WATER-QUALITY CHARACTERIZATION OF THE SPRING RIVER BASIN, SOUTHWESTERN MISSOURI AND SOUTHEASTERN KANSAS

By Jerri V. Davis and John G. Schumacher

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CONVERSION FACTORS AND VERTICAL DATUM

Multily	by	To obtain
	Length	
inch	25.4	millimeter
foot	0.3048	meter
mile	1.609	kilometer
foot per mile	0.1894	meter per kilometer
	Area	
acre	4,047	square meter
	0.4047	hectare
	0.004047	square kilometer
square mile	2.590	square kilometer
	Volume	
cubic yard	0.7646	cubic meter
	Flow	
cubic foot per second	28.3	liter per second
	0.02832	cubic meter per second
	Mass	
ton, short	0.9072	megagram or metric ton
	Temperature	
degree Fahrenheit	5/9 (°F - 32)	degree Celsius

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

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ABSTRACT

An appraisal of the surface-water quality in the Spring River basin in southwestern Missouri and southeastern Kansas was made using existing water-quality data collected from the early 1960's to September 1987 by the U.S. Geological Survey and the Kansas Department of Health and Environment at selected sites in the basin. Emphasis was given to data collected at six long-term monitoring stations (Spring River near Waco, Missouri; Center Creek near Carterville, Missouri; Center Creek near Smithfield, Missouri; Turkey Creek near Joplin, Missouri; Shoal Creek near Galena, Kansas; and Spring River near Baxter Springs, Kansas) and three ancillary stations (Cow Creek near Weir, Kansas; Brush Creek near Weir, Kansas; and Short Creek at Galena, Kansas).

Water-quality characteristics of the basin were described using summary statistics, analysis of variance and multiple-comparison procedures, and correlation analysis. Results indicated that Cow, Brush, Turkey, and Short Creeks, which are all tributary streams to the Spring River, are significantly affected by lead-zinc or coal mining, municipal wastes, and industrial wastes. Generally, small median pH values (3.9 to 7.5) and large median concentrations of calcium [76 to 120 mg/L (milligrams per liter)], sodium (19 to 70 mg/L), sulfate (110 to 540 mg/L), dissolved manganese [150 to 4,000 μg/L (micrograms per liter)], and dissolved zinc (30 to 49,000 μg/L) characterize the water quality of these streams. Short Creek at Galena also had large median concentrations of total ammonia (18 mg/L), total phosphorus (39 mg/L), and dissolved cadmium (280 μg/L). Center Creek has been affected to a lesser extent by mining activities in the large Oronogo-Duenweg lead-zinc mining belt located between the two Center Creek sampling stations, as evidenced by significant increases in median specific conductance values [350 to 405 μS/cm (microsiemens per centimeter at 25 degrees Celsius)] and median concentrations of calcium (56 to 72 mg/L), sulfate (24 to 56 mg/L), and dissolved zinc (53 to 420 μg/L) from Center Creek near Carterville, Missouri, to Center Creek near Smithfield, Missouri. Center Creek also is affected by discharges containing large concentrations of nitrite plus nitrate and ammonia from fertilizer and explosives manufacturing plants and seepage from phospho-gypsum piles near Grove Creek upstream from Carterville, Missouri.

The effect these contaminated tributary streams have on the Spring River is apparent from a comparison of the water-quality data collected at the Spring River sampling stations located near Waco, Missouri, and Baxter Springs, Kansas. There are significant increases in median specific conductance values (321 to 360 μS/cm) and median concentrations of calcium (55 to 59 mg/L), sodium (6.7 to 9.6 mg/L), sulfate (21 to 54 mg/L), total nitrite plus nitrate (1.7 to 2.4 mg/L), total ammonia (0.05 to 0.14 mg/L), total phosphorus (0.17 to 0.26 mg/L), dissolved manganese (30 to 150 μg/L), and dissolved zinc (30 to 310 μg/L), and decreases in median pH values (7.9 to 7.5) and median alkalinity concentrations (128 to 108 mg/L) from the upstream station near Waco, Missouri, to the downstream station near Baxter Springs, Kansas.

A comparison of median instantaneous constituent loads at the long-term monitoring and ancillary stations indicated that Short Creek is the largest single source of total phosphorus and dissolved zinc loads in the Spring River basin. Center Creek contributes a substantial dissolved zinc and total nitrite plus nitrate load. Cow Creek, which is affected significantly by surface coal mining, contributes most of the dissolved manganese load to the Spring River near Baxter Springs.

Baseline water-quality characteristics for the Spring River basin are best represented by the Spring River near Waco, Missouri, and Shoal Creek near Galena, Kansas. Samples collected at Shoal Creek near Galena generally had the smallest concentrations of major constituents, nutrients, and trace constituents. The slightly larger constituent concentrations detected on the Spring River near Waco are attributed to differences in geology, topography, and land use. Actual baseline constituent concentrations were determined from data collected at low and medium stream discharges.

Seasonal Kendall trend analysis results indicate that chloride concentrations are increasing at the Spring River near Waco, Missouri, and at both Center Creek stations, probably because of activities associated with basin development. Total phosphorus concentrations are decreasing at both Center Creek stations, at Shoal Creek near Galena, and at the Spring River near Baxter Springs, Kansas. Decreased use of phosphate detergents or aging of phospho-gypsum piles near Grove and Short Creeks may be responsible for this apparent trend. At the stations affected by lead-zinc mining, trends related to the cessation of mining were seen. Specific conductance and sulfate concentrations are decreasing at both Center Creek stations and Turkey Creek near Joplin, Missouri; sulfate concentrations are decreasing at the Spring River near Baxter Springs; pH is increasing at both Center Creek stations and the Spring River near Baxter Springs; and dissolved zinc concentrations are decreasing at Center Creek near Smithfield, Missouri.

INTRODUCTION

The Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) was a comprehensive program enacted to clean up the Nation's waters. The law mandated the development and implementation of state stream water-quality management plans to ensure that streams remain suitable for recreation, aquatic life, and general municipal and industrial water use. During the first few years after the enactment of Public Law 92-500, emphasis was placed on point sources of pollution, particularly industrial and municipal discharges. Point sources are controlled by the issuance of permits under the National Pollution Discharge Elimination System (NPDES) and are monitored to ensure compliance with regulations.

The authority to administer the NPDES program in the State of Missouri was granted to the Department of Natural Resources, Division of Environmental Quality (DNR-DEQ). Point-source discharges have been divided by DNR-DEQ into four categories: (1) publicly owned facilities, (2) industrial and mining facilities, (3) privately owned facilities, and (4) wastewater-treatment plants. All of these facilities must obtain NPDES permits that limit the kinds and quantities of pollutants in each wastewater discharge.

Large quantities of water-quality data have been collected in the Spring River basin by various State and Federal agencies and stored in paper and computer files. To provide the basis for establishment of water-quality based permit limits to be included in the NPDES permits for the Spring River basin, the U.S. Geological Survey (USGS), in cooperation with the Missouri DNR-DEQ, consolidated and analyzed existing water-quality information and data for the basin.

Purpose, Scope, and Methodology

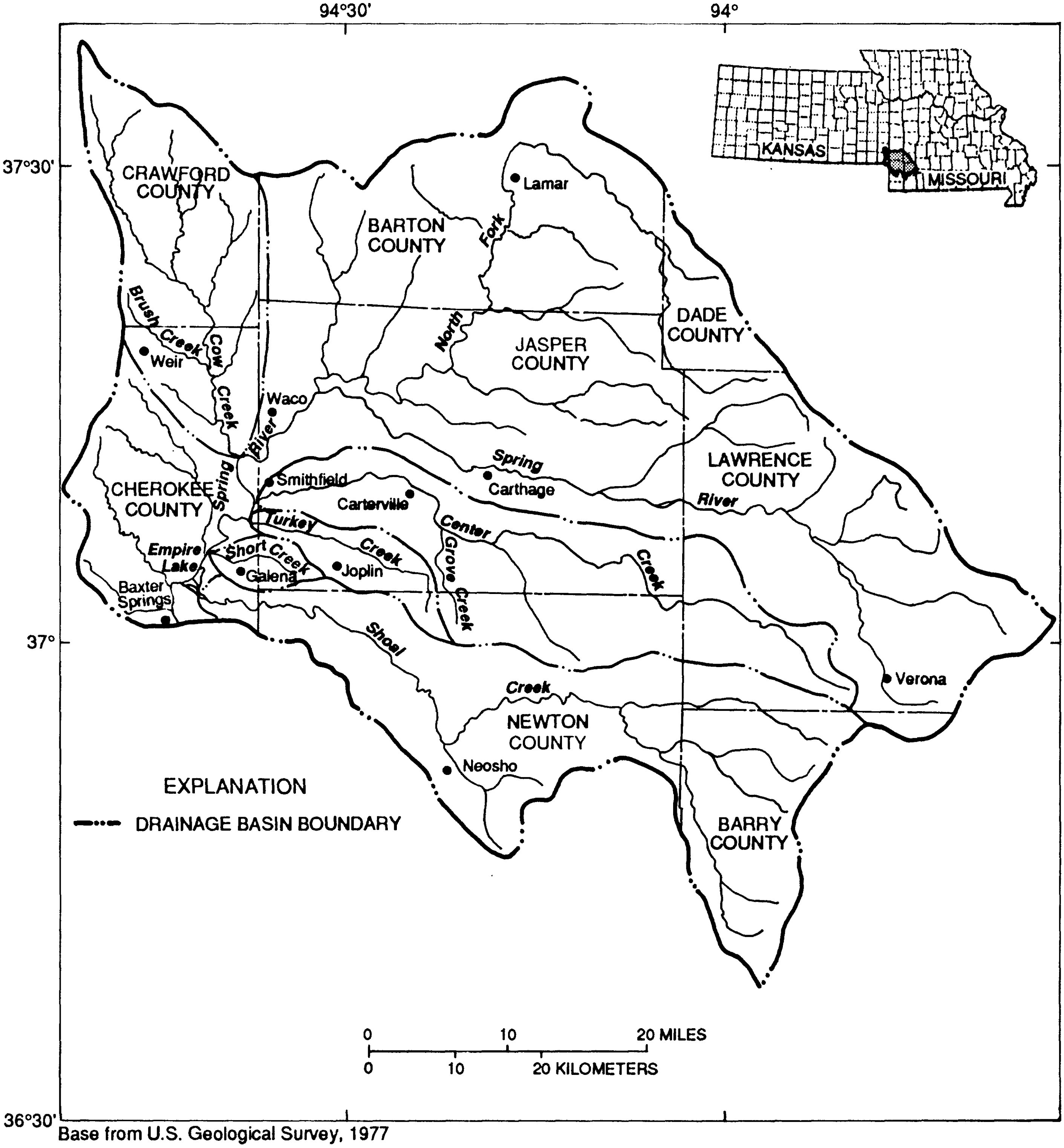
The principal objective of this report is to present a compilation and analyses of historical water-quality information and data for the Spring River basin in southwestern Missouri and southeastern Kansas (fig. 1). The compilation and analyses were done to:

1. Describe water-quality characteristics of the basin,

2. Determine baseline water-quality characteristics for the purpose of establishing NPDES permit limits, and

3. Detect water-quality trends in the basin.

Existing water-quality data, collected as part of long-term monitoring efforts by State and Federal agencies and from previous investigations by various governmental agencies, were compiled for the Spring River basin. To determine the suitability of the data for compilation and analysis, they were evaluated using statistical methods. Consideration also was given to sample collection methods, analytical methods, and laboratory quality control and quality assurance programs. Extensive



Base from U.S. Geological Survey, 1977

Figure 1.--The Spring River basin.

statistical analysis of the final data set was done to describe existing water-quality conditions in the basin, determine background and development-induced water-quality characteristics, and detect long-term trends of selected chemical constituents.

Descriptions of existing water-quality conditions were based on summary statistics, which indicate spatial variations in water quality; analysis of variance (ANOVA) and multiple-comparison tests, which detect significant differences between specific sampling sites in the basin; correlation analysis, which describes the statistical relation of various physical properties and chemical constituents to discharge; and calculation of median instantaneous loads, which can indicate relative effects of various subbasins on the Spring River.

Baseline water-quality characteristics were determined from evaluation of the summary statistics, particularly the median (50th percentile) concentrations of selected chemical constituents that coincide with instantaneous discharge measurements between the 25th and 75th percentiles and the 5th percentile or less. Constituent values and concentrations associated with discharges between the 25th and 75th percentiles are representative of average stream conditions. Those constituent values and concentrations associated with the 5th percentile or less are representative of stream base-flow conditions when much of the discharge originates from ground-water sources. By considering only constituent concentrations for this range of instantaneous discharge, a truer baseline can be determined because the possible dilution or loading effects of storm runoff will be minimized.

Trend analyses of selected chemical constituents were done using the Seasonal Kendall test (Hirsch and others, 1982; Crawford and others, 1983), which removes the effects of discharge and seasonality before testing for trends. Seasonal effects also were considered independently using ANOVA to detect significant seasonal differences in the data. Finally, a thorough search and review of pertinent literature provided information relating the results of the statistical analyses to natural basin characteristics that affect water quality or to development-induced water-quality problems.

Previous Investigations

Numerous reports on the Spring River basin area have been published by various State, Federal, and local governmental agencies. Reports pertinent to this study include statewide and region-specific water-quality reports. The interest generated by the basin primarily is because of the Tri-State lead-zinc district, which is almost wholly contained within the Spring River basin.

The Missouri Water Quality Management Plan (Missouri Department of Natural Resources, 1979a), a statewide report required by Section 208 of Public Law 92-500, identifies specific segments of streams affected by point and nonpoint sources of pollution and presents a strategy for controlling these sources of pollution to make improvements in the quality of the waters of the State. The Missouri DNR is responsible for ensuring that Section 208 planning is performed throughout the State in accordance with the Federal law. Areawide planning was initiated for regions identified as having specific problems because of severe point and nonpoint pollution. During the spring of 1975, parts of Jasper and Newton Counties (fig. 1) were designated for areawide planning because of nonpoint problems associated with abandoned lead-zinc mines.

The Ozark Gateway Council of Governments (OGCOG) was given responsibility for Section 208 planning in this region. Three reports were published by the OGCOG as part of the Section 208 planning. One of these was a study done by the USGS in cooperation with the OGCOG to locate sources of mine-related pollution and evaluate the effect of abandoned mines and tailings piles on ground and surface waters in the Joplin area (Barks, 1977). A second study lists alternative means of controlling the mine-related water-quality problems in Joplin area streams (Warner, 1977). In a final report (Stewart, 1980), the results of the two previous investigations were reviewed and summarized.

A document series, the Missouri Water Quality Basin Plans, was published in accordance with Section 303(e) of Public Law 92-500 by the Missouri DNR for each of the hydrological basins in the State. Each basin plan is updated biannually and was prepared "to serve as a management tool which would identify the basin's water-quality problems and set forth a remedial program to alleviate these problems" (Missouri Department of Natural Resources, 1979a, p. 121). The scope of these plans is limited to the development of point-source pollution abatement strategies. Volume 8 (Missouri Department of Natural Resources, 1984a) of the basin plan series covers the Spring River basin.

The water resources of the Missouri part of the study area were evaluated in three separate studies. The USGS, in cooperation with the Missouri Division of Geology and Land Survey (DGLS), appraised all sources of water in the Joplin area, regarding their potential for development and the effects of human activities on the system (Feder and others, 1969). Because of this study, the possible contamination of surface and ground waters by mine-related effluents and erosion of mine-mill waste areas was examined. A stream survey of the Elk, James, and Spring River basins, conducted by the Missouri Clean Water Commission during 1964 to 1965 in cooperation with the Missouri Department of Conservation and the Missouri DGLS, resulted in the publication of two reports (Dieffenbach and Ryck, 1976; Vineyard, 1974) and two supplemental appendices (Missouri Clean Water Commission and others, 1973, 1974). Data on the physical, chemical, and bacterial quality of surface waters, as well as the bottom-dwelling invertebrate communities, or benthos, were collected. An investigation of the trace-constituent content of the water resources of the Springfield and Joplin areas was done through a grant from the USGS's Water Resources Research program. A master's thesis (Garrison, 1974) and two reports (Proctor and others, 1973a, 1973b) were published.

In Kansas, interest in the Spring River basin is considerable because of the interstate nature of the Spring River and its primary tributaries (fig. 1). An assessment of the water resources in the Kansas part of the study area (Spruill, 1987) was done by the USGS, in cooperation with the Kansas Department of Health and Environment (KDHE). The water-quality characteristics of ground and surface waters and the type and extent of chemical contamination were defined, and the hydrology and geochemistry of the area were described. Chemical and biological data, collected in the Spring River basin by the KDHE (Kansas Department of Health and Environment, 1980) to investigate the effects of lead-zinc mine drainage on the water quality, were to be used to initiate future water-quality studies and for water resources planning in the basin. Statistical summaries of water-quality data for streams and strip pits in the coal-mined northwestern part of the basin also have been published (Bevans and Diaz, 1980; Pope and Diaz, 1982).

Two water-quality studies have been conducted because of the proposed construction of a reservoir on Center Creek by the U.S. Army Corps of Engineers (U.S. Army Corps of Engineers, 1970) in the Spring River basin. The USGS, in cooperation with the U.S. Army Corps of Engineers, assessed the water quality in the proposed project area (Barks and Berkas, 1979) and the effects of the proposed reservoir on water resources in lower Center Creek basin (Berkas and Barks, 1980).

DESCRIPTION OF THE SPRING RIVER BASIN

The Spring River basin drains approximately 2,090 mi^2 (square miles) of southwestern Missouri and 530 mi^2 of southeastern Kansas, with the remainder of the basin in northeastern Oklahoma where the Spring River is a tributary to the Grand River. The study area (fig. 1) includes all of Jasper County and parts of Barry, Barton, Dade, Lawrence, and Newton Counties in Missouri and parts of Cherokee and Crawford Counties in Kansas. Principal tributaries to the Spring River originating in the Missouri part of the study area include the North Fork Spring River and Center, Turkey, Short, and Shoal Creeks. With the exception of the North Fork Spring River, the tributaries are typical Ozark-type streams characterized by alternating pools and riffles, and mixed sand, gravel, and boulder bottoms. Base flows are sustained during dry weather by springs originating in the headwater areas. Flow is in a westerly direction to the junction with the Spring River just inside the Kansas state line. In Kansas, Cow Creek, and its tributary, Brush Creek, originate in the northwestern part of the basin and flow in a southeasterly direction. Both creeks are typical plains-type streams, as is the North Fork Spring River, characterized by few riffles and low velocity, uniform flow and mixed mud, silt, gravel, boulder, and bedrock bottoms. Base flows are poorly sustained during dry weather. Physical and hydrologic characteristics of the Spring River and principal tributaries are given in table 1.

Development of lead and zinc resources in the basin began about 1850 in Missouri and spread into southeastern Kansas and northwestern Oklahoma. The area became known as the Tri-State District. Production of lead and zinc concentrates in Missouri peaked between 1900 and 1910 and ceased by 1957 after most of the rich ores had been depleted. The peak production year for Kansas was 1926. By the early 1960's major production ended and the last mine in Kansas, located in the Picher field just west of the study area, closed during 1970. From 1850 to 1970, Missouri produced about 40 percent and Kansas produced about 24 percent of the approximate 460 million tons of lead and zinc ores mined in the Tri-State District (Spruill, 1987).

The location of major lead and zinc mines in the study area are shown in figure 2. Center Creek drains about 70 percent, Turkey Creek drains about 18 percent, and Short Creek drains about 5 percent of the lead-zinc mined area in Missouri (Barks, 1977). Tailings piles, or wastes from the milling operations located near the underground mines, are deposited throughout these basins (table 2). About 1.0 percent of the land surface in the Center Creek basin, 2.0 percent of the land surface in the Turkey Creek basin, and 1.6 percent of the land surface in the Short Creek basin is or has been covered with tailings. Stewart (1980) estimated that 80 percent of this material has been removed, leaving approximately 8,000,000 yd^3 (cubic yards) of waste products in the study area (McFarland and Brown, 1983). The tailings are an important economic asset and are sold for railroad ballast, road metal, asphalt mixes, domestic concrete aggregate, roofing granules, fill material, and rip-rap.

In addition to lead and zinc production, other mineral resources have been developed in the basin. Marble for building facades has been quarried in the area since the last century. The principal marble producing area is near Carthage, Missouri (fig. 1). Limestone and dolomite quarries are located in all counties in the basin. From the late 1800's to about 1969, large parts of the Cow Creek basin were strip mined for the underlying coal beds (fig. 2). Substantial coal reserves are reported to be present in Jasper and Barton Counties in Missouri (U.S. Army Corps of Engineers, 1970).

The climate in the Spring River basin is characterized as continental, with moderate winters and long, warm summers. The mean monthly temperature during January is between 30° and 40 °F (degrees Fahrenheit) and during August is between 80° and 90 °F; the mean annual temperature is 58 °F. The basin receives approximately 40 in. (inches) of rain annually and 12 to 16 in. of snow. Peak rainfall and 60 percent of all floods occur in the spring months of April, May, and June (Gann and others, 1974). Minimum rainfall occurs in late fall and winter, which also is when floods are least likely (Missouri Department of Natural Resources, 1986a). It is estimated that approximately 10 in., or 25 percent of the average annual precipitation, is available to streamflow and ground-water recharge, and the remaining 75 percent is lost, primarily to evapotranspiration.

Joplin, Missouri [population 38,900 (Missouri Department of Natural Resources, 1986a)], located mostly within the Turkey and Short Creek basins (fig. 1), is the largest urban center in the basin. Joplin and Neosho, Missouri (fig. 1), are the only communities in the basin that derive their public-water supply from a surface-water source, Shoal Creek.

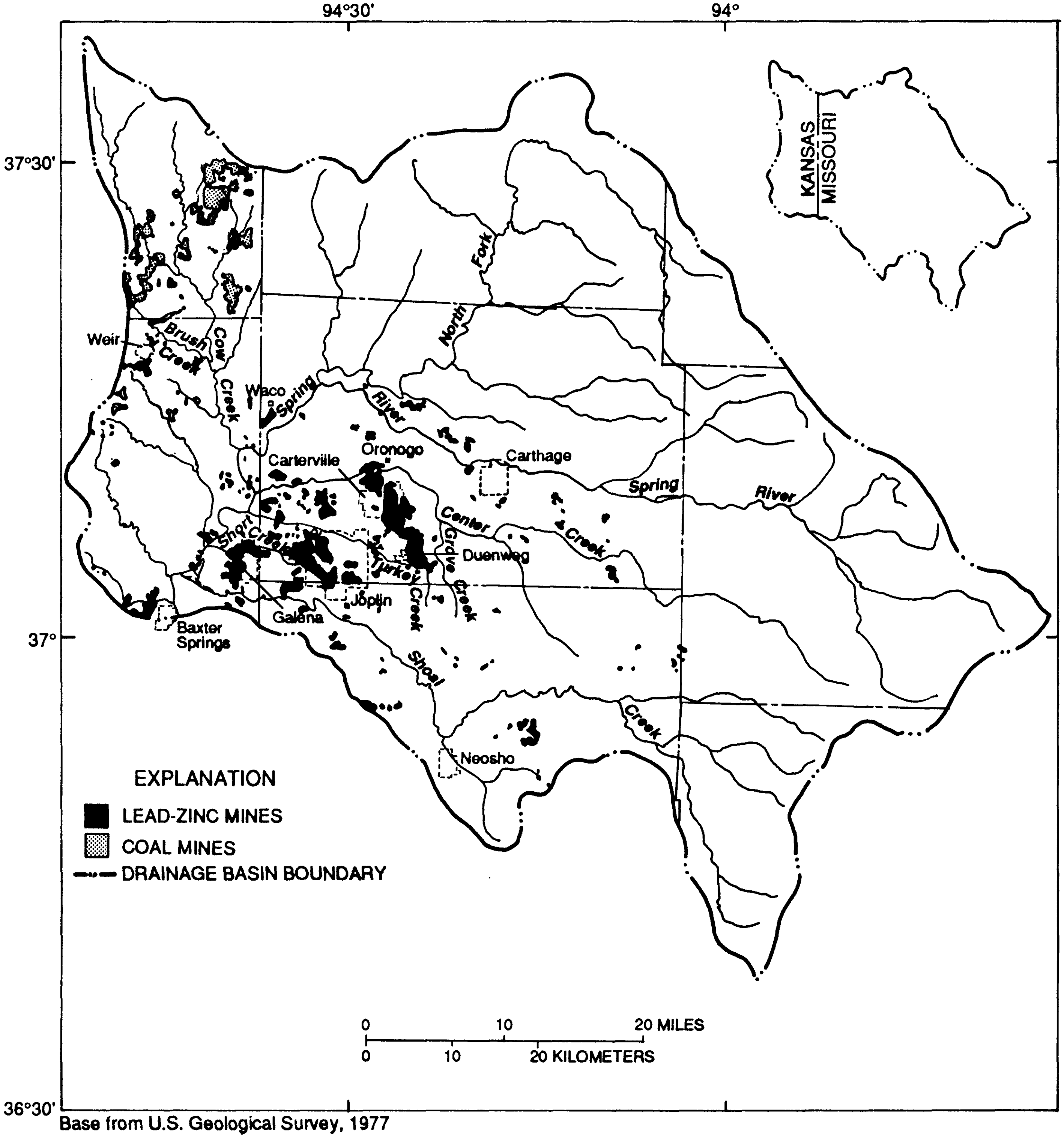
Land use in the basin primarily is agricultural, both row crop and pastureland, and hardwood forest (table 3; Missouri Department of Natural Resources, 1984a; Mike Butler, Kansas Department of Health and Environment, oral commun., 1989). Agricultural land use increases in a north and westerly direction, with approximately 85 percent of the North Fork Spring River basin in row crop and pastureland, and only 15 percent in hardwood forest. Forestland increases to around 50 percent in the central and southern part of the basin, with the exception of the Short and Turkey Creek basins, which are 50 percent urbanized.

Table 1.--*Physical and hydrologic characteristics of the Spring River and principal tributaries*

[Data from Vineyard (1974), Barks (1977), Bevans and Diaz (1980), Kansas Department of Health and Environment (1980), and Missouri Department of Natural Resources (1984a); mi^2, square mile; mi, mile; ft^3/s, cubic foot per second; --, no data]

Stream	Drainage area (mi^2)			Length (mi)			Discharge (ft^3/s)[a]
	Missouri	Kansas	Total	Missouri	Kansas	Total	
North Fork Spring River	709	0	709	63	0	63	--
Center Creek	302	0	302	54	0	54	122
Turkey Creek	45	1.0	46	17	1.0	18	30
Short Creek	8.0	10	18	5.7	4.3	10	3.8
Shoal Creek	490	12	502	62	7.0	69	257
Cow Creek	0	251	251	0	40	40	76
Brush Creek	0	30	30	0	13	13	1.9
Spring River and other tributaries	538	226	764	88	21	109	806

[a] Median of instantaneous discharges measured at time of sample collection at most downstream water-quality sampling stations in the basin (fig. 4).



Base from U.S. Geological Survey, 1977

Figure 2.--Location of lead-zinc and coal mines in the Spring River basin.

Table 2.--*Volume and area of tailings piles located in the Center, Turkey, and Short Creek basins*

[Data from Barks (1977); yd^3, cubic yard]

Stream	Original tailings volume (yd^3)	Tailings area (acres)	Percentage of total drainage area
Center Creek	38,000,000	1,970	1.0
Turkey Creek	10,000,000	600	2.0
Short Creek	2,900,000	185	1.6

Table 3.--*Land use in the Spring River basin*

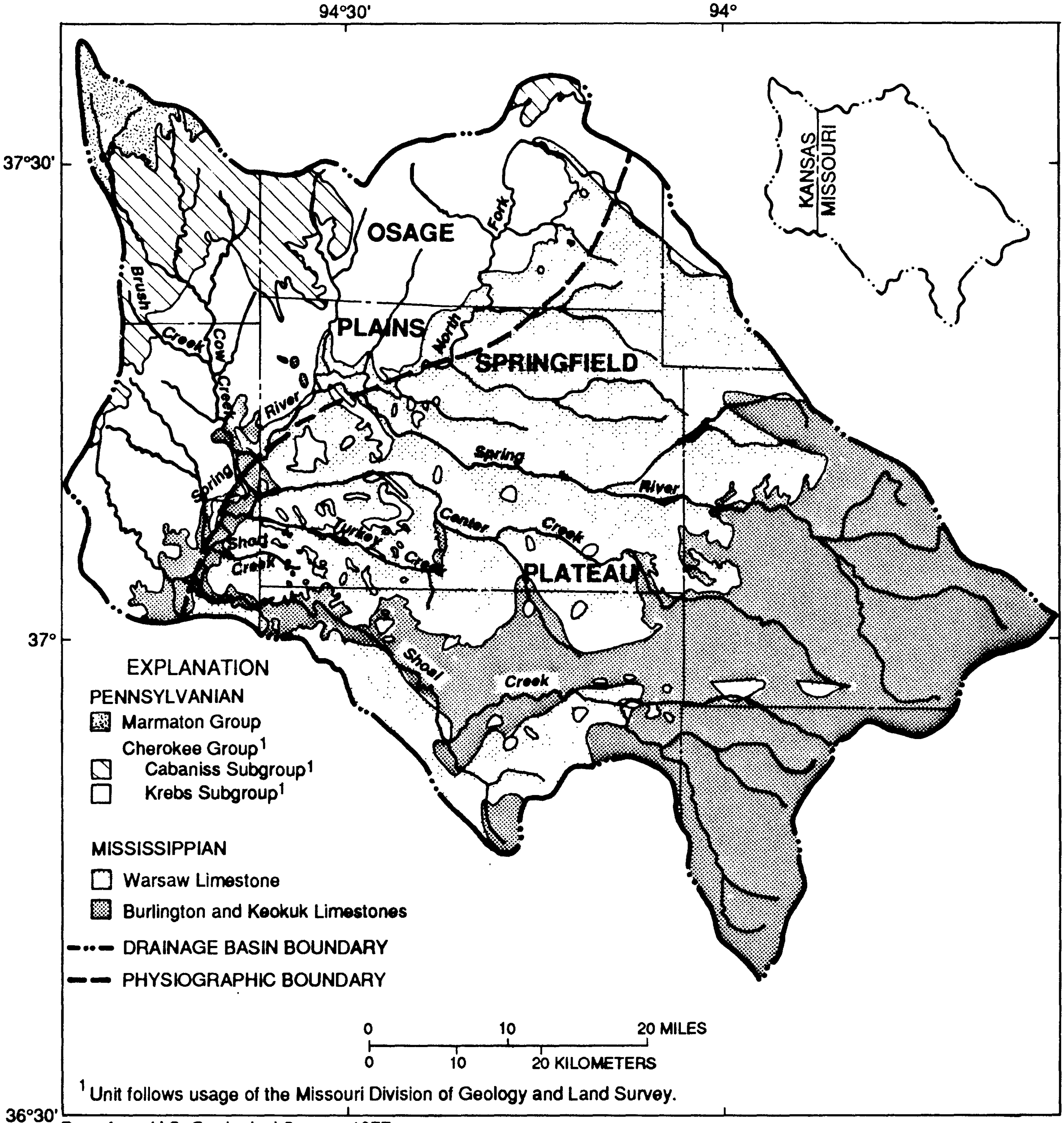
	Land use category, in percent			
Stream	Agricultural	Forest	Urban	Mining activities
North Fork Spring River	85	15	a	b
Center Creek	50	45	a	5
Turkey and Short Creeks	24	24	50	2
Shoal Creek	55	45	a	b
Spring River and other tributaries in Missouri	70	30	a	b
Spring River and other tributaries in Kansas	84	5	6	5

[a] No major urban areas.

[b] No major mining activities.

The Spring River basin lies on the northwestern flank of the Ozark Uplift. Areas east of the Spring River lie within the Springfield Plateau section of the Ozark Plateaus physiographic province (fig. 3). Areas west and north of the Spring River lie within the Osage Plains section of the Central Lowlands physiographic province (Fenneman, 1938). The topography is one of gently rolling uplands dissected by early-mature stream valleys trending into prairie to the north and west. Elevations range from near 800 ft (feet) above sea level in the west along the Spring River near Baxter Springs, Kansas, to more than 1,500 ft in the southeastern part of the basin. Major stream valleys commonly are 100 to 150 ft from ridgetop to valley floor with generally greater relief towards the southeast. Regional dips are shallow towards the northwest, between 15 and 20 ft/mi (feet per mile). A series of gentle parallel folds trending southeast to northwest are present within the basin. The most intensely mineralized areas, such as the Oronogo-Duenweg belt, are associated with the syncline part of these folds (Brichta, 1960).

The principal rocks in the study area are of Paleozoic (Mississippian and Pennsylvanian) age. The thickness of sedimentary rocks ranges from less than 1,200 ft in areas of granitic basement-rock highs to more than 2,000 ft towards the southwest (Spruill, 1987). Outcrops in the east predominately are weathered Burlington and Keokuk Limestones of Mississippian age (fig. 3). These limestones are the primary host units for the extensive lead and zinc mineralization in the region. Many outliers of Pennsylvanian rocks are present throughout the east as paleo-sink and valley fills. Streams in this



Base from U.S. Geological Survey, 1977

Figure 3.--Physiography and general geology of the Spring River basin.

area have well-sustained base flows from springs emerging primarily from the Burlington and Keokuk Limestones. The Burlington and Keokuk Limestones are undivided in the basin, as they are throughout most of the State. The lower limestone, the Burlington Limestone, is a light-colored, extremely coarse crystalline, fossiliferous limestone. The lower part of the Burlington is quarried for agricultural lime, road metal, and lime manufacture. Upper parts of the Burlington are moderately cherty and are less desirable for commercial purposes. The overlying Keokuk Limestone is a bluish-gray medium to fine crystalline, medium-bedded limestone that contains abundant chert in layers and as nodules.

Mineralization in the Tri-State District is restricted almost exclusively to localized brecciated areas within the Keokuk Limestone and overlying Warsaw Limestone of Mississippian age (fig. 3; Brockie and others, 1968). Only two minerals, galena (PbS) and sphalerite (ZnS), were commercially mined in the district. Other associated minerals include chalcopyrite, pyrite, marcasite, calcite, dolomite, and quartz. In the eastern part of the district, shallow oxidized deposits consisting of smithsonite ($ZnCO_3$), hemimorphite ($Zn_4Si_2O_7 \cdot H_2O$), and cerussite ($PbCO_3$) were mined during the earlier years of the mining era but were not economically significant.

West of the Spring River and in the northern part of the basin, including the North Fork Spring River, the principal exposed rocks are sandstones and shales of the Pennsylvanian Cherokee Group[1] (fig. 3). In the northern part of the basin, isolated strip mining of thin coal beds within the Krebs Subgroup[1] of the Cherokee Group has occurred. Extensive strip mining of coal has occurred in the northwestern part of the study area within the Cow Creek basin (fig. 2). Streams in the western part of the study area typically are ephemeral as Pennsylvanian rocks contribute little to base flows because of their relatively impervious nature (Spruill, 1987).

Three major soil associations are present within the study area (U.S. Soil Conservation Service, 1972). The Bodine-Baxter association coincides with the Springfield Plateau and predominately is in the east. These soils are composed of deep, gently sloping soils with clayey subsoils and cherty soils derived from the underlying cherty limestones of Mississippian age. The Parsons-Dennis association is a claypan primarily formed from weathered shales of Pennsylvanian age and generally coincides with the Osage Plains in the west. The Dennis-Bates association is composed of deep, gently sloping soils with clayey and loamy subsoils derived from Pennsylvanian shales and sandstones and is in the northwestern part of the study area.

Because the base flows of Center Creek, Shoal Creek, and the Spring River are sustained by springs originating in Mississippian limestones, the waters in these basins, where the chemical quality has not been affected by waste discharges, are a calcium-bicarbonate type. The dissolved solids concentrations ranged from about 130 to 200 mg/L (milligrams per liter; Feder and others, 1969), with the larger concentrations occurring during low flow. The water is characterized as a hard, moderately mineralized type and, other than turbidity during high flows, is relatively clear most of the time. These streams provide ideal aquatic habitat and generally support a large, diverse population of clean-water benthic organisms. An average calcium to magnesium ratio of 10:1 milliequivalents per liter reflects the calcium carbonate mineralogy of the limestone bedrock in these basins. This is in contrast to a calcium to magnesium ratio of approximately 1:1 (Hem, 1985) detected in surface waters on the Ozark Plateaus where the bedrock formations are dolomite (calcium-magnesium carbonate) of Cambrian and Ordovician age.

Although the dissolved solids and chemical character of the unaffected surface waters in Center Creek, Shoal Creek, and the Spring River are similar, slight differences do exist. The results of specific conductance measurements made on relatively unaffected segments during seepage runs on each

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

stream (Feder and others, 1969) indicated that the dissolved solids concentration increased slightly from Shoal Creek to Center Creek to Spring River. These differences largely were because of the time the water is underground before it is discharged to the stream by springs or seeps. Based on the large number of springs and the higher base flow in Shoal Creek and the limited number of springs and low base flow in much of the Spring River drainage (Feder and others, 1969), it is evident that there is more extensive solution development in the Shoal Creek basin.

Another factor contributing to localized variations in the chemical character of the water in these basins is mineralized solution features in the Mississippian limestones. Water that has flowed through sulfide-mineralized areas before being discharged to the surface will have a larger dissolved solids concentration. This increase principally is because of calcium and sulfate, but magnesium concentrations may increase if dolomitization occurred during the mineralization process. Iron and zinc also may be solubilized, but only small quantities remain in solution.

The North Fork Spring River, as well as streams on the west side of the Spring River in Kansas, are plains-type streams underlain by bedrock of relatively impervious Pennsylvanian shales. Flow is not sustained by ground-water inflow during the dry seasons, and it is not uncommon for the streams to go completely dry. Although the dissolved solids concentration is in the same range as the Ozark-type streams in the area, sulfate is more predominant because of sulfide minerals in the Pennsylvanian bedrock. The water is a hard, moderately mineralized calcium-sulfate-bicarbonate type and generally is turbid because of suspended clay particles. The turbidity, mud bands, slower velocities, and lack of riffles cause an overall decrease in the diversity and number of clean-water benthic organisms and provide a less-than-ideal aquatic habitat.

WATER-QUALITY PROBLEMS ON THE SPRING RIVER AND TRIBUTARIES

During the mining era, the ore-bearing zones were, for the most part, below the natural ground-water level. Flooding of the mines was a constant problem, and the mines had to be pumped continually to keep the water levels below the mine workings. Dewatering the mines exposed sulfide minerals to oxygen from the circulation of atmospheric air and oxygenated water from surface sources. Oxidation of insoluble sulfide minerals resulted in the formation of sulfuric acid and a corresponding rise in the acidity of the mine water. Other minerals, including all of the metallic ores, were readily solubilized in waters with pH values that may have been as small as 2.5 to 3.0.

Acid-mine water was pumped directly into streams in the Tri-State District, resulting in a degradation of water quality. Gibson (1972, p. 85), referring to water problems during the intermediate mining period between the years 1900 and 1930, states that "Water high in iron sulfide discharged into streams, polluted the waters, destroyed wildlife and vegetation, and produced much litigation." Smith (1905, p. 77) reported that "a number of streams of the Joplin district....have been polluted to a greater or less extent by water pumped from the mines." Haworth (1904, p. 94) noted that water from Shoal Creek, which had been used for domestic-water supplies in the Galena area, became "perceptibly contaminated with iron sulphate and zinc sulphate, making it somewhat objectionable." Dewatering of the mine workings ceased when the mining operations ceased in the 1960's, and the mine shafts subsequently filled with water. Although mine-related water-quality problems continue to be of great concern in the Spring River basin, the water quality also has been affected by industrial and municipal development in the basin.

Center Creek

Extensive documentation is available that describes the water-quality problems in the Center Creek basin. Center Creek is a classified stream (Missouri Department of Natural Resources, 1984a) designated for aquatic life protection, fishing, livestock and wildlife watering, boating, irrigation, and whole-body-contact recreation (swimming). The Oronogo-Duenweg mining belt (fig. 2), which is about 2 mi (miles) wide and 10 mi long, is located almost entirely in the basin, with the exception of the southwestern edge that is in the Turkey Creek basin. Mine-related discharges have affected the lower 18 river mi of Center Creek from Carterville to the mouth as evidenced by large concentrations of calcium, sulfate, dissolved solids, and zinc. During base-flow conditions, contamination results from discharges from artesian flowing mine shafts in the Carterville-Oronogo area and subsurface seepage of mine water into Center Creek near Oronogo. During high-flow conditions, seepage and runoff from the tailings areas contribute to the contamination (Barks, 1977).

Nitrogen fertilizers and explosives are manufactured at three industrial complexes located in the Center Creek basin, two near Grove Creek, a small tributary (fig. 1), and one near Center Creek two river mi downstream from Grove Creek. Wastes containing large concentrations of nitrate and ammonia are discharged into Grove Creek and Center Creek, and occasionally, the ammonia standard is exceeded in Center Creek downstream from Grove Creek (Missouri Department of Natural Resources, 1984a), particularly during low-flow conditions. The large concentrations of nitrate and ammonia, as well as phosphorus and fluoride, also are attributable to spills, leaks, and stack emissions, which enter the surface-water system by shallow ground water and surface runoff and to surface runoff from phospho-gypsum piles located near Grove Creek. Before 1968, mine water, which was used by one of the industrial plants during extended droughts, was discharged to Grove Creek, substantially augmenting the base flow of Grove Creek and Center Creek downstream from Grove Creek (Feder and others, 1969). This may have contributed to the mine-related water-quality problems between Grove Creek and Carterville.

Biological and chemical surveys done on Center Creek during 1961 (Academy of Natural Sciences of Philadelphia, 1961), 1964 to 1965 (Vineyard, 1974; Dieffenbach and Ryck, 1976), 1969, 1970, 1971, (Missouri Department of Natural Resources, 1970a, 1970b, 1971), 1974 (Howland, 1974), 1978 to 1979 (Kansas Department of Health and Environment, 1980), and 1983 to 1985 (Academy of Natural Science of Philadelphia, 1986) clearly indicate the effects these various sources of contamination have on the water quality. All surveys indicate that the water quality of Center Creek upstream from Grove Creek is good, both in terms of chemical quality and the density, diversity, and composition of benthic invertebrates. However, the chemical quality and the benthic invertebrate population deteriorate rapidly downstream from Grove Creek, as a result of municipal, industrial, and mine-related point and nonpoint source discharges. The fecal coliform, fluoride, ammonia, and zinc standards frequently are exceeded in this part of the stream. Improvements were detected in the chemical and biological quality in Center Creek immediately downstream from Grove Creek during the 1974 survey and again during the 1983 to 1985 survey because of process elimination or modifications, improvements in housekeeping practices, and recycling of waste discharges by the industries located in the vicinity. No improvements were seen in the benthic invertebrate population from Carterville, Missouri, to the mouth of Center Creek, even as late as the 1978 to 1979 survey, which most likely can be attributed to the frequently large dissolved zinc concentrations in this segment (Howland, 1974).

Turkey Creek

Turkey Creek (fig. 1) has been described as Missouri's most contaminated interstate stream (Vineyard, 1974). Two secondary wastewater-treatment facilities located near the creek, the Lone Elm and Turkey Creek Wastewater Treatment Plants, process municipal and industrial wastes from Joplin. One small spring is located in the upper part of the basin, and during dry weather, most of the base flow is treated wastewater from the plants. The reach of the stream below the wastewater-treatment facilities to the Spring River often has small dissolved oxygen concentrations, large concentrations of nutrients, deposited solids, excessive algae, floating scum, and large fecal coliform counts. The entire length of Turkey Creek that has perennial flow is affected by water discharging from abandoned mines and tailings piles (fig. 2), but because of the numerous alterations and contributions to the natural flow, it is difficult to determine the specific sources of contamination from the mining area. As in Center Creek, large concentrations of calcium, sulfate, dissolved solids, and zinc are caused by mine-water discharge and seepage during low flow and are sustained by tailings area runoff during high flow (Barks, 1977). Contributing to the water-quality problems are metal-plating and organic wastes discharged to Turkey Creek by industrial plants located in the vicinity (Missouri Department of Natural Resources, 1984a).

Biological and chemical surveys were done on Turkey Creek during 1958 to 1959 (Neel, 1961), 1964 to 1965 (Vineyard, 1974; Dieffenbach and Ryck, 1976), 1969 (Missouri Department of Natural Resources, 1970b), and 1978 to 1979 (Kansas Department of Health and Environment, 1980). Results of all four surveys indicate that the water quality in Turkey Creek is poor. A small density and nondiverse benthic community consisted almost entirely of pollution-tolerant varieties, which is expected in a stream affected by lead-zinc mining and where flow predominantly is secondary wastewater-treatment plant effluent.

Short Creek

Water-quality problems on Short Creek, a small intermittent stream, are caused by a combination of mine-water seepage, seepage from a 40-acre phospho-gypsum pile, and runoff from an abandoned lead and zinc smelter. Seepage from the phospho-gypsum pile has a small pH and large concentrations of sulfate, fluoride, phosphorus, and trace constituents, particularly cadmium and zinc. Downstream from the phospho-gypsum pile, concentrations of sulfate, cadmium, and zinc continue to increase, indicating that mine-water seepage also is an important source of these constituents (Farmers Chemical Company, 1985). Spruill (1987, p. 38) states that of Turkey, Center, and Short Creeks, "Short Creek exhibited the most severe water-quality effects of mine drainage." Biological and chemical surveys done on Short Creek during 1969 (Missouri Department of Natural Resources, 1970b) and 1978 to 1979 (Kansas Department of Health and Environment, 1980) substantiate this statement. The creek is almost totally devoid of aquatic life with the exception of dense growths of a trace-constituent tolerant species of filamentous algae (Kansas Department of Health and Environment, 1980). This algae was growing along the entire length of Short Creek downstream from the phospho-gypsum pile and undoubtedly is the result of large nutrient concentrations.

Shoal Creek

Shoal Creek, the most southern major tributary in the Spring River basin (fig. 1), has seven identified beneficial uses, including irrigation of croplands, livestock and wildlife watering, protection of aquatic life and fishing, coldwater sport fishery, whole-body-contact recreation, drinking-water supply, and limited-water-contact recreation (canoeing, boating; Missouri Department of Natural Resources, 1984a). Shoal Creek, which is impounded, along with the Spring River, approximately 1.5 river mi upstream from its junction to form Empire Lake (fig. 1), is the only true Ozarkian stream in Kansas (Kansas Department of Health and Environment, 1980). Rolling Ozark hills, picturesque mill dams, bedrock riffles, gently eddying pools, and long shaded reaches characterize this scenic resource. Grand Falls, located on Shoal Creek south of Joplin, has been described as having the greatest height and width of any continuously flowing falls in Missouri (Beveridge, 1980). The results of chemical and biological surveys done during 1958 to 1959 (Neel, 1961), 1964 to 1965 (Vineyard, 1974; Dieffenbach and Ryck, 1976), 1969 (Missouri Department of Natural Resources, 1970b), and 1978 to 1979 (Kansas Department of Health and Environment, 1980) indicate that the water quality of Shoal Creek is excellent. A dense, diverse benthic invertebrate population composed of at least 40 percent clean-water types was supported at most sampling locations.

Small reaches of the stream have been affected by the discharge of treated municipal wastes, particularly from Neosho and Joplin, as indicated by algal growth, sludge deposits, large fecal coliform counts, and the absence of pollution-intolerant benthic invertebrate species. Concern was expressed about the water quality in Shoal Creek because of waste effluents entering the creek upstream from Joplin, the effect of individual sewage-disposal systems, and the effluent from the Joplin Shoal Creek Wastewater Treatment Plant in a report by the Missouri DNR (1970c). At that time, treated sewage from the Shoal Creek plant was discharged into the reservoir upstream from Grand Falls, only 200 to 300 ft downstream from the Joplin water-supply intake. Fecal coliform counts in this area frequently exceeded the water-quality standard of 200 colonies per 100 mL (milliliters) for a stream used for whole-body-contact recreation. Effluents from the new Joplin Shoal Creek plant, which went into operation in March 1987, are discharged downstream from Grand Falls, near the Missouri-Kansas state line. Similar problems were reported for the Neosho Wastewater Treatment Plant, which was closed in September 1975, because the effluent was not of the desired quality (Sarai, 1976). Shoal Creek fully recovered from the effects of the wastewater discharge within one year after the plant ceased operations. A new Neosho wastewater-treatment plant is now operating on Shoal Creek. The effluent is being carefully monitored to ensure that aquatic life and the drinking-water supply are protected.

Spring River

The Spring River (fig. 1), upstream from its junction with the North Fork Spring River, is an Ozark-type stream. Municipal and industrial discharges, particularly in the vicinity of Carthage, affect reaches of the stream, as indicated by a decrease in the density, diversity, and number of clean-water type benthic invertebrates (Vineyard, 1974; Dieffenbach and Ryck, 1976). Near Verona, a chemical plant produced substantial quantities of dioxin as a by-product of their operation. Barks and others (1983) indicated that dioxin is present in soils, streambed sediments, and fish near Verona. Residents of the area were advised to limit consumption of fish from the Spring River (Missouri Department of Natural Resources, written commun., 1982) after results of a U.S. Environmental Protection Agency (USEPA) investigation detected concentrations as large as 18 ppt (parts per trillion) in fish fillet samples and as much as 52 ppt in whole-fish samples. The U.S. Food and Drug Administration dioxin advisory suggests decreased consumption when dioxin concentrations in fish fillets range from 25 to 50 ppt and no consumption when dioxin concentrations in fish fillets are greater than 50 ppt. More recent fish-flesh sampling indicates that dioxin concentrations are decreasing (Missouri Department of Natural Resources, 1984a).

Downstream from the North Fork, the Spring River is typical of an eastern Kansas plains river. This segment of the river is broader, more turbid, has less relief, and slower velocities, which all contribute to problems with sediment deposition. Chemical and biological samples collected on the Spring River near Waco, Missouri (fig. 1; Vineyard, 1974; Dieffenbach and Ryck, 1976; Missouri Department of Natural Resources, 1970b; Kansas Department of Health and Environment, 1980), indicate that the water quality here generally is good. However, even though the benthic invertebrate population consisted of at least 44 percent clean-water types, the diversity was small and the community structure was different from that at other polluted or unpolluted stations on the upper Spring River. This probably is because of habitat differences caused by slower current and greater turbidity.

After the Spring River crosses the Missouri-Kansas state line, it is affected by surface coal-mine drainage, lead-zinc mine drainage, and municipal and industrial discharges that enter the river from Cow, Brush, Center, Turkey, and Short Creeks. According to a stream survey conducted during 1978 to 1979 (Kansas Department of Health and Environment, 1980), the benthic invertebrate population was diverse and composed of 46 percent clean-water types downstream from the junction of Center Creek, indicating that the river adequately assimilates the surface coal-mine drainage and municipal wastes from Brush and Cow Creeks and the lead-zinc mine drainage from Center Creek. Downstream from Turkey and Short Creeks, however, this is not the case. Empire Lake possibly is a sink for both nutrients and trace constituents entering the river from Turkey and Short Creeks, and the large phosphorus loads from Short Creek may contribute to the continual aquatic weed problem on the lake. Spruill (1987) noted that concentrations of sulfate, manganese, and zinc increased in Empire Lake with respect to upstream stations on the Spring River. Concentrations of these constituents were smaller in samples analyzed from the Spring River near Baxter Springs, Kansas, downstream from Empire Lake, indicating either chemical transformations within the lake or dilution by Shoal Creek. Results of the stream survey indicate that the water quality does improve at Baxter Springs, Kansas. However, the benthic invertebrate population, which consisted of 49 percent clean-water organisms, exhibited a significant decrease in diversity and the pollution sensitive mayfly-stonefly group. This was attributed to chronic exposure to zinc.

SELECTION OF DATA FOR WATER-QUALITY CHARACTERIZATION

Extensive water-quality data have been collected in the Spring River basin from the early 1960's to September 1987 by various State and Federal agencies. Sources of data for this study include the USGS in Missouri and Kansas, KDHE, the Missouri DNR-DEQ, and the USEPA. Three types of data were compiled: (1) synoptic, (2) ancillary, and (3) long-term monitoring.

Synoptic sampling stations are scattered throughout the basin, but for the most part, synoptic data were collected for special projects and only one or two samples per site were collected. These data were not used in the final project data set but can be obtained from the office of the USGS in Rolla, Missouri.

Data were collected at the ancillary sampling stations (fig. 4) on a regular basis, but only for a short or irregular period of time. Insufficient data exist for trend analysis, but the available data can be used to support the results of other statistical tests. Ancillary sites are located on Cow (no. 2), Brush (no. 3), and Short Creeks (no. 7). The samples were collected by the USGS and the analyses done by either the USGS National Water-Quality Laboratory in Denver, Colorado, or a USGS-approved cooperator laboratory.

Six long-term monitoring stations (fig. 4) have been operated in the Spring River basin since the 1960's by the USGS or simultaneously by the USGS and the KDHE on Center Creek (nos. 4 and 5), Turkey Creek (no. 6), Shoal Creek (no. 8), and the Spring River (nos. 1 and 9). Samples were collected by both agencies and analyzed by a USGS or USGS-approved cooperator laboratory or by the KDHE laboratory.

Sufficient data exist at these six locations for a thorough statistical analysis, including trend analysis. Information about the long-term monitoring and ancillary stations is listed in table 4. All data from the ancillary and long-term monitoring stations have been entered into computer files and are available upon request from the USGS in Rolla, Missouri.

The locations of the long-term monitoring and ancillary stations (fig. 4) were chosen to monitor water-quality conditions in the Spring River basin. Cow Creek near Weir, Kansas (no. 2), and Brush Creek near Weir, Kansas (no. 3), are both downstream from surface coal mines. Turkey Creek near Joplin, Missouri (no. 6), is downstream from Joplin's Lone Elm and Turkey Creek Wastewater Treatment Plants and most of the lead-zinc mines in the Turkey Creek basin. Short Creek at Galena, Kansas (no. 7), is downstream from the phospho-gypsum pile, an abandoned lead and zinc smelter, and most of the lead-zinc mines in the Short Creek basin. Shoal Creek near Galena, Kansas (no. 8), is downstream from Neosho and Joplin. Two sampling stations are located on both Center Creek and the Spring River. Center Creek near Carterville, Missouri (no. 4), is downstream from Grove Creek but is on the eastern edge of the Oronogo-Duenweg mining belt (fig. 2) and is minimally affected by lead-zinc mine drainage. Center Creek near Smithfield, Missouri (no. 5), is downstream from Grove Creek and the mining belt and is affected by both. The Spring River near Waco, Missouri (no. 1), is upstream from all the major tributaries, with the exception of the North Fork Spring River; the Spring River near Baxter Springs, Kansas (no. 9), is downstream from all the major tributaries. The water at this station

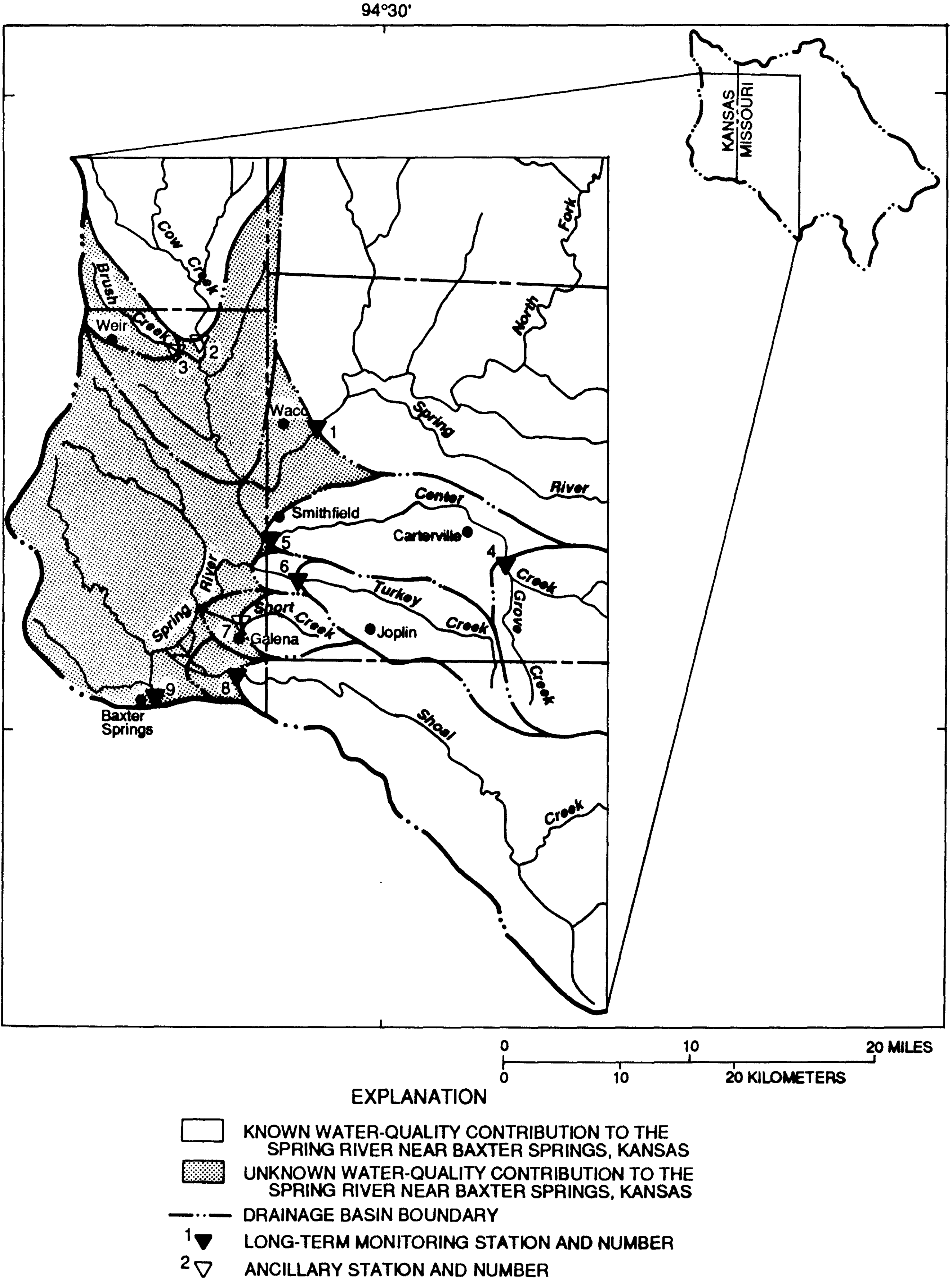

Figure 4.--Areas of known and unknown water-quality contribution to the Spring River near Baxter Springs, Kansas, and location of water-quality sampling stations in the Spring River basin.

Table 4.--*Long-term monitoring and ancillary stations*

[DDMMSS, degrees, minutes, seconds; mi^2, square miles; USGS, U.S. Geological Survey; KDHE, Kansas Department of Health and Environment; e, estimated]

Map number (fig. 4)	Station name	U.S. Geological Survey station identification number	Latitude and longitude (DDMMSS)	County	Drainage area (mi^2)	Sample collection and analysis[a]
1	Spring River near Waco, Missouri	07186000	37° 14' 44" 94° 33' 58"	Jasper	1,164	USGS KDHE
2	Cow Creek near Weir, Kansas	07186040	37° 18' 35" 94° 40' 48"	Cherokee	170	USGS
3	Brush Creek near Weir, Kansas	07186050	37° 18' 32" 94° 42' 19"	Cherokee	30.0	USGS
4	Center Creek near Carterville, Missouri	07186400	37° 08' 26" 94° 22' 57"	Jasper	232	USGS
5	Center Creek near Smithfield, Missouri	07186480	37° 09' 20" 94° 36' 10"	Jasper	297 e	USGS KDHE
6	Turkey Creek near Joplin, Missouri	07186600	37° 07' 15" 94° 34' 55"	Jasper	41.8	USGS KDHE
7	Short Creek at Galena, Kansas	370503094382200	37° 05' 03" 94° 38' 22"	Cherokee	13.0e	USGS
8	Shoal Creek near near Galena, Kansas	07187560	37° 02' 31" 94° 38' 34"	Cherokee	494 e	USGS KDHE
9	Spring River near Baxter Springs, Kansas	07187600	37° 01' 25" 94° 43' 15"	Cherokee	2,510	USGS KDHE

[a] The analyses were done by USGS laboratories in Little Rock, Arkansas; Lincoln, Nebraska; Salt Lake City, Utah; and Denver, Colorado; and by USGS-approved cooperator laboratories.

is a composite consisting of contributions from the upper Spring River and all its tributaries in Kansas and Missouri. By comparing water-quality data collected on the Spring River near Waco to data collected downstream near Baxter Springs, the effect of the tributary streams on the water quality of the Spring River can be assessed.

The availability of the USGS and KDHE water-quality data is shown in figure 5. Data from the two sources were combined to form a broader and more consistent data base for evaluating water-quality conditions in the Spring River basin. To determine the suitability of the KDHE data (samples collected and analyzed by KDHE) for inclusion in the project data set, consideration was given to sample collection, handling, and preservation techniques, analytical methods, and laboratory quality control and quality assurance practices.

The USGS samples were collected using techniques described by Guy and Norman (1970) for the collection of suspended sediment samples. The objective of using these techniques to collect water-quality samples is to obtain a sample that is representative of the flow in the stream cross section, both vertically and laterally. Depth-integrated water samples are collected at several points in the stream cross section and then composited to represent the entire stream cross section. The KDHE used a Biochemical Oxygen Demand sampler (American Public Health Association and others, 1985, p. 417) and collected one sample at the centroid of flow. This method of sample collection may not be suitable for total constituents unless the stream is well mixed.

Sample handling and preservation techniques are used to stabilize the sample so that it retains its original character as nearly as possible. Preservation requirements vary and have changed through the years, but essentially involve filtering or addition of reagents to stop biological action and precipitation or solution of chemical constituents. Sample handling and preservation techniques used by the USGS and KDHE are listed in table 5. Samples collected by the USGS to be analyzed for dissolved constituents were filtered onsite; samples collected by the KDHE were not filtered onsite and were allowed to settle before analysis.

Samples collected by the USGS were analyzed according to methods described by Rainwater and Thatcher (1960), Brown and others (1970), Skougstad and others (1979), and Fishman and Friedman (1985). The KDHE analytical methods are described in "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1965, 1971, 1976, 1981, and 1985) and "Methods for Chemical Analysis of Water and Waste" (U.S. Environmental Protection Agency, 1974, 1979, and 1983).

Table 5.--*Sample preservatives used by the U.S. Geological Survey and by the Kansas Department of Health and Environment*

[USGS, U.S. Geological Survey; KDHE, Kansas Department of Health and Environment; °C, degrees Celsius]

Constituent	USGS	KDHE
Anions	Filtered, untreated	Chilled to 4 °C
Cations	Filtered, acidified with nitric acid	Chilled to 4 °C
Nutrients	Mercuric chloride tablet or ampoule	Acidified with sulfuric acid to pH 2
Trace constituents	Filtered, acidified with nitric acid for dissolved Acidified with nitric acid for total-recoverable	Acidified with nitric and hydrochloric acid

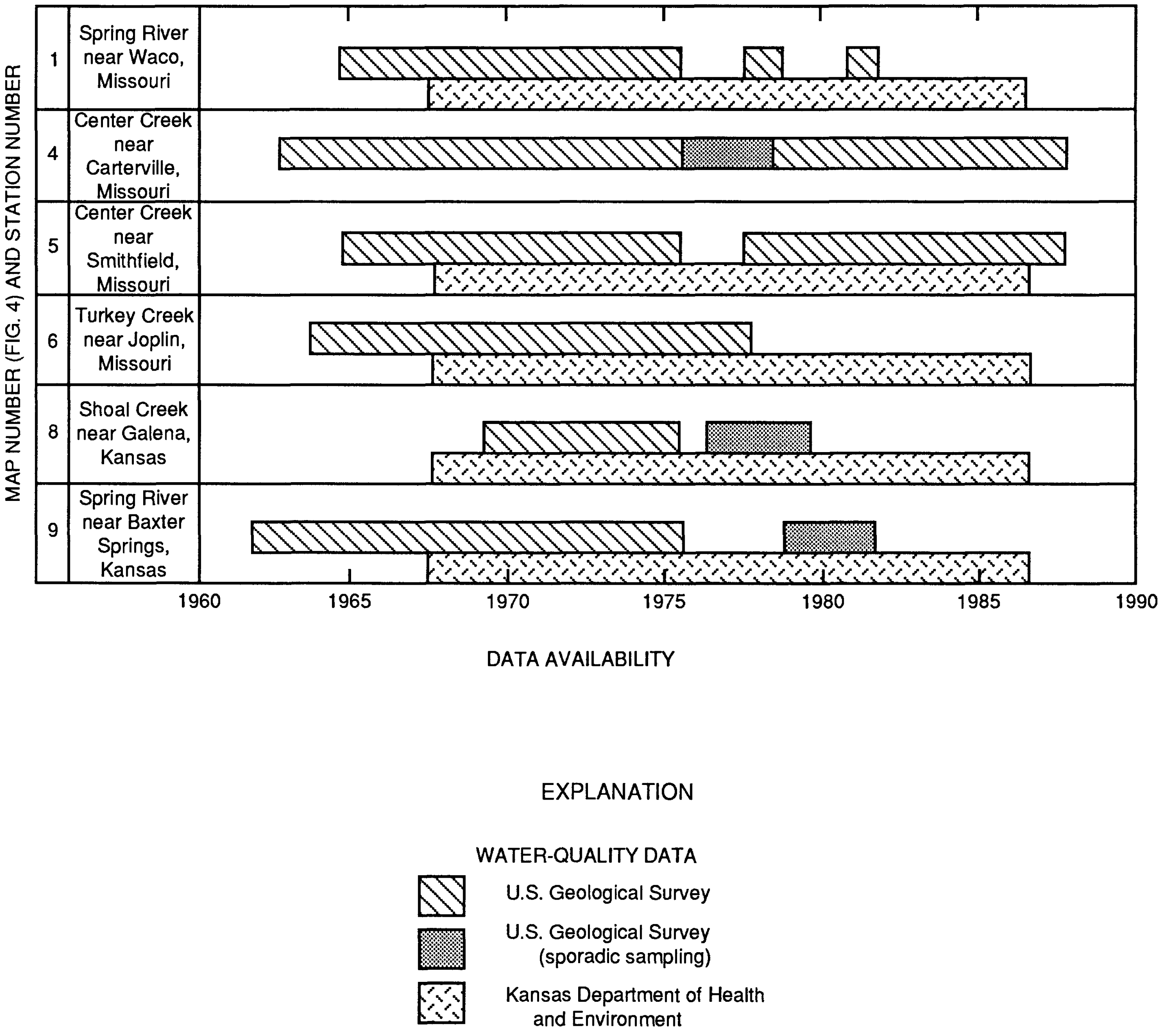

Figure 5.--Availability of long-term monitoring water-quality data.

The KDHE laboratory is a USGS-approved laboratory. This involves participation in the USGS Standard Reference Water Sample (SRWS) program, as well as internal quality control (QC) measures including field duplicates, laboratory duplicates, spikes, blanks, standards, and QC samples of known constituent concentration. The KDHE laboratory also participates in the USEPA Water Protection and Water Supply sample programs.

To determine if the sample collection, handling, or preservation techniques or analytical methods employed by the two agencies affected the data, a statistical comparison of the two data sets was done. Center Creek near Smithfield, Missouri (fig. 4, no. 5), was chosen for the comparison because the data from both agencies cover approximately the same time (fig. 5). A few of the constituents were not analyzed by both laboratories through the entire period of record; for these constituents, only the overlapping periods of record were considered. Because water-quality data often are not normally distributed, a t-test was performed on the jointly rank-transformed data (Iman and Conover, 1983). The results indicate that for most of the constituents, the USGS and KDHE data are not statistically different at the 0.05 level of probability (table 6). Exceptions are pH, chloride, dissolved solids, suspended solids, total ammonia, and several of the dissolved trace constituents.

Further investigation indicated that the statistical differences in these constituents could be attributed to sample collection or handling techniques, or analytical methodology. The pH was determined onsite by USGS personnel, whereas the pH of KDHE samples was determined in the laboratory. The USGS dissolved solids concentrations were from direct analysis [residue on evaporation at 180 °C (degrees Celsius)]; the KDHE dissolved solids concentrations were the sum of the cations and anions. Different sampling methodologies explain the difference in the concentration of suspended solids because the samples collected by the USGS were more representative of the stream cross section. Sample handling explains the difference in some of the dissolved trace constituents. USGS samples collected for dissolved trace-constituent analysis were filtered onsite and then acidified with nitric acid, which prevents the trace constituents from precipitating out of solution. The KDHE samples were acidified with nitric plus hydrochloric acid (HCl) but were not filtered onsite. The samples were allowed to settle in the laboratory and the supernatant decanted before analysis. Because these samples were acidified before filtering, trace constituents associated with suspended material may be solubilized, increasing the dissolved trace-constituent concentration in the sample. Statistical differences in the chloride and total ammonia concentrations are attributable to analytical methodology. The KDHE has adopted the same automated method used by the USGS for chloride and total ammonia (Fishman and Friedman, 1985), and after 1978, there is no statistical difference in the USGS and KDHE chloride and total ammonia concentrations. The KDHE pH, dissolved solids, suspended solids, and dissolved trace-constituent data for the entire period of record were deleted from the project data set. Likewise, the KDHE chloride data collected before October 1978 and total ammonia data collected before July 1978 also were deleted.

WATER-QUALITY CHARACTERISTICS

Analysis of Spatial Characteristics

The quality of water in the Spring River basin varies greatly. This is a consequence of natural conditions, particularly differences in geology, as well as industrial, municipal, and mining waste inputs. Water-quality conditions can be evaluated using summary statistics, which indicate spatial variations in water quality. Whether or not these variations are statistically significant is determined by using one-way ANOVA and multiple-comparison procedures. In addition, summary statistics can be used to determine baseline water-quality characteristics. In this instance, baseline refers to the condition of a stream that has been minimally affected by human activities and is not intended to represent pristine, natural background conditions. Large, long-term variations in water quality from baseline may limit the overall suitability of a stream for many uses, and likewise, extreme short-term variations from baseline could imperil the use of a stream for water supply, industrial use, recreation, or aquatic life.

Table 6.--*Water-quality data collected by the U.S. Geological Survey and by the Kansas Department of Health and Environment at Center Creek near Smithfield, Missouri*

[USGS, U.S. Geological Survey; KDHE, Kansas Department of Health and Environment;
ft^3/s, cubic foot per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter;
--, no data; mL, milliliters; $CaCO_3$, calcium carbonate; ROE, residue on evaporation at 180 degrees Celsius; N, nitrogen; µg/L, micrograms per liter]

Physical property or constituent	USGS		KDHE		Results of t-test^{a,b}
	Number of samples	Median value or concentration	Number of samples	Median value or concentration	
Discharge (ft^3/s)	171	125	138	108	Not significant
Specific conductance (µS/cm)	171	410	166	400	Not significant
pH (standard units)	172	7.8	163	7.7	Significant
Temperature (°C)	166	15.2	158	16.0	Not significant
Dissolved oxygen (mg/L)	169	9.3	166	9.5	Not significant
Dissolved oxygen, percent saturation	168	90	--	--	--
Suspended solids (mg/L)	121	7	106	12	Significant
Fecal coliform (colonies per 100 mL)	158	70	--	--	--
Calcium (mg/L)	84	72	167	72	Not significant
Magnesium (mg/L)	84	3.3	167	3.2	Not significant
Sodium (mg/L)	84	8.2	167	8.0	Not significant
Potassium (mg/L)	83	1.7	167	1.9	Not significant
Alkalinity (mg/L as $CaCO_3$)	172	116	167	116	Not significant
Sulfate (mg/L)	84	60	166	55	Not significant
Chloride (mg/L)	85	8.7	167	10	Significant
Fluoride (mg/L)	33	.6	37	.8	Not significant
Dissolved solids (ROE, mg/L)	90	256	165	229	Significant
Total nitrite plus nitrate (mg/L as N)	132	4.7	104	5.0	Not significant
Total ammonia (mg/L as N)	132	^{c}.08	164	^{c}.16	Significant
Dissolved ammonia (mg/L as N)	22	.22	--	--	--
Total phosphorus (mg/L)	157	.14	104	.15	Not significant
Dissolved phosphorus (mg/L)	35	.19	--	--	--
Total-recoverable cadmium (µg/L)	52	^{c}3	--	--	--
Dissolved cadmium (µg/L)	54	^{c}1	20	^{c}2	Not significant
Dissolved chromium (µg/L)	30	^{c}5	13	d	Not significant

Table 6.--*Water-quality data collected by the U.S. Geological Survey and by the Kansas Department of Health and Environment at Center Creek near Smithfield, Missouri*--Continued

Physical property or constituent	USGS		KDHE		Results of t-test[a,b]
	Number of samples	Median value or concentration	Number of samples	Median value or concentration	
Total-recoverable copper (µg/L)	51	[c]5	--	--	--
Dissolved copper (µg/L)	83	[c]3	19	[c]20	Significant
Total-recoverable iron (µg/L)	52	240	--	--	--
Dissolved iron (µg/L)	86	[c]20	16	130	Significant
Total-recoverable lead (µg/L)	52	[c]9	--	--	--
Dissolved lead (µg/L)	90	[c]3	20	[c]15	Significant
Total-recoverable manganese (µg/L)	50	60	--	--	--
Dissolved manganese (µg/L)	99	50	16	[c]75	Not significant
Total-recoverable zinc (µg/L)	51	430	--	--	--
Dissolved zinc (µg/L)	94	420	20	620	Significant

[a] Not significant indicates no statistically significant difference at the 0.05 level of probability.

[b] Significant indicates statistically significant difference at the 0.05 level of probability.

[c] Value is estimated by using a log-probability regression to predict the values of data below the constituent detection limit.

[d] Number of observations larger than the detection limit is less than 5. Estimated values are considered unreliable and are not reported.

Summary statistics, including the maximum, minimum, mean, and the 95th, 75th, 50th (median), 25th, and 5th percentiles, were calculated for the six long-term monitoring and three ancillary stations (table 7, at the back of this report). The mean and percentiles for multiply-censored data were estimated using a log-probability regression procedure described by Gilliom and Helsel (1986) and Helsel and Cohn (1988). The method is used to estimate the values less than the detection limit of a constituent and then these values and the detected values are used to estimate the mean and percentiles. A parameter is considered censored if greater than 5 percent of the total number of data values are flagged with < (less than) or U (not detected) symbols. However, if the number of observations larger than the detection limit is less than 5, the estimated mean and percentiles are considered unreliable and are not reported.

ANOVA and multiple-comparison procedures were used to evaluate significant differences in physical properties and chemical constituent concentrations between the long-term monitoring stations. Insufficient data for the three ancillary stations precluded including them in the analysis. Although periods of record differ between the stations for various constituents, the period of record for physical properties, major constituents, and nutrients is similar at all long-term stations. To use as much of the data set as possible, the entire period of record for physical properties, major constituents, and nutrients was used. However, because large quantities of dissolved trace-constituent data were removed from the data set because of sample handling, dissimilarities in the period of record for these constituents occurred. To avoid bias and comparison of widely different periods of record in ANOVA and multiple- comparison procedures, the dissolved trace-constituent data used in these procedures were limited to samples collected between October 1968 and September 1981 for each station. One assumption for these procedures is that the data be normally distributed. Because the assumption of normality was not met for most constituents, nonparametric tests, based on analysis of ranked data, were used.

An ∝-level (alpha level) of 0.05 was used for ANOVA procedures and the null hypothesis, which is that all stations have equal mean ranks for a given constituent, was rejected for analyses with p-values (probability values) less than 0.05. The ∝-level is the significance level of the test and is established before looking at the data. The p-value is the attained significance level and is determined by the data (Iman and Conover, 1983).

To further examine differences in various constituent concentrations between stations, a Fisher's Protected Least Significant Difference Test was used in cases where the null hypothesis (ANOVA) was rejected (Snedecor and Cochran, 1980). The 6 stations have 15 possible pairwise comparisons between mean ranks. If an ∝-level of 0.05 is used for each possible comparison, the overall probability of a Type I error (detecting a false difference) could be as great as $[1 - (1 - \propto)^{15} = 0.54]$, assuming the null hypothesis actually is true. To control the overall error rate for the multiple-comparison procedures, the Bonferroni method of dividing the overall ∝-level desired by the number of possible pairwise comparisons was used. This procedure ensures that the probability of a Type I error over all possible comparisons is no larger than the desired overall ∝-level (Snedecor and Cochran, 1980). A possible disadvantage of this method is the conservative value of ∝ used (0.05/15=0.003), increasing the risk of a Type II error (accepting the null hypothesis when the null is false). The increased risk of a Type II error was judged acceptable considering the initial null hypothesis and study objectives.

The distribution of selected physical property values or constituent concentrations at the long-term monitoring and ancillary stations are shown using side-by-side boxplots (Tukey, 1977). A boxplot is a useful tool for visually examining the central tendency and dispersion of a group of data or for comparing two or more groups of data. An example of a boxplot is shown in figure 6. To construct a boxplot, the median value is plotted as a horizontal line, and a box is drawn from the 25th percentile to the 75th percentile. The box length equals the interquartile range (IQR). Vertical lines are then drawn from the quartiles to two "adjacent" values. The upper adjacent value is defined as the largest data point less than or equal to the upper quartile plus 1.5 times the IQR. Likewise, the lower adjacent value is the smallest data point greater than or equal to the lower quartile minus 1.5 times the IQR.

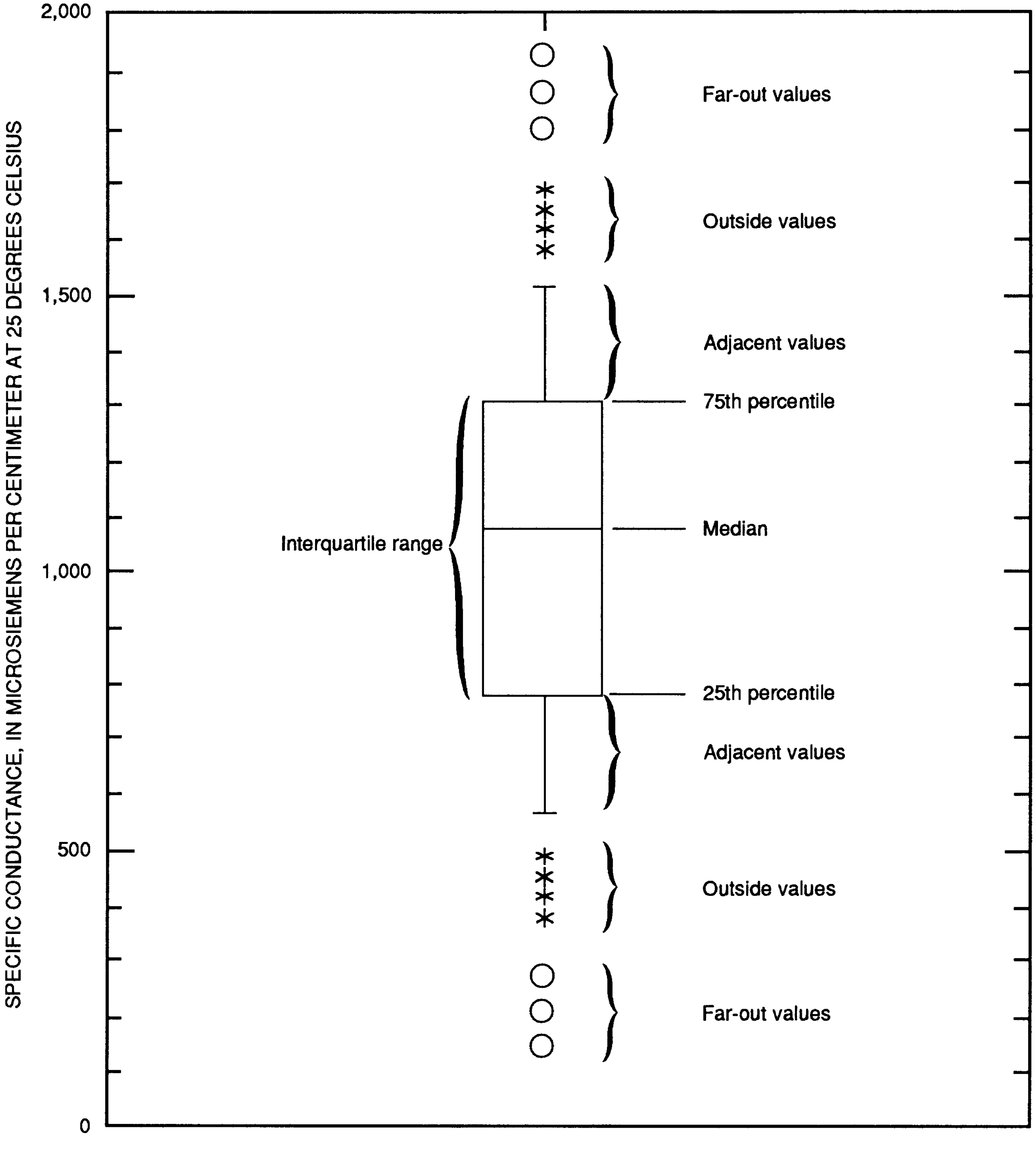

Figure 6.-- Boxplot example.

Values more extreme in either direction than the adjacent values are plotted individually. Those values equal to 1.5 to 3.0 times the IQR are called "outside values" and generally are represented by an asterisk; those values greater than 3.0 times the IQR are called "far-out values" and generally are represented by a circle.

The results of the analysis of variance and multiple-comparison tests are presented in a graphical format to aid in reader comprehension. An example of the format is given in figure 7.

Spatial variation in median water-quality constituent concentrations at the long-term monitoring and ancillary stations is presented in table 7. Results of ANOVA and multiple-comparison tests (fig. 8) indicate that many of these variations are significant at the long-term monitoring stations. Significant differences were detected at an overall ∝-level of 0.05 for nearly all physical and chemical constituents with the exception of temperature and dissolved copper and lead. Insufficient data were available for statistical tests on dissolved cadmium and chromium. Values computed for these constituents were based on a small number of samples collected at one or more stations, or constituent values had no variance. Generally, mean ranks for chemical constituents were smallest at Shoal Creek near Galena, Kansas (fig. 4, no. 8), the Spring River near Waco, Missouri (fig. 4, no. 1), and Center Creek near Carterville, Missouri (fig. 4, no. 4). In contrast, Turkey Creek near Joplin, Missouri (fig. 4, no. 6), and Center Creek near Smithfield, Missouri (fig. 4, no. 5), had among the largest mean ranks of chemical constituents, specific conductance, and dissolved solids. These stations, along with the Spring River near Baxter Springs, Kansas (fig. 4, no. 9), also had among the smallest mean ranks of pH.

The following discussion will focus on a comparison of median constituent concentrations and mean constituent ranks for various stations against constituent concentrations and ranks at Shoal Creek near Galena. Previous studies (Barks, 1977; Spruill, 1987) and the summary statistics (table 7) indicate this station represents baseline conditions within the basin. The relatively small median concentrations and low mean ranks for most chemical constituents and large median concentrations and high mean ranks for dissolved oxygen and pH at Shoal Creek near Galena corroborate the use of this station as representative of baseline conditions within the basin. Because of differences in basin geology, topography, and land use, a second baseline station at the Spring River near Waco also will be considered. The distribution of mean constituent ranks between the stations also will be related to differences in basin characteristics, such as geology and known effects of mining, industrial, and municipal sources.

Where appropriate, concentrations of various constituents at the long-term monitoring stations for the entire period of record are compared to Missouri water-quality standards (Missouri Department of Natural Resources, 1989) for the protection of aquatic life, livestock and wildlife watering, and whole-body-contact recreation (table 8). The percentage of samples for each station with concentrations exceeding a particular standard also is noted. Missouri water-quality standards are equal to or more stringent than the USEPA's quality criteria for water (U.S. Environmental Protection Agency, 1986). Shoal Creek is the only surface-water source for public-water supply in the basin; therefore, the drinking-water supply standards (Missouri Department of Natural Resources, 1989) are not included in table 8. The drinking-water supply standards were not exceeded in any of the samples collected at Shoal Creek near Galena, Kansas (fig. 4, no. 8).

Physical Properties

Physical properties including discharge, specific conductance, pH, water temperature, dissolved oxygen, and suspended solids contribute to the overall water quality of a stream. The pH value, water temperature, and dissolved oxygen affect the rates of chemical and biological activity. Summary statistics of the physical property data collected at the long-term monitoring and ancillary stations are listed in table 7.

EXPLANATION

▨ MEAN CONSTITUENT RANK

Shaded boxes in each column represent the relative mean constituent rank for each station. The absence of a shaded box in a column indicates that insufficient data were available for analysis. Stations with boxes shaded in the lowermost rows have among the smallest mean constituent ranks. Those stations with boxes shaded in the uppermost rows have among the largest mean constituent ranks. Two or more stations with boxes shaded in the same row indicate their respective mean constituent ranks are not significantly different at an alpha level of 0.05. Two shaded boxes in a column indicate that the mean constituent rank of the station is not statistically different at an alpha level of 0.05 from the mean constituent ranks of two or more other stations that have shaded boxes in the same rows. However, the mean constituent ranks of the other stations that are not in the same row are statistically different.

For example, Turkey Creek near Joplin, Missouri, has the only box shaded in the bottom row and consequently has a significantly smaller mean rank of dissolved oxygen than all other stations. Center Creek near Smithfield, Missouri, and Shoal Creek near Galena, Kansas, have boxes shaded in the fourth row and have significantly larger mean ranks of dissolved oxygen than all other stations. However, no significant difference was detected between the mean ranks of dissolved oxygen at these two stations. The mean rank of dissolved oxygen at the Spring River near Waco, Missouri, was not significantly different from the mean rank at Center Creek near Carterville, Missouri, or the mean rank at the Spring River near Baxter Springs, Kansas. However, the Spring River near Baxter Springs, Kansas, has a significantly larger mean rank of dissolved oxygen than Center Creek near Carterville, Missouri.

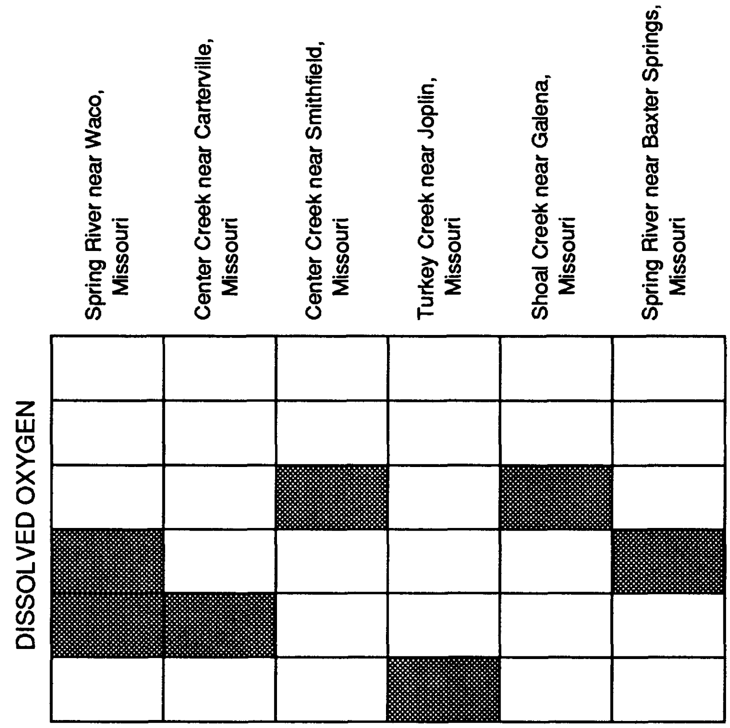

Figure 7.--Graphical representation of analysis of variance and multiple-comparison tests.

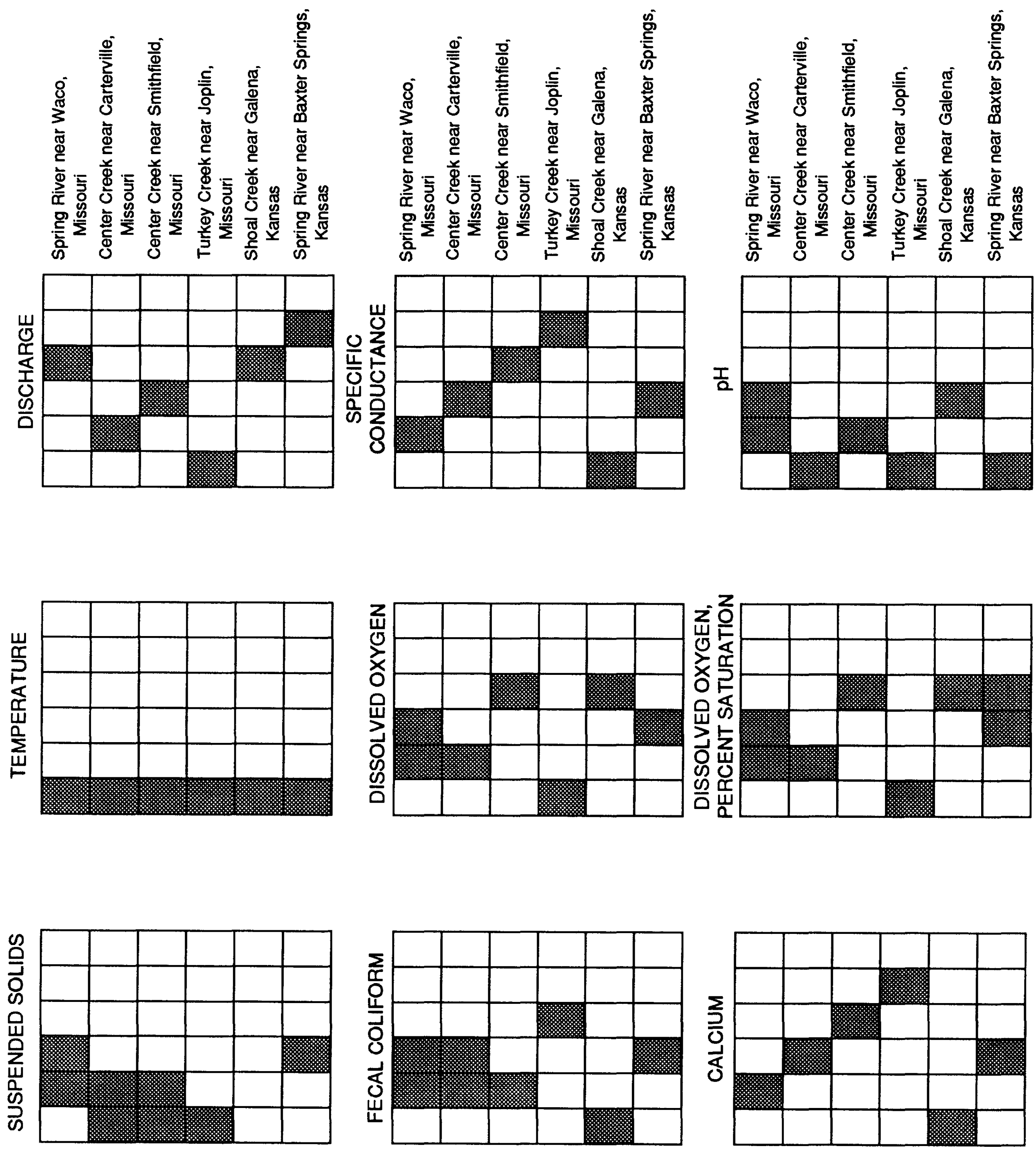

Figure 8.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between long-term monitoring stations (see figure 7 for explanation).

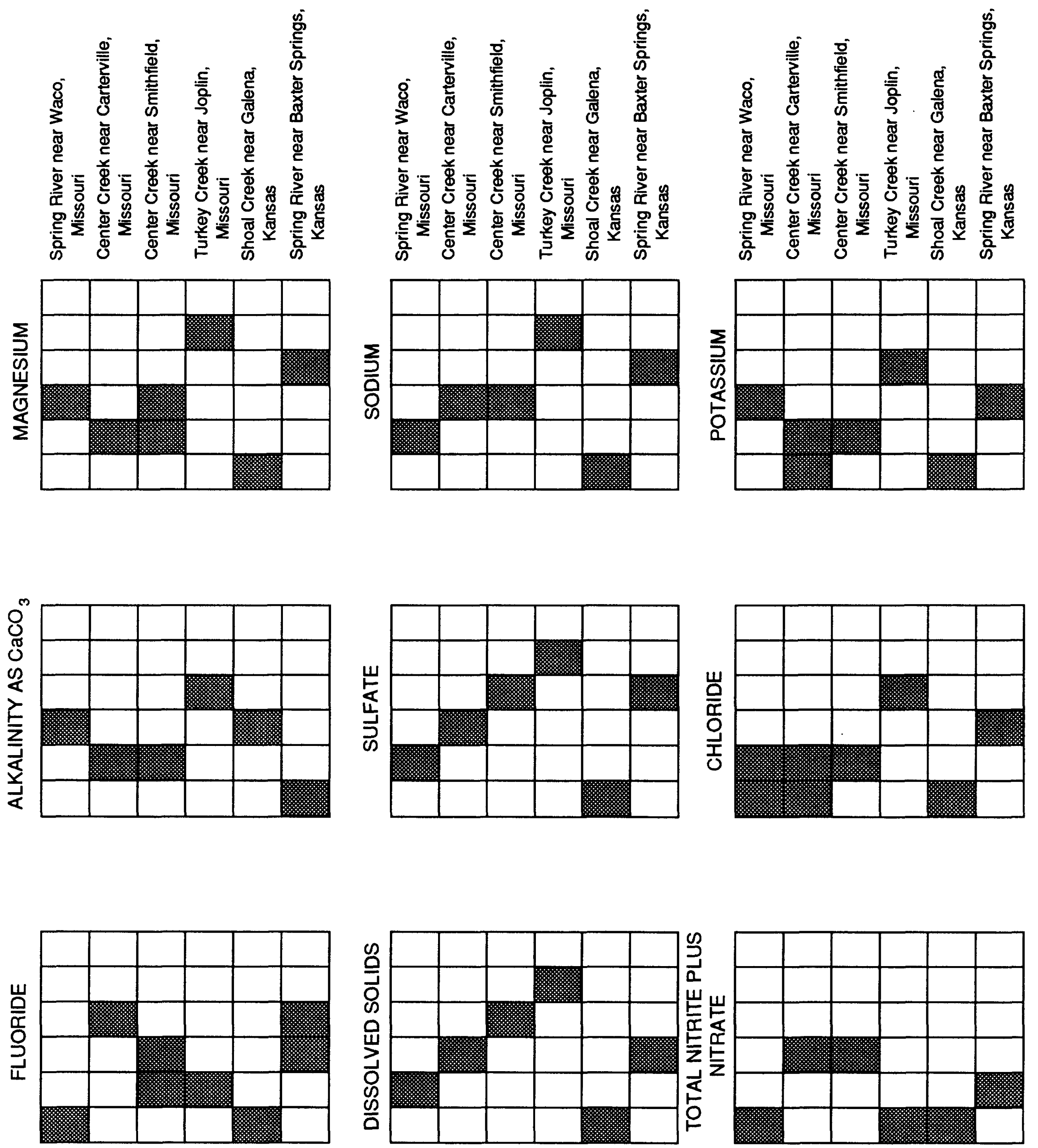

Figure 8.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between long-term monitoring stations--Continued.

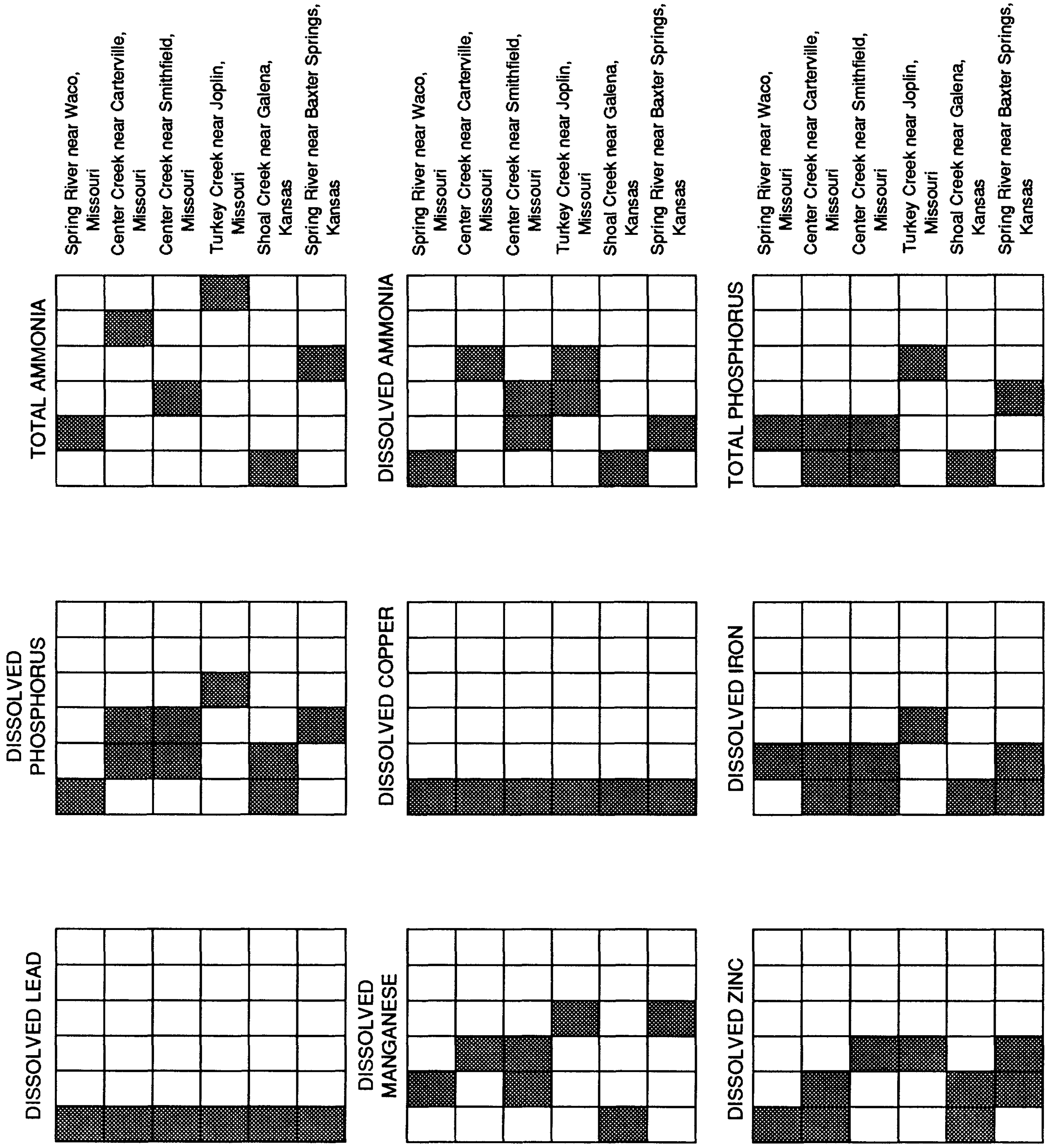

Figure 8.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between long-term monitoring stations--Continued.

Table 8.--*Missouri water-quality standards and measured constituent values from the long-term monitoring stations*

[mg/L, milligrams per liter; N, nitrogen; µg/L, micrograms per liter; mL, milliliters]

Aquatic life protection (Missouri standard)	Number of samples	Number of samples not in compliance with Missouri water-quality standard[a]	Percentage of samples not in compliance with Missouri water-quality standard[a]
Spring River near Waco, Missouri (fig. 4, no. 1)			
pH (6.5-9.0 standard units)	106	0	0
Dissolved oxygen (5.0 mg/L)	269	3	1
Total ammonia (mg/L as N)[b]	129	2	2
Dissolved lead (12-29 µg/L)[c]	57	4	7
Dissolved zinc (245-440 µg/L)[c]	68	5	7
Center Creek near Carterville, Missouri (fig. 4, no. 4)			
pH (6.5-9.0 standard units)	294	3	1
Dissolved oxygen (5.0 mg/L)	278	9	3
Total ammonia (mg/L as N)[b]	157	42	27
Dissolved lead (12-29 µg/L)[c]	141	12	9
Dissolved zinc (245-440 µg/L)[c]	164	25	15
Center Creek near Smithfield, Missouri (fig. 4, no. 5)			
pH (6.5-9.0 standard units)	172	0	0
Dissolved oxygen (5.0 mg/L)	335	2	.6
Total ammonia (mg/L as N)[b]	223	7	3
Dissolved lead (12-29 µg/L)[c]	73	5	7
Dissolved zinc (245-440 µg/L)[c]	77	50	65
Turkey Creek near Joplin, Missouri (fig. 4, no. 6)			
pH (6.5-9.0 standard units)	193	0	0
Dissolved oxygen (5.0 mg/L)	355	147	41
Total ammonia (mg/L as N)[b]	163	76	47
Dissolved lead (12-29 µg/L)[c]	98	10	10
Dissolved zinc (245-440 µg/L)[c]	111	46	41
Shoal Creek near Galena, Kansas (fig. 4, no. 8)			
pH (6.5-9.0 standard units)	45	0	0
Dissolved oxygen (5.0 mg/L)	210	1	.5
Total ammonia (mg/L as N)[b]	112	0	0
Dissolved lead (12-29 µg/L)[c]	2	0	0
Dissolved zinc (245-440 µg/L)[c]	6	0	0
Spring River near Baxter Springs, Kansas (fig. 4, no. 9)			
pH (6.5-9.0 standard units)	200	0	0
Dissolved oxygen (5.0 mg/L)	243	2	.8
Total ammonia (mg/L as N)[b]	112	2	2
Dissolved lead (12-29 µg/L)[c]	5	0	0
Dissolved zinc (245-440 µg/L)[c]	6	3	50

Table 8.--*Missouri water-quality standards and measured constituent values from the long-term monitoring stations*--Continued

Livestock and wildlife watering (Missouri standard)	Number of samples	Number of samples not in compliance with Missouri water-quality standard[a]	Percentage of samples not in compliance with Missouri water-quality standard[a]
Spring River near Waco, Missouri (fig. 4, no. 1)			
Fluoride (4.0 mg/L)	122	0	0
Center Creek near Carterville, Missouri (fig. 4, no. 4)			
Fluoride (4.0 mg/L)	199	62	31
Center Creek near Smithfield, Missouri (fig. 4, no. 5)			
Fluoride (4.0 mg/L)	123	8	6
Turkey Creek near Joplin, Missouri (fig. 4, no. 6)			
Fluoride (4.0 mg/L)	183	0	0
Shoal Creek near Galena, Kansas (fig. 4, no. 8)			
Fluoride (4.0 mg/L)	81	0	0
Spring River near Baxter Springs, Kansas (fig. 4, no. 9)			
Fluoride (4.0 mg/L)	190	3	2

Whole-body-contact recreation (Missouri standard)	Number of samples	Number of samples not in compliance with Missouri water-quality standard[a]	Percentage of samples not in compliance with Missouri water-quality standard[a]
Spring River near Waco, Missouri (fig. 4, no. 1)			
Fecal coliform bacteria (200 colonies per 100 mL)[d]	62	24	39
Center Creek near Carterville, Missouri (fig. 4, no. 4)			
Fecal coliform bacteria (200 colonies per 100 mL)[d]	191	65	34

Table 8.--*Missouri water-quality standards and measured constituent values from the long-term monitoring stations*--Continued

Whole-body-contact recreation (Missouri standard)	Number of samples	Number of samples not in compliance with Missouri water-quality standard[a]	Percentage of samples not in compliance with Missouri water-quality standard[a]
Center Creek near Smithfield, Missouri (fig. 4, no. 5)			
Fecal coliform bacteria (200 colonies per 100 mL)[d]	158	43	27
Turkey Creek near Joplin, Missouri (fig. 4, no. 6)			
Fecal coliform bacteria (200 colonies per 100 mL)[d]	115	81	70
Shoal Creek near Galena, Kansas (fig. 4, no. 8)			
Fecal coliform bacteria (200 colonies per 100 mL)[d]	32	8	25
Spring River near Baxter Springs, Kansas (fig. 4, no. 9)			
Fecal coliform bacteria (200 colonies per 100 mL)[d]	52	25	48

[a] Missouri water-quality standards are equal to or more strigent than the U.S. Environmental Protection Agency's quality criteria for water.

[b] The toxicity of ammonia is dependent on pH, temperature, and the concentrations of total ammonia. The Missouri water-quality standard for total ammonia varies with the pH value and temperature of the water. In this case, the standard referred to is the chronic criteria for total ammonia in a general, warm-water fishery.

[c] The toxicity of lead and zinc is dependent on the hardness of water and the concentration of lead or zinc. The Missouri water-quality standards for lead and zinc vary with the hardness of the water. The lead standard referred to is the chronic toxicity maximum in all classified waters. The zinc standard referred to is the chronic toxicity maximum in a general, warm-water fishery.

[d] The Missouri water-quality standard states that the fecal coliform bacteria count shall not exceed a geometric mean of 200 colonies per 100 mL during the recreational season from April 1 to October 31 in waters designated for whole-body-contact recreation.

Discharge

Discharge, expressed in ft^3/s (cubic feet per second), is a measure of the volume of water in a stream flowing past a specific location per unit time. Generally, changes in dissolved solids concentration are related to the rate of water discharge and the rate of change of discharge (Hem, 1985). If the chemical quality and discharge of a stream are closely related, water quality can be estimated from past water-quality records and discharge. Discharge data also can be used to estimate total solute discharges.

In the Spring River basin, median discharge values ranged from 1.9 ft^3/s at Brush Creek near Weir, Kansas (fig. 4, no. 3), to 806 ft^3/s at the Spring River near Baxter Springs, Kansas (fig 4, no. 9). Significant differences are detected in the mean ranks of discharge between the long-term monitoring stations (fig. 8). The distribution of mean ranks of discharge is directly related to drainage area as Turkey Creek near Joplin, Missouri (fig. 4, no. 6), has the lowest flows and the Spring River near Baxter Springs the largest. A significant increase in discharge is detected between the upstream Center Creek station near Carterville, Missouri (fig. 4, no. 4), and the downstream station near Smithfield, Missouri (fig. 4, no. 5). Contributions of flow from areas associated with the Oronogo-Duenweg mining belt are possible (fig. 2).

Specific conductance

Specific conductance, expressed in µS/cm (microsiemens per centimeter at 25 °C), is a measure of the ability of water to conduct an electrical current. Because it is a measure of the ionic strength of water, the specific conductance is related to the type and concentrations of ions in solution and can be used for approximating the dissolved solids concentration of water.

Median specific conductance values ranged from 280 µS/cm at Shoal Creek near Galena, Kansas (fig. 4, no. 8), to 1,070 µS/cm at Brush Creek near Weir (fig. 4, no. 3). Those streams profoundly affected by mining or industrial wastes, or both, as described previously, had the largest median specific conductance values: Cow Creek near Weir, Kansas (fig. 4, no. 2), 862 µS/cm; Brush Creek near Weir, 1,070 µS/cm; Turkey Creek near Joplin (fig. 4, no. 6), 620 µS/cm; and Short Creek at Galena, Kansas (fig. 4, no. 7), 740 µS/cm. The median specific conductance increased from 350 µS/cm at the upstream Center Creek station near Carterville (fig. 4, no. 4) to 405 µS/cm at the downstream Center Creek station near Smithfield (fig. 4, no. 5). Likewise, the median specific conductance increased from 321 µS/cm at the upstream Spring River station near Waco, Missouri (fig. 4, no. 1), to 360 µS/cm at the downstream Spring River station near Baxter Springs (fig. 4, no. 9), which is a smaller increase than would be expected when considering contributions of dissolved solids from Cow Creek, Brush Creek, Center Creek, Turkey Creek, and Short Creek. However, dilution of the Spring River by Shoal Creek undoubtedly accounts for this smaller than expected median value at the Baxter Springs station. The distribution of specific conductance values at the long-term monitoring and ancillary stations is shown in figure 9.

At the long-term monitoring stations, the distribution of mean ranks of specific conductance increase in the following order: Shoal Creek near Galena < Spring River near Waco < Center Creek near Carterville and Spring River near Baxter Springs < Center Creek near Smithfield < Turkey Creek near Joplin (fig. 8). The increase in specific conductance values between the upstream and downstream Center Creek and the Spring River stations is significant. The proposed baseline stations (Shoal Creek near Galena and the Spring River near Waco) have the smallest ranks of specific conductance and Center Creek near Smithfield and Turkey Creek near Joplin have the largest ranks of specific conductance.

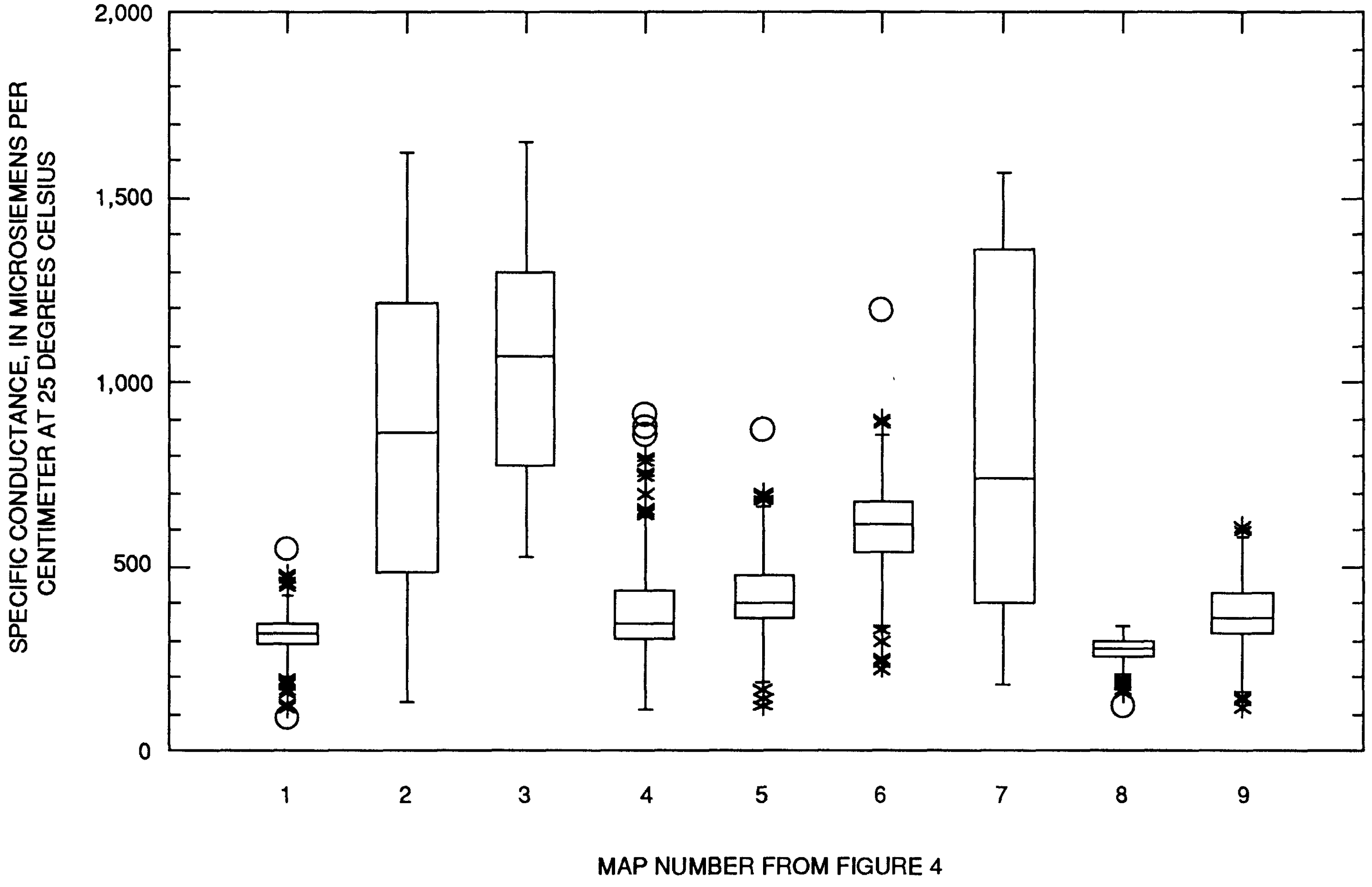

Figure 9.--Distribution of specific conductance values at the long-term monitoring and ancillary stations (see figure 6 for explanation).

pH

The pH value is a measure of the hydrogen ion activity in water and is an important factor regulating the rates of chemical and biological activity. In the Spring River basin, as in all natural waters, the principal factors regulating pH value are carbonate reactions. The degree of dissociation of weak acids or bases, some of which are toxic, is affected by changes in pH. For example, the dissociation of ammonia is increasingly inhibited by increasing pH and the water becomes more toxic as a result. The solubility of trace constituents contained in bottom sediments or in suspended sediments also generally increases with decreasing pH.

Median pH values at the long-term monitoring stations ranged from 7.5 at Turkey Creek near Joplin (fig. 4, no. 6) and the Spring River near Baxter Springs (fig. 4, no. 9) to 8.0 at Shoal Creek near Galena (fig. 4, no. 8); median pH values at the ancillary stations were 7.2 at Cow Creek near Weir (fig. 4, no. 2), 3.9 at Brush Creek near Weir (fig. 4, no. 3), and 6.2 at Short Creek at Galena (fig. 4, no. 7). Generally, the streams affected by mining, industrial, or municipal wastes had the lowest median pH values, particularly Brush and Short Creeks. An exception was the downstream Center Creek station near Smithfield (fig. 4, no. 5) where the median pH was 7.8. The state of Missouri criterion for the protection of aquatic life is a pH range of 6.5 to 9.0. At the Center Creek station near Carterville (fig. 4, no. 4), pH values of less than 6.5 were detected in three samples collected before 1968 (table 8), which may be because of the discharge of industrially used mine water into Grove Creek, as discussed previously. The distribution of pH values at the long-term monitoring and ancillary stations is shown in figure 10.

Shoal Creek near Galena and the Spring River near Waco have the largest pH ranks; and Center Creek near Carterville, Turkey Creek near Joplin, and the Spring River near Baxter Springs have the smallest pH ranks (fig. 8). The small pH ranks at Baxter Springs indicate significant contributions of hydrogen ions from sources not included in the ANOVA design, such as Short Creek in Missouri or Brush and Cow Creeks in Kansas (table 7). The small flows at Turkey Creek near Joplin as compared to the Spring River near Baxter Springs preclude Turkey Creek as being the principal source of hydrogen ions to Baxter Springs. The significant increase in pH value between the upstream and downstream stations on Center Creek contrasts earlier data that indicated substantial effects from several sources of mine discharge and tailings runoff between these sites (Barks, 1977). The indication is that, although mine seeps and tailings runoff significantly increase the specific conductance and trace-constituent concentrations between the upstream and downstream stations on Center Creek (fig. 8), pH values are not affected at Center Creek near Smithfield. The increases in pH may be because of rapid neutralization of acidic mine seeps and tailings runoff with carbonate minerals.

Temperature

The rates of most chemical reactions and biological processes increase with increasing temperature. Increased temperatures accelerate the biodegradation of organic material in water and bottom sediments, thereby affecting the self-purification processes in a stream. Various aquatic organisms have a temperature range within which survival is possible; therefore, temperature is one factor that determines the nature of the biological community in a stream. Maximum temperatures, which are the most stressful to aquatic organisms, generally are the growth-limiting factor in an aquatic environment.

The median temperature was 16.0 °C at all six long-term monitoring stations, 14.0 °C at Cow Creek near Weir, 15.5 °C at Brush Creek near Weir, and 21.5 °C at Short Creek at Galena. No significant differences in temperature are detected at the long-term monitoring stations (fig. 8). The anomalous median temperatures at the three ancillary stations reflect the small number of samples (table 7) that may not adequately represent daily and seasonal variations in stream temperature. In Missouri, the Spring River, Center Creek, Turkey Creek, and Shoal Creek have been classified for the protection of warm-water aquatic life. Reaches of the Spring River, Center Creek, and Shoal Creek, including the

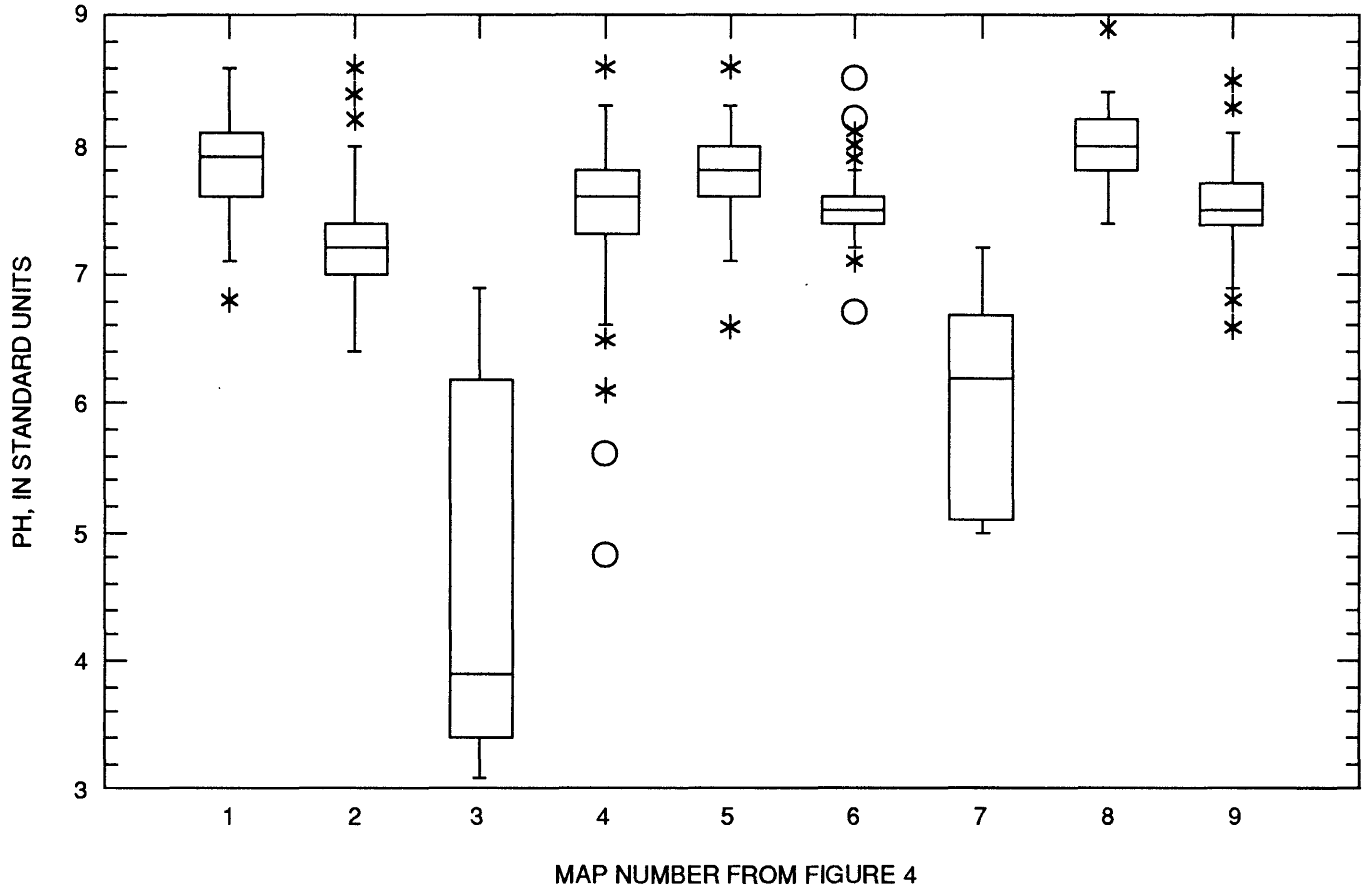

Figure 10.--Distribution of pH values at the long-term monitoring and ancillary stations (see figure 6 for explanation).

sampling stations, also have been designated for cool-water fisheries. At the headwaters of all three streams, the designation changes to cold-water fisheries. Maximum allowable temperatures for the three classifications are 32 °C, 29 °C, and 20 °C. The warm-water and cool-water temperature standards were infrequently exceeded; exceedance occurred during the summer months when ambient temperatures are high and flow is minimal and was not the result of contaminant sources. Short-term exceedance of the maximum allowable temperatures can be tolerated by most aquatic organisms.

Dissolved oxygen

Dissolved oxygen is required for survival by most forms of aquatic life, particularly fish, and also is necessary for chemical oxidation of naturally occurring organic materials, waste loads, and dissolved trace constituents, which precipitate as metal oxides. The concentration of dissolved oxygen in a stream is determined by water temperature, atmospheric pressure, plant photosynthesis, biological activity, chemical reactions, waste loads, and hydraulic properties that affect rates at which atmospheric oxygen can be supplied. The water quality and ability of a stream to support diverse aquatic life are directly related to dissolved oxygen concentrations.

Median dissolved oxygen concentrations ranged from 5.6 mg/L at Turkey Creek near Joplin to 9.4 mg/L at Center Creek near Smithfield and Shoal Creek near Galena. Those streams receiving substantial municipal waste loads had the lowest median concentrations: Turkey Creek near Joplin, 5.6 mg/L; Cow Creek near Weir, 6.2 mg/L; and Brush Creek near Weir, 7.8 mg/L. Although Shoal Creek receives municipal wastes from Neosho and Joplin, the flow and assimilative capacity are greater than for the aforementioned streams. The median dissolved oxygen concentration at the upstream Center Creek station (8.0 mg/L) was smaller than at the downstream station (9.4 mg/L), which probably was because of oxidation of ammonia from sources on Grove Creek (fig.1). There was little change in dissolved oxygen concentration between the upstream (8.4 mg/L) and the downstream (8.6 mg/L) Spring River stations, indicating that the Spring River has a good assimilative capacity. The rather large median at Short Creek at Galena (10.2 mg/L) probably was because of the small number of samples (table 7), which may not adequately represent daily and seasonal fluctuations in dissolved oxygen concentration.

The distribution of mean ranks of dissolved oxygen and percent oxygen saturation (fig. 8) are closely related, as expected. Shoal Creek near Galena and Center Creek near Smithfield have among the largest mean ranks and Turkey Creek near Joplin the smallest. The increase in dissolved oxygen concentrations between the upstream and downstream stations on Center Creek is significant. No differences are detected between the downstream Center Creek station near Smithfield and Shoal Creek near Galena, indicating near baseline concentration of dissolved oxygen and percent saturation at Smithfield and depressed concentrations at the upstream Center Creek station near Carterville. Although the distributions of dissolved oxygen and percent saturation seem reasonable, differences and similarities between the stations may not be indicative of actual conditions as both have large diurnal variations. It is unlikely that all sites were sampled during the same time of day under similar temperature and sunlight intensity conditions.

The minimum dissolved oxygen concentration required by the state of Missouri for the protection of aquatic life in warm-water and cool-water fisheries is 5.0 mg/L. This criterion level is adequate for the protection of fish throughout various stages of the life cycle from embryonic to adult. Measured dissolved oxygen concentrations were less than the standard only occasionally at five of the six long-term monitoring stations (table 8), predominantly in the summer and early fall when ambient air temperatures are high and stream discharge is minimal. At Turkey Creek near Joplin, the exceedance level was almost 42 percent and occurred throughout the year, although infrequently during the months of December, January, and February. The small dissolved oxygen concentration problems on Turkey Creek are because of the large volume of sewage effluent from the Lone Elm and Turkey Creek Wastewater Treatment Plants.

Suspended solids

Suspended solids describes the organic and inorganic particulate matter in water. Turbid streams are not only undesirable for recreation and aesthetic enjoyment, but also are less productive because of decreased light penetration. Fish populations are adversely affected by large suspended solids concentrations, either directly or indirectly by preventing the successful development of fish eggs and larvae or by decreasing the available food supply, primarily composed of benthic invertebrates. Concentrations of suspended solids are largest in streams draining basins where the soils are predominantly easily erodible clays.

Median suspended solids concentrations ranged from 4 mg/L at Turkey Creek near Joplin to 22 mg/L at the Spring River near Baxter Springs. Data were not available for the three ancillary stations and Shoal Creek near Galena. Feder and others (1969) stated that turbidity values for Shoal Creek ranged from 2 to 30 mg/L, indicating that the stream is clear most of the time. The larger median concentrations at the upstream (16 mg/L) and downstream Spring River stations are likely because of suspended solids contributions from plains-type streams draining basins where clay soils predominate.

No significant increases in concentrations of suspended solids that would be expected because of runoff from mined areas are detected between the upstream and downstream stations on Center Creek and the Spring River (fig. 8). Suspended solids concentrations at the Spring River near Baxter Springs are significantly larger than all sites except the upstream Spring River station near Waco. The lack of a significant increase in suspended solids concentrations between Waco and Baxter Springs may be because a significant part of the suspended material is being trapped within Empire Lake (fig. 1) before reaching Baxter Springs or because of dilution from Shoal Creek.

A suspended solids standard has not been established for Missouri. However, it is stated that "water contaminants shall not cause or contribute to turbidity that will cause substantial visible contrast with the natural appearance of the stream or interfere with beneficial uses...the stream bottom shall be free of materials which will adversely alter the composition of the benthos, interfere with the spawning of fish or development of their eggs, or adversely change the physical or chemical nature of the bottom" (Missouri Department of Natural Resources, 1989, p. 3).

Fecal Coliform Bacteria

The common bacterial species Escherichia coli occurs in the intestinal tracts of warm-blooded animals. Although fecal coliform bacteria are not pathogenic, their presence in water indicates fecal contamination and, therefore, the possible presence of other organisms that are pathogenic (Hem, 1985). Sources of fecal coliform contamination include municipal wastewater-treatment effluents, septic tanks, and animal wastes from feedlots and barnyards. Median fecal coliform counts at the long-term monitoring stations ranged from 38 colonies/100 mL (colonies per 100 milliliters) at Shoal Creek near Galena to 1,600 colonies/100 mL at Turkey Creek near Joplin (table 7). Although the median counts between the upstream (150 colonies/100 mL) and downstream (180 colonies/100 mL) Spring River stations increased and the median counts between the upstream (110 colonies/100 mL) and downstream (70 colonies/100 mL) Center Creek stations decreased, the differences are not significant (fig. 8). The large fecal coliform counts at Turkey Creek near Joplin are not unusual, because at low flow, effluent from the Lone Elm and Turkey Creek Wastewater Treatment Plants comprises most of the flow in Turkey Creek (Missouri Department of Natural Resources, 1984a). The Missouri water-quality criterion for fecal coliform bacteria states that the fecal coliform bacteria count shall not exceed a geometric mean of 200 colonies/100 mL during the recreational season from April 1 to October 31 in waters designated for whole-body-contact recreation. Although Turkey Creek is not designated for whole-body-contact recreation, a count of 200 colonies/100 mL was exceeded 70 percent of the time at Turkey Creek near Joplin (table 8).

Major Constituents

Hem (1985) defines major constituents as those substances that commonly occur in concentrations greater than 1.0 mg/L. The cations generally included in this category are calcium, magnesium, sodium, and potassium. The anions are sulfate, chloride, fluoride, and bicarbonate and carbonate, the primary contributors to alkalinity. Dissolved solids concentration, a gross measure of all the substances dissolved in water, is composed primarily of these cations and anions. Summary statistics of the major constituent data collected at the long-term monitoring and ancillary stations are listed in table 7.

Increases in calcium and sulfate concentrations commonly are associated with lead-zinc and coal mining because of the oxidation of sulfide minerals (primarily pyrite), subsequent production of sulfate (SO_4^{2-}) and hydrogen ions (H^+), and neutralization of the hydrogen ion by available carbonate minerals. Generalized, unbalanced forms for these reactions are:

$$\text{Oxidation} \qquad MS + O_2 = H_2O + M^{2+}_{(aq)} + SO_4^{2-} + H^+ \qquad (1)$$

$$\text{Neutralization} \qquad H^+ + XCO_{3(s)} = X^{2+} + HCO_3^-, \qquad (2)$$

where M can be a wide variety of trace constituents, such as iron, lead, or zinc, and X usually is calcium, magnesium, or both (as in dolomite). Median concentrations of calcium and sulfate were largest at those stations located in basins most affected by mining: Cow Creek near Weir (fig. 4, no. 2; 76 mg/L, 390 mg/L), Brush Creek near Weir (fig. 4, no. 3; 110 mg/L, 540 mg/L), Turkey Creek near Joplin (fig. 4, no. 6; 92 mg/L, 110 mg/L), and Short Creek at Galena (fig. 4, no. 7; 120 mg/L, 440 mg/L). Of the long-term monitoring stations, Turkey Creek near Joplin has the largest mean ranks for all major constituents (including calcium and sulfate), except fluoride. The distributions of calcium and sulfate ranks are the same as, or similar to, those for specific conductance and dissolved solids (fig. 8).

To a lesser extent, mining activities also have affected the water quality at the upstream and downstream Center Creek stations and the downstream Spring River station near Baxter Springs. Median calcium and sulfate concentrations were 56 mg/L and 24 mg/L at Center Creek near Carterville (fig. 4, no. 4), 72 mg/L and 56 mg/L at Center Creek near Smithfield (fig. 4, no. 5), and 59 mg/L and 54 mg/L at the Spring River near Baxter Springs (fig. 4, no. 9). By comparison, at the upstream Spring River station near Waco (fig. 4, no. 1) and Shoal Creek near Galena (fig. 4, no. 8), which are in basins essentially unaffected by mining activities, median calcium concentrations were 55 mg/L and 50 mg/L, and median sulfate concentrations were 21 mg/L and 10 mg/L. The mean ranks of these concentrations are significantly smaller than calcium and sulfate ranks at the other long-term monitoring stations. Also, the ranks of calcium and sulfate concentrations at the downstream Center Creek and the Spring River stations are significantly larger than the ranks at the upstream stations (fig. 8). The distribution of calcium and sulfate concentrations at the long-term monitoring and ancillary stations is shown in figures 11 and 12.

The small median alkalinity concentrations at Cow Creek near Weir (70 mg/L), Brush Creek near Weir (4 mg/L), and Short Creek at Galena (9 mg/L) were not unusual because these streams primarily drain Pennsylvanian sandstones and shales and also because acid-forming materials, which decrease alkalinity, have been exposed through coal and lead-zinc mining activities in these basins (eqs. 1 and 2). Chemical data collected from selected streams during low-flow conditions by Spruill (1987) indicate that streams east of the Spring River have larger alkalinity concentrations than those north and west of the Spring River. Of the long-term monitoring stations, the Spring River near Baxter Springs had the smallest median alkalinity concentration (108 mg/L) and mean ranks and Turkey Creek near

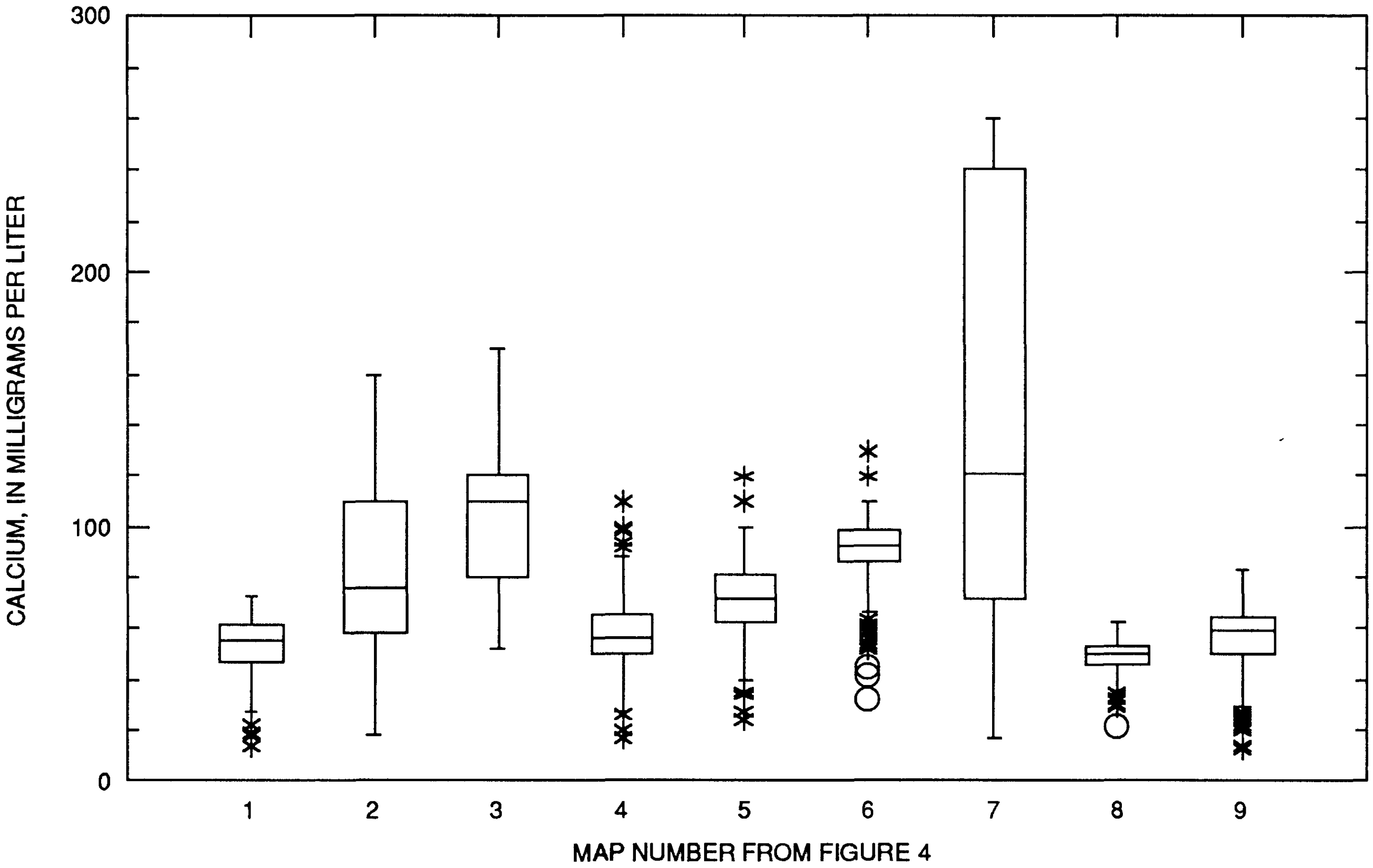

Figure 11.--Distribution of calcium concentrations at the long-term monitoring and ancillary stations (see figure 6 for explanation).

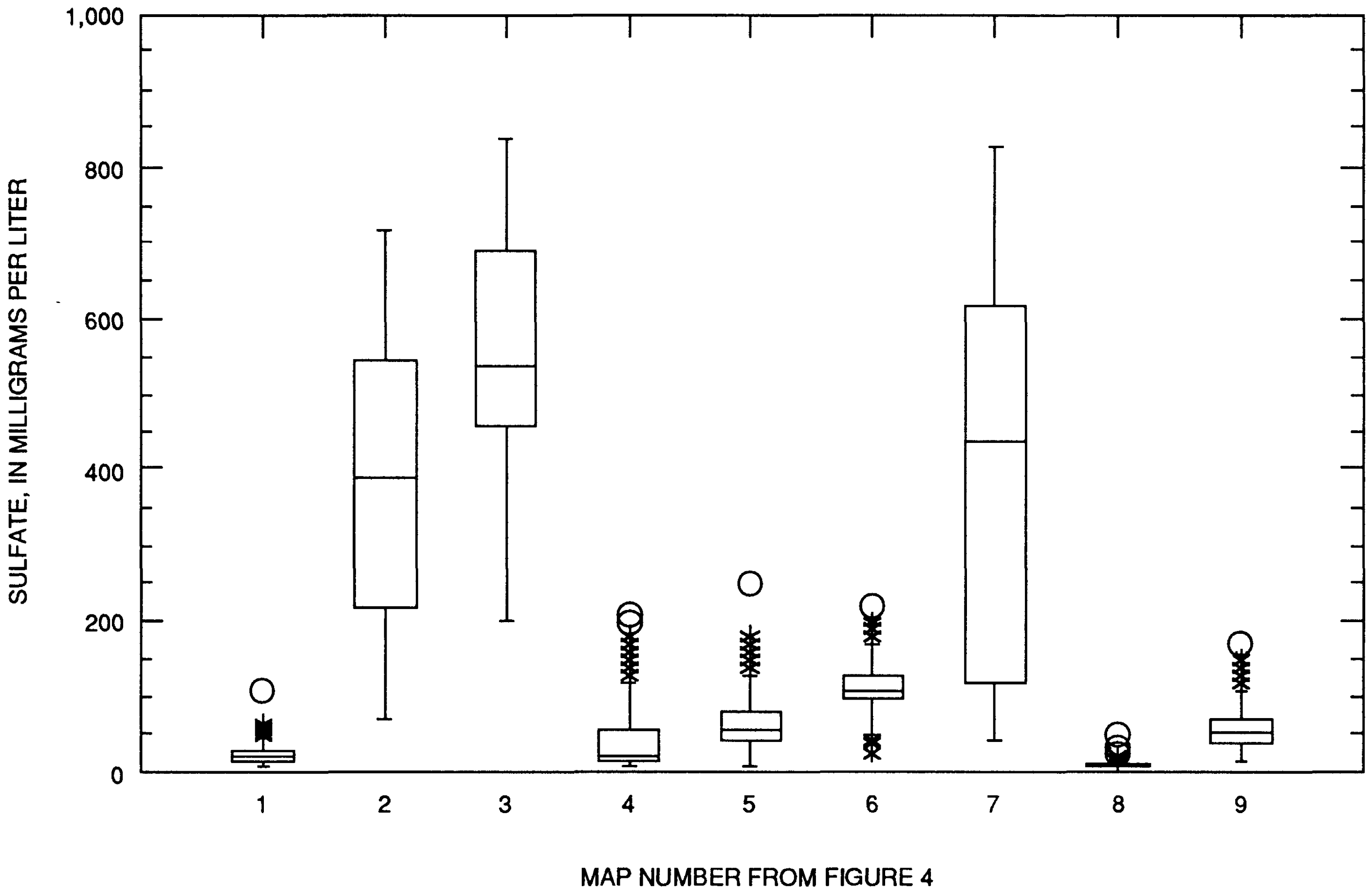

Figure 12.--Distribution of sulfate concentrations at the long-term monitoring and ancillary stations (see figure 6 for explanation).

Joplin the largest (152 mg/L; table 7; fig. 8). The significant decrease in alkalinity values from the Spring River near Waco to Baxter Springs probably was because of the effect of the aforementioned streams that drain Pennsylvanian sandstones and shales.

Sodium and chloride, although not generally associated with mining, are indicators of municipal and industrial wastes and urban runoff. A common source of both sodium and chloride is the application of road salt during winter months. Median concentrations of sodium and chloride were largest at Cow Creek near Weir (70 mg/L, 34 mg/L), Brush Creek near Weir (50 mg/L, 11 mg/L), Turkey Creek near Joplin (25 mg/L, 27 mg/L), and Short Creek at Galena (19 mg/L, 20 mg/L). There was a slight, significant increase between the upstream (6.7 mg/L, 9.6 mg/L) and downstream (9.6 mg/L, 11 mg/L) Spring River stations, whereas there was essentially no change between the upstream (8.8 mg/L, 8.4 mg/L) and downstream (8.0 mg/L, 9.4 mg/L) Center Creek stations (fig. 8). The lowest median concentration of sodium was at Shoal Creek near Galena (5.5 mg/L).

Median fluoride concentrations at the six long-term monitoring stations ranged from 0.1 mg/L at the Spring River near Waco and Shoal Creek near Galena to 0.7 mg/L at Center Creek near Carterville; the median fluoride concentrations at the three ancillary stations ranged from 0.6 mg/L at Brush Creek near Weir to 3.4 mg/L at Short Creek at Galena. The most common sources of fluoride in natural water are the minerals fluorite (CaF_2) and apatite [$Ca_5(Cl,F,OH)(PO_4)_3$]. Neither of these minerals has been identified as occurring naturally within the region; as a result, fluoride concentrations usually should be less than 1 mg/L, which was the concentration detected at both of the proposed baseline stations (Shoal Creek near Galena and Spring River near Waco). Apatite, however, commonly is used in the manufacture of phosphate fertilizers and as a source for salts of phosphoric acid (Cathcart, 1978). The phospho-gypsum piles along Grove Creek and Short Creek contain abundant apatite and are sources of not only phosphate but substantial quantities of fluoride. Both stations on Center Creek have significantly larger fluoride ranks than either of the proposed baseline stations. Substantial inputs of fluoride to the Spring River between Waco and Baxter Springs are indicated from the significant increase in fluoride ranks (fig. 8). Although the median fluoride concentration at Center Creek near Carterville was 0.7 mg/L, the Missouri water-quality standard of 4.0 mg/L for livestock and wildlife watering was exceeded 31 percent of the time before 1969 (table 8). The maximum fluoride concentration at Carterville was 40 mg/L. The standard was exceeded only 6 percent of the time at Center Creek near Smithfield before 1969 (table 8), where the maximum concentration was 21 mg/L, indicating dilution of the fluoride between Carterville and Smithfield.

Stiff diagrams (Stiff, 1951) commonly are used to illustrate the proportions of each ionic species contained in water and also to define water type. Cation-anion diagrams for the long-term monitoring and ancillary stations are shown in figure 13. Median concentrations (table 7) of the major constituents were used to construct the diagrams; alkalinity was converted to bicarbonate. At the Spring River near Waco, Center Creek near Carterville, and Shoal Creek near Galena, the water is a calcium-bicarbonate type, which is expected for these streams that are unaffected or only slightly affected by mining. The effects of mining are evident at the downstream Center Creek and Spring River stations where the water is a calcium-sulfate-bicarbonate type. The water types at Brush Creek near Weir and Cow Creek near Weir (sodium-magnesium-calcium-sulfate), Turkey Creek near Joplin (calcium-sulfate-bicarbonate), and Short Creek at Galena (calcium-sulfate) are typical in streams affected by industrial and municipal wastes and mining.

Nutrients

Nutrients are elements that are essential to plant growth. Aquatic vegetation, such as algae, depend on nitrogen and phosphorus compounds for a nutrient supply, but the availability of other required elements also may affect growth. Dense growths of algae, or algal blooms, usually occur when the concentration of nitrogen or phosphorus increases above normal, ambient concentrations. During an algal bloom, a lake or stream becomes undesirable for recreational use. After an algal bloom die-off, bacterial decomposition of dead algal cells, which sink to the bottom of lakes and slow moving

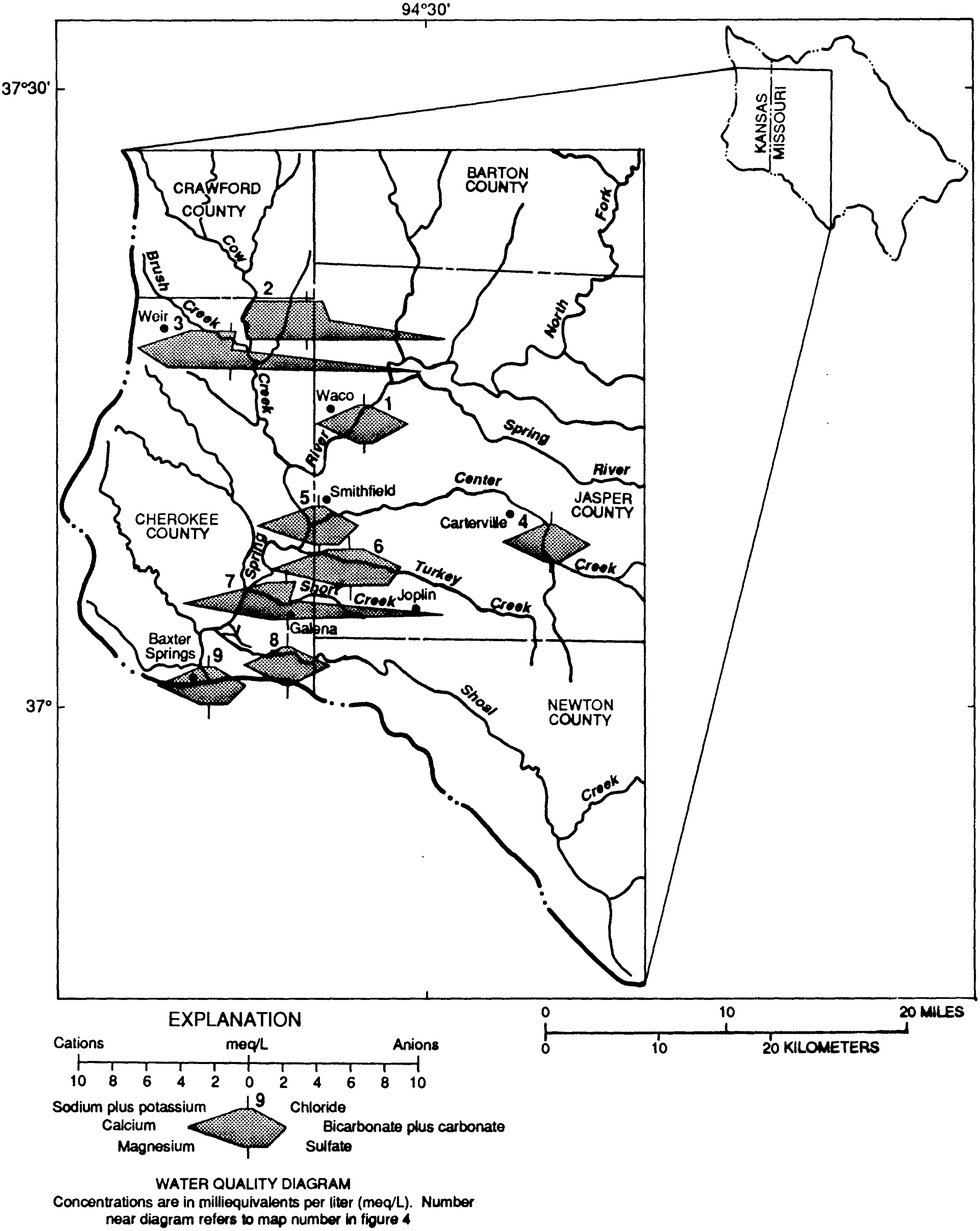

Figure 13.--Stiff diagrams for long-term monitoring and ancillary stations in the Spring River basin.

streams, can result in the depletion of dissolved oxygen, especially during the period of thermal stratification. The anoxic conditions can result in fish kills and other negative effects on aquatic life. Although nitrogen and phosphorus are both essential for algal growth, phosphorus availability is considered to be the limiting factor in many natural waters (Hem, 1985). Phosphorus-containing rocks are relatively insoluble and the chemistry of the element favors its precipitation in water, thereby limiting the quantity of phosphorus available for plant growth.

Nitrogen most commonly occurs in water as the nitrite (NO_2^-) and nitrate (NO_3^-) anions or the ammonium (NH_4^+) cation, although nitrite and ammonia are unstable in water and generally will oxidize to the nitrate form. The most common phosphorus compound in water is the orthophosphate ion (PO_4^{3-}). The dissolution of rock and soils by surface and ground water is a natural source for nitrogen and phosphorus in streams. Major anthropogenic sources are municipal and industrial wastewaters, septic tanks, fertilizers, and feedlot discharges. In addition, the use of phosphate detergents during the 1950's and 1960's increased the output of phosphate by wastewater-treatment plants. Summary statistics of the nutrient data collected at the long-term monitoring and ancillary stations are listed in table 7.

Median concentrations of total nitrite plus nitrate ranged from 1.2 mg/L at Turkey Creek near Joplin (fig. 4, no. 6) to 4.9 mg/L at both Center Creek stations (fig. 4, nos. 4 and 5). There were no total nitrite plus nitrate data available for the ancillary stations. Median total ammonia concentrations at the long-term monitoring stations ranged from 0.03 mg/L at Shoal Creek near Galena (fig. 4, no. 8) to 1.8 mg/L at Turkey Creek near Joplin. Median total phosphorus concentrations ranged from 0.13 mg/L at Center Creek near Carterville and Shoal Creek near Galena to 1.4 mg/L at Turkey Creek near Joplin. At Short Creek at Galena (fig. 4, no. 7), the large median total phosphorus concentration (39 mg/L) was principally because of seepage from the phospho-gypsum pile located nearby. Because the total ammonia data for Short Creek at Galena were collected between April 1976 and August 1979, the large median total ammonia concentration (18 mg/L) may not represent current (1991) conditions in the Short Creek basin. According to the Missouri DNR, the fertilizer plant located near Short Creek has not discharged process wastewater to the phospho-gypsum pile since before January 1979, at which time the company requested a modification of their NPDES permit to reflect this fact (E.H. Sears, Missouri Department of Natural Resources, oral commun., 1990).

Shoal Creek near Galena and the Spring River near Waco (fig. 4, no. 1) have among the smallest mean ranks for all nutrients included in the ANOVA design, and with the exception of total nitrite plus nitrate, Turkey Creek near Joplin has among the largest (fig. 8). The small total nitrite plus nitrate ranks and the large total and dissolved ammonia ranks indicate the predominance of reduced nitrogen species. During low flow, effluent from the Lone Elm and Turkey Creek Wastewater Treatment Plants comprises most of the flow in Turkey Creek (Missouri Department of Natural Resources, 1984a). Downstream from the treatment plants, the stream has had past problems with small dissolved oxygen and large ammonia concentrations. Biologic oxidation of ammonia by autotrophs has been shown to create a major demand on dissolved oxygen in aquatic systems (Dugdale and Dugdale, 1965).

Significant point sources for nitrate and ammonia have been identified by the Missouri DNR along Grove Creek and Center Creek upstream from Center Creek near Carterville (Missouri Department of Natural Resources, 1984a). The significantly larger mean ranks of total and dissolved ammonia and total nitrite plus nitrate at both stations on Center Creek, as compared to the proposed baseline stations, indicate substantial effects from those sources. The decrease in the ranks of both total and dissolved ammonia between the upstream and downstream Center Creek stations substantiates the effect of point sources upstream from Carterville. Unlike the mean ranks of total and dissolved ammonia, the ranks of total nitrite plus nitrate do not have corresponding decreases between Carterville and Smithfield. This is not unexpected because a downstream decrease in ammonia concentrations should result in increased, or at least constant, nitrate concentrations.

Mean ranks of total nitrite plus nitrate, total and dissolved ammonia, and total and dissolved phosphorus are significantly larger at the downstream Spring River station near Baxter Springs (fig. 4, no. 9) than at the upstream station near Waco, indicating substantial sources of these constituents within the basin. Although Turkey Creek near Joplin had larger values of total and dissolved phosphorus than the Spring River near Baxter Springs, its effect on the water quality at Baxter Springs probably was secondary to Short Creek, which had more than 30 times the concentration of total phosphorus between 1976 and 1982 (table 7).

Although the median total ammonia concentrations at Center Creek near Carterville (0.6 mg/L) and Turkey Creek near Joplin (1.8 mg/L) were not particularly large, the Missouri water-quality standard for the protection of aquatic life (the chronic criteria for total ammonia in a general, warm-water fishery) was exceeded 27 percent of the time at Center Creek near Carterville and 47 percent of the time at Turkey Creek near Joplin (table 8). Because the toxicity of ammonia is dependent on pH value and temperature, as well as the concentrations of total ammonia, the actual standard varies with the pH value and temperature of the water. The distribution of total nitrite plus nitrate, total ammonia, and total phosphorus concentrations at sampling stations in the Spring River basin are shown in figures 14, 15, and 16.

Trace Constituents

Hem (1985) defines trace constituents as those substances that always or nearly always occur in concentrations less than 1.0 mg/L. Small quantities of many trace constituents are essential for plant and animal life, but often these same trace constituents are toxic to aquatic life at concentrations only slightly larger than those that occur naturally. Trace constituents considered in this section are dissolved cadmium, chromium, copper, iron, lead, manganese, and zinc. Because total-recoverable concentrations depend on sample collection techniques, only dissolved trace constituents will be discussed. Summary statistics of the trace-constituent data collected at the long-term monitoring and ancillary stations are listed in table 7.

The oxidation of sulfide minerals, as shown in equation 1, creates acid conditions and may result in large concentrations of dissolved constituents in solution. However, in near neutral, moderately oxidizing waters, the concentrations of most trace constituents (such as iron and lead) are controlled by formation of insoluble compounds and would not necessarily be expected to correlate with sulfate concentrations in mine-affected areas. In contrast, zinc concentrations have no such controls and are limited by relatively soluble minerals, such as hydrozincite [$Zn_5(OH)_6(CO_3)_{2(s)}$] and smithsonite ($ZnCO_3$).

Median concentrations of dissolved cadmium, chromium, copper, and lead were at, or only slightly above, detection at all stations, with the exception of a median dissolved cadmium concentration of 280 μg/L (micrograms per liter) and a median dissolved copper concentration of 240 μg/L at Short Creek at Galena. The small concentrations are consistent with the limited solubility of these trace constituents at near-neutral pH. With the exception of Brush Creek near Weir, median dissolved iron concentrations were relatively small at all stations, ranging from 20 μg/L at both Center Creek stations, Short Creek at Galena, and Shoal Creek near Galena, to 80 μg/L at Turkey Creek near Joplin. Because of the extensive surface coal mining in the Brush Creek basin and the resulting low pH value of the water (table 7), the large median dissolved iron concentration at Brush Creek near Weir (2,600 μg/L) was not unexpected.

Dissolved iron ranks, although largest at Turkey Creek near Joplin, are nondistinct at the other long-term monitoring stations (fig. 8). The relatively nondistinct iron ranks, the generally small concentrations of dissolved iron, and the lack of significant increases between the upstream and downstream Center Creek and Spring River stations indicate small concentrations of available ferrous iron. Rapid oxidation of ferrous to ferric iron and precipitation may explain the small concentrations. Spruill (1987) indicated that concentrations of dissolved iron were small in Short Creek and reached

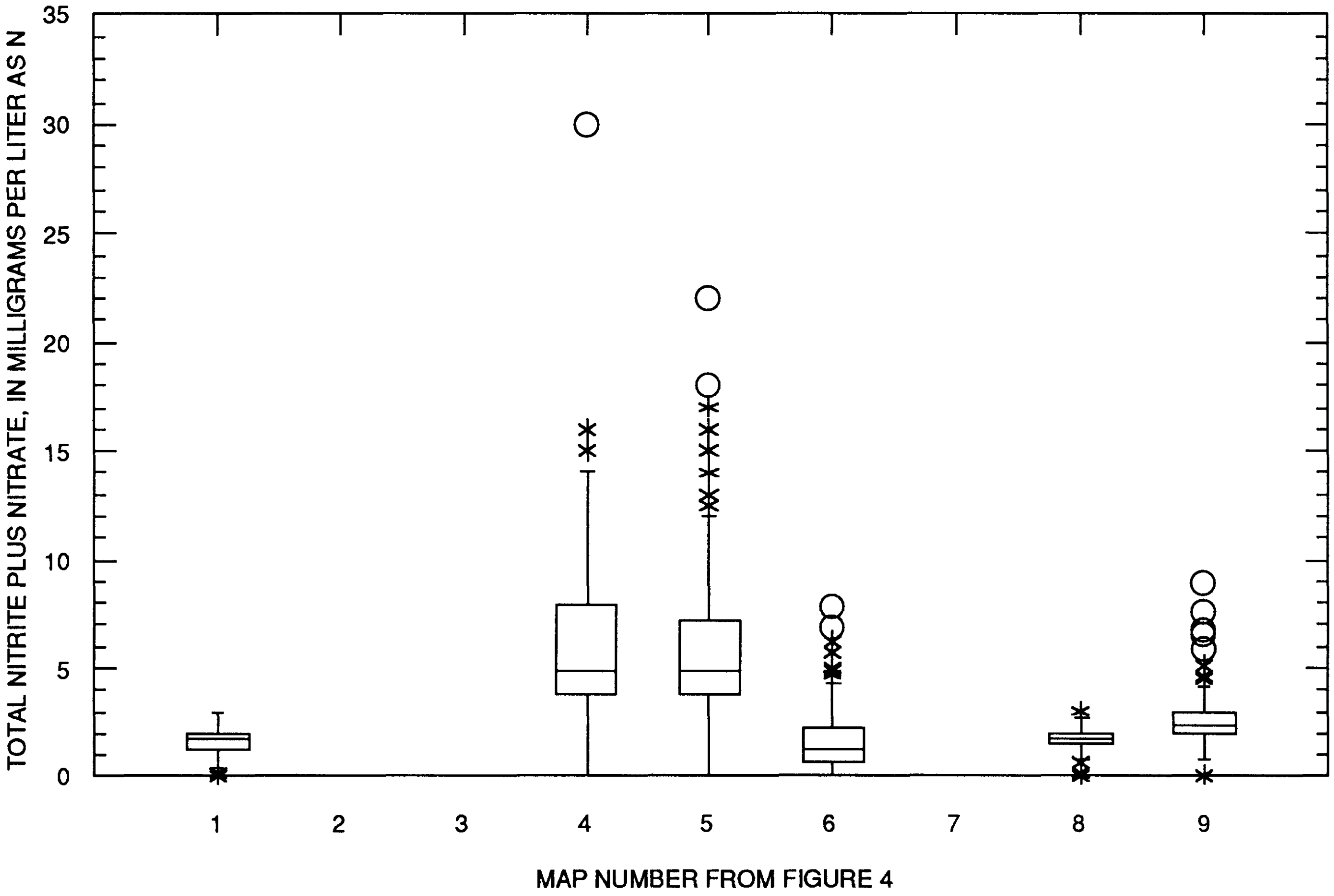

Figure 14.--Distribution of total nitrite plus nitrate concentrations at the long-term monitoring stations. (There were no total nitrite plus nitrate data available for the ancillary stations; see figure 6 for explanation.)

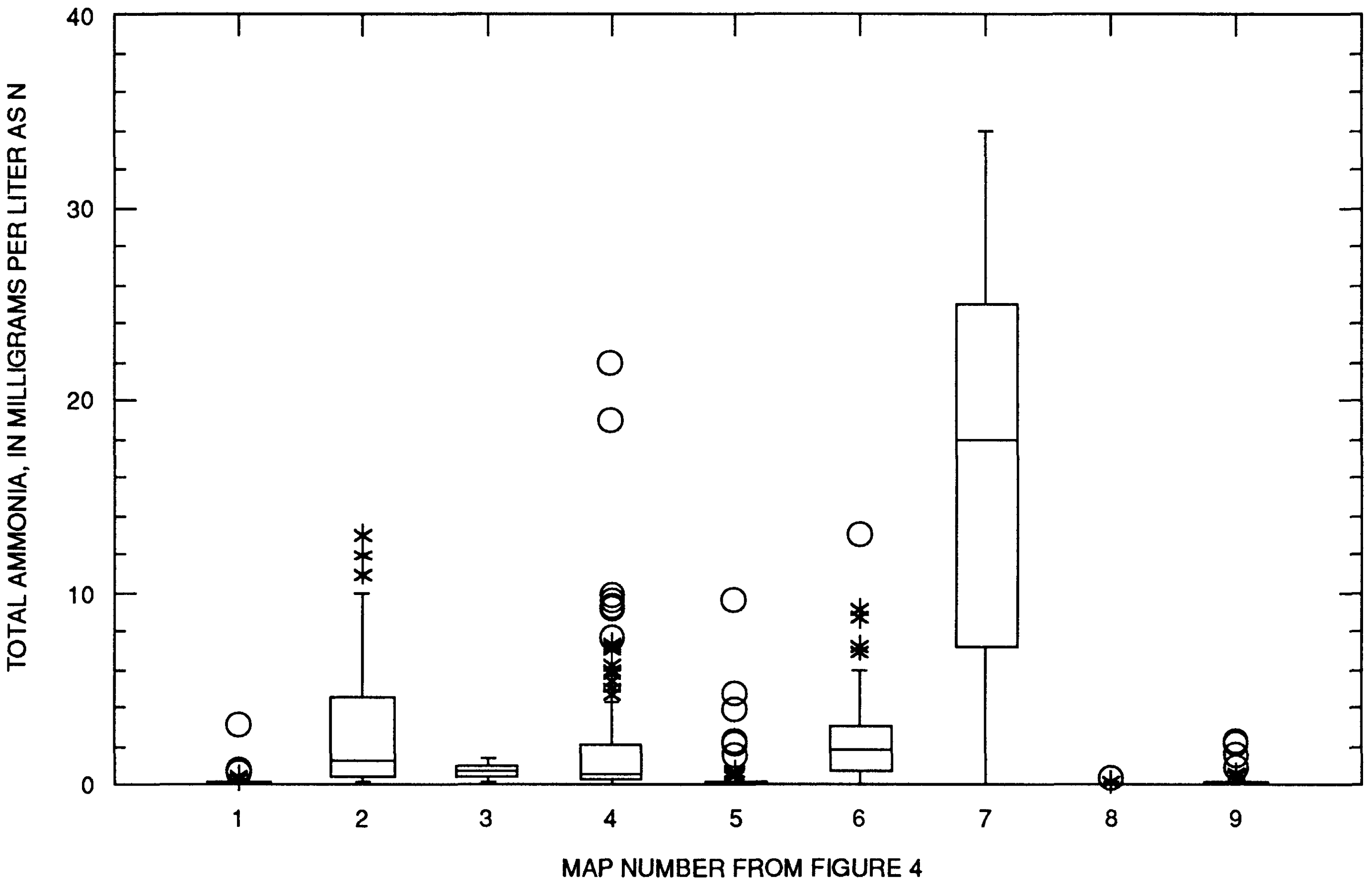

Figure 15.--Distribution of total ammonia concentrations at the long-term monitoring and ancillary stations (see figure 6 for explanation).

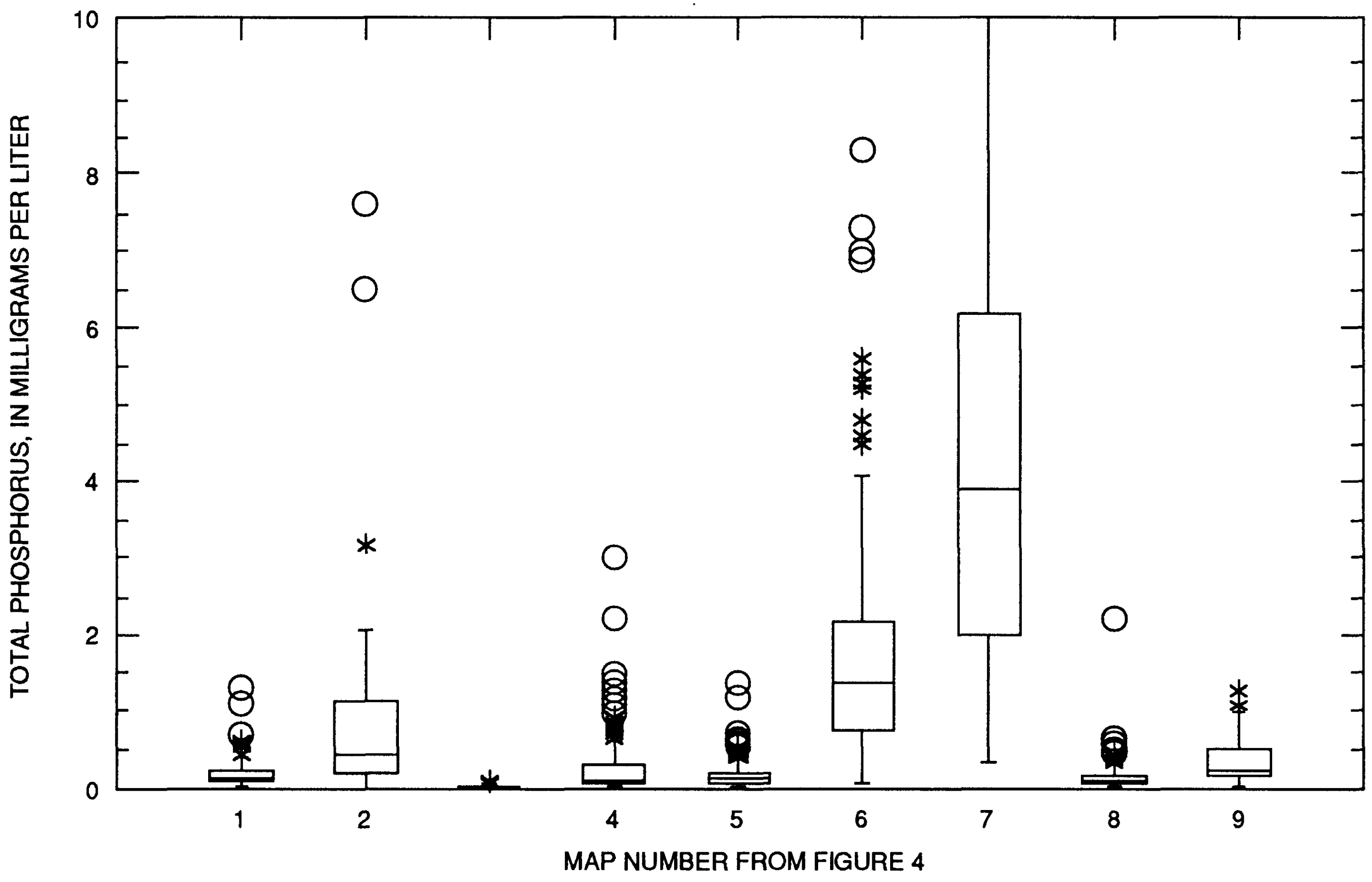

Figure 16.--Distribution of total phosphorus concentrations at the long-term monitoring and ancillary stations. (Concentrations for station 7 are divided by 10; see figure 6 for explanation.)

similar conclusions. Concentrations of dissolved iron do not seem to be affected by lead-zinc mining in streams with moderate dissolved oxygen concentrations and pH value. Also, according to Spruill (1987), oxidizing conditions exist in mines from the eastern part of the Spring River basin, and this may limit concentrations of dissolved iron in these areas.

At the long-term monitoring stations, median dissolved manganese concentrations ranged from 10 μg/L at Shoal Creek near Galena to 150 μg/L at Turkey Creek near Joplin and the Spring River near Baxter Springs. The difference in median concentrations between the upstream (60 μg/L) and downstream (50 μg/L) Center Creek stations was not appreciable, but the median dissolved manganese concentration increased from 30 μg/L at the upstream Spring River station near Waco to 150 μg/L at the downstream station near Baxter Springs. Median dissolved manganese concentrations were large at Cow Creek near Weir (2,400 μg/L), Brush Creek near Weir (4,000 μg/L), and Short Creek at Galena (3,000 μg/L).

Although Turkey Creek near Joplin has large concentrations of dissolved manganese (table 7), effects from lead-zinc mining are not readily evident based on the lack of significant differences in dissolved manganese ranks between the upstream and downstream stations on Center Creek and the downstream Center Creek station near Smithfield and the Spring River near Waco (fig. 8). Also, the large dissolved manganese ranks at the Spring River near Baxter Springs indicate substantial effects from other sources not evaluated in the ANOVA design, probably Cow, Brush, and Short Creeks. Because manganese often is associated with organic material (Slack and Feltz, 1968), the dissolved manganese concentrations at Turkey Creek near Joplin may be related to large quantities of organic matter from the wastewater-treatment facilities, aquatic plants, and leaf litter and small concentrations of dissolved oxygen, which would prevent the precipitation of manganese oxides.

Zinc, because of its solubility in water, often is used as an indicator of mining, along with calcium, sulfate, and dissolved solids. Median dissolved zinc concentrations at the long-term monitoring stations ranged from 30 μg/L at the Spring River near Waco (fig. 4, no. 1) to 420 μg/L at Center Creek near Smithfield (fig. 4, no. 5). The median concentration increased significantly from the upstream (fig. 4, no. 4; 53 μg/L) to the downstream (420 μg/L) station on Center Creek and from the upstream (30 μg/L) to the downstream (fig. 4, no 9; 310 μg/L) station on the Spring River, which can be attributed to the effects of lead-zinc mining. Only six samples were collected at Shoal Creek near Galena (fig. 4, no. 8) and the Spring River near Baxter Springs for dissolved zinc analysis, which makes the median values (40 μg/L at Shoal Creek) suspect. At the ancillary stations, the median dissolved zinc concentration was 30 μg/L at Cow Creek near Weir (fig. 4, no. 2), 250 μg/L at Brush Creek near Weir (fig. 4, no. 3), and 49,000 μg/L at Short Creek at Galena (fig. 4, no. 7). The distribution of dissolved zinc concentrations at the long-term monitoring and ancillary stations is shown in figure 17.

The large concentrations of dissolved zinc in Short Creek reflect the substantial effect from mining activities within this basin. The large concentrations of cadmium, a common trace impurity in sphalerite, and sulfate indicate the dissolution of large quantities of sphalerite in addition to other sulfide minerals. Proposed solubility limits on zinc concentrations in solution, such as smithsonite, have been proposed by Hem (1985). However, the low pH value and subsequent low availability of aqueous carbonate in Short Creek inhibit the precipitation of zinc carbonate phases. Equilibrium calculations using SOLMINEQ.88 (Kharaka and others, 1988) indicate undersaturation with respect to zinc carbonate phases and a theoretical upper limit of dissolved zinc in excess of 220,000 μg/L.

The minimal variability in mean ranks for dissolved zinc and lack of differences between Center Creek near Smithfield, Turkey Creek near Joplin, and the Spring River near Baxter Springs may indicate substantial effects from other sources (such as Short Creek) or may be the result of a Type I error caused by the small number of samples collected at Baxter Springs for dissolved zinc. However, significant effects on dissolved zinc concentrations attributable to mining are indicated between the baseline stations (Shoal Creek near Galena and the Spring River near Waco) and Center Creek near

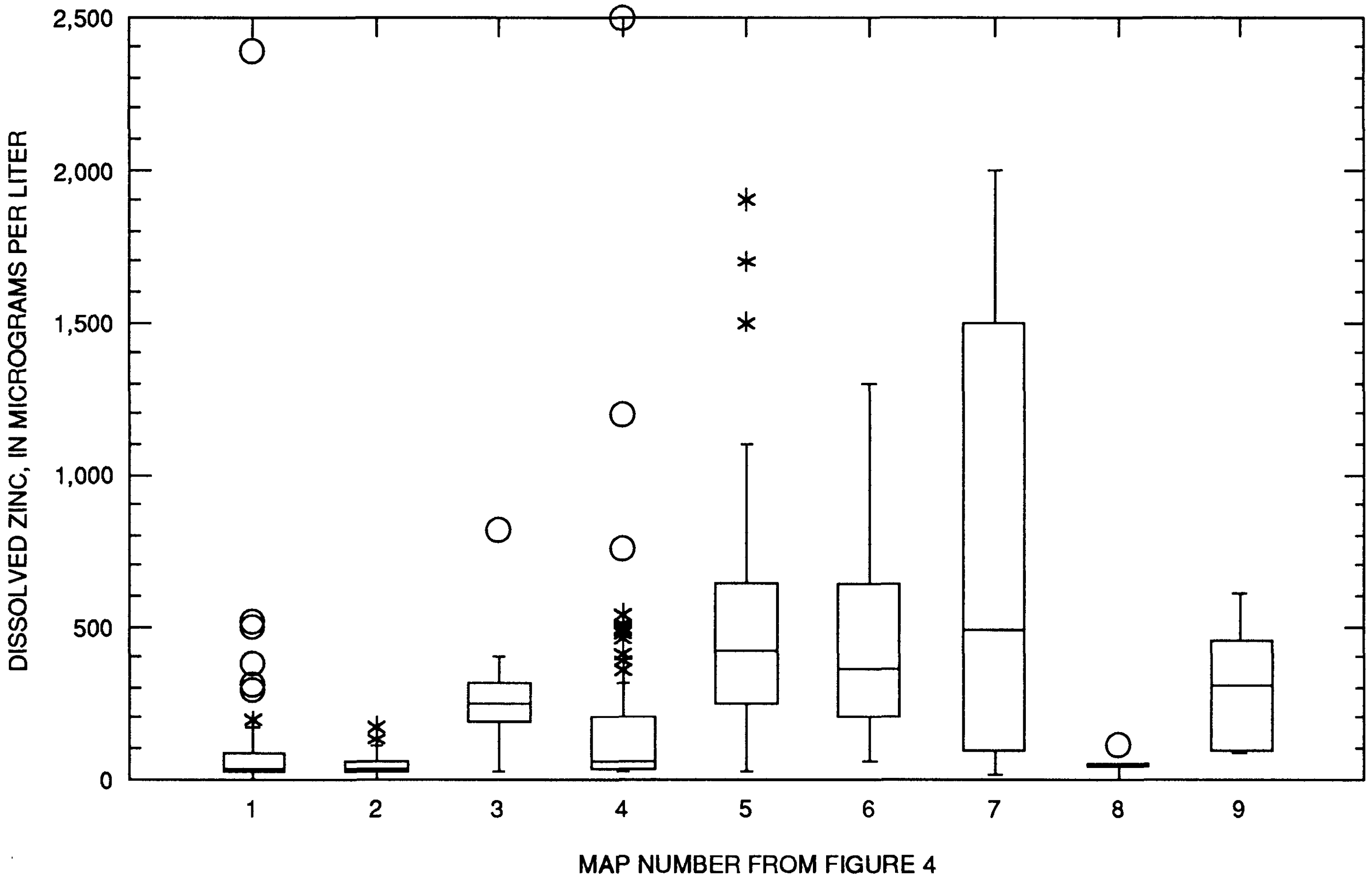

Figure 17.--Distribution of dissolved zinc concentrations at the long-term monitoring and ancillary stations. (Concentrations for station 7 are divided by 100; see figure 6 for explanation.)

Smithfield and Turkey Creek near Joplin (fig. 8). Like many other mining-related constituents, mean ranks of dissolved zinc at the downstream Center Creek station are significantly larger than at the upstream station.

The toxicity of zinc to aquatic animals, including fish and benthic invertebrates, depends on the hardness, dissolved oxygen concentration, and temperature of the water. The Missouri chronic toxicity maximum for zinc in a general, warm-water fishery ranges from 245 to 440 µg/L; the actual value is determined by the hardness of the water. This standard was exceeded a large percentage of the time (table 8) at Center Creek near Smithfield (65 percent), Turkey Creek near Joplin (41 percent), and the Spring River near Baxter Springs (50 percent, although this number is suspect because of the small number of samples; table 7). The frequent exceedance of the zinc standard was the likely reason for the almost total lack of a benthic invertebrate population in Center and Turkey Creeks. Also, the benthic invertebrate population in Turkey Creek probably was adversely affected by wastewater-treatment plant effluents.

Baseline Water-Quality Characteristics

Baseline water quality refers to the condition of a stream that has been minimally affected by human activities. It is apparent from an evaluation of the summary statistics (table 7) and the results of the ANOVA (fig. 8) that Shoal Creek near Galena, Kansas (fig. 4, no. 8), and the Spring River near Waco, Missouri (fig. 4, no. 1), have the smallest concentrations of major constituents (with the exception of alkalinity), nutrients, and trace constituents. The Spring River upstream from Cow Creek and Shoal Creek along its entire length are only minimally affected by human activities. Municipal point sources of pollution are the primary concerns in both basins. These problems usually are localized because dilution and large assimilative capacities minimize the overall effect. This is substantiated by inspection of the summary statistics for Shoal Creek near Galena and the Spring River near Waco.

The differences in water-quality characteristics between Shoal Creek near Galena and the Spring River near Waco primarily are because of differences in geology (fig. 3), topography, and land use (table 3). About 50 percent of the drainage area of the Spring River near Waco is in the plains, and discharge from plains-type streams makes up approximately 10 percent of the flow at Waco. This is in contrast to Shoal Creek, an entirely Ozark-type stream. Land use in the Spring River basin upstream from Waco is between 70 to 85 percent agricultural and only 15 to 30 percent forest; the Shoal Creek basin is 55 percent agricultural and 45 percent forest (Missouri Department of Natural Resources, 1984a). There seem to be two distinct water-quality baselines in the Spring River basin. A third baseline would be representative of streams in the basin that are 100 percent plains-type, but insufficient water-quality data were available for unaffected streams of this type. Based on the geology and topography in the Center Creek and Turkey Creek basins, the water quality for these streams should most closely resemble that of Shoal Creek, if the two streams were not affected by mining and municipal and industrial wastes. Likewise, at the downstream Spring River station near Baxter Springs, Kansas (fig. 4, no. 9), where approximately 50 percent of the drainage area is plains and 10 percent of the flow is from plains-type streams, the water quality should most closely resemble that at the Spring River near Waco.

The actual baseline values and concentrations for physical properties, chemical constituents, and fecal coliform bacteria probably are best represented by two numbers: (1) The median values for samples collected at discharges between the 25th and 75th percentile (medium flow, table 7); and (2) the median values for samples collected at discharges equal to or less than the 5th percentile (low flow, table 7). These values, along with the median values for samples collected at discharges equal to or greater than the 95th percentile (high flow), are listed in table 9 for the Spring River near Waco and Shoal Creek near Galena. The high-flow values are listed to indicate the effects of storm runoff on

Table 9.--*Median constituent concentrations for low, medium, and high flow samples at the Spring River near Waco, Missouri, and Shoal Creek near Galena, Kansas*

[Low flow is defined as less than the 5th percentile discharge listed in table 7; medium flow is defined as greater than the 25th percentile discharge but less than the 75th percentile discharge listed in table 7; high flow is defined as greater than the 95th percentile discharge listed in table 7; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; --, no data; mL, milliliters; $CaCO_3$, calcium carbonate; ROE, residue on evaporation at 180 degrees Celsius; N, nitrogen; <, less than; µg/L, micrograms per liter]

Physical property or constituent	Low flow		Medium flow		High flow	
	Number of samples	Median value or concentration	Number of samples	Median value or concentration	Number of samples	Median value or concentration
			Spring River near Waco, Missouri (fig. 4, no. 1)			
Specific conductance (µS/cm)	13	380	135	325	14	184
pH (standard units)	5	8.2	54	7.9	3	7.4
Temperature (°C)	13	9.0	130	18.0	11	8.0
Dissolved oxygen (mg/L)	13	11.0	134	8.0	14	9.2
Dissolved oxygen, percent saturation	5	89	53	80	3	73
Suspended solids (mg/L)	3	2	12	12	--	--
Fecal coliform (colonies per 100 mL)	5	10	31	160	3	2,300
Calcium (mg/L)	11	62	124	56	14	29
Magnesium (mg/L)	11	5.2	124	3.5	14	2.4
Sodium (mg/L)	11	11	124	6.8	14	4.4
Potassium (mg/L)	11	2.3	124	2.2	14	3.8
Alkalinity (mg/L as $CaCO_3$)	13	156	129	128	14	53
Sulfate (mg/L)	11	21	124	21	14	18
Chloride (mg/L)	10	16	124	10	14	6.1
Fluoride (mg/L)	4	.10	65	.10	6	.30
Dissolved solids (ROE, mg/L)	3	238	45	190	3	125
Total nitrite plus nitrate (mg/L as N)	10	1.3	65	1.9	10	1.2
Total ammonia (mg/L as N)	12	.04	54	.04	10	.14
Dissolved ammonia (mg/L as N)	--	--	19	<.01	--	--
Total phosphorus (mg/L)	12	.25	79	.15	10	.27

Table 9.--*Median constituent concentrations for low, medium, and high flow samples at the Spring River near Waco, Missouri, and Shoal Creek near Galena, Kansas*--Continued

Physical property or constituent	Low flow		Medium flow		High flow	
	Number of samples	Median value or concentration	Number of samples	Median value or concentration	Number of samples	Median value or concentration
Spring River near Waco, Missouri (fig. 4, no. 1)--Continued						
Dissolved phosphorus (mg/L)	1	0 .08	20	0 .10	2	0.12.
Total-recoverable cadmium (µg/L)	2	<2	12	3	--	--
Dissolved cadmium (µg/L)	2	<2	13	2	--	--
Dissolved chromium (µg/L)	1	<20	16	<20	3	<20
Total-recoverable copper (µg/L)	2	<20	12	<20	--	--
Dissolved copper (µg/L)	2	<20	27	<20	3	<20
Total-recoverable iron (µg/L)	2	250	12	480	1	6,800
Dissolved iron (µg/L)	3	20	30	35	3	70
Total-recoverable lead (µg/L)	2	7	9	10	--	--
Dissolved lead (µg/L)	3	<5	42	<5	3	5
Total-recoverable manganese (µg/L)	2	60	12	70	--	--
Dissolved manganese (µg/L)	3	20	52	30	3	30
Total-recoverable zinc (µg/L)	2	100	11	30	--	--
Dissolved zinc (µg/L)	3	20	44	35	3	20
Shoal Creek near Galena, Kansas (fig. 4, no. 8)						
Specific conductance (µS/cm)	9	320	93	280	12	215
pH (standard units)	3	8.2	21	8.1	3	7.8
Temperature (°C)	9	17.0	93	18.0	12	10.0
Dissolved oxygen (mg/L)	9	9.4	92	9.2	12	10.6
Dissolved oxygen, percent saturation	3	118	17	93	3	91
Suspended solids (mg/L)	--	--	--	--	--	--
Fecal coliform (colonies per 100 mL)	3	12	13	44	3	430
Calcium (mg/L)	9	52	92	51	12	38
Magnesium (mg/L)	9	3.7	92	3.0	12	2.0
Sodium (mg/L)	9	8.0	92	5.4	12	3.5

Table 9.--*Median constituent concentrations for low, medium, and high flow samples at the Spring River near Waco, Missouri, and Shoal Creek near Galena, Kansas*--Continued

Physical property or constituent	Low flow		Medium flow		High flow	
	Number of samples	Median value or concentration	Number of samples	Median value or concentration	Number of samples	Median value or concentration
Shoal Creek near Galena, Kansas (fig. 4, no. 8)--Continued						
Potassium (mg/L)	9	1.8	92	1.6	12	1.6
Alkalinity (mg/L as $CaCO_3$)	8	133	92	122	12	88
Sulfate (mg/L)	9	12	92	10	12	10
Chloride (mg/L)	7	13	54	8.0	4	5.0
Fluoride (mg/L)	4	.20	37	.10	8	.10
Dissolved solids (ROE, mg/L)	3	185	17	163	3	135
Total nitrite plus nitrate (mg/L as N)	5	1.7	49	1.6	4	1.8
Total ammonia (mg/L as N)	5	.07	48	.05	4	.02
Dissolved ammonia (mg/L as N)	3	<.01	9	<.01	--	--
Total phosphorus (mg/L)	8	.19	60	.12	5	.07
Dissolved phosphorus (mg/L)	3	.24	15	.13	2	.05
Total-recoverable cadmium (µg/L)	--	--	3	<2	--	--
Dissolved cadmium (µg/L)	--	--	2	<2	--	--
Dissolved chromium (µg/L)	--	--	4	<20	--	--
Total-recoverable copper (µg/L)	--	--	4	<20	--	--
Dissolved copper (µg/L)	--	--	4	<20	--	--
Total-recoverable iron (µg/L)	--	--	4	130	--	--
Dissolved iron (µg/L)	3	<20	19	20	3	20
Total-recoverable lead (µg/L)	--	--	2	<5	--	--
Dissolved lead (µg/L)	--	--	1	<5	--	--
Total-recoverable manganese (µg/L)	--	--	6	25	--	--
Dissolved manganese (µg/L)	3	20	19	10	3	<10
Total-recoverable zinc (µg/L)	--	--	4	80	--	--
Dissolved zinc (µg/L)	--	--	4	40	--	--

total and dissolved constituent concentrations and on fecal coliform bacteria counts and should not be considered a reliable indicator of high-flow conditions. At high flows, concentrations vary depending on whether the sample is collected on the rising or falling limb of the hydrograph.

Generally, median constituent values and concentrations for samples collected at medium flows vary insignificantly from the overall medians (table 7) and represent average stream conditions. As expected, low-flow values and concentrations are the largest, with the exception of fecal coliform, suspended solids, and total trace constituents, which usually increase with increasing flow. This is true only up to a certain point, however. Substantial flood flows eventually can result in decreasing concentrations of these constituents because of dilution effects. The low-flow values and concentrations are representative of stream base-flow conditions, when much of the discharge originates from ground-water sources. Median dissolved trace-constituent concentrations at the Spring River near Waco were at or near the detection limit at all stages, with the exception of dissolved iron concentrations, which seem to increase with flow. This probably is because of colloidal iron. The lack of dissolved trace-constituent data for Shoal Creek near Galena (table 7) makes it difficult to determine baseline trace-constituent concentrations with certainty. However, based on the dissolved iron and manganese concentrations at low and medium flows, it can be assumed that other trace-constituent concentrations also will be at or near the detection limit.

Relation of Water-Quality Constituents to Discharge

The concentrations of total-recoverable and dissolved chemical constituents in a stream are related to many factors including, but not limited to, climate, topography, geology, and biota. Two other important factors are (1) the capacity of the stream to transport large concentrations of suspended sediment and its associated matrix and adsorbed chemical constituents, and (2) the volume of water available to dilute dissolved chemical constituents (Rinella, 1986). Constituents associated with ground-water sources usually are inversely related to discharge, whereas those constituents derived from runoff sources, such as suspended solids, usually will be directly related to discharge. In addition, constituents associated with industrial, municipal, or agricultural activity may exhibit either positive or negative relations with discharge providing significant increases or decreases in these activities occur within the basin.

To evaluate general relations between constituent concentrations and discharge within the Spring River basin, Spearman rank correlation coefficients (nonparametric test) were computed at each of the six long-term monitoring stations (Iman and Conover, 1983). Values for constituents were individually ranked over the entire period of record at each station and matrixes of correlation coefficients were computed. Coefficients between all constituents and discharge for each station are listed in tables 10 to 15. The values of the correlation coefficient (r_s) range from -1.0 and 1.0. Positive values indicate a tendency for ranks of one constituent to increase as the ranks of the other constituent increase. When r_s is negative, there is a tendency for ranks of one constituent to decrease as the ranks of the other constituent increase.

Because pairwise deletion was used to remove observations with missing values in the correlation matrixes, it is possible that coefficients computed between constituents with substantial numbers of missing values may be computed between different subsets of the data. Because of this uncertainty, coefficients between constituents with small sample sizes as compared to the total number of samples for each station should be considered unreliable.

As expected, correlations between many of the major constituents and discharge are negative at each site. This indicates dilution of these constituents during high flow. Potassium, however, exhibits only slightly negative correlations at most sites except at the Spring River near Waco, Missouri (fig. 4, no. 1), where r_s is slightly positive (table 10). This tendency for potassium ranks to be nearly as large,

Table 10.--*Matrix of Spearman rank correlation coefficients between discharge and selected physical properties or constituents for the Spring River near Waco, Missouri*

[$CaCO_3$, calcium carbonate; N, nitrogen; --, no sample variance]

Physical property or constituent	Discharge correlation coefficient[a]	Number of sample pairs
Specific conductance	-0.74	260
pH	-.56	105
Temperature	-.22	260
Dissolved oxygen	.11	258
Dissolved oxygen, percent saturation	-.12	104
Suspended solids	.57	26
Fecal coliform	.59	62
Calcium	-.73	236
Magnesium	-.53	236
Sodium	-.54	237
Potassium	.18	237
Alkalinity as $CaCO_3$	-.81	248
Sulfate	.11	236
Chloride	-.47	161
Fluoride	.16	121
Dissolved solids	-.65	85
Total nitrite plus nitrate as N	.26	131
Total ammonia as N	.27	119
Dissolved ammonia as N	-.40	30
Total phosphorus	-.14	155
Dissolved phosphorus	-.42	35
Total-recoverable cadmium	.29	20
Dissolved cadmium	.14	21
Dissolved chromium	--	32
Total-recoverable copper	--	20
Dissolved copper	.05	50
Total-recoverable iron	.40	20
Dissolved iron	.59	53
Total-recoverable lead	.12	17
Dissolved lead	-.22	72
Total-recoverable manganese	.10	19
Dissolved manganese	.15	94
Total-recoverable zinc	-.02	19
Dissolved zinc	-.11	82

[a] Values of the Spearman rank correlation coefficient range from -1.0 to 1.0. Positive values indicate a tendency for the ranks of one constituent to increase as the ranks of the other constituent increase. Negative values indicate a tendency for the ranks of one constituent to decrease as the ranks of the other constituent increase.

Table 11.--*Matrix of Spearman rank correlation coefficients between discharge and selected physical properties or constituents for Center Creek near Carterville, Missouri*

[$CaCO_3$, calcium carbonate; N, nitrogen; --, no sample variance]

Physical property or constituent	Discharge correlation coefficient[a]	Number of sample pairs
Specific conductance	-0.92	292
pH	.18	292
Temperature	-.21	292
Dissolved oxygen	.11	277
Dissolved oxygen, percent saturation	.03	271
Suspended solids	.36	102
Fecal coliform	.36	191
Calcium	-.88	189
Magnesium	-.78	188
Sodium	-.92	196
Potassium	-.16	190
Alkalinity as $CaCO_3$	-.45	233
Sulfate	-.75	198
Chloride	-.77	198
Fluoride	-.50	197
Dissolved solids	-.89	197
Total nitrite plus nitrate as N	-.73	134
Total ammonia as N	-.47	157
Dissolved ammonia as N	-.44	56
Total phosphorus	-.24	183
Dissolved phosphorus	-.50	81
Total-recoverable cadmium	.12	38
Dissolved cadmium	.04	43
Dissolved chromium	-.33	75
Total-recoverable copper	--	38
Dissolved copper	-.15	108
Total-recoverable iron	.53	37
Dissolved iron	.21	107
Total-recoverable lead	.26	50
Dissolved lead	.04	148
Total-recoverable manganese	.14	38
Dissolved manganese	-.52	188
Total-recoverable zinc	-.16	50
Dissolved zinc	-.46	163

[a] Values of the Spearman rank correlation coefficient range from -1.0 to 1.0. Positive values indicate a tendency for the ranks of one constituent to increase as the ranks of the other constituent increase. Negative values indicate a tendency for the ranks of one constituent to decrease as the ranks of the other constituent increase.

Table 12.--*Matrix of Spearman rank correlation coefficients between discharge and selected physical properties or constituents for Center Creek near Smithfield, Missouri*

[$CaCO_3$, calcium carbonate; N, nitrogen; --, no sample variance]

Physical property or constituent	Discharge correlation coefficient[a]	Number of sample pairs
Specific conductance	-0.10	308
pH	-.10	171
Temperature	-.21	303
Dissolved oxygen	.05	306
Dissolved oxygen, percent saturation	-.19	167
Suspended solids	.33	121
Fecal coliform	.33	157
Calcium	-.71	221
Magnesium	-.53	221
Sodium	-.76	221
Potassium	-.16	220
Alkalinity as $CaCO_3$	-.44	309
Sulfate	-.58	220
Chloride	-.69	149
Fluoride	-.27	119
Dissolved solids	-.85	89
Total nitrite plus nitrate as N	-.55	212
Total ammonia as N	.12	198
Dissolved ammonia as N	-.32	21
Total phosphorus	-.17	236
Dissolved phosphorus	-.39	34
Total-recoverable cadmium	.29	52
Dissolved cadmium	-.04	54
Dissolved chromium	-.14	29
Total-recoverable copper	-.18	51
Dissolved copper	-.14	82
Total-recoverable iron	.27	52
Dissolved iron	.38	85
Total-recoverable lead	-.09	52
Dissolved lead	-.19	89
Total-recoverable manganese	-.01	50
Dissolved manganese	-.08	98
Total-recoverable zinc	.19	51
Dissolved zinc	.08	93

[a] Values of the Spearman rank correlation coefficient range from -1.0 to 1.0. Positive values indicate a tendency for the ranks of one constituent to increase as the ranks of the other constituent increase. Negative values indicate a tendency for the ranks of one constituent to decrease as the ranks of the other constituent increase.

Table 13.--*Matrix of Spearman rank correlation coefficients between discharge and selected physical properties or constituents for Turkey Creek near Joplin, Missouri*

[$CaCO_3$, calcium carbonate; N, nitrogen; --, no sample variance]

Physical property or constituent	Discharge correlation coefficient[a]	Number of sample pairs
Specific conductance	-0.57	329
pH	-.19	191
Temperature	-.11	329
Dissolved oxygen	.14	328
Dissolved oxygen, percent saturation	.13	190
Suspended solids	.54	34
Fecal coliform	.07	115
Calcium	-.49	280
Magnesium	-.49	280
Sodium	-.60	280
Potassium	-.46	280
Alkalinity as $CaCO_3$	-.58	284
Sulfate	-.31	307
Chloride	-.63	231
Fluoride	-.48	179
Dissolved solids	-.67	168
Total nitrite plus nitrate as N	.04	128
Total ammonia as N	-.24	136
Dissolved ammonia as N	-.42	44
Total phosphorus	-.42	175
Dissolved phosphorus	-.66	70
Total-recoverable cadmium	--	1
Dissolved cadmium	-.44	4
Dissolved chromium	-.12	69
Total-recoverable copper	--	1
Dissolved copper	-.11	66
Total-recoverable iron	--	1
Dissolved iron	-.31	70
Total-recoverable lead	1.00	2
Dissolved lead	-.18	98
Total-recoverable manganese	--	1
Dissolved manganese	.09	142
Total-recoverable zinc	1.00	2
Dissolved zinc	.42	111

[a] Values of the Spearman rank correlation coefficient range from -1.0 to 1.0. Positive values indicate a tendency for the ranks of one constituent to increase as the ranks of the other constituent increase. Negative values indicate a tendency for the ranks of one constituent to decrease as the ranks of the other constituent increase.

Table 14.--*Matrix of Spearman rank correlation coefficients between discharge and selected physical properties or constituents for Shoal Creek near Galena, Kansas*

[--, no sample variance; $CaCO_3$, calcium carbonate; N, nitrogen]

Physical property or constituent	Discharge correlation coefficient[a]	Number of sample pairs
Specific conductance	-0.78	181
pH	-.10	45
Temperature	-.18	180
Dissolved oxygen	.15	179
Dissolved oxygen, percent saturation	-.28	39
Suspended solids	--	0
Fecal coliform	.49	32
Calcium	-.65	180
Magnesium	-.43	180
Sodium	-.74	180
Potassium	-.12	180
Alkalinity as $CaCO_3$	-.79	179
Sulfate	-.13	179
Chloride	-.61	103
Fluoride	.16	81
Dissolved solids	-.73	39
Total nitrite plus nitrate as N	.44	86
Total ammonia as N	-.34	83
Dissolved ammonia as N	.03	22
Total phosphorus	-.35	115
Dissolved phosphorus	-.72	35
Total-recoverable cadmium	.21	4
Dissolved cadmium	--	3
Dissolved chromium	--	6
Total-recoverable copper	--	6
Dissolved copper	--	6
Total-recoverable iron	.34	6
Dissolved iron	.23	41
Total-recoverable lead	--	3
Dissolved lead	--	2
Total-recoverable manganese	.71	10
Dissolved manganese	-.22	41
Total-recoverable zinc	.39	6
Dissolved zinc	.18	6

[a] Values of the Spearman rank correlation coefficient range from -1.0 to 1.0. Positive values indicate a tendency for the ranks of one constituent to increase as the ranks of the other constituent increase. Negative values indicate a tendency for the ranks of one constituent to decrease as the ranks of the other constituent increase.

Table 15.--*Matrix of Spearman rank correlation coefficients between discharge and selected physical properties or constituents for the Spring River near Baxter Springs, Kansas*

[$CaCO_3$, calcium carbonate; N, nitrogen; --, no sample variance]

Physical property or constituent	Discharge correlation coefficient[a]	Number of sample pairs
Specific conductance	-0.65	275
pH	-.01	163
Temperature	-.18	239
Dissolved oxygen	.19	165
Dissolved oxygen, percent saturation	.69	12
Suspended solids	.18	31
Fecal coliform	.30	31
Calcium	-.68	245
Magnesium	-.24	246
Sodium	-.64	245
Potassium	-.21	243
Alkalinity as $CaCO_3$	-.45	272
Sulfate	-.34	272
Chloride	-.66	211
Fluoride	-.57	159
Dissolved solids	-.69	128
Total nitrite plus nitrate as N	-.63	71
Total ammonia as N	-.14	67
Dissolved ammonia as N	-.46	3
Total phosphorus	-.03	118
Dissolved phosphorus	-.53	11
Total-recoverable cadmium	--	3
Dissolved cadmium	.63	4
Dissolved chromium	--	3
Total-recoverable copper	--	3
Dissolved copper	--	3
Total-recoverable iron	-.34	15
Dissolved iron	-.07	49
Total-recoverable lead	1.00	2
Dissolved lead	--	3
Total-recoverable manganese	-.08	19
Dissolved manganese	.45	45
Total-recoverable zinc	1.00	3
Dissolved zinc	.81	4

[a] Values of the Spearman rank correlation coefficient range from -1.0 to 1.0. Positive values indicate a tendency for the ranks of one constituent to increase as the ranks of the other constituent increase. Negative values indicate a tendency for the ranks of one constituent to decrease as the ranks of the other constituent increase.

or larger, at high flows as compared to low flows is not unexpected. Hem (1985) noted potassium concentrations tend to increase with flow in most North American streams. This is thought to be caused by potassium being leached from organic matter and soils during runoff.

Ranks of total alkalinity exhibit moderate decreases with increasing flow at all stations and range from a minimum of -0.44 at Center Creek near Smithfield, Missouri (fig. 4, no. 5), to a maximum of -0.81 at the Spring River near Waco. Sulfate ranks also exhibit decreases with increasing flow at all sites except the Spring River near Waco, where r_s is slightly positive (0.11). Correlations between total alkalinity and discharge are most negative at the baseline stations [the Spring River near Waco and Shoal Creek near Galena, Kansas (fig. 4, no. 8)], whereas correlations between sulfate and discharge are positive or the least negative at these sites. With the exception of potassium, values of r_s between major constituents and discharge at the downstream Center Creek station near Smithfield are less negative than those at the upstream station near Carterville, Missouri (fig. 4, no. 4). In addition, median concentrations of most of these constituents were larger at Center Creek near Smithfield (table 7). Concentrations of many of these constituents may be somewhat maintained at higher discharges by runoff from tailings areas where a much larger surface area of exposed minerals containing many of these constituents exists.

Ranks of total nitrite plus nitrate exhibit positive relations with discharge at the Spring River near Waco (r_s = 0.26) and Shoal Creek near Galena (r_s = 0.44). Because there are few anthropogenic sources of nitrite and nitrate in these basins, the positive relations probably are related to soil leaching during runoff events. This contrasts the negative relations at the upstream (r_s = -0.73) and downstream (r_s = -0.55) Center Creek stations and the Spring River near Baxter Springs, Kansas (fig. 4, no. 9; r_s = -0.63), where anthropogenic sources are diluted with increasing discharge. Concentrations of total nitrite plus nitrate at Turkey Creek near Joplin (fig. 4, no. 6) exhibit no relation with discharge (r_s = 0.04). In contrast to total nitrite plus nitrate, relations between ranks of total ammonia and discharge are less negative or slightly positive at both Center Creek stations and the Spring River near Baxter Springs and more negative at Turkey Creek near Joplin (r_s = -0.24). Unlike total nitrite plus nitrate, ranks of total ammonia at Center Creek near Smithfield have little relation to flow (r_s = 0.12). Ranks of dissolved ammonia exhibit negative relations with flow at all sites except Shoal Creek near Galena where the small number of samples (22) renders interpretation unreliable.

The Missouri DNR (Missouri Department of Natural Resources, 1984a) indicated substantial effects on levels of ammonia and nitrate in Center Creek from fertilizer and explosives manufacturing plants along Center and Grove Creeks (upstream from the station near Carterville). The Missouri DNR also indicated the possibility of substantial quantities of ammonia and nitrate in runoff from industrial areas and stack emissions. The negative relations between total nitrite plus nitrate (r_s = -0.73), total ammonia (r_s = -0.47), and dissolved ammonia (r_s = -0.44) and discharge at Center Creek near Carterville indicate dilution of low-flow sources during runoff.

Correlations between most total-recoverable trace constituents and discharge are positive, as expected, although less than 30 samples were collected for determination of total-recoverable constituents at some stations, making these results somewhat unreliable. However, dissolved iron also is positively correlated with discharge at most sites. This may indicate significant quantities of colloidal iron during higher flows and probably is not related to mining, as both baseline stations (Spring River near Waco and Shoal Creek near Galena) also exhibit positive values of r_s.

Ranks of dissolved manganese have little relation with discharge at most stations except for Center Creek near Carterville and the Spring River near Baxter Springs. The relatively large negative relation between dissolved manganese and discharge at Carterville (r_s = -0.52) contrasts with that of most trace constituents, except dissolved zinc, and indicates runoff dilution of low-flow sources. The negative relation also parallels the decreases in nitrogen species with increasing flow. Because dissolved trace constituents generally are negatively correlated with discharge, the positive relation between ranks of dissolved manganese and discharge at the Spring River near Baxter Springs (r_s =

0.45) is anomalous and may be related to effects from the large concentrations in Cow and Brush Creeks in Kansas (table 7). Manganese also is associated with organic-rich sediments, aquatic plants, and leaf litter (Slack and Feltz, 1968).

Because of the small number of samples, correlation between dissolved zinc and discharge is unreliable at Shoal Creek near Galena and the Spring River near Baxter Springs. The Center Creek station near Carterville is upstream from most mined areas and the correlation between dissolved zinc and discharge is negative (r_s = -0.46). However, dissolved zinc exhibited essentially no relation to discharge (r_s = 0.08) downstream near Smithfield, indicating substantial runoff-derived sources between Carterville and Smithfield. Dissolved zinc is positively correlated with discharge at Turkey Creek near Joplin (r_s = 0.42), indicating significant effects from mined areas, industrial sites, or both, in that basin. This corroborates earlier work by Barks (1977) that indicated concentrations of dissolved trace constituents in Center Creek and Turkey Creek were sustained during high flows by runoff from tailing areas.

Analysis of Seasonal Characteristics

The ANOVA and multiple-comparison procedures were used to examine seasonal dependence of selected physical and chemical constituents at the six long-term monitoring stations. Because the major objective of these procedures was to examine intrastation variation, the entire period of record for each station was used. Seasons were defined as the following: winter--January, February, March; spring--April, May, June; summer--July, August, September; fall--October, November, December. Nonparametric tests on ranked data for each station were used. The ANOVA and multiple-comparison procedures used were identical to those described in the previous section, except the data were not joint ranked across all stations, and the α-level used in multiple-comparison tests of mean ranks was adjusted. In a possible pairwise comparison of four seasons, there are six possible unique comparisons. Therefore, the α-level for each comparison was adjusted by the Bonferroni method (0.05/6 = 0.0083) to ensure that the probability of a Type I error over all possible comparisons was no larger than the desired overall α-level of 0.05 (Snedecor and Cochran, 1980). Graphical summaries of the results of ANOVA and multiple comparison procedures for each of the six long-term monitoring stations are presented in figures 18 to 23.

Mean ranks of discharge closely follow the annual distribution of rainfall. The largest mean ranks of discharge for all sites are associated with the winter and spring seasons. No significant differences are detected between winter and spring flows. This may be because of the inclusion of higher flows in late March with the winter season and including lower flows in late June with the spring season.

Although no significant differences in discharge are detected between winter and spring, mean ranks of specific conductance are significantly smaller during the spring at the baseline stations [Shoal Creek near Galena, Kansas (fig. 4, no. 8), and the Spring River near Waco, Missouri (fig. 4, no. 1)] and at the downstream Spring River station near Baxter Springs, Kansas (fig. 4, no. 9). The largest ranks of specific conductance are associated with low flow that occurred during the summer and fall at both Center Creek stations (fig. 4, nos. 4 and 5) and Turkey Creek near Joplin, Missouri (fig. 4, no. 6). Large ranks of specific conductance also are associated with larger flows during the winter and with low flows during the summer and fall at the Spring River near Waco, Shoal Creek near Galena, and the Spring River near Baxter Springs.

No seasonal differences in pH ranks are detected. The distribution of dissolved oxygen at each station is inversely related to temperature. The largest ranks of dissolved oxygen are associated with the smallest temperature ranks during the fall and winter. Generally, mean ranks of major constituents are smaller during high flow (winter and spring) and larger during the summer and fall at most stations. No seasonal differences are detected in magnesium and chloride ranks at the Spring River near Waco, in calcium and sulfate ranks at Turkey Creek near Joplin, or in magnesium and sulfate ranks at Shoal Creek near Galena.

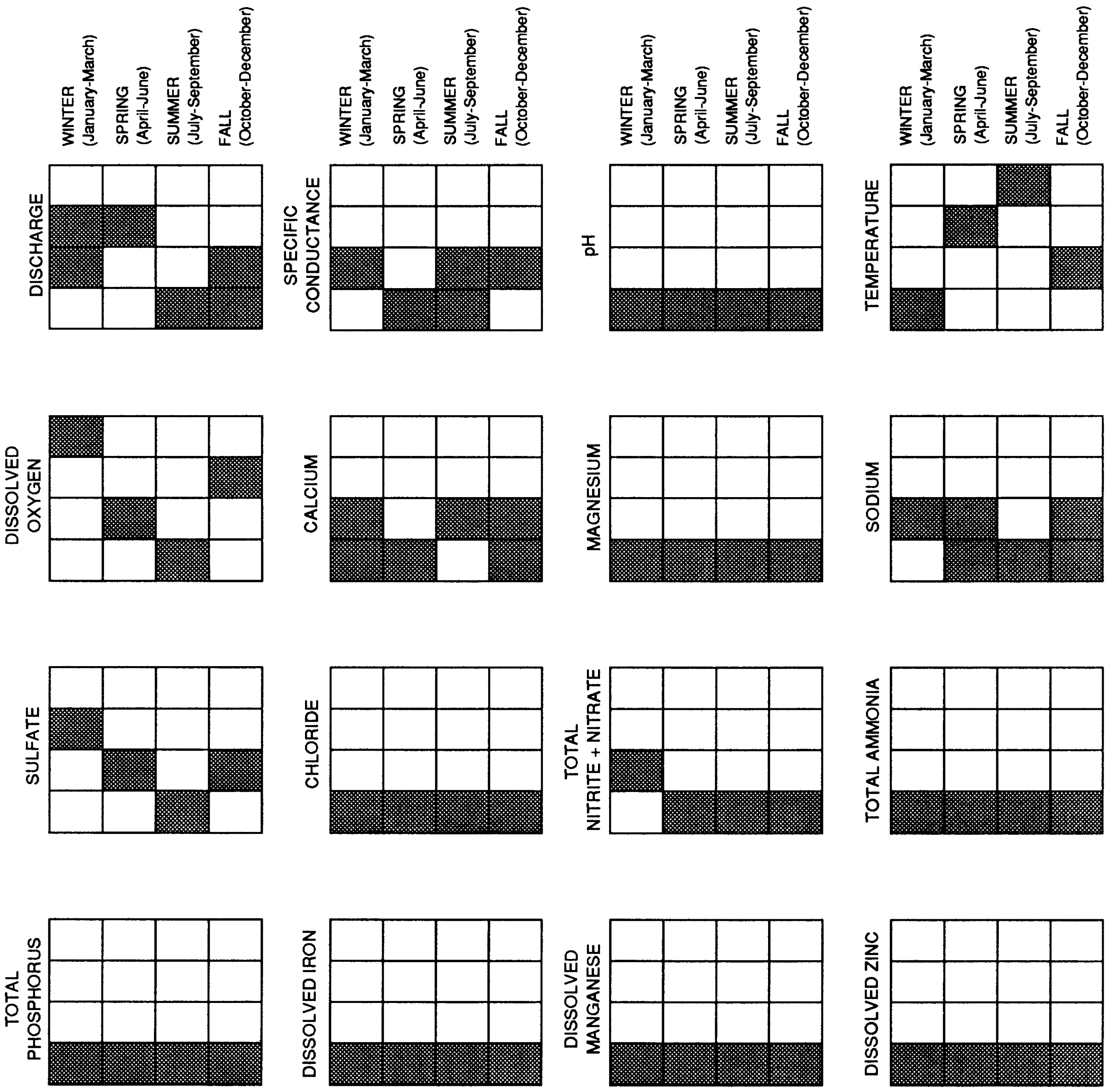

Figure 18.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between seasons for Spring River near Waco, Missouri (see figure 7 for explanation).

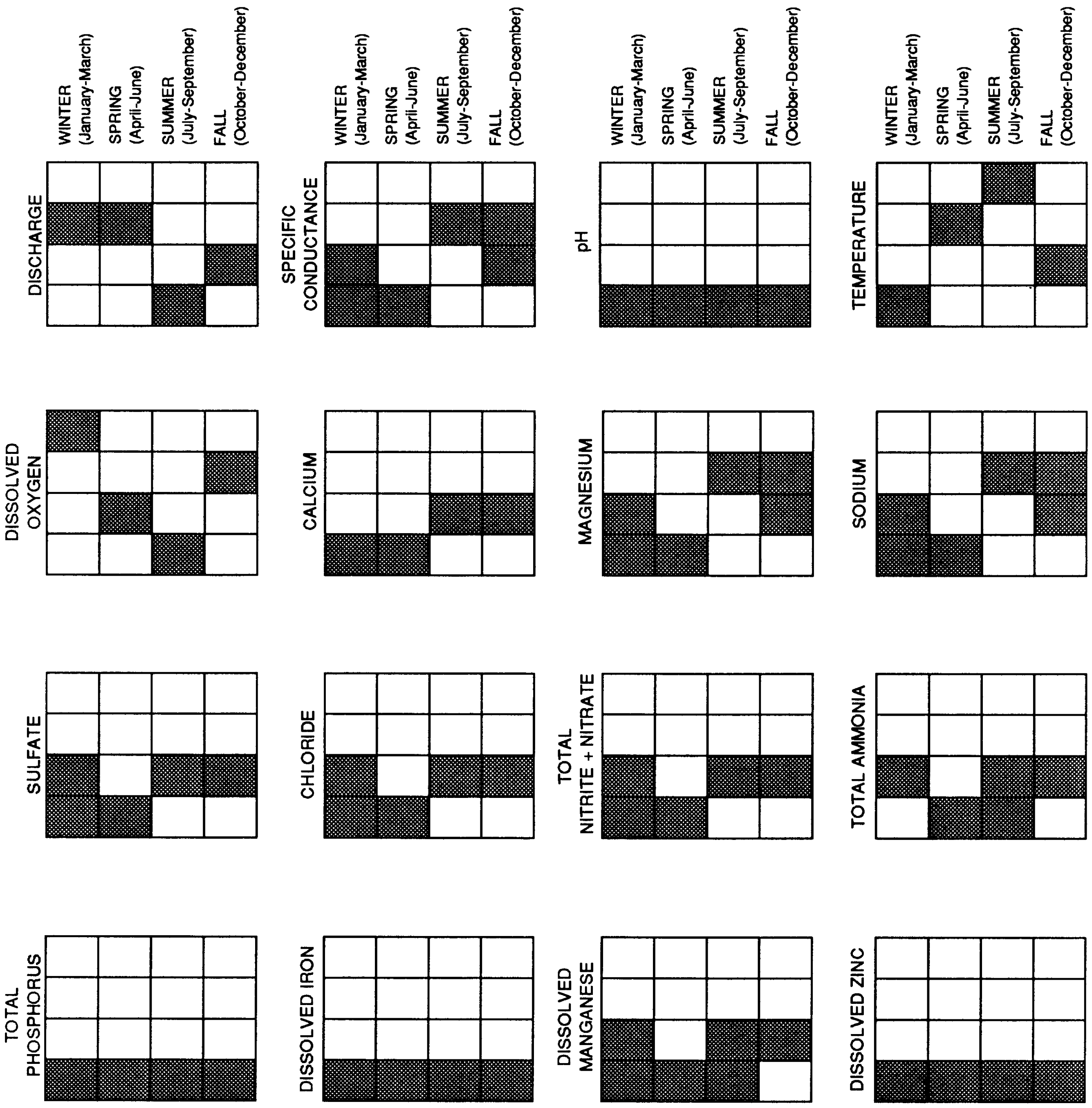

Figure 19.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between seasons for Center Creek near Carterville, Missouri (see figure 7 for explanation).

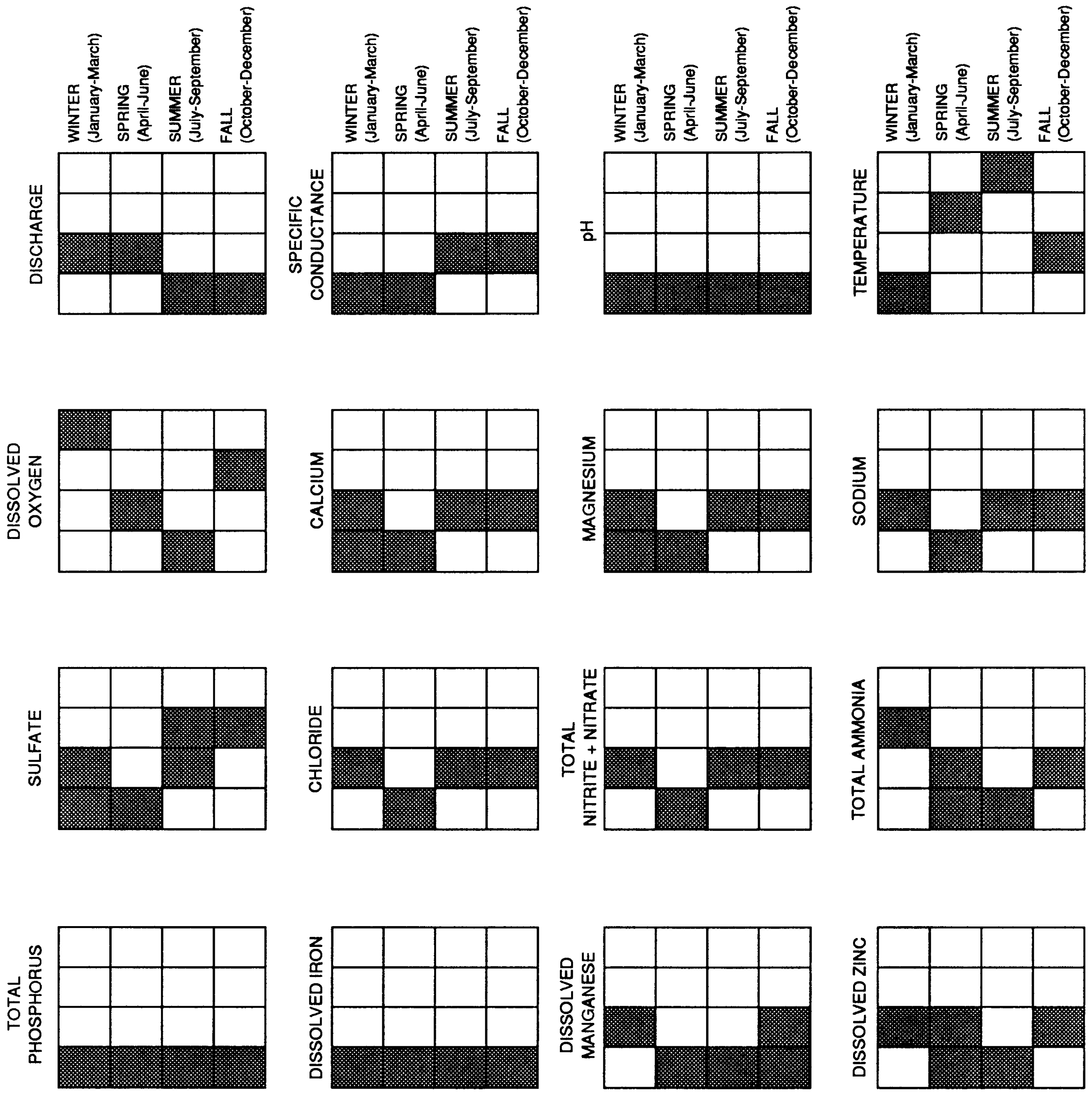

Figure 20.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between seasons for Center Creek near Smithfield, Missouri (see figure 7 for explanation).

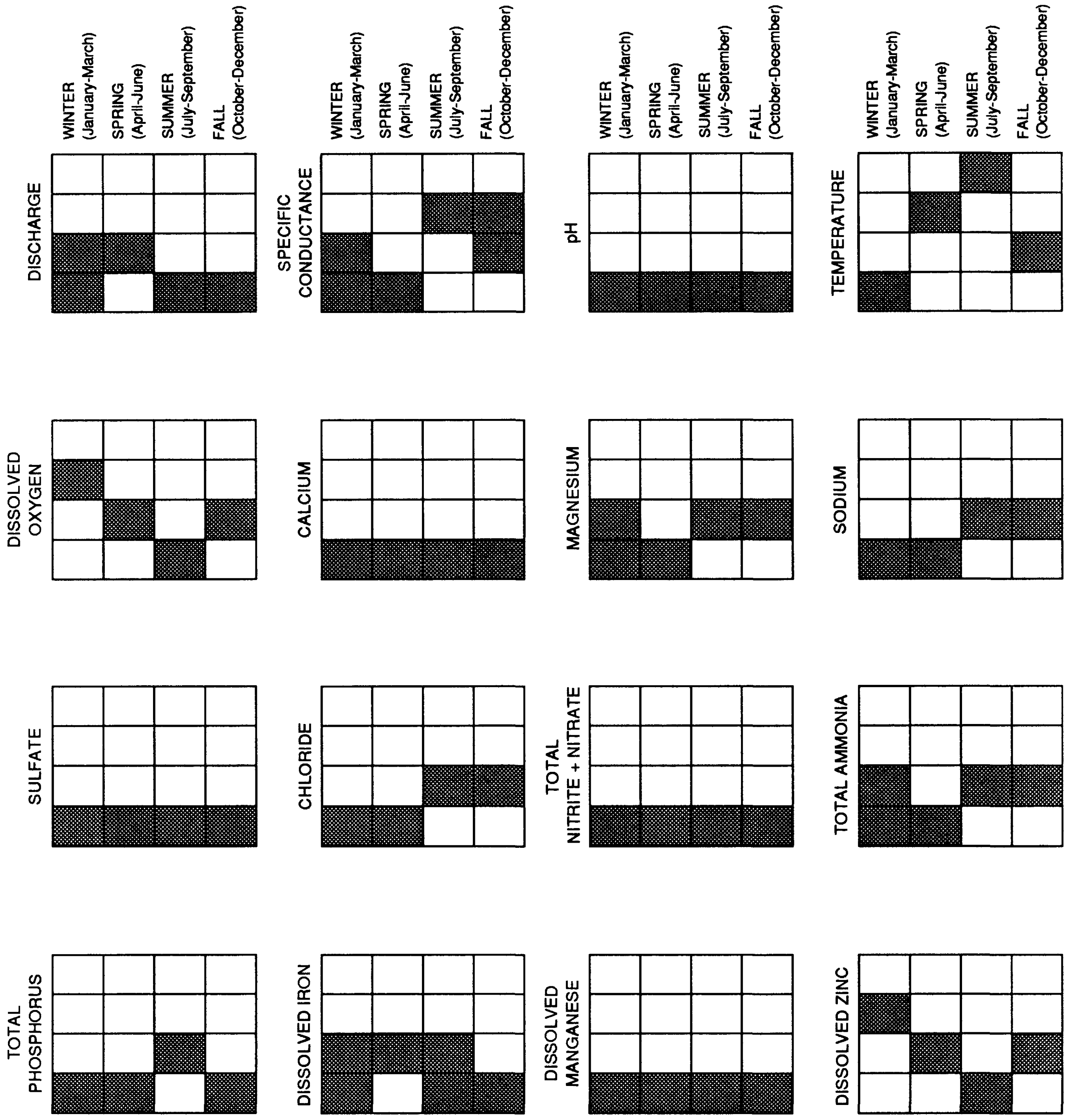

Figure 21.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between seasons for Turkey Creek near Joplin, Missouri (see figure 7 for explanation).

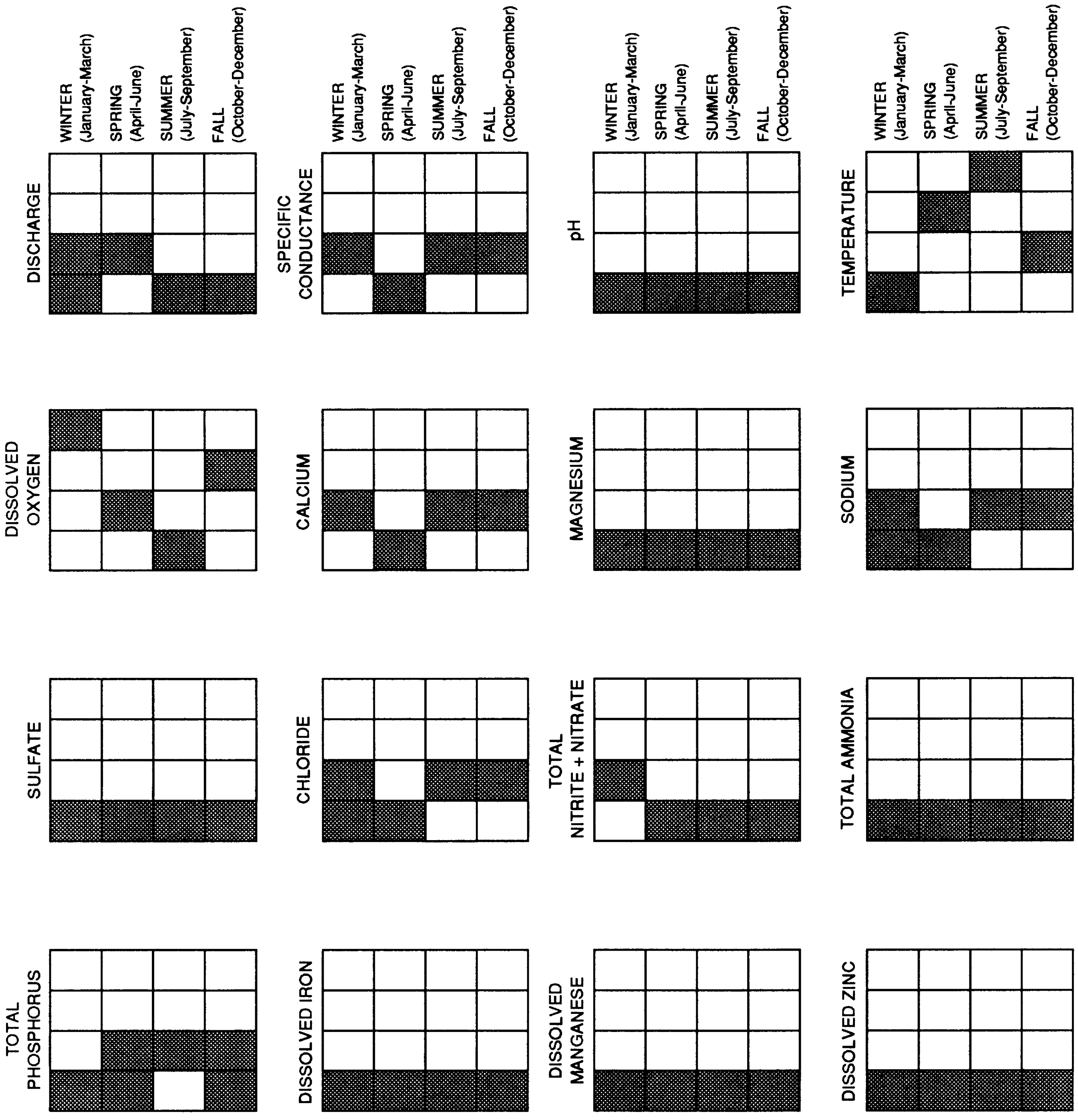

Figure 22.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between seasons for Shoal Creek near Galena, Kansas (see figure 7 for explanation).

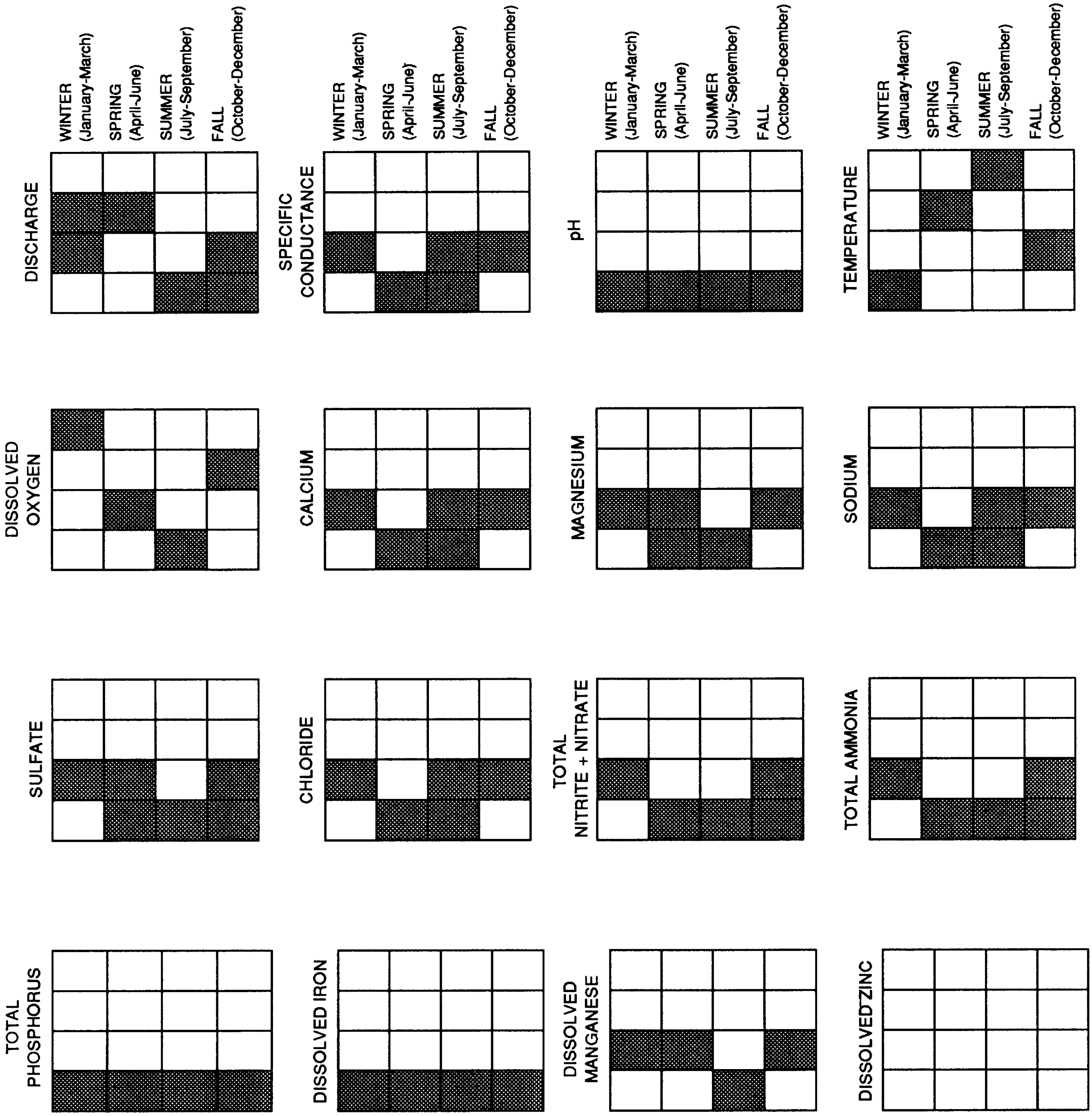

Figure 23.--Results of analysis of variance and multiple-comparison tests on mean ranks of selected constituents between seasons for Spring River near Baxter Springs, Kansas (see figure 7 for explanation).

The distribution of nitrogen species at the baseline stations (figs. 18 and 22) does not indicate dilution effects during the spring and increases during low flow like most major constituents. The lack of variation in the mean ranks of total ammonia at these stations may be because of the small concentrations at these sites and the lack of significant sources of reduced nitrogen. The larger mean ranks of total nitrite plus nitrate during the winter may be because of decreased biologic activity or plant uptake. Dugdale and Dugdale (1965) demonstrated the extensive assimilation of dissolved nitrogen species by fresh water algae during the late spring and summer months.

Mean ranks of total nitrite plus nitrate and total ammonia are among the smallest during the spring at both Center Creek stations (figs. 19 and 20). Ranks of total ammonia also are significantly smaller during the spring as compared to the summer and fall at Turkey Creek near Joplin (fig. 21). The smaller values of total nitrite plus nitrate during the spring indicate runoff dilution of low-flow sources and corroborate correlation data. The distributions of total ammonia at the Center Creek stations are similar to those of total nitrite plus nitrate; however, mean total ammonia ranks at Smithfield indicate greater variability and are smallest during the summer. This may indicate dilution in conjunction with biologic effects, such as assimilation, taking place between Carterville and Smithfield. The lack of significant seasonal variability in total nitrite plus nitrate ranks at Turkey Creek near Joplin, combined with the seasonal dependence of total ammonia ranks, probably is an artifact of the predominance of reduced nitrogen species. Mean ranks of total phosphorus indicate seasonal variation only at Turkey Creek near Joplin and Shoal Creek near Galena. Ranks of total phosphorus during the summer are among the largest at both stations.

Seasonal variation in ranks of dissolved iron is minimal because significant variation is detected only at Turkey Creek near Joplin (fig. 21). Ranks of dissolved iron during the spring are significantly larger than those during the fall and may indicate significant transport of colloidal ferric iron during higher flows. This would seem to contradict the slightly negative correlation (-0.31) between dissolved iron and discharge at this station (table 13); however, the limited variability between seasons may indicate other controlling mechanisms.

The effect of mining activities is evident in the seasonal variation of ranks of dissolved manganese and dissolved zinc. Those stations relatively unaffected by mining (Shoal Creek near Galena and Spring River near Waco) have no detectable seasonal variation, whereas those stations previously identified as being affected (both Center Creek stations, Turkey Creek near Joplin, and the Spring River near Baxter Springs) have significant seasonal variation in one or both constituents. Ranks of dissolved manganese are significantly larger during the fall than in the spring at Center Creek near Carterville. Because this trend was detected in most other constituents at Carterville, the smaller ranks in the spring probably reflect dilution of low-flow sources. Seasonal dissolved manganese ranks downstream at Smithfield have significant differences between the winter, spring, and summer seasons, with the largest values occurring during the winter months (fig. 20). Ranks of dissolved zinc at Turkey Creek near Joplin are smallest during the summer months and largest in the winter. The seasonal distribution of dissolved zinc at Center Creek near Smithfield is similar, except no difference is detected between the spring and summer. The tendency for larger ranks of dissolved zinc to occur during higher flows indicates substantial runoff effects from mined areas and corroborates the correlations between dissolved zinc and discharge at Center Creek near Smithfield (table 12) and Turkey Creek near Joplin (table 13).

Comparison of Instantaneous Loads

Although summary statistics and analysis of variance procedures identify subbasins with larger than baseline concentrations of selected constituents and identify relative concentration levels in a static sense, it is difficult to evaluate the effect of each subbasin on the Spring River. Streams with large concentrations of potentially harmful constituents but with small discharges, such as Turkey

Creek, may not have a significant effect on the Spring River. Likewise, streams with larger discharges and only slightly increased concentrations may have a large effect on the Spring River. Neither scenario can be distinguished by evaluation of concentration data alone.

To assess the relative effect of various subbasins on the Spring River, the median instantaneous loads for selected constituents were compared. Actual loads (tons per year) could not be calculated because of the lack of continuous discharge record data for most stations. As an alternative, instantaneous loads for selected constituents were calculated for the six long-term monitoring stations (fig. 4; table 4) and three ancillary stations, Cow Creek near Weir, Kansas (fig. 4, no. 2), Brush Creek near Weir, Kansas (fig. 4, no. 3), and Short Creek at Galena, Kansas (fig. 4, no. 7), using the entire period of record for each station. Equation 3 was used to compute instantaneous loads in g/s (grams per second) for major constituents and nutrients (mg/L); equation 4 was used to compute instantaneous loads in g/s for trace constituents (µg/L).

Major constituents and nutrients (mg/L):

$$LDC_i = C_i \text{ mg/L} \times \frac{1\text{g}}{1,000\text{mg}} \times (Q_i \text{ ft}^3\text{/s} \times 28.317 \text{ liter/ft}^3) \tag{3}$$

Trace constituents (µg/L):

$$LDC_i = C_i \text{ µg/L} \times \frac{1\text{g}}{10^6 \text{µg}} \times (Q_i \text{ ft}^3\text{/s} \times 28.317 \text{ liter/ft}^3), \tag{4}$$

where LDC_i is the instantaneous constituent load in g/s, C_i is the reported constituent concentration, and Q_i is discharge in $\text{ft}^3\text{/s}$.

Median instantaneous loads were computed for selected constituents by station (table 16). The sum of the median instantaneous loads for the seven subbasins (the Spring River near Waco, Missouri; Cow Creek near Weir, Kansas; Brush Creek near Weir, Kansas; Center Creek near Smithfield, Missouri; Turkey Creek near Joplin, Missouri; Short Creek at Galena, Kansas; and Shoal Creek near Galena, Kansas) were computed and are listed as total subbasin load for each constituent. The upstream Center Creek station near Carterville was not used in the calculations. It is listed in table 16 as a comparison for the downstream station near Smithfield. The percentage of the Spring River near Baxter Springs load accounted for by the seven subbasin stations listed above was computed for each constituent using the following equation:

$$\text{Percentage of Baxter Springs} = \frac{\sum_{j=1}^{7} LDC_i}{LDC_{i,\text{ Baxter}}} \times 100, \tag{5}$$

where j is each of the seven subbasin stations, LDC_i is the median instantaneous constituent load at each of the subbasin stations listed above, and $LDC_{i,\text{Baxter}}$ is the median instantaneous constituent load at the downstream Spring River station near Baxter Springs.

The percentage contribution from each subbasin station to the downstream station near Baxter Springs was calculated for each constituent by dividing the median instantaneous constituent load at each subbasin station by the median instantaneous constituent load at Baxter Springs and multiplying by 100 (table 16). The constituent loads for each subbasin also were normalized to the total subbasin loads. These values were computed by dividing the median instantaneous constituent load at each subbasin station by the total subbasin loads and multiplying by 100 (table 16).

Table 16.--*Median instantaneous loads for selected constituents between subbasin stations and the downstream Spring Rive station near Baxter Springs, Kansas*

[Loads are expressed in grams per second, percentage of the downstream station load at Baxter Springs, and as percentage of subbasin station load, excluding Center Creek near Carterville; ft^3/s, cubic feet per second; g/s, grams per second; <, less than; $CaCO_3$, calcium carbonate; --, no data; N, nitrogen]

		Discharge			Calcium			Magnesium		
Map number (fig. 4)	Station name	Discharge (ft^3/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]
1	Spring River near Waco, Missouri	332	41	40	532.048	37	42	35.147	27	33
2	Cow Creek near Weir, Kansas	76	9	9	50.064	3	4	28.034	21	27
3	Brush Creek near Weir, Kansas	1.9	<1	<1	4.757	<1	<1	2.472	2	2
4	Center Creek near Carterville, Missouri	103	13	13	136.318	9	11	8.130	6	8
5	Center Creek near Smithfield, Missouri	122	15	15	241.827	17	19	11.010	8	10
6	Turkey Creek near Joplin, Missouri	30	4	4	76.286	5	6	5.094	4	5
7	Short Creek at Galena, Kansas	3.8	<1	<1	12.154	1	1	1.716	1	2
8	Shoal Creek near Galena, Kansas	257	32	31	357.502	25	28	21.726	17	21
	Total subbasin load[c]	823 (102)			1,274.638 (87)			105.199 (80)		
9	Spring River near Baxter Springs, Kansas	806			1,457.306			131.295		

		Sodium			Potassium			Alkalinity as $CaCO_3$		
Map number (fig. 4)	Station name	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]
1	Spring River near Waco, Missouri	68.527	29	34	21.368	38	44	1,188.181	50	44
2	Cow Creek near Weir, Kansas	35.283	15	18	3.466	6	7	39.289	2	1
3	Brush Creek near Weir, Kansas	2.537	1	1	.306	1	1	.051	<1	<1
4	Center Creek near Carterville, Missouri	22.031	9	11	3.834	7	8	418.978	17	16
5	Center Creek near Smithfield, Missouri	31.092	13	16	6.371	11	13	405.216	17	15
6	Turkey Creek near Joplin, Missouri	21.096	9	11	4.811	9	10	136.941	6	5
7	Short Creek at Galena, Kansas	1.427	1	1	.773	1	2	.846	<1	<1
8	Shoal Creek near Galena, Kansas	39.960	17	20	11.824	21	24	902.604	38	34
	Total subbasin load[c]	198.922 (85)			48.919 (87)			2,673.128 (111)		
9	Spring River near Baxter Springs, Kansas	233.106			56.334			2,400.163		

Table 16.--*Median instantaneous loads for selected constituents between subbasin stations and the downstream Spring River station near Baxter Springs, Kansas*--Continued

		Sulfate			Chloride			Dissolved solids		
Map number (fig. 4)	Station name	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]
1	Spring River near Waco, Missouri	216.002	16	23	86.650	34	42	1,701.144	29	37
2	Cow Creek near Weir, Kansas	245.084	18	26	16.679	7	8	234.465	4	5
3	Brush Creek near Weir, Kansas	28.544	2	3	.442	<1	<1	28.476	<1	1
4	Center Creek near Carterville, Missouri	88.986	7	9	22.413	9	11	567.416	10	12
5	Center Creek near Smithfield, Missouri	221.439	17	24	30.809	12	15	1,019.412	18	22
6	Turkey Creek near Joplin, Missouri	95.711	7	10	19.907	8	10	293.138	5	6
7	Short Creek at Galena, Kansas	50.164	4	5	2.213	1	1	--	--	--
8	Shoal Creek near Galena, Kansas	85.234	6	9	51.469	20	25	1,310.511	23	29
	Total subbasin load[c]	942.178 (71)			208.169 (82)			4,587.146 (79)		
9	Spring River near Baxter Springs, Kansas	1,332.600			254.853			5,800.171		

		Total nitrite plus nitrate as N			Total ammonia as N			Total phosphorus		
Map number (fig. 4)	Station name	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]
1	Spring River near Waco, Missouri	15.886	25	34	0.389	7	9	1.444	17	18
2	Cow Creek near Weir, Kansas	--	--	--	.985	19	23	.258	3	3
3	Brush Creek near Weir, Kansas	--	--	--	.037	1	1	.009	<1	<1
4	Center Creek near Carterville, Missouri	20.691	32	44	3.589	69	82	.582	7	7
5	Center Creek near Smithfield, Missouri	18.829	30	40	.373	7	9	.549	7	7
6	Turkey Creek near Joplin, Missouri	.338	2	3	1.256	24	29	1.223	15	16
7	Short Creek at Galena, Kansas	--	--	--	1.031	20	24	3.627	43	46
8	Shoal Creek near Galena, Kansas	10.770	17	23	.283	5	6	.779	9	10
	Total subbasin load[c]	46.823 (73)			4.354 (83)			7.889 (94)		
9	Spring River near Baxter Springs, Kansas	63.761			5.239			8.423		

Table 16.--*Median instantaneous loads for selected constituents between subbasin stations and the downstream Spring River station near Baxter Springs, Kansas*--Continued

		Dissolved iron			Dissolved lead			Dissolved manganese		
Map number (fig. 4)	Station name	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]
1	Spring River near Waco, Missouri	0.334	21	42	0.085	60	47	0.283	9	8
2	Cow Creek near Weir, Kansas	.053	3	7	.010	7	6	2.505	82	68
3	Brush Creek near Weir, Kansas	.073	5	9	.007	5	4	.160	5	4
4	Center Creek near Carterville, Missouri	.110	7	14	.025	18	14	.269	9	7
5	Center Creek near Smithfield, Missouri	.091	6	12	.027	19	15	.197	6	5
6	Turkey Creek near Joplin, Missouri	.069	4	9	.007	5	4	.113	4	3
7	Short Creek at Galena, Kansas	.004	<1	1	.008	6	4	.297	10	8
8	Shoal Creek near Galena, Kansas	.165	10	21	.035	25	20	.127	4	3
	Total subbasin load[c]	.789 (49)			.179 (126)			3.682 (121)		
9	Spring River near Baxter Springs, Kansas	1.596			.142			3.054		

		Dissolved zinc		
Map number (fig. 4)	Station name	Load (g/s)	Percentage of downstream station[a]	Percentage of subbasin stations[b]
1	Spring River near Waco, Missouri	0.372	11	3
2	Cow Creek near Weir, Kansas	.039	1	<1
3	Brush Creek near Weir Kansas	.014	<1	<1
4	Center Creek near Carterville, Missouri	.259	7	2
5	Center Creek near Smithfield, Missouri	1.487	43	13
6	Turkey Creek near Joplin, Missouri	.246	7	2
7	Short Creek at Galena, Kansas	8.920	257	79
8	Shoal Creek near Galena, Kansas	.196	6	2
	Total subbasin load[c]	11.247 (325)		
9	Spring River near Baxter Springs, Kansas	3.474		

[a] The sum total of the percentages of downstream station (not including Center Creek near Carterville, Missouri) may not equal the percentage of Spring River near Baxter Springs, Kansas, because of rounding.

[b] The sum total of the percentages of subbasin stations may not equal 100 percent because of rounding.

[c] Value in parentheses indicates percentage of discharge or load at Spring River near Baxter Springs, Kansas.

The comparison of median instantaneous loads can be interpreted as a semi-quantitative indicator of the effect of a particular tributary on the Spring River. Subbasins with a small percent contribution of median discharge, but a relatively large contribution of the median load for a specific constituent, may be of concern, providing the following conditions can be assumed or nearly approximated:

1. Random sampling was done throughout the entire hydrograph.
2. The subbasins sampled represent most of the flow at the Spring River near Baxter Springs.
3. Subbasin sampling stations represent most of the flow and area within the subbasin.
4. Constituent concentrations are more or less conservative.
5. No large changes in constituent concentrations are noted with time.
6. The number of samples collected is relatively large.

Assumptions 1 and 6 may not be met at all sites. For example, after the deletion of the KDHE trace-constituent data, there were only 5 samples for dissolved lead and 6 for dissolved zinc at the Spring River near Baxter Springs, and Short Creek at Galena was sampled only 14 times. The data must be scrutinized carefully and the values shown (table 16) should only be construed as relative estimates of loads under median-flow conditions. For analysis of dissolved lead and zinc, a more meaningful comparison would be the subbasin percentages that are normalized to the total median subbasin loads instead of the downstream percentage values.

Nearly 87 percent of the surface area of the Spring River basin upstream from Baxter Springs, Kansas, is represented by the seven subbasin stations (fig. 4). Because one of the more significant factors affecting runoff volume in a basin is drainage area (assuming uniformity in precipitation and basin characteristics), stations draining the unshaded region in figure 4 may represent, on the average, most of the runoff volume at Baxter Springs. The percentage of base flow at Baxter Springs contributed by the subbasin stations probably is much larger because streams draining most of the shaded region in figure 4 are ephemeral for much of the year (Spruill, 1987).

The sum of median instantaneous discharges at the seven subbasin stations (823 ft^3/s) exceeded the median discharge at the Spring River near Baxter Springs (806 ft^3/s; table 16) only slightly (2 percent), indicating that during the period of record, the seven subbasin stations represented most of the flow at the downstream station near Baxter Springs. However, because the total number of discharge measurements made at each station exceeded the number of water-quality analyses for most constituents, it is possible that the subset of those discharge measurements paired with each water-quality constituent may not represent the central tendency of the total number of discharge measurements at each station. Also, because most of the total annual constituent loads from a basin occur at high flows, it is important to determine if water-quality sampling was biased toward lower or higher flows. The medians of the discharge measurements paired with each water-quality constituent analyses (hereafter defined as the median constituent sampling discharge) were calculated and compared to the median of the total discharge measurements at each subbasin station (table 17).

For example, a total of 101 discharge measurements were made at Cow Creek near Weir, Kansas. The median of these 101 measurements was 76 ft^3/s. The number of water-quality analyses and the corresponding discharge measurements paired with them is much smaller, however, and ranged from zero for the number of total nitrite plus nitrate analyses to 48 for dissolved iron, manganese, and zinc (table 7 and 17). If the subset of discharge measurements paired with water-quality analyses is representative of the total number of discharge measurements at Cow Creek (101), the median constituent sampling discharges should be similar to the median of the total discharge measurements (76 ft^3/s) at the station. This is not true at Cow Creek, because the median constituent sampling discharges were much smaller and ranged from 12 ft^3/s for dissolved solids to 29 ft^3/s for dissolved iron, manganese, and zinc. This indicates that water-quality sampling at Cow Creek was biased toward lower discharges. If the relation between instantaneous load and discharge is positive for a given constituent at Cow Creek, the median instantaneous load listed in table 16 is biased toward low

Table 17.-- *Median constituent discharge values at the long-term monitoring and ancillary stations in the Spring River basin*
[ft^3/s, cubic feet per second; NA, not applicable; CaCO$_3$, calcium carbonate; N, nitrogen; NC, not computed]

		Discharge (ft^3/s)		Median constituent discharge (ft^3/s)						
Map number (fig. 4)	Station name	Total measurements	Median value	Calcium	Magnesium	Sodium	Potassium	Alkalinity as CaCO$_3$	Chloride	Sulfate
1	Spring River near Waco, Missouri	271	332	346	346	346	346	341	339	346
2	Cow Creek near Weir, Kansas	101	76	16	16	17	17	16	16	16
3	Brush Creek near Weir, Kansas	38	2	2	2	2	2	2	2	2
4	Center Creek near Carterville, Missouri	294	103	87	88	87	87	125	87	87
5	Center Creek near Smithfield, Missouri	309	122	108	109	109	110	122	108	108
6	Turkey Creek near Joplin, Missouri	330	30	30	30	30	30	31	26	28
7	Short Creek at Galena, Kansas	14	4	3	3	3	3	4	4	4
8	Shoal Creek near Galena, Kansas	181	257	257	257	257	257	257	250	257
	Total subbasin	1,233	823	761	762	763	764	772	744	760
9	Spring River near Baxter Springs, Kansas	283	806	827	821	815	815	806	805	808
	Percentage of Spring River near Baxter Springs, Kansas	NA	102	92	93	94	94	96	92	94

		Median constituent discharge (ft^3/s)							
Map number (fig. 4)	Station name	Dissolved solids	Total nitrite plus nitrate as N	Total ammonia as N	Total phosphorus	Dissolved iron	Dissolved lead	Dissolved manganese	Dissolved zinc
1	Spring River near Waco, Missouri	310	351	404	327	285	327	284	269
2	Cow Creek near Weir, Kansas	12	NC	15	21	29	23	29	29
3	Brush Creek near Weir, Kansas	1	NC	2	2	2	2	2	2
4	Center Creek near Carterville, Missouri	90	135	133	122	135	128	88	111
5	Center Creek near Smithfield, Missouri	134	124	120	121	130	130	125	125
6	Turkey Creek near Joplin, Missouri	26	30	28	30	29	30	26	27
7	Short Creek at Galena, Kansas	NC	NC	3	3	3	12	3	3
8	Shoal Creek near Galena, Kansas	260	251	250	238	256	245	256	173
	Total subbasin	743	756	822	742	734	768	725	628
9	Spring River near Baxter Springs, Kansas	807	827	926	807	1,420	1,000	1,500	752
	Percentage of Spring River near Baxter Springs, Kansas	92	91	89	92	52	77	48	84

discharge. A comparison between median constituent sampling discharges and the median of the total discharge measurements (table 17) does not indicate similar bias in water-quality sampling at the other subbasin stations.

Except for discharges at Center Creek near Carterville and the Spring River near Baxter Springs, the median constituent sampling discharges at the subbasin stations were summed and reported as the total subbasin constituent sampling discharge for each of the selected constituents (table 17). The percentage of the Spring River near Baxter Springs constituent sampling discharge contributed by the subbasin stations was calculated by dividing the total median subbasin constituent sampling discharge by the median constituent sampling discharge at Baxter Springs and multiplying by 100 (table 17).

Constituent sampling discharges at the Spring River near Baxter Springs, Kansas, ranged from 89 to 96 percent for all constituents except for those constituent sampling discharges associated with trace constituents. The small percentages for dissolved iron (52), lead (77), and manganese (48) are partially attributable to the median constituent sampling discharges for these constituents at the Spring River near Baxter Springs, which ranged from 124 percent or 1,000 ft^3/s (dissolved lead) to 186 percent or 1,500 ft^3/s (dissolved manganese) of the median discharge for the period of record (806 ft^3/s). The large median constituent sampling discharge for dissolved lead was because of the extremely small number of samples collected at the Spring River near Baxter Springs (table 7). Because of the smaller number of samples collected for the trace constituents at most stations, the total subbasin median constituent sampling discharges for the trace constituents were 7 to 24 percent smaller than the median of the total discharge measurements at the subbasin stations. Because the subbasin stations contributed relatively small percentages of the median constituent sampling discharges at the Spring River near Baxter Springs for dissolved iron, lead, and manganese, and because of the small number of samples collected, the percentage of the Spring River near Baxter Springs loads associated with these constituents is considered unreliable (table 16).

The sum of median instantaneous constituent loads at the seven subbasin stations generally was within about 20 percent of the median loads at the downstream Spring River station near Baxter Springs (fig. 24; table 16). The Spring River near Waco contributed 41 percent and Shoal Creek near Galena contributed 32 percent of the median flow at Spring River near Baxter Springs. Therefore, these stations contributed a substantial part of the median instantaneous loads of calcium, magnesium, sodium, potassium, alkalinity, chloride, dissolved solids, dissolved iron, and dissolved lead at Baxter Springs (table 16). Other subbasins also may have contributed substantial loads to the Spring River because of differences in geology, land use, or mining, industrial, and municipal effects. For example, the median discharge at Short Creek at Galena contributed less than 1 percent of the median discharge at Baxter Springs, yet it contributed about 20 percent of the total ammonia, 43 percent of the total phosphorus, and substantial quantities of dissolved zinc (79 percent of the total subbasin load; fig. 24). Cow Creek near Weir contributed less than 10 percent of the median discharge at Baxter Springs; however, it contributed 21 percent of the magnesium and substantial quantities of dissolved manganese (68 percent of the total subbasin load; fig. 24).

Median instantaneous loads of calcium at the downstream Spring River station near Baxter Springs and most subbasin stations were an order of magnitude greater than magnesium loads. This is because of the predominance of limestone within the region. The small calcium to magnesium ratios at both Brush Creek near Weir and Cow Creek near Weir were expressed as larger than expected magnesium loads (table 16). Brush Creek near Weir contributed less than 1 percent and Cow Creek near Weir contributed 9 percent of the median discharge at Baxter Springs; however, Brush Creek contributed 2 percent and Cow Creek contributed 21 percent of the median magnesium load. Large numbers of spoil piles associated with coal-strip mining activities may supplement base flows in these basins during dry weather (Spruill, 1987). A common mineral in coal spoil is gypsum, and calcium to magnesium ratios in seeps from coal spoil areas in Missouri commonly are near 1.0 to 1.6. Equilibrium calculations using SOLMINEQ.88 (Kharaka and others, 1988) indicate these streams were

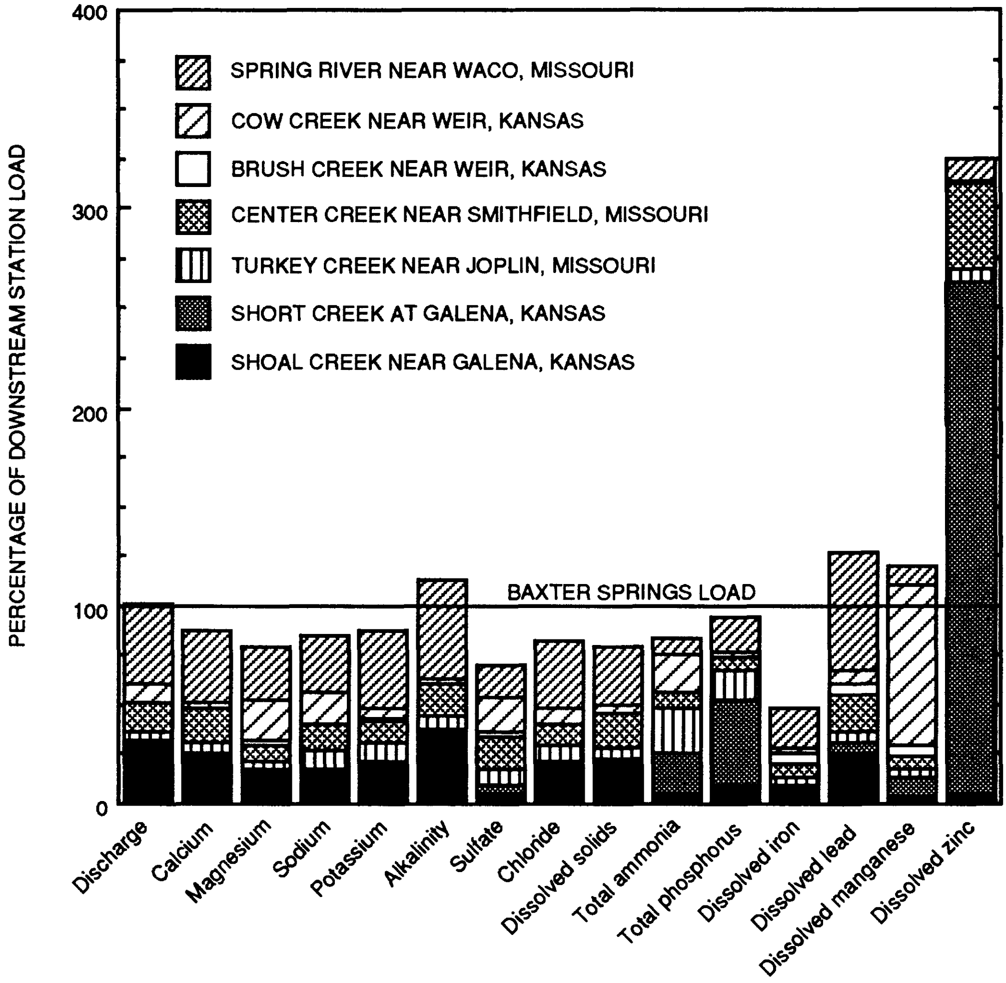

Figure 24.--Median instantaneous loads for selected constituents as a function of the downstream Spring River station near Baxter Springs, Kansas.

supersaturated with gypsum. The small calcium to magnesium ratios and substantial magnesium loads at Cow Creek near Weir (fig. 24) probably are related to controls on calcium, and not preferential dissolution of magnesium-rich minerals.

A comparison between the median instantaneous loads at the upstream Center Creek station near Carterville and the downstream station near Smithfield indicated a decrease in the total ammonia load between these two stations (fig. 25). Simple inorganic oxidation was not indicated because the median loads (table 16) and concentrations of total nitrite plus nitrate (table 7; fig. 8) were nearly the same between the two stations. A combination of oxidation to other forms, such as nitrite or nitrate, and subsequent dilution, coupled with biologic consumption, may explain the decreased ammonia loads at Smithfield. Center Creek near Carterville represented nearly one-third of the median total nitrite plus nitrate load in the basin but represented less than 15 percent of the median flow. Cow Creek near Weir, Turkey Creek near Joplin, and Short Creek at Galena also had substantial median loads of total ammonia (table 16). Effects from wastewater-treatment effluents were indicated in Cow Creek and Turkey Creek (Kansas Department of Health and Environment, 1980), while the fertilizer manufacturing plant near Joplin was identified as the principal source of total ammonia on Short Creek.

Total phosphorus concentrations usually average about 0.025 mg/L in natural, unaffected streams (Meybeck, 1979). The large median concentration of total phosphorus in Short Creek at Galena (39 mg/L; table 7) and large median load (table 16; fig. 24) indicated substantial industrial or municipal effects. Large concentrations (14 mg/L) in the Snake River in northeastern Oregon have been attributed to municipal waste disposal (Laird, 1964). Phosphorus concentrations as large as 30 mg/L in Peace Creek in Florida are attributed to mining of phosphate ore (Hem, 1985). The large increases in phosphorus and sulfate concentrations downstream from the phospho-gypsum waste pile indicated the waste pile is a significant contributor of phosphorus and sulfate to Short Creek (Farmers Chemical Company, 1985). Data collected by Farmers Chemical Company (1985) indicated that seep water from the phospho-gypsum pile was acidic (pH 3.8). However, the site owner also indicated that seepage from mines downstream was equally significant in contributing sulfate to Short Creek, as dilution effects were not observed downstream from the waste pile. The large concentrations (table 7) and median loads (table 16) of total phosphorus and dissolved zinc, as compared to other mining affected areas (Cow Creek, Brush Creek, Center Creek, and Turkey Creek), and low pH values in seep water, which may inhibit trace-constituent precipitation or adsorption reactions, indicated this waste pile and possible mine seepage through it contributed substantial loads of phosphorus and zinc to Spring River near Baxter Springs (Farmers Chemical Company, 1985).

Cow Creek near Weir contributed substantial loads of dissolved manganese to the Spring River, representing more than 80 percent of the median instantaneous load at the downstream Spring River station near Baxter Springs and 68 percent of the normalized subbasin load (table 16). The minimal contributions from other mined areas, such as Center Creek near Smithfield and Turkey Creek near Joplin, and decreases in the dissolved manganese load in Center Creek between the upstream and downstream stations indicated that coal-strip mining and not lead-zinc mining was the primary source of dissolved manganese at the Spring River near Baxter Springs.

Effects of coal and lead-zinc mining activities are reflected in the contributions of median sulfate, dissolved solids, and dissolved zinc loads to the Spring River near Baxter Springs. The median sulfate loads at Brush Creek near Weir and Cow Creek near Weir were larger than expected (2 and 18 percent of the median sulfate load at the Spring River near Baxter Springs), and, similar to dissolved manganese loads, probably were from coal-strip mining activities. The effect of lead-zinc mining in the Oronogo-Duenweg mining belt (fig. 2) was indicated in the increases in median loads of calcium, sulfate, dissolved solids, and dissolved zinc in Center Creek between Carterville and Smithfield (table 16; fig. 25). However, no large increase in the median load of dissolved lead was detected, and the median loads of dissolved iron and manganese decreased slightly from Carterville (0.11 and 0.27 g/s)

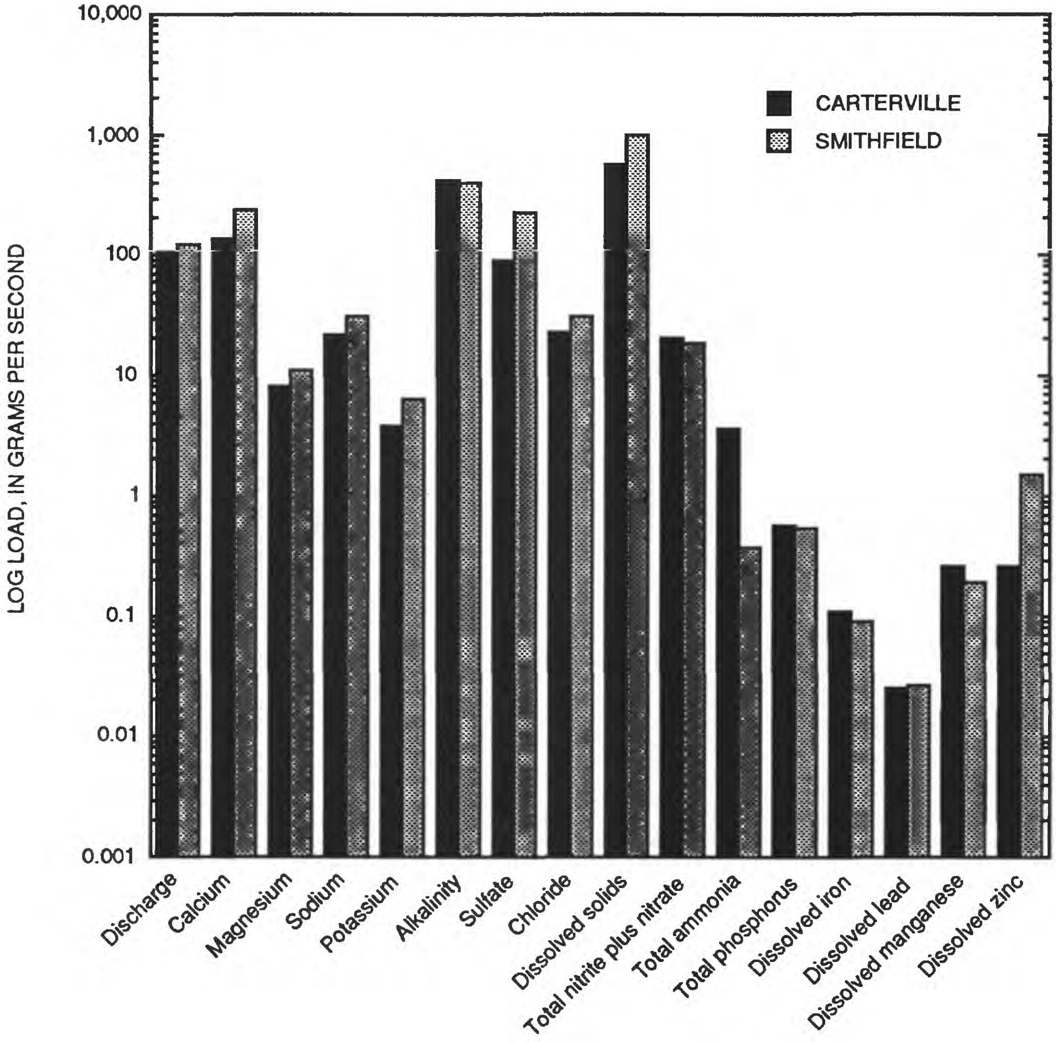

Figure 25.--Constituent loads at Center Creek near Carterville, Missouri, and Center Creek near Smithfield, Missouri.

to Smithfield (0.09 and 0.20 g/s). The lack of large differences in median loads of dissolved lead probably is attributable to solubility controls on dissolved lead concentrations, such as lead hydroxide [$Pb(OH)_2$] (Hem, 1985) and lead phosphate species.

Large concentrations of dissolved iron and manganese are possible in coal-strip mined areas. However, the large loads of dissolved manganese, as compared to the much smaller loads of dissolved iron at Cow Creek near Weir (table 16; fig. 24), may have been because of the kinetics of reactions controlling the solubility of these trace constituents in oxidizing environments. Although iron and manganese form relatively insoluble oxides in oxidizing environments, the kinetics of manganese oxidation are much slower than the rates for iron (Lewis, 1976; Hem, 1985). It is possible that much of the dissolved iron may have been removed from the stream before reaching the subbasin sampling station; manganese, because of its slower reaction kinetics, may have remained in solution until reaching the subbasin sampling station.

Median instantaneous loads of dissolved zinc at the subbasin stations exceeded the median load at the Spring River near Baxter Springs by more than 300 percent. This is likely because of the small number of samples collected for dissolved zinc analysis at Baxter Springs. Although comparisons of percent zinc loads at Baxter Springs are unreliable (such as in fig. 24), a comparison of the normalized subbasin percentages for dissolved zinc loads indicates Short Creek contributed most of the dissolved zinc load to the Spring River near Baxter Springs (table 16). Similar conclusions were reached in an evaluation of low-flow samples by Spruill (1987). Barks (1977) indicated uncertainty in distinguishing between mining effects and effects from the waste phospho-gypsum pile near Short Creek. According to Farmers Chemical Company (1985), the phospho-gypsum pile is a source of sulfate, cadmium, and zinc in Short Creek. However, shallow ground water from abandoned lead-zinc mining areas, which recharges Short Creek near Galena, Kansas (fig. 1), also is an important source of these constituents in Short Creek. As stated previously in the section on the analysis of spatial characteristics, in addition to the availability of sulfide minerals, the low pH value and small alkalinity concentrations in Short Creek (table 7) inhibit the precipitation of zinc carbonate.

Trends in Water Quality

The water quality in the Spring River basin has been affected by a combination of lead-zinc and coal mining and municipal and industrial wastes. Urban and industrial development create new demands on existing wastewater-treatment facilities that could eventually contribute to further changes in water quality. However, effective water-quality laws limit the volume and content of industrial and municipal effluents discharged to streams, which would tend to minimize any changes. Another factor to consider in the Spring River basin is that lead-zinc mining activities ceased in the early 1960's, and it is possible that mining related water-quality effects are decreasing with time. Knowledge of significant water-quality trends is important for evaluating existing wastewater-treatment facilities and for determining NPDES permit limits.

Trend data should be interpreted in general terms, because the results may be affected by other factors. Significant trend results indicate that a constituent concentration is increasing or decreasing with time. The supposed trend in some instances may be due to changes or improvements in an analytical method, changes in sample preservation, or changes in sample collection techniques.

The Seasonal Kendall test (Hirsch and others, 1982; Crawford and others, 1983) was used to determine monotonic time trends of water-quality constituents in the Spring River basin. This nonparametric test is based on ranks of data values and is applicable to data sets with seasonality, missing values, and censored values. The actual procedure compares data pairs of constituent values and time of collection. If the constituent concentration is larger for the latter of two data pairs, a plus is scored, and if the latter value is smaller, a minus is scored (Smith and others, 1982). Equal occurrences of pluses and minuses indicate no trend. An upward trend is likely if there are significantly more pluses than minuses, and likewise, a downward trend is indicated if there are significantly more minuses than pluses. The Seasonal Kendall test also removes seasonal effects (discussed in the section on the analysis of seasonal variation) by comparing only data pairs of the same specified time period. In this report, the specified time period is the month, and therefore, only data pairs from the same month are compared. The magnitude of the trend is expressed as a slope (change per unit time).

As indicated in the earlier section on correlation analysis, constituent concentrations commonly are correlated positively or negatively with stream discharge. Perceived trends may be the result of fluctuations in flow because of droughts or wetter than normal years. Anomalously high or low flows also may mask a significant trend. Flow-adjustment procedures (Hirsch and others, 1982) are used to remove constituent concentration variations because of flow. This involves the use of least-squares regression to determine the relation of constituent concentration to some function of discharge. If a significant relation exists, the residuals from this regression are considered to have the effects of discharge removed. The Seasonal Kendall test for trend is then applied to these residuals.

The results of the Seasonal Kendall trend analysis for selected water-quality constituents from the long-term monitoring stations are listed in table 18. The entire period of record (fig. 5; table 7) was used at each station. To avoid some of the bias caused by changes or improvements in an analytical method, data values less than or equal to the largest constituent detection limit for censored data were set equal to that detection limit. The Seasonal Kendall test was first done on data unadjusted for flow. The relation of constituent concentration to discharge, if any, was then determined using one of the two following models:

$$C = a + b\,(Q) \qquad \text{Linear} \tag{6}$$

$$C = a + b\,(\log Q) \qquad \text{Log-linear,} \tag{7}$$

where C is the predicted constituent concentration, a and b are regression coefficients, and Q is the discharge. If neither of the models resulted in a significant fit at an α-level of 0.05, then no flow adjustment was done. Likewise, if both models were significant, then the model with the smallest p-value was used for flow adjustment.

At the stations affected by lead-zinc mining [Center Creek near Carterville, Missouri (fig. 4, no. 4); Center Creek near Smithfield, Missouri (fig. 4, no. 5); Turkey Creek near Joplin, Missouri (fig. 4, no. 6); and the downstream Spring River station near Baxter Springs, Kansas (fig. 4, no. 9)], sulfate concentrations have significant ($p < 0.05$) downward trends. With the exception of the Spring River near Baxter Springs, specific conductance also has significant downward trends at these stations. There also is a downward specific conductance trend at the Spring River near Baxter Springs, but the p-value (0.074) is slightly greater than the significance level of 0.05. The pH values have significant increases at both Center Creek stations and the Spring River near Baxter Springs; calcium concentrations have significant decreases at Center Creek near Smithfield and Turkey Creek near Joplin; and dissolved manganese and zinc concentrations at Center Creek near Smithfield have a significant downward trend. Because of insufficient dissolved zinc data for the Spring River near Baxter Springs, a dissolved zinc trend could not be determined at this station. These apparent trends indicate, that at least with respect to lead-zinc mining effects, the water quality is improving with time.

Other factors could be involved, however, particularly at the upstream Center Creek station near Carterville and Turkey Creek near Joplin. The station near Carterville, which is on the edge of the Oronogo-Duenweg mining belt (fig. 2), is not affected significantly by mining. The trends at the station, including downward trends in dissolved iron and manganese concentrations, seem to indicate improvements in water quality related to the cessation of mining. However, these apparent trends also could be related to improvements in housekeeping practices, diversion of gray water to land application, or process elimination or modifications by the industries located along Grove Creek (Greg Perkins, Missouri Department of Natural Resources, oral commun., 1990). The lack of a significant

Table 18.--*Results of the Seasonal Kendall analysis for the long-term monitoring stations*

[Underlining indicates trend is significant at p = 0.05 level; ft³/s, cubic feet per second; NA, not applicable; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; NC, not computed; mL, milliliters; N, nitrogen; µg/L, micrograms per liter]

			Unadjusted for flow				Flow adjusted		
Physical property or constituent	Number of samples	Median	Kendall's Tau	Slope[a]	p-value[b]	Flow model	Kendall's Tau	Slope[a]	p-value[b]
			Spring River near Waco, Missouri (fig. 4, no. 1)						
Discharge (ft³/s)	271	332	0.073	4.21	0.427	NA	NA	NA	NA
Specific conductance (µS/cm)	271	321	.016	.08	.857	(c)	0.088	0.61	0.164
pH (standard units)	106	7.9	.085	.00	.450	(c)	.092	.01	.438
Dissolved oxygen (mg/L)	269	8.4	.225	.06	.000	NC	NC	NC	NC
Fecal coliform (colonies per 100 mL)	62	150	.084	2.48	.502	(d)	.024	3.74	.909
Calcium (mg/L)	247	55	.105	.22	.106	(c)	.201	.29	.010
Magnesium (mg/L)	247	3.5	.067	.02	.434	(c)	.154	.03	.070
Sodium (mg/L)	248	6.7	.082	.03	.418	(c)	.184	.05	.090
Sulfate (mg/L)	247	21	.084	.14	.364	NC	NC	NC	NC
Chloride (mg/L)	172	9.6	.250	.17	.048	(c)	.401	.22	.003
Total nitrite plus nitrate (mg/L)	139	1.7	.077	.01	.383	(d)	.092	.02	.342
Total ammonia (mg/L as N)	129	.05	.002	.00	1.000	NC	NC	NC	NC
Total phosphorus (mg/L)	165	.17	-.169	.00	.061	(d)	-.152	.00	.151
Dissolved iron (µg/L)	53	49	.248	2.00	.149	(c)	.153	1.51	.352
Dissolved manganese (µg/L)	95	30	.188	1.67	.106	NC	NC	NC	NC
Dissolved zinc (µg/L)	82	30	-.102	.00	.523	NC	NC	NC	NC
			Center Creek near Carterville, Missouri (fig. 4, no. 4)						
Discharge (ft³/s)	294	103	0.202	2.26	0.055	NA	NA	NA	NA
Specific conductance (µS/cm)	294	350	-.262	-4.47	.014	(c)	-0.208	-2.18	0.011
pH (standard units)	294	7.6	.386	.02	.000	(c)	.346	.02	.000
Dissolved oxygen (mg/L)	278	8.0	.006	.00	.938	NC	NC	NC	NC
Fecal coliform (colonies per 100 mL)	191	110	.095	1.37	.270	(d)	-.066	-5.44	.593
Calcium (mg/L)	191	56	-.258	-.67	.029	(c)	-.032	-.06	.690
Magnesium (mg/L)	190	3.1	-.239	-.04	.022	(c)	-.021	.00	.770
Sodium (mg/L)	198	8.8	-.219	-.17	.043	(c)	.110	.07	.167
Sulfate (mg/L)	200	24	-.519	-1.64	.000	(c)	-.217	-1.14	.019
Chloride (mg/L)	200	8.4	-.029	-.01	.770	(c)	.245	.13	.008
Total nitrite plus nitrate (mg/L)	134	4.9	-.105	-.05	.454	(c)	-.201	-.13	.097
Total ammonia (mg/L as N)	157	.61	-.262	-.05	.119	(c)	-.311	-.12	.017
Total phosphorus (mg/L)	183	.13	-.539	-.02	.000	(c)	-.520	-.02	.000
Dissolved iron (µg/L)	107	20	-.066	.00	.396	(d)	-.194	-.92	.017
Dissolved manganese (µg/L)	190	60	-.364	-6.37	.001	(c)	-.176	-4.84	.046
Dissolved zinc (µg/L)	164	53	-.328	-4.00	.012	(c)	-.143	-5.42	.186

Table 18.--*Results of the Seasonal Kendall analysis for the long-term monitoring stations*--Continued

Physical property or constituent	Number of samples	Median	Unadjusted for flow: Kendall's Tau	Unadjusted for flow: Slope[a]	Unadjusted for flow: p-value[b]	Flow model	Flow adjusted: Kendall's Tau	Flow adjusted: Slope[a]	Flow adjusted: p-value[b]
Center Creek near Smithfield, Missouri (fig. 4, no. 5)									
Discharge (ft^3/s)	309	122	0.036	0.62	0.745	NA	NA	NA	NA
Specific conductance (µS/cm)	337	405	-.215	-4.38	.056	(c)	-0.305	-3.28	0.007
pH (standard units)	172	7.8	.243	.02	.002	(d)	.271	.02	.002
Dissolved oxygen (mg/L)	335	9.4	.175	.04	.012	(d)	.167	.04	.012
Fecal coliform (colonies per 100 mL)	158	70	.088	.92	.235	(c)	-.043	-5.12	.691
Calcium (mg/L)	251	72	-.197	-.64	.079	(c)	-.300	-.60	.016
Magnesium (mg/L)	251	3.3	-.073	-.02	.471	(c)	-.108	-.02	.360
Sodium (mg/L)	251	8.0	-.031	-.02	.789	(c)	.006	.00	.964
Sulfate (mg/L)	250	56	-.338	-1.81	.006	(c)	-.344	-1.70	.005
Chloride (mg/L)	175	9.4	.022	.00	.868	(c)	.221	.15	.045
Total nitrite plus nitrate (mg/L)	236	4.9	-.147	-.11	.294	(c)	-.100	-.05	.421
Total ammonia (mg/L as N)	223	.10	-.200	.00	.089	(c)	-.084	.00	.358
Total phosphorus (mg/L)	261	.15	-.423	-.01	.000	(c)	-.437	-.01	.000
Dissolved iron (µg/L)	86	20	.014	.00	.913	NC	NC	NC	NC
Dissolved manganese (µg/L)	99	50	-.317	-3.33	.002	NC	NC	NC	NC
Dissolved zinc (µg/L)	94	420	-.391	-26.67	.001	NC	NC	NC	NC
Turkey Creek near Joplin, Missouri (fig. 4, no. 6)									
Discharge (ft^3/s)	330	30	0.138	0.60	0.165	NA	NA	NA	NA
Specific conductance (µS/cm)	360	620	-.381	-8.67	.000	(c)	-0.365	-7.98	0.001
pH (standard units)	193	7.5	-.107	.00	.199	(d)	-.073	.00	.355
Dissolved oxygen (mg/L)	355	5.6	-.111	-.05	.221	(c)	-.141	-.06	.168
Fecal coliform (colonies per 100 mL)	115	1600	NC	NC	NC	NC	NC	NC	NC
Calcium (mg/L)	311	92	-.395	-.88	.000	(d)	-.408	-1.04	.000
Magnesium (mg/L)	311	5.8	-.313	-.09	.000	(c)	-.323	-.10	.000
Sodium (mg/L)	311	25	-.223	-.53	.016	(c)	-.195	-.44	.071
Sulfate (mg/L)	338	110	-.503	-3.00	.000	(d)	-.485	-3.11	.000
Chloride (mg/L)	260	27	-.150	-.40	.124	(c)	-.108	-.24	.351
Total nitrite plus nitrate (mg/L)	148	1.2	-.120	-.04	.330	NC	NC	NC	NC
Total ammonia (mg/L as N)	163	1.8	.183	.07	.104	(c)	.228	.15	.116
Total phosphorus (mg/L)	201	1.4	-.051	-.01	.487	(c)	-.149	-.04	.074
Dissolved iron (µg/L)	70	80	-.276	-12.88	.083	NC	NC	NC	NC
Dissolved manganese (µg/L)	144	150	.211	1.00	.117	NC	NC	NC	NC
Dissolved zinc (µg/L)	112	360	-.019	.00	.845	(c)	-.012	-1.74	.932

Table 18.--*Results of the Seasonal Kendall analysis for the long-term monitoring stations*--Continued

Physical property or constituent	Number of samples	Median	Unadjusted for flow: Kendall's Tau	Unadjusted for flow: Slope[a]	Unadjusted for flow: p-value[b]	Flow model	Flow adjusted: Kendall's Tau	Flow adjusted: Slope[a]	Flow adjusted: p-value[b]
Shoal Creek near Galena, Kansas (fig. 4, no. 8)									
Discharge (ft^3/s)	181	257	-0.069	-3.39	0.590	NA	NA	NA	NA
Specific conductance (µS/cm)	212	280	.003	.00	.982	(c)	0.012	0.06	0.894
pH (standard units)	45	8.0	-.178	-.02	.318	NC	NC	NC	NC
Dissolved oxygen (mg/L)	210	9.4	.096	.03	.361	NC	NC	NC	NC
Fecal coliform (colonies per 100 mL)	32	38	.343	17.00	.158	NC	NC	NC	NC
Calcium (mg/L)	211	50	.127	.14	.159	(d)	.155	.15	.137
Magnesium (mg/L)	211	3.0	.014	.00	.891	(c)	-.006	.00	.969
Sodium (mg/L)	211	5.5	.136	.05	.189	(c)	.164	.06	.130
Sulfate (mg/L)	211	10	-.071	.00	.408	NC	NC	NC	NC
Chloride (mg/L)	135	8.8	.111	.10	.405	(c)	.288	.24	.059
Total nitrite plus nitrate (mg/L)	116	1.7	.212	.03	.095	(c)	.142	.02	.130
Total ammonia (mg/L as N)	112	.03	-.214	.00	.180	(d)	-.009	.00	.979
Total phosphorus (mg/L)	146	.13	-.164	.00	.158	(c)	-.327	-.01	.029
Dissolved iron (µg/L)	41	20	.126	.00	.497	NC	NC	NC	NC
Dissolved manganese (µg/L)	41	10	-.136	.00	.370	NC	NC	NC	NC
Dissolved zinc (µg/L)	6	40	NC	NC	NC	NC	NC	NC	NC
Spring River near Baxter Springs, Kansas (fig. 4, no. 9)									
Discharge (ft^3/s)	283	806	0.102	14.38	0.269	NA	NA	NA	NA
Specific conductance (µS/cm)	353	360	-.246	-3.38	.008	(c)	-0.148	-1.56	0.074
pH (standard units)	200	7.5	.186	.02	.014	NC	NC	NC	NC
Dissolved oxygen (mg/L)	243	8.6	.284	.08	.002	(c)	.160	.06	.018
Fecal coliform (colonies per 100 mL)	52	180	.333	44.50	.081	(c)	-.517	-109.34	.133
Calcium (mg/L)	318	59	-.134	-.25	.076	(c)	-.057	-.07	.449
Magnesium (mg/L)	320	5.2	-.198	-.08	.029	(c)	-.205	-.09	.034
Sodium (mg/L)	319	9.6	-.126	-.08	.143	(c)	-.038	-.02	.563
Sulfate (mg/L)	350	54	-.247	-1.00	.006	(c)	-.188	-.79	.043
Chloride (mg/L)	289	11	-.090	-.06	.313	(c)	.081	.05	.388

Table 18.--*Results of the Seasonal Kendall analysis for the long-term monitoring stations*--Continued

Physical property or constituent	Number of samples	Median	Unadjusted for flow: Kendall's Tau	Unadjusted for flow: Slope[a]	Unadjusted for flow: p-value[b]	Flow model	Flow.adjusted: Kendall's Tau	Flow.adjusted: Slope[a]	Flow.adjusted: p-value[b]
Spring River near Baxter Springs, Kansas (fig. 4, no. 9)--Continued									
Total nitrite plus nitrate (mg/L)	116	2.4	-0.090	-0.02	0.516	(c)	0.006	0.00	0.000
Total ammonia (mg/L as N)	112	.14	-.235	-.01	.137	NC	NC	NC	NC
Total phosphorus (mg/L)	192	.26	-.475	-.02	.001	NC	NC	NC	NC
Dissolved iron (µg/L)	73	50	-.142	-.91	.382	NC	NC	NC	NC
Dissolved manganese (µg/L)	67	150	.114	4.55	.430	(c)	.000	.21	.000
Dissolved zinc (µg/L)	6	310	NC	NC	NC	NC	NC	NC	NC

[a] The slope (change per unit time) is expressed in constituent units per year.

[b] 0.05 level of probability.

[c] The relation of constituent concentration to discharge was determined using the following log-linear model: C = a+b (log Q), where C is the predicted constituent concentration, Q is the discharge, and a and b are regression coefficients.

[d] The relation of constituent concentration to discharge was determined using the following linear model: C = a+b (Q), where C is the predicted constituent concentration, Q is the discharge, and a and b are regression coefficients.

zinc trend and the downward total ammonia trend indicates that this may be the case. The water quality in Turkey Creek is not only affected by lead-zinc mining but also municipal, organic, and metal-plating wastes, which make it difficult to interpret trend results at Turkey Creek near Joplin.

Other trends are more basinwide. Chloride has a significant upward trend at the upstream Spring River station near Waco, Missouri (fig. 4, no. 1), and at both Center Creek stations. There also is an upward chloride trend at Shoal Creek near Galena, Kansas (fig. 4, no. 8), but the p-value (0.059) is slightly greater than the significance level of 0.05. This possibly is because of increased development in the Spring River basin. Total phosphorus has significant downward trends at both Center Creek stations, Shoal Creek near Galena, and the Spring River near Baxter Springs. Decreased use of phosphate detergents during the 1970's partially may account for the decreasing concentrations of total phosphorus. Also, as no new material has been added to the phospho-gypsum piles near Grove and Short Creeks since the early 1970's, the downward total phosphorus trends at Carterville, Smithfield, and Baxter Springs probably are because of the aging of the phospho-gypsum piles, which has resulted in declining phosphate concentrations in pile leachate (E.H. Sears, oral commun., 1990). Significant increases in dissolved oxygen concentrations are noted at the upstream and downstream Spring River stations and at Center Creek near Smithfield, indicating decreases in organic loading, possibly as a result of improvements in wastewater treatment.

Discharge did not have any significant upward or downward trends at any of the six stations. There is an upward trend at Center Creek near Carterville, but the p-value (0.055) is slightly greater than the significance level of 0.05. The borderline significance does indicate that there is a tendency toward an increase in discharge with time at Carterville, which may be the result of basin development. The effect that discharge can have on trend analysis results is indicated by Center Creek near Carterville (table 18). Calcium, magnesium, sodium, and dissolved zinc have significant downward trends before flow adjustment but not after flow-adjustment procedures are applied. Likewise, chloride, total ammonia, and dissolved iron do not have any significant trends before flow adjustment but do after.

SUMMARY

The Spring River basin drains approximately 2,090 mi^2 of southwestern Missouri and 530 mi^2 of southeastern Kansas. Principal tributaries to the Spring River originating in the Missouri part of the study area include the North Fork Spring River and Center, Turkey, Short, and Shoal Creeks. Cow Creek, and its tributary Brush Creek, are the principal tributaries originating in Kansas. With the exception of Cow and Brush Creeks and the North Fork Spring River, which are plains-type streams, the tributaries are typical Ozark-type streams characterized by alternating pools and riffles, and mixed sand, gravel, and boulder bottoms.

The base flows of Center Creek, Shoal Creek, and the Spring River are sustained by springs originating in Mississippian limestones. Where the chemical quality has not been affected by waste discharges, the waters in these basins are a calcium-bicarbonate type with an average calcium to magnesium ratio of 10:1 milliequivalents per liter. This is in contrast to a calcium to magnesium ratio of approximately 1:1 detected in surface waters on the Ozark Plateaus where the bedrock formations are dolomites of Cambrian and Ordovician age. Dissolved solids concentrations ranged from about 130 to 200 mg/L and tended to increase slightly from Shoal Creek to Center Creek to the Spring River. The plains-type streams are underlain by bedrock of relatively impervious Pennsylvanian shales, and base flows are poorly sustained during dry weather. The dissolved solids concentration is in the same range as the Ozark-type streams in the area, but sulfate is more predominant because of sulfide minerals in the Pennsylvanian bedrock.

There are extensive water-quality problems in the Spring River basin. Development of lead and zinc resources in the basin began about 1850 in Missouri and spread into southeastern Kansas and northwestern Oklahoma, into what is called the Tri-State District. Center Creek drains about 70 percent, Turkey Creek drains about 18 percent, and Short Creek drains about 5 percent of the lead-zinc mined areas in Missouri. Mine-related discharges, characterized by large concentrations of calcium, sulfate, dissolved solids, and zinc, have affected the lower 18 river mi of Center Creek and Turkey and Short Creeks along their entire lengths. Municipal or industrial wastes also have affected these streams. Shoal Creek has been minimally affected by municipal point sources of pollution. The Spring River upstream from its junction with Cow and Brush Creeks, which are significantly affected by surface coal mining, and Center, Turkey, and Short Creeks also is minimally affected by municipal and industrial sources of pollution. These problems usually are localized because of dilution and large assimilative capacities. The water quality of the Spring River deteriorates downstream from the affected tributary streams, but improves downstream near Baxter Springs, Kansas, probably because of dilution by Shoal Creek, or because of Empire Lake, which may be a sink for nutrients and trace constituents.

Large quantities of water-quality data have been collected in the Spring River basin. The project data set consisted of data for six long-term monitoring stations (the Spring River near Waco, Missouri; Center Creek near Carterville, Missouri; Center Creek near Smithfield, Missouri; Turkey Creek near Joplin, Missouri; Shoal Creek near Galena, Kansas; and the Spring River near Baxter Springs, Kansas) and three ancillary stations (Cow Creek near Weir, Kansas; Brush Creek near Weir, Kansas; and Short Creek at Galena, Kansas). Data for the long-term monitoring stations have been collected simultaneously by the USGS and KDHE from the early 1960's to September 1987. The two sources of data were combined after first considering sample collection, handling, and preservation techniques, analytical methods, and laboratory quality control and quality assurance practices. A statistical comparison of the two data sets indicated that most constituents were not statistically different at the 0.05 level of probability.

Summary statistics, which indicate spatial variations in water quality, were calculated for the six long-term monitoring and three ancillary stations to describe water-quality conditions in the Spring River basin. To determine whether or not these variations were statistically significant, ANOVA and multiple-comparison procedures were used. Generally, streams most significantly affected by lead-zinc or coal mining, municipal wastes, and industrial wastes had the smallest median pH values (3.9 to 7.5) and largest median specific conductance values (620 to 1,070 μS/cm), particularly Cow Creek near Weir, Brush Creek near Weir, Turkey Creek near Joplin, and Short Creek at Galena. A median pH of 7.8 at Center Creek near Smithfield, downstream from the Oronogo-Duenweg mining belt, indicated that acid formed by the dissolution of sulfide minerals was neutralized by carbonate rocks. Median specific conductance values significantly increased downstream from Carterville to Smithfield on Center Creek (350 to 405 μS/cm) and from Waco to Baxter Springs on the Spring River (321 to 360 μS/cm). Median pH values were largest (7.9 and 8.0) and median specific conductance values were smallest (321 and 280 μS/cm) at the Spring River near Waco and at Shoal Creek near Galena. Median dissolved oxygen concentrations were smallest at Cow Creek near Weir (6.2 mg/L), Brush Creek near Weir (7.8 mg/L), and Turkey Creek near Joplin (5.6 mg/L), all of which receive substantial municipal waste loads. Significant increases in median dissolved oxygen concentrations were detected on Center Creek between Carterville (8.0 mg/L) and Smithfield (9.4 mg/L), indicating that Center Creek somewhat recovers from the effects of the industries located near Grove and Center Creeks.

Large median concentrations of the major constituents, particularly calcium (76 to 120 mg/L) and sulfate (110 to 540 mg/L), which are commonly associated with lead-zinc and coal mining, were detected at Cow Creek near Weir, Brush Creek near Weir, Turkey Creek near Joplin, and Short Creek at Galena. Between Carterville and Smithfield on Center Creek and Waco and Baxter Springs on the Spring River, median calcium (56 to 72 mg/L on Center Creek and 55 to 59 mg/L on the Spring River) and sulfate (24 to 56 mg/L on Center Creek and 21 to 54 mg/L on the Spring River) concentrations significantly increased. Median concentrations of sodium (19 to 70 mg/L), an indicator of municipal and industrial wastes and urban runoff, were largest at Cow Creek near Weir, Brush Creek near Weir, Turkey Creek near Joplin, and Short Creek at Galena. Generally, the smallest median major constituent concentrations were detected at the Spring River near Waco and Shoal Creek near Galena.

Median total nitrite plus nitrate (1.7 to 2.4 mg/L), total ammonia (0.05 to 0.14 mg/L), dissolved ammonia (0 to 0.23 mg/L), total phosphorus (0.17 to 0.26 mg/L), and dissolved phosphorus (0.10 to 0.28 mg/L) concentrations were significantly larger at the downstream Spring River station near Baxter Springs than at the upstream station near Waco, indicating substantial sources of these constituents within the basin. Median total and dissolved ammonia concentrations significantly decreased on Center Creek from Carterville (0.61 and 1.2 mg/L) to Smithfield (0.10 and 0.22 mg/L), further substantiating that Center Creek somewhat recovers from the effects of the industries located near Grove and Center Creeks. The Missouri water-quality standard for ammonia was exceeded 27 percent of the time at Carterville and 47 percent of the time at Turkey Creek near Joplin. Effluents from a fertilizer manufacturing plant located near Grove Creek upstream from Carterville and municipal wastewater-treatment effluents on Turkey Creek probably were responsible for the frequent large total ammonia concentrations. As determined by the ANOVA and multiple-comparison procedures, Turkey Creek near Joplin had among the smallest total nitrite plus nitrate concentrations and among the largest total and dissolved ammonia concentrations, indicating the predominance of reduced nitrogen species from wastewater-treatment plants.

Median concentrations of dissolved cadmium, chromium, copper, iron, and lead were at, or only slightly above, detection at all stations, with the exception of large median dissolved cadmium and copper concentrations at Short Creek at Galena (280 and 240 µg/L) and a large median dissolved iron concentration at Brush Creek near Weir (2,600 µg/L). Large median dissolved manganese concentrations at Cow Creek near Weir (2,400 µg/L), Brush Creek near Weir (4,000 µg/L) and Short Creek at Galena (3,000 µg/L) indicated that these tributary streams probably were responsible for the significant increase in the dissolved manganese concentration between the Spring River near Waco (30 µg/L) and the Spring River near Baxter Springs (150 µg/L). Median concentrations of dissolved zinc, which often is used as an indicator of mining effects, significantly increased from Carterville to Smithfield on Center Creek (53 to 420 µg/L) and Waco to Baxter Springs on the Spring River (30 to 310 µg/L). The frequent exceedance of the Missouri water-quality standard for zinc for the protection of aquatic life was the likely reason for the almost total lack of benthic invertebrate populations at Center Creek near Smithfield and Turkey Creek near Joplin. Also, the benthic invertebrate population on Turkey Creek probably was affected adversely by wastewater-treatment plant effluents. Generally, the smallest median trace-constituent concentrations were detected at the Spring River near Waco and at Shoal Creek near Galena.

From an evaluation of the summary statistics and the results of the ANOVA and multiple-comparison tests, it is evident that Shoal Creek near Galena and the Spring River near Waco have the smallest concentrations of major constituents, nutrients, and trace constituents. Differences in water-quality characteristics between the two likely are attributable to differences in geology, topography, and land use. There seems to be two distinct water-quality baselines for the Spring River basin, as represented by the Spring River near Waco and Shoal Creek near Galena. Actual baseline constituent concentrations were determined by calculating the median constituent values for samples collected at discharges between the 25th and 75th percentiles and at discharges less than the 5th percentile.

Correlations between most water-quality constituents and discharge indicate substantial effects from lead-zinc mining at the downstream Center Creek station near Smithfield and Turkey Creek near Joplin. Concentrations of major cations, anions, and most dissolved trace constituents at Center Creek near Smithfield are somewhat sustained at higher flows by runoff from tailings areas upstream. With the exception of potassium, values of Spearman rank correlation coefficients between most major constituents, including specific conductance, and discharge are less negative at Smithfield than those upstream from most mined areas at Center Creek near Carterville. Positive relations between dissolved zinc and discharge ($r_s = 0.42$) at Turkey Creek near Joplin indicate substantial effects from mined areas, industrial sites, or both. Negative relations between total nitrite and nitrate, total ammonia, and dissolved ammonia and discharge at Center Creek near Carterville indicate dilution of low-flow effluent discharges along Grove and Center Creeks upstream from Carterville during runoff.

The Spring River near Waco and Shoal Creek near Galena represent most of the flow in the Spring River basin. Comparison of median period of record discharges and median instantaneous constituent loads at the long-term monitoring and ancillary stations indicated that the Spring River near Waco and Shoal Creek near Galena represented over 70 percent of the median period of record discharge at the Spring River near Baxter Springs, Kansas. Therefore, these two stations contributed a significant part of the median instantaneous loads of calcium, magnesium, sodium, potassium, alkalinity, chloride, dissolved solids, dissolved iron, and dissolved lead at Baxter Springs. Effects from industries along Grove Creek on loads of total nitrite plus nitrate were indicated. Center Creek near Carterville represented nearly one-third of the median load in the basin but represented less than 15 percent of the median flow. Although Grove Creek had a substantial effect on concentrations of total ammonia at Center Creek near Carterville, a ten-fold decrease in total ammonia loads occurred downstream at Center Creek near Smithfield. Substantial effects on loads of total ammonia, total phosphorus, and dissolved zinc from industrial discharges, seepage from a phospho-gypsum waste pile, or lead-zinc mining were indicated by the Short Creek data. Short Creek at Galena represented less than 1 percent of the median flow at Spring River near Baxter Springs; however, it seemed to be the largest single source of total phosphorus and dissolved zinc loads in the Spring River basin. Median loads of dissolved iron, lead, and manganese did not seem to be affected by lead-zinc mining in the basin. However, Cow Creek near Weir had substantial effects from coal-strip mined areas on loads of magnesium and dissolved manganese and contributed most of the dissolved manganese load at Spring River near Baxter Springs.

The Seasonal Kendall test was used to determine monotonic time trends of water-quality constituents at the long-term monitoring stations. Flow-adjustment procedures were used if there was a significant relation between constituent concentration and discharge. Chloride concentrations have an upward trend at the Spring River near Waco and both Center Creek stations, probably because of increased development in the basin. Total phosphorus concentrations are decreasing at both Center Creek stations, Shoal Creek near Galena, and the downstream Spring River station near Baxter Springs, probably because of the decreased use of phosphate detergents and the aging of phospho-gypsum waste piles located near Grove Creek and Short Creek, which has resulted in declining phosphate concentrations in pile leachate.

At the stations affected by lead-zinc mining (Center Creek near Carterville, Center Creek near Smithfield, Turkey Creek near Joplin, and the Spring River near Baxter Springs), sulfate concentrations have significant downward trends. With the exception of the Spring River near Baxter Springs, specific conductance also has significant downward trends at these stations. The pH values are increasing at Center Creek near Carterville, Center Creek near Smithfield, and the Spring River near Baxter Springs; calcium concentrations are decreasing at Center Creek near Smithfield and Turkey Creek near Joplin; and dissolved zinc has a significant downward trend at Center Creek near Smithfield. These apparent trends indicate that the water quality is improving with time, at least with respect to lead-zinc mining effects.

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ADDITIONAL DATA

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*

[ft^3/s, cubic foot per second; µS/cm, microsiemens per centimeter at 25 degrees Celsius; °C, degrees Celsius; mg/L, milligrams per liter; mL, milliliter; CaCO$_3$, calcium carbonate; e, value is estimated by using a log-probability regression to predict the values of data less than the detection limit; ROE, residue on evaporation at 180 degrees Celsius; N, nitrogen; µg/L, micrograms per liter; --, no data]

	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
Physical property or constituent	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Spring River near Waco, Missouri (fig. 4, no. 1; data collected from September 1964 to July 1986)									
Discharge (ft^3/s)	271	17,300	36	970	3,970	864	332	141	58
Specific conductance (µS/cm)	271	544	92	317	410	350	321	290	194
pH (standard units)	106	8.6	6.8	a	8.3	8.1	7.9	7.6	7.3
Temperature (°C)	262	30.5	0.0	14.9	27.0	22.5	16.0	7.0	2.0
Dissolved oxygen (mg/L)	269	17.6	2.0	8.8	13.0	10.7	8.4	6.8	5.7
Dissolved oxygen, percent saturation	104	129	54	83	110	90	80	72	63
Suspended solids (mg/L)	26	280	1	38	168	25	16	7	1
Fecal coliform (colonies per 100 mL)	62	15,000	2	950	5,000	420	150	49	4
Calcium (mg/L)	247	73	14	53	67	61	55	47	30
Magnesium (mg/L)	247	10	.9	3.8	6.2	4.4	3.5	3.0	1.8
Sodium (mg/L)	248	16	1.7	7.2	12	8.0	6.7	5.8	4.2
Potassium (mg/L)	248	7.1	.9	2.6	4.8	2.9	2.3	2.0	1.5
Alkalinity (mg/L as CaCO$_3$)	258	196	24	121	159	144	128	104	58
Sulfate (mg/L)	247	110	6.5	23	44	28	21	15	10
Chloride (mg/L)	172	21	2.3	10	17	12	9.6	7.3	5.0
Fluoride (mg/L)	122	1.2	b	.17e	.40e	.20e	.10e	.10e	.04e
Dissolved solids (ROE, mg/L)	86	243	41	187	234	210	190	177	132
Total nitrite plus nitrate (mg/L as N)	139	3.0	.10	1.7	2.5	2.0	1.7	1.3	.73
Total ammonia (mg/L as N)	129	3.1	b	.12e	.38e	.13e	.05e	.01e	.004e
Dissolved ammonia (mg/L as N)	31	1.8	.00	.08	.16	.04	.00	.00	.00

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Spring River near Waco, Missouri (fig. 4, no. 1; data collected from September 1964 to July 1986)--Continued									
Total phosphorus (mg/L)	165	1.3	0.02	0.21	0.52	0.26	0.17	0.12	0.06
Dissolved phosphorus (mg/L)	35	.60	.00	.12	.28	.13	.10	.06	.00
Total-recoverable cadmium (μg/L)	20	30	b	3.76e	9.00e	3.00e	2.50e	.96e	.32e
Dissolved cadmium (μg/L)	21	5	b	2.20e	4.00e	3.00e	2.00e	1.23e	.77e
Dissolved chromium (μg/L)	32	39	b	8.07e	23.44e	10.00e	5.70e	2.30e	.83e
Total-recoverable copper (μg/L)	20	13	b	5.34e	12.00e	6.00e	5.00e	3.26e	1.59e
Dissolved copper (μg/L)	50	160	b	14.00e	51.50e	11.52e	4.00e	1.86e	.32e
Total-recoverable iron (μg/L)	20	8,000	4	1,300	4,800	1,600	480	220	4
Dissolved iron (μg/L)	53	300	b	50.06e	110.00e	70.00e	49.00e	10.62e	6.25e
Total-recoverable lead (μg/L)	17	52	b	13.78e	43.00e	18.00e	10.00e	5.00e	1.62e
Dissolved lead (μg/L)	72	80	b	8.77e	34.50e	10.00e	4.00e	1.39e	.37e
Total-recoverable manganese (μg/L)	19	170	20	83	160	120	70	45	20
Dissolved manganese (μg/L)	95	430	0	46	120	50	30	20	0
Total-recoverable zinc (μg/L)	19	470	b	132.63e	435.00e	150.00e	70.00e	16.30e	5.00e
Dissolved zinc (μg/L)	82	2,400	0	90	330	70	30	20	0
Cow Creek near Weir, Kansas (fig. 4, no. 2; data collected from April 1976 to November 1982)									
Discharge (ft^3/s)	101	9,350	2.6	738	3,340	703	76	12	3.6
Specific conductance (μS/cm)	92	1,620	135	856	1,500	1,220	862	482	185
pH (standard units)	69	8.6	6.4	a	8.1	7.4	7.2	7.0	6.6
Temperature (°C)	82	30.0	0.0	14.3	27.0	20.0	14.0	8.5	0.8
Dissolved oxygen (mg/L)	46	12.8	1.0	6.4	9.8	8.2	6.2	4.8	2.2
Dissolved oxygen, percent saturation	--	--	--	--	--	--	--	--	--
Suspended solids (mg/L)	--	--	--	--	--	--	--	--	--
Fecal coliform (colonies per 100 mL)	--	--	--	--	--	--	--	--	--
Calcium (mg/L)	38	160	18	83	140	110	76	58	19
Magnesium (mg/L)	38	81	6.0	42	80	58	43	25	6.5

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Cow Creek near Weir, Kansas (fig. 4, no. 2; data collected from April 1976 to November 1982)--Continued									
Sodium (mg/L)	35	110	5.8	60	100	89	70	28	7.2
Potassium (mg/L)	35	14	3.1	7.5	13	9.5	7.0	5.0	3.3
Alkalinity (mg/L as $CaCO_3$)	38	189	14	79	160	100	70	49	20
Sulfate (mg/L)	40	720	70	380	680	540	390	220	91
Chloride (mg/L)	40	96	4.0	38	80	56	34	16	5.0
Fluoride (mg/L)	39	1.0	.20	.60	.90	.80	.70	.50	.20
Dissolved solids (ROE, mg/L)	3	728	687	c	c	c	c	c	c
Total nitrite plus nitrate (mg/L as N)	--	--	--	--	--	--	--	--	--
Total ammonia (mg/L as N)	32	13	.19	3.3	12	4.6	1.2	.43	.22
Dissolved ammonia (mg/L as N)	17	11	.28	3.2	11	3.6	1.7	.51	.28
Total phosphorus (mg/L)	31	7.6	.02	1.1	4.8	1.2	.46	.20	.04
Dissolved phosphorus (mg/L)	--	--	--	--	--	--	--	--	--
Total-recoverable cadmium (μg/L)	47	d	d	d	d	d	d	d	d
Dissolved cadmium (μg/L)	44	d	d	d	d	d	d	d	d
Dissolved chromium (μg/L)	48	d	d	d	d	d	d	d	d
Total-recoverable copper (μg/L)	49	40	b	12.17e	20.00e	14.41e	10.77e	8.63e	5.55e
Dissolved copper (μg/L)	48	20	b	10.68e	14.33e	11.89e	10.18e	9.15e	7.31e
Total-recoverable iron (μg/L)	49	16,000	360	3,200	10,000	4,300	1,600	820	400
Dissolved iron (μg/L)	48	1,300	b	138.68e	435.00e	170.00e	65.00e	20.00e	6.27e
Total-recoverable lead (μg/L)	44	320	b	35.30e	74.03e	39.38e	20.56e	17.42e	9.01e
Dissolved lead (μg/L)	30	80	b	14.46e	20.00e	20.00e	11.26e	7.33e	3.71e
Total-recoverable manganese (μg/L)	49	7,000	310	2,800	6,000	4,100	2,300	1,300	380
Dissolved manganese (μg/L)	48	7,000	220	2,700	6,000	4,400	2,400	1,000	260
Total-recoverable zinc (μg/L)	49	370	b	103.38e	280.00e	160.00e	80.00e	40.00e	13.35e
Dissolved zinc (μg/L)	48	170	b	40.33e	105.00e	60.00e	30.00e	14.97e	6.16e

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Brush Creek near Weir, Kansas (fig. 4, no. 3; data collected from April 1976 to March 1980)									
Discharge (ft^3/s)	38	153	0.12	16	100	8.0	1.9	0.55	0.12
Specific conductance (µS/cm)	38	1,650	525	1,080	1,540	1,300	1,070	775	612
pH (standard units)	36	6.9	3.1	a	6.9	6.2	3.9	3.4	3.2
Temperature (°C)	38	26.5	0.0	14.3	26.0	20.5	15.5	7.0	0.0
Dissolved oxygen (mg/L)	33	12.8	3.5	8.1	11.6	9.6	7.8	6.4	4.2
Dissolved oxygen, percent saturation	--	--	--	--	--	--	--	--	--
Suspended solids (mg/L)	--	--	--	--	--	--	--	--	--
Fecal coliform (colonies per 100 mL)	--	--	--	--	--	--	--	--	--
Calcium (mg/L)	34	170	52	100	140	120	110	80	53
Magnesium (mg/L)	34	68	20	46	66	54	45	33	24
Sodium (mg/L)	31	67	16	46	67	56	50	34	18
Potassium (mg/L)	31	10	3.8	6.0	8.6	7.0	6.0	5.0	3.9
Alkalinity (mg/L as $CaCO_3$)	35	42	b	9.06e	36.00e	8.00e	4.38e	1.92e	.45e
Sulfate (mg/L)	35	840	200	550	780	690	540	460	260
Chloride (mg/L)	34	16	8.0	11	15	13	11	10	8.0
Fluoride (mg/L)	34	.90	.20	.60	.80	.80	.60	.60	.20
Dissolved solids (ROE, mg/L)	3	838	510	c	c	c	c	c	c
Total nitrite plus nitrate (mg/L as N)	1	.07	f	f	f	f	f	f	f
Total ammonia (mg/L as N)	30	1.4	.18	.80	1.4	1.1	.80	.52	.20
Dissolved ammonia (mg/L as N)	16	1.6	.25	.81	1.4	.99	.78	.56	.25
Total phosphorus (mg/L)	27	.13	b	.04e	.12e	.04e	.02e	.01e	.002e
Dissolved phosphorus (mg/L)	--	--	--	--	--	--	--	--	--
Total-recoverable cadmium (µg/L)	32	d	d	d	d	d	d	d	d
Dissolved cadmium (µg/L)	31	d	d	d	d	d	d	d	d
Dissolved chromium (µg/L)	36	d	d	d	d	d	d	d	d

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Brush Creek near Weir, Kansas (fig. 4, no. 3; data collected from April 1976 to March 1980)--Continued									
Total-recoverable copper (µg/L)	36	d	d	d	d	d	d	d	d
Dissolved copper (µg/L)	36	d	d	d	d	d	d	d	d
Total-recoverable iron (µg/L)	35	14,000	890	4,100	12,000	4,400	3,500	1,600	900
Dissolved iron (µg/L)	36	14,000	10	3,000	9,600	3,900	2,600	530	65
Total-recoverable lead (µg/L)	30	120	b	30.22e	76.76e	36.47e	20.00e	14.82e	7.18e
Dissolved lead (µg/L)	25	98	b	15.36e	45.00e	20.00e	7.46e	3.43e	1.01e
Total-recoverable manganese (µg/L)	36	7,200	910	3,800	6,400	4,800	4,100	2,700	920
Dissolved manganese (µg/L)	36	7,300	900	3,800	6,400	4,800	4,000	2,700	900
Total-recoverable zinc (µg/L)	36	800	30	260	380	320	260	190	45
Dissolved zinc (µg/L)	35	820	20	260	400	320	250	180	25
Center Creek near Carterville, Missouri (fig. 4, no. 4; data collected from October 1962 to September 1987)									
Discharge (ft^3/s)	294	4,910	16	226	805	234	103	48	25
Specific conductance (µS/cm)	294	910	111	385	642	440	350	304	242
pH (standard units)	294	8.6	4.8	a	8.0	7.8	7.6	7.3	6.8
Temperature (°C)	294	29.5	0.0	15.4	26.5	21.5	16.0	9.0	3.5
Dissolved oxygen (mg/L)	278	15.0	3.8	8.4	12.4	10.0	8.0	6.4	5.0
Dissolved oxygen, percent saturation	272	149	38	80	104	90	80	69	57
Suspended solids (mg/L)	102	921	1	27	47	16	9	4	1
Fecal coliform (colonies per 100 mL)	191	29,000	1	800	2,500	280	110	36	4
Calcium (mg/L)	191	110	17	58	88	66	56	50	40
Magnesium (mg/L)	190	15	.70	3.7	8.2	4.0	3.1	2.5	2.0
Sodium (mg/L)	198	29	2.1	10	20	13	8.8	5.5	3.8
Potassium (mg/L)	192	4.6	.2	1.8	2.8	2.1	1.7	1.4	1.2
Alkalinity (mg/L as $CaCO_3$)	234	141	8	110	135	123	115	102	65
Sulfate (mg/L)	200	210	6.0	43	130	57	24	15	10
Chloride (mg/L)	200	28	2.3	9.6	18	11	8.4	6.8	4.6

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Center Creek near Carterville, Missouri (fig. 4, no. 4; data collected from October 1962 to September 1987)--Continued									
Fluoride (mg/L)	199	40	0.00	6.1	30	7.5	0.70	0.30	0.20
Dissolved solids (ROE, mg/L)	199	537	70	243	430	284	216	185	142
Total nitrite plus nitrate (mg/L as N)	134	30	.10	6.0	12	7.9	4.9	3.8	1.7
Total ammonia (mg/L as N)	157	22	.01	1.9	8.1	2.1	.61	.30	.04
Dissolved ammonia (mg/L as N)	56	8.5	.00	2.2	6.7	3.8	1.2	.65	.005
Total phosphorus (mg/L)	183	3.0	.02	.27	.97	.31	.13	.09	.05
Dissolved phosphorus (mg/L)	81	2.2	.00	.28	.81	.32	.16	.10	.06
Total-recoverable cadmium (µg/L)	38	55	b	2.67e	8.00e	2.00e	.44e	.12e	.02e
Dissolved cadmium (µg/L)	43	31	b	1.81e	2.50e	.44e	.08e	.01e	.00e
Dissolved chromium (µg/L)	75	60	b	11.32e	35.00e	11.98e	8.56e	5.00e	2.00e
Total-recoverable copper (µg/L)	38	14	b	5.84e	12.50e	8.00e	5.00e	3.23e	2.01e
Dissolved copper (µg/L)	109	270	b	21.92e	120.00e	20.00e	5.22e	2.23e	.53e
Total-recoverable iron (µg/L)	37	4,300	10	530	2,800	430	260	160	25
Dissolved iron (µg/L)	107	360	b	37.95e	130.00e	38.50e	20.00e	9.75e	3.64e
Total-recoverable lead (µg/L)	50	730	b	27.09e	84.00e	11.00e	4.00e	1.57e	.20e
Dissolved lead (µg/L)	149	390	b	12.22e	40.50e	8.00e	3.00e	.73e	.15e
Total-recoverable manganese (µg/L)	38	420	10	86	330	70	51	30	10
Dissolved manganese (µg/L)	190	1,200	0	160	680	200	60	24	0
Total-recoverable zinc (µg/L)	50	610	20	89	310	90	40	30	20
Dissolved zinc (µg/L)	164	2,500	0	180	540	200	53	30	11
Center Creek near Smithfield, Missouri (fig. 4, no. 5; data collected from September 1964 to September 1987)									
Discharge (ft^3/s)	309	7,540	18	313	960	293	122	65	34
Specific conductance (µS/cm)	337	868	123	423	596	481	405	360	286
pH (standard units)	172	8.6	6.6	a	8.2	8.0	7.8	7.6	7.4
Temperature (°C)	324	30.0	0.0	15.3	27.0	22.0	16.0	8.0	3.2
Dissolved oxygen (mg/L)	335	15.7	3.6	9.4	12.8	10.8	9.4	7.9	6.6

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Center Creek near Smithfield, Missouri (fig. 4, no. 5; data collected from September 1964 to September 1987)--Continued									
Dissolved oxygen, percent saturation	168	153	33	91	118	100	90	83	68
Suspended solids (mg/L)	121	328	1	16	40	14	7	4	1
Fecal coliform (colonies per 100 mL)	158	11,000	2	450	2,000	220	70	20	3
Calcium (mg/L)	251	120	24	73	99	81	72	63	50
Magnesium (mg/L)	251	11	1.1	3.6	6.0	4.2	3.3	2.8	1.8
Sodium (mg/L)	251	33	2.2	9.5	20	12	8.0	6.1	4.0
Potassium (mg/L)	250	5.2	.8	1.9	3.0	2.2	1.8	1.5	1.2
Alkalinity (mg/L as $CaCO_3$)	339	168	26	113	135	124	116	107	78
Sulfate (mg/L)	250	250	5.0	67	140	81	56	43	31
Chloride (mg/L)	175	26	3.3	10	18	12	9.4	7.5	5.0
Fluoride (mg/L)	123	21	.00	1.2	4.6	.80	.40	.30	.20
Dissolved solids (ROE, mg/L)	90	492	166	275	416	317	256	228	189
Total nitrite plus nitrate (mg/L as N)	236	22	.20	5.7	12	7.2	4.9	3.8	2.4
Total ammonia (mg/L as N)	223	9.6	b	.31e	1.20e	.22e	.10e	.03e	.005e
Dissolved ammonia (mg/L as N)	22	16	.00	2.1	8.2	2.0	.22	.02	.00
Total phosphorus (mg/L)	261	1.4	.01	.19	.50	.22	.15	.10	.06
Dissolved phosphorus (mg/L)	35	1.3	.04	.24	.58	.28	.19	.12	.06
Total-recoverable cadmium (µg/L)	52	92	b	5.85e	21.50e	4.00e	3.00e	1.23e	.49e
Dissolved cadmium (mg/L)	54	10	b	1.89e	4.50e	3.00e	1.19e	.71e	.29e
Dissolved chromium (µg/L)	30	30	b	7.31e	17.27e	10.00e	5.24e	3.21e	1.73e
Total-recoverable copper (µg/L)	51	21	b	6.14e	14.00e	7.00e	5.00e	3.77e	2.00e
Dissolved copper (µg/L)	83	190	b	11.84e	55.00e	6.50e	3.00e	1.10e	.29e
Total-recoverable iron (µg/L)	52	4,200	60	550	1,600	580	240	160	85
Dissolved iron (µg/L)	86	730	b	37.82e	80.00e	40.00e	20.00e	8.00e	2.64e
Total-recoverable lead (µg/L)	52	270	b	23.14e	61.00e	18.00e	9.00e	6.00e	1.12e

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Center Creek near Smithfield, Missouri (fig. 4, no. 5; data collected from September 1964 to September 1987)--Continued									
Dissolved lead (µg/L)	90	130	b	7.37e	25.00e	7.00e	2.77e	1.00e	0.28e
Total-recoverable manganese (µg/L)	50	800	20	89	160	110	60	44	25
Dissolved manganese (µg/L)	99	400	0	66	180	80	50	30	14
Total-recoverable zinc (µg/L)	51	1,400	50	500	1,000	600	430	320	100
Dissolved zinc (µg/L)	94	1,900	7	480	1,000	640	420	240	35
Turkey Creek near Joplin, Missouri (fig. 4, no. 6; data collected from August 1963 to July 1986)									
Discharge (ft^3/s)	330	955	3.0	42	104	52	30	18	6.9
Specific conductance (µS/cm)	360	1,190	226	611	805	678	620	540	413
pH (standard units)	193	8.5	6.7	a	8.0	7.6	7.5	7.4	7.2
Temperature (°C)	351	33.0	1.0	15.6	26.0	22.0	16.0	9.0	5.0
Dissolved oxygen (mg/L)	355	16.7	.3	5.8	10.1	7.8	5.6	3.8	1.6
Dissolved oxygen, percent saturation	191	134	11	56	97	68	55	41	23
Suspended solids (mg/L)	34	55	1	11	46	10	4	2	1
Fecal coliform (colonies per 100 mL)	115	1,000,000	2	22,000	69,000	9,200	1,600	110	10
Calcium (mg/L)	311	130	32	92	120	99	92	86	66
Magnesium (mg/L)	311	13	1.0	6.0	9.1	6.7	5.8	5.0	3.8
Sodium (mg/L)	311	65	4.7	27	50	36	25	17	11
Potassium (mg/L)	311	20	1.9	6.6	13	8.3	5.8	4.0	2.8
Alkalinity (mg/L as $CaCO_3$)	313	222	54	151	194	166	152	138	104
Sulfate (mg/L)	338	220	27	120	180	130	110	98	75
Chloride (mg/L)	260	110	4.4	29	52	36	27	19	12
Fluoride (mg/L)	183	4.0	.00	.40	.90	.50	.40	.30	.20
Dissolved solids (ROE, mg/L)	170	610	148	415	548	466	424	357	281
Total nitrite plus nitrate (mg/L as N)	148	7.8	.10	1.8	5.0	2.2	1.2	.76	.19
Total ammonia (mg/L as N)	163	13	.00	2.2	5.8	3.2	1.8	.76	.14
Dissolved ammonia (mg/L as N)	44	5.2	b	1.43e	3.75e	1.90e	.98e	.54e	.12e

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Turkey Creek near Joplin, Missouri (fig. 4, no. 6; data collected from August 1963 to July 1986)--Continued									
Total phosphorus (mg/L)	201	8.3	0.08	1.7	4.6	2.2	1.4	0.77	0.31
Dissolved phosphorus (mg/L)	70	6.6	.15	1.6	3.9	2.0	1.2	.73	.24
Total-recoverable cadmium (μg/L)	1	7	f	f	f	f	f	f	f
Dissolved cadmium (μg/L)	5	d	d	d	d	d	d	d	d
Dissolved chromium (μg/L)	70	130	b	9.66e	20.00e	10.00e	4.82e	2.02e	.76e
Total-recoverable copper (μg/L)	1	11	f	f	f	f	f	f	f
Dissolved copper (μg/L)	66	190	b	26.37e	100.00e	30.00e	13.22e	6.00e	1.67e
Total-recoverable iron (μg/L)	1	410	f	f	f	f	f	f	f
Dissolved iron (μg/L)	70	330	b	98.03e	265.00e	120.00e	80.00e	50.00e	16.40e
Total-recoverable lead (μg/L)	2	27	12	c	c	c	c	c	c
Dissolved lead (μg/L)	99	350	b	14.50e	50.00e	10.00e	5.00e	1.55e	.31e
Total-recoverable manganese (μg/L)	1	110	f	f	f	f	f	f	f
Dissolved manganese (μg/L)	144	540	b	154.05e	305.00e	210.00e	150.00e	80.00e	20.00e
Total-recoverable zinc (μg/L)	2	620	240	c	c	c	c	c	c
Dissolved zinc (μg/L)	112	1,300	0	440	940	640	360	200	95
Short Creek at Galena, Kansas (fig. 4, no. 7; data collected from April 1976 to March 1982)									
Discharge (ft^3/s)	14	800	0.98	70	440	15	3.8	1.9	0.98
Specific conductance (μS/cm)	13	1,570	180	927	1,540	1,360	740	400	180
pH (standard units)	13	7.2	5.0	a	7.1	6.7	6.2	5.1	5.0
Temperature (°C)	13	34.0	6.0	20.2	32.0	26.0	21.5	14.0	6.0
Dissolved oxygen (mg/L)	8	12.2	8.4	10.2	12.1	11.4	10.2	8.9	8.4
Dissolved oxygen, percent saturation	--	--	--	--	--	--	--	--	--
Suspended solids (mg/L)	--	--	--	--	--	--	--	--	--
Fecal coliform (colonies per 100 mL)	--	--	--	--	--	--	--	--	--
Calcium (mg/L)	12	260	17	140	250	240	120	72	17
Magnesium (mg/L)	12	81	1.3	21	76	20	11	6.8	1.3

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
Physical property or constituent	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Short Creek at Galena, Kansas (fig. 4, no. 7; data collected from April 1976 to March 1982)--Continued									
Sodium (mg/L)	11	27	3.0	17	26	23	19	10	3.0
Potassium (mg/L)	11	16	2.0	9.4	15	13	12	5.0	2.0
Alkalinity (mg/L as $CaCO_3$)	14	44	4	17	44	32	9	5	4
Sulfate (mg/L)	14	830	43	420	780	620	440	120	43
Chloride (mg/L)	14	32	4.0	19	31	27	20	11	4.0
Fluoride (mg/L)	8	6.0	.20	3.3	6.0	5.8	3.4	1.0	.20
Dissolved solids (ROE, mg/L)	1	251	f	f	f	f	f	f	f
Total nitrite plus nitrate (mg/L as N)	--	--	--	--	--	--	--	--	--
Total ammonia (mg/L as N)	9	34	b	16.69e	30.00e	25.00e	18.00e	7.20e	1.92e
Dissolved ammonia (mg/L as N)	3	21	.19	c	c	c	c	c	c
Total phosphorus (mg/L)	10	100	3.6	46	95	62	39	20	3.6
Dissolved copper (µg/L)	13	6,500	20	1,200	4,600	1,600	240	30	20
Total-recoverable iron (µg/L)	14	5,100	40	1,300	5,000	1,200	640	380	40
Dissolved iron (µg/L)	13	170	b	45.34e	160.00e	60.00e	20.00e	7.74e	2.18e
Total-recoverable lead (µg/L)	14	24,000	b	3,537.78e	21,500.00e	800.00e	124.59e	40.00e	5.69e
Dissolved lead (µg/L)	8	d	d	d	d	d	d	d	d
Total-recoverable manganese (µg/L)	14	4,900	620	2,400	4,200	3,500	2,600	1,100	620
Dissolved manganese (µg/L)	13	4,900	150	2,300	4,200	3,400	3,000	930	150
Total-recoverable zinc (µg/L)	14	200,000	6,900	87,000	200,000	150,000	56,000	22,000	6,900
Dissolved zinc (µg/L)	13	200,000	1,800	85,000	200,000	150,000	49,000	9,200	1,800
Shoal Creek near Galena, Kansas (fig. 4, no. 8; data collected from July 1967 to July 1986)									
Discharge (ft^3/s)	181	3,860	45	454	1,365	543	257	133	78
Specific conductance (µS/cm)	212	340	126	278	320	300	280	260	216
pH (standard units)	45	8.9	7.4	a	8.3	8.2	8.0	7.8	7.6
Temperature (°C)	202	30.0	0.0	15.6	27.0	23.0	16.0	9.0	2.2
Dissolved oxygen (mg/L)	210	14.0	1.1	9.6	13.0	10.9	9.4	8.1	6.6

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics: Number of samples	Maximum	Minimum	Mean	Percentage of samples in which values were less than or equal to those shown: 95	75	(Median) 50	25	5
Shoal Creek near Galena, Kansas (fig. 4, no. 8; data collected from July 1967 to July 1986)--Continued									
Dissolved oxygen, percent saturation	39	133	61	95	124	104	93	84	67
Suspended solids (mg/L)	--	--	--	--	--	--	--	--	--
Fecal coliform (colonies per 100 mL)	32	29,000	1	1,100	1,740	210	38	14	2
Calcium (mg/L)	211	63	22	49	56	53	50	46	38
Magnesium (mg/L)	211	40	.9	3.1	4.6	3.5	3.0	2.3	1.4
Sodium (mg/L)	211	10	1.8	5.6	8.1	6.6	5.5	4.5	3.4
Potassium (mg/L)	211	6.4	.9	1.8	2.6	2.0	1.7	1.4	1.1
Alkalinity (mg/L as $CaCO_3$)	211	174	45	119	140	131	122	110	86
Sulfate (mg/L)	211	50	b	11.28e	18.00e	13.00e	10.00e	8.90e	6.76e
Chloride (mg/L)	135	15	2.1	8.7	13	11	8.8	6.5	4.4
Fluoride (mg/L)	81	.4	b	.12e	.20e	.10e	.10e	.10e	.05e
Dissolved solids (ROE, mg/L)	39	200	119	164	188	178	164	150	127
Total nitrite plus nitrate (mg/L as N)	116	3.0	.10	1.7	2.5	2.0	1.7	1.5	.80
Total ammonia (mg/L) as N	112	.27	b	.05e	.14e	.07e	.03e	.01e	.004e
Dissolved ammonia (mg/L as N)	23	.12	b	.02e	.10e	.02e	.004e	.001e	.000e
Dissolved phosphorus (mg/L)	1	5.0	f	f	f	f	f	f	f
Total-recoverable cadmium (μg/L)	14	930	30	490	920	800	380	230	30
Dissolved cadmium (μg/L)	12	900	b	426.81e	875.00e	800.00e	280.00e	95.00e	31.77e
Dissolved chromium (μg/L)	13	d	d	d	d	d	d	d	d
Total-recoverable copper (μg/L)	14	6,700	60	1,400	4,800	1,700	960	480	60
Total phosphorus (mg/L)	146	2.2	.01	.17	.40	.18	.13	.08	.06
Dissolved phosphorus (mg/L)	35	.44	.05	.15	.32	.18	.14	.09	.05
Total-recoverable cadmium (μg/L)	5	d	d	d	d	d	d	d	d
Dissolved cadmium (μg/L)	3	d	d	d	d	d	d	d	d
Dissolved chromium (μg/L)	6	d	d	d	d	d	d	d	d

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Shoal Creek near Galena, Kansas (fig. 4, no. 8; data collected from July 1967 to July 1986)--Continued									
Total-recoverable copper (μg/L)	7	d	d	d	d	d	d	d	d
Dissolved copper (μg/L)	6	d	d	d	d	d	d	d	d
Total-recoverable iron (μg/L)	7	240	90	160	220	180	160	130	90
Dissolved iron (μg/L)	41	70	b	23.90e	55.00e	30.00e	20.00e	10.00e	6.13e
Total-recoverable lead (μg/L)	4	d	d	d	d	d	d	d	d
Dissolved lead (μg/L)	2	d	d	d	d	d	d	d	d
Total-recoverable manganese (μg/L)	11	60	b	27.74e	50.00e	30.00e	30.00e	20.00e	11.34e
Dissolved manganese (μg/L)	41	100	b	20.06e	50.00e	30.00e	10.00e	5.77e	2.09e
Total-recoverable zinc (μg/L)	7	300	60	110	200	90	80	75	60
Dissolved zinc (μg/L)	6	110	40	53	80	50	40	40	40
Spring River near Baxter Springs, Kansas (fig. 4, no. 9; data collected from October 1961 to July 1986)									
Discharge (ft^3/s)	283	29,400	69	1,950	6,500	1,790	806	358	180
Specific conductance (μS/cm)	353	610	120	372	516	430	360	320	230
pH (standard units)	200	8.5	6.6	a	8.0	7.7	7.5	7.4	7.1
Temperature (°C)	308	32.5	0.0	16.4	29.2	24.0	16.0	8.5	3.0
Dissolved oxygen (mg/L)	243	14.3	4.2	8.9	12.5	10.4	8.6	7.3	6.0
Dissolved oxygen, percent saturation	39	131	57	86	113	90	84	78	64
Suspended solids (mg/L)	35	227	3	40	154	43	22	16	6
Fecal coliform (colonies per 100 mL)	52	11,000	1	780	2,600	460	180	73	4
Calcium (mg/L)	318	83	13	57	74	65	59	50	32
Magnesium (mg/L)	320	17	1.7	5.8	10	7.0	5.2	4.1	2.9
Sodium (mg/L)	319	27	3.1	10	20	12	9.6	7.5	5.0
Potassium (mg/L)	317	6.0	1.1	2.7	4.2	3.1	2.6	2.1	1.6
Alkalinity (mg/L as $CaCO_3$)	350	164	24	103	133	118	108	90	58
Sulfate (mg/L)	350	170	17	60	110	72	54	41	29
Chloride (mg/L)	289	48	3.7	12	21	14	11	9.0	5.5

Table 7.--*Summary statistics of selected physical properties and constituents for long-term monitoring and ancillary stations in the Spring River basin*--Continued

Physical property or constituent	Descriptive statistics				Percentage of samples in which values were less than or equal to those shown				
	Number of samples	Maximum	Minimum	Mean	95	75	(Median) 50	25	5
Spring River near Baxter Springs, Kansas (fig. 4, no. 9; data collected from October 1961 to July 1986)									
Fluoride (mg/L)	190	5.2	0.00	0.80	3.4	0.90	0.50	0.30	0.10
Dissolved solids (ROE, mg/L)	161	400	86	246	343	279	245	202	168
Total nitrite plus nitrate (mg/L as N)	116	8.9	.10	2.6	4.8	2.9	2.4	2.0	1.3
Total ammonia (mg/L as N)	112	2.2	b	.23e	.59e	.25e	.14e	.08e	.02e
Dissolved ammonia (mg/L as N)	25	1.7	.00	.48	1.6	.62	.23	.10	.01
Total phosphorus (mg/L)	192	1.3	.01	.37	.90	.52	.26	.18	.10
Dissolved phosphorus (mg/L)	34	.98	.01	.33	.70	.50	.28	.18	.02
Total-recoverable cadmium (µg/L)	3	d	d	d	d	d	d	d	d
Dissolved cadmium (µg/L)	6	d	d	d	d	d	d	d	d
Dissolved chromium (µg/L)	3	d	d	d	d	d	d	d	d
Total-recoverable copper (µg/L)	3	d	d	d	d	d	d	d	d
Dissolved copper (µg/L)	5	d	d	d	d	d	d	d	d
Total-recoverable iron (µg/L)	15	660	10	180	620	160	70	55	10
Dissolved iron (µg/L)	73	1,600	0	76	150	70	50	20	0
Total-recoverable lead (µg/L)	2	d	d	d	d	d	d	d	d
Dissolved lead (µg/L)	5	d	d	d	d	d	d	d	d
Total-recoverable manganese (µg/L)	23	260	0	130	240	220	150	40	0
Dissolved manganese (µg/L)	67	530	0	140	280	200	150	95	0
Total-recoverable zinc (µg/L)	3	350	200	c	c	c	c	c	c
Dissolved zinc (µg/L)	6	610	80	310	530	450	310	90	80

[a] Mean pH will not satisfactorily summarize the typical hydrogen ion concentration if pH is not normally distributed.

[b] The minimum of censored properties is an estimated value and is not reported.

[c] If the total number of observations is greater than 1 and less than or equal to 5, only the maximum and minimum are reported.

[d] If the number of observations above the detection limit is less than 5, the estimated values are considered unreliable and are not reported.

[f] If the number of observations is equal to 1, only the maximum is reported.