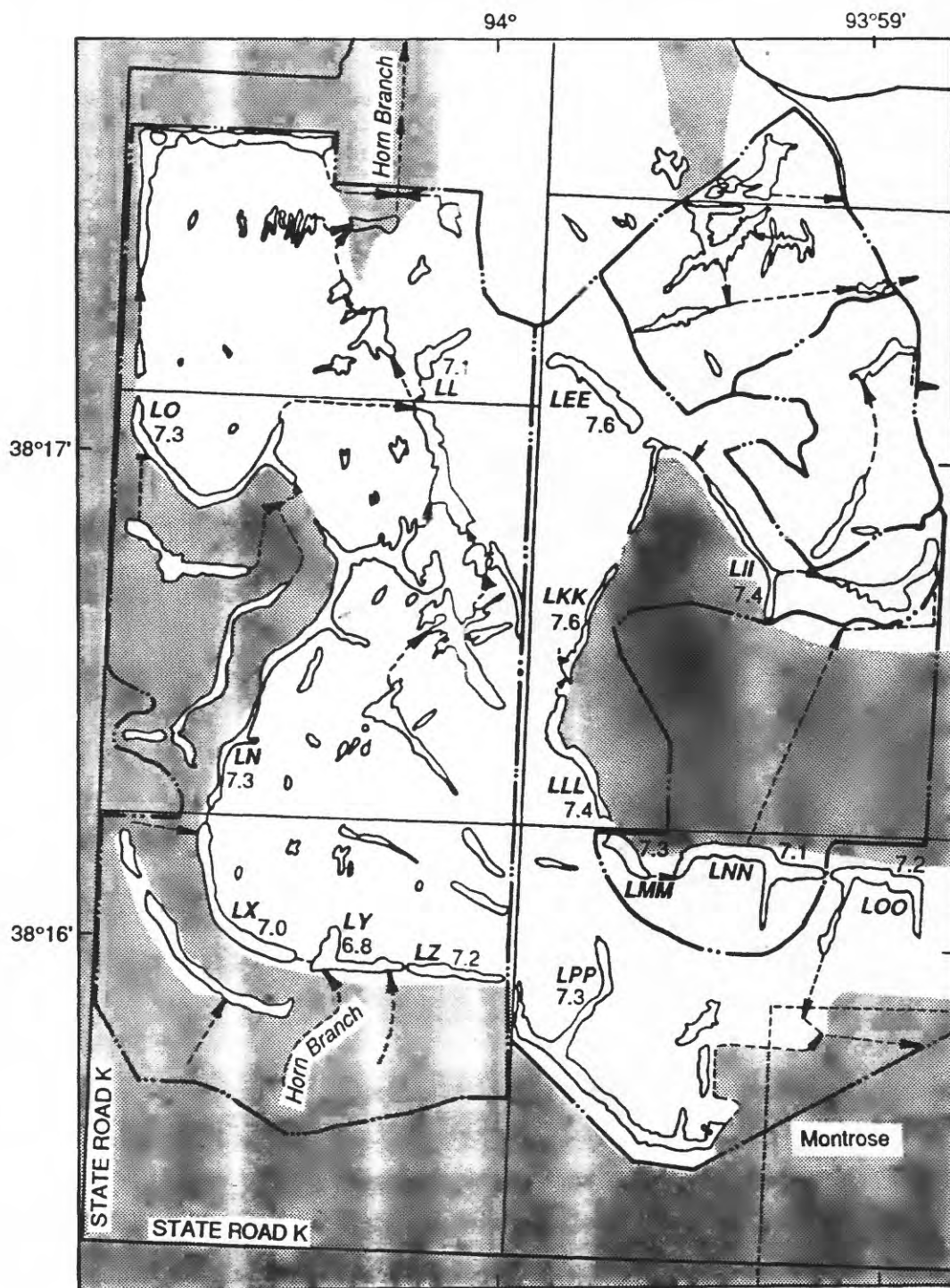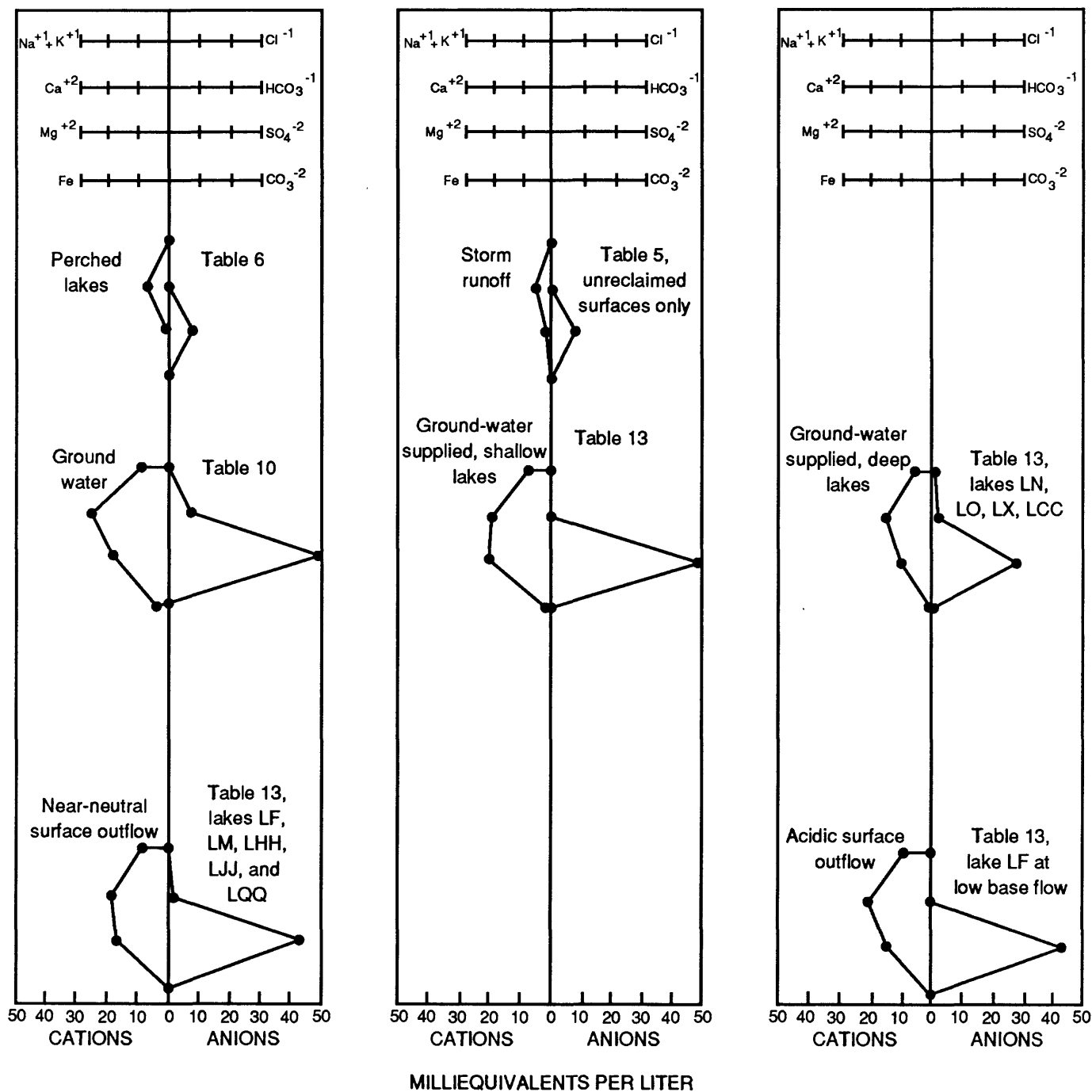
Figure 19.--pH value of deep lakes, September 1984.

Continuous pH data collected at site Q3 from June 29 to December 15, 1984, and from March 20 to June 25, 1985, and frequent instantaneous pH measurements collected during other periods ranged from 6.2 to 8.4. Drainage from lakes LII, LJJ, LKK, and LLL were included in the flow at G3. All instantaneous measurements of pH of the outflows from these last-cut, ground-water-supplied lakes always were greater than 6.0 (figs. 7-9).

Lake LGG had the lowest measured pH in the study area of 2.7 (table 13). Outflow from LGG contributed to the low pH of 3.5 at lake LFF on April 18, 1985 (fig. 7), which then drained out of the study area. Small quantities of the outflow from lake LQQ also left the study area. The pH value of this lake fluctuated depending on the relative contributions from acidic lake LRR and the near-neutral lakes LCC and LDD and the seeps between lakes LCC and LQQ.

Geochemical Processes and Conditions Occurring on Unreclaimed Spoil

Geochemical conditions and processes occurring in and on unreclaimed mine spoil in the study area are summarized in figures 20 and 21. The water-quality patterns of storm runoff and perched lakes are similar. Both waters are acidified by dissolution of ferric-sulfate and HSO_4^{-1} salts (acidic water is identified in figure 20 by the absence of HCO_3^{-1}). Dissolution of calcite and secondary gypsum are the most likely sources of Ca^{+2} detected in runoff. Near the surface where oxygen is available, iron-disulfide oxidation acidifies spoil. After this water reaches the water table, O_2 concentrations at depth are depleted, and calcite and siderite are dissolved, neutralizing acidic recharge and increasing concentrations of Ca^{+2}, Mg^{+2}, SO_4^{-2}, and Fe^{+2}. Consequently, the water-quality pattern for ground water has a characteristic shape, which also can be seen in ground-water-supplied lakes and in base flows draining the spoil. The resulting surface outflows from unreclaimed spoil are mixtures of acidic and near-neutral base flows, acidic runoff from unvegetated spoil, and near-neutral runoff unmined areas. Effects of acidic runoff are minimized by lakes with small or no outflows that trap acidic runoff and increase base flows. However, base flow from shallow, acidic, ground-water-supplied lakes occasionally acidifies receiving streams for a considerable distance downstream, primarily during late summer months. The pH value of base flow depends on the relative contribution of the deep, near-neutral lakes and the shallow, acidic lakes.

Figure 20.--Pattern plots of mean concentrations of selected constituents in storm runoff, perched lakes, ground water, shallow ground-water-supplied lakes, deep ground-water-supplied lakes, and two types of surface outflow leaving the study area.
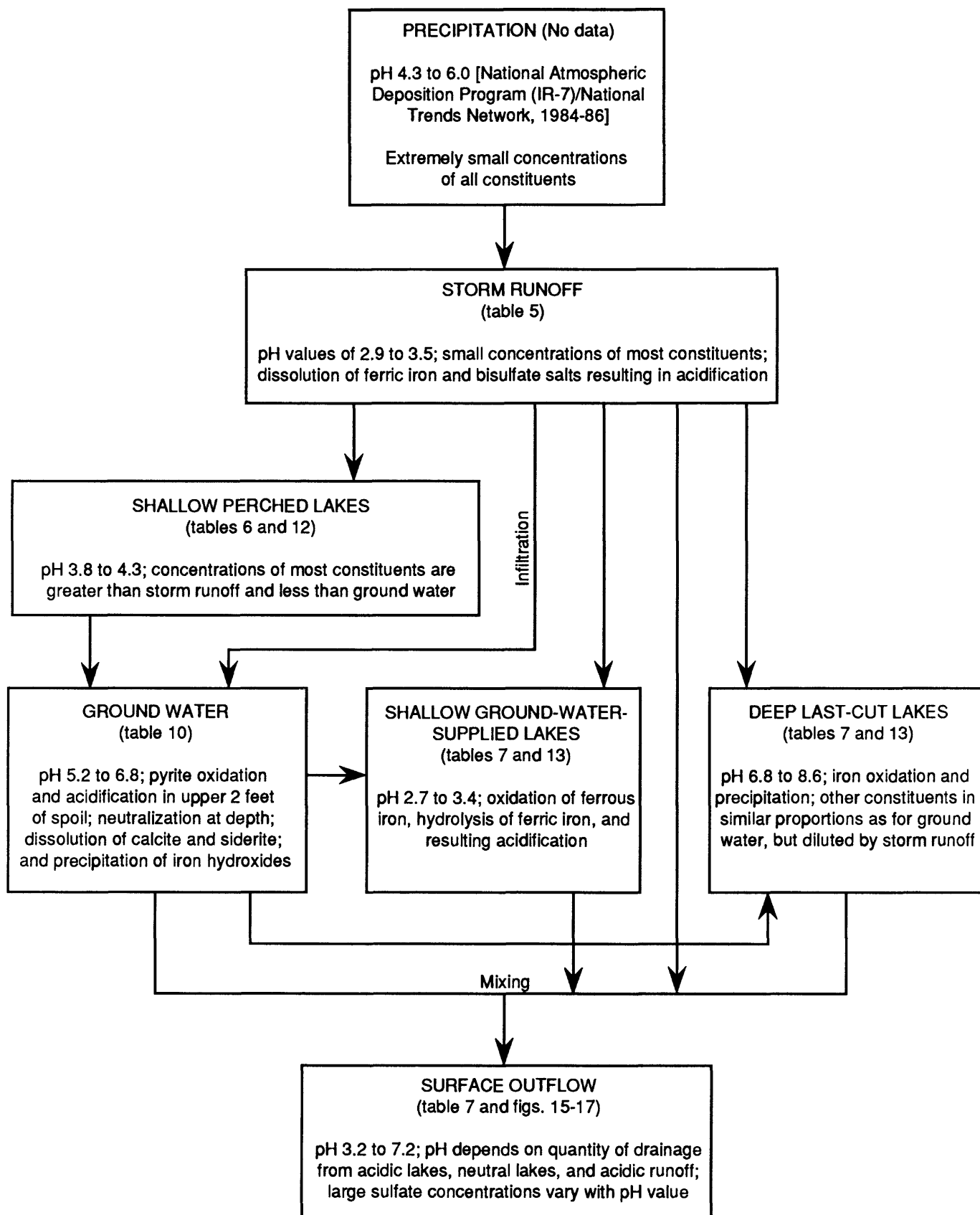
PRECIPITATION (No data)

pH 4.3 to 6.0 [National Atmospheric Deposition Program (IR-7)/National Trends Network, 1984-86]

Extremely small concentrations of all constituents

STORM RUNOFF
(table 5)

pH values of 2.9 to 3.5; small concentrations of most constituents; dissolution of ferric iron and bisulfate salts resulting in acidification

Infiltration

SHALLOW PERCHED LAKES
(tables 6 and 12)

pH 3.8 to 4.3; concentrations of most constituents are greater than storm runoff and less than ground water

GROUND WATER
(table 10)

pH 5.2 to 6.8; pyrite oxidation and acidification in upper 2 feet of spoil; neutralization at depth; dissolution of calcite and siderite; and precipitation of iron hydroxides

SHALLOW GROUND-WATER-SUPPLIED LAKES
(tables 7 and 13)

pH 2.7 to 3.4; oxidation of ferrous iron, hydrolysis of ferric iron, and resulting acidification

DEEP LAST-CUT LAKES
(tables 7 and 13)

pH 6.8 to 8.6; iron oxidation and precipitation; other constituents in similar proportions as for ground water, but diluted by storm runoff

Mixing

SURFACE OUTFLOW
(table 7 and figs. 15-17)

pH 3.2 to 7.2; pH depends on quantity of drainage from acidic lakes, neutral lakes, and acidic runoff; large sulfate concentrations vary with pH value

Figure 21.--Flow chart of evolution of water chemistry in mined area.

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SUMMARY AND CONCLUSIONS

The 2,400 acres of abandoned surface-mined land northwest of Montrose, Missouri, contained more than 100 lakes and 1,200 acres of barren, acidic spoil. More than one-half of the lakes had pH values less than 4.0. Most of the acidic spoil was drained by Horn Branch.

Surface drainage was mostly from lake to lake until it left the mined area. A part of the mined area has internal drainage (20 percent of the Horn Branch basin) due to ridges of spoil material that block drainage paths. Consequently, unit peak discharges were 28 and 53 percent less than 2 larger unmined areas nearby. As the lakes that trapped runoff filled with sediment from the rapidly eroding spoil, the capability to reduce runoff in the mined area decreased. Forty-seven percent of the runoff from the Horn Branch basin was caused by precipitation falling directly on lakes having outflow.

Ground water in the spoil had a water-table surface and was bounded on the bottom and sides by Pennsylvanian rocks of low permeability. The sides of the spoil aquifer usually were marked by linear, last-cut lakes that fully penetrated the aquifer and received ground-water discharge. The saturated spoil averaged 30 ft thick. The direction of ground-water flow in the spoil was controlled by the location and altitude of lakes recharging the spoil relative to the altitude of last-cut lakes receiving ground water from the spoil. Most of the recharge to the spoil aquifer came from leakage from shallow lakes formed between ridges of spoil. Consequently, as these ridges erode and the lakes disappear, ground-water levels and base-flow volumes will decrease.

Samples of overland runoff from bare mine spoil and fly ash had pH values between 2.9 and 3.5. Two runoff samples from revegetated spoil had pH values 2 to 3 units higher than runoff from bare spoil, which indicates that successful revegetation of spoil substantially increases the pH value of runoff. Although overland runoff was more dilute than any other water in the mine, substantial Ca^{+2} and SO_4^{-2} concentrations in five samples from bare mine spoil indicate secondary gypsum quickly dissolved in runoff. The pH value of streamflow leaving the mine was only minimally affected by acidic overland runoff because the large quantity of near-neutral lake water in the stream system moderated fluctuations in pH. Also, areas of internal drainage prevented much acidic runoff from reaching streams. One large 3-in. rainfall on May 13, 1985, decreased the pH value in Horn Branch to 4.8, but runoff sometimes increased the pH value in Horn Branch if prestorm values were less than 5.0. The higher pH values were caused by flushing of near-neutral water from several large lakes upstream, such as lakes LN, LO, LX, LY, and LZ.

The pH of ground water was usually between 5.7 and 6.8, except in fly ash and near a few acidic recharge lakes where the pH was less than 4.0 during wet weather. Ground water usually was not acidic because oxygen was not present in sufficient quantities to oxidize pyrite in the spoil. A few feet below the surface and at depth, carbonate rocks were present in sufficient quantity to neutralize the acidic recharge from lakes or the spoil surface. As this acidic recharge dissolved calcium carbonate at depth, the water became saturated with gypsum. Calcite also reached saturation if the pH was greater than 6.4. Concentrations of dissolved SO_4^{-2} in ground water were large, partly because of the tendency of SO_4^{-2} to form ion pairs such as aqueous calcium, magnesium, and iron sulfate. Reducing conditions in the spoil allowed concentrations of Fe^{+2} to average 93 mg/L, which oxidized and formed precipitates of Fe^{+3} minerals in the few shallow lakes that received ground-water discharge.

Samples of perched lakes had pH values between 2.8 and 4.3. The pH of lakes averaging more than 9 ft deep was greater than 6.0, probably because the deeper lakes received larger quantities of near-neutral runoff from unmined and topsoiled areas and they received ground water with lower Fe to HCO_3^{-1} ratios. A few shallow lakes intercepted the water table and received ground-water discharge. Water in these lakes was acidified to a pH between 2.7 and 3.4 and produced sustained outflows that had pronounced effects downstream. The pH of base flow in Horn Branch where it left the mine (site Q1) was lowered to less than 4.0 during the dry summer months by sustained outflow from shallow, ground-water-supplied lakes. The rest of the year, outflows from the near-neutral lake LN were large enough to dominate the water chemistry in the downstream reaches of Horn Branch.

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