

# Geochemistry of Natural Waters of the Blue Grass Region, Kentucky

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GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1700

*Prepared in cooperation with the Department of Economic Development of Kentucky and the Kentucky Geological Survey*



**UNITED STATES DEPARTMENT OF THE INTERIOR**

**STEWART L. UDALL, *Secretary***

**GEOLOGICAL SURVEY**

**Thomas B. Nolan, *Director***

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# GEOCHEMISTRY OF NATURAL WATERS OF THE BLUE GRASS REGION, KENTUCKY

By G. E. HENDRICKSON and R. A. KRIEGER

## ABSTRACT

The Blue Grass region includes most of the outcrop area of rocks of Ordovician, Silurian, and Devonian ages in the north-central part of Kentucky. The region is generally of moderate relief and was developed by erosion of beds that lie nearly flat and that are composed chiefly of limestone and shale. Most of the region is drained by the Kentucky and Licking Rivers which rise in the Eastern Coal Field and flow northwestward through the Blue Grass region to discharge into the Ohio River. The Salt River and other minor streams originating within the Blue Grass drain the remainder of the region.

The dissolved substances contained in natural waters are derived from all materials with which the water comes in contact, including the atmosphere, vegetation, soil, and rock. Rainwater in the Blue Grass region contains small amounts of dissolved materials, generally less than 20 ppm (parts per million). As it percolates through the soil, rainwater dissolves additional materials, probably about 100–200 ppm. The water percolating through the soil to the underlying rocks dissolves carbon dioxide from the soil air, and the dissolved carbon dioxide increases the rate of solution of the calcareous material in the rocks. Inasmuch as the unfractured limestone of the Blue Grass is nearly impermeable, the water enters the rocks through fractures, chiefly vertical joints, and enlarges these fractures by solution. The most vigorous solution is at the base of the soil where the water contains large amounts of dissolved carbon dioxide. As the water moves downward, the carbon dioxide is used up, solution becomes less vigorous, and the size of solution openings diminishes until, generally at depths of 100 feet or less, solution enlargement of fractures cannot be detected. Although the most obvious source of dissolved solids in ground water of the Blue Grass region is the calcareous material dissolved from the rocks, other materials in the rocks and soils, especially the clay minerals and the metallic sulfides, are dissolved by or react with the percolating waters to modify the chemical character of the water. The water moving through the solution openings at shallow depths discharges to springs and streams, generally within a few miles of the point of entrance. This water is generally of the calcium magnesium bicarbonate type and contains 200–400 ppm dissolved solids.

At greater depths, circulation of the ground water is slower, and the waters are more highly mineralized. At depths greater than 50–200 feet below local stream level, all ground water is of the sodium chloride type and too highly mineralized for domestic use. The depth to saline waters is largely dependent upon the amount of shale in the bedrock, for the shale restricts the zone of relatively rapid circulation to shallow depths. Saline waters in the Blue Grass region contain as much as 195,000 ppm dissolved solids. The origin of the saline waters of the Blue Grass region is still a subject of speculation; however, the saline waters probably are modified connate marine waters.

Surface water in the Blue Grass region is composed of surface- and ground-water runoff, and the relative amounts of the two components are constantly changing owing chiefly to changes in the rates of precipitation and evapotranspiration. In the winter and early spring, the soil is relatively saturated with water, and heavy rains run off rapidly over the surface to cause flood discharges in the streams. Relatively little of this flood discharge is derived from ground water. In late summer and early fall, vegetation has reduced the amount of moisture held in the soil so that most of the rainfall is absorbed by the soil and relatively little reaches the streams as surface runoff. Most of the discharge to streams, during this period, is derived from ground water.

Because surface runoff is in contact with earth materials a relatively short time, the water discharged during flood stages is relatively low in concentration of dissolved solids. In late summer and early fall, when stream discharge is low and ground water makes up a large part of the discharge, the concentration of dissolved solids generally is relatively high. The relation between discharge and dissolved solids is not a simple one, however, and is affected by other factors such as rising and falling stages, season of year, and length of time between stream rises.

Although the concentration of dissolved solids generally decreases with increased stream discharge, the decrease in concentration is very small in proportion to the increase in stream discharge. Consequently, the quantity of dissolved material carried away by streams is much greater during floods than at low flows.

The water in streams originating in the Blue Grass region invariably is of the calcium magnesium bicarbonate type and similar in most respects to the shallow ground water in the region. Dissolved solids generally range from 100 to 250 ppm. Water in the two large streams originating in the Eastern Coal Field generally enters the Blue Grass region containing relatively large amounts of sulfate in proportion to bicarbonate. The high sulfate content presumably is due in part to acid mine waters entering the streams. As the streams flow through the Blue Grass region, the proportion of sulfate decreases as the typical bicarbonate waters of the Blue Grass region make up larger parts of the total flow.

## INTRODUCTION

This report describes changes in the chemical character of water in the Blue Grass region as it falls to the ground as rain or snow, runs off on the surface into streams, and percolates underground through soils and rocks. The information presented should be useful to all users of water in the Blue Grass region and should be of interest to anyone concerned with the geochemistry of water in limestone terranes.

This report is the result of a joint investigation by the Ground Water and Quality of Water Branches of the U.S. Geological Survey. Water-resources investigations in Kentucky now are made by the U.S. Geological Survey in cooperation with the Kentucky Geological Survey, but at the time this investigation was begun the Department of Economic Development was the cooperating State agency. The Kentucky Geological Survey's interests in the cooperative investigations are represented by Dr. W. W. Hagan, State Geologist and Director of the Kentucky Geological Survey.

### LOCATION AND EXTENT OF AREA

As defined in this report, the Blue Grass region includes the entire outcrop area of rocks of Ordovician, Silurian, and Devonian age in Kentucky except for a few isolated outcrops along the Green, Barren, and Cumberland Rivers in the Mississippian Plateau region. It also includes small areas of outcrop of Mississippian and Pennsylvanian rocks. Thus, it includes the physiographic subdivisions McFarlan termed Inner Blue Grass, Eden shale belt, Outer Blue Grass, and most of the area called the Knobs (McFarlan, 1943, p. 167-174). The location and boundaries of the area are shown on the map, plate 1. The area includes all of 43 counties except the alluvial terraces along the Ohio River. The total area is about 11,000 square miles.

### PREVIOUS INVESTIGATIONS

This is the first comprehensive study of the geochemistry of the natural waters in the Blue Grass region, although several previous reports on the geology and ground-water resources of the State present information on the chemical character of ground water and the chemical composition of the rocks in the region. Matson (1909) described the ground-water resources of this region. That report also included a chapter on chemical character of the waters by Chase Palmer. The chemical character of public and industrial water supplies of the region is described in a report by Palmquist and Hall (1953). Several reports of the Kentucky Geological Survey include chemical analyses of rocks and of waters in the area. A series of reconnaissance reports by Palmquist and Hall (1960 a-f) include brief descriptions of the chemical character of ground water in the rock formations of the region.

### ACKNOWLEDGMENTS

Appreciation is expressed for the cooperation of local residents, well drillers, and owners and operators of public and industrial water supplies who furnished information about their wells and springs and permitted the collection of water samples. The section on soil chemistry was reviewed by Dr. H. H. Bailey of the College of Agriculture, University of Kentucky, and by Mr. J. H. Havens of the Kentucky Department of Highways. Mr. Havens also furnished most of the data on clay minerals described in this report. The parts of the report on clay minerals were reviewed by Dr. R. E. Grim of the University of Illinois, and the discussion of rock weathering was reviewed by Dr. W. D. Keller of the University of Missouri. The authors are grateful for the generous assistance and helpful suggestions of all reviewers. The text of the report has been revised since these early reviews.

### METHODS OF INVESTIGATION AND PRESENTATION OF DATA

This report is based on the interpretation of data obtained from various sources. Most of the data on chemical character of ground and surface water is from samples collected and analyzed by the U.S. Geological Survey personnel for other investigations; a few water samples were collected and analyzed especially for this study. Data on the chemical character of rocks were obtained from publications of the Kentucky Geological Survey, unpublished records of the Kentucky Highway Department, and from rock analyses made especially for this study by the U.S. Geological Survey. Data on the chemical character of the soils are from published and unpublished records of the Kentucky Agricultural Experiment Station and the U.S. Department of Agriculture.

Selected data are presented in both tabular and graphic form. The tables of chemical analyses include analyses made by the Geological Survey of water from wells and springs in the area and some selected analyses of surface water. Representative analyses of rocks, made by the Kentucky Geological Survey and of soils made by the U.S. Department of Agriculture, are also included. Chemical analyses of water are illustrated by means of diamond-field diagrams and bar diagrams. Maps of the area illustrate the general geology, the correlation of chemical character of water with geologic units, and changes in the chemical character of surface water as it moves downstream.

Chemical analyses of waters are reported in tables in parts per million (ppm) by weight. Relations and ratios of dissolved constituents presented in the illustrations are also expressed in parts per million by weight. Bar diagrams (pls. 4, 6) and diamond-field diagrams (figs. 12, 13, 14) are based on equivalents per million (epm) because these diagrams cannot be conveniently drawn on other units. Equivalents per million is an expression of concentration in terms of the combining or reacting capacity of the ions. It is the number of unit equivalent weights of an ion contained in 1 million unit weights of water.

Chemical analyses of soils are reported in percentage by weight as in the original sources. Chemical analyses of rocks have been converted to parts per million by weight for the purpose of comparison with analyses of ground-water samples.

### WELL-NUMBERING SYSTEM

Wells, springs, and borings are numbered in the system used by the Ground Water Branch in Kentucky. The State is divided into rectangles by a grid of 5-minute meridians of longitude and 5-minute parallels of latitude. Each rectangle is numbered from its longitude

and latitude at its southeast corner. Within each 5-minute rectangle the wells are numbered in the order in which they were inventoried. Thus, well 8505-3810-1 is the first well inventoried in the 5-minute rectangle bounded on the east by long  $85^{\circ}05'$  W. and on the south by lat  $38^{\circ}10'$  N. (See fig. 1.)

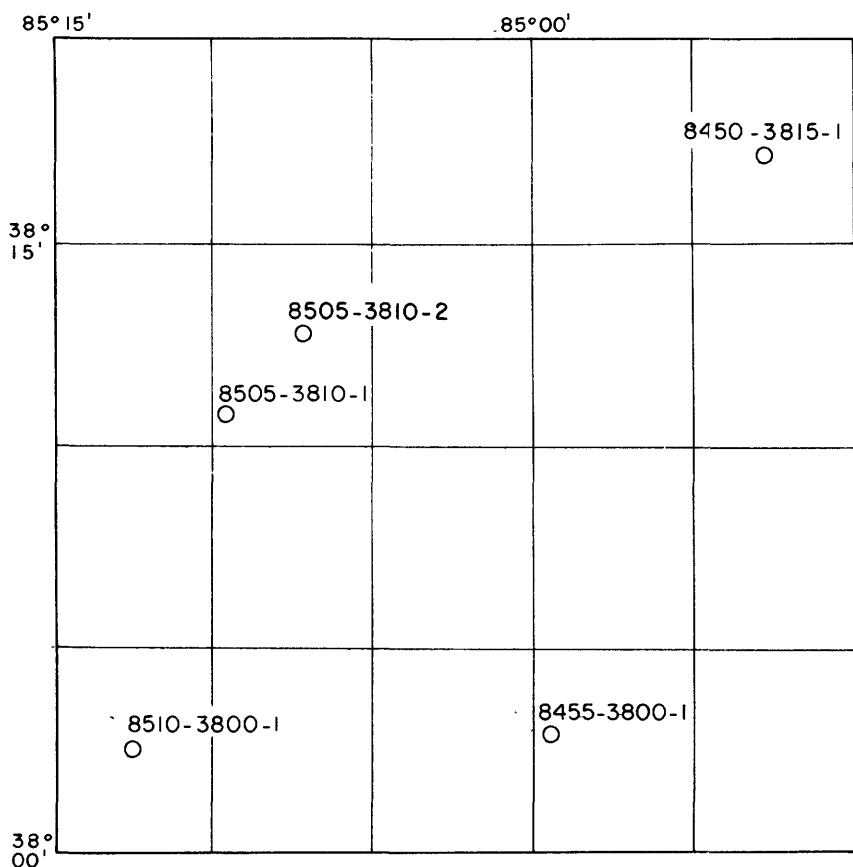


FIGURE 1.—Diagram illustrating well-numbering system.

The only variation in this well-numbering system is in Jefferson County, which includes the city of Louisville, where the density of wells makes it necessary to subdivide each 5-minute rectangle into twenty-five 1-minute rectangles. With the exception of a small area at the extreme southwestern tip, the entire county lies between long  $85^{\circ}$  and  $86^{\circ}$  W. and lat  $38^{\circ}$  and  $39^{\circ}$  N. Therefore, the 1-minute rectangles can be designated by minutes only. Thus, well number 48-13-2 is the second well inventoried in the 1-minute rectangle bounded on the east by long  $85^{\circ}48'$  W. and on the south by lat



38°13' N. Where a 1-minute rectangle overlaps the boundary between Jefferson and an adjacent county, the 1-minute numbering system is used in Jefferson County and the 5-minute system is used in the adjacent county. This is the only area where the wells in a given quadrangle are not numbered consecutively without regard to county lines.

### PHYSIOGRAPHY

The Blue Grass region proper consists of the Inner Blue Grass, the Eden shale belt, and the Outer Blue Grass; however, for the purpose of this report, it is defined to include also the Knobs region of McFarlan (1943, p. 167-174). Plate 2 is a map of the Blue Grass region showing the physiographic subdivisions. The boundaries of the subdivisions are simplified in this map to show the general relations. More detailed boundaries of the areas are shown on plate 6. As used in this report the Blue Grass region includes roughly the same area as Penneman and Johnson's (1946) Lexington Plain section of the Interior Low Plateaus physiographic province. The Blue Grass region is, for the most part, an area of rolling uplands ranging in altitude from less than 800 feet in the northwest to about a thousand feet in the southeast. The major streams, such as the Kentucky and Licking Rivers, are entrenched to depths of 200-500 feet in the rolling uplands.

The Inner Blue Grass, as described in this report, includes almost all of the area of outcrop of Ordovician rocks, chiefly limestone, of the High Bridge group, Lexington group, and Cynthiana formation except for narrow exposures of these units that extend north along the Kentucky and Licking Rivers. It is surrounded by the Eden shale belt. As defined, it includes an area of about 800 square miles.

The limestone of the High Bridge group, Lexington group, and parts of the Cynthiana formation generally are less shaly and more soluble than the overlying rocks; therefore, solution features are better developed in the Inner Blue Grass than in other parts of the Blue Grass region. Sinkholes, caverns, and sinking streams are fairly common. Most of the sinkholes are less than 1,000 feet in diameter and 20-30 feet deep. All the explored caves are small, and most sinking streams drain only a few square miles. There are several large springs in the region. The Inner Blue Grass typically is gently rolling except in areas where shaly limestone crops out and in the vicinity of large streams, especially the Kentucky and Licking Rivers. In shaly areas and near large streams, the hill slopes are steep and the ridges are narrow. The ridges broaden away from the river, and at distances of more than a mile the effect of dissection by the major rivers is hardly noticeable, and the gently rolling topography prevails.

The Eden shale belt includes the following: nearly all of the outcrop area of the Eden group, in the valleys some of the area of outcrop

of the Cynthiana formation, and, on the ridgetops, some of the area of outcrop of the Maysville group. The shale belt surrounds the Inner Blue Grass and separates it from the Outer Blue Grass. It is irregular in outline and ranges in width from about 5 to 30 miles. It is wider on the northwest and west than on the southeast and east. In contrast to the rolling plains of the Inner and Outer Blue Grass, the Eden shale belt is characterized by steep-sided hills and narrow valleys and ridgetops. Drainage lines are closely spaced, valley walls are steep, and flat or rolling interstream areas are rare. The boundaries of the Eden shale belt may be recognized easily in the field and are conspicuous on the new, 1:24,000-scale topographic quadrangles of the Geological Survey. Sinkholes and subsurface drainage are rare in this area. Runoff from the shale is rapid, and the smaller streams generally cease flowing in dry weather. Springs are small, and most of these also cease flowing in dry weather.

The Outer Blue Grass includes most of the area of outcrop of the limestone and shale of the Maysville and Richmond groups of Ordovician age, limestone and shale of Silurian age, and limestone of Devonian age. The Outer Blue Grass forms an irregular belt around the outside of the Eden shale belt. It is bordered on the east, west, and south by the Knobs region and on the north by the terraces of the Ohio River. It ranges in width from about 5 to 30 miles and generally is wider on the west and north than on the east and south. Like the Inner Blue Grass, the Outer Blue Grass typically is an area of gently rolling hills. Because there is a greater amount of shaly limestone in the underlying rocks, the areas of more rugged topography are of greater extent and are better developed in the Outer Blue Grass than in the Inner Blue Grass. The shaly limestone restricts the circulation of ground water, and consequently, sinkholes and underground streams are not well developed in the Outer Blue Grass. As in the Inner Blue Grass, the local relief is greater in the vicinity of the major streams, especially the Kentucky, Licking, and Ohio Rivers. Springs are numerous in the Outer Blue Grass, but the discharge of the springs generally is smaller than the discharge of springs in the Inner Blue Grass. Many of the springs go dry in dry weather.

The Knobs is a narrow belt of hills, generally less than 10 miles wide, around the east, south, and west of the Outer Blue Grass. It is transitional on the east with the Eastern Coal Field region and on the south and west with the Mississippian Plateau region. The rocks underlying the Knobs are chiefly shale but include some sandstone and limestone. On the west the Knobs, as defined in this report, is underlain by rocks of Devonian and Mississippian age; on the east it is underlain by rocks ranging from Late Ordovician to Pennsylvanian in age. Typically the topography is conical hills separated by broad,

relatively flat stream valleys. The conical hills generally are capped by resistant sandstone and limestone; the hill slopes and broad valleys are underlain by easily eroded shale. Runoff generally is rapid. Springs are small, and most go dry in dry weather.

A typical land-surface profile across the Knobs would show a transition from the rolling hills of the Outer Blue Grass, through the typical Knobs topography of conical hills with broad, flat lowlands, to the high plateaus developed on Mississippian limestone to the west and south and Pennsylvanian sandstone to the east.

### DRAINAGE

All the streams in the Blue Grass region drain to the Ohio River. The headwaters of the Licking River are in the Pennsylvanian rocks of the mountains of eastern Kentucky. From there, the Licking flows across a narrow belt of Mississippian, Devonian, and Silurian rocks and drains a large area of Ordovician rocks in the eastern part of the Blue Grass region (pl. 3). It joins the Ohio River at Covington. The drainage basin of the Licking includes a moderate area of the Eastern Coal Field, a small area of the Knobs, a large area of the Outer Blue Grass and Eden shale belt, and a small area of the Inner Blue Grass (pl. 6).

The headwaters of the Kentucky River also are in the Pennsylvanian rocks of the mountains of eastern Kentucky. From the mountains the Kentucky crosses a belt of Mississippian, Devonian, and Silurian rocks and drains a large area of Ordovician rocks in the central part of the Blue Grass region (pl. 3). It joins the Ohio River at Carrollton. The drainage basin of the Kentucky includes a large area of the Eastern Coal Field, a small area of the Knobs, a large area of the Outer Blue Grass and the Eden shale belt, and most of the area of the Inner Blue Grass (pl. 6).

The Salt River heads in Ordovician rocks in the western part of the Blue Grass region. The Salt flows westward out of the area of Ordovician rocks, crosses a belt of Silurian, Devonian, and Mississippian rocks and enters the Ohio River south of Louisville (pl. 3). The drainage basin of the Salt includes a fairly large area of the Eden shale belt and Outer Blue Grass, a small area of the Knobs, and a small area of the Mississippian Plateau.

The remainder of the Blue Grass region is drained by minor tributaries of the Ohio River.

### GENERAL GEOLOGY

Rocks exposed in the Blue Grass region range in age from Ordovician to Pennsylvanian. Rocks of Pennsylvanian age, however, crop out only in small areas on hilltops at the eastern edge of the

Knobs, and they are not described in this report. The alluvial deposits along the Ohio River have been excluded from this discussion because they form a well-defined unit that will be described in another report. The alluvial deposits along other streams in the region are described under the heading "Soils and mantle materials." The areas of outcrop of the geologic units are shown on the geologic map (pl. 3).

### STRUCTURE

The major structural feature of the Blue Grass region is the Cincinnati arch, whose axis extends from central Tennessee, northeastward to the central part of the Blue Grass region. Here it splits, one branch extending northwestward through Boone County and one extending northward through Pendleton County (pl. 3). The axis of the arch is not horizontal but rises and plunges to form two domes, the Jessamine dome and the Nashville dome, which are separated by a broad saddle. The center of the Jessamine dome is in Jessamine County in the heart of the Inner Blue Grass. The center of the Nashville dome is in Tennessee, and the trough of the saddle is in Cumberland County, Ky., about 50 miles south of the Blue Grass region. The rocks dip generally outward from the Jessamine dome. The regional dip ranges from 10 to 40 feet per mile and is generally steeper to the east and west than to the north and south. Superimposed on the regional dip are numerous minor flexures, which are relatively inconspicuous because the dip of the rocks is generally less than 100 feet per mile.

The major fault systems of the Blue Grass region are the Kentucky River fault zone and the West Hickman fault zone, which for the most part are more or less parallel to the axis of the Cincinnati arch in the east-central part of the region. There are many minor displacements in the region. In most of the region the rocks are fractured by two major sets of approximately vertical joints, one roughly parallel to the direction of the regional dip and one approximately at right angles to it. Straight reaches of the streams, generally parallel to one of the joint systems, probably are due to solution along the joints.

### SUMMARY OF STRATIGRAPHY

More than 90 percent of the Blue Grass area is underlain by rocks of Ordovician age. The oldest exposed rock, of the High Bridge group, is chiefly massive limestone that contains very little shale. Disconformably overlying the High Bridge is the Lexington group, which consists chiefly of limestone but contains moderate amounts of shale. The Cynthiana formation overlies the Lexington with little or no disconformity and is similar to the Lexington except that it contains more shale. The Eden group contains more shale than the Cynthiana and

in places may consist of more than 90 percent shale. Thus, the proportion of shale increases upward from rocks of the High Bridge group through the Eden group. The Maysville group consists of limestone and shale in approximately equal amounts. The Richmond group, which overlies the Maysville, is predominantly shale and shaly limestone, but the proportion of shale in the Richmond is not as great as in the Eden.

Rocks of Silurian age rest unconformably on Ordovician rocks on the flanks of the Jessamine dome in the western, southern, and eastern parts of the Blue Grass region. On the west side of the dome, the Silurian rocks consist chiefly of limestone and some shale. On the east side of the dome, shale predominates in the Silurian and only minor amounts of limestone are present.

Rocks of Devonian age rest unconformably on rocks of Silurian and Ordovician age on the western, southern, and eastern flanks of the region. On both sides of the Jessamine dome, the Devonian consists of a lower limestone unit overlain by a thick unit of black shale.

Rocks of Mississippian age that cap the Knobs around the outer edge of the Blue Grass region except on the north consist chiefly of shale, siltstone, and sandstone but include some limestone.

Rocks of Pennsylvanian age also cap some of the Knobs on the east side of the region, but they are of little hydrologic importance in the region.

### GENERAL HYDROLOGY

All natural waters of present economic importance in the Blue Grass region are derived from rain or snow. The two largest streams of the region, the Kentucky and Licking Rivers, have their headwaters in the Pennsylvanian rocks of the Eastern Coal Field. Except for these two streams, nearly all potable waters in the Blue Grass region are derived from precipitation within the region. Water in some of the deeper aquifers may have entered the rocks at considerable distances beyond the region, or it may be modified connate water, but the water in the deeper rocks generally is highly saline and is not used at the present time.

### HYDROLOGIC CYCLE

Part of the rain falling on the ground soaks into the soil, and when the rain falls faster than it can soak in, or when the soil already is saturated, part of it runs overland into streams or ponds. Part of the water entering the soil evaporates, part is held by capillary forces until used by plants (transpired), and part seeps downward to be added to the ground-water body in the zone of saturation. In the zone of saturation, water moves slowly to discharge at points of lower elevation.

The speed of ground-water movement is controlled chiefly by the hydraulic gradient from the point of recharge to the point of discharge and by the size and nature of the openings through which it moves. In the Blue Grass region, water moves very slowly through the intergranular openings in shale and sandstone, more rapidly through fractures in limestone and sandstone, and most rapidly through fractures in limestone which have been enlarged by solution. Generally, openings enlarged by solution are restricted to a shallow depth zone not more than 100 feet below the local drainage level. Where limestone is interbedded with shale, solution channels may be restricted to even shallower zones, in places only a few feet below the local drainage. Thus, the speed of ground-water flow in the Blue Grass region generally decreases with increasing depth and with increasing amounts of shale interbedded with the limestone.

Eventually, the ground water discharges as springs or into surface-water bodies or is discharged by evaporation and transpiration. Seepage and spring flow are the sources of streamflow during dry periods. When streams cease flowing in dry weather it may be assumed that some ground water moves through the streambed deposits below the surface, but probably most ground-water discharge at these times is by evapotranspiration. Most water entering the streams eventually flows to the sea, but some of it is evaporated, some is used by plants along the streams, and during high stages some may recharge the ground-water body. The hydrologic cycle is complex and in any specific area is controlled by many factors such as climate, the nature of the earth materials, the topography, and the vegetation. Figure 2 is a generalized diagram illustrating the hydrologic cycle in the Blue Grass region.

If we assume no subsurface inflow or outflow to or from the region and no change in the amount of water stored underground (including ground water and soil moisture), the amount of stream runoff plus the amount of water lost by evaporation and transpiration will equal the amount of precipitation in a given area. In the Blue Grass region, which is bordered by shale and shaly limestone, the amount of subsurface inflow and outflow is extremely small. Changes in storage over a period of several years tend to cancel out. The average annual runoff from several small drainage basins in the Blue Grass region over a period of record of 17-18 years was about 15 inches. The average annual precipitation in the region is about 43 inches. Therefore, the average annual loss of water by evaporation and transpiration is estimated at about 28 inches.

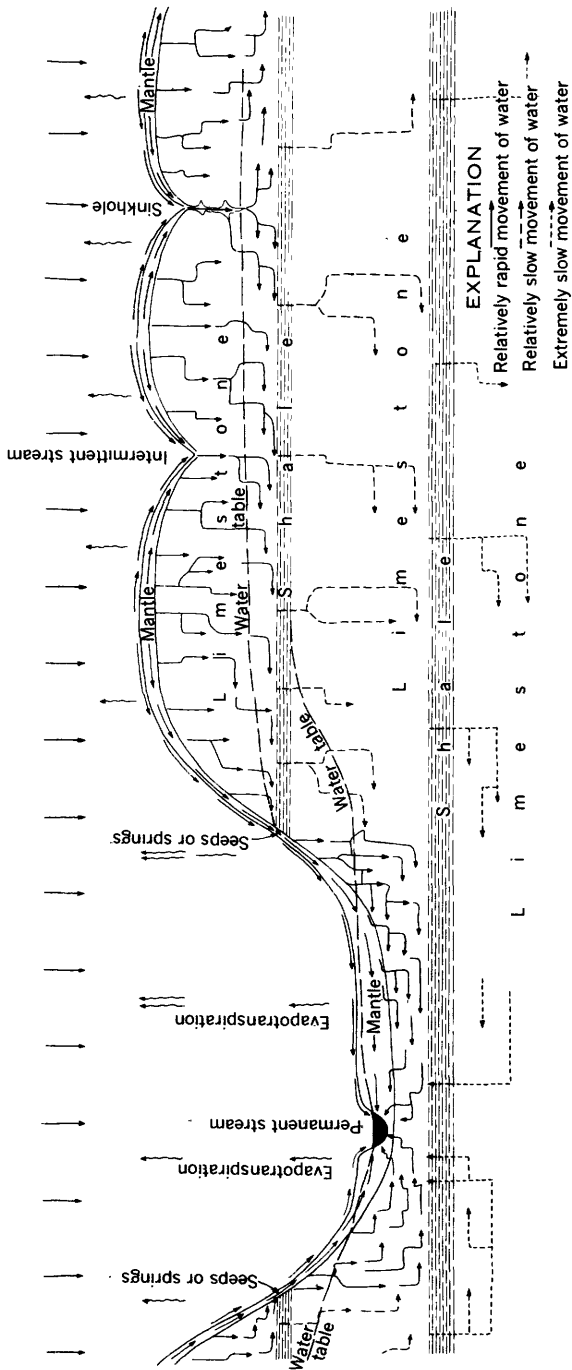


FIGURE 2.—Generalized diagram showing typical movement of ground water in the Blue Grass region, Kentucky.

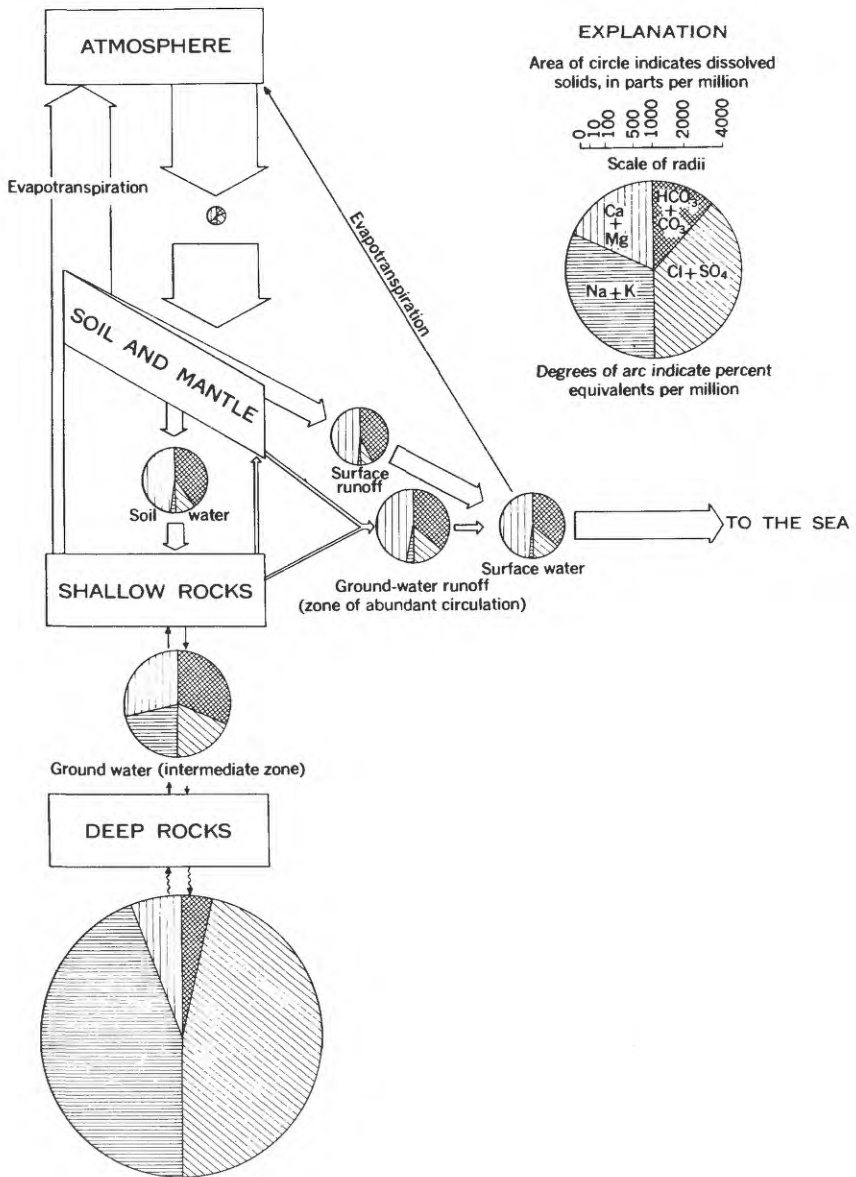


FIGURE 3.—Geochemical cycle of water in the Blue Grass region, Kentucky.

### GEOCHEMICAL CYCLE

The movement of the water in the hydrologic cycle, described on pages 10–11, is accompanied by changes in the chemical quality of the water as illustrated in figure 3. The rain falling to the ground



contains small amounts of solids and gases dissolved from the atmosphere. In percolating through the soil or running off on the surface, the water dissolves materials from the soil and may be moderately high in dissolved solids before it reaches the bedrock. Moreover, percolating waters also dissolve carbon dioxide from the soil air in which carbon dioxide concentrations may be several times greater than in the atmosphere owing to organic activity. The soil-water solution may be further concentrated as water is removed by evaporation or transpiration. The dissolved materials taken into plants through the roots may be returned to the earth when the plants die and decay, or the dissolved materials may be removed when cultivated plants are harvested.

The water that percolates downward through the soil into the underlying rocks dissolves additional materials from the rocks. The amount of material dissolved from the rocks depends chiefly on the amount of water in circulation, the concentration and composition of materials already dissolved in the water, the chemical composition of the rocks, the nature of the openings through which the water moves, the distance the water moves, and its rate of movement. In the Blue Grass region, the shallow ground waters generally move faster than the deep waters, and, because a greater quantity of more dilute water is in contact with the rock, larger quantities of materials are dissolved. However, because the quantities of water involved are so large, the waters do not become highly mineralized. The deep waters generally move greater distances more slowly than the shallow waters and through smaller openings. They are in contact with the rock materials for a longer period of time and, consequently, become more highly mineralized than the shallow waters; however, the high mineral content of some of the deep waters may be due to factors other than distance and rate of circulation. The possible sources of saline waters are discussed on pages 79-82. As the water discharges from the rocks as springs or seeps, it may dissolve additional material from the soil and mantle overlying the rock.

Except for the material removed by the harvesting of crops and the small amount blown away by the wind, nearly all dissolved materials removed from the Blue Grass region are carried by streams. Thus, the dissolved materials in the streams are a composite of the materials contained in the rainwater, those leached from the soils or rocks, and those brought up from great depths through deep wells or permeable zones along faults.

Dissolved materials may be precipitated in openings in the soil or rocks, as a cement around clastic particles, as vein fillings in fractures in the rocks, or as cavern deposits.

Although the changes in the chemical character of water have been described as cyclic, most of the dissolved materials discharged to the sea will return to the land only by tectonic uplift in geologic time. The natural waters of the region are attacking the earth materials and removing them as suspended particles and dissolved substances in the streams. A very small amount of this material may return as airborne material, including salts in rainwater, generally referred to as "cyclic salts," but most of it will remain in the ocean as dissolved materials or will be deposited as sediments on the floor of the sea.

### GROUND WATER

Ground water of economic importance in the Blue Grass region generally occurs in fractures in limestone and in the intergranular pore spaces in siltstone, sandstone, and unconsolidated soil and mantle material. Most of the water obtained from wells in the Blue Grass region comes from fractures in limestone beds. These fractures include joints, which are near perpendicular, and openings along bedding planes which are near horizontal. Near the surface, these fractures have been enlarged by solution, and the most productive wells are those which intersect large openings developed by solution. The openings range in size from paper-thin cracks to caverns several feet in diameter, but few wells intersect openings more than 1 inch wide. Figure 4 is a photograph showing solution openings of relatively large size in the limestone below Dix Dam, Ky.

The depth of effective solution appears to be limited to the depth of abundant ground-water circulation, and the depth of relatively abundant ground-water circulation is controlled largely by the topography and the character of the bedrock. Shale beds restrict or retard the downward percolation of water and tend to limit the zone of abundant circulation, and consequently, development of solution openings to shallow depths.

Ground water in the zone of abundant circulation generally is of the calcium magnesium bicarbonate type.<sup>1</sup> Fresh water is limited to the zone of abundant circulation; at depths greater than about 50–200 feet below the level of local streams saline or sulfurous waters are likely to occur. This is true especially where shale beds occur below the local streams.

The relation between the chemical character of the ground water and the depth of the source of the water is apparent in all parts of the Blue Grass region. With few exceptions, the springs in the region

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<sup>1</sup> In this report the term calcium magnesium bicarbonate type is used to designate a water in which calcium and magnesium together constitute more than half of the total concentration of cations and bicarbonate constitutes more than half of the total concentration of anions (in equivalents per million). Similarly, the term sodium chloride type designates water in which sodium constitutes more than half of the concentration of cations and chloride constitutes more than half of the concentration of anions.



FIGURE 4.—Solution openings in the High Bridge limestone below Dix Dam, Ky.

discharge from the shallow zone of abundant circulation. Accordingly, water from 95 percent of the springs sampled in the Blue Grass region is of the calcium magnesium bicarbonate type and is low in chloride, sulfate, and specific conductance.<sup>2</sup> Most dug wells extend only a few feet below the water table and, therefore, are in the zone of abundant circulation.

<sup>2</sup> Specific conductance is a measure of the capacity of water to conduct an electric current. It varies with concentration and degree of ionization of dissolved constituents and with temperature.

*Comparison of chemical character of water from drilled and dug wells and springs in the Blue Grass region, Kentucky*

Source	Number of samples	Percent Ca Mg HCO <sub>3</sub> type	Percent containing more than 250 ppm of chloride	Percent containing more than 250 ppm of sulfate	Percent exceeding 1,000 micromhos specific conductance
Drilled wells-----	120	62	19	11	34
Dug wells-----	60	73	2	2	13
Springs-----	76	95	1	1	1

Water from 73 percent of the dug wells in the Blue Grass region is of the calcium magnesium bicarbonate type. Only 2 percent of the samples from dug wells contain more than 250 ppm of chloride or sulfate, and only 13 percent have a specific conductance greater than 1,000 micromhos at 25°C. Because more wells are dug in shaly rocks than in limestone, probably more of the dug wells extend below the zone of abundant circulation than their depth would suggest. Drilled wells produce water from openings at any depth from the water table to the bottom of the well. Generally it is impracticable, and sometimes impossible, to determine the depth to the water-bearing openings in drilled wells unless the well is visited at the time it is being drilled. Because drilled wells are, however, generally deeper than dug wells more of them tap zones of sluggish circulation in which the waters are highly mineralized. Sixty-two percent of the samples from drilled wells in the Blue Grass region are of the calcium magnesium bicarbonate type, but 19 percent of the samples contain more than 250 ppm of chloride, and 11 percent contain more than 250 ppm of sulfate. Thirty-four percent have a specific conductance greater than 1,000 micromhos.

#### SURFACE WATER

The two largest streams in the region, the Kentucky and the Licking Rivers, have their headwaters in the Eastern Coal Field and derive their water from both the Eastern Coal Field and Blue Grass regions. Records of discharge and chemical character of some of the smaller streams, however, are more typical of the Blue Grass region.

The ground-water storage capacity of the rocks of the Blue Grass region is very small; consequently, the flow of the smaller streams during dry periods becomes very small or ceases entirely. On the other hand, owing to a generally low infiltration rate and small storage capacity, floods are common during periods of heavy rain.

The surface waters that drain the Blue Grass region typically are of the calcium magnesium bicarbonate type. This is true of all streams whose drainage area is entirely within the Blue Grass region.

Because the headwaters of the Kentucky and Licking Rivers are in the Pennsylvanian rocks of the Eastern Coal Field, the waters of these streams are of mixed type and are generally higher in sulfate than waters from streams originating in the Blue Grass region.

The chemical character of surface water may be influenced by two types of discharge. Surface runoff, because it moves rapidly over the ground to streams, generally picks up a relatively small amount of dissolved materials; ground-water discharge generally moves much more slowly than surface runoff and generally picks up larger quantities of dissolved materials. Because the low flow of streams is predominately ground-water discharge, the concentrations of dissolved materials is generally greater at low than at high flows.

### CHEMISTRY OF WATER IN THE ATMOSPHERE

The atmosphere is composed chiefly of nitrogen and oxygen, but contains also water vapor, argon, carbon dioxide, and other gases. In addition, the atmosphere contains varying amounts of solids in suspension. The amounts vary considerably with time and place and are affected by many factors including the season of the year, proximity of industrial cities or the ocean, velocity of the wind, area of denuded land, and the chemical character of exposed earth materials. Atmospheric water, falling to the earth as rain or snow or condensing as dew, contains very little dissolved materials, but it is not absolutely pure.

Dissolved gases in rainwater consist of about 63 percent nitrogen by volume, 34 percent oxygen, and 3 percent carbon dioxide and other gases (Rankama and Sahama, 1950, p. 312). One sample of rainwater collected in the Blue Grass region had a carbon dioxide content of 16 ppm. The carbon dioxide content of rainwater is important in that a high carbon dioxide content results in rapid solution of carbonate rocks.

Chemical analyses of four samples of rainwater collected in the Blue Grass region as part of this investigation are shown in table 1. The bicarbonate, which ranged from 3 to 8 ppm, probably was derived in part from dissolved carbon dioxide and in part from calcareous dust in the air. The sulfate, which ranged from 0.2 to 4.1 ppm, may have been derived from dust or possibly from industrial smoke. The chloride, which ranged from 0 to 2.2 ppm, probably was derived from industrial contamination or from salt particles brought inland from the Gulf of Mexico. The pH of the samples ranged from 5.5 to 6.2, indicating that rainwater in this region is weakly acid and becomes neutral or alkaline only after it has dissolved carbonate materials from the soils or rocks.

TABLE 1.—*Chemical analyses of rainwater, Blue Grass region, Kentucky*

[Analyses by U.S. Geol. Survey. Chemical constituents in parts per million]

Chemical constituents	At Middletown, Aug. 3, 1956	Near La Grange and Shelbyville, Aug. 31, 1956	Near Buckner, Oct. 26, 1956	Near Shelbyville, Nov. 20, 1956
Silica (SiO <sub>2</sub> )			0.2	0.1
Iron (Fe)			.21	.00
Manganese (Mn)			.22	
Calcium (Ca)			2.1	.6
Magnesium (Mg)			.3	.4
Sodium (Na)			.8	.7
Potassium (K)			.4	1.4
Bicarbonate (HCO <sub>3</sub> )	8	3	5	4.4
Carbonate (CO <sub>3</sub> )	0	0	0	0
Sulfate (SO <sub>4</sub> )	2.8	2.4	4.1	.2
Chloride (Cl)	1.1	2.2	1.8	.0
Fluoride (F)			.1	.1
Nitrate (NO <sub>3</sub> )			1.0	0.1
Carbon dioxide (CO <sub>2</sub> )		16		
Dissolved solids (calc.)			14	6
Hardness as CaCO <sub>3</sub>			6	3
Specific conductance (micromhos at 25°C)	24.9	20.9	36	12
pH	5.6	5.5	5.6	6.2
Color			2	1
Remarks	Gray precipitate formed around neck of bottle (probably suspended matter). Collected near beginning of a heavy summer shower.	Composite sample from two loca- tions. Collected near end of a light rain.	Air temperature 55°F. Collected near begin- ning of a light rain.	Collected during prolonged driz- zle.

It has been suggested that most, or all, of the chloride in river water is derived from salts transported by the atmosphere from the ocean and deposited on the land by precipitation. This question could be resolved on a local basis by computing the amount of chloride deposited by precipitation in a given drainage basin and the amount of chloride carried out of the basin by the stream. The data required for these computations are periodic analyses of rainwater and river water in the basin and continuous measurements of rainfall and stream discharge. All data required are available for several drainage basins in Kentucky except periodic chemical analyses of rainwater. A few analyses suggest that the average chloride content of rainwater in Kentucky may be about 1.0 ppm. If we accept this figure as an average, the amount of chloride deposited by rainfall during the water year October 1949 through September 1950 on the drainage basin (3,330 square miles) of the Licking River above Butler was about 15,000 tons. The amount of chloride discharged from this basin during the same period was about 35,000 tons. Discharge of water from the basin during this period was about 30 inches, which is considerably higher than the average for this stream. Consequently, only part of the chloride discharged by the streams is derived from the atmosphere.

### CHEMISTRY OF WATER IN THE SOILS AND MANTLE

For the purpose of this report, all unconsolidated materials overlying the bedrock have been classed as soil and mantle material. This includes a small amount of glacial material and alluvial deposits, usually described as geologic units. As indicated on page 3, the alluvial deposits along the Ohio River are not described in this report. The soils and mantle of the Blue Grass region were formed by the weathering of the limestone, shale, and sandstone bedrock. Some of the weathered material remained in place, and some was transported and deposited by water, wind, or ice. More than 90 percent of the soils of the Blue Grass region were formed from rock material that weathered in place. The thickness of residual soil or mantle at a given location is controlled by the type and thickness of the rock weathered and the rate of removal of the soil by erosion. A greater thickness of such soils is to be expected on rolling lands of low relief than on steep hillsides where erosion removes the soil almost as fast as it is formed.

### CHEMICAL COMPOSITION OF THE SOILS

The chemical composition of the soils of the Blue Grass is important in that it influences the chemical character of the waters percolating through them. Chemical analysis and clay-mineral analyses of soils of the Blue Grass were obtained from published and unpublished records of the U.S. Department of Agriculture, Kentucky Agricultural Experiment Station, and Kentucky Department of Highways. Chemical analyses of 10 soils from the Blue Grass region are given in table 2. These analyses were abstracted from county soil survey reports published by the U.S. Department of Agriculture. The samples are identified by soil series. Because exact locations of the samples are not indicated, the underlying geologic units cannot be determined.

Analyses of the clay-mineral fractions of 24 samples of soil from the Blue Grass region showed illite as the dominant clay mineral in all but one of the samples. The clay-mineral fractions of 16 of the samples were 100 percent illite. Seven of the samples contained 10-47 percent kaolinite in the clay-mineral fraction, and one sample contained 90 percent kaolinite. Montmorillonite was not detected in any of the samples. The collection and determinations of clay-mineral content of these samples were made by the X-ray diffraction method by J. H. Havens, Robert Deen, and others of the Kentucky Department of Highways.

TABLE 2.—*Chemical analyses of typical soils of the Blue Grass region, Kentucky*  
[Percentage composition by weight]

Description	Depth (inches)	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Ignition loss at 700° C	N	S	H <sub>2</sub> O at 104°- 110° C
<b>Maury silt loam 1</b>															
Reddish-brown silt loam.....	0-7	72.90	1.23	4.24	9.48	0.53	0.75	1.46	1.38	0.33	0.77	6.49	0.215	0.051	2.66
Do.....	7-17	73.29	1.28	4.68	11.52	.48	.68	1.07	1.41	.44	.68	5.05	.121	.028	2.60
Reddish-brown silty clay loam containing iron and manganese pellets.....	17-34	65.00	1.41	7.27	16.58	.53	.73	1.55	1.10	.05	.90	5.97	.079	.021	4.16
Do.....	34-66	57.52	1.15	8.94	18.61	.72	.86	1.37	.91	.10	1.61	7.07	.076	.038	4.66
Dark-chocolate-brown clay loam.....	66-72	37.32	.94	10.62	20.27	1.25	10.10	.86	.96	11.16	11.30	7.77	.065	.027	4.28
Do.....	72-86	38.84	.89	10.34	20.34	.91	9.92	1.44	1.41	.16	10.30	7.38	.058	.024	4.12
Parent material of dark-brown plastic clay.....	86-104	41.04	.99	10.01	19.27	1.07	9.69	1.42	2.36	.17	9.63	6.75	.049	.020	4.00
Dark-chocolate-brown silty clay.....	104-130	29.14	.52	8.50	16.86	.99	18.61	1.12	1.44	.24	15.72	6.29	.052	.037	3.92
Do.....	104-130	36.02	.83	9.09	16.58	.91	14.05	1.24	1.75	.18	12.55	6.29	.048	.031	3.32
Dark-brown silty clay material over bed- rock.....	130-144	15.42	.31	5.11	9.44	1.36	29.56	.95	.89	.14	24.93	4.10	.031	.067	1.94
<b>Maury silt loam 2</b>															
.....	0-5 1/2	74.53	1.09	3.57	9.91	0.43	0.62	0.69	1.27	0.32	0.51	7.30	0.217	0.040	2.50
.....	5 1/2-10	76.82	1.15	3.42	10.35	.37	.54	.72	1.26	.23	.43	4.84	.111	.021	2.02
.....	10-16	74.55	1.23	3.94	11.16	.23	.51	.70	1.28	.26	.45	4.27	.067	.011	2.54
.....	16-28	70.09	1.23	5.22	14.22	.22	.54	.88	1.27	.13	.52	5.12	.062	.004	3.56
.....	28-40	68.09	1.15	6.11	14.36	.23	.47	.86	1.41	.13	.62	5.43	.062	.009	4.24
.....	40-56	63.58	1.10	7.03	16.23	.29	1.02	1.06	1.55	.14	1.27	5.93	.063	.009	4.56
.....	56-63	51.27	.81	8.82	22.11	.23	1.60	1.52	2.20	.16	1.98	8.01	.069	.010	7.36
.....	63-73	47.32	.64	8.53	19.48	.43	6.53	1.31	2.07	.20	5.16	6.73	.048	.053	6.18
.....	73-79	49.37	.60	6.51	17.75	.26	7.18	1.31	2.37	.12	5.31	6.89	.079	.064	6.18
.....	79-88	46.18	.59	4.28	9.53	.27	4.8	.16	1.37	.29	.47	4.21	.17	-----	1.79
.....	8-20	74.84	1.02	5.08	11.10	.24	.52	.54	1.39	.17	.95	4.45	.07	-----	1.93
.....	20-40	66.24	1.03	7.29	14.99	.29	1.45	.77	1.38	.11	1.06	5.45	.07	-----	2.95
.....	40-58	56.69	1.02	8.71	19.49	.33	3.39	.98	1.64	.03	1.06	6.50	.07	-----	3.70
.....	58-70	49.83	.98	6.84	20.24	.28	9.75	1.21	2.26	.08	.96	7.33	.06	-----	3.31
<b>Hagerstown silt loam 1</b>															
Grayish-brown silt loam with mealy struc- ture.....	0-7	73.47	1.23	4.26	9.38	0.16	0.67	0.82	1.16	0.24	0.55	7.01	0.232	0.038	2.14
Brown silt loam.....	7-14	74.85	1.38	4.72	11.61	.17	.52	.86	1.17	.18	.49	4.69	.095	.023	1.86
Brown heavy silt loam.....	14-22	68.72	1.44	6.26	12.12	.39	.65	1.45	1.16	.33	.53	5.06	.067	.017	2.14
Reddish-brown silt loam with mealy struc- ture.....	22-50	57.91	1.40	13.57	13.41	.81	.53	.90	.92	.13	1.31	7.01	.062	.033	3.34

See footnotes at end of table.



TABLE 2.—*Chemical analyses of typical soils of the Blue Grass region, Kentucky—Continued*

[Percentage composition by weight]

Description	Depth (inches)	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Ignition loss at 700° C	N	S	H <sub>2</sub> O at 104° 110° C
<b>Hagerstown silt loam—Continued</b>															
Brick-red color. Iron and manganese material.	50-82	49.59	1.50	25.23	12.45	1.11	.53	.77	.77	.18	1.84	7.54	.039	.011	3.48
Yellowish-gray material with brownish-red and black splotches.	82-96	48.56	1.55	26.06	11.84	.38	.50	.95	.92	.16	2.18	7.51	.040	.048	3.30
Gray silty clay.	96-102	60.35	1.65	12.98	13.29	.35	.56	.86	1.18	.21	1.25	6.06	.034	.011	2.94
Yellow silty clay.	102-128	57.15	1.34	9.84	20.38	.14	.59	1.90	3.02	.24	1.20	6.12	.042	.023	3.24
Silty clay loam with brown and black splotches.	128-139	47.24	1.19	10.36	17.97	.22	5.63	1.65	2.46	.21	6.11	6.00	.045	.029	2.96
Brown gritty silty clay.	139-146	31.49	.62	9.90	17.44	.64	18.00	1.18	1.61	.21	14.60	6.36	.047	.066	3.22
Brown sandy clay loam.	146-192	25.39	.51	7.60	7.66	.47	24.75	1.70	1.00	.29	21.10	4.64	.049	.014	2.80
<b>Mercer silt loam 1</b>															
Grayish-brown silt loam.	0-7	78.44	1.47	4.26	7.71	0.22	0.55	0.74	1.08	0.30	0.32	5.22	0.131	0.014	1.48
Rust-brown silt loam with yellow-gray splotches.	7-20	73.05	1.44	6.51	12.75	.02	.88	1.12	1.19	.17	.19	4.68	.047	.038	2.56
Loose brown silt loam.	20-36	68.42	1.56	7.83	15.22	.01	.63	1.35	1.17	.19	.21	5.29	.036	.021	3.66
Rust-brown and yellow silt loam.	36-54	57.75	1.32	8.50	21.17	.01	.63	1.85	1.90	.25	.19	7.42	.039	.021	5.18
Bluish-gray and pale-yellow very plastic clay.	54-76	57.45	1.10	7.20	22.38	.01	.88	2.00	2.89	.29	.29	7.05	.032	.024	4.68
Rust-brown clay with gray splotches.	76-86	56.85	1.07	5.76	19.96	.08	1.17	2.66	2.82	.49	.44	5.67	.030	.017	4.74
Blue, yellow, and brown gritty clay.	86-96	53.92	1.05	9.11	20.72	.08	1.54	2.36	2.66	.40	.70	6.21	.030	.016	4.64
Alkaline yellow clay, with small blue and dark-brown splotches, over bedrock.	96-116	54.31	1.09	7.84	19.64	.04	3.19	2.29	3.01	.35	.68	6.69	.032	.021	3.78
<b>Mercer silt loam, profile 1<sup>2</sup></b>															
	0-7	80.59	1.22	2.91	7.11	0.14	0.30	1.13	1.38	0.31	0.10	4.19	0.104	0.015	1.24
	7-12	76.00	1.19	4.19	10.41	.08	.24	.43	1.57	.33	.08	3.88	.056	.009	1.94
	12-18	74.52	1.26	6.59	9.25	.03	.27	.46	1.64	.30	.08	4.11	.046	.010	2.12
	18-24	69.04	1.32	3.94	14.87	.03	.27	.83	1.70	.27	.09	5.10	.040	.009	3.58
	24-29	66.70	1.32	6.66	12.65	.10	.27	.65	1.64	.22	.09	4.87	.032	.005	3.58
	29-33	62.85	1.00	7.20	17.42	.14	.66	1.24	1.77	.31	.07	6.37	.033	.002	5.24
	33-42	56.29	1.00	7.54	21.53	.10	1.41	1.69	2.29	.33	.12	7.36	.035	.005	6.26

Mercer silt loam, profile 2

0-6	79.32	1.24	2.74	7.95	0.13	0.45	0.58	1.41	0.51	0.12	5.60	0.151	0.017	1.78
6-13	79.10	1.24	3.00	9.38	.08	.30	.55	1.48	.44	.09	3.68	.061	.004	1.50
13-24	69.80	1.15	5.81	14.64	.03	.27	.96	1.70	.43	.08	5.05	.044	.004	3.84
24+	57.99	.99	6.67	21.20	.02	.60	1.35	2.05	.32	.06	7.20	.035	.002	6.40

Loradale silt loam<sup>1</sup>

0-7	74.57	1.43	5.33	9.70	0.38	0.76	0.94	1.12	0.15	0.59	5.46	0.154	0.025	1.92
7-17	74.34	1.43	4.56	10.56	.11	.64	1.23	1.47	.44	.43	4.76	.110	.022	2.12
17-26	69.55	1.39	6.34	12.91	.26	.65	1.20	1.50	.40	.43	5.04	.064	.021	2.72
26-36	62.66	1.60	10.02	16.35	.45	.62	1.33	1.34	.22	.65	6.08	.062	.015	3.26
36-48	51.64	1.31	13.30	21.38	.12	.66	1.64	1.99	.18	.93	7.34	.093	.014	4.60
48-84	48.69	1.11	14.99	21.74	.08	.63	1.67	2.57	.34	1.09	7.43	.051	.016	5.04

Laradale silt loam

84-114	52.48	1.14	12.40	20.27	.19	.62	2.12	3.18	.24	1.17	7.07	.044	.011	3.84
114-168	55.59	1.14	9.85	19.85	.20	1.15	2.19	3.83	.26	1.06	5.92	.040	.012	3.32
168-182	55.53	1.08	8.73	19.66	.21	1.42	2.55	4.70	.19	.72	5.00	.047	.019	2.72

Eden silty clay loam<sup>2</sup>

0-8	58.63	1.04	5.37	15.06	0.21	0.88	1.35	3.49	0.47	0.27	9.50	0.248	0.029	3.90
8-37	64.44	.89	7.10	20.15	.15	1.23	1.96	4.01	.44	.21	7.06	.094	.011	3.30
17-26	32.21	.94	3.91	20.30	.11	3.72	1.75	4.03	.41	.36	7.81	.068	.010	3.88

Eden clay<sup>3</sup>

0-6	71.78	1.25	2.95	11.91	---	0.84	1.22	2.72	---	0.21	5.81	---	---	---
6-18	64.34	.86	4.07	16.18	---	.87	1.63	3.25	---	.33	5.68	---	---	---
0-6	60.02	1.00	4.71	16.77	---	.90	2.10	5.12	---	.22	7.03	---	---	---

Eden silt loam<sup>3</sup>

0-6	80.06	1.10	2.00	8.67	---	0.24	0.56	1.82	---	0.13	4.45	---	---	---
6-18	74.20	1.10	2.88	12.75	---	.21	.52	1.95	---	.13	4.69	---	---	---
0-6	80.82	.95	1.80	8.98	---	.26	.45	1.84	---	.17	4.21	---	---	---
6-18	73.04	1.16	3.03	12.66	---	.35	.78	2.05	---	.15	5.03	---	---	---

<sup>1</sup> Analyses from Higbee, H. W., and Venable, K. S., 1931, Soil survey of Fayette County, Ky.: U.S. Dept. Agriculture, Bur. Chemistry and Soils, p. 35-36.<sup>2</sup> Analyses from Higbee, H. W., Wrather, Yandall, and Boatright, W. C., 1930, Soil survey of Mercer County, Ky.: U.S. Dept. Agriculture, No. 23, ser. 1930, p. 47-48.<sup>3</sup> Analyses from Van Duyne, Cornelius, Schoemann, L. R., and Averitt, S. C., 1919, Soil survey of Shelby County, Ky.: U.S. Dept. Agriculture, Bur. Soils, p. 64.

**CHEMICAL CHARACTER OF SOIL WATER**

In most of the area of recharge, water percolates through soil or mantle materials before it reaches the ground-water body. Few data are available on the quantities of substances dissolved from the soil under natural conditions in the Blue Grass region, but information on the relative amounts of materials dissolved from samples of typical soils in the laboratory is listed in tables 3 and 4. The water samples reported in table 3 were obtained by allowing water to percolate through undisturbed samples of soil which were taken by driving an aluminum tube, 4 inches in diameter and 5 feet long, sharpened on one end, into the soil to a depth of 12 inches. The sampling tube was returned to the laboratory with the sample inside, where it was suspended from an overhead support, and water was poured into the tube until it reached a level a few inches from the top. Rainwater collected near Shelbyville on November 20, 1956 (see table 1) was used in one of the tests. All other tests were made with distilled water. The water percolated through the soil samples in 1-16 hours under a head of about 1-4 feet into a sample bottle below. A plastic funnel that fitted snugly on the base of the tube and into the mouth of the bottle kept evaporation loss to a minimum.

The water collected in this manner is not typical of water percolated through the soil under natural conditions. Because of the artificially induced head, the water will pass through the soil in the tubes much more rapidly than it would under natural conditions; consequently, the quantities of dissolved substances will be smaller. In addition, the substitution of distilled water for rainwater in all but one of the tests probably changes both the total and relative amounts of materials dissolved. Soil 7 was leached first with distilled water, and later the same sample was leached with rainwater. The leach obtained by percolating rainwater contained more than double the amount of dissolved solids of the leach obtained by percolating distilled water. The relative amounts of calcium and sulfate in the two samples were approximately the same, but the relative amount of bicarbonate was more than twice as great in the distilled water sample. The relative concentration of nitrate was much greater in the rainwater sample. The concentrations of magnesium, sodium, potassium, and chloride probably are too small in both samples to justify comparisons.

Table 4 lists analyses of leach from disturbed soil samples leached with distilled water. Most of the soil samples are duplicates of the samples listed in table 3. These soils were placed in bottles filled with distilled water, agitated to allow thorough mixing, and allowed to stand for 3 days. Because the distilled water remained in contact with the disturbed soil for a longer period of time than with the

TABLE 3.—*Chemical analyses of water percolated through undisturbed typical soil samples, Blue Grass region, Kentucky*  
 [Analyses by the U.S. Geol. Survey. Chemical constituents in parts per million. All samples leached with distilled water except as noted]

Soil	Location	Date of collection of soil samples	Source of soil	Silica (SiO <sub>2</sub> )	Iron (Fe)	Manganese (Mn)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO <sub>3</sub> )	Sulfate (SO <sub>4</sub> )	Chloride (Cl)	Fluoride (F)	Nitrate (NO <sub>3</sub> )	Dissolved solids (calculated)	Hardness as CaCO <sub>3</sub>		pH
																	Ca, Mg	Noncarbonate	
7----	Near Frankfort, Franklin County, Ky.	Aug. 29, 1956	Soil over Lexington group. <sup>1</sup>	2.2	0.03	0.00	3.9	0.4	1.1	0.4	11	2.0	0.2	----	0.7	16	11	2	6.1
7----	do.	do.	Soil over Lexington group. <sup>2</sup>	1.5	.10	-----	8.0	.6	.0	.8	11	4.0	.0	0.4	17	38	22	14	6.2
2----	Near Bridgeport, Franklin County, Ky.	do.	Soil over Cynthiana formation.	.7	.01	.00	1.0	.1	.5	.3	4	1.4	.2	-----	.5	7	3	0	6.0
1----	Near Peytona, Shelby County, Ky.	Aug. 21, 1956	Soil over Eden group. <sup>3</sup>	.5	.36	.00	1.5	.3	.6	.2	7	2.5	.2	.3	.1	10	5	0	5.8
1----	do.	Aug. 28, 1956	Soil over shale of the Eden group. <sup>4</sup>	1.2	.57	.00	2.1	.5	.4	.4	6	2.1	.2	.4	.1	11	7	2	6.0
8----	Near Graefenburg, Franklin County, Ky.	Aug. 29, 1956	Soil over Eden group.	2.7	.00	.00	3.2	.1	1.1	.5	10	2.0	.2	-----	.5	15	8	0	6.2
3----	Shelbyville, Shelby County, Ky.	Aug. 28, 1956	Soil over Maysville	4.5	.06	.00	14	.9	1.0	.2	31	14	.6	.2	.6	51	39	13	6.6
4----	Near Buckner, Oldham County, Ky.	do.	Soil over Sandus limestone of the Richmond group.	.6	.10	.00	.4	.3	.4	.4	3	2.3	.5	-----	.2	7	2	0	5.1
5----	Near Louisville, Jefferson County, Ky.	do.	Soil over Louisville limestone of Silurian age.	12	.01	.00	6.3	.9	.5	.4	8	14	.9	.2	.0	39	19	13	6.0

<sup>1</sup> One gallon obtained in 5 hours. This is first water sample percolated through the soil.

<sup>2</sup> This is second gallon collected under 2-1 ft of head overnight.

<sup>3</sup> This is second water sample percolated through the soil. (Table 2, collected near Shelbyville, Nov. 20, 1956.)

<sup>4</sup> About three-fourths gallon passed through in 1 hour under 3-4 ft of head.

TABLE 4.—*Chemical analyses of distilled-water leach of disturbed soils of the Blue Grass region, Kentucky*  
 [Analyses by the U. S. Geol. Survey. Chemical constituents in parts per million]

Soil	Location	Soil depth (in.)	Silica (SiO <sub>2</sub> )	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO <sub>3</sub> )	Sulfate (SO <sub>4</sub> )	Chloride (Cl)	Nitrate (NO <sub>3</sub> )	Dissolved solids (residue at 180°C)	Hardness as CaCO <sub>3</sub>	
													Calcium, magnesium	Non-carbonate
7	Near Frankfort, Franklin County, Ky.	0-12	3.0	10	0.9	0.8	1.1	37	2.3	0.0	0.0	50	29	0
2	Near Bridgeport, Franklin County, Ky.	12-18	3.6	9.8	.5	1.6	.7	32	2.0	.2	.1	40	26	0
2	do.	0-12	3.8	7.8	.6	.5	.9	28	2.6	.0	.1	43	22	0
8	Near Graefenburg, Franklin County, Ky.	0-12	4.7	13	.8	.5	.8	45	2.1	.0	.2	57	36	0
3	Shelbyville, Shelby County, Ky.	0-12	3.2	7.1	1.0	.2	.8	26	4.4	.0	.0	36	22	1
4	Near Buckner, Oldham County, Ky.	0-12	4.2	1.4	.8	1.0	.6	9	4.0	1.0	.0	20	7	0
5	Near Louisville, Jefferson County, Ky.	0-12	6.2	19	1.7	.9	2.9	73	4.1	1.0	.1	77	54	0

undisturbed soil, the disturbed soil yielded a greater amount of dissolved substances than did the undisturbed soil.

A comparison of the analyses of the leaches in tables 3 and 4 with the analyses of soils in table 2 shows that the calcium in the topsoils generally is more soluble than the magnesium. Magnesium (as  $MgO$ ) generally is greater than calcium (as  $CaO$ ) in the upper 12 inches of soil, whereas the water leached from the upper 12 inches of soil generally contains much larger quantities of calcium than magnesium. This indicates that, unlike calcium, most of the magnesium in the soils does not occur as carbonate but is fixed in the clay minerals. The low concentration of potassium in the leaches as compared with the soils suggests that most of the potassium also is tied up in the clay minerals.

Although the analyses listed in tables 3 and 4 are not representative of the chemical character of soil water under natural conditions, they do indicate the more soluble materials contained in the soil and, to some degree, the probable relative concentrations of these materials in soil water. From these data, it appears probable that the water in soils of the Blue Grass region generally is of the calcium magnesium bicarbonate type. The soil water probably contains more sulfate and less chloride in relation to dissolved solids than does the water from most of the wells and springs listed in table 7.

An analysis of one sample of water obtained from a saturated soil near Goose Creek in Jefferson County is listed below:

*Chemical constituents in parts per million*

Silica ( $SiO_2$ )	10	Dissolved solids:	
Iron (Fe)	.05	Sum calculated from determined constituents	282
Manganese (Mn)	.01	Residue on evaporation at 180° C.	288
Calcium (Ca)	54	Hardness as $CaCO_3$ :	
Magnesium (Mg)	25	Calcium magnesium	238
Sodium (Na)	8.7	Noncarbonate	41
Potassium (K)	1.5	Free carbon dioxide ( $CO_2$ )	55
Bicarbonate ( $HCO_3$ )	240	Specific conductance (micro-mhos at 25° C)	486
Carbonate ( $CO_3$ )	0	pH	7.3
Sulfate ( $SO_4$ )	41	Color	5
Chloride (Cl)	9.5		
Fluoride (F)	.1		
Nitrate ( $NO_3$ )	14		

The soil water reported above presumably was discharging to the creek, and the concentration of dissolved solids may be greater than would be normal for most areas in the Blue Grass region. The concentration of dissolved solids in most soil waters in the Blue Grass is estimated to be in the order of 100–200 ppm.

## CHEMICAL CHARACTER OF WATER IN ALLUVIAL MATERIALS

Alluvial materials along streams tributary to the Ohio River are classified in this report as part of the soil and mantle. These materials generally consist of clay, silt, and sand with minor amounts of gravel. The older deposits underlie higher terraces and generally are farther removed from the stream than the younger alluvium. The chemical composition of the alluvial materials is related to the age of the deposits. The older deposits generally are more acid and contain less calcium and magnesium carbonate than the younger deposits.

The chemical character of water in these materials probably reflects the differences in chemical composition of the older and younger alluvium. Water in the older alluvium would presumably be lower in pH and lower in calcium, magnesium, and bicarbonate than water in the younger alluvium.

*Chemical analyses of water from four wells tapping alluvial materials in the Blue Grass region*

[Chemical constituents in parts per million]

Well	8335-3805-1	8500-3835-5	8450-3805-3	8350-3750-1
Date collected	4-28-53	8-20-53	6-4-52	5-1-57
Silica (SiO <sub>2</sub> )			10	
Iron (Fe)	1.8	.36	2.7	3.9
Manganese (Mn)			1.1	
Calcium (Ca)			75	
Magnesium (Mg)			8.6	
Sodium (Na)			3.0	
Potassium (K)			.8	
Bicarbonate (HCO <sub>3</sub> )	430	375	250	106
Carbonate (CO <sub>3</sub> )	0		0	0
Sulfate (SO <sub>4</sub> )	146	38	12	8.8
Chloride (Cl)	152	15	7.0	12
Fluoride (F)	.1	.3	.1	.1
Nitrate (NO <sub>3</sub> )	3.4	5.6	2.4	.5
Dissolved solids			260	
Hardness as CaCO <sub>3</sub>	270	321	223	75
Noncarbonate			18	0
Specific conductance (micromhos at 25°C)	1,390	664	448	213
pH			7.5	6.3
Color			4	

Unfortunately, few data are available on the chemical character of ground water in these materials. Few wells are finished in the alluvial materials in the Blue Grass region, and most of the wells that

tap these deposits are on high terraces underlain by the Cumberland soils, which are the oldest and most acid of the alluvial soils of the Blue Grass region. Most of the wells in the alluvium are drilled to bedrock, and some may obtain part of their water from the consolidated rocks.

Two of the samples, the one with the highest and the one with the lowest specific conductance, are high in bicarbonate and low in hardness. These probably are of the sodium bicarbonate type. The other two samples are of the calcium magnesium bicarbonates type and are similar to water from shallow wells in the consolidated rocks of the Blue Grass region.

The chemical character of ground water in the alluvium is influenced by additions of water from three sources: water percolating through the soil from precipitation on the surface, water discharging from bedrock through the alluvium to the stream, and water entering the alluvium from the stream during floods.

Water percolating through the soil to the underlying alluvium probably contains smaller amounts of dissolved solids than that entering the alluvium from the bedrock. Water entering the alluvium from floodwaters of the stream would, of course, be similar in chemical composition to that of the floodwaters. Water entering the alluvium may dissolve additional materials from the alluvium, and ion exchange with the clay minerals of the alluvium may occur.

The chemical character of ground water in the alluvium along smaller streams probably is similar to the chemical character of the water in the stream, especially at times of low flow.

## CHEMISTRY OF WATER IN THE ROCKS

### CHEMICAL COMPOSITION OF THE ROCKS

The chemical composition of the rocks determines the substances that are available for solution by the water moving through them. Table 5 is a collection of selected chemical analyses of rocks of Kentucky compiled from reports of the Kentucky Geological Survey. Most of the samples were obtained from the Blue Grass region, and all are of rocks that occur in the Blue Grass region.

The analyses in table 6 were made especially for this investigation. The samples were selected as typical of the rock units by the authors and were analyzed by Henry Kramer of the Geological Survey.



TABLE 5.—*Chemical analyses of rocks of Kentucky compiled from Kentucky Geological Survey reports*

[Reference: 1, Richardson, 1923; 2, Easton, 1913; 3, Richardson, 1927; 4, Richardson, 1920. Analytical results converted to parts per million by R. A. Krieger; geology revised by W. N. Palmquist, Jr.]

Geologic source	County	Sand and in-soluble silicates (as SiO <sub>2</sub> )	FeO <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , and Mn <sub>2</sub> O <sub>3</sub> (as Fe)	Iron (Fe)	Aluminum (Al)	Titanium (Ti)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Carbonate (CO <sub>3</sub> )	Sulfate (SO <sub>4</sub> )	Phosphate (PO <sub>4</sub> )	Reference	Remarks
High Bridge group <sup>1</sup> .....	Anderson.....	22,800	-----	1,940	4,340	-----	363,500	17,300	-----	-----	582,400	Trace	-----	1	Limestone from Kentucky River cliffs. Middle of Tyrone limestone formation.
Do.....	Clark.....	35,200	4,060	-----	-----	-----	242,900	93,700	1,860	3,110	588,500	1,490	2,770	1	Mouth of Lower Howards Creek.
Do.....	Fayette.....	15,800	2,660	-----	-----	-----	382,700	5,930	355	1,600	579,000	1,990	2,440	3	14½ miles from Lexington.
Do.....	Jessamine.....	38,400	-----	3,360	265	-----	355,400	12,700	-----	-----	-----	0	3,350	1	Tyrone limestone (Birdseye). High Bridge. Camp Nelson limestone.
Do.....	Woodford.....	24,800	6,860	-----	-----	-----	239,400	106,300	592	3,320	613,300	1,920	-----	1	Shylocks Ferry. Oregon limestone.
Do.....	do.....	21,800	4,410	3,360	0	-----	379,000	5,680	2,370	1,910	572,900	3,600	Trace	1	Shylocks Ferry.
Lexington (?) group.....	do.....	10,000	-----	-----	-----	0	382,900	2,780	-----	-----	-----	0	5,630	1	West of Old Crow district on Glenn Creek. Benson limestone or Lower Cynthiana formation.
High Bridge or Lexington group.	Jessamine.....	535,200	-----	13,400	104,300	1,200	16,500	28,900	2,370	55,700	-----	Trace	2,010	2	¼ mile northeast of High Bridge.
Do.....	Fayette.....	49,800	22,600	-----	-----	-----	310,500	29,000	1,110	2,660	529,000	37,400	9,380	1	Clay under limestone. On Elk horn River below Lexington.
Lexington group or Cynthiana formation.	Jessamine.....	584,000	-----	37,000	92,600	3,600	20,300	11,500	4,370	35,400	-----	None	10,700	2	Tyrone limestone. 9 miles south of Lexington. Clay.
Do.....	do.....	588,000	-----	41,500	92,400	4,200	17,000	10,100	5,990	32,600	-----	None	12,100	2	Do.
Cynthiana formation.	Nicholas.....	13,800	6,300	-----	-----	0	379,700	5,200	-----	-----	-----	0	4,020	1	Pleasant Valley. Point Pleasant limestone member.
Do.....	Robertson.....	933,900	29,000	-----	-----	-----	440	580	888	1,660	-----	9,600	1,210	4	Blue Licks Battleground. Sandstone (?)
Do.....	do.....	14,500	2,000	-----	-----	-----	390,000	2,020	1,530	540	585,100	2,160	1,240	1	Sample from Cane Ridge.
Eden group.....	Bourbon.....	28,800	11,600	-----	-----	-----	364,900	10,600	1,100	1,660	567,600	3,230	2,440	1	Sample from near Augusta limestone.
Do.....	Bracken.....	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Do.....	Grant.....	525,000	-----	44,800	89,400	3,000	12,200	12,400	10,700	47,100	-----	None	4,420	2	North of Masson. Upper Utica. Yellow calcareous shale.

Eden(?) group.....	Bracken.....	471,600	-----	15,100	39,500	0	130,800	20,000	4,900	14,500	-----	Trace	14,300	1	1/4 mile east of Foster Flag Station near Richmond. Garrard sandstone.
Do.....	Madison.....	735,800	-----	19,000	65,200	0	12,400	5,400	17,800	17,700	-----	0	0	1	1/2 mile east of Foster Station. Garrard sandstone (westward).
Richmond group.....	Clark.....	48,000	-----	21,500	14,700	-----	215,800	98,700	-----	-----	-----	Trace	1,870	1	2 1/2 miles west of Indian Fields. Lower 20 ft of Richmond group.
Do.....	do.....	447,700	-----	28,000	74,200	2,400	72,800	42,800	1,340	16,000	-----	Trace	Trace	2	West of Indian Fields. Green clay shale.
Do.....	Jefferson.....	144,800	31,300	-----	-----	-----	208,300	91,300	2,290	5,060	530,700	3,600	2,810	1	3 miles from Middletown. Sandstone.
Slurian system.....	Clark.....	556,800	-----	40,800	111,500	3,000	12,700	14,200	3,710	40,500	6,950	Trace	Trace	2	1 mile west of Indian Fields. Estill clay member of Crab Orchard group.
Do.....	do.....	584,800	-----	50,400	102,400	2,700	5,820	13,600	6,590	38,000	-----	Trace	Trace	2	1 mile west of Indian Fields. Crab Orchard group. "Not an average clay."
Do.....	Jefferson.....	40,300	15,500	-----	-----	0	218,300	105,500	-----	-----	-----	0	402	1	1 1/2 miles east of Anchorage. Upper Laurel dolomite.
Do.....	do.....	38,800	-----	3,150	13,300	300	304,400	44,500	-----	-----	-----	0	0	1	Florida Heights quarry. Louisville limestone.
Do.....	do.....	56,400	-----	7,000	14,500	480	230,900	86,900	-----	-----	-----	4,200	Trace	1	1/4 mile east of Tucker. Lower Laurel dolomite.
Do.....	Oldham.....	57,200	-----	7,280	12,100	480	205,300	113,000	-----	-----	-----	900	Trace	1	2 miles east of LaGrange. Osgood formation.
Do.....	do.....	10,000	4,970	-----	-----	0	386,500	5,200	-----	-----	-----	Trace	1,610	1	1 1/2 miles northwest of Beards.
Do.....	Powell.....	373,000	-----	38,500	82,800	3,000	42,400	13,300	2,440	29,600	-----	1,440	3,480	2	East of Virden. Crab Orchard group. Clay.
Devonian system.....	Clark.....	57,900	-----	160,600	335,400	2,700	7,170	Trace	2,150	45,600	-----	Trace	None	2	2 miles south of Indian Fields. Clay.
Do.....	do.....	444,000	-----	172,800	60,200	4,500	1,040	2,280	1,920	16,500	-----	6,720	1,740	2	2 1/2 miles east of Indian Fields. Ohio shale residue.
Mississippian system.....	Rowan.....	855,200	-----	12,500	37,100	4,200	-----	-----	-----	-----	-----	-----	-----	4	Blue Grass quarries, Freestone, Sandstone.
Do.....	do.....	931,300	-----	11,200	6,310	-----	2,320	754	-----	-----	17,400	-----	-----	1	Farmers Station. Kinderhook(?) group or New Providence(?) group.

## 32 GEOCHEMISTRY OF WATERS OF BLUE GRASS REGION

TABLE 6.—*Chemical analyses of limestone and shale of the Blue Grass region, Kentucky*

[Analyses by the U.S. Geol. Survey. Chemical constituents in parts per million to nearest 100 ppm]

Sample	County	Location <sup>1</sup>	Geologic unit	Silica (SiO <sub>2</sub> )	Calcium (Ca)	Magnesium (Mg)	Chloride (Cl)
CL-1-----	Jefferson	8535-3820	Louisville limestone-----	-----	200,200	100,800	100
CL-2-----	do	8535-3820	Waldron shale-----	295,000	-----	-----	700
CL-3-----	do	8535-3820	Laurel dolomite-----	-----	225,800	107,400	200
CL-4-----	Oldham	8525-3820	Limestone of Richmond group-----	-----	176,100	85,800	100
CL-5-----	do	8525-3820	Shale of Richmond group-----	218,000	-----	-----	100
CL-6-----	Shelby	8510-3810	Shale of Maysville group-----	243,000	-----	-----	100
CL-7-----	do	8510-3810	Limestone of Maysville group-----	-----	358,600	6,000	<100
CL-8-----	Franklin	8455-3805	Shale of Eden group-----	546,000	-----	-----	100
CL-9-----	do	8455-3805	Limestone of Eden group-----	-----	379,100	5,700	<100
CL-10-----	do	8500-3805	Limestone of Cynthiana formation-----	-----	365,700	10,800	<100
CL-11-----	do	8500-3805	Shale of Cynthiana formation-----	384,000	-----	-----	100
CL-12-----	do	8450-3810	Limestone of Lexington group-----	-----	383,400	2,760	<100
CL-13-----	do	8450-3810	Shale of Lexington group-----	244,000	-----	-----	100
CL-14-----	do	8450-3810	Limestone of High Bridge group-----	-----	379,900	4,920	100
CL-15-----	do	8450-3810	Shale of High Bridge group-----	560,000	-----	-----	1,400

<sup>1</sup> Longitude and latitude of the southeast corner of the 5-minute quadrangle in which sample was collected.

Most of the limestone of the Blue Grass region is high in calcium and relatively low in magnesium (table 6). Only a few samples contain more than 100,000 ppm of magnesium, and most of these are of rocks of Silurian age. The relatively low magnesium-calcium ratios in the rocks are reflected to some degree in low magnesium-calcium ratios in natural waters. Impurities in the limestone are chiefly sand and insoluble silicates. Probably the chief influence of these impurities on the chemical character of natural waters is through ion exchange between percolating waters and the clay minerals. Ion exchange with the clay minerals in the shale also affects the chemical character of natural waters. Most of the shale of the Blue Grass region contains moderate amounts of soluble calcareous material (table 5). Only the black shale of Devonian age and shale of Mississippian age are relatively free of soluble calcium and magnesium carbonate.

### CHEMICAL CHARACTER OF WATER IN THE CONSOLIDATED ROCKS

Water moves through rocks in both the zone of aeration and the zone of saturation, that is, above and below the water table. Following is an analysis of the wet-weather discharge from a solution channel in the Louisville limestone above the Waldron shale at a roadcut along U.S. Highway 42 near Louisville.

*Chemical constituents in parts per million*

Silica (SiO <sub>2</sub> )-----	9.5	Phosphate (PO <sub>4</sub> )-----	0.02
Iron (Fe)-----	.07	Dissolved solids:	
Manganese (Mn)-----	.00	Calculated from determined	
Calcium (Ca)-----	53	constituents-----	232
Magnesium (Mg)-----	20	Residue on evaporation at	
Sodium (Na)-----	1.6	180°C-----	227
Potassium (K)-----	.6	Hardness as CaCO <sub>3</sub> :	
Bicarbonate (HCO <sub>3</sub> )-----	208	Calcium, magnesium-----	214
Carbonate (CO <sub>3</sub> )-----	0	Noncarbonate-----	44
Sulfate (SO <sub>4</sub> )-----	24	Specific conductance (micro-	
Chloride (Cl)-----	3.4	mhos at 25°C)-----	395
Fluoride (F)-----	.2	pH-----	7.2
Nitrate (NO <sub>3</sub> )-----	17	Color-----	1

This sample may be typical of vadose water (water in the zone of aeration) in the Blue Grass region. Because samples of water from the zone of aeration generally are difficult to obtain, the discussion that follows is generally confined to the chemical character of water in the zone of saturation in consolidated rocks.

Most of the analyses of ground water used as basic data in this report were obtained and analyzed by the Geological Survey for earlier investigations. Only a few were collected specifically for this study. Results of comprehensive analyses of ground-water samples are listed in table 7. Where analyses of several samples from the same well or spring are available, only two, the highest and lowest in dissolved solids, are listed. Partial analyses are not listed in this table, but partial analyses were used as data for some of the illustrations.

The chemical character of ground water in the Blue Grass region is shown graphically on plate 4 and figures 5-14. Plate 4 is a map of the Blue Grass region that shows by means of bar diagrams the concentration of the various constituents in representative samples of ground water. Each constituent is represented by a part of a bar graph that is proportional to the concentration of the constituent, in equivalents per million, in the water sample. The ratios, by weight, of various cations and anions in ground waters of the Blue Grass region are shown graphically in figures 5-11. The ratios of the various constituents were computed from comprehensive analyses of ground-water samples. Many of these are repeat samples from the same well or spring, and not all are given in table 7.

TABLE 7.—*Chemical analyses of selected ground water of the Blue Grass region*

[Analyses by U. S. Geol. Survey. Chemical constituents in part per million. The geologic units are in ascending order, from oldest to youngest, the analyses within each unit are in descending order of total dissolved solids. Type of well: Dr, drilled; Du, dug; S, spring]

Well	Type of well	Date of collection	Silica (SiO <sub>2</sub> )	Aluminum (Al)	Iron (Fe)	Manganese (Mn)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potash (K)	Lithium (Li)	Bicarbonate (HCO <sub>3</sub> )	Carbonate (CO <sub>3</sub> )	Sulfate (SO <sub>4</sub> )	Chloride (Cl)	Fluoride (F)	Nitrate (NO <sub>3</sub> )	Phosphate (PO <sub>4</sub> )	Dissolved solids (residue on evaporation at 180° C)	Calcium, magnesium	Noncarbonate	Hardness as CaCO <sub>3</sub>	Specific conductance (micromhos at 25° C)	pH
High bridge group																								
8445-3800-4	Dr	9-28-55	7.8	---	1.3	0.19	121	8.7	2.0	1.2	---	342	0	38	2.5	0.2	25	---	---	375	338	57	618	7.3
8435-3750-50	Dr	9-19-51	4.4	---	10	.00	82	14	15	2.2	---	222	0	75	26	.2	1.0	---	---	347	262	80	590	7.6
3745-16	Dr	9-19-51	6.4	---	.47	.00	82	14	5.3	2.1	---	260	0	49	9.5	.2	1.7	---	---	310	262	49	507	8.0
8430-3750-23	Dr	8-23-51	11	---	.17	.36	86	12	8.5	2.2	---	306	0	26	9.0	.2	5.0	---	---	307	264	13	526	7.4
	Dr	9-28-55	11	---	.24	.00	90	6.1	2.7	.7	---	278	0	14	3.5	.2	12	0.09	---	283	250	22	470	7.4
	Dr	4-19-56	9.0	---	.65	.10	61	4.3	1.8	.6	---	174	0	14	3.0	.2	11	---	---	199	170	27	328	7.3
Lexington group																								
8435-3755-31	Dr	8-4-56	10	---	0.09	.00	141	55	341	82	0.2	231	0	43	848	.8	1.0	---	---	1,720	578	389	3,010	7.7
	Dr	10-18-55	8.0	---	1.2	.00	48	27	19	2.3	---	229	0	45	22	.9	.5	---	---	288	231	43	510	7.6
27	Dr	8-13-52	9.6	---	.13	.00	60	38	176	9.6	---	309	0	41	290	.8	.0	---	---	795	309	53	1,480	7.0
8415-3800-11	Dr	3-1-54	7.5	---	.65	.00	102	22	60	3.3	---	312	0	78	99	.8	.3	---	---	528	345	59	903	7.3
9	Dr	3-1-54	6.9	---	.24	.00	119	20	30	2.3	---	292	0	112	59	.7	2.2	---	---	513	382	140	825	7.2
8415-3800-16	Dr	10-26-54	8.0	---	.19	.05	94	17	60	4.9	---	313	0	75	72	.7	1.8	---	---	490	307	48	842	7.4
12	Dr	10-26-54	8.0	---	.03	.00	98	29	42	3.6	---	348	0	65	69	.7	.5	---	---	488	364	79	834	7.5
8435-3755-30	Dr	1-13-56	9.1	---	1.0	.04	75	24	62	1.2	---	238	0	42	30	.7	.5	---	---	464	286	91	887	7.2
	Dr	4-19-56	9.1	---	1.5	.03	58	22	17	2.1	---	324	0	42	30	.1	4.1	---	---	297	235	64	712	7.3
8435-3735-2	Dr	10-3-51	8.1	---	.20	.00	117	17	20	7.7	---	364	0	73	30	.1	4.1	---	---	458	380	64	712	7.3
	Dr	7-11-51	9.0	---	.17	.00	86	22	33	4.0	---	297	0	69	35	.7	.9	---	---	380	292	47	675	6.7
8415-3820-1	Dr	2-13-52	7.4	---	.19	.00	96	16	16	2.7	---	288	0	73	35	.7	.9	---	---	376	304	60	606	7.9
8435-3800-1	Dr	9-28-55	8.9	---	.39	.11	103	9.1	16	4.8	---	288	0	28	31	.2	1.7	0.09	---	380	294	58	628	7.2
8430-3805-27	S	9-28-55	8.9	---	.47	.15	69	7.0	3.2	1.4	---	183	0	38	7.7	.2	.9	---	---	217	201	51	593	7.3
	S	4-19-56	9.2	---	.21	.02	92	8.0	17	1.4	---	201	0	47	32	.5	.3	---	---	363	262	98	562	6.8
	S	12-27-51	8.3	---	.16	.01	53	3.9	2.0	1.0	---	143	0	25	3.5	.2	11	---	---	201	162	44	329	8.0
2310-51	S	8-9-56	14	---	.29	.10	92	14	14	.7	---	253	0	54	25	.2	6.3	---	---	356	287	80	713	7.5
8440-3800-2	Dr	4-20-56	6.8	---	.29	.24	68	8.9	5.8	.7	---	188	0	46	56	.8	.1	---	---	348	206	52	442	7.4
	Dr	10-22-54	8.6	---	.03	.00	54	23	41	4.2	---	226	0	54	56	.8	.1	---	---	348	228	44	626	7.6
8415-3800-17	Dr	1-2-52	8.7	---	.06	.00	62	31	16	4.2	---	316	0	30	24	.2	1.0	---	---	345	280	23	589	7.9
8450-3765-1	Dr	2-13-52	8.9	---	1.6	.48	90	14	16	2.2	---	307	0	37	17	.4	2.3	---	---	340	282	31	572	7.3
8430-3810-29	Dr	2-21-52	7.8	---	.37	.00	59	29	21	3.3	---	302	0	45	18	.9	.9	---	---	325	266	19	573	7.7



TABLE 7.—*Chemical analyses of selected ground water of the Blue Grass region—Continued*

[Analyses by U.S. Geol. Survey. Chemical constituents in part per million. The geologic units are in ascending order, from oldest to youngest, the analyses within each unit are in descending order of total dissolved solids. Type of well: Dr, drilled; Du, dug; S, spring]

Well	Type of well	Date of collection	Silica (SiO <sub>2</sub> )	Aluminum (Al)	Iron (Fe)	Manganese (Mn)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potash (K)	Lithium (Li)	Bicarbonate (HC O <sub>3</sub> )	Carbonate (C O <sub>3</sub> )	Sulfate (SO <sub>4</sub> )	Chloride (Cl)	Fluoride (F)	Nitrate (NO <sub>3</sub> )	Phosphate (P O )	Dissolved solids (rest- due on evaporation at 180° C)	Calcium, mar- nesium	Hardness as CaCO <sub>3</sub>	Specific conductance (micromhos at 25° C)	pH	
Maysville group																								
3515-3810-2	Dr	10-31-56	8.3	---	0.40	---	623	258	5,000	40	---	169	0	804	8,940	2.8	66	---	115,800	2,670	2,530	25,300	7.3	
3520-3755-1	Dr	4-17-56	2.7	0.0	3.89	0.00	320	80	807	22	---	0	0	1.4	2,200	.4	.9	---	4,000	1,130	1,130	6,960	2.8	
3435-3735-1	Dr	1-14-56	3.5	---	3.3	.16	25	15	96	6.8	---	252	0	98	93	.7	.7	---	367	124	0	700	7.6	
9430-3900-73	Dr	10-3-51	9.4	---	.16	.00	86	35	128	15	---	428	0	114	142	.2	2.7	---	720	360	8	1,180	7.2	
3515-3810-1	Dr	1-19-50	8.0	---	.11	.00	97	23	26	---	---	268	0	114	17	.6	36	---	461	337	117	708	7.5	
3515-3810-1	Dr	8-7-56	10	---	.14	.00	108	18	14	---	---	309	0	56	25	.1	35	---	418	343	90	711	7.2	
3510-3800-2	Du	4-19-56	9.4	---	.14	.00	92	18	9.5	2.0	---	278	0	41	16	.2	34	---	349	304	76	586	7.6	
3515-3750-1	Du	1-13-56	11	---	.27	.07	97	8.2	9.3	7.0	---	184	0	66	13	.0	86	---	390	276	125	616	7.7	
3515-3750-1	Du	4-19-56	12	---	.11	.00	87	8.7	7.9	8.7	---	168	0	56	13	.1	75	---	368	253	115	538	7.2	
3510-3805-3	S	2-13-52	6.2	---	.50	.09	93	12	16	7.4	---	278	0	65	15	.2	9.4	---	364	282	54	592	7.6	
3510-3805-3	S	10-30-56	11	---	.02	.00	90	8.3	5.6	1.6	---	261	0	28	7.0	.1	17	---	305	259	44	518	7.4	
3510-3805-3	S	1-12-56	2.9	---	3.1	.17	26	5.7	3.7	.7	---	82	0	21	5.5	.1	2.8	---	114	88	21	202	7.8	
9440-3730-1	S	10-3-51	4.6	---	.88	.00	30	14	6.5	2.4	---	152	0	1.7	12	.1	1.6	---	153	134	8	285	7.6	
Richmond group																								
8528-3812-1	Dr	10-30-56	11	---	0.14	0.00	26	12	259	9.0	0.8	511	0	20	180	0.2	3.7	---	764	115	0	1,340	7.5	
3813-1	Dr	4-18-56	9.9	---	.19	.02	26	13	194	7.1	---	480	0	13	96	.7	2.5	---	603	118	0	1,040	7.6	
8520-3805-8	Du	8-8-56	55	---	.01	.00	52	19	102	5.2	.4	462	0	16	34	.8	.1	---	496	208	0	795	8.0	
8520-3805-8	Du	1-12-56	12	---	.29	.04	48	18	97	7.2	---	436	0	13	36	.0	.0	---	442	194	0	777	7.2	
3813-56	Du	9-16-55	8.7	---	.65	.04	129	13	7.0	6.3	---	296	0	62	8.2	.1	107	---	495	375	133	795	8.2	
3813-56	Du	3-13-56	7.1	---	1.0	.06	113	11	5.7	5.5	---	228	0	52	8.8	.1	105	---	429	327	140	664	7.6	
3820-9	S	8-7-56	20	---	.04	.14	82	44	7.5	1.0	---	388	0	36	10	.1	41	---	425	386	68	724	7.6	
3810-11	S	4-18-56	13	---	.04	.00	58	36	5.5	.8	---	292	0	28	7.0	.1	26	---	309	293	54	638	7.3	
3810-11	Du	3-13-56	9.0	---	.59	.00	82	12	31	5.2	---	134	0	55	38	.0	125	---	418	254	144	663	7.3	
3810-11	Du	9-16-55	13	---	.24	.01	75	12	19	2.6	---	207	0	28	21	.0	71	---	337	236	67	546	7.8	

4	Du	8-8-56	34	---	---	0.00	66	15	10	1.2	---	232	0	26	7.2	1.1	18	---	226	36	465	8.0
---	Du	4-20-56	8.7	---	---	.70	00	52	3.4	1.4	---	157	0	25	6.3	.1	22	---	179	50	348	7.5
---	Dr	2-21-52	8.7	---	---	.52	00	61	3.6	.9	---	289	0	15	8.0	.1	27	---	280	43	521	7.9

Silurian system

530-3814-1	Dr	8-7-56	4.8	---	14	0.18	338	222	39	8.0	---	386	0	1,420	38	0.0	---	2,460	1,760	1,440	2,660	7.0	
8-17-56	Dr	5.0	---	---	14	.07	328	221	42	9.3	---	400	0	1,360	35	.3	---	2,360	1,730	1,400	2,510	7.1	
4-4-56	Dr	8.8	0	1.1	.03	116	59	570	17	12	305	0	51	1,110	.5	.5	0	2,190	284	3,930	7.6		
1-14-56	Dr	20	---	.13	.00	49	25	114	5.9	---	378	0	91	56	.6	.6	---	528	225	0	901	7.5	
1-14-56	Dr	14	---	.25	.00	68	28	94	4.9	---	356	0	93	46	.6	2.0	---	505	260	0	853	7.4	
1-14-56	S	14	---	.02	.00	68	37	6.8	4.4	---	320	0	28	10	.1	.48	---	352	322	60	825	7.7	
2-14-52	S	11	---	.17	.00	61	34	5.2	1.2	---	283	0	19	23	.1	.37	---	312	290	52	544	7.7	
10-30-56	S	13	---	.02	.06	80	24	14	4.3	1.5	---	304	0	23	26	.0	.36	---	360	298	49	639	7.4
4-18-56	S	12	---	.05	.00	61	18	14	4.3	1.0	---	188	0	11	11	.1	.19	---	210	194	40	567	8.0
1-4-55	S	11	---	.01	.00	48	34	9.0	1.1	---	291	0	20	11	.1	.44	---	361	293	54	587	8.2	
2-14-52	S	11	---	.17	.00	61	34	5.2	1.2	---	283	0	19	23	.1	.37	---	312	290	52	544	7.7	
3-17-53	S	11	---	.49	.00	52	29	3.1	1.0	---	226	0	29	5.0	.1	.21	---	275	248	49	460	8.3	
529-3815-1	S	7.5	---	.3	.00	37	30	1.2	.6	---	224	0	16	2.0	.0	6.0	---	216	215	32	393	7.9	
530-3750-1	S	---	---	.14	.00	41	22	1.9	.5	---	202	0	29	2.5	.2	.18	---	205	194	27	369	7.8	
2-20-52	S	9.2	---	.52	.00	35	22	1.6	.6	---	198	0	8.6	1.9	.1	.14	---	185	177	16	335	7.9	
525-3745-4	S	9.5	---	.80	.24	29	16	1.4	.3	---	165	0	1.5	1.2	.1	4.8	---	140	138	3	266	7.3	
2-20-52	S	9.5	---	.80	.24	29	16	1.4	.3	---	165	0	1.5	1.2	.1	4.8	---	140	138	3	266	7.3	
9-28-54	S	7.8	---	.03	.00	24	11	.9	.5	---	96	0	5.4	2.0	.0	.22	---	109	103	26	209	7.7	

Devonian system

455-3735-5	Dr	11-27-56	12	0.2	4.6	0.55	37	38	850	11	3.8	760	0	264	880	1.0	8.8	.1	2,520	249	0	4,340	7.3
350-3745-3	Dr	11-27-56	8.8	.1	.46	.02	34	11	180	6.9	1.0	448	0	47	114	.4	.8	.0	381	130	59	1,080	7.7
430-3725-1	Dr	10-3-51	11	---	.34	.00	66	31	19	3.8	.4	284	0	86	20	.2	26	.1	336	286	81	594	7.3
355-3745-1	S	11-27-56	18	0	.03	.00	91	7.3	5.9	3.5	---	215	0	14	4.6	.2	4.5	---	340	257	31	524	7.6
533-3817-1	Dr	8-7-56	15	---	.04	.00	63	37	2.9	.4	---	340	0	14	2.9	.1	20	---	324	309	31	567	7.6
541-3807-1	Dr	1-27-56	11	---	.00	.00	67	36	2.1	1.9	---	342	0	14	5.3	.5	17	---	309	315	35	559	7.5
541-3807-2	Dr	11-29-56	9.7	1	.23	.02	57	33	15	1.9	.8	360	0	9.8	12	.2	.0	---	312	278	0	561	7.7
510-3730-2	Du	11-27-56	13	.1	.74	.04	53	15	18	14	.7	186	0	73	5.3	.5	9.5	.0	300	194	42	499	7.7
541-3805-1	Dr	8-6-56	46	---	25	.82	41	19	13	2.7	---	185	0	41	17	.2	.1	---	267	180	29	422	6.8
541-3805-1	Dr	4-17-56	37	---	15	.12	36	20	13	2.5	---	188	0	41	18	.2	.1	---	252	172	34	393	6.7
535-3815-1	Dr	8-7-56	15	---	.45	.11	50	24	8.7	1.3	---	188	0	18	12	.1	26	---	279	248	43	492	7.3
535-3815-1	S	8-7-56	8.8	---	.45	.11	50	22	5.7	1.2	---	218	0	18	8.5	.1	18	---	230	215	37	417	7.2
330-3820-3	S	1-5-55	22	1.5	.01	.19	15	7.5	36	3.5	.3	3.2	0	128	21	.2	.5	.0	250	78	75	373	4.9

Mississippian system

8410-3730-1	S	8-22-51	7.6	---	.16	.00	40	3.4	0.5	0.2	---	138	0	2.0	1.0	0.0	1.0	---	126	114	1	226	7.3
8340-3745-1	S	7-25-51	6.5	---	.20	.00	14	1.0	1.0	.9	---	49	0	2.2	1.4	.0	.8	---	52	38	0	83.3	6.5
8340-3745-1	S	1-5-55	5.2	.0	.01	.00	8.7	1.0	.5	.9	---	29	0	2.8	.5	.0	1.0	.0	33	26	2	57.2	7.4

\* Sample not filtered; iron content caused by introduction of acid into well.



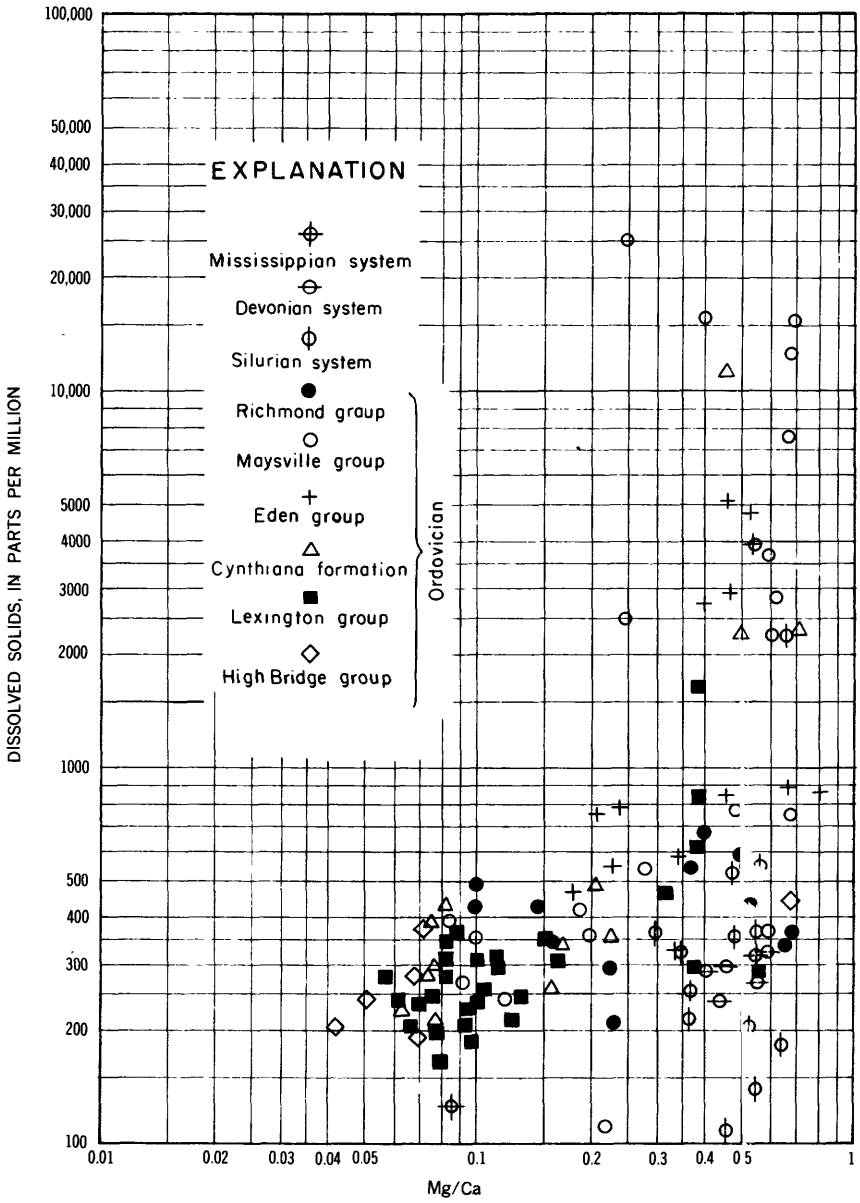


FIGURE 5.—Relation of dissolved solids and magnesium-calcium ratios, by weight, of samples of ground water from the Blue Grass region, Kentucky.

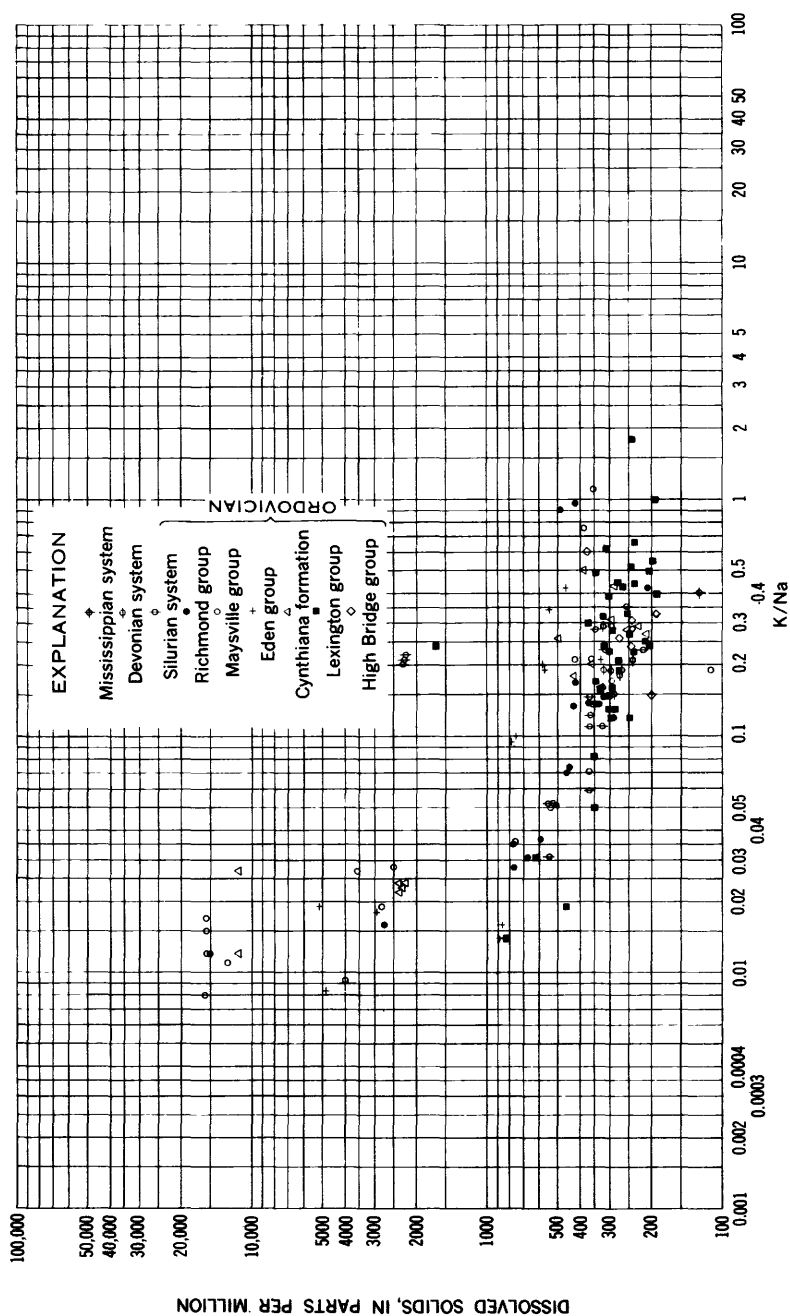


FIGURE 6.—Relation of dissolved solids and potassium-sodium ratios, by weight, of samples of ground water from the Blue Grass region. Kentucky.

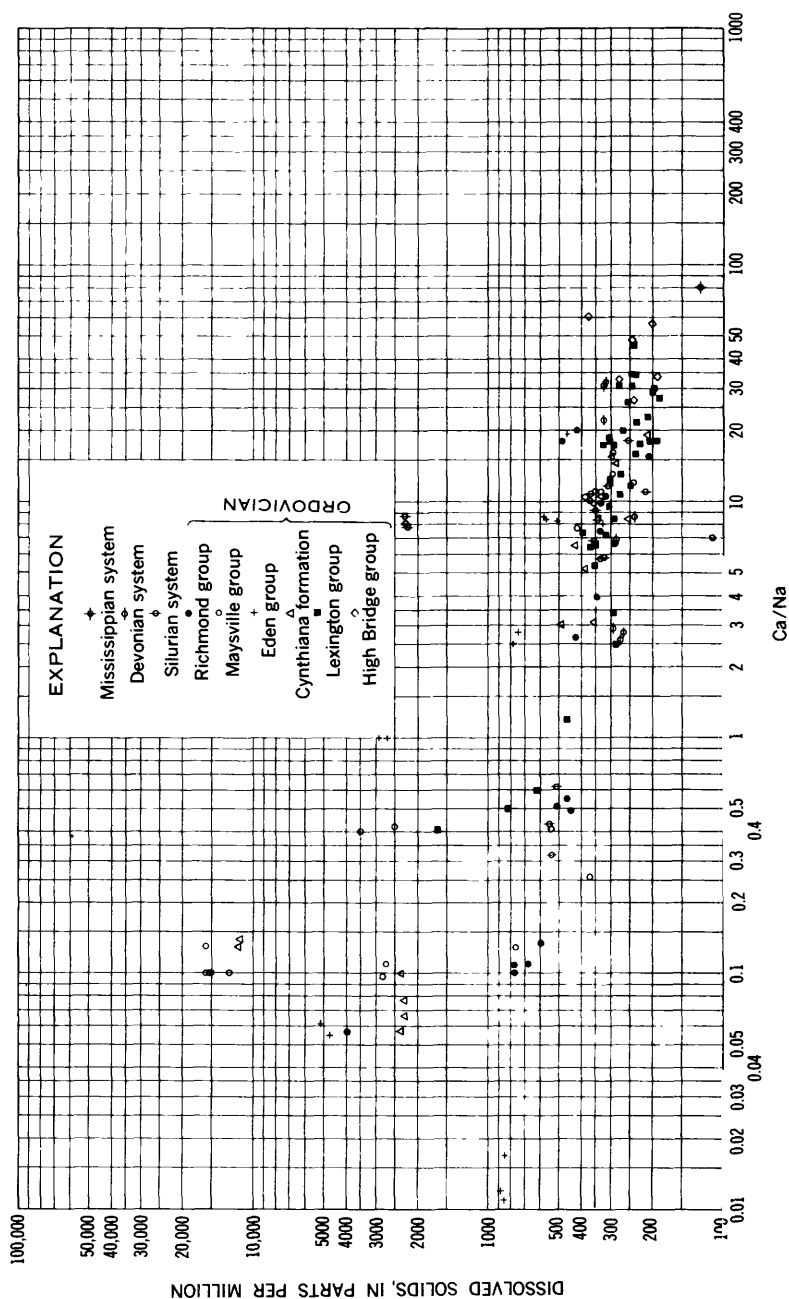


FIGURE 7.—Relation of dissolved solids and calcium-sodium ratios, by weight, of samples of ground water from the Blue Grass region, Kentucky.

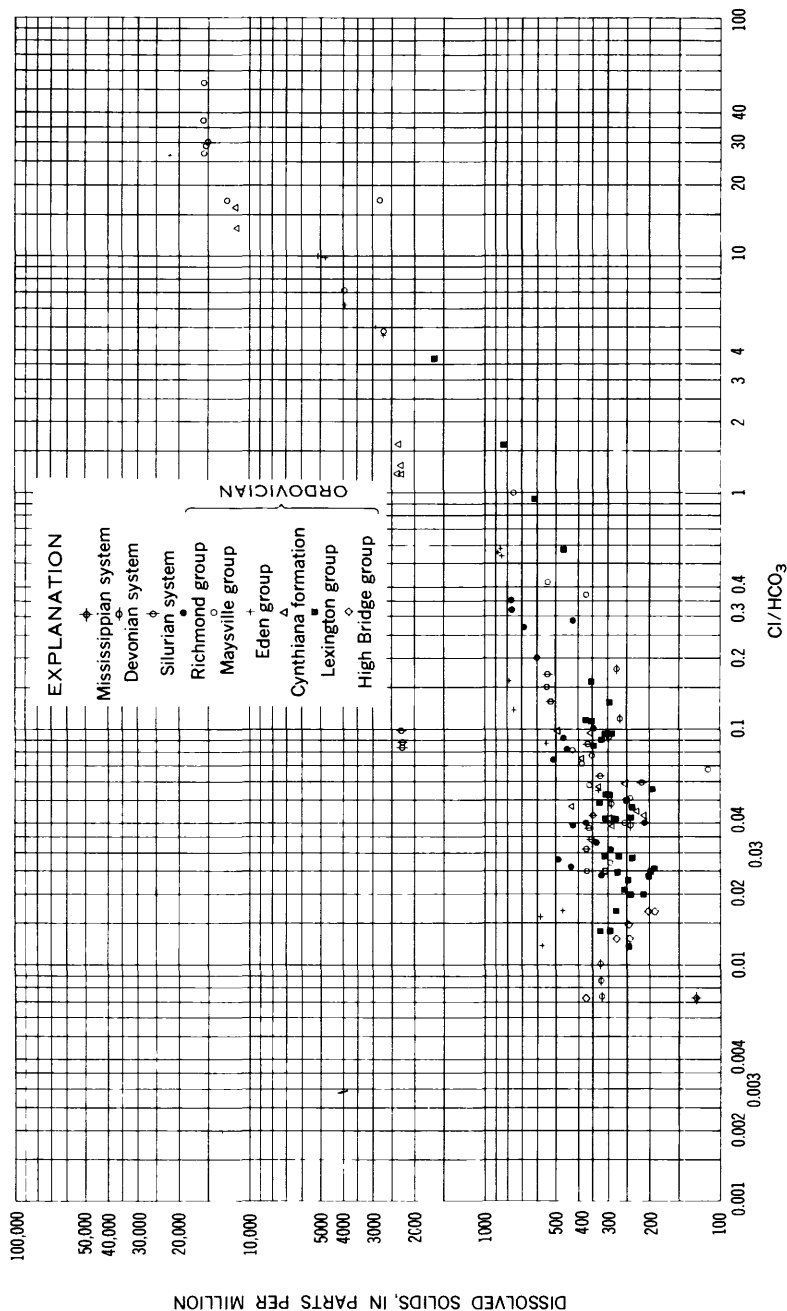


FIGURE 8.—Relation of dissolved solids and chloride-bicarbonate ratios, by weight, of samples of ground water from the Blue Grass region, Kentucky.

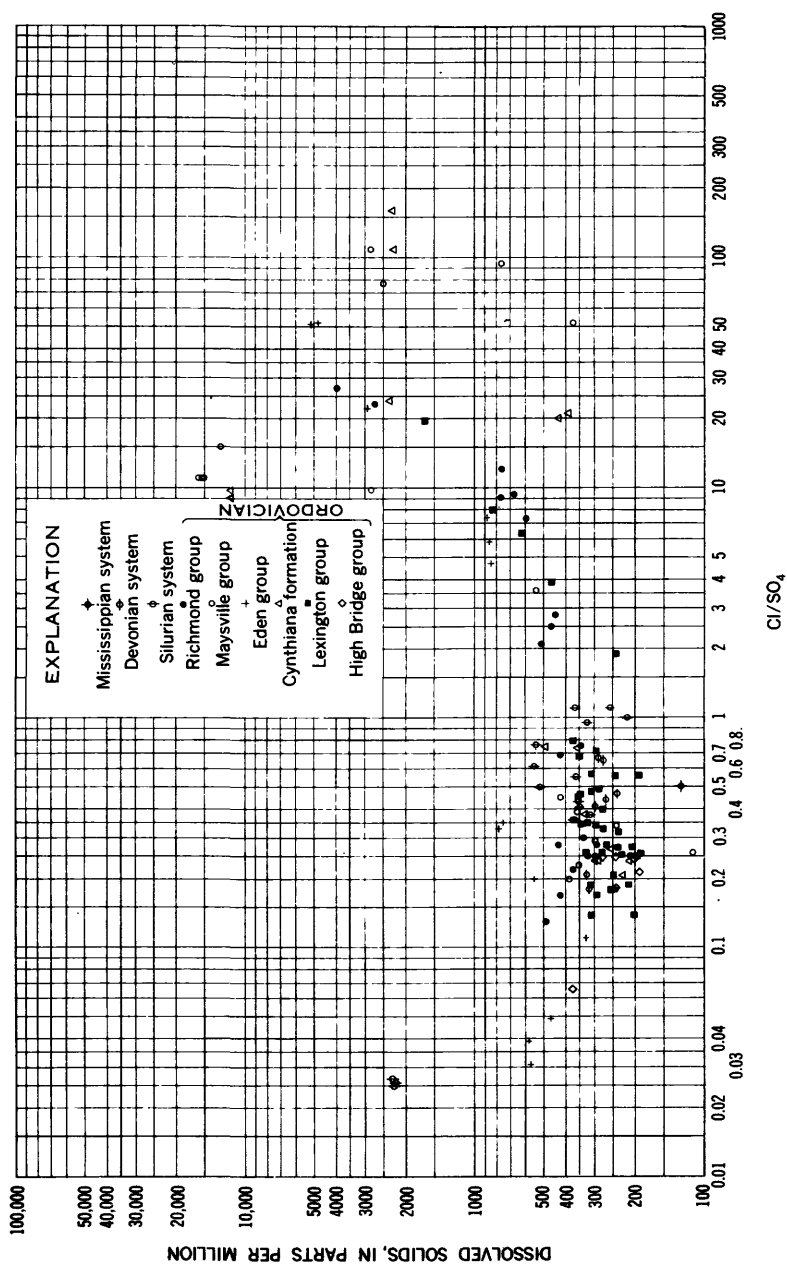


FIGURE 9.—Relation of dissolved solids and chloride-sulfate ratios, by weight, of samples of ground water from the Blue Grass region, Kentucky.

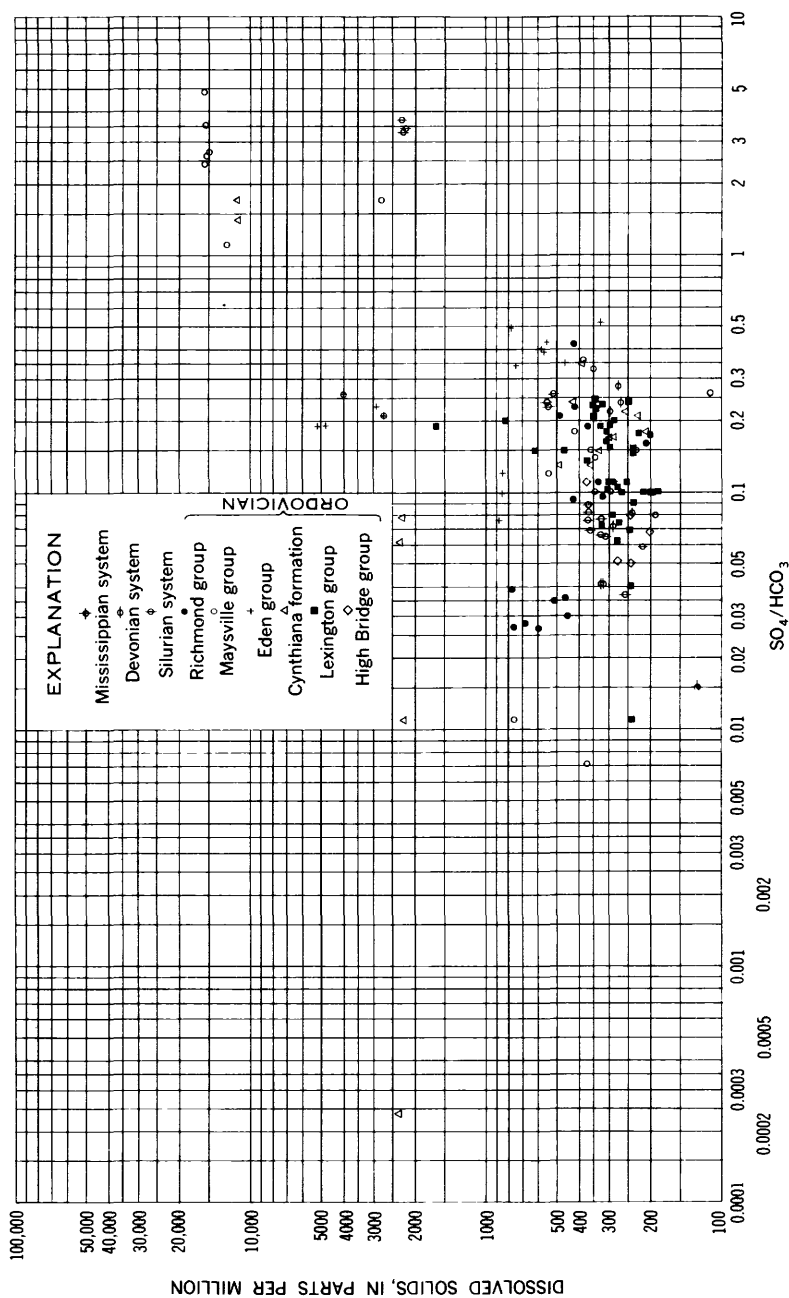


FIGURE 10.—Relation of dissolved solids and sulfate-bicarbonate ratios, by weight, of samples of ground water from the Blue Grass region, Kentucky.

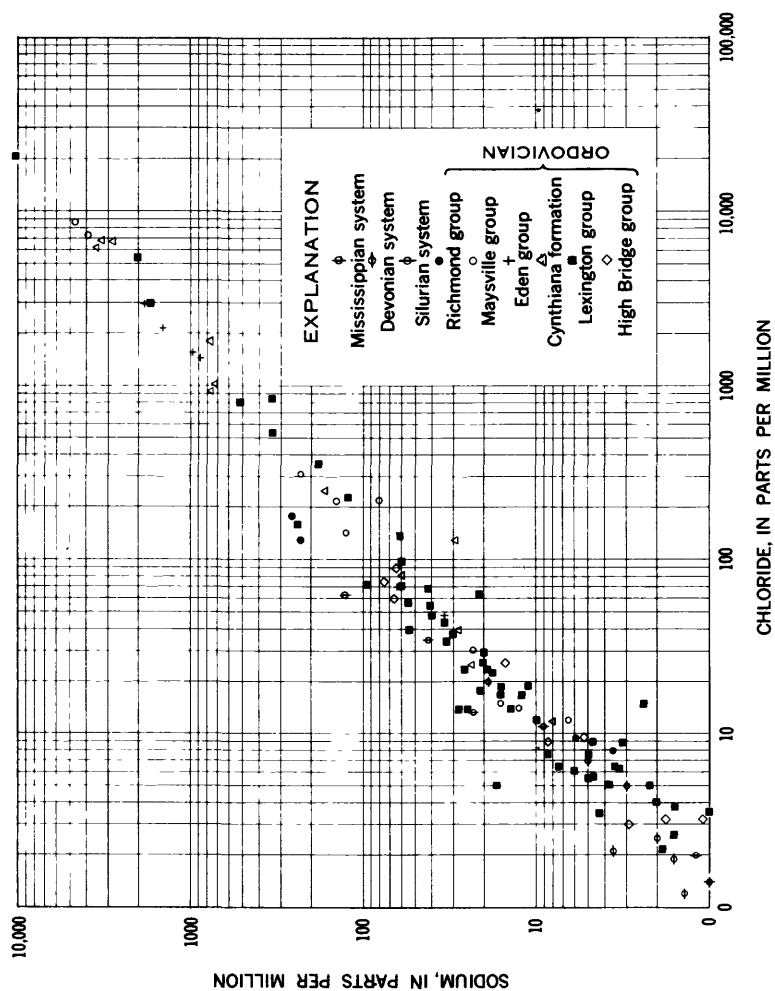


Figure 11.—Correlation of sodium and chloride concentrations in ground water of the Blue Grass region, Kentucky.

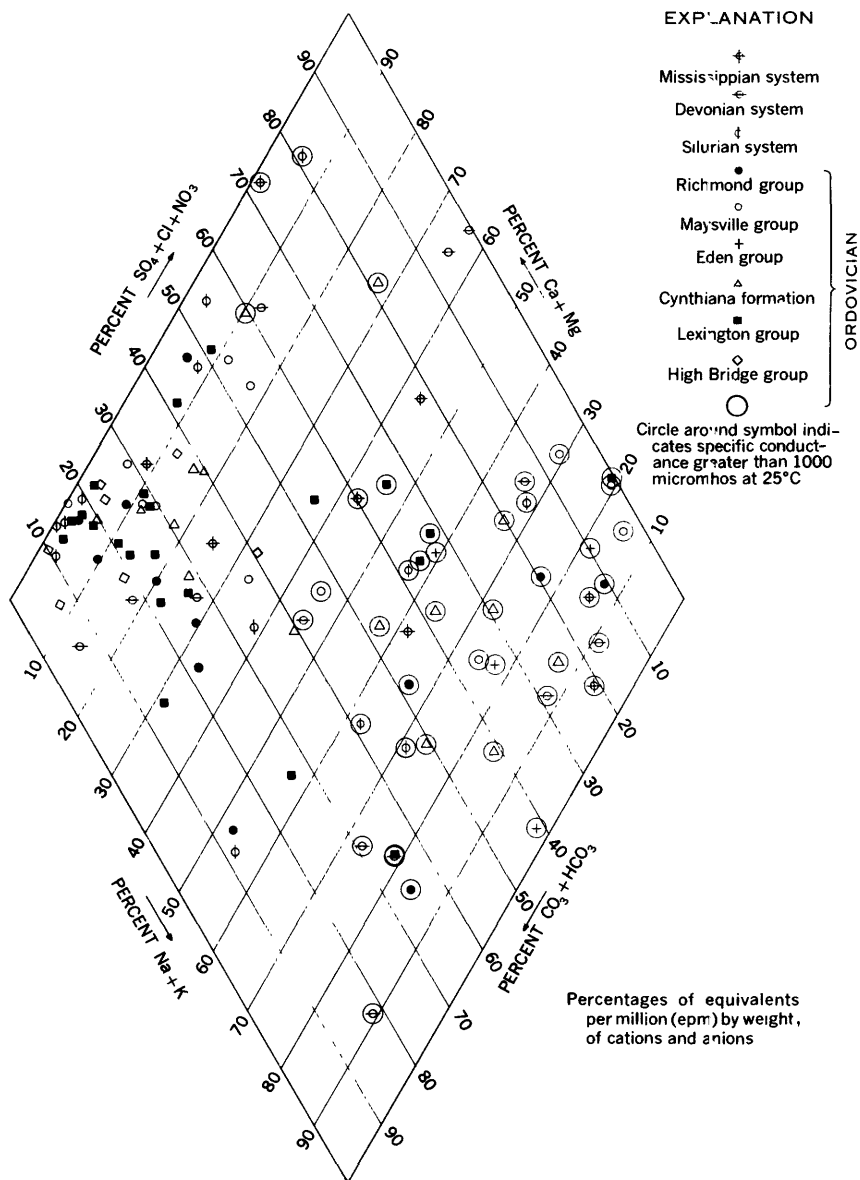


FIGURE 12.—Chemical character of water from drilled wells in the Blue Grass region, Kentucky.

Figures 12-14 are diamond-field diagrams which show the general chemical character of ground waters from the different geologic units in the Blue Grass region. Most, but not all, analyses listed in table 7 are plotted on the diagrams. Where points are closely spaced



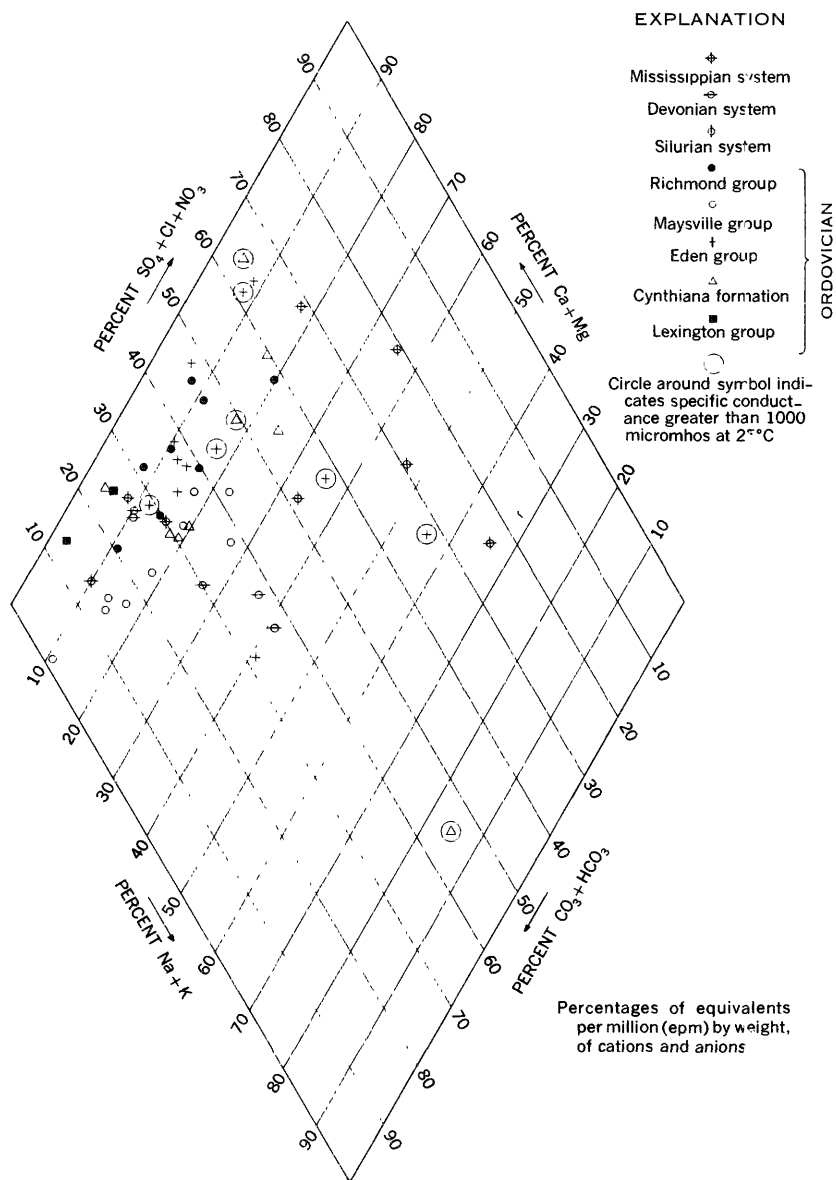


FIGURE 13.—Chemical character of water from dug wells in the Blue Grass region, Kentucky.

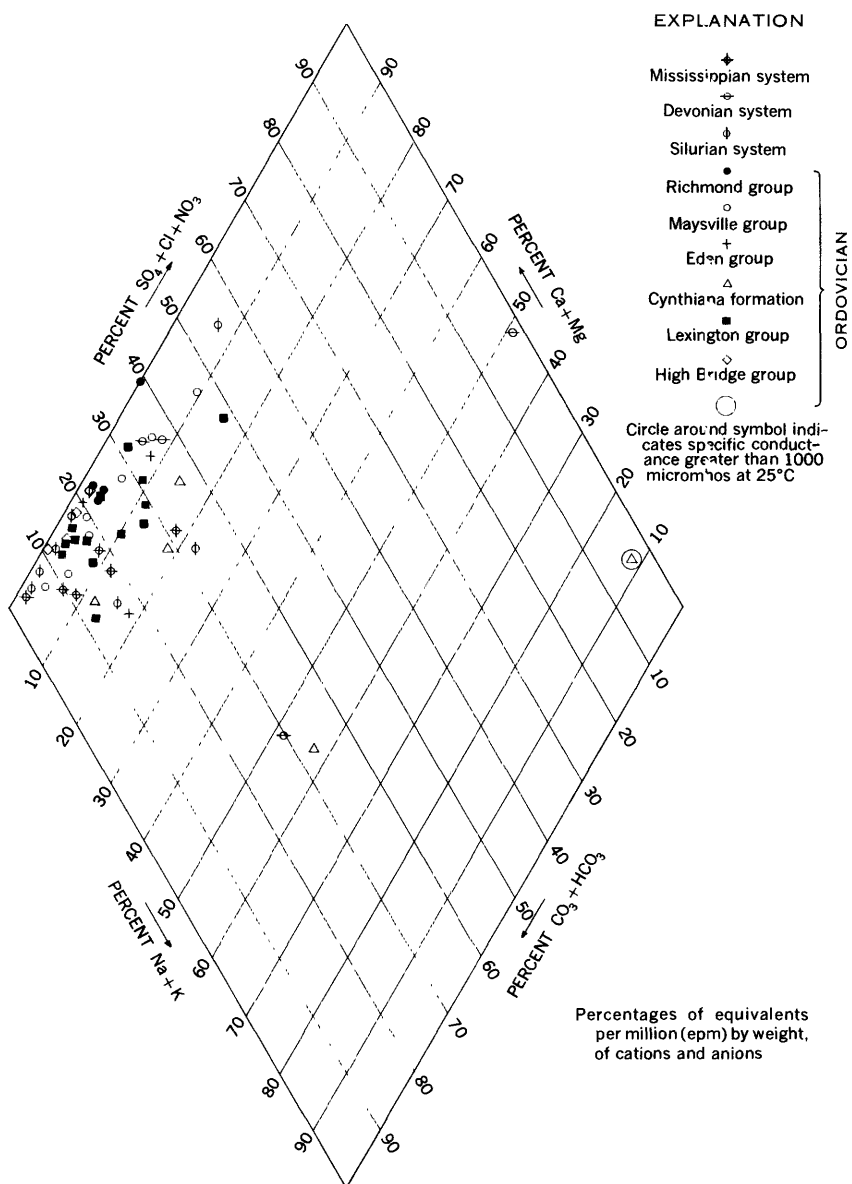


FIGURE 14.—Chemical character of water from springs in the Blue Grass region, Kentucky.

on the diagram a few of the analyses have been omitted. In addition, a number of partial analyses not listed in table 7 are included in the diagrams.

Each point on the diamond field represents a sample of water from a well or spring, and the position of the point indicates the chemical character of that sample. The points are plotted on the basis of percentages of equivalents per million of the cations and anions in the sample. Because water is a chemically balanced system, the total of the cations in equivalents per million is equal to the total of the anions. Only two groups each of cations and anions can be shown on the diamond field. Of the cations, calcium is grouped with magnesium and sodium with potassium because they are similar chemically and because they were not separated in partial analyses. In partial analyses, the value in equivalents per million of calcium plus magnesium is computed by dividing the value of calcium magnesium hardness in parts per million by 50. The value in equivalents per million of sodium plus potassium is computed by subtracting the value in equivalents per million of calcium plus magnesium from the total equivalents per million of the anions. Of the anions, bicarbonate and carbonate are somewhat similar chemically and are grouped together in the diagram. Of necessity, all the other major anions must be placed in the one remaining group. Thus sulfate, chloride, and nitrate are lumped together in the diagram.

Samples of natural waters of the Blue Grass are classified according to the predominant cation and anion, or group of cations and anions, that they contain. Because of the grouping of the ions in the diagrams, the classification of samples indicated in figures 12, 13, and 14 is very general. For example, samples that are represented in the left quarter of the diamond could be classed as the following types: calcium carbonate, calcium bicarbonate, magnesium carbonate, magnesium bicarbonate, or any combination of the above. The analyses listed in table 7, however, show that few samples contain significant amounts of carbonate. Therefore, we may classify these samples as calcium bicarbonate or magnesium bicarbonate type. Separate determinations of calcium and magnesium have not been made in partial analyses. For convenience, however, samples plotted in the left quarter of the diagram are classified as calcium magnesium bicarbonate types of samples.

Although samples plotted in the right quarter of the diagram also are subject to various classifications, most in the Blue Grass region are of the sodium chloride type. Potassium is a minor constituent in all waters of the Blue Grass, and sodium sulfate and sodium nitrate waters are unknown in this region. Most samples plotted in the top

quarter are calcium magnesium sulfate waters, and most samples in the bottom quarter are sodium bicarbonate waters.

In each of the three diagrams (figs. 12, 13, 14), the points are concentrated in the left quarter of the diagram (calcium magnesium bicarbonate type). With few exceptions, the calcium magnesium bicarbonate waters are relatively low in dissolved solids as indicated by specific conductance values of less than 1,000 micromhos at 25° C. Most of the samples having a specific conductance greater than 1,000 micromhos are in the right quarter of the diagram and are sodium chloride type waters. A relatively small number of samples plot in the top quarter (calcium magnesium sulfate waters) and fewer still in the bottom quarter (sodium bicarbonate type). Samples plotted in the top and bottom quarters generally are higher in dissolved solids than the samples of the calcium magnesium bicarbonate type and lower in dissolved solids than the samples of the sodium chloride type.

To summarize: The consolidated rocks of the Blue Grass region contain two major types of ground water—calcium magnesium bicarbonate waters of relatively low mineralization and sodium chloride waters of relatively high mineralization. Calcium magnesium sulfate waters and sodium bicarbonate waters, of moderate mineralization, are not common in the Blue Grass region.

The concentration of points in the left quarter of the diagram is greatest in figure 14, which represents samples from springs, and is least in figure 12, which represents samples from drilled wells. Conversely, the concentration of points in the right quarter is greatest in figure 12 and is least in figures 13 and 14. As indicated previously, the source of water for most springs is in the zone of abundant circulation, and almost all water in this zone is fresh and of the calcium magnesium bicarbonate type. Drilled wells may tap aquifers below the zone of abundant circulation which yield highly mineralized water generally of the sodium chloride type.

In general, most water in the Blue Grass region of equal mineralization are similar in relative amounts of dissolved constituents. However, there are some apparent differences in the chemical character of waters from the different geologic units. These differences are described in succeeding paragraphs.

#### HIGH BRIDGE GROUP

Ground-water from the High Bridge group is generally of the calcium magnesium bicarbonate type, as are most dilute ground waters of the Blue Grass region (figs. 12, 13, and 14). None of the samples analyzed were highly mineralized, but deep waters in the High Bridge group, especially at considerable depths below drainage, probably are highly mineralized and of the sodium chloride type. Magnesium-

calcium ratios of water from the High Bridge group generally are low (fig. 5), although magnesium-calcium ratios in the limestone of the High Bridge group are in the same range as those from most other geologic units in the Blue Grass region (tables 5, 6). Magnesium-calcium ratios in Blue Grass waters generally increase as mineralization increases, and the generally low magnesium-calcium ratios of High Bridge waters are no doubt due chiefly to their low mineral content. Potassium-sodium ratios in waters of the Blue Grass generally decline with increasing mineralization (fig. 6). The moderately high potassium-sodium ratio of High Bridge waters is related to their low mineralization. Because most of the potassium in rocks of the Blue Grass is fixed in the clay minerals, the potassium-sodium ratios in natural waters show little or no relation to potassium-sodium ratios in the rocks. In ground waters of the Blue Grass (fig. 7), calcium-sodium ratios generally decrease and chloride-bicarbonate and chloride-sulfate ratios (figs. 8, 9) generally increase as mineralization increases. Calcium-sodium ratios are high and chloride-bicarbonate and chloride-sulfate ratios are low in High Bridge waters because of their low mineralization.

#### LEXINGTON GROUP

Most samples of water from the Lexington group are calcium magnesium bicarbonate waters of low mineralization, but some of the samples are more highly mineralized and of the sodium chloride type (figs. 12, 13, and 14). A few samples of intermediate mineral content are calcium magnesium sulfate or sodium bicarbonate waters. More of the samples of water from the Lexington have higher magnesium-calcium ratios (greater than 0.3) than samples from the High Bridge group, chiefly because more of the Lexington samples are highly mineralized. Potassium-sodium ratios of Lexington waters (fig. 6) decline with increased mineralization, but in dilute water they may be higher than those of the waters in all other units of the region. Calcium-sodium ratios of Lexington waters generally are lower and chloride-bicarbonate and chloride-sulfate ratios higher than in waters of the High Bridge group.

#### CYNTHIANA FORMATION

Samples of water from the Cynthiana formation are of diverse types as indicated by the scatter of points on figures 12, 13, and 14. The samples are similar to those of other units in that most dilute waters are of the calcium magnesium bicarbonate type and most concentrated waters are of the sodium chloride type. One apparent difference in the waters from the Cynthiana formation as compared with those of the High Bridge and Lexington groups is that waters from some of the dug wells and springs are highly mineralized, whereas

waters from dug wells and springs in the older formations are dilute. The water from one spring in the Cynthiana has a dissolved-solids content of 11,500 ppm. Magnesium-calcium ratios of most of the ground-water samples from the Cynthiana are higher than many of those from the older formations because the samples of Cynthiana are relatively highly mineralized. Potassium-sodium ratios of the Cynthiana ground waters are generally low but are in the same range as in other waters of equal mineralization. Chloride-bicarbonate and chloride-sulfate ratios of Cynthiana waters increase with mineralization, and they range higher than do those of waters of the High Bridge or Lexington groups.

#### EDEN GROUP

Ground waters from most drilled wells in the Eden are highly mineralized and generally are of the sodium chloride type (fig. 12). Ground waters from some dug wells are also relatively high in dissolved solids and are of the calcium magnesium sulfate or sodium chloride type (fig. 13). Dilute waters from springs and dug wells are chiefly of the calcium magnesium bicarbonate type (fig. 14). Although the Eden group contains more shale than any of the underlying Ordovician units, some limestone of the Eden is remarkably pure. The magnesium-calcium ratios of three samples of limestone of the Eden group (tables 5, 6) are low in comparison with most limestone of the Blue Grass region. Magnesium-calcium ratios of ground waters from the Eden are, however, relatively high because of the generally high mineralization of the ground waters. Potassium-sodium and calcium-sodium ratios of most samples of ground water from the Eden are low because of the high mineralization of the waters. Calcium-sodium ratios of Eden waters range much lower than those of the waters of all other rocks of the Blue Grass region. Chloride-bicarbonate and chloride-sulfate ratios of Eden waters generally are high for the same reason.

#### MAYSVILLE AND RICHMOND GROUPS

Most dilute ground waters of the Maysville and Richmond groups are of the calcium magnesium bicarbonate type (figs. 12, 13, 14), but a few are of the calcium sulfate type. Highly mineralized waters of the Maysville and Richmond groups are of the sodium chloride type. Magnesium-calcium ratios of three samples of limestone of the Richmond group are higher than those in most samples of older limestone (tables 5, 6). Magnesium-calcium ratios of ground water from the Richmond also are slightly higher in waters of low mineralization (less than 400 ppm dissolved solids) than in waters from older rocks. Magnesium-calcium ratios of waters from the Maysville are in the same range as those of other waters of similar mineralization.

### SILURIAN SYSTEM

Most dilute ground waters of the Silurian rocks are calcium magnesium bicarbonate waters, although a few are of the calcium magnesium sulfate or sodium bicarbonate type (figs. 12, 13, 14). Few samples of water from the Silurian are highly mineralized, but highly mineralized waters probably occur generally at depth in the Silurian, especially on the east side of the Cincinnati arch where the Silurian is predominantly shaly. The relatively high magnesium-calcium ratios of Silurian limestone (tables 5, 6) are reflected in the relatively high magnesium-calcium ratios of dilute Silurian waters (fig. 5), especially at concentrations of dissolved solids less than 300 ppm.

### DEVONIAN SYSTEM

Samples of water from Devonian rocks of the Blue Grass are widely scattered in the diamond field diagrams of figures 12, 13, 14. Although most dilute waters of the Devonian plot in the left quarter of the diagrams, others are scattered in each of the remaining quarters. One sample plotted in the right quarter of the diagram (spring 8330-3820-3) was the only sodium sulfate type water collected in the Blue Grass. More highly mineralized waters from the Devonian generally are sodium chloride or sodium bicarbonate types. The ratios of various dissolved constituents in Devonian waters (figs. 5-11) appear to be about the same as those of other geologic units.

### MISSISSIPPIAN SYSTEM

The plots of both dilute and highly mineralized ground waters from dug and drilled wells in the Mississippian system are widely scattered (figs. 12, 13, 14), although none are of the sodium bicarbonate type. Plots of waters from springs are somewhat scattered, but all are dilute and of the calcium magnesium bicarbonate type.

## WEATHERING OF ROCKS AND SOILS AS A SOURCE OF DISSOLVED MATERIALS IN NATURAL WATERS OF THE BLUE GRASS REGION

The dissolved materials in fresh natural waters of the Blue Grass region are derived chiefly from weathering of rocks and soils. Other sources are the small amount of dissolved material carried in rainwater and an undetermined contribution from highly mineralized waters, possibly connate, which occur at depth everywhere in the region. Because the highly mineralized waters occur only where circulation of ground water is retarded, the contribution from these waters is probably small except in areas along faults where mineral springs occur.

### RATE OF WEATHERING

Neglecting the effect of cyclic salts in rainwater and contributions from connate waters, the chemical composition of residual soils reflects

the chemical composition of the rocks less the soluble products carried away in the natural waters plus other materials, chiefly organic, introduced in the soil-forming process. A comparison of the chemical composition of the rocks, soils, and dissolved materials carried by streams makes possible an estimate of the rate of reduction of the land surface by chemical weathering and the rate of soil formation in the region.

The quantity of dissolved solids carried by a stream draining a limestone area indicates, in a general way, the rate of lowering of the surface of the drainage area by solution. The rate of lowering of the surface of Salt River basin above Shepherdsville by solution was about 0.00005 feet per year for the period October 1, 1952, to September 30, 1956 (page 116).

The soils of the Salt River basin include about 90 percent sand, silt, and clay. If all of this relatively insoluble material were derived from the weathering of relatively pure limestone containing only about 5 percent of such material (table 5), it would take about 30,000 years to produce 1 inch of soil. Because the drainage basin of Salt River also includes outcrops of shale and shaly limestone which contain much more than 5 percent of insoluble material, soil formation may be much more rapid than the above figures indicate.

#### ZONES OF WEATHERING

Weathering occurs wherever earth materials are not in equilibrium with their environment (Keller, 1957, p. 5). Thus, weathering probably occurs in the Blue Grass region from the surface to at least the depths where only saline waters occur. The rate of weathering, however, is not constant but is much more rapid near the surface, where fresh water in large amounts moves through the earth materials.

Weathering takes place in both the rocks and the soils. Weathering of the rocks is most active at the soil-rock contact. The effect of weathering at the soil-rock contact is illustrated in figure 15, which shows a pinnacle surface resulting from such weathering. Below this contact, weathering is most active along the fracture openings enlarged by solution and decreases with depth as the size of the fracture openings decreases. Because water also moves through intergranular openings, weathering also occurs throughout the mass of the rock to at least the depths of fresh-water circulation. Movement of water through intergranular openings is very slow, however, and weathering is correspondingly slow. Because beds of shale between limestone units restrict the solution openings to shallow depths, the zone of relatively rapid weathering is limited to shallow depths in areas where shale is abundant.





FIGURE 15.—Weathering of limestone at soil-rock contact, in quarry at Louisville, Ky.

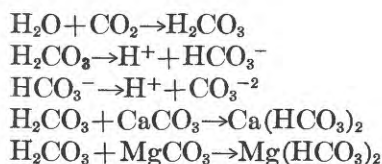
Weathering of the soils probably is most rapid at the top of the subsoil, where the clay minerals formed by the weathering of the rock are weathered further to simpler compounds and some of the soluble products are leached away. Organic activity, which promotes weathering, is, of course, most prevalent at and near the surface.

#### PROCESSES OF WEATHERING

The processes most effective in the chemical weathering of rocks and soils in the Blue Grass region include carbonation, simple solution, oxidation, reduction, hydrolysis, and ion exchange.

##### CARBONATION AS THE DOMINANT PROCESS OF WEATHERING OF LIMESTONE OF THE BLUE GRASS REGION

Weathering of limestone in a humid region usually is described as a process of solution; the relatively insoluble impurities of the limestone form the residual soil. Weathering of limestone, at least in shallow zones where the action is relatively rapid, however, is not solely a process of simple solution, for limestone is only very slightly soluble in cold water. Water entering the rocks from the overlying soil is charged with carbon dioxide. The process by which the limestone is brought into solution by this charged water is called carbonation (Keller, 1957, p. 43). The process is illustrated in the following chemical reactions:



The bicarbonates of calcium and magnesium are much more soluble than the carbonates and in shallow zones are readily carried away by circulating waters. Carbonation is most active where the water first enters the rocks because here the water is more highly charged with carbon dioxide and is slightly acid. In quarry faces in the Inner Blue Grass, solution openings, several inches to several feet in width at the top, can be seen to pinch out with depth, and at depths below a few tens of feet are generally paper thin. The water enters minute openings along joints and bedding planes and enlarges these openings as it dissolves the rock walls. Carbonation is not necessarily limited to shallow depths, however, for sulfuric acid formed by the oxidation of sulfides may react with the limestone to form carbonic acid. Carbonation also is effective in removing calcium and magnesium carbonate from calcareous shale.

#### **SIMPLE SOLUTION IN THE ROCKS AND SOILS OF THE BLUE GRASS REGION**

As ground water descends, it loses some of its free carbon dioxide and becomes moderately alkaline as it dissolves the limestone. Consequently, the process of carbonation is retarded, and at some undetermined depth it is possible that simple solution may become dominant. As indicated above, however, other weathering processes may release carbon dioxide at depth to further the carbonation process.

To determine the more soluble constituents in rocks of the Blue Grass region, eight samples of limestone and seven of shale were crushed and leached for 30 days with distilled water, and the leach was analyzed (table 8). Undoubtedly, the crushing of the rocks caused the release of constituents in different proportions than would be induced by natural waters circulating through the rocks. With few exceptions, potassium exceeded sodium in the leaches, whereas in all natural waters of similar concentration in the Blue Grass the sodium greatly exceeds the potassium. Magnesium-calcium ratios are also generally higher in the leaches than in natural waters. Most striking is the high sulfate content of the leaches which exceeded the computed bicarbonate content in about half of the samples. Chloride in the leaches was generally less than in natural waters of like concentrations.

As a result of leaching experiments on limestone from Illinois, Lamar and Shrode (1953) concluded that calcium and sulfate ions in the leaches came from intercrystal deposits of calcium sulfate, but the other ions probably came chiefly from intracrystal fluid inclusions. Possibly the sulfate in the Blue Grass leach also came from intercrystalline gypsum. The gypsum may have been formed by the action on limestone of sulfuric acid derived from the weathering of

TABLE 8.—*Solubility of crushed rock in distilled water, Blue Grass region, Kentucky*

[Analyses by U. S. Geol. Survey. Leaching time=30 days]

Sam- ple	Geologic unit	Rock analysis (ppm)				Amount of rock dissolved												Per- cent of total chlor- ide ex- tract- ed		
		Silica	Cal- cium	Mag- nesium	Chlo- ride	Calcium		Mag- nesium		Sodium		Potassium		Sulfate		Chloride			Computed bicarbonate	
						ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm	ppm	epm		ppm	epm
1	Slurian, Louisville lime- stone	200, 200	100, 800	100	100	400	19.96	280	23.03	26	1.13	52	1.33	1,420	29.56	22	0.56	935	15.33	22
2	Slurian, Waldron shale	295, 000	100, 800	700	100	398	19.85	139	11.43	23	1.00	159	4.07	1,110	23.11	12	.34	790	12.90	1.7
3	Slurian, Laurel dolomite	225, 800	107, 400	200	100	139	6.94	179	14.72	20	.87	24	.61	417	8.69	25	.71	780	12.74	13
4	Richmond group, Saluda limestone	176, 100	85, 800	100	100	139	6.94	80	6.58	23	1.00	61	1.54	139	2.89	11	.28	790	12.79	11
5	Richmond group, shale of Liberty formation	218, 000	100, 800	100	100	540	26.95	210	16.45	27	1.17	90	2.30	1,150	23.94	5	.14	1,390	22.89	5.0
6	Maysville group, shale	243, 000	100, 800	100	100	2,080	100.0	180	14.80	21	.91	84	2.15	4,970	103.47	8	.23	880	14.42	8.0
7	Maysville group, lime- stone	358, 600	6, 000	100	100	879	43.86	110	9.05	25	1.09	28	.72	2,080	43.30	18	.51	665	10.91	>18
8	Eden group, shale	546, 000	100, 800	100	100	719	35.88	190	15.62	20	.87	72	1.84	1,710	35.60	5	.14	1,130	18.47	5.0
9	Eden group, limestone	379, 100	5, 700	100	100	260	12.97	71	5.84	41	1.78	14	.36	480	9.99	32	.90	610	10.06	>32
10	Cynthiana formation, limestone	365, 700	10, 800	100	100	249	12.33	57	4.69	39	1.70	19	.49	479	9.97	50	1.41	480	7.83	>50
11	Cynthiana formation, shale	384, 000	10, 800	100	100	1,120	55.89	150	12.34	25	1.09	75	1.92	2,530	52.67	8	.23	1,120	18.34	10
12	Lexington group, lime- stone	383, 400	2, 760	100	100	137	6.84	17	1.40	27	1.17	4	.10	76	1.58	25	.70	440	7.23	>25
13	Lexington group, shale	244, 000	2, 760	100	100	1,040	51.90	95	7.81	31	1.35	36	.92	1,800	37.47	4	.11	1,490	24.40	4.0
14	High Bridge group, lime- stone	379, 900	4, 920	100	100	180	7.98	45	3.70	75	3.26	20	.51	310	6.45	72	2.12	420	6.88	75
15	High Bridge group, shale	560, 000	4, 920	1,400	1,400	1,190	55.99	290	22.07	949	43.87	470	12.92	7,010	145.24	219	5.92	420	6.88	15
16	High Bridge group, shale	560, 000	4, 920	1,400	1,400	1,060	52.89	428	35.20	936	40.70	618	15.81	6,790	141.36	219	6.18	420	6.88	16

1 Sample as above except crushed to pass 0.25 mm sieve. All others crushed to pass 0.50 mm sieve.

pyrite (p. 58). The sodium and chloride from the limestone may have been derived in part from intracrystal fluid inclusions, but it appears unlikely that this is the source of these elements in the shale. In this connection it should be noted that the amount of chloride leached from the limestone is, with but one exception, greater than the amount of chloride leached from shale of the same geologic unit. The single exception is the sample of shale from the High Bridge group. The high sodium and chloride in this sample may be due to the salt in the water of deposition, which, owing to its great depth below the surface, has never been flushed out. Part of the potassium leached from the limestone may be derived also from intracrystalline fluid inclusions, but some may have entered solution by ion exchange with the clay-mineral impurities of the limestone. The potassium leached from the shale, which exceeds that derived from the limestone in every unit, is almost certainly derived largely from ion exchange with the clay minerals. Crushing of the rocks undoubtedly increased the number of broken bonds and thus favored ion exchange with the leaching solution (Grim, 1953, p. 138). The bicarbonate in the leach (computed by difference from total cations and content of sulfate and chloride) may be derived in part from carbonation of the limestone due to the release of carbon dioxide in the formation of gypsum.

Seven samples of soils were collected in the outcrop areas of the major rock units of the Blue Grass region and were leached with distilled water for 3 days to determine the water-soluble constituents. Analyses of the leaches from the soils (table 4) indicated soluble materials in greatly different proportions than in those obtained from the crushed-rock samples. Magnesium-calcium and potassium-sodium ratios were much lower in the leaches from the soils than in the leaches from the crushed rock; the sulfate was much lower and bicarbonate correspondingly higher.

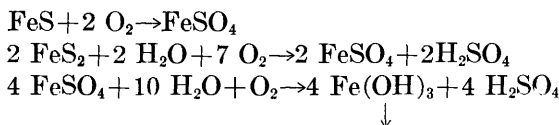
Magnesium-calcium ratios were somewhat lower and potassium-sodium ratios slightly higher in the soil leaches than in natural waters of like mineralization. With these exceptions, the amounts of dissolved constituents in the leaches closely resembled those in natural waters.

The closer resemblance of leaches of soils to natural waters as compared to the leaches of crushed rock probably is due to the crushing of the rocks, which presented materials for solution in different proportions than would occur in weathering under natural conditions.

#### OXIDATION OF IRON SULFIDE IN ROCKS AND SOILS OF THE BLUE GRASS REGION

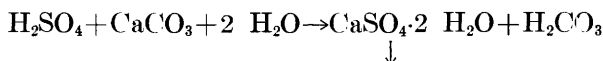
Much of the limestone and shale and some of the soils of the Blue Grass region contain small to moderate amounts of iron sulfide. Oxidation of this sulfide is a weathering process that is important

to this study chiefly because of the further effects of the products of oxidation. Pyrite (FeS) and other iron sulfides oxidize to form sulfuric acid and hydrous iron oxides. The following equations indicate some of the possible reactions:

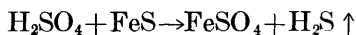


Between pH 7 and 6,  $\text{Fe}(\text{OH})_3$  is relatively insoluble. At lower pH values, the solubility increases until at pH 3 or less,  $\text{Fe}(\text{OH})_3$  is fairly soluble.

The sulfuric acid derived from these reactions is a potent weathering agent that reacts with calcium carbonate to form gypsum and carbonic acid.



The gypsum may be deposited in fracture openings, solution cavities, or intergranular pore spaces. Deposits of gypsum are common in caves of the Blue-Grass region. Gypsum is more soluble than calcite and may be carried away in solution by circulating water. The carbonic acid resulting from the reaction of sulfuric acid with the limestone further attacks the limestone by the process of carbonation as described on page 54. The sulfuric acid also may react with the ferrous sulfide to evolve hydrogen sulfide gas.



The hydrogen sulfide gas given off in this reaction may be one source of hydrogen sulfide detected by its odor in waters from many wells and springs in the Bluegrass. Sulfuric acid also may combine with the clay mineral illite in the shale and soil of the Blue Grass region to produce alums rich in potassium and sodium (Keller, 1957, p. 40).

#### HYDROLYSIS OF SILICATE MINERALS IN ROCKS AND SOILS OF THE BLUE GRASS REGION

Except for the minor impurities in limestone, silicate minerals in the Blue Grass region generally are present chiefly in the shale and in the soil. The silicate minerals in the shale presumably are chiefly the clay minerals, although small amounts of mica are present. Because the clay minerals in the shale were formed chiefly by hydrolysis of other silicate minerals, they probably are little affected by hydrolysis. The chief clay mineral of shale of the Blue Grass is illite.

The chief clay mineral of the subsoils of the region also is illite, which suggests that little alteration of the clay minerals occurs during weathering of the shale. Hydrolysis of the mica in the shale probably forms additional illite as the weathered product.

#### ION EXCHANGE IN CLAY MINERALS OF THE ROCKS AND SOILS OF THE BLUE GRASS REGION

As the clay minerals in the shale and soil of the region are a product of weathering, they may be considered relatively immune to further alteration by weathering. Clay minerals, along with other earth materials, however, are stable only as long as they are in equilibrium with their environment.

Natural waters, charged with varying amounts of magnesium, calcium, potassium, and sodium, provide a constant source of exchangeable cations to the clay minerals. A detailed discussion of the factors controlling ion exchange is included in Grim (1953, p. 126-159). The ion-exchange capacities of the three major groups of clay minerals are in the order montmorillonite > illite > kaolinite. Illite, as indicated on page 66, is the major clay-mineral constituent of the rocks and soils of the Blue Grass, although kaolinite makes up a considerable part of the clay minerals of some of the soils and is present in some of the rocks. Montmorillonite is locally present in small amounts in rocks and may be present in some of the soil. Marshall (1949) has shown that the bonding energies of cations adsorbed by a clay mineral are related to the position of the cation in relation to the crystal surfaces of the clay mineral. In montmorillonite, most of the cations are on basal plane surfaces, whereas in illite most of the cations are at the edges of the crystals.

Data obtained in the present investigation are insufficient to determine in detail the effects of ion exchange on the dissolved load of natural waters in the Blue Grass region. Experiments similar to the work of Woodruff (1955) on the ionic exchange between clay and dilute salt solutions probably would yield much useful data, especially if natural conditions were simulated.

It appears that the sodium bicarbonate waters that occur in the rocks of the Eden group and some other units may be the result of ion exchange in which the calcium and magnesium ions derived from the solution of limestone are exchanged for sodium ions that are loosely held in the clay minerals of the shale. The source of the sodium ions in the clays probably is the saline waters that occur at depth in the region.

Closely related to ion exchange is the removal of potassium from circulating waters by weathered illite. Weathering of the illite removes some of its original potassium resulting in a "degraded" illite (Grim, 1953, p. 152). Plants may also remove potassium from

the illite by ion exchange through the plant rootlets. The degraded clays are effective in removing potassium from solution to rebuild the normal illite structure. In a somewhat similar manner, degraded chlorite or montmorillonite may remove magnesium from solution.

### SOLUBLE PRODUCTS OF WEATHERING

The soluble products of weathering are carried away by natural waters percolating through the soils and rocks and discharging to the streams. The dissolved constituents in waters percolating through the soils and rocks and carried by the streams have been described in preceding sections. The following discussion will attempt to describe and account for changes in the dissolved materials as the water moves from the atmosphere through the soils and rocks to the streams of the region.

The water falling to the earth as rain generally contains small amounts of bicarbonate, sulfate, and chloride and some free carbon dioxide (table 1). As it percolates through the soil, the water picks up additional materials until it contains dissolved solids estimated to range from 100 to 300 ppm. The substances leached from the soils in the probable order of decreasing concentrations are bicarbonate, calcium, sulfate, silica, magnesium, chloride, potassium, nitrate, and iron. As compared to ground water in the underlying rocks, the soil water entering the rocks probably is relatively higher in calcium, bicarbonate, and nitrate and lower in sodium and chloride. It is generally charged with carbon dioxide and may be moderately acid, whereas most ground water in the Blue Grass region is somewhat alkaline. The dissolved material in the soil water entering the underlying rocks varies with the texture and thickness of the soil, the availability of soluble salts, the carbon dioxide content of the soil, air, and water, the soil temperature, and the rate of percolation through the soil. The availability of soluble salts may vary with time and may be strongly influenced by the length of time between heavy rains. During rainless periods the soluble salts formed on the surface by weathering can accumulate. Soluble salts deposited by evaporating ground water also accumulate during these periods. The rate of percolation is determined largely by the texture of the soil but may be influenced also by plant roots that upon decay provide easy routes of percolation.

As the water percolates from the soil into openings in the underlying rocks, it dissolves additional materials from the rocks. Not all water entering the rocks, however, has percolated through soil or mantle materials, for some water enters the rocks through sinkholes, and this water may have had only brief surface contact with the soil. In addition, some recharge takes place in valleys and gulleys

where rock crops out. The relative amounts of water recharged by percolation through soil and by direct entry into outcropping rocks has not been determined, but it may have an appreciable effect on the chemical character of the ground water.

The water that enters the rocks as surface runoff through sinkholes and in gulleys or valleys where rock crops out probably is lower in dissolved solids and may contain smaller amounts of free carbon dioxide than water that percolates through the soil into the rocks. The chemical character of this water probably resembles that of the floodwaters of small streams such as Elkhorn Creek (table 13). This water is low in dissolved solids and is moderately alkaline. Because sinkholes generally are better developed in the Inner Blue Grass than in the other subregions, a larger proportion of recharge probably occurs through sinkholes in the Inner Blue Grass.

In those areas where the water table is above the bottom of the soil and mantle, water moves in the zone of saturation from the soils to the rocks and from the rocks to the soils. In most of the Blue Grass region, however, water moves downward through the soil to the rocks and continues downward through a zone of unsaturated rock before it reaches the water table. After heavy rains, water may move through the large shallow openings at a relatively rapid rate and discharge from openings along cliffs or steep hillsides without penetrating to the principal ground-water body. An analysis of a sample of such a wet-weather flow is presented on page 33. The water is low in dissolved solids and only slightly alkaline. This sample was obtained from the Outer Blue Grass, but it probably is typical of rapidly circulating water in any of the limestone areas of the Blue Grass. Water from large springs is characteristic also of rapidly circulating ground water, particularly water from those springs that respond quickly to rainfall. For this reason, spring waters generally are lower in dissolved solids than the well waters.

As waters descend, their solutional activity is weakened, but this does not mean that additional materials are not dissolved during deep circulation. Waters at depth move slowly and are in contact with the rock for long periods of time. Because the openings are extremely narrow, the surface area of contact between water and rock is correspondingly large. Because openings along fractures are virtually absent at great depth, it is possible that a substantial part of the ground-water movement at depth is through intergranular openings. The deeper waters in the Inner Blue Grass region are more mineralized than the shallow waters. The increase of mineralization with depth is more pronounced where shaly beds restrict the downward motion of ground water (fig. 2). This is, of course, because the shale restricts the relatively abundant circulation of ground water to shallow depths.



Another possible cause of the increasing mineralization with depth is the presence of concentrated brines below the depth of rapid circulation. Mixing of brines with descending fresh ground waters would be expected to cause increasing mineralization with depth. The origin of the highly saline waters will be discussed in a later section.

At greater depths where the water is more mineralized, the relative amounts of different constituents change. The magnesium-calcium ratios generally increase with increasing mineralization, at least to concentrations of about 5,000 ppm of dissolved solids (fig. 5). Potassium-sodium ratios (fig. 6) generally decline as mineralization increases. Calcium-sodium ratios (fig. 7) generally decline with increasing mineralization, at least to concentrations of about 10,000 ppm of dissolved solids. Chloride-bicarbonate ratios (fig. 8) and chloride-sulfate ratios (fig. 9) generally increase as mineralization increases, but sulfate-bicarbonate ratios (fig. 10) show little correlation with mineralization.

The magnesium-calcium ratios of the waters entering the rocks from the overlying soil is low, probably because most of the magnesium is fixed in the clay minerals. As the water enters the rocks and moves through the openings, it dissolves relatively more magnesium than calcium. According to Grim (1953, p. 356), montmorillonite is generally absent in sedimentary rocks older than Mesozoic. It appears that clay minerals, other than montmorillonite, have little power to fix magnesium, and, therefore, most of the magnesium dissolved in percolating ground water remains in solution. Magnesium-calcium ratios of spring water are generally lower than those of well water of equal total mineralization, at least in the Inner Blue Grass. At dissolved-solids concentrations of more than 10,000 ppm, magnesium-calcium ratios decline with increasing mineralization, possibly because at very high concentrations magnesium may be fixed in the clay minerals.

The potassium-sodium ratios of waters entering the rocks from the overlying soil probably are relatively high in comparison to these ratios in ground waters, not because the potassium content is especially high, but because the sodium content is low. The ratios in soil waters may be appreciably affected by the sodium content of rain-water. As the waters percolate through the openings in the rocks, they dissolve additional sodium compounds. The concentration of sodium is plotted against the concentration of chloride in ground waters in figure 11. The correlation suggests the possibility that most of the sodium dissolved in ground waters was obtained from the solution of sodium chloride in the rocks. Another possible source of the sodium and chloride is the saline water at depth, which may be modified connate marine water. The concentration of potassium

increases very little as the water percolates through the rocks, presumably because most of the potassium in the rocks is fixed in the clay minerals (illite). Potassium in soluble compounds may be dissolved but apparently is removed from solution by ion exchange with the clay minerals. The relatively high potassium content of the distilled-water leach of rock samples (table 8) suggests that soluble potassium compounds may be present in the limestone and especially in the shale. The solubility of the potassium may have been increased, however, by breaking down the clay minerals in the crushing of the rock samples. It seems evident that most of the potassium dissolved is lost again by ion exchange. Probably the movement of water accelerates removal of potassium. In highly saline waters, the concentration of potassium may be as much as several hundred parts per million, but it is generally less than 0.5 percent, by weight, of the dissolved solids. Concentrations of sodium may be more than 40,000 ppm in highly saline waters and may be more than 30 percent, by weight, of the dissolved solids.

Calcium-sodium ratios of waters entering the rocks from the overlying soil probably are moderately high as they are in most dilute ground waters of the region. As the water percolates through the rocks, the calcium-sodium ratios decline as mineralization increases, but the decline is not so sharp as that of the potassium-sodium ratios. The reason for this is that the calcium content increases with increased mineralization at a greater rate than does the potassium but at a lower rate than does the sodium. Apparently neither the calcium nor the sodium is fixed to any great extent by the clay minerals, but the sodium in the rocks may be in combination with chloride and, therefore, is much more soluble than the calcium which is present as carbonate. Concentrations of calcium may be more than 12,000 ppm in the saline waters, more than 8 percent by weight of the dissolved solids in saline waters, and more than 15 percent by weight in the more dilute waters of the Blue Grass region.

Water percolating through the soil to the rocks in the Blue Grass region is generally low in chloride content. As it percolates through the rocks it may dissolve substantial amounts of chloride. The chloride content of rocks in the Blue Grass ranges from less than 100 ppm to 200 ppm in the limestone and from 100 ppm to 1,400 ppm in the shale. The greatest concentration determined was in a shale bed in the High Bridge group. The concentration of chloride increases quite uniformly with the increase in dissolved solids.

The chloride content of the rocks is great enough to account for very high concentrations of chloride in the ground water, if we assume that a large part of it can be dissolved by ground water. If solution of the chloride from limestone can be effected only along solution

openings in the rocks, large quantities of limestone must be dissolved to yield high concentrations of chloride. There undoubtedly is some intergranular permeability in the limestone, however, and given enough time water could percolate through these openings, dissolving out the chloride and leaving behind most of the calcium carbonate.

Water percolating through the soil into the rocks probably contains greater amounts of sulfate than chloride. As the water moves through openings in the rock, it picks up additional sulfate, but the increase is by no means uniform. The source of most of the sulfate probably is pyrite, which is moderately abundant in much of the limestone and shale of the region. Oxidation of pyrite is most active above the water table where abundant oxygen is available. Probably part of the sulfate is redeposited as gypsum. Sulfur also may be lost, possibly in large amounts, as hydrogen sulfide gas that escapes to the air at springs. The characteristic odor of hydrogen sulfide in many of the springs and wells of the region supports this supposition. According to R. E. Grim (oral communication, 1957), sulfate may be fixed in kaolinite by substitution of sulfate for silica in the silicate lattice. Hydrogen sulfide may be formed also by reduction of sulfate by bacteria. Because concentrations of sulfate show little correlation with dissolved solids and concentrations of chloride show rather uniform increase with increasing dissolved solids, it may follow that any correlation in chloride-sulfate ratios with dissolved solids is due chiefly to the chloride content.

Waters percolating through the soils in the Blue Grass region probably contain much greater concentrations of bicarbonate than of sulfate or chloride. As the water moves through the rocks, it dissolves additional carbonates, and the concentrations of bicarbonate increase but not so rapidly nor so uniformly as the chloride. Because bicarbonate increases less rapidly than chloride with increasing mineralization, the chloride-bicarbonate ratio in ground waters in the Blue Grass generally increases with mineralization.

The preceding section indicates how the amount and proportions of the different dissolved constituents change as the water moves from the soil into the rocks and through deeper zones in the rocks. The dissolved material in the water percolating through the rocks may be redeposited in openings in the rocks or soils or it may be left on the surface when the ground water is discharged by evapotranspiration. However, the ultimate disposal of most of this dissolved material is its removal from the region as the dissolved load of streams. Because of the larger openings and shorter paths in shallow zones, most of the ground water entering the streams has not penetrated more than a few tens of feet below stream level. Consequently, the ground water discharged to streams generally is less mineralized than that from the

deeper wells. The more deeply circulating ground water that discharges to the streams may be very highly mineralized, but this water generally is mixed with much larger quantities of dilute shallow water before it enters the stream. Part of the water (storm runoff) reaching the stream after periods of heavy rains has been in contact only with the soils before reaching the streams. This water generally is lower in dissolved materials than the ground-water discharge.

The chemical character of most discharging ground waters is similar to that of the more dilute waters from wells tapping the same aquifer. The concentrations of dissolved solids generally are low, and the relative amounts of silica, calcium, magnesium, and bicarbonate generally are high. In late winter and early spring, when increased recharge raises the water table, the slope of the water table toward the streams steepens and ground-water discharge increases. At this time, much of the ground water is moving at a relatively rapid rate and through relatively large openings. Consequently, the ground-water discharge to the stream is relatively low in dissolved solids. In late summer and early fall, the water table is generally relatively low, the slope of the water table to the streams is less steep, and ground water moves more slowly and through smaller openings. The ground-water discharge to the streams at this time is relatively high in dissolved solids.

The discharge of most streams at low flow consists chiefly of ground-water discharge, and the chemical character of the stream waters at low flow is very similar to that of ground water in shallow wells or springs. Much of the ground water discharged to streams percolates through mantle materials to reach the stream and may gain, lose, or exchange materials with the mantle. As the water comes in contact with the air, it almost immediately loses much of its iron and manganese, which precipitate as oxides. Hydrogen sulfide or carbon dioxide gas may be discharged to the air.

Water discharged to the atmosphere by evaporation or transpiration loses all its dissolved solids in the soil or plants. In the Blue Grass region, especially where limestone is interrupted by shaly beds, discharge of ground water by evaporation and transpiration may be of large magnitude. Impeded in its downward movement by the shaly beds, ground water moves laterally to discharge on hillsides where the limestone-shale contact is near the surface. Visible springs or seeps occur only where and when the discharge is sufficient to exceed local evaporation and transpiration. Probably a much greater amount of ground water is lost by evaporation and transpiration than is discharged to visible springs and seeps, especially during the growing season.

Much of the material left in the plants returns eventually to the soil when the plants decay unless the plants are removed as crops. Most of the material left in the soil by the evaporating ground water is readily soluble, and much of it is flushed out in the surface runoff during heavy rains. This material, redissolved by surface runoff, may account in part for the relatively small fluctuation in chemical character of water with large fluctuations in runoff.

#### RESIDUES OF WEATHERING—THE SOILS

A description of the insoluble residues from the Lexington limestone of the Blue Grass region is from a paper by Young, Havens, and Gregge (1949, p. 23-24). The material of the quarry was highly organic as shown by the insoluble residues and the rich fossiliferous nature of the rock. Silica, the dominant mineral, often replaced entire fossils. Crystalline quartz, galena, pyrite, and mica were the minor minerals in the residues. Clay, which was prominent in every fraction, was principally illite; however, once pure kaolinite was observed.

Chemical analyses of Maury soils (table 2), which generally overlie limestone of the Lexington group, show that the comparatively soluble calcium and magnesium carbonates are largely removed by percolating waters. Only in the subsoil immediately overlying bedrock do the carbonates of the alkaline earths make up an appreciable part of the mantle. Some of the chert and crystalline quartz reported in the "insoluble residue" is dissolved, but most of it remains in the soil in sand, silt, and clay-sized particles. The silica is concentrated in the topsoil by the leaching of the more soluble elements and by the downward movement of the clay fraction. The downward movement of the clay fraction is evidenced by the concentration of alumina at a depth of about 4-6 feet. Iron oxide is also concentrated at this depth, and the silica content is low. In the pH range from 4.5 to 7.0, the general range in Blue Grass soils, silica is moderately soluble, but alumina is very slightly soluble. As stated above, however, the silica is concentrated in the topsoil, whereas the alumina is concentrated in the subsoil at a depth of 4-6 feet. It is apparent, therefore, that the separation of the alumina and silica must have been accomplished either by solutions of pH lower than 4.5 or by a process other than solution and precipitation. If the alumina was removed from the topsoil by solution in percolating waters high in organic acids, the alumina presumably would be precipitated at greater depth when the pH of the waters increased by solution of calcium and magnesium carbonate in the subsoil.

Another, and more probable, explanation of the concentration of alumina in the subsoil is that the downward movement of the clay

minerals is chiefly as a colloid sol, carried down by percolating waters. This would account for the concentration of alumina at depth and could account for the concentration of iron oxide. According to Moore and Maynard (1929, p. 277), iron is generally transported as a ferric oxide hydrosol stabilized by organic colloids in cold natural surface waters.

The clay fraction of the insoluble residues from limestones of the Lexington group is chiefly illite but includes some kaolinite. Apparently the clay minerals are altered but little in the weathering process, as the clay minerals in the subsoil overlying limestone in the Blue Grass are also chiefly illite and some kaolinite. Probably some of the potassium in the illite is removed by leaching or by action of plant roots leaving a "degraded" illite in the topsoil (Grim, 1953, p. 152). Inasmuch as calcium and magnesium, which tend to inhibit formation of kaolinite (Keller, 1957, p. 63), are largely removed from the topsoil, the topsoil may contain more kaolinite than the subsoil.

The metallic sulfides, chiefly pyrite, in the insoluble residue probably are altered to metallic oxides with the release of hydrogen sulfide gas. Sulfuric acid, which also may be formed from this reaction, accelerates the solution of the limestone. The small amount of mica in the insoluble residue probably weathers to illite.

Weathering of other limestone of the Blue Grass probably is similar to that of the Lexington limestone. Differences in the relative amounts of calcium and magnesium carbonate in the limestone and differences in the composition of the insoluble residues are reflected in differences in the chemical composition of the soils. No clay-mineral analyses of insoluble residues of Mississippian limestone from the Blue Grass region are available; however, clay-mineral analyses of insoluble residues from Mississippian limestone outside the Blue Grass region (Havens and others, 1949) indicate that montmorillonite as well as illite may be a common constituent. As outcrop areas of Mississippian rocks in the Blue Grass region are small, a discussion of the effect of the differences in clay minerals in these rocks will not be undertaken in this report.

Residues of shale may be markedly different from those of limestone. The shale is the product of chemical weathering of an earlier geologic time and has undergone transportation to the site of deposition, diagenesis after deposition, and compaction by overlying sediments. The clay minerals of the shale may thus show the influence of each of these earlier environments. Exposure of the shale to the weathering processes imposes a new environment, but the meager data available indicate that illite is the major clay mineral in the soils as well as in the shale from which the soils are derived. As stated above (page 67), calcium and magnesium tend to inhibit formation of kaolinite.

It is possible, therefore, that the leaching of calcium and magnesium from the calcareous shale in the soil-forming process may make possible a greater concentration of kaolinite in the soils than in the shale from which they are derived.

A comparison of the analyses of shale of the Blue Grass with analyses of residual soil overlying the shale indicates that much of the calcium and magnesium have been leached from the shale. The percentage of calcium removed is greater than that of magnesium, indicating that some of the magnesium is in relatively insoluble form, probably as a constituent of clay minerals. Although some of the silica has undoubtedly been leached from the shale in the weathering process, silica is more concentrated in the topsoil than in the parent shale because of its relative insolubility and the flocculating action of calcium and magnesium. Probably a part of the clay-mineral fraction of the topsoil has been carried down as a colloid sol. Aluminum and iron oxide have been removed from the topsoil but concentrated in the subsoil. Potassium also has been leached or removed by plants from the topsoil, probably resulting in a "degraded" illite.

The change in volume involved in the weathering of shale probably is not large. Some of the rock materials have been removed by solution, but organic material has been added to the soil. Allowing for changes in specific gravity, weathering of 1 inch of shale probably would produce about 1 inch of soil.

Except for the Devonian black shale, shale bedrock in the Blue Grass is generally interbedded with limestone. The relative proportion of shale and limestone determines the nature of the weathering. Thus, the amount of rock weathered to produce 1 inch of soil ranges from about 1 to 18 inches.

Sandstone forms a very small part of the bedrock in the Blue Grass region. Probably most of it contains 80-90 percent sand, silt, and clay. Cementing materials may be iron oxide or calcium carbonate. Weathering of the sandstone consists chiefly of leaching of the more soluble cementing materials, leaving the less soluble sand, silt, and clay in the soil. Because of the difference in specific gravity, weathering of 1 inch of sandstone probably would produce more than 1 inch of soil.

The transported soils have been subjected to a new environment of weathering for a comparatively short time, and adjustment to this environment is incomplete. Weathering of transported materials consists chiefly of leaching of calcium and magnesium carbonate and leaching of iron oxide from the topsoil and precipitation of iron oxide in the subsoil. The leaching of the calcium and magnesium carbonate results in an acid soil, and the precipitation of iron oxide results in a red subsoil. Thus the older soils, which have undergone weathering

for a greater period of time, are more acid and have redder subsoils than the younger soils. The older soils probably contain more kaolinite than the younger soils; the younger soils may contain greater amounts of illite. The older soils are topographically higher than the younger soils.

### SALINE WATERS

Saline waters are found in many parts of the Blue Grass region, and saline waters probably underlie the zone of active ground-water circulation everywhere in the region. Most known analyses of saline waters from the Blue Grass region indicate dissolved solids of less than 35,000 ppm. However, analysis of one brine sample, which was obtained from a well in Powell County, near the edge of the Blue Grass region as defined in this report, indicates dissolved solids of about 195,000 ppm (McGrain and Thomas, 1951, p. 14). Several of the analyses of saline waters from deep oil tests in other parts of the State indicate concentrations of dissolved solids of more than 100,000 ppm. No doubt similar saline waters of very high mineralization underlie much of the Blue Grass region. In this report, all waters having a dissolved solids of more than 1,000 ppm are considered to be saline; all waters having a dissolved solids greater than that of sea water (about 35,000 ppm) are called brines.

### OCCURRENCE

Saline waters generally are reached in the Blue Grass region at depths of 50–200 feet below the altitude of local streams. A few wells produce saline water from rocks above the local stream level. Fresh water has been reported from a few wells that are several hundred feet deep, but it has been impossible to determine the depths at which the fresh water enters these wells. Saline waters are known to occur also at shallow depths in the vicinity of some of the major faults in the region (Hamilton, 1950), saline waters may be near the surface in the vicinity of some abandoned deep wells. Saline springs in the Blue Grass region are positive evidence of shallow saline waters in some localities (Matson, 1909, p. 203–210). Not all of these springs are in the vicinity of known faults, and the sources of these shallow saline waters are not known. Additional data on the temperatures of these waters may throw some light on the depths of the sources of the springs.

The depth at which saline waters are found is related to the amount of shale in the bedrock. If a considerable thickness of shale immediately underlies the local drainage in a given area, it is almost hopeless to attempt to obtain a supply of fresh water in that area. Where thick massive pure limestone strata, uninterrupted by shale,



underlie the local drainage, fresh water may be obtained at considerable depth.

### CHEMICAL CHARACTER OF SALINE WATERS

Because few chemical analyses of brines from the Blue Grass are available, analyses of brines from surrounding regions in Kentucky are used for comparison with the saline waters of the Blue Grass (table 9). All brines and most saline waters of Kentucky are of the sodium chloride type; sodium and chloride make up 80-90 percent by weight of the dissolved solids. The relative abundance of the different dissolved materials in the saline waters and brines may provide a clue to their origin.

The brine analyses listed in the tables and plotted on the diagrams are from formations ranging in age from Ordovician to Pennsylvanian. If there are differences in the chemical character of brines from different formations, these differences are largely masked by variations in individual samples. Hoskins (1947) stated that the quantities of many constituents of West Virginia brines varied quite uniformly with density, no matter from which producing horizon the brine might come. In this report, brines from all formations will be considered as a unit.

In the discussion that follows, references to brines will include waters from formations in various parts of Kentucky; references to saline waters less mineralized than brines will include only waters from the Blue Grass region. Comparison with nonsaline waters of the Blue Grass will be made for the purpose of determining the origin of the saline waters and brines.

### SILICA, ALUMINUM, IRON, AND MANGANESE

There appears to be little correlation between the amount of dissolved solids and concentrations of silica, aluminum, iron, and manganese in the saline waters. Silica ranges from less than 1 to about 50 ppm in both the fresh and saline waters, but most samples contain less than 20 ppm of silica. Aluminum is reported in few analyses of fresh waters. In brines, aluminum ranges from 1.5 to 84 ppm. One brine sample contained 56 ppm of iron. Iron generally is higher in saline than in fresh waters. Most samples of saline waters, however, contain only a few parts per million of iron. Manganese is reported in few samples of saline waters. Where reported, it ranges from a few thousandths to a few tenths part per million.

### CALCIUM

Figure 16 is a plot of calcium and magnesium against dissolved solids in fresh and saline ground waters of the Blue Grass and of brines in various parts of Kentucky.



Calcium makes up about 15 percent, by weight, of the dissolved solids of waters having a salinity of 1,000 ppm. As salinity increases, the percentage, by weight, of calcium generally declines to less than 3 in waters having a salinity of 10,000 ppm. The relative amount of calcium increases again in the brines and is more than 7 percent, by weight, in waters having a dissolved-solids content greater than 100,000 ppm. The percentage, by weight, of calcium in sea water is 1.2, which is less than that of most of the saline ground waters. Because the percentage of calcium is higher in both fresh waters and very concentrated brines than it is in the moderately saline ground waters, it is apparent that the intermediate waters cannot be accounted for as a simple mixture of fresh waters and concentrated brines.

#### MAGNESIUM

The percentage, by weight, of magnesium in dissolved solids of fresh ground waters of the Blue Grass generally ranges from about 2 to 10, depending to some extent on the chemical character of the underlying rocks. The plot of magnesium in this range is more scattered than is the plot of calcium. In waters in which the dissolved solids ranges from 1,000 to more than 150,000 ppm, magnesium content generally ranges from 1 to 2 percent of dissolved solids, by weight. Magnesium constitutes 3.7 percent, by weight, of the dissolved solids in sea water. This is greater than that of any of the saline waters of Kentucky.

The magnesium-calcium ratios of fresh waters of the Blue Grass generally increase as mineralization increases to about 0.7 at a dissolved-solids concentration of 1,000 ppm. The magnesium-calcium ratios of most saline waters containing less than 35,000 ppm of dissolved solids range from 0.4 to 0.7. At dissolved-solids concentrations greater than 35,000 ppm, magnesium-calcium ratios generally decline and range from 0.2 to 0.3 at concentrations greater than 100,000 ppm. The magnesium-calcium ratio of sea water is 3.18, which is much greater than that of any of the saline waters of Kentucky.

#### SODIUM

The relation of sodium and potassium to dissolved solids in fresh and saline waters is shown graphically in figure 17. Sodium constitutes less than 1 percent of the dissolved solids, by weight, of some fresh water samples from the Blue Grass. The percentage of sodium increases sharply as mineralization increases to about 30 percent, by weight, at 1,000 ppm of dissolved solids. Sodium constitutes 30 to 34 percent, by weight, of the dissolved solids of most saline waters from the moderately saline waters to the concentrated brines. The percentage of sodium declines slightly in the brines containing more than 100,000 ppm of dissolved solids. Sodium content of sea water

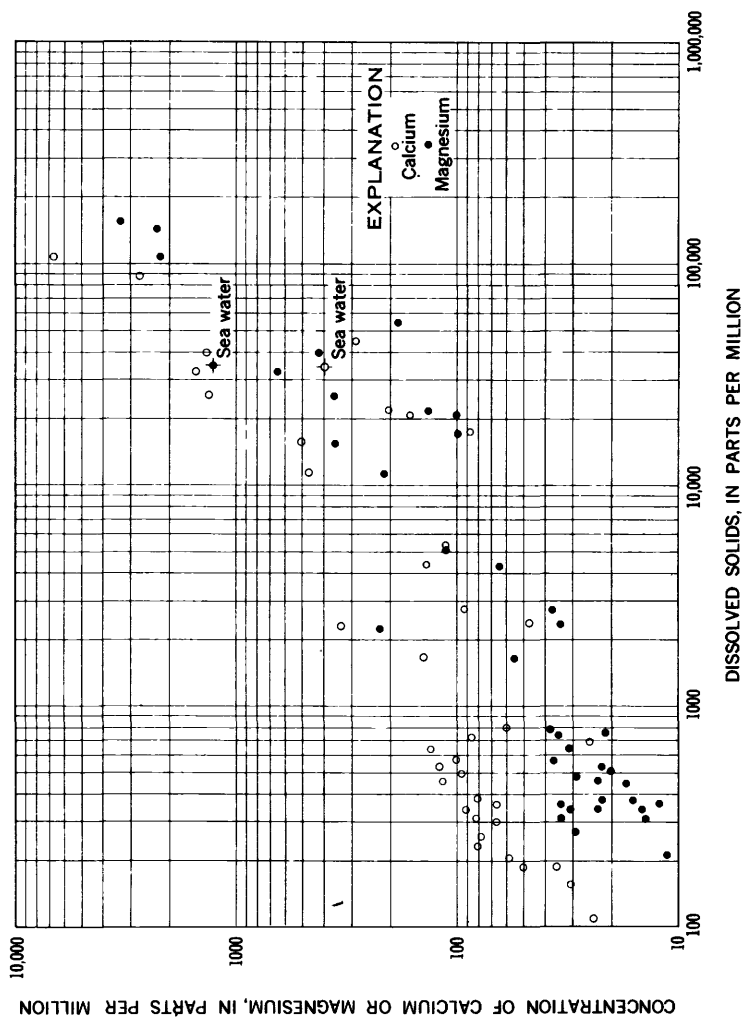


Figure 16.—Correlation of calcium and magnesium concentrations and dissolved solids in fresh and saline waters in the Blue Grass region and in brines in various parts of Kentucky.

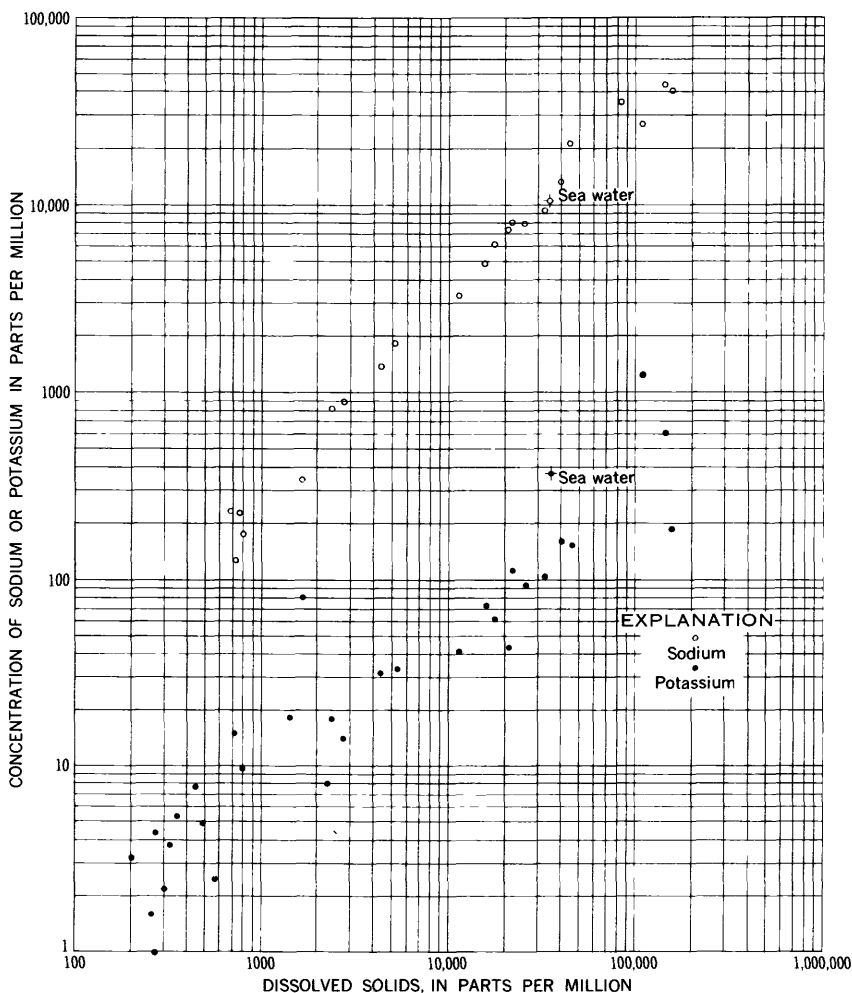


FIGURE 17.—Correlation of sodium and potassium concentrations and dissolved solids in fresh and saline water in the Blue Grass region and in brines in various parts of Kentucky.

is slightly more than 30 percent, by weight, of dissolved solids and is similar to that of the saline waters of Kentucky of like concentration of dissolved solids.

The ratio of calcium to sodium in fresh ground waters of the Blue Grass generally ranges from about 1 to 20. It is greater than five in most samples. With few exceptions, the ratio of calcium to sodium is less than one in saline waters of Kentucky. The ratio of calcium to sodium in saline waters increases with increased mineralization from about 0.1 in the moderately saline waters to more than 0.3 in the concentrated brines. The calcium-sodium ratio in sea water is less

than 0.04, which is considerably less than that of most ground waters of similar mineralization.

The ratio of magnesium to sodium in fresh and saline waters shows little correlation with dissolved solids. The magnesium-sodium ratio in saline waters ranges from less than 0.01 to about 0.08. The magnesium-sodium ratio of sea water is about 0.12.

#### POTASSIUM

The relation of potassium content to dissolved solids (fig. 17) is more variable than that of sodium. The potassium content of fresh waters generally ranges from about 0.2 to 2 percent of dissolved solids, by weight. In most saline waters, potassium ranges from 0.3 to 0.6 percent of dissolved solids. One sample of saline water from a spring in the Blue Grass contains 98 ppm of potassium, which constitutes about 1 percent of the dissolved solids of this sample. Potassium makes up 1.1 percent, by weight, of the dissolved solids of sea water.

The ratios of potassium to sodium in fresh waters of the Blue Grass generally range from about 0.1 to about 1 and generally decline with increasing dissolved solids. The ratio of potassium to sodium in saline waters is generally less than 0.02, although some saline waters have a potassium-sodium ratio greater than 0.2. The potassium-sodium ratio of sea water is about 0.036.

#### STRONTIUM AND BARIUM

Strontium and barium generally have not been determined in fresh waters of the Blue Grass. Because barite ( $\text{BaSO}_4$ ) is an important vein mineral in parts of the Blue Grass (Robinson, 1931, p. 28), barium may be present locally in fresh ground waters in very small amounts. However, barium sulfate is only very slightly soluble in fresh water. It is noted that none of the analyses of saline waters that report barium also report sulfate. In the concentrated brines of Kentucky, the strontium content may be as great as 832 ppm, constituting 0.5 percent of the dissolved solids, by weight, and the barium content may be as great as 155 ppm, constituting about 0.1 percent, by weight, of the dissolved solids. The strontium and the barium contents are considerably greater in most Kentucky brines than in sea water.

#### BICARBONATE AND CARBONATE

Bicarbonate makes up more than 50 percent of the dissolved solids, by weight, in almost all fresh waters of the Blue Grass region. In most saline waters, bicarbonate constitutes less than 10 percent of the dissolved solids, by weight, and in most brines it constitutes less than 1 percent, by weight, of the dissolved solids (fig. 18). The percentage of bicarbonate generally declines as mineralization increases. In saline waters of low pH, bicarbonate generally is low,

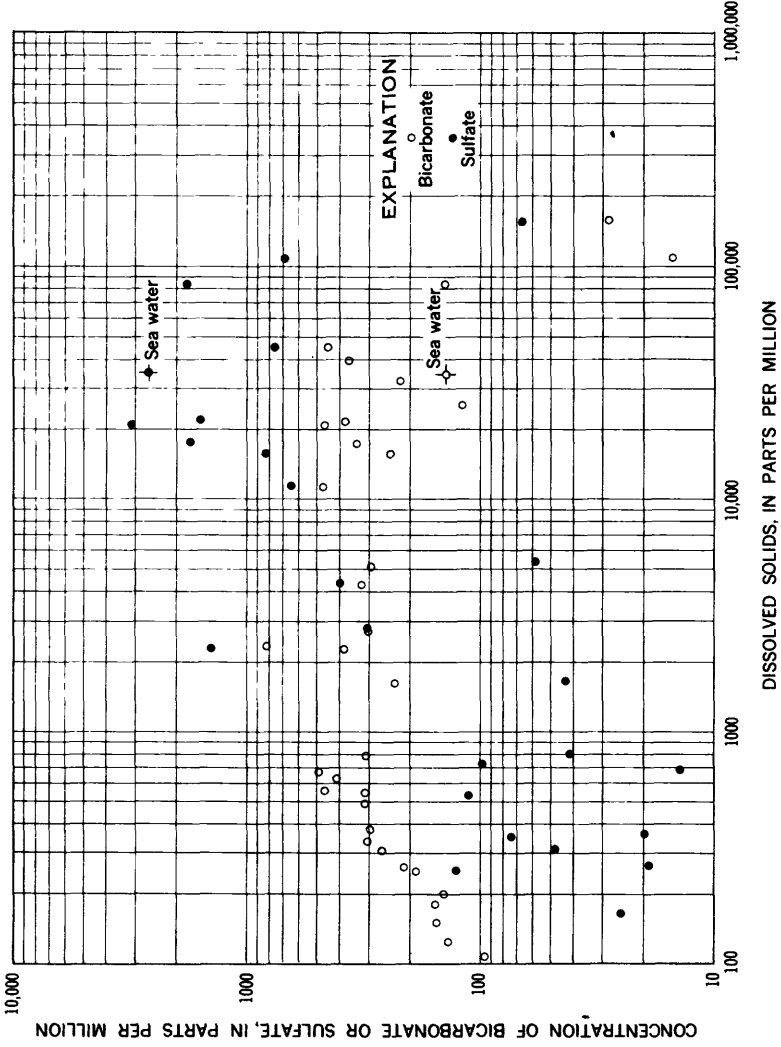


FIGURE 18.—Correlation of bicarbonate and sulfate concentrations and dissolved solids in fresh and saline waters in the Blue Grass region and in brines in various parts of Kentucky.

and one brine sample contained no bicarbonate or carbonate. Bicarbonate makes up 0.4 percent, by weight, of the dissolved solids of sea water. Carbonate is rarely present in significant amounts in fresh or saline waters in Kentucky.

#### SULFATE

Sulfate content ranges widely in fresh waters of the Blue Grass region, making up more than 50 percent of the dissolved solids, by weight, in a few samples, and less than 1 percent of the dissolved solids in others. Although a few of the brines in Kentucky contain more than 3,000 ppm of sulfate, there appears to be little correlation between sulfate content and dissolved solids in the saline waters of Kentucky (fig. 18). Sulfate makes up less than 5 percent of the dissolved solids in most saline waters and less than 1 percent in most brines. Where barium is present in appreciable amounts, sulfate is generally absent. Sulfate makes up 7.6 percent, by weight, of the dissolved solids in sea water. This is greater than in most saline ground waters in this range of dissolved solids.

Because neither the sulfate nor bicarbonate content shows a marked correlation with dissolved solids in saline waters, it is obvious that the sulfate-bicarbonate ratio shows little correlation with dissolved solids.

#### CHLORIDE

Chloride in the fresh waters of the Blue Grass region increases from less than 5 percent of dissolved solids, by weight, in the dilute fresh waters to more than 30 percent at concentrations of dissolved solids near 1,000 ppm. The amount of chloride in the dissolved solids of most saline waters containing between 1,000 and 30,000 ppm of dissolved solids ranges from 50 to 60 percent (fig. 19). At concentrations of dissolved solids greater than 30,000 ppm, the chloride content is as great as 75 percent, by weight, of the dissolved solids. The percentage of chloride, by weight, in the dissolved solids of sea water is 55.2, which is near that of saline ground waters of equal concentration.

The ratios of bicarbonate and sulfate to chloride generally decline as dissolved solids increase. This is because chloride generally increases as mineralization increases, whereas the bicarbonate and sulfate content of saline waters show little relation to increased mineralization.

#### FLUORIDE, BROMIDE, AND IODIDE

Although chloride makes up more than 50 percent, by weight, of the dissolved solids of almost all saline waters in Kentucky, the remaining halogens, fluoride, bromide, and iodide together constitute less than 1 percent of the dissolved solids, by weight. Concentrations of fluoride are reported in few of the analyses and, where



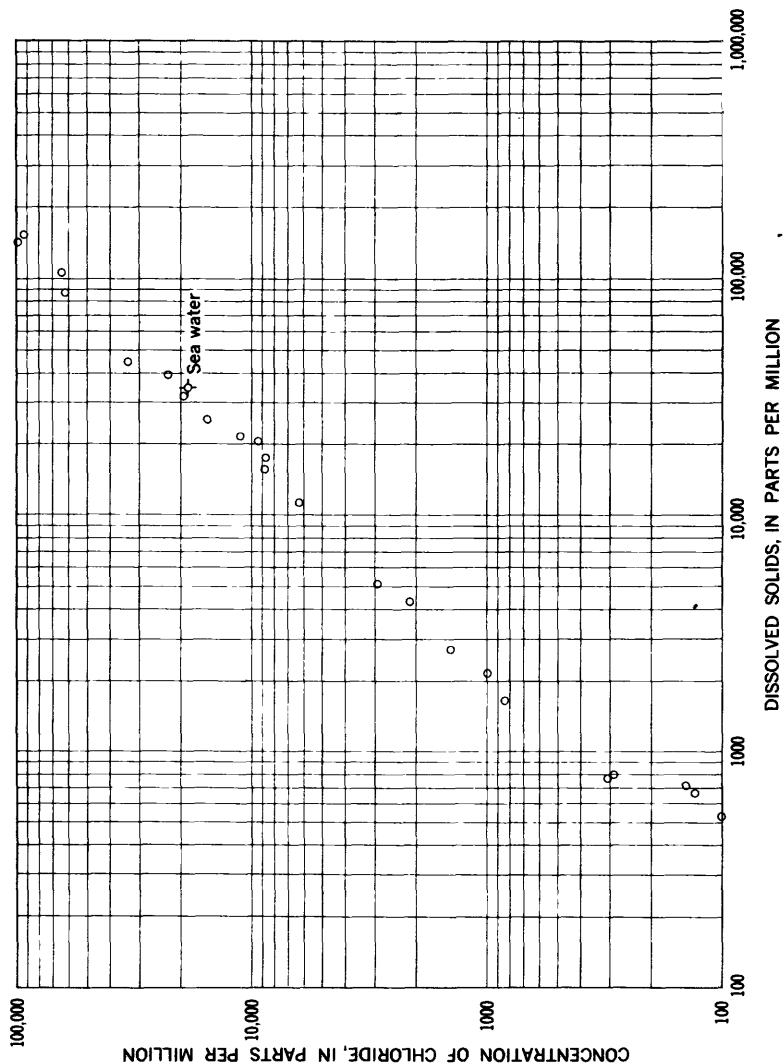


FIGURE 19.—Correlation of chloride concentrations and dissolved solids in fresh and saline waters in the Blue Grass region and in brines in various parts of Kentucky.

reported, they generally range from a few tenths to about 4 ppm; the fluoride content of sea water is 1.3 ppm.

Bromide content exceeds 1,000 ppm in some brines and makes up about 0.2 to more than 0.5 percent of the dissolved solids, by weight. The percentage of bromide generally increases with dissolved solids. Bromide makes up 0.2 percent, by weight, of the dissolved solids of sea water, but generally is not reported in analyses of fresh water.

Iodide exceeds 50 ppm in some Kentucky brines and makes up as much as 0.06 percent of the dissolved solids, by weight. Iodide makes up 0.05 percent of the dissolved solids of sea water.

#### NITRATE AND BORATE

Nitrate is reported in few analyses of saline waters of Kentucky. The concentration of nitrate appears to have little of any relation to the dissolved solids content.

Borate ( $\text{BO}_3$ ) is reported in a few of the analyses of Kentucky brines. As much as 70 ppm or 0.05 percent of dissolved solids, by weight, is reported in one brine sample.

#### pH VALUE

Most moderately saline waters of Kentucky are alkaline, the pH values ranging from 7.0 to 7.7. Some of the more concentrated brines are acid, however, and have reported pH values as low as 4.2. The pH of sea water ranges from 7.5 to 8.4.

#### ORIGIN

The origin of highly saline waters in inland areas far from any known deposits of salt has been the subject of considerable speculation. Saline waters of inland areas commonly have been explained as connate, that is, fossil sea waters.

It is apparent that the highly concentrated Kentucky brines could not be unaltered fossil sea waters unless the ancient seas were much more highly mineralized than the ocean is at present. Under arid conditions, sea water could become highly mineralized where shallow seas were isolated by bars or were left by the general retreat of the major seas. Such conditions existed in Late Silurian time in Ohio, New York, and Ontario, where salt and gypsum were deposited as evaporites. Presumably, deposition of sand, silt, and clay could occur in these highly saline shallow seas. Subsequent subsidence of the land could result in burial of the sediments and included brines under new deposits.

Although the salinity of the ocean possibly has varied during geologic time, the relative amounts of the different dissolved substances probably have changed but little (Sverdrup and others, 1942). The relative amounts of the dissolved substances are remarkably uniform

in present-day oceans, even where there are appreciable differences in dissolved solids. If it is assumed that Kentucky brines are connate waters, unaltered except by evaporation, the relative amounts of the dissolved substances should be the same in the brines as in the oceans, the only differences being due to precipitation as solubility limits were exceeded. Clarke (1924, p. 220) showed that evaporation of Mediterranean Sea waters results in a brine that is higher in magnesium and lower in calcium than sea water. Conversely, Kentucky brines are higher in relative amounts of calcium and lower in magnesium than sea water. Sulfate is also higher in the more concentrated brine obtained by evaporating sea water, whereas sulfate is much lower in Kentucky brines than in sea water.

Matson (1909, p. 49) concluded that the highly mineralized waters of the Blue Grass region probably are derived from meteoric sources. His statement follows:

The numerous joints in the limestone probably furnish a natural means of escape for the mineral waters, but the amount escaping from a channel must as a rule be less than that taken out by an ordinary well. The almost universal connection of the channels with the surface, which is indicated by the entrance of surface water after pumping, shows that water is probably derived from meteoric sources, the mineralization being due, as suggested, to the slow circulation of the water and the great length of time it remains in contact with the soluble materials of the limestone.

The entrance of surface water, according to Matson, is indicated by the replacement of mineralized water with fresh water after a well has been pumped for a time. In recent investigations, reports of mineralized waters being replaced by fresh waters after pumping are rare. On the contrary, most reports indicate that where changes in chemical character occur the water increases in mineralization with continued pumping.

Chemical analyses of samples of water from well 8435-3755-31, near Lexington, provide an example of increased mineralization with continued pumping. Because this well yielded too little water, it was deepened to 144 feet in 1954 and pumped for several days at about 5 gpm. A sample of water taken in March 1954, several days after pumping began, was highly mineralized sodium chloride water containing 34,400 ppm dissolved solids. Because of the salty water, the well was never used, but a hand pump was left on the well. In October 1955, a sample collected from this well, after a long period of no pumping, was a calcium magnesium bicarbonates water containing only 287 ppm of dissolved solids. In August 1956, two additional samples were taken from this well; one was collected as soon as pumping began and one after 20 minutes of pumping. Both of these were sodium chloride waters, but the sample collected at the start of the

pumping contained 358 ppm of chloride and dissolved solids of 834 ppm, whereas the sample collected after 20 minutes of pumping contained 848 ppm of chloride and dissolved solids of 1,640 ppm. Continued pumping of this well evidently brings in more highly mineralized water, probably from the deeper rocks penetrated by the well. The increased mineralization with pumping does not disprove Matson's hypothesis that the mineralized waters are of meteoric origin, but it does cast doubt on one line of evidence used in support of the hypothesis.

Another approach to the question of meteoric source of saline waters in the Blue Grass is to examine chemical analyses of Blue Grass rocks to determine if the saline waters could be derived from them. Unfortunately, none of the analyses of rocks available in the literature included determinations of chloride. Fifteen samples of marine sedimentary rocks from the Blue Grass region, eight of limestone and seven of shale, were collected as a part of this investigation and analyzed for chloride by the U.S. Geological Survey (table 6). The chloride content of the limestone samples ranged from less than 100 ppm to 200 ppm. The chloride content of the shale ranged from 100 to 1,400 ppm. Most of the rock samples analyzed for chloride were collected from roadcuts less than 20 feet below the soil zone. The highest chloride content was found in a shale sample from near the floor of a deep quarry. It is possible that rocks collected from greater depths would contain larger amounts of chloride.

Although the openings that furnish appreciable amounts of water to wells and springs in the Blue Grass are along fractures in the rocks, there is undoubtedly some movement of water through intergranular openings in the limestone and shale. If meteoric waters, slowly percolating through these intergranular openings, could take into solution the more soluble sodium chloride contained in the rocks without dissolving large amounts of the calcium carbonate and other rock minerals, then, in geologic time, highly concentrated sodium chloride waters could result. The occurrence of fresh waters at shallow depth and saline waters at greater depth is in accordance with this view for the shallow waters move at relatively high speeds through fractures in the rocks, whereas the deeper waters move very slowly, and much of the movement may be through intergranular openings. Unfortunately, this correlation is not definitive, for the same relation of chemical character with depth would hold true if the waters were of connate or modified connate origin. Even if the sodium and chloride in saline waters of the Blue Grass had been dissolved from the rocks by slowly circulating meteoric waters, the saline waters would be only once removed from modified connate waters, for the probable source

of the sodium and chloride in the rocks is dissolved material in the waters of deposition.

Most authorities now agree that inland brines not associated with evaporite deposits are derived from connate marine waters which have been concentrated and modified after deposition. The mechanism of concentration and modification, however, is still a subject of controversy. An evaluation of the relative merits of the different hypotheses is beyond the scope of this paper. As more data are obtained on the composition of brines in various formations in different physiographic provinces, and further advances in the knowledge of clay mineralogy are made, additional hypotheses on the origin of the brines undoubtedly will be offered. The work of Marshall (1949), Woodruff (1955), and others on energies of exchange of ions may prove of the greatest significance when applied to the problem of the origin of the brines.

### **FLUCTUATIONS IN CHEMICAL CHARACTER OF GROUND WATER**

An analysis of a water sample from a well, spring, or stream indicates the chemical character of the water at the time of sampling but does not necessarily indicate the character of water from that source at any other time. Fluctuations in chemical character of water from a given source may range from almost undetectable changes in the waters from some artesian wells and springs to drastic changes in both degree of mineralization and type of water from other wells, springs, and streams. In the Blue Grass region, the chemical character of waters from streams generally fluctuates more than the chemical character of waters from wells. Fluctuations in concentration of dissolved solids of the order of 100 percent are common in stream waters, whereas fluctuations in waters from most wells are of the order of 10–50 percent. Under certain condition, however, dissolved solids in waters from wells in the Blue Grass region may fluctuate several hundred percent. Fluctuations in chemical character of water from springs generally are intermediate between those from wells and streams.

Selected wells and springs in the Blue Grass were sampled periodically for this investigation. The wells and springs were selected to represent various types of water in various aquifers of the region. Comprehensive chemical analyses of the samples containing the greatest and the least concentration of dissolved solids from each of these wells and springs are included in table 7. Plate 5 and figure 20 are graphs showing typical fluctuations in chemical character of water from some of these wells and springs. A few of the analyses plotted in these graphs are not comprehensive analyses and are not included in table 7.

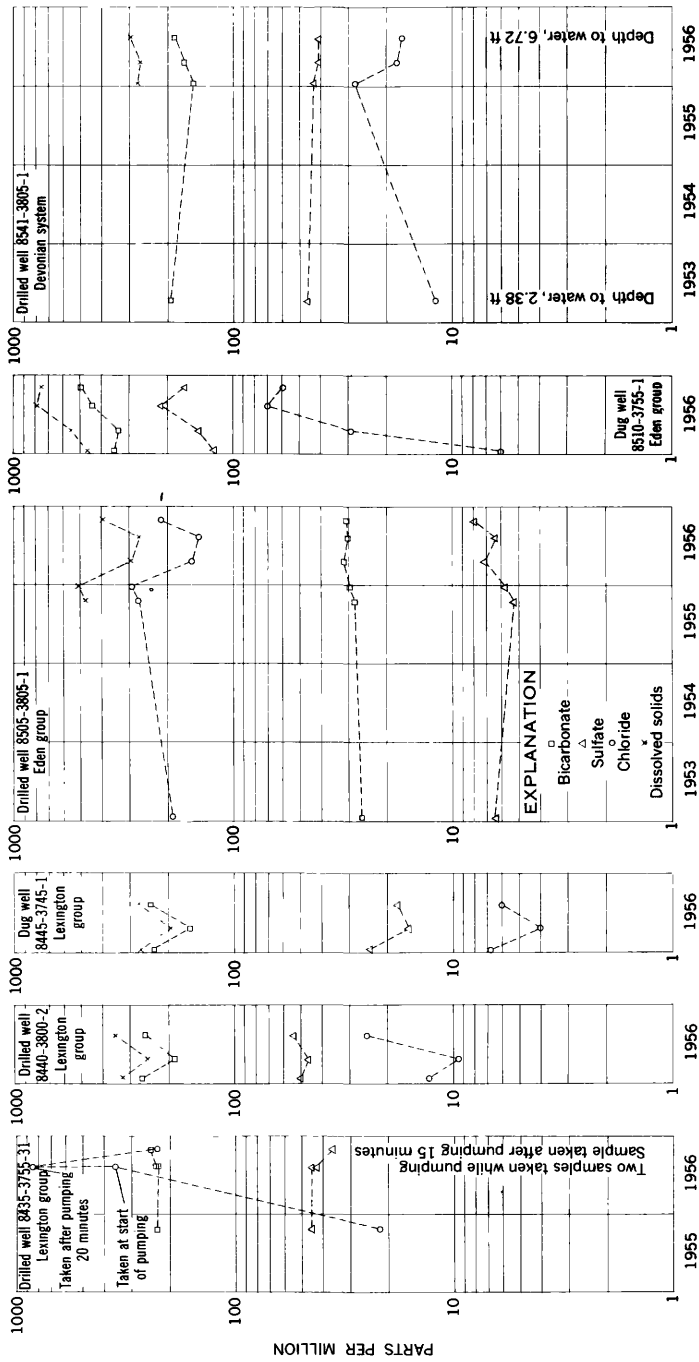


FIGURE 20.—Fluctuations in concentrations of dissolved constituents in water from selected wells of the Blue Grass region, Kentucky.

**FLUCTUATIONS IN CHEMICAL CHARACTER OF WATER CAUSED BY CHANGES IN RATE OF RECHARGE**

The major cause of fluctuations in chemical character of water from wells and springs in the Blue Grass is the fluctuation in the rate of recharge to the ground-water body. The fluctuations in the rate of recharge that affect the chemical character of the water are reflected also in changes in water level in wells and changes in the rate of discharge in springs. Unfortunately, data on depth to water in wells and discharge of springs were not always obtained at the times the wells and springs were sampled.

Changes in the rate of recharge may be of short duration, such as those caused by local storms; seasonal, such as those caused chiefly by seasonal changes in soil moisture; or long-term changes lasting several years, such as those caused by a succession of dry or wet years. Chemical analyses of ground waters in the Blue Grass show the effect of seasonal changes in rate of recharge, but sampling generally was not frequent enough to show in detail the effect of short-term changes or extensive enough to show the effect of long-term changes.

Local storms influence the rate of ground-water recharge and thereby the chemical character of the ground water. Heavy local rains may be expected to cause a decrease in the dissolved-solids content, especially in the shallow zone of rapid circulation. At greater depths, the immediate effect of local rains probably decreases until it is indistinguishable. In sinkhole areas, the effect of local rains may be more apparent than in areas where shaly beds prevent sinkhole development. This would be especially true during the growing season when little recharge is received by percolation through the soil.

Fluctuations in chemical character of water caused by local storms are greater in most springs than in wells but generally are not as great as in surface waters. Most springs in the Blue Grass are fed by waters in the shallow zone of rapid circulation; fluctuations in recharge are quickly reflected in fluctuations in chemical character of water. The speed with which recharge due to local storms is effective is apparent in many springs that yield large quantities of turbid water immediately after heavy rains. In general, the greater the fluctuation in discharge of a spring, the greater the immediate effect of local precipitation and the greater the fluctuation in the chemical character of the water. Springs flowing from shaly limestone generally yield less water, and the yield fluctuates less than in springs from thick limestone, however, some of these small springs may cease flowing altogether in late summer. Spring 8435-3835-2 generally yields less than 1 gpm from shaly beds of the Eden group (p. 5). The yield of this spring generally fluctuates very little, and the dissolved constituents of the water also fluctuate but little. On the other hand,

Russell Cave Spring (8425-3805-50) and Silver Spring (8430-3805-27) yield several hundred to several thousand gallons per minute from limestone of the Lexington group. The discharge of these springs fluctuates considerably, and the dissolved constituents of the water also fluctuate considerably (fig. 21).

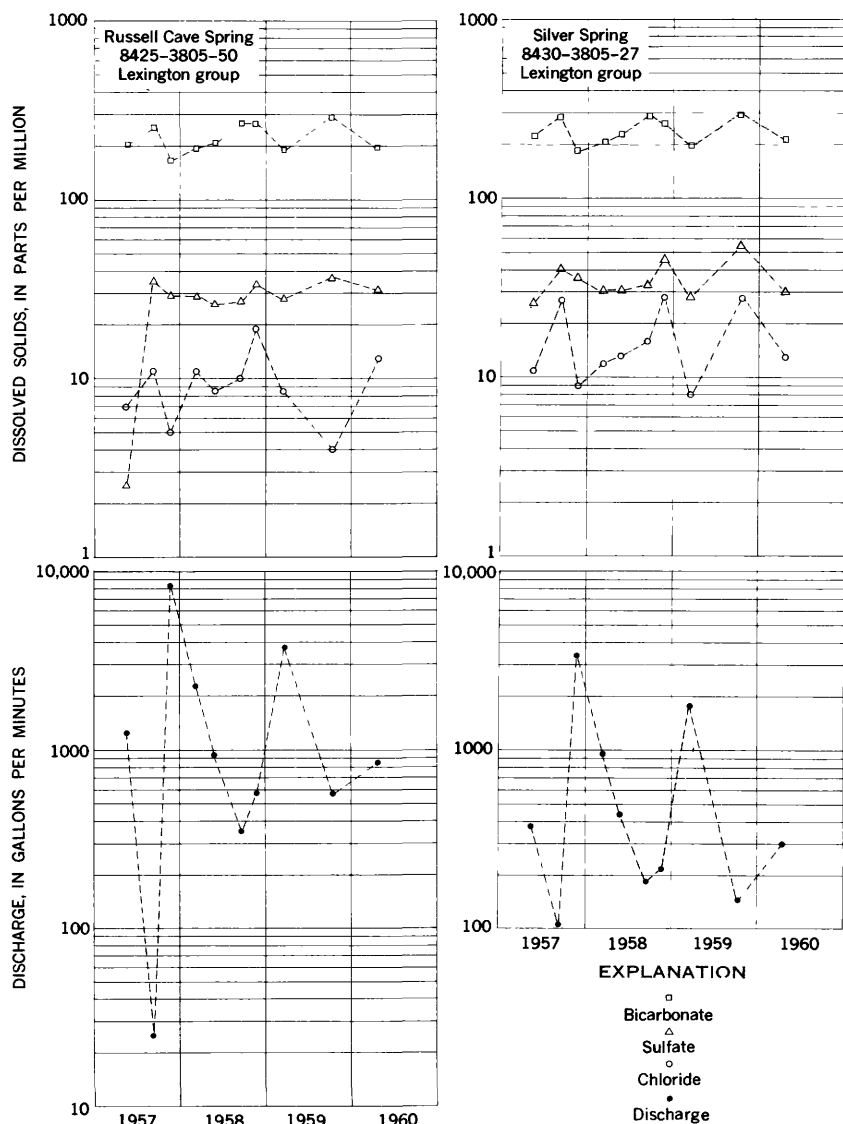


FIGURE 21.—Fluctuations in concentrations of dissolved constituents and discharge of two springs in the Blue Grass region, Kentucky.



Spring 8500-3830-3 (pl. 5) is not typical of the Blue Grass, although others like it have been found. This spring yields saline water from a source below the zone of rapid circulation. The chemical character of water from this spring is affected little, if any, by local recharge, and fluctuations in concentrations of dissolved materials are very slight.

Seasonal changes in chemical character of water from wells and springs generally are due to seasonal changes in the rate of recharge. Although rainfall in the Blue Grass is nearly uniform throughout the year, recharge generally is greater in late winter and early spring. At this time, the soil-moisture deficiency that accumulated during the growing season has been overcome, and much of the water entering the ground percolates through the soil into the underlying rock. As the growing season begins, the plant roots remove moisture from the soil, and most of the water entering the ground is held in the soil zone. During the growing season, soil moisture generally continues to decline, and recharge becomes progressively smaller until killing frosts in the fall stop most of the removal of water by growing plants. Recharge does not increase immediately on the close of the growing season, for the soil-moisture deficiency must first be overcome. If precipitation is below normal in the fall, appreciable recharge may be delayed until late winter or early spring. The rates of discharge in the two springs plotted in figure 21 show the effect of seasonal trends in recharge, although the seasonal effects are partly masked by the short-term effects of local storms.

The effect of seasonal recharge on fluctuations in chemical character of water is generally of greater magnitude in springs in the zone of rapid circulation than in wells that obtain water from openings at considerable depth below the surface. The reason for this relation is that the water entering the wells has been in contact longer with earth materials, and the effect of dilution by increments of seasonal recharge is dampened by mixing and by solution of and reactions with the earth materials. Exceptions to this general rule are waters from deep drilled wells which are mixtures of two distinct types of water. Fluctuations in chemical character of water in these wells are greater than fluctuations in all other natural waters of the region.

The most obvious change in the chemical character of ground waters of the region is the decrease of dissolved solids with an increase in the rate of recharge. The added increment of recharge which has been in contact with earth materials a relatively short time, is relatively low in dissolved solids. Thus it mixes with and lowers the dissolved solids of the shallow ground-water body that yields water to most wells in the area. Dissolved solids generally are low in the late winter or early spring when the rate of recharge is high. As the growing

season progresses, the rate of recharge declines and the dissolved solids increase (pl. 5; figs. 20, 21).

Although the dissolved-solids content of ground waters generally decreases with increasing recharge, the relation may not be a simple one. Recharge through sinkholes, during local storms, may carry material dissolved from the surface of the soil, and the relation of dissolved-solids content to rate of recharge may be similar to that of surface streams of the Blue Grass (p. 113 to 115).

The relation of the concentration of the various dissolved constituents to rate of recharge is complex also. In dilute waters of the Blue Grass, concentrations of bicarbonate generally decrease with increasing recharge. Concentrations of sulfate and chloride, however, may increase or decrease with increasing recharge. This is especially noticeable in the water from springs. The occasional increase of sulfate content of spring water with increasing recharge may be due to the flushing of sulfate salts by surface runoff that drains into sinkholes.

A detailed study of seasonal and short-term fluctuations in the chemical character of ground water would require analyses of samples collected daily or at even shorter intervals. The results of such a study could be useful to determine favorable times for withdrawal of water where quality requirements are especially stringent.

#### CHANGES DUE TO MIXED SOURCES

The most extreme fluctuations in chemical character of natural waters of the Blue Grass are due to changes in the relative amounts of two or more distinctly different types of waters. Most of these appear to be mixtures of fresh waters of the calcium magnesium bicarbonate type from a shallow source and saline waters of the sodium chloride type from a deeper source. The changes in the relative amounts of the different types of water are due mostly to changes in the amount of recharge or changes in the amount of discharge from the well by pumping. The effect of changes in relative amounts of the fresh and saline waters due to changes in recharge are illustrated by well 8505-3805-1 (fig. 20). Dissolved solids are highest in late fall and early winter and lowest in spring and midsummer. The effect of greater recharge in late winter and early spring apparently is retarded because movement of water through the shaly beds of the Eden group is slow. Thus, the lowest dissolved-solids content occurs in summer, several months later than in most shallow wells that top the zone of rapid circulation. The fluctuations in dissolved solids presumably are due to mixing of different types of water because the percentage of chloride, by weight, is much higher and the percentage of bicarbonate much lower in the more concentrated samples than

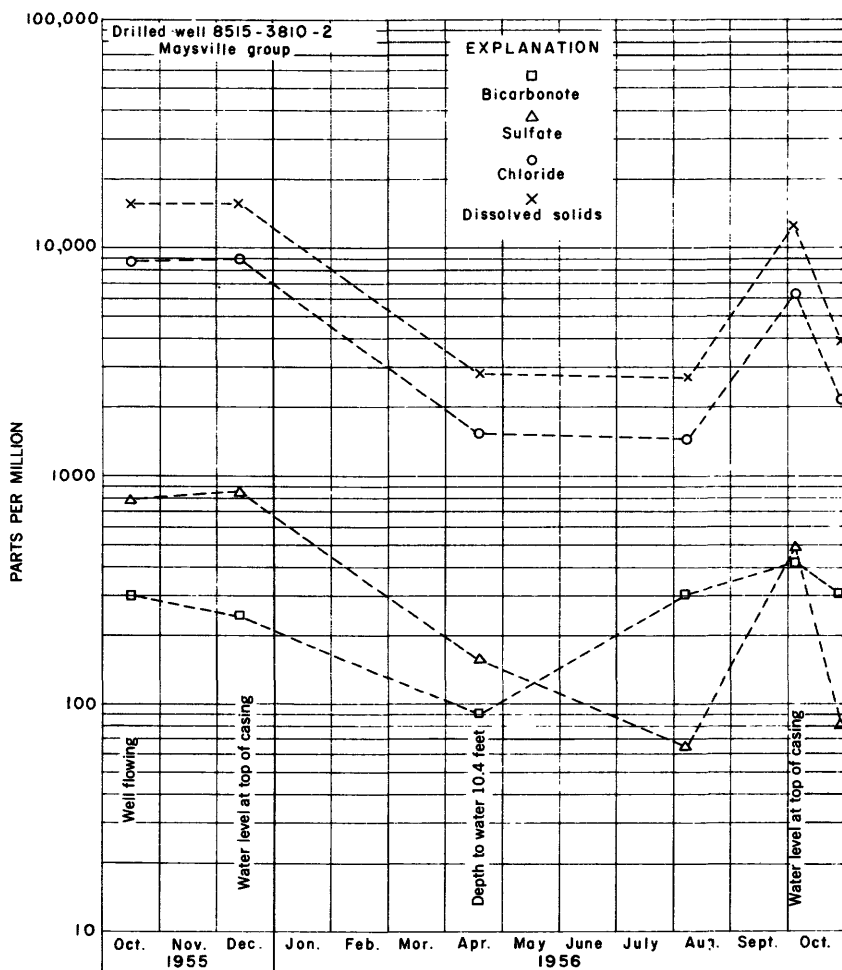


FIGURE 22.—Fluctuations in concentrations of dissolved constituents in a well obtaining water from deep and shallow sources.

in the relatively dilute samples. Likewise, the percentage, by weight, of sodium is greater and the percentage of calcium and magnesium smaller in the concentrated samples.

The extreme fluctuations in chemical character of water in well 8515-3810-2 (fig. 22) appear to be due to mixing of sources of water controlled by changes in the water level in the well. When the well is flowing or the water level is at the top of the casing, the water apparently is chiefly from a relatively deep zone and the dissolved-solids content is about 15,000 ppm. When the head in the deep zone declines, the water level declines. Then shallow ground water or surface water under higher head apparently enters the well, and the dissolved-

solids content declines to less than 3,000 ppm (fig. 22). Further evidence of the shallow source of the less mineralized water in this well is the increase in concentration of dissolved solids with increasing depth. All the samples plotted in figure 22 were collected by hand dipping a container at the top of the casing. On October 4, 1956, when the water level was at land surface, three samples were taken from the well, one at the surface, one at a depth of 18 feet, and one at a depth of 37 feet. The concentration of dissolved solids increased from 12,600 ppm at the surface to 15,100 ppm at 18 feet and 15,700 ppm at 37 feet. Chloride content increased from 7,140 ppm at the surface to 8,510 ppm at 18 feet and 8,790 ppm at 37 feet. Bicarbonate, probably derived chiefly from a shallow source, decreased from 430 ppm at the surface to 283 ppm at 18 feet and then increased again to 326 ppm at 37 feet.

The effect of changes in relative amounts of fresh and saline waters due to pumping is described above in the discussion of saline waters. The increase in dissolved solids in water from well 8435-3755-31 (fig. 20) indicates that highly mineralized water enters the well when water is removed by pumping. Although a few reports have been received of water becoming less saline with pumping, no data in support of these reports are available.

### SURFACE WATER

Surface water in the creeks and rivers in a general way consists of two components, surface runoff and ground-water discharge. The proportion of these changes almost continuously. Surface runoff responds quickly to precipitation, but ground-water discharge generally has a much delayed response. Consequently, streamflow at times may be composed almost entirely of surface runoff and at other times entirely of ground-water discharge. The dissolved material in the stream water may be derived almost entirely from surface runoff or entirely from ground water, or it may be a mixture of the two.

In most places the surface runoff generally has a dissolved-solids content lower than that of ground-water discharge because ground water is in contact with more unweathered materials and for a longer period of time. Moreover, water infiltrating the soil and passing into the rocks below receives a heavy charge of carbon dioxide within the root zone. Ground water, as a result, has more solvent power than surface runoff. As the proportion of the surface-runoff and ground-water components change, the dissolved-solids content also changes; thus there commonly is a definite relation between stream stage and the dissolved-solids concentration. In small streams, the relation is relatively simple because streamflow corresponds closely to the rate

and duration of precipitation, and the drainage areas commonly are relatively small and homogeneous. In large streams such as the Kentucky River, the relation is more complicated. The drainage basin of such a river is so large that precipitation often occurs only in a small part of the basin. As the distance between the storm area and the sampling station increases, the mass of water in the channel tends to flatten out and the crest of the flood becomes less sharp. The Kentucky River has additional complications because many dams store water in the channel. This stored water must be moved out by the advancing floodwaters before a lower dissolved-solids content is attained.

The Blue Grass region is drained by two large streams and a number of smaller ones. The two large streams, the Licking and Kentucky Rivers, head in the Eastern Coal Field. Water draining from the Eastern Coal Field, a region underlain largely by sandstone and shale, is different in chemical character from water from the Blue Grass, which is chiefly a limestone terrane. Several smaller streams, such as Elkhorn Creek, Beech Fork, and the upper part of the Salt River, drain areas that are entirely within the Blue Grass.

The location of the sampling stations and sampling frequency are shown in table 10. Most of the chemical analyses have been published in a series of reports by Lamar and Laird (1953), Lamar, Krieger, and Collier (1955), Collier and Krieger (1958), and the U.S. Geological Survey (1954-60). Some of the remaining data are included in this report, and some are available in the open files of the U.S. Geological Survey, Columbus, Ohio, and Louisville, Ky.

The location of the sampling stations is shown on plate 6. At each location a bar graph of an analysis at a high and a low flow is shown. The bars show the concentration of the principal constituents in equivalents per million. For most samples, several other constituents and physical properties were also determined. The height of the bars is an indication of the concentration of dissolved solids. The small streams vary more in dissolved solids than do the large streams. Streams draining the Eastern Coal Field and parts of the Knobs region contain relatively large amounts of sodium and chloride or sulfate. Streams draining only the Outer Blue Grass are of the calcium magnesium bicarbonate type and may have relatively more magnesium than other areas. Most of these latter streams are small and their low flow is fairly high in dissolved solids. Streams draining the Outer Blue Grass and the Eden shale belt are of the calcium magnesium bicarbonate type and low in sodium. The streams that drain only the Inner Blue Grass are fairly high in dissolved solids and

are typically calcium magnesium bicarbonate in type. The chemical character of the water of individual stream basins is discussed in the sections that follow.

TABLE 10.—*Surface-water sampling stations in the Blue Grass region*

[Stations listed in downstream order; tributary streams indented]

Map No. (see pl. 6)	Sampling station	Sampling		Period of record
		Type	Frequency	
Licking River basin				
1-----	Licking River at Farmers-----	Chemical	Periodic	Sept. 1949-Aug. 1950
2-----	Triplett Creek at Morehead-----	do	Spot	Nov. 1951, Feb. 1952
3-----	Licking River at Blue Lick Springs-----	do	do	Dec. 1950, Feb. 1951
4-----	North fork Licking River near Lewisburg-----	do	do	Nov. 1951, Apr. 1952
5-----	Licking River at McKinneysburg-----	do	do	Sept. 1949, Jan. 1950
		do	Daily	Oct. 1952-Sept. 1956
		Sediment	do	Do.
6-----	South fork Licking River at Cynthiana-----	Chemical	Spot	Sept. 1949, Jan. 1950
		do	Periodic	Oct. 1950-Aug. 1951
7-----	Licking River at Butler-----	do	Daily	Oct. 1949-Sept. 1950
8-----	Licking River at Covington-----	do	do	Sept. 1949, 1950.
Kentucky River basin				
9-----	Red River at Clay City-----	Chemical	Spot	Aug. 1949, Feb. 1950
10-----	Kentucky River at lock 10, near Winchester-----	do	do	Do.
11-----	Kentucky River at lock 8, near Camp Nelson-----	do	do	Do.
12-----	Dix River near Danville-----	do	do	Do.
13-----	Kentucky River at lock 6, at Salvisa (Warwick)-----	do	do	Do.
14-----	Kentucky River at lock 4, at Frankfort-----	do	do	Aug. 1949
		do	Daily	Oct. 1949-Sept. 1956
		Sediment	do	Oct. 1952-Sept. 1956
15-----	North Elkhorn Creek near Georgetown-----	Chemical	Spot	Nov. 1950, Feb. 1951
16-----	South Elkhorn Creek at Fort Spring-----	do	do	Do.
17-----	Elkhorn Creek near Frankfort-----	do	do	Aug. 1949
		do	Periodic	Oct. 1949-Sept. 1950
18-----	Kentucky River at lock 2, at Lockport-----	do	Spot	Aug. 1949, Jan. 1950
19-----	Eagle Creek at Sadieville-----	do	do	Do.
20-----	Eagle Creek at Glencoe-----	do	do	Aug. 1949, Mar. 1950
21-----	Kentucky River at Carrollton-----	do	Daily	Sept. 18-29, 1950
Harrods Creek basin				
22-----	Harrods Creek near Prospect-----	Chemical	Spot	June, July, Sept., Oct. 1952
Salt River basin				
23-----	Salt River near Van Buren-----	Chemical	Spot	Sept. 1949, Feb. 1950
24-----	Floyds Fork at Fishersville-----	do	do	Nov. 1950, Feb. 1951
		do	Periodic	June 1952-Aug. 1953
25-----	Salt River at Shepherdsville-----	do	Spot	Sept. 1949
		do	Periodic	Oct. 1949-Sept. 1950
		do	Daily	Oct. 1952-Sept. 1956
		Sediment	do	Do.
26-----	Rolling Fork near Lebanon-----	Chemical	Spot	Nov. 1950, Mar. 1951
27-----	Beech Fork at Bardstown-----	do	do	Dec. 1950, Feb. 1951
28-----	Rolling Fork near Boston-----	do	do	Sept. 1949, Feb. 1950
		do	Periodic	Oct. 1950-Sept. 1951

# CHEMICAL CHARACTER OF WATER IN STREAMS DRAINING SMALL BASINS OF UNIFORM GEOLOGY

## INNER BLUE GRASS, ELKHORN CREEK BASIN BASIN DESCRIPTION

The Elkhorn Creek basin lies almost entirely in the Inner Blue Grass (pl. 6). The Cynthiana formation underlies the higher parts of the area and the higher divides between creeks. The Cynthiana formation is underlain by rocks of the Lexington group, which overlies rocks of the High Bridge group. The Lexington group and the High Bridge group are exposed along the sides of valleys, especially in the lower part of the basin.

The Elkhorn Creek basin has an undulating to gently rolling surface and the surface altitude generally ranges from 470 feet to 1,000 feet. The land is largely in pasture and cultivated crops. Numerous sink-holes in the upper part of the basin give rise to a sizeable underground drainage system (Hamilton, 1950, p. 30). Layers of shale and clay in many places prevent deep penetration of infiltrating ground water, and springs and seeps occur along the sides of valleys.

Surface-water flow in the Elkhorn Creek basin is measured at three gaging stations: North Elkhorn Creek near Georgetown, South Elkhorn Creek at Fort Spring, and Elkhorn Creek near Frankfort. Characteristics of flow at each of the three stations (U.S. Geol. Survey, 1958, p. 373, 375, 376) are given in the following table. The flow of Elkhorn Creek near Frankfort is augmented by discharge of sewage from Lexington.

Station	Drainage area (sq mi)	Period of record (years)	Average discharge (cfs)	Maximum discharge (cfs)	Minimum discharge (cfs)
North Elkhorn Creek near Georgetown	119	1950-56	145	6,480	0
South Elkhorn Creek at Fort Spring	22.8	1950-56 1915-18	28.8	11,280	0
Elkhorn Creek near Frankfort	474	1940-56	576	22,400	0

<sup>1</sup> As revised in U.S. Geol. Survey Water-Supply Paper 1625, p. 355.

## CHEMICAL CHARACTERISTICS OF THE GROUND WATER

Samples of ground water were obtained from the Lexington group, Cynthiana formation, and Eden group in the Elkhorn Creek basin. Examination of the analyses shows the water from the Lexington group to be of the calcium magnesium bicarbonate type and of uniform composition. The uniformity of composition suggests only minor variation in the chemical character of the rock. A few partial analyses of water samples from the Cynthiana formation and the Eden group

are similar to analyses of water from the Lexington group. Periodic analyses of springs show that some ground water is not consistent in chemical composition. Springs respond rapidly to precipitation, however, especially in an area where sinkholes are common.

#### CHEMICAL CHARACTERISTICS OF THE SURFACE WATER

Two water samples for chemical analysis were collected from North Elkhorn Creek near Georgetown, 2 samples from South Elkhorn Creek at Fort Spring, and 11 samples from Elkhorn Creek near Frankfort. Samples were taken at a low and a high flow, and from Elkhorn Creek near Frankfort, at several intermediate flows. The small number of samples makes it possible to determine only general trends in chemical character of the water in the streams.

The Lexington sewage-disposal plant is located on a tributary to Elkhorn Creek. The effluent probably contributes sodium, chloride, and nitrate, particularly to the dissolved minerals of Elkhorn Creek. At low flows, the effect may be considerable. Chemical analyses of the waters of Elkhorn Creek have been published by Lamar and Laird (1953).

The relation between discharge and dissolved constituents in the Elkhorn Creek basin is not clear cut. On a plot of discharge against specific conductance of Elkhorn Creek near Frankfort (fig. 23) the points are widely scattered and only a vague suggestion of a trend is noticeable. Samples from North Elkhorn and South Elkhorn Creeks indicate that these streams contain less dissolved solids than Elkhorn Creek near Frankfort.

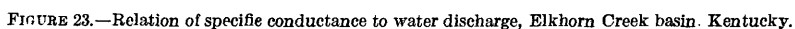
Ratios of various chemical and related data were calculated for the samples from the three stations (table 11). Except for specific conductance, which is expressed in micromhos at 25°C, all chemical and related data used are expressed in parts per million. Where many samples had been analyzed, as for Elkhorn Creek near Frankfort, some statistical treatment was possible.

One method of measuring the degree of variation from the arithmetic mean ( $\bar{X}$ ) is to find the standard deviation  $\sigma = \sqrt{\frac{\sum(X^2)}{N}}$ , where  $N$  is the number of samples. The amount of variation can be found by calculating the coefficient of variation ( $V$ ) according to the formula:  $V = \frac{\sigma}{\bar{X}} \times 100$ . The coefficient of variation, which is a measure of the closeness of grouping of data around the mean, is expressed in percentage; thus the greater the percentage value, the greater is the variation from the mean. In table 11,  $V$  for the dissolved solids-specific conductance ratio for Elkhorn Creek near Frankfort was only 3.2 percent. Silica-specific conductance



TABLE 11.—*Ratios between various dissolved constituents and properties in surface water, Elkhorn Creek basin, Kentucky*  
 [DS=dissolved solids; sp. c.=specific conductance]

Date of collection	DS sp. c.	Calcium sp. c.	Magne- sium sp. c.	Bicarbo- nate sp. c.	Sulfate sp. c.	Chloride sp. c.	Silica sp. c.	Magne- sium Calcium	Calcium Sulfate	Hardness bicarbo- nate	Sodium plus potassium chloride
<b>North Elkhorn Creek near Georgetown</b>											
Nov. 6, 1950.....	0.575	0.182	0.016	0.590	0.038	0.011	0.016	0.088	4.800	0.884	0.841
Feb. 22, 1951.....	.606	.177	.013	.520	.031	.010	.022	.076	3.462	.955	1.000
<b>South Elkhorn Creek at Fort Spring</b>											
Nov. 6, 1950.....	0.575	0.189	0.010	0.578	0.029	0.016	0.019	0.054	6.584	0.884	0.647
Feb. 22, 1951.....	.610	.175	.011	.488	.049	.008	.028	.063	3.553	.952	1.611
<b>Elkhorn Creek near Frankfort</b>											
Aug. 17, 1949.....	0.612	0.151	0.015	0.487	0.062	0.045	0.012	0.102	2.444	0.941	0.846
Oct. 10, 1949.....	.578	.133	.015	.435	.061	.057	.001	.113	2.179	.910	-----
Nov. 14, 1949.....	.608	.121	.015	.363	.060	.081	.001	.123	2.000	1.005	.886
Dec. 20, 1949.....	.613	.173	.015	.453	.070	.015	.017	.087	2.476	1.088	.667
Jan. 31, 1950.....	.612	.175	.014	.455	.068	.013	.016	.081	2.571	1.020	1.307
Mar. 9, 1950.....	.603	.176	.016	.461	.073	.018	.008	.091	2.417	1.092	.552
Apr. 17, 1950.....	.568	.169	.014	.464	.062	.018	.004	.082	2.714	1.032	1.226
May 22, 1950.....	.585	.172	.015	.513	.061	.017	.007	.087	2.857	.961	.933
June 28, 1950.....	.623	.175	.010	.546	.052	.013	.013	.078	3.368	.900	1.771
Aug. 8, 1950.....	.568	.173	.010	.450	.047	.016	.009	.058	3.667	1.046	1.383
Sept. 7, 1950.....	.592	.153	.014	.471	.056	.044	.020	.090	2.739	.933	.889
Statistic or parameter:											
Mean ( $\bar{X}$ ).....	0.597	0.161	0.014	0.464	0.061	0.031	0.010	0.090	2.676	0.903	1.046
Standard deviations ( $\sigma$ ).....	.019	.019	.002	.046	.008	.023	.006	.017	.487	.068	.351
Coefficient variable ( $V$ ), in per- cent.....	3.2	11.8	14.3	9.9	13.1	74.2	60.0	18.9	18.2	6.8	33.6



and chloride-specific conductance had  $V$  values of 60.0 and 74.2 percent, respectively. Values of this magnitude are beyond the area of reasonable relation. It seems that as the relative concentration of an ion decreases, the coefficient of variation of the ratio between the ion and specific conductance increases. There is a reasonably close relation between hardness and bicarbonate and a

moderate one between magnesium and calcium and between calcium and sulfate. The relation between sodium plus potassium and chloride is less definite.

The water in the Elkhorn Creek basin is of the calcium magnesium bicarbonate type, which is typical of water draining a limestone terrane. Among the anions, sulfate is generally of secondary importance and is a minor constituent in comparison with bicarbonate. The samples were all moderately hard to very hard. Color, according to the platinum-cobalt scale (Rainwater and Thatcher, 1930. p. 155), at the station near Frankfort increases from about 4 at high flows to about 15 at low flows perhaps due to the sewage from Lexington.

At times during low flows, the water in the stream may be entirely derived from ground water. A method suggested by F. F. Schrader<sup>2</sup> was used to determine the discharge below which one could be reasonably sure that the flow was due to ground water. For the Elkhorn Creek basin, wholly ground-water flow could be expected at discharges less than the values given as follows:

	<i>Cubic feet per second</i>
North Elkhorn Creek near Georgetown.....	0.05
South Elkhorn Creek at Fort Spring.....	.0
Elkhorn Creek near Frankfort.....	7.6

These figures are believed to be conservative. Discharges at the time all the samples were taken were greater than the above flows. Therefore, all samples may contain some surface runoff. Comparison between the chemical analyses of surface-water samples and ground-water samples shows that at a flow of 27 cfs near Frankfort, the dissolved-solids content of Elkhorn Creek is about equal to that of the more dilute samples of ground water from the Lexington group. The ratios of various constituents to specific conductance are more variable in ground water than in surface water. It would appear that simple dilutions generally take place in surface water, whereas more complex reactions take place in ground water. Variations in ground water are probably due to local differences in conditions of recharge, porosity and permeability of the rock, and chemical properties of the rock. Surface-water uniformity may be due to mixing in the stream so that samples collected are a blend of all water entering the stream above the sampling station.

#### EDEN SHALE BELT AND OUTER BLUE GRASS, BEECH FORK BASIN

##### BASIN DESCRIPTION

Beech Fork is a tributary of Rolling Fork, the principal tributary of the Salt River. This discussion is confined to the Beech Fork

<sup>2</sup> F. F. Schrader, district engineer, U.S. Geological Survey, Louisville, Ky, suggested the use of the median of the mean flows for the lowest 10 consecutive days each year for the period of record.

basin above Bardstown, which for simplicity will be called Beech Fork basin. The basin above the gaging station at Bardstown is pear shaped and covers 664 square miles. The upper one-third of the drainage area is in the Eden shale belt. Here the land is sharply rolling and the runoff is rapid. The remainder of the area is in the Outer Blue Grass where the land is undulating to rolling and the runoff is not as rapid.

A significant part of the Beech Fork basin is so steeply rolling that surface runoff is rapid. Consequently, infiltration into the soil and into the underlying rocks accounts for only a small percentage of the precipitation. In dry seasons, ground water is discharged almost entirely by evapotranspiration, and no stream flow occurs in the upper part of the basin. Ground-water contribution to low flows of Beech Fork is confined mostly to the lower part of the basin.

Ground water was sampled from rocks that have been classified into seven geologic units. These range in age from the Lexington group of the Ordovician system through black shale of the Devonian system. Most of the waters are of the calcium magnesium bicarbonate type. Exceptions are one sample from the Cynthiana formation and one from the Eden group that contained more sulfate than bicarbonate. In addition, one sample from the Maysville group contains about equal amounts of sulfate and chloride, which were about five times greater than the bicarbonate. Samples from the Devonian black shale generally contained large amounts of sulfate or chloride, or both.

#### CHEMICAL CHARACTERISTICS OF THE SURFACE WATER

Surface-water discharge from the Beech Fork basin is measured at two stations, Beech Fork near Springfield and Beech Fork at Bardstown. The drainage area above the Springfield station is 85.9 square miles and above the Bardstown station 664 square miles. Flow records at these two stations (U.S. Geol. Survey, 1958, p. 393, 394) are as follows:

	Period of record	Discharge (cfs)		
		Maximum	Minimum	Average
Beech Fork near Springfield.....	September 1952- September 1956.	3, 560	0	85. 8
Beech Fork at Bardstown.....	November 1939- September 1956.	27, 100	0	871

According to the method described on page 96, flows of about 0.7 cfs or less at the Bardstown station are certain to consist entirely of ground-water discharge. Neither of the two spot samples was obtained at such low discharges. The sample taken December 5, 1950, was obtained during a flow of 2,770 cfs and the sample taken February 13, 1951, at 15,200 cfs. Therefore, both samples represent streamflow consisting largely of surface runoff. For analyses, see table 12.

TABLE 12.—*Chemical analyses of surface water, Beech Fork at Bardstown, Ky.*  
[Analyses by U.S. Geol. Survey. Chemical constituents in parts per million]

	Sample collected	
	Dec. 5, 1950	Feb. 13, 1951
Instantaneous discharge (cfs)-----	2,770	15,200
Silica (SiO <sub>2</sub> )-----	6.2	3.4
Iron (Fe)-----	.25	.16
Calcium (Ca)-----	51	27
Magnesium (Mg)-----	7.8	3.9
Sodium (Na) and potassium (K)-----	2.3	1.0
Bicarbonate (HCO <sub>3</sub> )-----	166	86
Carbonate (CO <sub>3</sub> )-----	0	0
Sulfate (SO <sub>4</sub> )-----	21	10
Chloride (Cl)-----	2.2	1.5
Fluoride (F)-----	.0	.1
Nitrate (NO <sub>3</sub> )-----	4.0	3.0
Dissolved solids (residue on evaporation at 180° C)-----	184	99
Hardness (as CaCO <sub>3</sub> ):		
Calcium, magnesium-----	160	84
Non-carbonate-----	23	13
Specific conductance (micromhos at 25° C)-----	315	172
pH-----	7.7	7.5
Color-----	25	7

Both samples are calcium bicarbonate type water having dissolved-solids contents that seem high in relation to the discharge. This may be due, however, to flushing of salts deposited by evaporation and transpiration from the streambed, streambanks, and soils. Low flows of about 10 cfs or less may be so high in mineralization as to approach or exceed the mineralization of the dilute ground-water samples. Ratios between various elements and the specific conductance show a simple dilution at high discharges. Comparison of the chemical character of water in Elkhorn Creek with that in Beech Fork indicates that they are similar at comparable discharges.

#### EDEN SHALE BELT, OUTER BLUE GRASS, AND KNOBS, SALT RIVER BASIN

The largest drainage basin entirely within the Blue Grass region is that of the Salt River upstream from the gaging station at Shepherdsville, Bullitt County. Included in the basin are parts of the Eden shale belt, the Outer Blue Grass, and the Knobs. The topography ranges from undulating to steep and hilly. In the upper part of the basin the shale of the Eden shale belt is eroded to form steep hills. Most of the lower part of the basin is gently rolling, but there are a few steep isolated "Knobs" near Shepherdsville.

The Salt River rises in Boyle County west of Danville and flows north to near Lawrenceburg in Anderson County. There it turns sharply westward to join the Ohio River south of Louisville. Upstream from Shepherdsville, the principal tributaries are Prashears Creek, which joins the Salt River at Taylorsville, and Floyds Fork, which joins the river 2.6 miles upstream from Shepherdsville. Downstream from Shepherdsville, Rolling Fork joins the Salt River.

Exposed in the basin and underlying the soils are rocks of the Ordovician, Silurian, and Devonian age. Ordovician rocks exposed in most of the basin consist of the Eden, Maysville, and Pichmond groups. The Cynthiana formation and Lexington group are exposed in a small area in the upper part of the basin. Ordovician rocks underlie about 90 percent of the drainage area above Shepherdsville. At the edge of the Outer Blue Grass and in the Knobs, rocks of Silurian and Devonian age crop out.

In the drainage area upstream from Shepherdsville, precipitation is measured at Anchorage, Shepherdsville, Shelbyville, Taylorsville, and Van Buren. Only at Anchorage (59 years) and Shelbyville (68 years) have records been kept long enough to determine the long-term mean precipitation. Mean precipitation at Anchorage was 43.63 inches for the period 1931 to 1955 and at Shelbyville was 46.56 inches. Average discharge of the Salt River at Shepherdsville for the 18 years ending September 30, 1956, was 1,531 cfs. The mean precipitation of the basin amounts to approximately 2,886,000 acre-feet and average run off about 1,108,000 acre-feet. As the drainage basin above Shepherdsville covers 1,197 square miles (area redetermined in 1960), the average flow of the Salt River at Shepherdsville was 38 percent of the long-term mean precipitation.

*Surface-water records in the Salt River basin excluding Rolling Fork*

[U.S. Geol. Survey, 1958, p. 385, 386, 389-391]

Gaging station	Period of record	Discharge (cfs)		
		Maximum	Minimum	Average
Salt River near Harrodsburg----	Sept. 1952–Sept. 1956.	4, 140	0	42. 1
Salt River near Van Buren-----	Oct. 1938–Sept. 1956.	14, 700	0	238
Plum Creek at Waterford-----	Dec. 1953–Sept. 1956.	6, 040	0	<sup>1</sup> 33. 1
Floyds Fork at Fisherville-----	Aug. 1944–Sept. 1956.	11, 500	0	176
Salt River at Shepherdsville-----	May 1938–Sept. 1956.	50, 000	0	1, 531

<sup>1</sup> Computed.

As in most streams, much of the flow consists of surface runoff. According to the method described on page 96, the discharge, which is considered to be made up entirely of ground water (ground-water base flow), for Salt River near Van Buren is 0 cfs and for Salt River at Shepherdsville, 0.7 cfs. These discharges, when compared with average flow, indicate that the Salt River basin has a runoff somewhat characteristic of a metal roof. Most of the 58 percent of the precipitation that does not run off is lost through evaporation and transpiration.

#### INFLUENCE OF GROUND WATER ON THE SALT RIVER

Ground water in the Salt River basin is a minor contributor to the flow of Salt River. According to the method of Schrader (see p. 96), a flow of 0.7 cfs or less will be of ground-water discharge only. One can arrive at the conclusion that ground-water influence on the chemical character of the Salt River is not direct and probably is quite small. This conclusion seems to be borne out by the chemical-quality record at Shepherdsville.

Ground water, however, has an effect on the chemical character of the river water in an indirect way. Ground waters in the basin are of calcium magnesium bicarbonate or sodium chloride types. The sodium chloride waters generally have a high dissolved mineral content. During dry periods, seepage may bring salts to the surface where the water evaporates. The salts then can be washed into the stream when overland flow resumes. This accounts for the occurrence of unusually high values for dissolved solids in some streams in the early stages of a rise or flood.

#### CHEMICAL CHARACTERISTICS OF SALT RIVER

Chemical analyses of the surface waters in the Salt River basin above Shepherdsville are given in table 13. The basic data have been published in Lamar and others (1953, 1955), Collier and Krieger (1958), and U.S. Geological Survey (1956-60). Sampling procedures and analytical methods are described by Rainwater and Thatcher (1960). A summary of the chemical character of surface waters in the Salt River basin above Shepherdsville is given in table 13.

Salt River has a name it appears not to deserve. It is not a sodium chloride type water. Compared with most streams in arid regions, the mineralization of the Salt River is quite low. The Salt River discharges water of the calcium bicarbonate type in which magnesium and sulfate are the predominant secondary ions. Two samples from the Salt River near Van Buren were taken at discharges of 0.8 and about 1,200 cfs. The ratios of dissolved solids and various ions to specific conductance are about the same at both rates of flow. The exception is that at the higher flow, sulfate constituted a larger part and bicarbonate a smaller part of the total anions. With this excep-

TABLE 13.—*Summary of chemical analyses of surface water, Salt River basin, Kentucky*

[Analyses by the U.S. Geol. Survey. Chemical constituents in parts per million. As the composite periods during a year range from 1 day to 31 days, the analysis for a composite sample was weighted by the number of days in the composite period. The average of these weighted values is the time-weighted average.]

Date of collection	Mean discharge (cfs)	Silica (SiO <sub>2</sub> )	Iron (Fe)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Bicarbonate (HCO <sub>3</sub> )	Carbonate (CO <sub>3</sub> )	Sulfate (SO <sub>4</sub> )	Chloride (Cl)	Fluoride (F)	Nitrate (NO <sub>3</sub> )	Dissolved solids (residue on evaporation at 180° C)	Hardness as CaCO <sub>3</sub>		Specific conductance (microhmhos at 25° C)	pH	Color
															Calcium	Noncarbonate			
Floyds Fork at Fisherville																			
Aug. 4, 1953 <sup>1</sup>	0.2	4.9	0.08	51	2.7	2.0	3.3	148	0	17	3.0	0.3	1.7	155	138	17	274	7.6	15
Nov. 25, 1950 <sup>2</sup>	123	7.8	.01	71	19	2.5	2.4	274	0	26	3.6	.0	5.0	269	257	31	458	8.1	7
Average <sup>3</sup>		4.3	.04	56	13	3.3	2.4	197	0	30	4.5	.1	3.1	220	192	30	389		6
Salt River at Shepherdsville																			
Oct. 1, 1952-Sept. 30, 1953:																			
July 19-21, 1953 <sup>4</sup>	877	7.7	0.03	30	4.3	3.4	2.5	96	0	14	3.6	0.2	5.1	121	93	14	185	7.2	7
Dec. 21-31, 1952 <sup>4</sup>	395	17	.01	64	11	6.2	2.1	190	0	40	12	.1	13	258	208	49	433	7.2	4
1953 Water year <sup>4</sup>	1,209	7.3	.05	49	8.3	3.8	2.3	161	0	22	5.1	.1	5.9	191	156	24	321		8
Oct. 1, 1953-Sept. 30, 1954:																			
Sept. 20-21, 1954 <sup>4</sup>	11,730	4.4	.13	27	4.6	1.8	4.0	84	0	9.1	3.0	.3	6.4	95	87	17	176	7.4	10
Feb. 11-20, 1954 <sup>4</sup>	91.1	6.3	.01	72	9.0	5.2	1.8	188	0	44	7.0	.1	18	268	216	63	433	7.3	6
1954 Water year <sup>4</sup>	346	5.3	.02	55	7.9	3.9	3.0	162	0	30	5.5	.3	7.6	207	170	37	343		13
Oct. 1, 1954-Sept. 30, 1955:																			
Mar. 16-17, 1955 <sup>4</sup>	11,180	7.6	.09	32	5.0	1.9	2.9	110	0	13	4.0		5.9	135	100	10	226	7.2	
Dec. 21-27, 1954 <sup>4</sup>	267	7.3	.03	83	11	3.8	2.5	240	0	42	5.9	.2	8.4	287	253	56	494	8.0	12
1955 Water year <sup>4</sup>	1,622	7.0	.03	57	9.1	3.6	2.6	182	0	24	4.9	.2	6.0	212	180	30	353		11
Oct. 1, 1955-Sept. 30, 1956:																			
July 25-31, 1956 <sup>4</sup>	1,128	8.2	.05	35	2.6	1.2	3.1	98	0	14	2.4	.4	5.5	129	98	18	205	7.2	22
Dec. 17-31, 1955 <sup>4</sup>	143	7.0	.01	83	15	4.3	2.3	272	0	40	7.5	.2	6.2	304	269	46	529	7.6	2
1956 Water year <sup>4</sup>	1,360	7.6	.04	56	10	3.6	2.8	186	0	26	4.8	.2	4.2	215	181	28	362		8

<sup>1</sup> Sample with minimum dissolved solids.<sup>2</sup> Sample with maximum dissolved solids.<sup>3</sup> Average of 13 samples.<sup>4</sup> Composite sample with minimum dissolved solids.<sup>5</sup> Composite sample with maximum dissolved solids.<sup>6</sup> Average of composited samples.<sup>7</sup> Time-weighted average of composited samples.



tion, the higher flow was mainly a simple dilution of the dissolved materials.

Data for Floyds Fork at Fisherville are based on 13 samples taken over a 3-year period. The quality of water was similar to that of the Salt River near Van Buren, except that dissolved-solids content generally was higher in samples from Floyds Fork. Silica and iron at both stations were low, as were chloride, fluoride, and nitrate. All samples were slightly basic as the lowest pH was 7.2.

At Shepherdsville, the greater number of samples over a longer period of time gave data that showed greater variation and wider extremes of mineral content of the water. As at the two upstream stations, the Salt River at Shepherdsville was a calcium bicarbonate water in which sulfate was relatively high; all other ions were generally low. The hardness of the waters in the drainage basin ranges from moderately hard to very hard. Potassium exceeded sodium at times on a parts-per-million basis without relation to discharge. This may be due to heavy application of potash fertilizer in the tobacco fields. No sodium chloride type waters were found at the points sampled. Dissolved solids averaged about 200 ppm for most years.

A statistical treatment was used to determine the relations between specific conductance and various constituents and between the different constituents. The ratios were calculated from parts-per-million values to promote uniformity in expressing concentrations of the constituents. This form also made it easier to calculate loads of dissolved solids which are taken up in detail in the section beginning on page 112.

Ratios, means ( $\bar{X}$ ), standard deviations ( $\sigma$ ), and coefficients of variation ( $V$ ) are given in table 14. A low coefficient indicates that the two statistics are closely related. For example,  $V$  for dissolved solids-specific conductance for Floyds Fork at Fisherville was 6.9 percent, whereas  $V$  for chloride:specific conductance was 93 percent. Dissolved-solids content was closely related to specific conductance, but chloride was not. Also, magnesium and calcium were less closely related to each other than were calcium and magnesium together (hardness) to bicarbonate. Another inference based on the value of  $V$  for sodium:chloride is that sodium and chloride are derived in part from other compounds than the salt, sodium chloride.

Similar comparisons can also be made for the Salt River at Shepherdsville but with some additional deductions. Coefficients of variation for Shepherdsville are generally lower than for Floyds Fork. At Shepherdsville, 124 composite samples were analyzed; at Fisherville, 13 spot samples were analyzed. Composite samples tend to suppress extremes in variation, and their greater number at Shepherdsville make the parameters more consistent.

TABLE 14.—*Ratios between various dissolved constituents and properties in surface water, Salt River basin, Kentucky*  
 [DS=dissolved solids; sp. c.=specific conductance]

Date of collection	DS sp. c.	Ca sp. c.	Mg sp. c.	Na sp. c.	HCO <sub>3</sub> sp. c.	SO <sub>4</sub> sp. c.	Cl sp. c.	SiO <sub>2</sub> sp. c.	Mg Ca	Ca SO <sub>4</sub>	Hardness HCO <sub>3</sub>	Na Cl	Na+K Cl
<b>Floyds Fork at Fisherville</b>													
Nov. 25, 1950.	0.587	0.155	0.041	0.012	0.598	0.057	0.008	0.017	0.298	2.731	0.938	0.945	0.684
Feb. 14, 1951.	.576	.142	.027	.006	.537	.061	.008	.017	.189	2.316	.867	---	3.200
June 11, 1952.	.579	.132	.045	.006	.546	.078	.013	.009	.359	1.697	.940	---	---
July 24, 1952.	.595	.157	.019	.006	.496	.077	.010	.025	.123	2.048	.474	.571	---
Sept. 26, 1952.	.583	.151	.024	.009	.462	.109	.012	.006	.157	1.385	1.036	.762	---
Oct. 30, 1952.	.596	.159	.023	.007	.467	.122	.015	.003	.144	1.306	1.053	.467	---
Dec. 24, 1952.	.448	.111	.030	.006	.349	.077	.013	.009	.271	1.439	1.151	.443	---
Jan. 23, 1953.	.574	.145	.036	.006	.494	.080	.010	.013	.250	1.818	1.044	.575	---
Mar. 10, 1953.	.579	.146	.036	.009	.526	.074	.010	.010	.246	1.968	.982	.900	---
Apr. 9, 1953.	.563	.146	.038	.007	.547	.066	.010	.010	.263	2.192	.949	.650	---
June 5, 1953.	.594	.122	.048	.014	.541	.059	.019	.007	.363	2.074	.927	.753	---
July 16, 1953.	.550	.135	.041	.009	.544	.067	.011	.009	.304	2.000	.914	.816	---
Aug. 4, 1953.	.566	.186	.010	.007	.540	.062	.062	.018	.053	3.000	.932	.667	---
Statistic or parameter:													
Mean ( $\bar{X}$ )	0.568	0.145	0.032	0.008	0.511	0.076	0.015	0.012	0.231	1.998	0.939	0.686	---
Standard deviation ( $\sigma$ )	.039	.019	.011	.003	.061	.019	.014	.006	.094	.498	.159	.167	---
Coefficient variable ( $V$ ), in per- cent.	6.9	13.1	34.4	37.5	11.9	25.0	93.3	50.0	40.7	24.9	16.9	24.3	---
<b>Salt River at Shepherdsville</b>													
Number of samples ( $N$ )	124	124	124	124	124	124	124	124	124	124	124	124	---
Mean ( $\bar{X}$ )	0.602	0.157	0.025	0.012	0.492	0.075	0.016	0.020	0.162	2.203	1.010	0.798	---
Standard deviation ( $\sigma$ )	.025	.010	.005	.004	.340	.033	.033	.019	.031	.543	.575	.305	---
Coefficient variable ( $V$ ), in percent.	4.2	6.4	20.0	33.3	8.1	10.7	50.0	96.0	25.3	24.6	7.4	38.6	---

**CHEMICAL COMPOSITION OF WATER OF LARGE STREAMS  
DRAINING AREAS PARTLY IN THE BLUE GRASS REGION**

The Blue Grass region does not include the entire drainage basins of two larger streams. The upper part of the drainage basins of the Licking and the Kentucky Rivers are in the Eastern Coal Field. The geology, topography, and land use of the Eastern Coal Field is such that water draining from it has different chemical characteristics than waters of the Blue Grass region. Consequently, waters of the Licking and the Kentucky Rivers at sampling points in the Blue Grass region are mixtures of two types. For this reason, they are not strictly characteristic of a limestone terrane.

Daily and periodic sampling stations have been maintained in the two river basins as follows:

In addition, a number of spot samples were collected from the two rivers and various tributaries in the Blue Grass and Eastern Coal Field regions.

Sampling station	Type of sampling	Period
Licking River near Salyersville <sup>1</sup> -----	Periodic-----	Oct. 1951-Sept. 1952.
Licking River at Farmers <sup>2</sup> -----	-----do-----	Sept. 1949-Aug. 1950.
Licking River at McKinneysburg-----	Daily-----	Oct. 1952-Sept. 1956.
South Fork Licking River at Cynthiana.	Periodic-----	Oct. 1950-Aug. 1951.
Licking River at Butler-----	Daily-----	Oct. 1949-Sept. 1950.
North Fork Kentucky River at Hazard. <sup>1</sup>	Periodic-----	Nov. 1949-Aug. 1950.
Kentucky River at Lock 14, at Heidelberg. <sup>1</sup>	-----do-----	Oct. 1950-Aug. 1951.
Kentucky River at Lock 4, at Frankfort.	Daily-----	Oct. 1949-Sept. 1956.
Elkhorn Creek near Frankfort-----	Periodic-----	Oct. 1949-Sept. 1950.

<sup>1</sup> In Eastern Coal Field.

<sup>2</sup> In Blue Grass region, but the flow is almost entirely made up of water from the Eastern Coal Field.

**LICKING RIVER BASIN**

The Licking River drains two regions in Kentucky. About one-fourth of the basin lies in the Eastern Coal Field, which is underlain mainly by sandstone, limestone, and shale of Mississippian and Pennsylvanian age. The remainder drains the eastern one-third of the Blue Grass region. Rocks exposed in the Blue Grass section of the basin range in age from Ordovician through Quaternary. Silurian and Devonian shale is exposed in the knobs at the rim of the Blue Grass region and limestone locally interbedded with shale is exposed in the rest of the Blue Grass section.

Flow of the Licking River from the Eastern Coal Field is measured at Farmers. The area of the Licking River basin is 3,655 square miles. Mean discharge and drainage areas at important stations (U.S. Geol.

Survey, 1958, p. 320, 324, 326, 327; U.S. Geol. Survey, 1957, p. 450) are given in the table below:

Station	Drainage area (sq mi)	Period of record	Mean discharge (cfs)
Licking River at Farmers-----	826	1938-56	1, 051
Licking River at McKinneysburg-----	2, 280	1924-25, 1939-56	2, 931
South Fork Licking River at Cynthiana-----	615	1938-56	743
Licking River at Catawba-----	3, 250	1915-17, 1928-56	4, 123
Licking River at Butler-----	3, 330	1938-42	3, 506

<sup>1</sup> Computed.

#### CHEMICAL CHARACTERISTICS OF SURFACE WATERS OF THE LICKING RIVER BASIN

In the Eastern Coal Field, oil-field brines and acid coal-mine drainage influence the chemical character of the water. Samples taken from the Licking River at Salyersville and at Farmers and from the Triplett Creek at Morehead show waters from these sources to be present. On plate 7, the major ions are shown in equivalents per million. High and low flows may be different in chemical character as shown by high and low flow samples of the Licking River at Salyersville.

Monthly samples taken at Farmers (table 15) show the variation in composition that occurs with time. The dissolved solids-specific conductance ratio is most consistent with a coefficient of variation of 7.7 percent. Of course, the dissolved-solids content and specific conductance should be consistent as they are interdependent. Variations in the calcium-specific conductance and magnesium-specific conductance ratios is slightly larger. More variable are the dissolved matter such as sulfate, chloride and sodium which are derived from oil-field brines and mine drainage. This is the type of water entering the Blue Grass region from the upper Licking River basin.

Chemical quality of water in the Blue Grass region is typical for water of a limestone terrane. Calcium and bicarbonate ions make up about two-thirds or more of the dissolved mineral matter as shown on plate 7. The South Fork Licking River, which drains a central area of the Blue Grass region, is highest in relative amounts of calcium and bicarbonate.

The ion to specific-conductance ratios of table 15 show that the influence of Eastern Coal Field drainage diminishes with distance downstream. For instance, the mean bicarbonate-specific conductance ratio is 0.353 at Farmers, 0.450 at McKinneysburg, and 0.486 at Butler. Sulfate-specific conductance ratios decline from 0.115 at Farmers, 0.091 at McKinneysburg, and to 0.080 at Butler. Chloride shows a similar decline. Ratios of stations on the main stem tend to approach the ratios of the station at Butler.

TABLE 15.—*Ratios between various dissolved constituents and properties in surface water, Licking River basin, Kentucky*

[DS=dissolved solids; sp. c.=specific conductance]

Sampling period	Statistic or parameter	DS sp. c.	Ca sp. c.	Mg sp. c.	Na sp. c.	HCO <sub>3</sub> sp. c.	SO <sub>4</sub> sp. c.	Cl sp. c.	SiO <sub>2</sub> sp. c.	Mg Ca	Ca SO <sub>4</sub>	Hard- ness HCO <sub>3</sub>	Na Cl	Na+K Cl
<b>Licking River at Farmers</b>														
Sept. 1949-Aug. 1950.	Number of samples (N).....	11	11	11	11	11	11	11	11	11	11	11	1	10
	Mean ( $\bar{X}$ ).....	.638	.095	.031	-----	.453	.115	.053	.071	.328	1.012	1.065	-----	1.436
	Standard deviation ( $\sigma$ ).....	.049	.017	.006	-----	.079	.039	.020	.028	.080	.655	.272	-----	1.060
	Coefficient variable ( $V$ ), in percent.....	7.7	17.9	19.4	-----	22.4	33.9	37.7	39.4	15.2	64.7	25.5	-----	73.8
<b>Licking River at McKinneysburg</b>														
Oct. 1952-Sept. 1956.	Number of samples (N).....	153	153	153	153	153	153	152	153	153	153	153	152	-----
	Mean ( $\bar{X}$ ).....	.614	.140	.027	.016	.450	.091	.021	.040	.191	1.660	1.038	.814	-----
	Standard deviation ( $\sigma$ ).....	.039	.010	.004	.004	.052	.025	.007	.018	.038	.505	.111	.199	-----
	Coefficient variable ( $V$ ), in percent.....	6.4	7.1	14.8	25.0	11.6	27.5	33.3	45.0	19.9	30.4	10.7	24.4	-----
<b>South Fork Licking River at Cynthiana</b>														
Sept. 1949-Aug. 1951.	Number of samples (N).....	12	12	12	5	12	12	12	12	12	12	12	5	7
	Mean ( $\bar{X}$ ).....	.596	.165	.020	.015	.516	.069	.013	.024	.126	2.574	.967	.827	1.676
	Standard deviation ( $\sigma$ ).....	.020	.015	.007	.005	.044	.020	.006	.026	.054	.726	.062	.392	.142
	Coefficient variable ( $V$ ), in percent.....	3.4	9.1	35.0	33.3	8.5	29.0	46.2	108.3	42.8	28.2	6.5	47.4	8.5
<b>Licking River at Butler</b>														
Oct. 1949-Sept. 1950.	Number of samples (N).....	36	36	36	-----	36	36	36	36	36	36	36	6	30
	Mean ( $\bar{X}$ ).....	.615	.146	.025	-----	.486	.080	.019	.032	.172	1.892	.959	1.063	1.521
	Standard deviation ( $\sigma$ ).....	.024	.011	.008	-----	.036	.014	.013	.014	.025	.396	.071	.560	.905
	Coefficient variable ( $V$ ), in percent.....	3.9	7.5	32.0	-----	7.4	17.5	68.4	43.8	14.5	21.0	7.4	52.7	59.5

Basic data on the chemical composition of waters of the Licking River basin have been published in Lamar and others (1953, 1955), Collier and Krieger (1958), and U.S. Geological Survey (1955-60).

In essence, the drainage from the Eastern Coal Field, which is influenced by brines and coal-mine drainage, becomes altered by more consistent calcium magnesium bicarbonate waters of the Blue Grass region.

#### KENTUCKY RIVER BASIN

Like the Licking River basin, the Kentucky River drains a part of the Eastern Coal Field region before entering the Blue Grass region. Between 40 and 50 percent of the basin is in the Eastern Coal Field. Coal mines active and inactive, are plentiful in the upper Kentucky River basin. Some oil and gas is also produced in this area.

Rocks of the upper Kentucky River basin consist mainly of sandstone and shale of Mississippian and Pennsylvanian age. The area of the Blue Grass region drained by the Kentucky River consists of a strip cutting across the heart of the Blue Grass. Accordingly, the limestone interbedded with shale in this section ranges in age from Ordovician to Mississippian.

Flow of the Kentucky River is measured at a number of points on the main stem and important tributaries. A list of these stations, their drainage areas and mean discharges (U.S. Geol. Survey, 1958, p. 356, 363, 368, 369, 372, 376, 378, 380) are given in the table below. The flow from the Eastern Coal Field is measured essentially by the station at Heidelberg.

Station	Drainage area (sq mi)	Period of record	Mean discharge (cfs)
North Fork Kentucky River at Hazard.....	466	1940-56	519
Kentucky River at lock 14, at Heidelberg....	2, 657	1925-31, 1938-56	3, 490
Kentucky River at lock 8, near Camp Nelson..	4, 414	1939-56	5, 550
Dix River near Danville.....	316	1942-56	445
Kentucky River at lock 4, at Frankfort.....	5, 412	1925-30, 1932-56	7, 044
Elkhorn Creek near Frankfort.....	474	1915-18, 1940-56	576
Kentucky River at lock 2, at Lockport.....	6, 181	1925-30, 1932-37, 1939-56	8, 206
Eagle Creek at Glencoe.....	438	1915-18, 1928-31, 1938-56	507

The effect of mine drainage is shown by the percentage composition of the low and high flow samples obtained from the North Fork Kentucky River at Hazard (pl. 8). Sulfate makes up about two-thirds in equivalent parts per million of the total anions present.

Dilution by the South and Middle Forks of the Kentucky River reduces this to about a half at Heidelberg. There is little coal mining in these latter two subbasins. With dilution of the sulfate content, there seems to be a general increase in dissolved mineral matter in the lower reaches of the Kentucky River. Tributaries like Elkhorn Creek and Eagle Creek are relatively high in dissolved solids. However, these Blue Grass streams are definitely of the calcium bicarbonate type. The chemical characteristics of the Elkhorn Creek basin were discussed in an earlier section of this report.

The mass of data obtained on a regular basis from monthly and daily sampling stations was reduced to the form given in table 16. The basic data have been published in Lamar and others (1953, 1955), Collier and Krieger (1958), and U.S. Geological Survey (1955-60). The increasing calcium-specific conductance ratios downstream show that calcium makes up an increasingly larger part of the dissolved mineral matter in the Blue Grass section of the basin. Magnesium, on the other hand, makes up a decreasingly smaller part of the dissolved solids. This is confirmed even more strongly by the Magnesium-calcium ratio which is 0.485 at Hazard 0.446 at Heidelberg, and only 0.222 at Frankfort. The relative concentration of sulfate decreases downstream as shown by the sulfate-specific conductance and the calcium-sulfate ratios. The coefficients of variation indicate that concentrations of calcium, magnesium, and silica in relation to specific conductance and the ratio of calcium to sulfate are more variable downstream, whereas most of the others do not have a consistent trend from Hazard to Frankfort. In general, the chemical characteristics of the Kentucky River at Frankfort tend to approach the character of Elkhorn Creek at Frankfort. The latter stream and Dix River are more typical in chemical character of streams draining a limestone terrane.

#### CHEMICAL EROSION

The movement of water in and over the rocks to the streams, down the streams, and to the ocean is a means of removing vast quantities of mineral matter from land to sea. The process is slow at the start but becomes rapid once the water and its minerals reach the stream. Upon reaching the stream, the mineral load can be measured easily in three forms: fluvial sediment, colloidal matter, and dissolved material in ionic form. A full treatment of fluvial sediment is beyond the scope of this report. As data on the tonnage of suspended sediment were available for three of the largest streams in the Blue Grass region, however, sediment-load data are included for comparison purposes.

TABLE 16.—*Ratios between various dissolved constituents and properties in surface water, Kentucky River basin*

[D. S. = dissolved solids; Sp. C. = specific conductance]

Sampling period	Statistic or parameter	D. S. Sp. C.	Ca Sp. C.	Mg Sp. C.	Na Sp. C.	HCO <sub>3</sub> Sp. C.	SO <sub>4</sub> Sp. C.	Cl Sp. C.	SiO <sub>2</sub> Sp. C.	Mg Ca	Ca SO <sub>4</sub>	Hard. HCO <sub>3</sub>	Na Cl	Na+K Cl
<b>North Fork Kentucky River at Hazard</b>														
Aug. 1949-Aug. 1950	Number of samples (N)	10	10	10	10	10	10	10	10	10	10	10	10	10
	Mean ( $\bar{X}$ )	0.646	0.082	0.040	-----	0.145	0.320	0.018	0.036	0.485	0.259	2.536	-----	3.210
	Standard deviation ( $\sigma$ )	.031	.003	.003	-----	.023	.029	.005	.017	.037	.024	.387	-----	1.090
	Coefficient variable in percent (V)	4.8	3.6	7.5	-----	15.9	9.1	27.8	47.2	7.6	9.3	14.9	-----	34.0
<b>Kentucky River at Lock 14, at Heidelberg</b>														
Aug. 1949-July 1951	Number of samples (N)	9	9	9	-----	9	9	9	9	9	9	9	4	5
	Mean ( $\bar{X}$ )	0.642	0.080	0.035	-----	0.192	0.244	0.034	0.056	0.446	0.349	1.870	3.237	1.712
	Standard deviation ( $\sigma$ )	.032	.006	.005	-----	.041	.060	.033	.028	.065	.062	.420	3.155	1.905
	Coefficient variable in percent (V)	8.1	7.5	14.3	-----	21.4	24.6	97.0	50.0	19.0	29.2	22.4	98.4	53.0
<b>Kentucky River at Lock 4, at Frankfort</b>														
Oct. 1949-Sept. 1956	Number of samples (N)	241	240	240	173	242	241	241	223	242	241	242	175	-----
	Mean ( $\bar{X}$ )	0.600	0.125	0.028	0.029	0.381	0.115	0.036	0.039	0.222	1.160	1.103	0.817	-----
	Standard deviation ( $\sigma$ )	.035	.014	.003	.009	.069	.026	.018	.024	.048	.376	.147	.254	-----
	Coefficient variable in percent (V)	5.8	11.2	10.7	31.0	15.5	22.6	50.0	61.5	21.6	32.4	13.3	31.1	-----
<b>Elkhorn Creek near Frankfort</b>														
Aug. 1949-Sept. 1950	Number of samples (N)	11	11	11	-----	11	11	11	11	11	11	11	-----	10
	Mean ( $\bar{X}$ )	0.597	0.161	0.014	-----	0.464	0.061	0.031	0.010	0.090	2.676	0.933	-----	1.046
	Standard deviation ( $\sigma$ )	.019	.019	.002	-----	.046	.008	.023	.006	.017	.457	.068	-----	.351
	Coefficient variable in percent (V)	3.2	11.8	14.3	-----	9.9	13.1	74.2	60.0	18.9	18.2	6.8	-----	33.6



## OCCURRENCE OF THE ELEMENTS

## FORM AND CONCENTRATION IN ROCKS AND SOILS

The rocks of the Blue Grass region consist mainly of calcium limestone and magnesian limestone interbedded with shale. Consequently, calcium and magnesium occur almost entirely as simple carbonates. More complicated calcium and magnesium minerals, if present, may be found mostly in the shale. No true dolomite was found among the rock analyses examined for this report. The limestone richest in magnesium has a ratio of 100 calcium atoms to 91 magnesium atoms. Calcium and magnesium, at least briefly, may be in the form of sulfates in areas around oxidizing sulfides. It is a common practice to apply lime to the soils of the Blue Grass region which adds to the supply of limestone available for solution.

Sodium and potassium are found in the rock analyses reported, but the mineral form was not determined. Analyses of seven simple limestones of the Blue Grass (table 6) had median values of 1,530 ppm sodium and 1,910 ppm potassium. Ten analyses of shale and clay had median values of 3,080 ppm sodium and 36,700 ppm potassium (table 6). A principal source of these elements in the waters of the Blue Grass region is the brine that occurs at relatively shallow depths.

The average abundance of sulfur, according to Rankama and Sahama (1950, p. 226) is 1,100 ppm in limestone, 2,600 ppm in shale, and 2,800 ppm in sandstone. Sulfur as S computed from  $\text{SO}_4$ , in carbonate rocks in the Blue Grass ranged from 0 to 15,160 ppm (table 5 and Richardson, 1923). In shale and clay, the abundance was usually reported in trace quantities, but one Devonian shale contained 2,720 ppm sulfur (Easton, 1913). Much of the sulfur apparently occurs as iron and manganese sulfides, which oxidize readily to sulfate. Some sulfur probably occurs also as alkaline earth sulfates. Soil analyses show sulfur generally to be more abundant in the top 7 inches of soil. This may be due to fertilization or to plant residues.

Rankama and Sahama (1950, p. 765) stated that the chloride content of sedimentary rocks is practically unknown. According to our data, the concentration generally is low. In the Blue Grass region, limestone generally contains less chloride than shale. One sample of shale from the Highbridge group contained 1,400 ppm. The chloride content of brines or connate waters is as much as two or more times the abundance found in sea water. The chloride content of soils is generally low. Soils obtain much of their chloride from rainwater and from fertilizers, especially potash fertilizers. Tobacco, a common crop in the area, requires rather large applications of potash.

Silicon is one of the most abundant elements. In carbonate rocks, quartz is not uncommon. Silicon, occurring as silicates in clay

minerals, is a basic constituent of shale. In sandstone, silica is the principal mineral compound. Chemical analyses of limestone, shale, and sandstone of rocks of the Blue Grass area show their ranges of silica content to be as follows:

<i>Rock</i>	<i>Range of silica content, percent</i>
Limestone-----	1. 0-5. 7
Shale-----	21. 8-56. 0
Sandstone-----	47. 2-93. 3

In the soils of the area, silica content generally ranges from 65 to 92 percent of the mineral matter. Silicon is present as quartz grains and in the clay minerals.

#### FORM AND CONCENTRATION IN SURFACE WATERS

Silicon is believed to occur in several forms in water depending on pH and the alkali-silica ratio. A discussion of the various forms of silicon in water is given by Hem (1959, p. 53-57). It appears that under the conditions present in streams of the Blue Grass region, silicon occurs in one or more forms in the ionic and colloidal states. The reported concentrations of silica are generally less than 10 ppm, although amounts of 22 ppm and 24 ppm were reported for the Kentucky River at Frankfort.

The remainder of the determined constituents occur in water in the ionic state. Iron as  $\text{Fe}^{+3}$  generally occurs in amounts less than 0.10 ppm in surface waters and as  $\text{Fe}^{+2}$  in higher amounts in ground water. The cations calcium, magnesium, sodium, and potassium and the anions bicarbonate, sulfate, and chloride vary in concentration with the season and rate of discharge of the particular stream. These variations will be taken up in some detail in the sections that follow.

#### MOVEMENT OF THE ELEMENTS

The movement of dissolved material is an important geochemical process. The rivers draining the Blue Grass region are the most important means of removing the products of weathering from the region. The removal of these products is a complicated one as it depends on many factors. The rate of removal from any one area depends largely on the amount and rate of streamflow and time of the year. In the sections that follow, three of the characteristics of chemical erosion of the land surface will be described. These three characteristics are: (1) The dissolved loads of various streams, (2) the variation in dissolved material with changes in discharge, and (3) the seasonal variations that occur in the amount of dissolved material in the streams.

## DISSOLVED LOAD

The dissolved-load calculations have been made only for daily sampling stations. The methods of sampling, of compositing of daily samples, and of analysis are described adequately by Rainwater and Thatcher (1960, p. 3-25, 32-39) and Hem (1959, p. 14-18). Specific conductance was the only property measured daily. From the relations between specific conductance and dissolved solids, a mean-daily concentration of dissolved solids in parts per million was obtained. The mean-daily values for dissolved solids and discharge were then used to calculate daily dissolved load. Suspended-sediment figures are based on a daily determination of sediment concentration and were calculated in a similar manner. No attempt was made to determine that part of the load due to municipal, industrial, and agricultural wastes.

The dissolved load was measured at three sampling stations: Licking River at McKinneysburg, Kentucky River at Lock 4 at Frankfort, and Salt River at Shepherdsville. The dissolved and suspended loads for these stations are given in table 17. The total load as used in this report includes only the dissolved solids and suspended sediment. It does not include the sediment transported as bed or saltation load.

TABLE 17.—*Dissolved loads of streams of the Blue Grass region, Kentucky*

Sampling period	Water discharge (cu ft x 10)	Total load, <sup>1</sup> (tons)	Dissolved load		Suspended sediment load		
			Tons	Percent of total load	Tons	Percent of total load	
Licking River at McKinneysburg							
Oct. 1, 1952-Sept. 30, 1953	68.71	819,000	207,000	25.3	612,000	74.7	
Oct. 1, 1953-Sept. 30, 1954	25.85	398,000	92,200	23.2	305,000	76.8	
Oct. 1, 1954-Sept. 30, 1955	98.63	2,248,000	328,000	14.6	1,920,000	85.4	
Oct. 1, 1955-Sept. 30, 1956	117.85	2,609,000	319,000	12.2	2,290,000	87.8	
Total	311.05	6,074,000	946,200	15.6	5,128,000	84.4	
Kentucky River at lock 4, at Frankfort							
Oct. 1, 1949-Sept. 30, 1950	339.41		1,040,000				
Oct. 1, 1950-Sept. 30, 1951	288.57		936,000				
Oct. 1, 1951-Sept. 30, 1952	297.99		900,000				
Oct. 1, 1952-Sept. 30, 1953	178.56	1,680,000	580,000	34.5	1,100,000	65.5	
Oct. 1, 1953-Sept. 30, 1954	77.10	594,000	277,000	46.6	317,000	53.4	
Oct. 1, 1954-Sept. 30, 1955	249.29	4,633,000	833,000	18.0	3,800,000	82.0	
Oct. 1, 1955-Sept. 30, 1956	248.72	4,204,000	814,000	19.4	3,390,000	80.6	
Total	1,679.64	11,111,000	<sup>2</sup> 2,504,000 5,380,000	<sup>2</sup> 22.5	8,607,000	77.5	
Salt River at Shepherdsville							
Oct. 1, 1952-Sept. 30, 1953	38.14	795,000	199,000	25.0	596,000	75.0	
Oct. 1, 1953-Sept. 30, 1954	10.89	357,700	58,700	16.4	299,000	83.6	
Oct. 1, 1954-Sept. 30, 1955	50.71	1,630,000	280,000	17.2	1,350,000	82.8	
Oct. 1, 1955-Sept. 30, 1956	44.15	962,600	76,600	8.0	886,000	92.0	
Total	143.89	3,745,300	614,300	16.4	3,131,000	83.6	

<sup>1</sup> Does not include material transported as bed or saltation load.<sup>2</sup> October 1952 to September 1956 only.

The dissolved load composes only a small part of the total load. For the Licking River it averaged 15.6 percent, for the Kentucky River 22.5 percent, and for the Salt River 16.4 percent. The part varies widely from one year to the next. Maximum and minimum values do not occur during the same years for the three stations. For example, dissolved loads made up the highest fraction of the total load in the 1954 water year at Frankfort, but the largest fraction occurred in 1953 at McKinneysburg and Shepherdsville. The minimum fraction of dissolved load showed a similar pattern. For 4 comparable years, 1953-56, the average yield of dissolved solids was 104 tons per square mile per year at McKinneysburg, 116 tons at Frankfort, and 125 tons at Shepherdsville. Yield of dissolved solids apparently is not a direct function of basin size.

Dissolved load is a function of water discharge as shown in figure 24. The relation is almost a straight line for the Licking, the Kentucky, and the Salt Rivers. The Salt River carries a slightly greater dissolved load per cubic foot of water than either of the other two streams. At 1,000 cfs-days per month the Salt River carries 1.3 times as much dissolved material as the Licking River. At 100,000 cfs-days per month, the load is about 1.7 times that of the Licking River and about 1.5 times that of the Kentucky River.

#### VARIATION IN DISSOLVED LOAD

The dissolved load of a stream depends on the season and water discharge. During the winter months the greatest daily and monthly loads of dissolved solids occur. The load for this quarter makes up about 60 percent of the yearly load as shown in table 18. During the spring quarter of April, May, and June, about 20-25 percent of the yearly load is removed from the basin. The remaining 15-20 percent of the yearly load is about equally divided between the summer and fall quarters. Water discharge has a similar distribution pattern. However, when a season of above-normal flows occurs as during July-September 1950 at Frankfort, there is an above-normal dissolved load.

In general a high dissolved load occurs during periods of sustained medium to high flow. Sediment loads, on the other hand, are high when a large flood or series of floods occur during the month. Dissolved-solids concentrations decrease for a day or so after sudden high stages and then rapidly return to about the normal concentration for the season. Sediment concentrations, on the other hand, increase sharply during the rising stages of a flood and then decrease to a normal concentration.

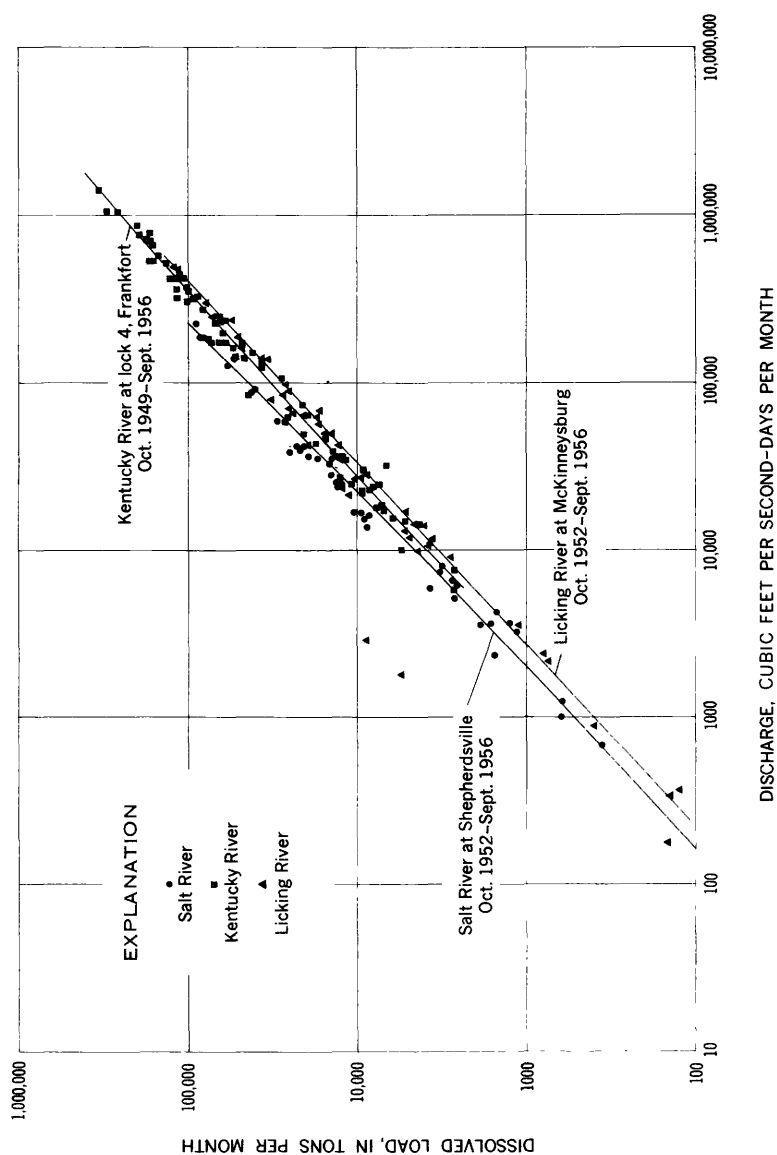


FIGURE 24.—Relation between dissolved load and water discharge for the Blue Grass region, Kentucky.

TABLE 18.—*Seasonal dissolved loads of Blue Grass region streams*

Water year	October to December		January to March		April to June		July to September	
	Tons	Yearly load (percent)	Tons	Yearly load (percent)	Tons	Yearly load (percent)	Tons	Yearly load (percent)
<b>Licking River at McKinneysburg</b>								
1953-----	15,100	7.3	120,000	57.9	66,400	32.0	5,780	2.8
1954-----	622	.7	43,700	47.4	38,300	41.5	9,630	10.4
1955-----	30,000	9.1	222,000	67.6	39,700	12.1	36,500	11.1
1956-----	29,100	7.5	221,000	56.7	101,000	25.9	38,500	9.9
Total-----	74,800	7.4	607,000	59.6	245,000	24.1	90,400	8.9
<b>Kentucky River at Lock 4, at Frankfort</b>								
1950-----	152,000	14.6	516,000	49.5	212,000	20.3	162,000	15.5
1951-----	266,000	28.4	496,000	53.0	145,000	15.5	29,000	3.1
1952-----	283,000	31.4	453,000	50.3	143,000	15.9	20,800	2.3
1953-----	72,500	12.5	278,000	47.9	208,000	35.9	27,300	3.7
1954-----	13,700	4.9	141,000	50.9	97,200	35.1	25,200	9.1
1955-----	93,000	11.2	570,000	68.4	102,000	12.2	68,500	8.2
1956-----	22,400	2.8	514,000	63.1	214,000	26.3	64,100	7.9
Total (1953-56) ..	202,000	8.1	1,500,000	60.0	621,000	24.8	179,000	7.2
Total (7 yr.)-----	903,000	16.8	2,970,000	55.2	1,120,000	20.8	397,000	7.3
<b>Salt River at Shepherdsville</b>								
1953-----	15,400	7.8	106,000	53.4	72,800	36.6	4,400	2.2
1954-----	862	1.5	25,800	44.0	21,100	36.0	10,900	18.6
1955-----	25,800	9.2	190,000	67.8	47,000	16.8	17,200	6.1
1956-----	20,100	8.7	166,000	71.8	36,400	15.8	8,610	3.7
Total-----	62,600	8.1	488,000	63.5	177,000	23.0	47,100	5.3

## LOWERING OF THE LAND SURFACE

The load of dissolved solids and suspended sediment is evidence of erosion of the earth's crust. Removal of the products of weathering by water lowers the land surface a small amount each year. As given in table 17, only about 15-22 percent of the material removed is in dissolved form. In considering erosion of the land surface in the Blue Grass region, it should be remembered that only the Salt River basin upstream from Shepherdsville lies entirely in the region. It was not possible at this time to determine the part of the mineral load derived only from the Blue Grass in the Licking and Kentucky River basins.

In calculating the values for lowering of the land surface, a density of 2.64 was assumed for the rock in the basin. The same density was also used for the suspended sediment. Contributions to the dissolved load by pollution and other wastes were taken to be part of the natural erosional process. The volume of material removed is given as follows:

*Mineral material removed per square mile per year*

Station and period	Dissolved load		Suspended load	
	Tons	Cubic feet	Tons	Cubic feet
Licking River at McKinneysburg Oct. 1, 1952–Sept. 30, 1956-----	104	1, 260	462	6, 850
Kentucky River at Lock 4 at Frankfort:				
Oct. 1, 1952–Sept. 30, 1956-----	116	1, 400	398	4, 820
Oct. 1, 1949–Sept. 30, 1956-----	142	1, 720	-----	-----
Salt River at Shepherdsville Oct. 1, 1952–Sept. 30, 1956-----	125	1, 520	635	7, 700

The removal of dissolved and sedimentary material can also be expressed in terms of lowering of the land surface. For the period of record, the land surface was lowered as follows:

Rates of erosion between the Eastern Coal Field and the Blue Grass region may be different because of differences in topography, rock, vegetation, and other factors. It appears from the table above that erosion, particularly as suspended sediment, is greater in the Blue Grass region than in the Eastern Coal Field. The greater rate of erosion in the Blue Grass region was determined earlier by Collier and Krieger (1958, p. 15–18) by a different method.

Station and period	Average lowering of the land surface (ft per yr)		
	Dissolved	Suspended sediment	Total
Licking River at McKinneysburg Oct. 1, 1952–Sept. 30, 1956-----	0. 00004	0. 0002	0. 0002
Kentucky River at Lock 4, at Frankfort:			
Oct. 1, 1952–Sept. 30, 1956-----	. 00005	. 0002	. 0002
Oct. 1, 1949–Sept. 30, 1956-----	. 00006	-----	-----
Salt River at Shepherdsville Oct. 1, 1952–Sept. 30, 1956-----	. 00005	. 0003	. 0004

**GROUND WATER AND THE DISSOLVED SOLIDS OF STREAMS**

The dissolved load of a stream is made up of two components, dissolved solids from overland runoff and from ground water discharge. The part of the dissolved load contributed by both is variable, depending on the season and the stage of the river. During low-flow periods, as in late summer and early fall, the dissolved solids may be derived entirely from ground water. At flood stages, as during the winter, the dissolved solids may be derived almost entirely from overland runoff. The method of determining the contribution of ground water to the dissolved load of a stream has been described by Durum (1953). However, Durum's procedure was modified to suit the milder and more humid conditions of Kentucky. A hydrograph

and ground-water discharge curve was prepared as shown on plate 9 for Salt River at Shepherdsville. Similar hydrographs were prepared for each year at Licking River at McKinneysburg and Kentucky River at Lock 4, at Frankfort. Specific conductance was plotted against mean daily discharge for those days when the hydrographs of runoff and ground-water discharge coincided. This curve for the Salt River at Shepherdsville is shown in figure 25. The low-flow data was assumed to be composed entirely of ground water. It was necessary to fit three curves to the data to define the relation of specific conductance to water discharge, one curve for spring and early summer, one curve for late summer and early fall, and another for the winter period. Low flows in the spring and early summer are more dilute than comparable low flows in the fall.

The seasonal effects on the mineral content of low flows can be explained by examination of the yearly pattern of recharge, ground-water discharge, and surface runoff. In late summer and early fall, runoff is low, recharge is generally nonexistent, the level of ground water is at the lowest, and evapotranspiration is high. The shallow ground water is higher in dissolved minerals because it has been in contact with the rocks for several months and evapotranspiration accumulates salts near the surface of the soil. In the winter, surface runoff and recharge to the ground-water body become dominant components of the hydrologic cycle. Surface runoff at this time is relatively dilute because of its contact with leached soils and exposed rocks. Recharge flushes the soils and rocks of accumulated soluble salts. It also pushes out by circulation the more saline ground waters that have been draining to the streams during the summer and fall. Consequently, the lower flows during the early winter months may have a continued high mineral content. By spring, the more mineralized ground waters that move readily to the stream have been replaced by the fresher recharge of the winter months. Ground-water discharge or low flows of this season, consequently, are more dilute than comparable low flows of the late summer and fall. This cycle of events had to be considered in estimating the dissolved mineral content of ground-water discharge.

From 124 composite samples of surface water, the following relation of specific conductance to dissolved solids was obtained (table 14):

$$K \times 0.602 = DS$$

Where:  $K$  = Specific conductance in micromhos at 25°C.

$DS$  = Dissolved solids in ppm.

Using the mean daily ground-water discharge, the relation of low-flow discharge to specific conductance, and the relation of specific



conductance to dissolved solids, the dissolved load of ground-water discharge was obtained. These data are given in table 19 for the Licking River at McKinneysburg and in table 20 for the Salt River at Shepherdsville.

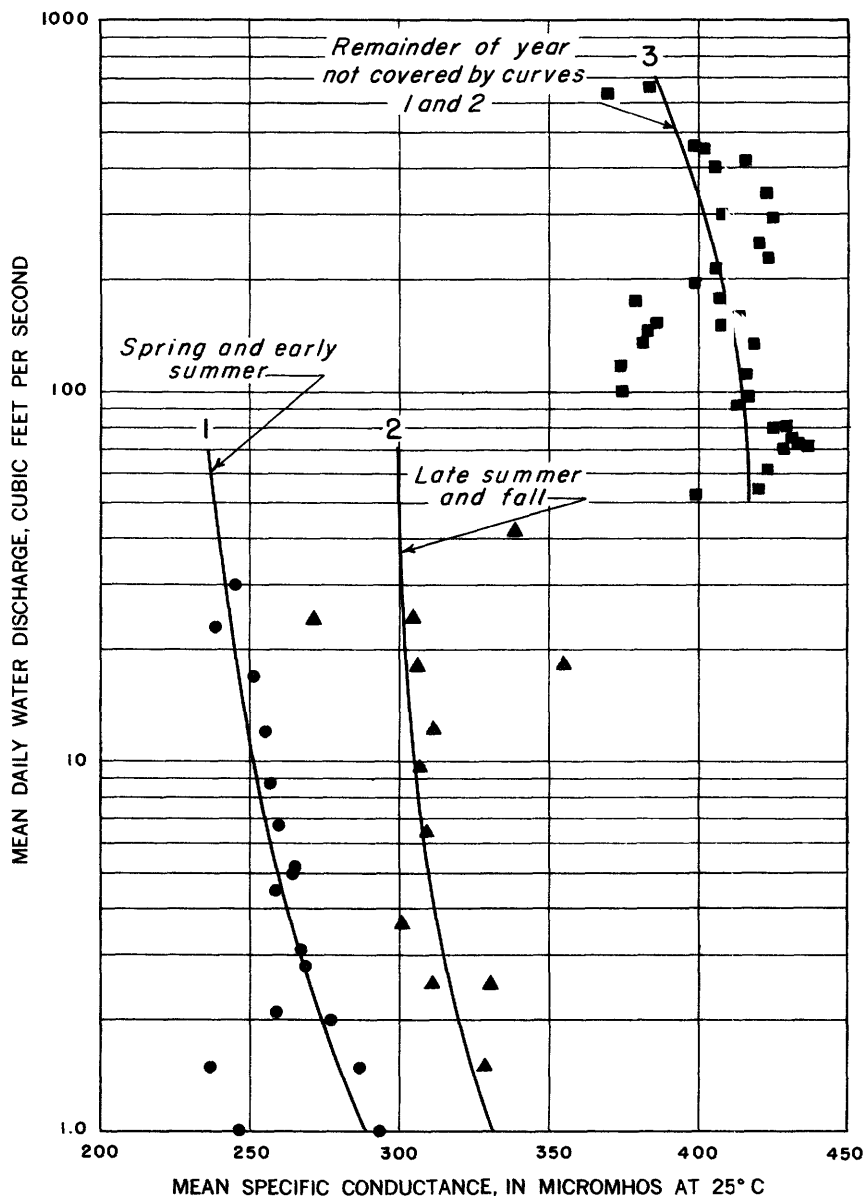


FIGURE 25.—Relation of specific conductance to low-flow discharge, Salt River at Shepherdsville, Ky., October 1952-September 1954.

TABLE 19.—Ground-water discharge and runoff characteristics, Licking River at McKinneysburg, Ky., Oct. 1, 1952 to Sept. 30, 1954

Water year	Water discharge, cfs-days			Percentage of total water discharge		Dissolved load, tons per month			Percentage of dissolved load	
	Total	Ground-water runoff	Surface runoff	Ground-water runoff	Surface runoff	Total	Ground-water runoff	Surface runoff	Ground-water runoff	Surface runoff
<b>1952-53</b>										
October 1952.....	370.9	250	120	67	33	126	95	31	75	25
November.....	5,636.8	950	4,700	17	83	1,820	305	1,520	17	83
December.....	43,238	9,580	33,600	22	78	13,100	2,650	10,500	20	80
January 1953.....	163,674	25,700	138,000	16	84	47,800	6,820	41,000	14	86
February.....	68,098	31,000	37,100	46	54	16,800	8,160	8,620	48	52
March.....	242,540	55,800	187,000	23	77	55,200	14,600	40,600	26	74
April.....	99,330	40,000	59,300	40	60	26,500	10,600	15,900	40	60
May.....	139,304	32,200	107,000	23	77	36,000	8,520	27,400	24	76
June.....	14,396	8,370	6,000	58	42	3,990	2,320	1,670	58	42
July.....	9,062	4,840	4,230	53	47	2,810	1,400	1,410	50	50
August.....	9,140	1,410	7,730	15	85	2,800	1,460	1,340	16	84
September.....	474.6	410	60	86	14	177	150	27	85	15
Total.....	795,264.3	210,510	584,840	26	74	207,123	56,080	151,018	27	73
<b>1953-54</b>										
October 1953.....	189.0	170	20	90	10	81	66	15	81	19
November.....	328.0	160	170	49	51	146	62	84	42	58
December.....	882	440	440	50	50	395	158	237	40	60
January 1954.....	34,866	1,110	33,800	3	97	12,500	366	12,100	3	97
February.....	11,225	3,600	3,620	50	50	3,800	1,580	2,220	42	58
March.....	85,058	21,600	63,500	25	75	27,400	5,700	21,600	21	79
April.....	57,446	21,600	31,800	44	56	16,700	6,860	9,890	41	59
May.....	63,543	21,600	41,700	34	66	17,100	5,760	11,300	34	66
June.....	14,275	4,230	10,000	30	70	4,520	1,230	3,290	27	73
July.....	2,383	1,210	1,170	51	49	803	393	410	49	51
August.....	11,936	2,770	9,160	23	77	3,640	843	2,800	23	77
September.....	17,253	1,670	15,600	10	90	5,250	532	4,660	10	90
Total.....	299,284.0	86,160	213,080	29	71	92,375	23,590	68,596	26	74

TABLE 20.—Ground-water discharge and runoff characteristics, Salt River at Shepherdsville, Ky., Oct. 1, 1952 to Sept. 30, 1954

Water year	Water discharge, cfs-days			Percentage of total water discharge		Dissolved load, tons per month			Percentage of dissolved load	
	Total	Ground-water runoff	Surface runoff	Ground-water runoff	Surface runoff	Total	Ground-water runoff	Surface runoff	Ground-water runoff	Surface runoff
<b>1952-53</b>										
October 1952.....	112.7	( <sup>1</sup> )	894			56				
November.....	999.9	4,160	28,500	11	89	622	59	583	9	91
December.....	32,736	14,300	73,200	13	87	14,700	2,710	12,000	18	82
January 1953.....	87,494	11,200	5,690	16	84	42,400	9,120	33,300	22	78
February.....	106,891	13,200	124,000	66	34	10,600	7,220	3,340	68	32
March.....	137,267	16,500	42,500	10	90	53,200	8,450	44,800	16	84
April.....	59,042	17,700	72,300	28	72	29,800	10,500	19,300	35	65
May.....	90,029	1,840	3,280	20	80	40,300	11,200	29,100	28	72
June.....	5,127	7,300	7,300	36	64	2,700	1,040	1,670	38	62
July.....	8,019	526	3,150	9	91	3,130	284	2,840	9	91
August.....	3,675.0	( <sup>1</sup> )		14	86	1,270	209	1,060	16	84
September.....	2.3					1				
Total.....	441,394.9	80,253	360,814	18	82	198,779	50,762	147,973	26	74
<b>1953-54</b>										
October 1953.....	0	( <sup>1</sup> )	363	2	98	0	5	242	2	98
November.....	372.2	241	997	19	81	247	120	496	19	81
December.....	1,238.0	2,200	25,700	2	98	12,600	323	12,200	2	98
January 1954.....	5,813	4,720	3,610	38	62	3,790	1,500	2,290	40	60
February.....	26,402	6,250	18,600	28	72	9,520	3,150	6,370	33	67
March.....	24,852	10,281	4,380	25	75	13,300	4,130	9,170	31	69
April.....	10,281	1,050	2,470	43	57	5,920	2,780	3,140	47	53
May.....	3,523.1	66	604	30	70	1,480	410	1,480	22	78
June.....	4,237.6	15	4,170	10	90	1,357	29	328	8	92
July.....	31,906.6		31,900	0	100	1,520	33	1,490	2	98
August.....						9,010	8	9,000	0	100
September.....										
Total.....	126,063.7	19,652	106,314	16	84	58,760	12,488	46,206	21	79

<sup>1</sup> Less than 1.0 cfs each day.

The annual water discharge of the Licking River at McKinneysburg in 1954 was about 38 percent of the discharge in 1953. The mean discharge for the water year 1954 was only about 28 percent of the 18-year average; for 1953, it was about 74 percent of average. The runoff in 1954 was one of the lowest on record. In spite of this, the ratio of ground-water discharge to surface runoff was almost constant for 1953 and 1954. The ratio of annual dissolved load from ground water to annual dissolved load from surface runoff was similar. The bulk of the water and dissolved load is contributed by surface runoff.

In the Salt River basin conditions are somewhat different. Surface runoff comprises a greater share of the total water discharge than in the Licking River basin because runoff is more rapid and infiltration less in the Salt River basin than in other major basins in the Blue Grass region. Ground water in the Salt River basin, however, contributes a greater share to the dissolved load, in proportion to ground-water discharge, than it does in the Licking River basin. This is shown as follows for the 2-year period: Ground water above McKinneysburg contributes 27 percent of the water and 27 percent of the dissolved load, whereas at Shepherdsville ground water contributes only 18 percent of the water but 24 percent of the dissolved load.

Station	Water year	Contribution by ground water to—	
		Water discharge (percent)	Dissolved load (percent)
Licking River at McKinneysburg-----	1953	26	27
	1954	29	26
Average-----		27	27
Salt River at Shepherdsville-----	1953	18	26
	1954	16	21
Average-----		18	24

The first 6 months or so of the water year are periods of low ground-water discharge in relation to the total discharge of the streams. As a result, the contribution of ground water to the dissolved load of streams is relatively low. Ground-water recharge takes place chiefly in the winter and early spring. Soil-moisture deficiencies must be made up before recharge to the ground water can take place. Where sinkholes occur, recharge of ground water can occur at almost any time. In the last 6 months of the water year, ground-water discharge contributes a relatively greater proportion of the total flow and the

dissolved load. For the McKinneysburg station, 1953 water year, the average part contributed by ground water is as follows:

	Ground-water contribution to—	
	Water discharge (percent)	Dissolved load (percent)
October–March, 1953.....	23	24
April–September, 1953.....	32	32

#### CYCLIC VARIATIONS

The relation between daily water discharge and specific conductance was found to have a pattern that could not be resolved into a straight line, or the hyperbolic function of Durum (1953). There proved to be a cyclic sequence of events that take place during the rising and falling stages of a flood. Between floods the relation was simple. At first thought, a cyclic relation appears to be directly opposed to the straight-line relation of figure 24, but this is not so. The data in figure 24 are based on total monthly dissolved load which masks the daily variations during a flood. For a detailed description of the cycle, the reader is referred to a paper by Hendrickson and Krieger (1960). Only a brief explanation will be given here.

#### THE BASIC CYCLE

The basic cycle is relatively simple. It is a counterclockwise curve of varying shape that results from plotting specific conductance against water discharge in sequence for the rising and falling stages of a flood. Such a curve is shown in figure 26. The shape changes with the change in rate of water discharge and specific conductance and the time interval between floods.

A single flood cycle can be divided into three phases as shown. The first phase is that part of the curve from *A* to *B*. During this phase, water discharge increases rapidly but the conductance of the water changes very little. Apparently the water coming into the stream dissolves readily soluble material from the soil and streambed and includes, perhaps, shallow ground waters. In addition, "old" water in the channel may constitute an appreciable part of the initial rise in stage. The phase from *B* to *C* occurs because of a rapid decrease in conductance with little change in discharge. The water coming into the stream in this phase has a decreasing amount of soluble material. Moreover, at the time the stream is near peak stage, water is moving from the stream into the banks. This retards ground-water discharge. As a result, the dissolved-solids content of the stream decreases greatly without much change in discharge.

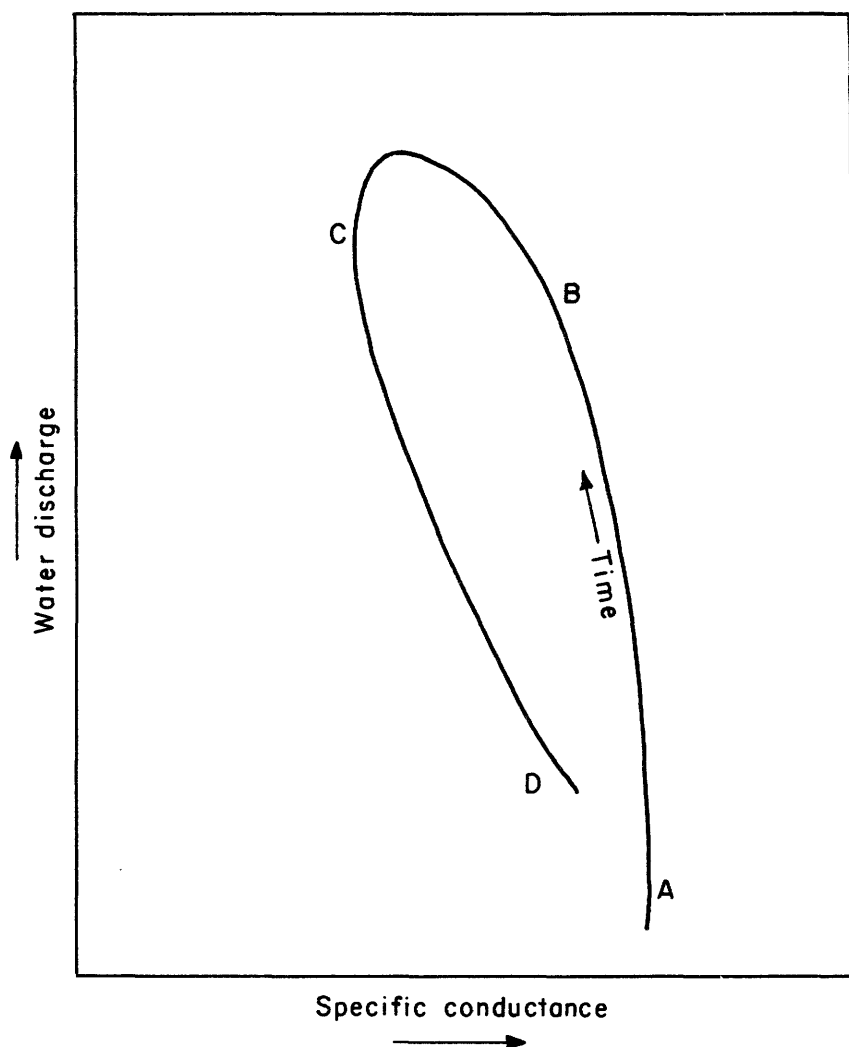


FIGURE 26.—Relation between specific conductance and water discharge during a single flood.

The third phase, *CD*, is marked by a decrease in discharge and an increase in conductance so that the curve approaches the origin of the cycle. The fall in stage causes water stored in the banks to move into the stream. Ground water containing a higher concentration of dissolved minerals once again discharges into the stream. During this phase ground water makes up an increasingly larger part of the stream flow.

## VARIATIONS IN THE CYCLE

There seems to be a curve of individual size and shape for each flood. To illustrate the point, a few of the floods of the Salt River at Shepherdsville are represented by the curves in figure 27. Some curves developed in as little as 5 days (curve 3), whereas others required 19 days (curve 5). Curves, such as 9, did not develop fully because of the occurrence of another flood which interrupted the full development of the first flood.

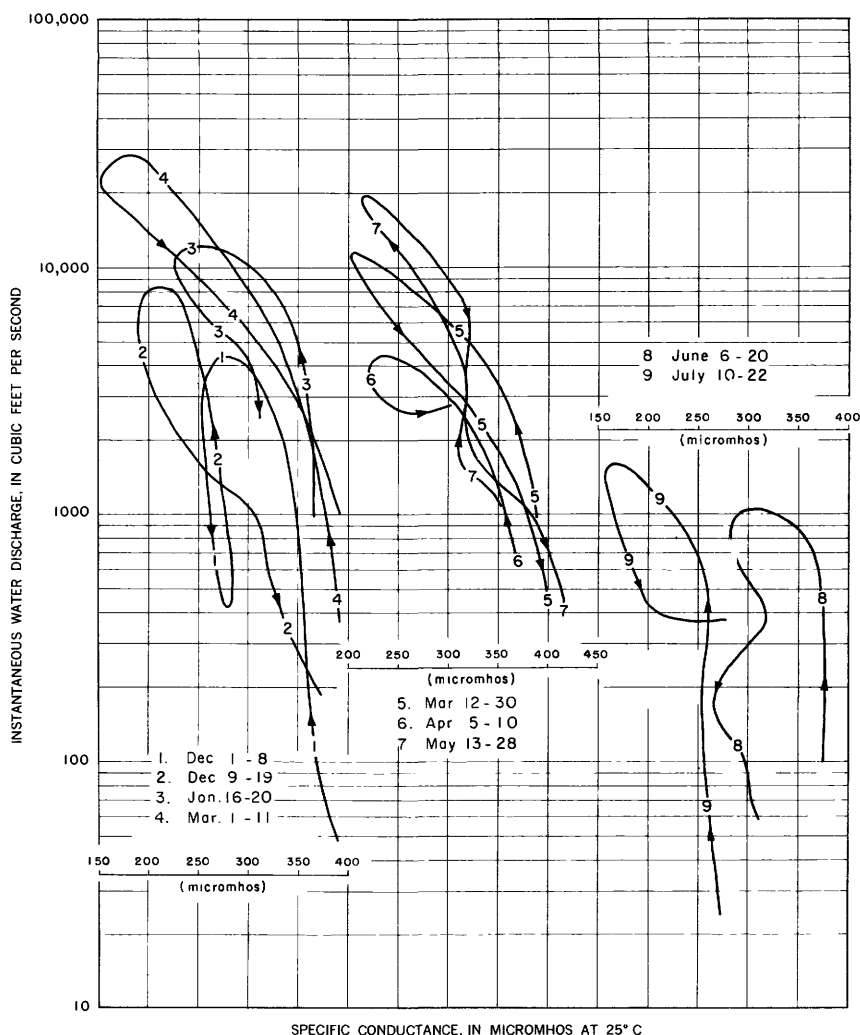


FIGURE 27.—Selected curves showing relation between water discharge and specific conductance for 1953 water year, Salt River at Shepherdsville, Ky.

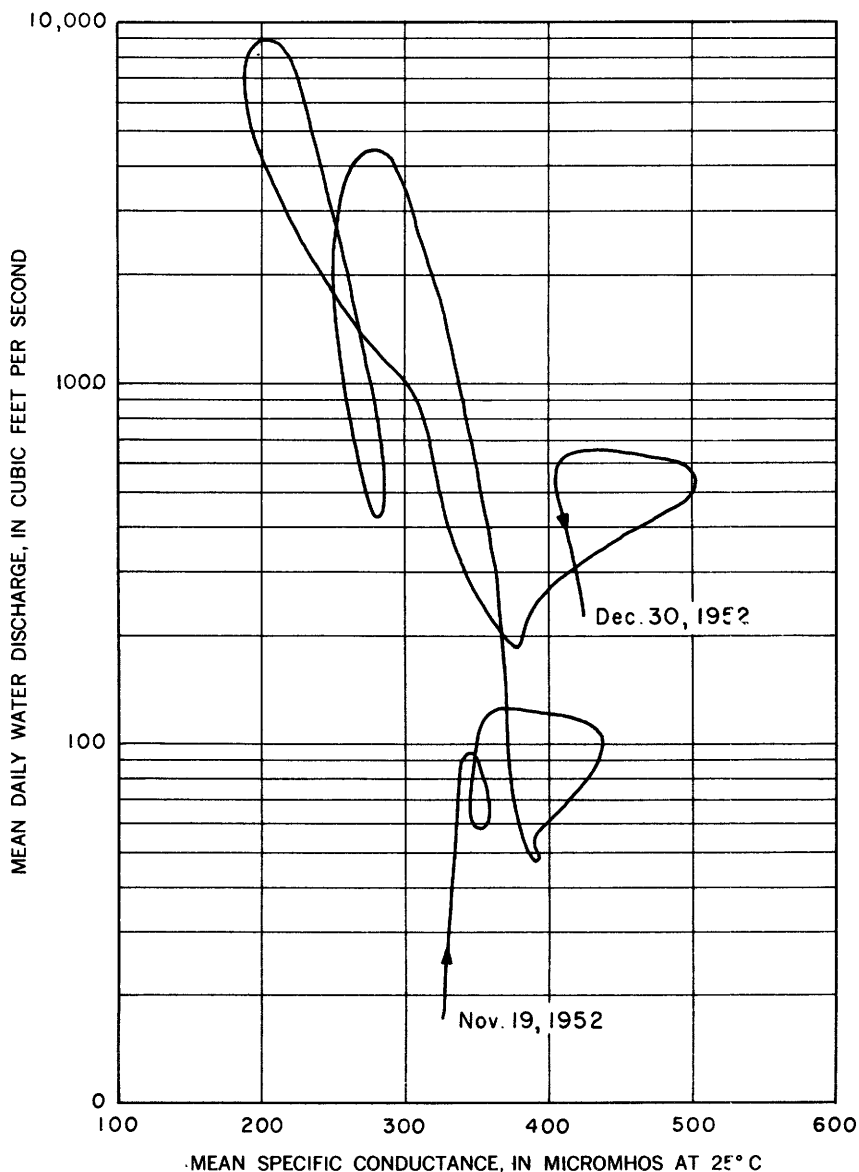


FIGURE 28.—Continuous curve showing relation between water discharge and specific conductance for November 19–December 30, 1952, Salt River at Shepherdsville, Ky.

A continuous plot of the period from November 19 to December 30, 1952, at Shepherdsville, is probably the best proof of why no simple relation between conductance and discharge exists. This period, shown in figure 28, provided a maze of cycles. If the data for



each sample had been plotted as a point, the result would have been a group of scattered and seemingly unrelated points. It is interesting to note that the first two loops in the curve are clockwise. The record shows that these floods occurred after a prolonged period of low flow. Daily discharges of less than 1.0 cfs were common. The floods that occurred were small so that apparently there was not sufficient water to flush and dilute the accumulation of dissolved salts and concentrated ground water.

### OBSERVATIONS AND CONCLUSIONS

1. Rainwater in the Blue Grass region probably does not contain enough chloride to account for all that is discharged from Blue Grass streams.

2. Much of the potassium and magnesium in the soils is fixed in the clay minerals, and little is leached by percolating soil waters. Much of the sodium and chloride in the soils is present in soluble salts or loosely held as exchangeable ions, and relatively large amounts are dissolved by percolating soil waters.

3. Soil waters in the Blue Grass region probably are similar in chemical character to the dilute ground waters of the region; that is, they are generally of the calcium magnesium bicarbonate type. The magnesium-calcium ratios generally are lower, and potassium-sodium ratios generally higher than in most ground waters of the region.

4. Most dilute ground waters of the Blue Grass are of the calcium magnesium bicarbonate type; most saline ground waters are of the sodium chloride type.

5. Magnesium-calcium ratios in ground waters of the Blue Grass generally increase, and potassium-sodium ratios generally decrease as mineralization increases.

6. Magnesium-calcium ratios of dilute ground waters from the Silurian and Devonian rocks generally are higher than those from the Ordovician rocks of the Blue Grass.

7. Magnesium-calcium ratios of most of the ground waters of the Blue Grass are higher than those of the limestones but lower than those of the shales, probably because the magnesium in limestones is combined with carbonate, whereas most of the magnesium in the shales is fixed in the clay minerals.

8. Potassium-sodium ratios of the ground waters of the Blue Grass generally are lower than potassium-sodium ratios in both limestones and shales, probably because the potassium is fixed in the clay minerals, whereas the sodium is present as sodium chloride or is loosely held in the clay minerals.

9. The rate of reduction of the land surface by solution in the Blue Grass region is about 0.00005 feet per year.

10. It would take about 30,000 years to produce 1 inch of soil by weathering of limestones in the Blue Grass region at the present rate.

11. Weathering of limestones in the Blue Grass is relatively rapid in shallow zones where the waters are charged with carbon dioxide. In deeper zones weathering of limestones is extremely slow.

12. Weathering of limestones probably is accelerated by acids formed in the oxidation of pyrite.

13. Gypsum, which may be present in fracture openings, solution cavities, and intergranular pore spaces in the rocks of the Blue Grass, probably is derived from weathering of pyrite and the reaction of the liberated sulfuric acid with calcium carbonate.

14. Silica is concentrated in the topsoils of the Blue Grass region, whereas alumina is concentrated at a depth of 4-6 feet. The silica is concentrated in the topsoil by leaching of the more soluble elements and the downward movement of the clay fraction, probably as a colloidal sol carried down by percolating waters.

15. The concentrations of dissolved solids in the brines may be more than five times the concentration in sea water.

16. The moderately saline waters were formed by some process other than simple mixture of fresh meteoric water and concentrated brines.

17. The chemical composition of brines of a given density is remarkably uniform regardless of the producing aquifer.

18. Fluctuations in chemical character of ground waters in the Blue Grass region generally are smaller than fluctuations in the chemical character of water of streams. However, in ground waters of mixed types, fluctuations in the chemical character of the waters may be very great.

19. Except in ground waters of mixed types, fluctuations in the composition of spring waters generally are greater than those in well waters.

20. Fluctuations in composition of water are generally greater in shallow than in deep wells.

21. In general, the greater the fluctuation in discharge of a spring, the greater the fluctuation in the chemical character of the water.

22. Although the Blue Grass region is a limestone terrane and calcium magnesium bicarbonate type waters predominate, other types of waters are found also. Drainage from the Eastern Coal Field into the Blue Grass region contributes large amounts of sulfate to water in the streams. Some small streams show the effects of wastes discharged into the stream.

23. The chemical character of small streams shows a greater variation than large streams. However, most of the large streams are regulated by low dams, and the uniformity of the large streams may be more apparent than real.

24. The load of dissolved solids makes up about 15–20 percent of the total load of the stream on a yearly basis. During low flows, the dissolved load makes up as much as 98 percent of the total load.

25. Denudation in the Salt River basin, based on a 4-year average, was approximately 1,500 cu ft per sq mi per year by chemical erosion and 7,700 cu ft per sq mi per year by physical erosion.

26. There is a cyclic relation between water discharge and the concentration of dissolved mineral matter. At the beginning of a rise in stage the concentration of most stream waters remains constant or increases slightly, but near the crest of the rise, or a little later, the concentration decreases. Before the flow returns to normal, the concentration is about equal to or perhaps more than before the rise in stage. Consequently, the dissolved-solids concentration cannot be readily estimated from the discharge alone.

27. The concentration of dissolved minerals in the streams at low flows varies with the season of the year. Concentration of dissolved solids is lower in late spring and early summer than the concentration of equal flows in late summer and early fall.

28. The relation between the dissolved constituents and specific conductance in streams is most consistent at low and medium concentrations of dissolved solids.

29. In the Blue Grass region, ground water discharge makes up about 15 to 30 percent of the yearly flow of the streams depending on topography, amount and rate of precipitation, and the porosity and permeability of the soils and rocks.

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**Hendrickson, Gerth Edison, 1916-**

Geochemistry of natural waters of the Blue Grass region, Kentucky, by G. E. Hendrickson and R. A. Krieger. Washington, U.S. Govt. Print. Off., 1964.

vii, 134 p. illus., maps (1 col.) diagrs., tables. 24 cm. (U.S. Geological Survey. Water-supply paper 1700.)

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Prepared in cooperation with the Dept. of Economic Development of Kentucky and the Kentucky Geological Survey.

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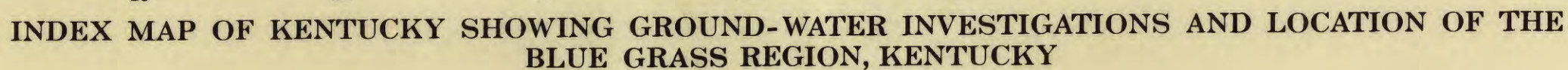
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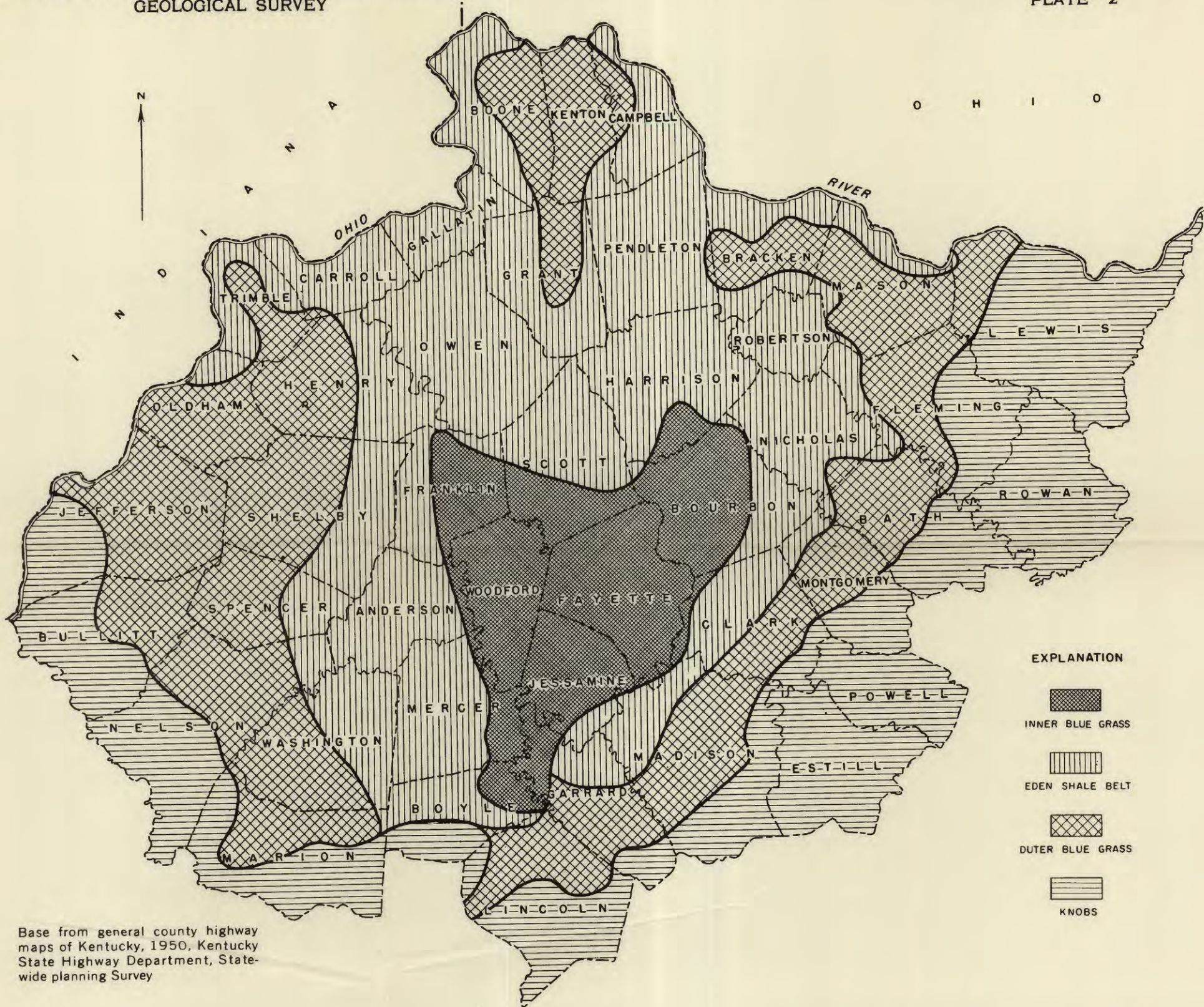




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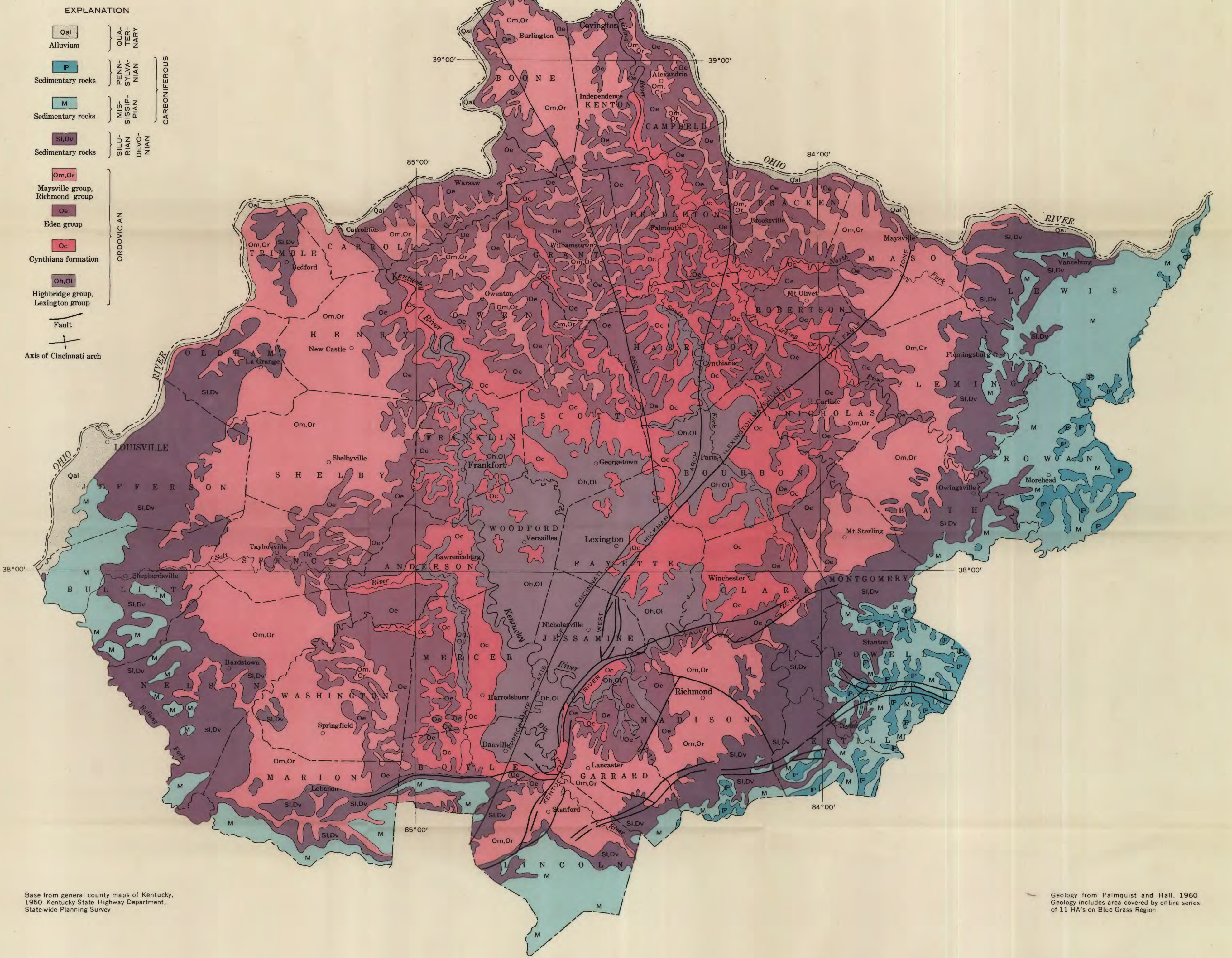


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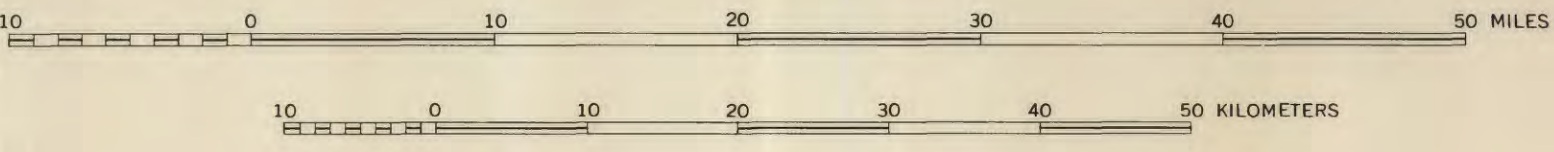


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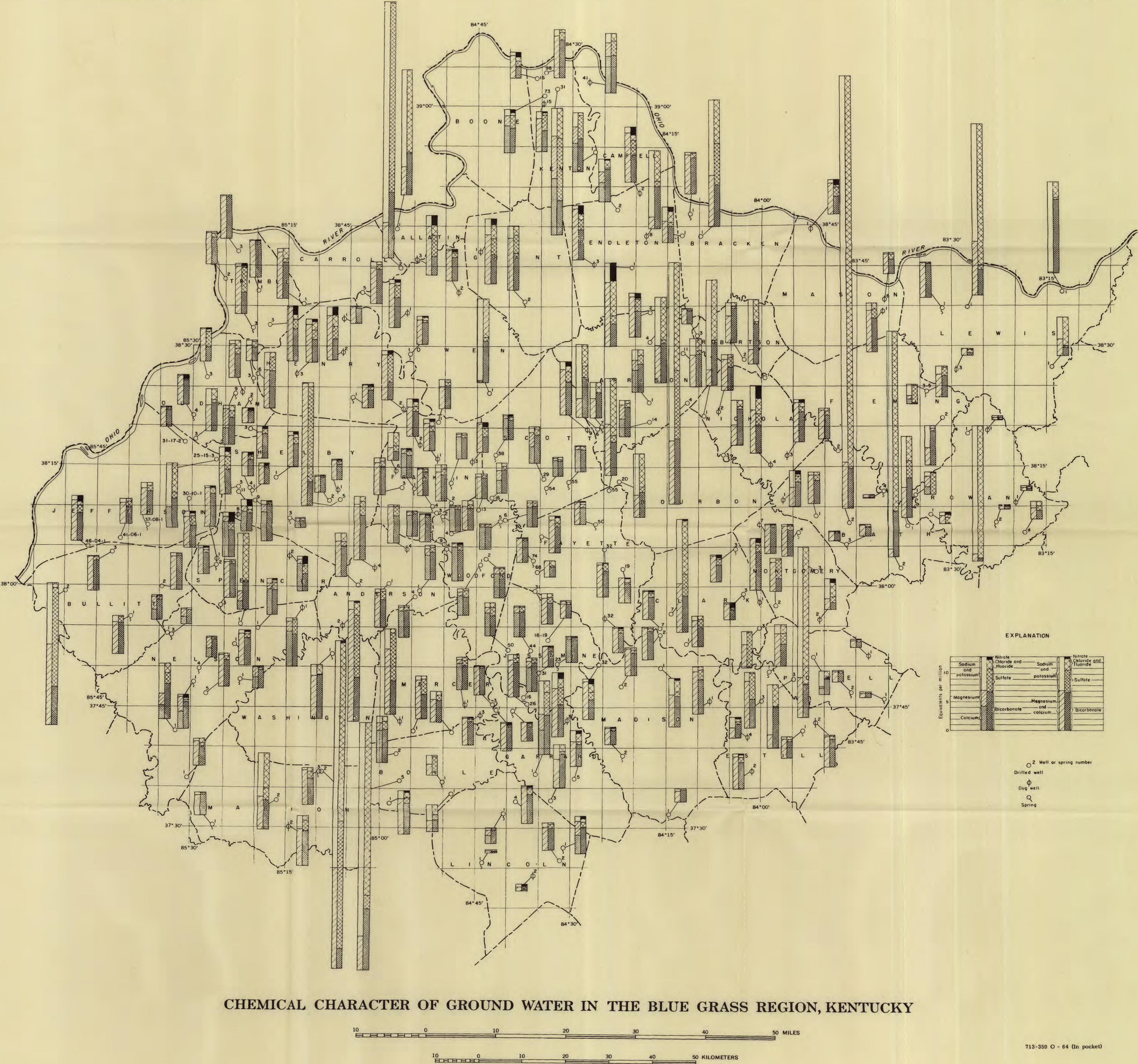
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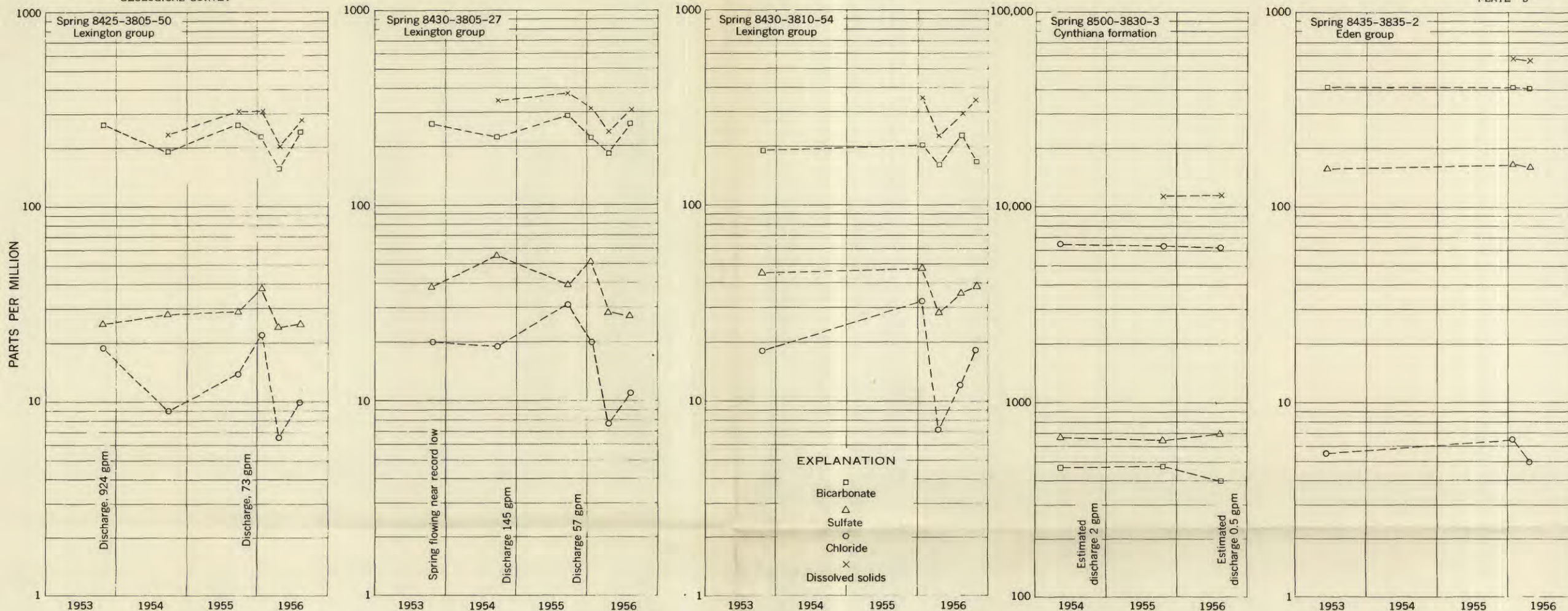
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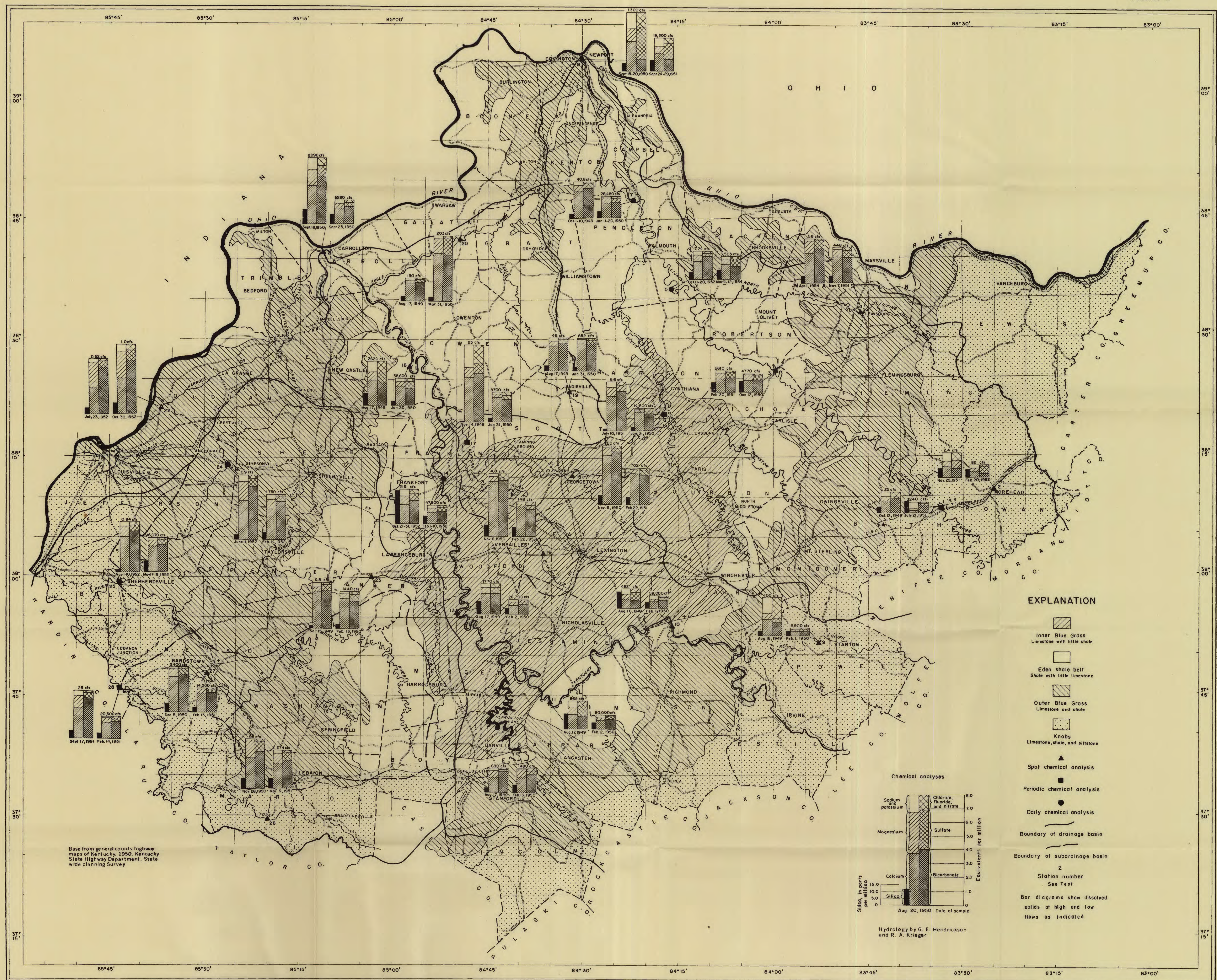




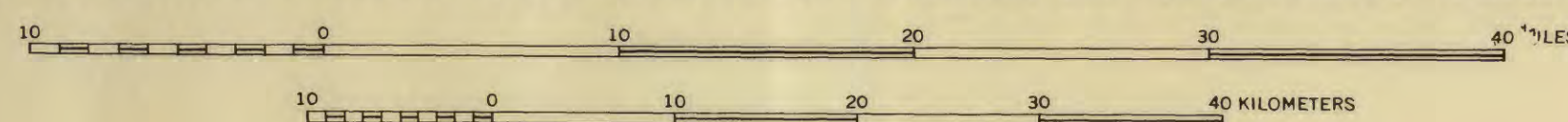


FLUCTUATIONS IN CONCENTRATIONS OF DISSOLVED CONSTITUENTS IN WATER FROM SELECTED SPRINGS OF  
THE BLUE GRASS REGION, KENTUCKY

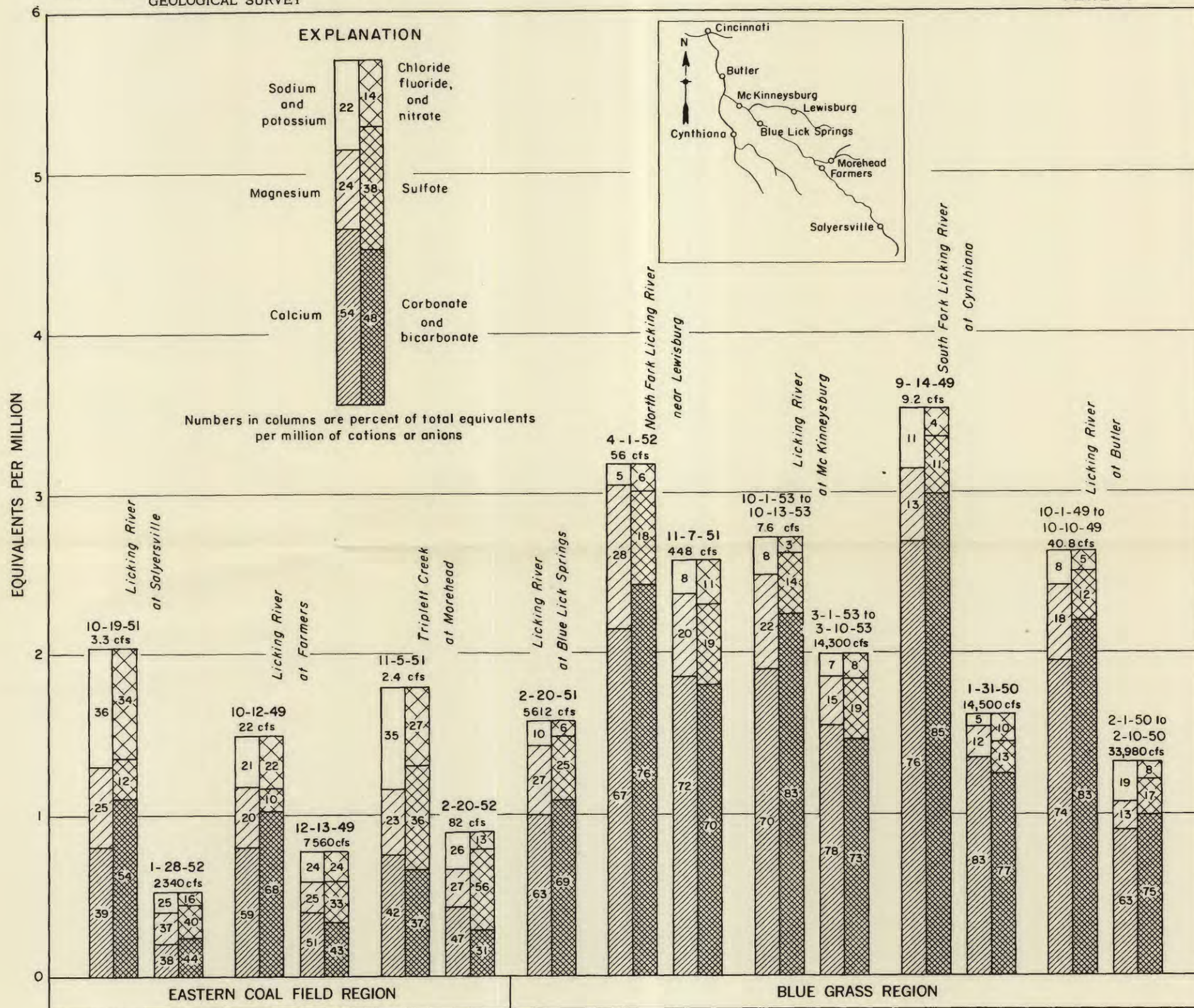




MAP SHOWING CHEMICAL CHARACTER OF STREAM WATER AND SURFACE WATER AT SAMPLING STATIONS, BLUE GRASS REGION, KENTUCKY

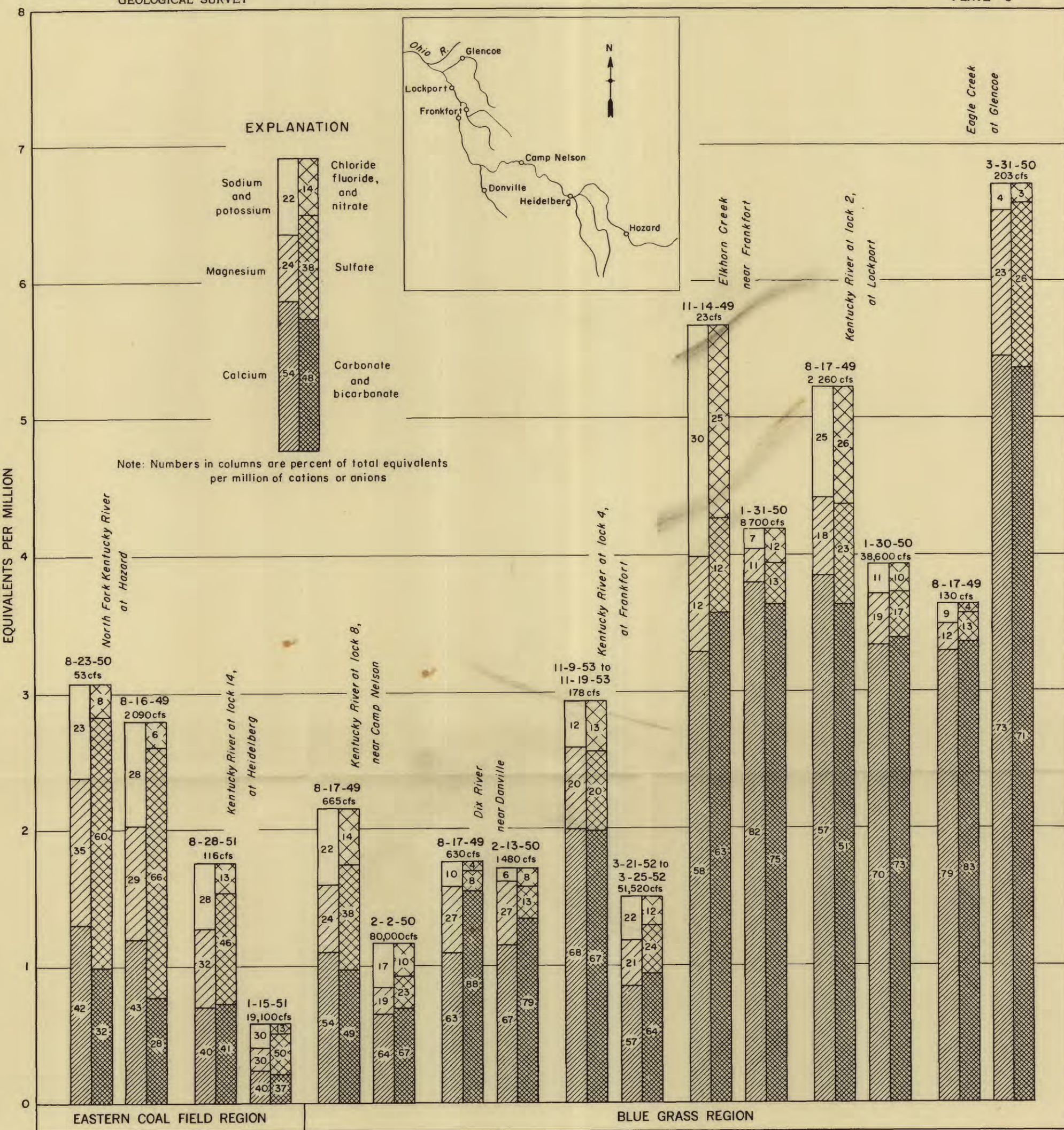






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AT LOW AND HIGH RATES OF DISCHARGE

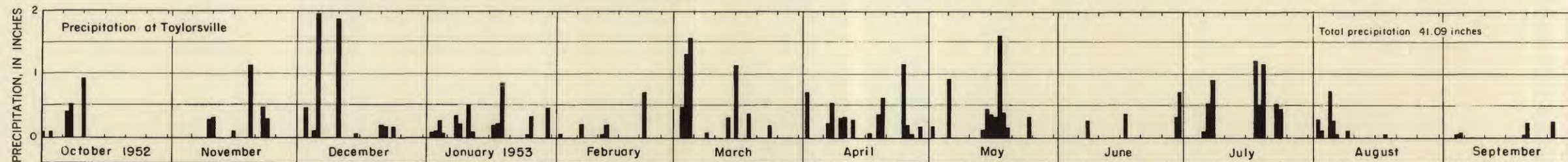
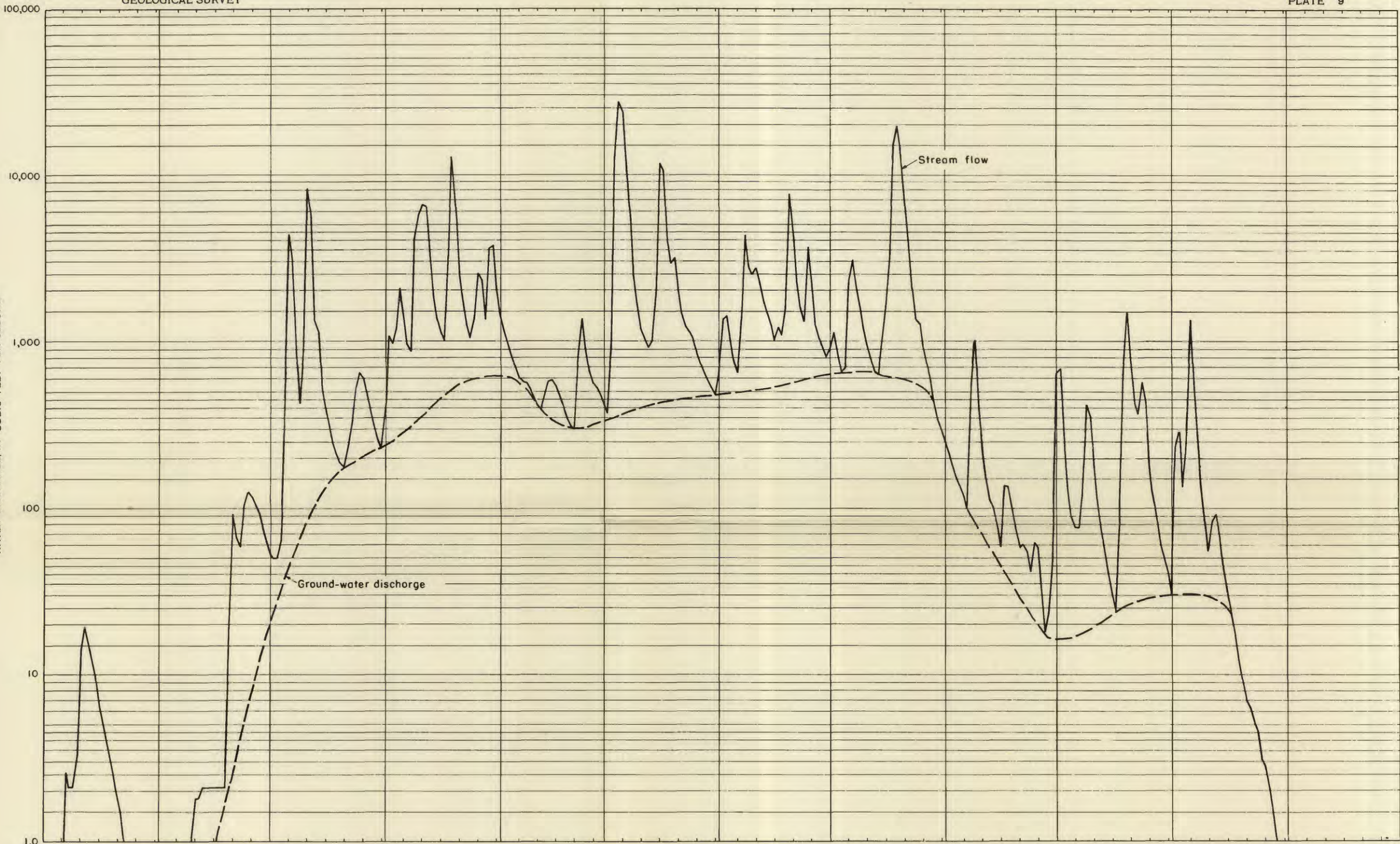




CHEMICAL CHARACTERISTICS OF SURFACE WATER, KENTUCKY RIVER BASIN, KENTUCKY  
AT LOW AND HIGH RATES OF DISCHARGE



WATER DISCHARGE, IN CUBIC FEET PER SECOND



RELATION OF MEAN DAILY RUNOFF TO GROUND-WATER DISCHARGE, SALT RIVER AT SHEPHERDSVILLE, OCTOBER 1, 1952  
TO SEPTEMBER 30, 1953