GEOCHEMISTRY OF GROUND WATER IN THE SOUTHEASTERN COASTAL PLAIN AQUIFER SYSTEM IN MISSISSIPPI, ALABAMA, GEORGIA, AND SOUTH CAROLINA

REGIONAL AQUIFER-SYSTEM ANALYSIS

U. S. GEOLOGICAL SURVEY PROFESSIONAL PAPER 1410-D

Geochemistry of Ground Water in the Southeastern Coastal Plain Aquifer System in Mississippi, Alabama, Georgia, and South Carolina

By ROGER W. LEE

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FOREWORD

THE REGIONAL AQUIFER-SYSTEM ANALYSIS PROGRAM

The Regional Aquifer-System Analysis (RASA) Program was started in 1978 following a congressional mandate to develop quantitative appraisals of the major ground-water systems of the United States. The RASA Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which in aggregate underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system and accordingly transcend the political subdivisions to which investigations have often arbitrarily been limited in the past. The broad objective for each study is to assemble geologic, hydrologic, and geochemical information, to analyze and develop an understanding of the system, and to develop predictive capabilities that will contribute to the effective management of the system. The use of computer simulation is an important element of the RASA studies, both to develop an understanding of the natural, undisturbed hydrologic system and the changes brought about in it by human activities, and to provide a means of predicting the regional effects of future pumping or other stresses.

The final interpretive results of the RASA Program are presented in a series of U.S. Geological Survey Professional Papers that describe the geology, hydrology, and geochemistry of each regional aquifer system. Each study within the RASA Program is assigned a single Professional Paper number, and where the volume of interpretive material warrants, separate topical chapters that consider the principal elements of the investigation may be published. The series of RASA interpretive reports begins with Professional Paper 1400 and thereafter will continue in numerical sequence as the interpretive products of subsequent studies become available.

Robert M. Hirsch

Robert M. Hirsch
Acting Director

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[Plates are in pocket]

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CONVERSION FACTORS AND VERTICAL DATUM

For readers who wish to convert measurements from the inch-pound system of units to the metric system of units, the conversion factors are listed below:

Multiply inch-pound units	*By*	*To obtain metric units*
square miles (mi^2)	2.590	square kilometer (km^2)
foot per day (ft/d)	0.3048	meter per day (m/d)
foot per mile (ft/mi)	.1894	meter per kilometer (m/km)
foot per year (ft/yr)	.3048	meter per year (m/yr)

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

GEOCHEMISTRY OF GROUND WATER IN THE SOUTHEASTERN COASTAL PLAIN AQUIFER SYSTEM IN MISSISSIPPI, ALABAMA, GEORGIA, AND SOUTH CAROLINA

By Roger W. Lee

ABSTRACT

The chemistry of ground water in Upper Cretaceous and Tertiary rocks of the Southeastern Coastal Plain was delineated in four regionally extensive aquifers. Concentrations of dissolved solids increase in a downgradient direction, initially as a result of water-rock interactions; farther downgradient, concentrations increase to as much as 100,000 milligrams per liter as a result of mixing with saline waters. Concentrations of dissolved iron are generally less than 0.5 milligrams per liter, but they may exceed 15 milligrams per liter in areas just downgradient from recharge areas or 5 milligrams per liter farther downgradient in high-salinity areas. Ground-water chemistry is predominantly calcium bicarbonate facies upgradient, sodium bicarbonate facies farther downgradient, and sodium chloride facies in the deep, downgradient parts of the aquifers.

Chemical evolution was generally defined by mass-transfer models of water-rock interactions. Four families of reaction models were considered; they demonstrate chemical processes ranging from feldspar hydrolysis with almost no calcite dissolution in upgradient reaction zones to some feldspar hydrolysis and calcite saturation in the upgradient, partly oxidized ground-water zone. Concentration of dissolved iron in the ground water is controlled by siderite and pyrite solubilities. Evolution of ground water to sodium bicarbonate facies primarily involves a process of calcite dissolution and calcium-for-sodium cation exchange, enhanced by carbon dioxide emanation from the decay of sedimentary organic matter such as lignite.

Carbon-14 measurements and geochemical-model adjustment indicate that in some areas the age of ground water may exceed 40,000 years. Ground-water velocities estimated from adjusted carbon-14 ages are 3 feet per year in the Black Warrior River aquifer, 13 feet per year in the Chattahoochee River aquifer, and 18 feet per year in the Pearl River aquifer. These rates agree favorably with velocities of about 1, 10, and 15 feet per year, respectively, derived from a ground-water flow model constructed during this study.

INTRODUCTION

BACKGROUND

The Southeastern Coastal Plain aquifer system provides water over an area of about 130,000 square miles (mi^2) in the Southeastern United States. It extends from the southwestern flank of the Cape Fear arch in North Carolina to the Mississippi embayment in northern Mississippi. The Southeastern Coastal Plain aquifer system adjoins four other regional aquifer systems: the Northern Atlantic Coastal Plain aquifer system to the northeast, the Floridan aquifer system to the south and southeast, and the Mississippi embayment and coastal lowlands aquifer systems to the west and southwest.

The Southeastern Coastal Plain aquifer system is composed of clastic sediments of Cretaceous and Tertiary age in South Carolina, Georgia, Alabama, Mississippi, and adjacent areas of northern Florida. The sediments that make up the aquifer system have been subdivided regionally into four aquifers and three intervening confining units, some of which are hydraulically interconnected with the interfingering and locally overlying Floridan aquifer system (Renken, 1984). The composition, texture, and bedding character of the major units vary from place to place. The sand aquifers of the system are massive to thinly bedded, fine to coarse grained, quartzose, and locally feldspathic, and in places they include limestone beds. Chalk, clay, shale, and mudstone form the three confining units that separate the four major aquifers. Locally, the major aquifers have been subdivided into smaller aquifers of subregional extent.

PURPOSE AND SCOPE

This is one of several chapters of a U.S. Geological Survey Professional Paper describing different aspects of the Southeastern Coastal Plain aquifer system (fig. 1) and the results of computer simulations of ground-water flow in the aquifer system. This chapter focuses on the

Base from U.S. Geological Survey National Atlas, 1970

FIGURE 1.—Location of the area of study for the Southeastern Coastal Plain Regional Aquifer-System Analysis.

geochemistry of the aquifer system. It describes (1) the water chemistry in the Southeastern Coastal Plain aquifer system and (2) the major geochemical processes in the aquifers, and the magnitude of those processes.

Water chemistry and geochemical processes in sand aquifers in Cretaceous and Tertiary rocks in Mississippi, Alabama, Georgia, South Carolina, and southeastern North Carolina were investigated. Maps were prepared to show the areal distribution of some chemical parameters, including dissolved-solids, dissolved-iron, and dissolved-chloride concentrations, and hydrochemical facies. Separate maps were prepared for each of the regional aquifers in the aquifer system. These aquifers have been delineated in a regional geohydrologic framework (Renken, 1984) (pl. 1) that correlates the major aquifers and confining units with geologic units in each State in the study area. The Black Warrior River and Pearl River aquifers in the western part of the study area were subdivided, on the basis of chemical variations, into lower, middle, and upper water-bearing zones, whereas the Chattahoochee River aquifer was represented as a single aquifer.

Chemical data used for the maps were collected by State and Federal agencies during the last half century and have been published in county or State reports in each State in the study area. Many of the usable data were entered in the Water Data Storage and Retrieval System (WATSTORE), part of the nationwide data base of the U.S. Geological Survey. Chemical data for the maps of the aquifer system were selected on the basis of the following criteria: well location, geologic unit, and the necessary chemical constituents. Chemical analyses that included major cations and anions and had a cation-anion balance of less than ±10 percent error were required for construction of the hydrochemical facies maps.

On the basis of subsurface delineations of aquifers and confining units and directions of ground-water flow, seven flow paths were sampled for additional geochemical data. Mineral-water relationships were analyzed using speciation calculations of WATEQ2, a computerized chemical model described by Ball and others (1980), and mass-balance calculations for samples from along flow paths in the same aquifer. Application of speciation and mass-balance calculations to the observed chemical data allowed evaluation of geochemical models for the systems considered. As a further constraint on geochemical models, carbon-13 cycling among the gas, liquid, and solid phases was included in the mass-balance models.

HYDROGEOLOGIC SETTING

The Southeastern Coastal Plain aquifer system has been divided into four regional aquifers—the Chickasawhay River, Black Warrior River, Chattahoochee River, and Pearl River aquifers. These regional aquifers are separated by three regional confining units that consist of clay, chalk, or other low-permeability materials (Renken, 1984). The uppermost aquifer, the Chickasawhay River aquifer, is of limited extent as a regional aquifer and is not discussed in this paper.

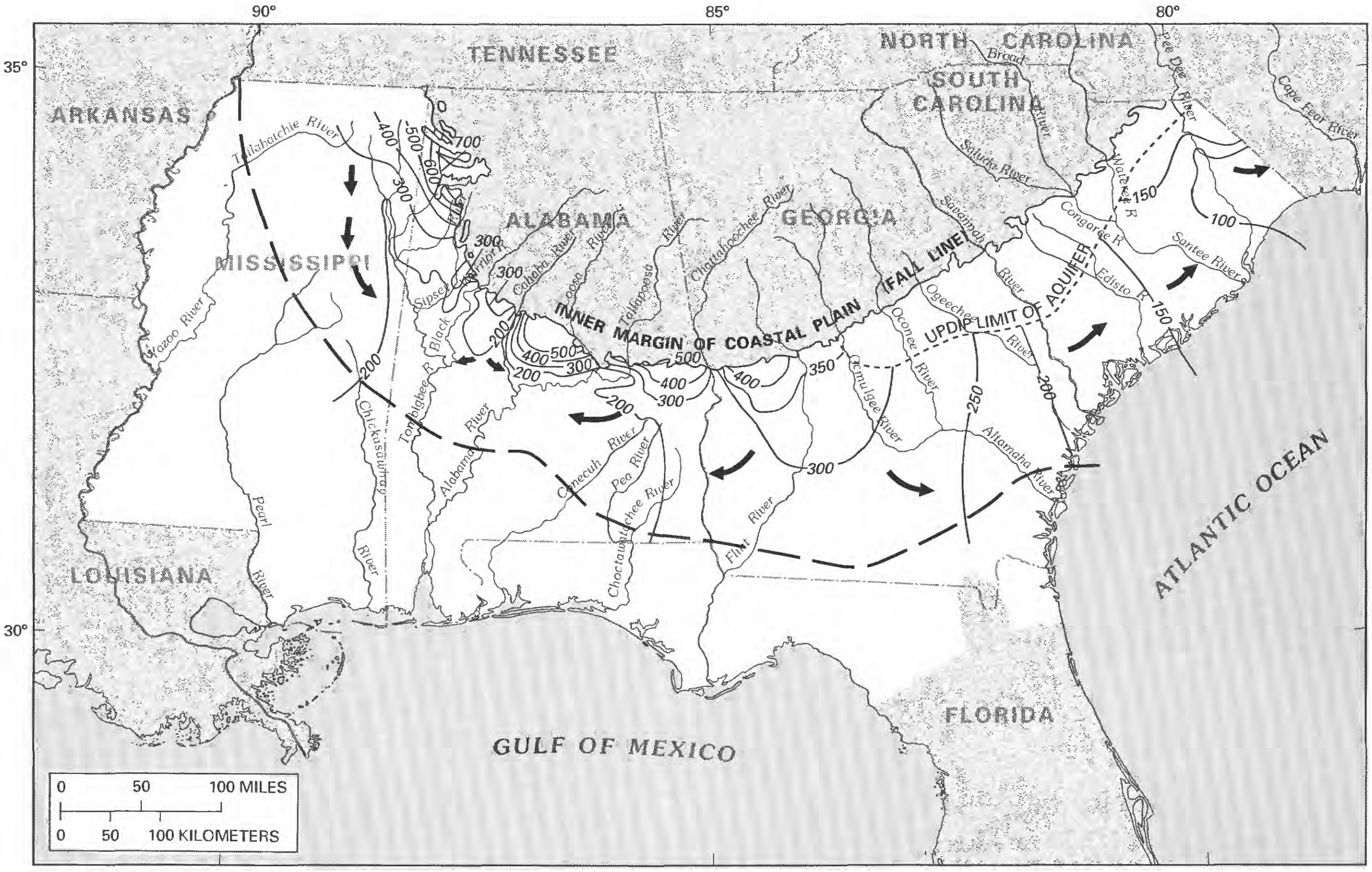
Black Warrior River regional aquifer.—The Black Warrior River aquifer is the basal hydrogeologic unit in the Southeastern Coastal Plain aquifer system (Renken, 1984). This regionally extensive aquifer is composed of sand and shale of Late Cretaceous age deposited in deltaic and associated nearshore environments. To understand better the complexity of the water chemistry of this aquifer, it has been further subdivided for this report into three water-bearing zones—lower, middle, and upper. The geology and hydrology of these three water-bearing zones have been reported statewide for Mississippi (Boswell, 1977, 1978, 1979; Wasson, 1980; Gandl, 1982) and for various counties for Alabama (Carlston, 1942; Paulson and others, 1962; Wahl, 1965; Gardner, 1981). A potentiometric surface map of the Black Warrior River aquifer (Barker, 1985) shows generalized ground-water flow paths (flow directions), including one that approximately parallels the coast of South Carolina (fig. 2).

The upper water-bearing zone of the Black Warrior River aquifer, described as the Eutaw-McShan aquifer system by Boswell (1977), is composed of all or part of two geologic formations recognizable in outcrop and subsurface: (1) a basal sand in the Eutaw Formation and (2) sand of the McShan Formation. Throughout much of the study area where these geologic units are present, no clay confining unit separates the overlying Eutaw Formation and the underlying McShan Formation in the subsurface or outcrop. This strongly suggests, and previous studies (Boswell, 1977; Gardner, 1981) indicate, that these sands make up a single water-bearing zone. A sand present near the top of the Eutaw Formation in parts of Georgia is separated from a basal sand in the same formation by intervening clay (Renken, 1984). The upper sand in the Eutaw Formation hydrologically is part of the Chattahoochee River aquifer, whereas the basal sand hydrologically is part of the Black Warrior River aquifer.

The middle water-bearing zone of the Black Warrior River aquifer consists of sands of the Gordo Formation, which is the upper formation of the Tuscaloosa Group; it is distinguishable in the subsurface in Mississippi and Alabama (Boswell, 1978). This middle zone extends slightly farther north in the subsurface in Mississippi than the lower zone. Eastward into Georgia and South Carolina, the middle zone is not well defined in the subsurface, and to the east it is generally undifferentiated, although locally the Tuscaloosa and Atkinson Formations in Georgia and the Cape Fear Formation in South Carolina, all of Late Cretaceous age, have been described. Chemical data from deep wells in southern Georgia indicate the presence of upper and lower water-bearing zones in the Black Warrior River aquifer. Data for the lower zone are not extensive; therefore, data for only the upper zone were used in this study. All chemical data for the Black Warrior River aquifer for Georgia and South Carolina, and locally for equivalent aquifers in North Carolina, are combined with data for the middle zone for Mississippi and Alabama.

The lower water-bearing zone of the Black Warrior River aquifer is composed of sands in the Coker Formation of the Tuscaloosa Group in Mississippi and Alabama. This zone is underlain by Paleozoic basement rock in updip areas and crops out at the inner Coastal Plain margin (Fall Line). Downdip, the lower zone may include the so-called massive sand in the Coker, for which few data are available but which locally produces freshwater in the area of Noxubee County, Miss. The zone is distinguishable in the subsurface throughout Mississippi and Alabama, but it is not well defined eastward into Georgia and South Carolina, where it may merge with overlying sands to form a single water-bearing unit. The zone is limited in extent in Mississippi and is not present in the subsurface north and northwest of Calhoun, Chickasaw, and Monroe Counties, Miss. (Gandl, 1982). Throughout most of its extent in Mississippi and Alabama, the lower zone is separated from the middle water-bearing zone by intervening clay confining beds (Boswell, 1978).

Regional ground-water flow patterns are similar in all three water-bearing zones. Recharge to the Black Warrior River aquifer occurs in outcrop areas near the Fall Line, and ground water flows down the hydraulic gradient, which generally correlates with the seaward dip of the geologic units (Boswell, 1977, 1978, 1979; Gardner, 1981; Gandl, 1982). The geologic formations that make up the Black Warrior River aquifer do not crop out from



Base from U.S. Geological Survey National Atlas, 1970

EXPLANATION

—*100*—	**Potentiometric contour**—Shows altitude at which water would have stood in tightly cased wells, pre-1950. Contour interval 50 feet in Georgia and South Carolina, 100 feet in Alabama and Mississippi. Datum is sea level
— —	**Southern extent of ground-water containing less than 10,000 milligrams per liter dissolved solids**
⟶	**General direction of ground-water flow**

FIGURE 2.—Area of Southeastern Coastal Plain aquifer system and the potentiometric surface, flow direction, and downdip limit of ground water containing less than 10,000 milligrams per liter dissolved solids in the Black Warrior River aquifer.

central Georgia eastward into South Carolina. In these areas, most of the recharge to the Black Warrior River aquifer occurs in Georgia; ground water flows southeastward, and then eastward and northeastward into South Carolina (fig. 2) (Barker, 1985).

Chattahoochee River regional aquifer.—The Chattahoochee River aquifer is composed of sand and shale of Late Cretaceous and early Tertiary age that were deposited in fluvial, deltaic, and associated nearshore environments. Head differences among sands of the aquifer are small enough to consider the sands part of a single aquifer (Stricker and others, 1985b). Chemical data for ground water in the aquifer are well distributed areally but poorly distributed vertically. Locally, some vertical chemical differences exist in the sands that make up the aquifer; however, the chemical data show that for a regional appraisal, most of the geologic units can be considered a single aquifer. The named geologic units making up the Chattahoochee River aquifer are shown on plate 1, which is taken from Renken (1984).

In Mississippi, the Ripley Formation is part of the Chattahoochee River aquifer. However, in Alabama the Ripley sands are calcareous, are limited in extent, and grade laterally southeastward to chalk. In eastern Alabama and western Georgia, where the subsurface geology is more complex, the chalk grades eastward to interbedded sands and clays. The major named sands included in the aquifer in eastern Alabama and western Georgia are the Blufftown Formation, the Cusseta Sand, the Ripley Formation, and the Providence Sand, all of

Late Cretaceous age, and the Clayton Formation, of Paleocene age (pl. 1).

In eastern Georgia and throughout South Carolina, major sands included in the Chattahoochee River aquifer (pl. 1) are the Middendorf Formation, the Black Creek Formation and its unnamed coastal-area equivalent sediments, and the Peedee Formation, all of Late Cretaceous age. Units of Paleocene age in the eastern half of the study area are not considered part of the aquifer. Laterally equivalent aquifers in North Carolina are considered to be part of the Northern Atlantic Coastal Plain aquifer system. However, some water moves from these aquifers southward into the Chattahoochee River aquifer, thus affecting the geochemistry of its water.

Throughout the study area, the Chattahoochee River aquifer generally consists of a series of lenticular to wedge-shaped sand bodies interbedded with low-permeability rocks (Renken, 1984). Although the individual sand bodies that make up the aquifer form a series of discrete subregional aquifers in some areas, they are hydraulically interconnected to varying degrees on a regional scale. In the eastern half of the study area, the aquifer consists of alluvial, deltaic, and marginal marine to marine deposits of fine- to coarse-grained quartz sand that is commonly fossiliferous, glauconitic, micaceous, phosphatic, and feldspathic. Sand horizons within the aquifer are typically interbedded with dark, calcareous, carbonaceous, chalky shale, clay, and mudstone.

In eastern Alabama and western Georgia, the sandy limestone and calcareous sand of the Clayton Formation are interconnected with permeable, predominantly clastic horizons of the Chattahoochee River aquifer, and are therefore included as part of the aquifer even though the Clayton consists largely of carbonate rocks. In a large part of the western half of the study area, particularly central and western Alabama and east-central Mississippi, the Chattahoochee River aquifer is nonexistent. In northern Mississippi, the Ripley Formation, which makes up the aquifer there, is marine, glauconitic, fine- to coarse-grained, calcareous, fossiliferous sand.

In Mississippi and Alabama, dark, massive marine clay of the Porters Creek Formation (Paleocene) and calcareous to noncalcareous shale, chalky limestone, chalk, and carbonaceous clay of the Selma Group (Late Cretaceous) form the upper confining unit of the Chattahoochee River aquifer. In the eastern part of the study area, fissile, carbonaceous clay and shale that are part of the Eutaw Formation of eastern Alabama and Georgia, and varicolored clay of the upper part of the Cape Fear Formation (Late Cretaceous age) in the subsurface of eastern South Carolina, form the lower confining unit of the aquifer.

Seaward of the Fall Line, sand units of the Chattahoochee River aquifer commonly crop out along the inner margin of the Coastal Plain. In eastern Alabama, Georgia, and South Carolina, the Fall Line is the contact between sands of the aquifer and crystalline basement rock. The wedge-shaped body of sediments that constitutes the aquifer thickens seaward to a maximum of about 2,000 feet (ft). Recharge to the aquifer generally occurs by rainfall in outcrop areas. Water entering the aquifer near the Fall Line flows toward adjacent coastal areas. Locally, small streams in outcrop areas may provide some recharge or may be drains; larger streams, such as the Chattahoochee and Savannah Rivers, are regional ground-water drains. Downgradient, saline waters are present in sands of the aquifer. Ground-water withdrawals from wells completed in sands near the freshwater-saltwater interface may degrade the quality of drinking water supplies by withdrawing freshwater mixed with saltwater as a result of pumping.

Pearl River regional aquifer.—The upper hydrogeologic unit of the Southeastern Coastal Plain aquifer system has been named the Pearl River aquifer (Renken, 1984). This regionally extensive aquifer is composed of sand, shale, and some limestone of Tertiary age deposited in deltaic and associated nearshore environments. The aquifer consists of massive to thinly laminated, very fine to coarse, glauconitic, calcareous, quartz sand of middle Paleocene to late Eocene age. The geology and hydrology of the Tertiary sediments in Mississippi have been studied, and detailed subsurface information and appropriate water quality data are available (Boswell, 1976a, 1976b; Newcome, 1976; Spiers, 1977a, 1977b; Wasson, 1980; Gandl, 1982). To understand better the complexity of the water chemistry, the Pearl River aquifer in Mississippi has been further subdivided into three water-bearing zones—lower, middle, and upper. Few vertical chemical differences are apparent from water-chemistry data for the Pearl River aquifer in Alabama, Georgia, and South Carolina. Most of the data closely resemble data for the middle water-bearing zone in Mississippi; therefore, these data are mapped as an extension of the middle water-bearing zone from Mississippi. The upper and lower zones in Mississippi and western Alabama are mapped separately.

The upper water-bearing zone of the Pearl River aquifer is limited to Mississippi and western Alabama; it is made up of the Sparta Sand, the Cockfield Formation, and the Cook Mountain Formation. The latter formation contains less extensive water-bearing sands than the other two, but it has been included in the upper zone on the basis of available chemical data for water from the formation. The Sparta Sand and Cockfield Formation previously have been reported as separate aquifers throughout Mississippi (Newcome, 1976; Spiers, 1977a). However, they are known to be interconnected hydrologically in many places, especially in central Mississippi, where the Cook Mountain Formation is sandy. Some areas of vertical chemical difference are present locally, but on a regional basis, the chemical data may be combined for these three units.

The middle water-bearing zone of the Pearl River aquifer consists of several permeable zones in Mississippi that are grouped with Tertiary sand and limestone in Alabama, Georgia, and South Carolina. In Mississippi, chemical data for the middle water-bearing zone are from the Winona Sand, the Tallahatta Formation (Spiers, 1977b), the Meridian Sand Member of the Tallahatta Formation, lower Eocene-age sands (Boswell, 1976b), the Basic City Shale, and the Neshoba Sand Member of the Tallahatta Formation. In Alabama, chemical data for the middle water-bearing zone are from the Gosport Sand and the Lisbon, Tallahatta, Tuscahoma, Nanafalia, and Naheola Formations. However, the Naheola Formation regionally is a confining unit in Alabama, as shown on plate 1. In Georgia, chemical data for the middle water-bearing zone are from the Barnwell, McBean, Lisbon, Tallahatta, Tuscahoma, and Nanafalia Formations. In South Carolina, chemical data for the middle water-bearing zone are from the Barnwell, McBean, and Black Mingo Formations. Other geologic units are present in the middle water-bearing zone in these States, but available ground-water chemical data are generally limited to the named formations.

The lower water-bearing zone of the Pearl River aquifer occurs principally in Mississippi. It is differentiated primarily on the basis of water quality data from lowermost Eocene-age sands (Boswell, 1976a). Additional chemical data from the Tuscahoma Formation are included on the map of the lower zone.

Regional ground-water flow patterns are similar in all three water-bearing zones of the Pearl River aquifer. Recharge to the aquifer occurs in outcrop areas, and ground water flows down the hydraulic gradient, which generally correlates with the seaward dip of the geologic units. Most of the Tertiary formations crop out seaward along the Fall Line. Ground-water flow generally is toward the Mississippi River in central Mississippi, toward the Gulf of Mexico in southern Mississippi, Alabama, and western Georgia, and toward the Atlantic Ocean in eastern Georgia and South Carolina (Cederstrom and others, 1979; Stricker and others, 1985a).

GENERAL WATER CHEMISTRY

The ground water in the Southeastern Coastal Plain aquifer system meets Environmental Protection Agency drinking water standards (U.S. Environmental Protection Agency, 1977) in many places. Concentrations of dissolved solids in excess of 500 milligrams per liter (mg/L) occur as a result of mineral-water interactions in the aquifers, or of mixing of fresh ground water with saline water present in the deeper parts of the water-bearing zones. Where concentrations of dissolved solids are less than about 500 mg/L, most of the waters are dominated by sodium and bicarbonate ions (Lee, 1985). In deeper parts of the aquifers, sodium and chloride ions dominate (Cederstrom and others, 1979), and concentrations of dissolved solids may exceed 10,000 mg/L. Concentrations of dissolved iron may reach 15 mg/L in freshwater areas in noncalcareous sands; such water usually must be treated to remove iron before it is used.

Maps of concentrations of dissolved solids, dissolved iron, dissolved chloride, and hydrochemical facies were constructed to illustrate the spatial distributions of principal water-quality parameters in the Southeastern Coastal Plain. These maps and parameters are described below.

DISSOLVED SOLIDS

Maps of concentrations of dissolved solids in the various aquifers were prepared using values of residue on evaporation at 180 °C, if available, or calculated dissolved solids if no residue on evaporation was recorded. Concentrations of dissolved solids in ground waters generally increase with distance from the area of outcrop where recharge occurs. In recharge areas, concentrations in ground water may be less than 50 mg/L, or near the concentration of dissolved solids in rainfall (Junge and Werby, 1958). Waters having concentrations greater than 50 mg/L but less than 500 mg/L in the Southeastern Coastal Plain aquifer system principally are the result of water-rock interactions (Lee, 1985). Concentrations greater than about 500 mg/L generally are the result of the combined effects of water-rock interactions and mixing with saline water. Saline water may contain dissolved solids greater than 100,000 mg/L in places, with sodium and chloride the dominant ions in ground water from the deeper, downgradient parts of the aquifers. In southern Mississippi, salt domes have caused local increases in the concentrations of dissolved solids in ground water (Spiers and Gandl, 1980).

DISSOLVED CHLORIDE

The distribution of dissolved chloride in the Southeastern Coastal Plain aquifer system shows the extent of freshwater flushing of brines or relict seawater. In southern Mississippi, high concentrations of dissolved chloride in some areas reflect the influence of salt domes; in other areas, the pronounced increase in chloride concentrations indicates mixing of meteoric ground water with saline water. Farther downgradient, beyond the mixing zone, sparse chemical data show that sodium chloride brines are present in the deeper parts of the aquifers. Maps of concentrations of dissolved chloride show trends similar to trends in concentrations of dissolved solids where dissolved solids exceed 500 mg/L. This suggests that increases in dissolved-solids concentrations above 500 mg/L are caused by mixing with chloride-rich saline waters.

DISSOLVED IRON

Dissolved iron is present in ground water throughout the Southeastern Coastal Plain and in places may exceed concentrations of 15 mg/L. Concentrations greater than 0.1 mg/L are principally in localized narrow bands in or near the areas of outcrop of the water-bearing zones. As reducing conditions develop within the aquifer downgradient from recharge areas, concentrations may increase to 1 mg/L, and locally may exceed 15 mg/L. Concentrations may then decrease to less than 0.1 mg/L farther downgradient, suggesting that iron oxyhydroxide minerals are first dissolved and then precipitated as other iron minerals downgradient (Lee, 1985). Even farther downgradient, concentrations may again increase, because iron solubility increases with increasing dissolved chloride.

Dissolved-iron data are poorly distributed throughout the study area and are generally not accurate within limits of ±5 percent, especially for waters containing elevated concentrations of iron. Ferric hydroxide minerals ($Fe(OH)_3$) may precipitate from solution after ground-water samples are exposed to the atmosphere, causing losses in the amount of iron in solution and resulting in lower measured concentrations. Although a large contour interval (100, 1,000, and 10,000 micrograms per liter (μg/L)) was used in mapping the iron concentrations, dissolved iron should be interpreted with caution.

HYDROCHEMICAL FACIES

The term "hydrochemical facies" refers to a classification of natural waters based on the proportions of major cations and anions in the water (Back, 1961). Piper (1953) devised a way to depict graphically the major ion chemistry of water samples (fig. 3). Dominance is determined from the percentage of milliequivalents of each major cation (calcium, magnesium, and sodium plus potassium trilinear) and each major anion (chloride, sulfate, and bicarbonate plus carbonate trilinear) in solution. Thus, in water dominated by calcium and bicarbonate, the calcium ion accounts for more than 50 percent of the total milliequivalents of cations, and the bicarbonate (plus carbonate) ion accounts for more than 50 percent of the milliequivalents of total anions. (This differs slightly from the nomenclature of Back, 1961.) The cations (or anions) of a water analysis define a point in the appropriate field of the trilinear part of the diagram in figure 3. A multiple-ion designation in decreasing order of dominance is used for water containing no cations or anions that individually amount to 50 percent or more of the total cations or anions. For example, a magnesium-calcium-chloride-sulfate water is a water containing magnesium ion in greater concentration than calcium ion and chloride ion in greater concentration than sulfate ion; however, none of the ions constitutes more than 50 percent of the total milliequivalents of cations or anions. Both the cation and anion trilinear plots of this water analysis would be in the no-dominant-cation and no-dominant-anion fields of figure 3. The locations of the various cation-anion dominances of the water samples collected during this study were mapped to show areal distribution of the hydrochemical facies.

Three hydrochemical facies dominate the ground water in the study area: calcium bicarbonate, sodium bicarbonate, and sodium chloride. In ground water containing very low ion concentrations, analytical errors or minor changes in the chemistry of recharge (rainfall) may cause apparent "shifts" in the hydrochemical facies that are unrelated to flow and to the general chemistry of water in the aquifers. Thus, low dissolved-solids concentrations led to a fourth classification for some parts of the recharge areas: variable or no dominant cations or anions.

Near recharge areas, calcium bicarbonate is the dominant facies of the low-dissolved-solids waters. Downgradient, sodium and bicarbonate are the prevalent ions, owing to water-rock interactions of principally calcite dissolution and cation exchange of calcium ion for sodium ion (Lee, 1985). Farther downgradient, where dissolved-solids concentrations exceed about 500 mg/L, sodium and chloride are the dominant ions, probably because of mixing with saline waters present in the deep, downgradient parts of the water-bearing zones. Although sulfate may dominate locally near outcrop areas, neither dissolved magnesium nor sulfate is present in quantities large enough to affect the hydrochemical facies in these areas. Because such occurrences do not represent regional patterns, they have been included with the variable or no dominant facies.

CONCEPTS, THEORY, AND METHODOLOGY

Existing mineralogic, petrologic, or chemical descriptions of sands of the Southeastern Coastal Plain aquifer system are limited to generalized lithologic characteriza-

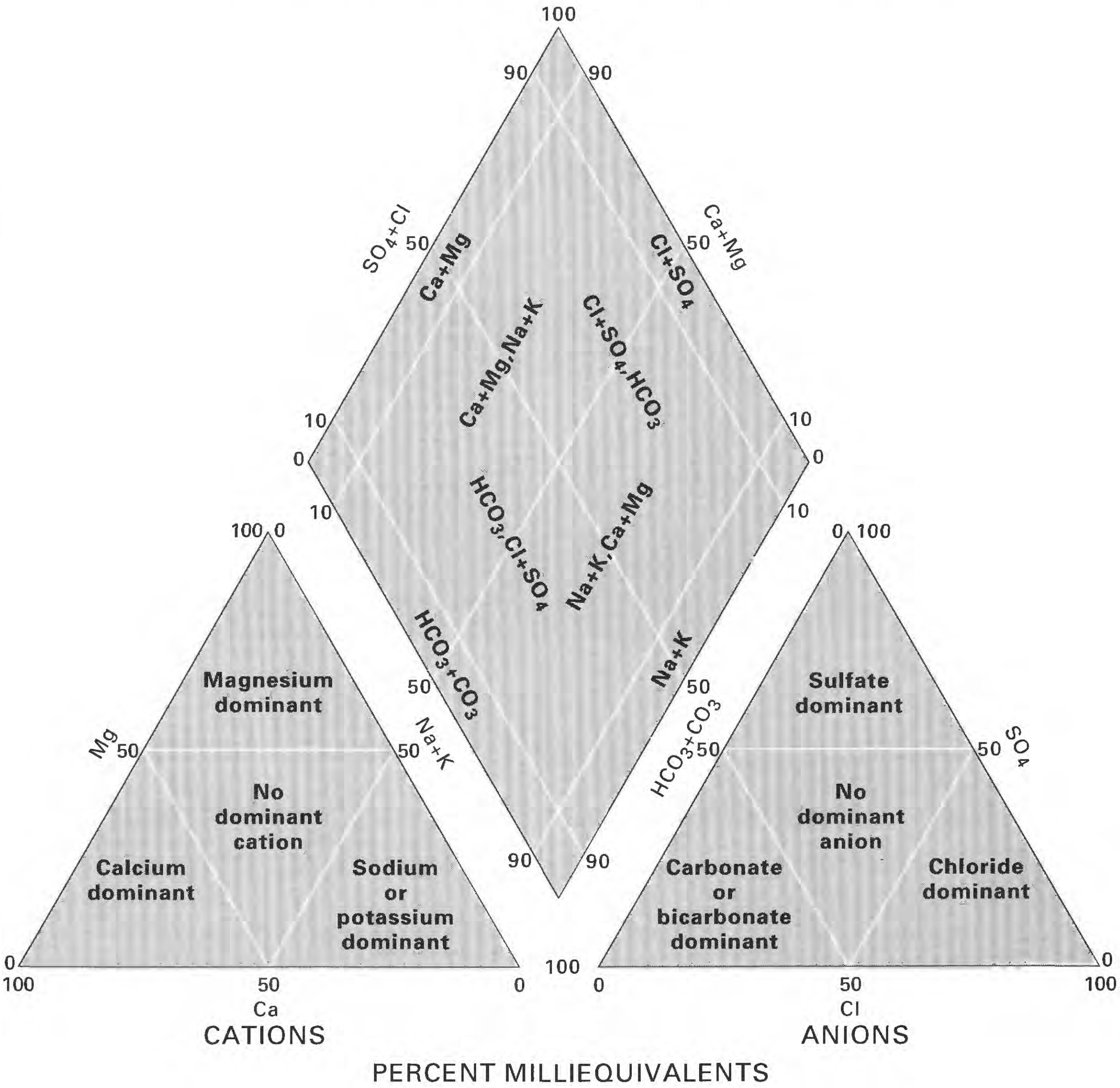
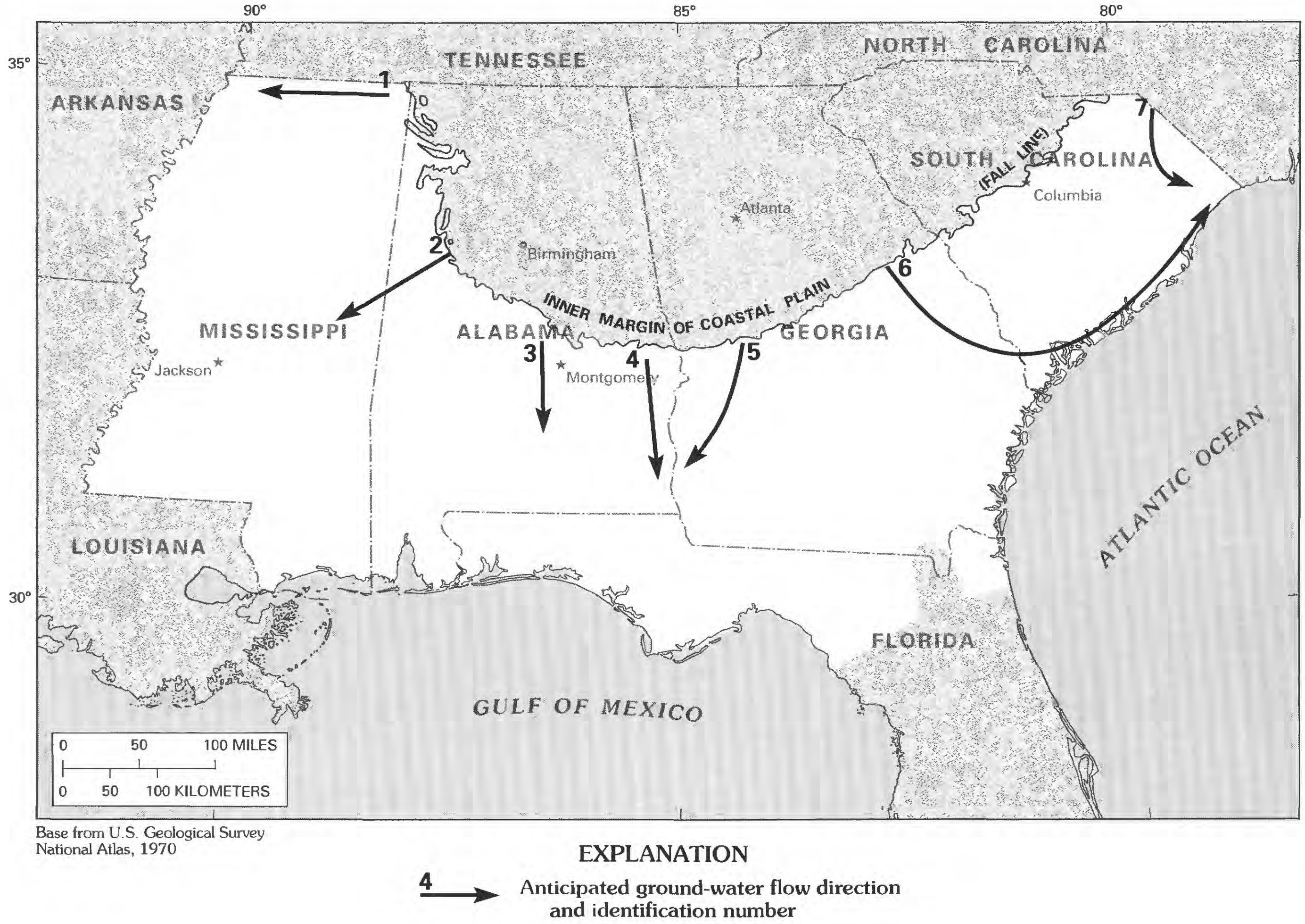


FIGURE 3.—Modified Piper diagram (Piper, 1953) depicting classification scheme for hydrochemical facies of water.

tions. As part of this study, subsurface cores from Coastal Plain sands were taken during deep drilling and testing in 1981–82 in Marion County (Reid, Renken, and others, 1986) and Dorchester County, S.C. (Reid, Aucott, and others, 1986). Selected core samples were analyzed for bulk mineralogy and for clay mineral identification using a petrographic microscope and X-ray diffraction techniques (Grim, 1968). Results were used to corroborate the presence of solid phase constituents participating in chemical evolution and mass transfer in the ground waters of the Coastal Plain aquifers. These core samples, and information derived from them, are described for the various water-bearing zones under "Mineralogy and Petrology."

AQUIFER MINERALOGY

Supporting evidence of water-rock interactions was provided by Hanor and Helton (Louisiana State University, written commun., 1986), who described mineral assemblages and diagenesis in cores and cuttings from Cretaceous sediments in eastern Mississippi and western Alabama. In this study, petrologic descriptions of thin sections, clay mineralogy by X-ray diffraction, and scanning electron microscopy were used to define mineral assemblages in the Eutaw and McShan Formations, the Gordo Formation, and the Coker Formation in eastern Mississippi and western Alabama. In general, mineral assemblages varied from near outcrop to downdip areas.



Base from U.S. Geological Survey
National Atlas, 1970

FIGURE 4.—Location of ground-water flow paths sampled.

Detrital feldspars altering to kaolinite was the dominant diagenetic process updip. Downdip, smectite clays were dominant, with some of the clays formed authigenically. In updip areas, secondary iron mineralization was generally absent; however, in deeper, downdip parts of the aquifers, siderite was observed as a mineral precipitate. In very deep downdip areas, pyrite was observed as a mineral precipitate, with no siderite present. These observations correlate well with geochemical reaction zones derived from models of the water chemistry in the aquifers (Lee, 1985). Models of aqueous geochemistry corroborate authigenesis of kaolinite, smectite, siderite, and pyrite found in the same locations in the water-bearing zone along a specific flow path (Lee, 1985). Although this work was limited in extent, it does provide a basis of comparison and corroboration of aqueous geochemical models with aquifer mineralogy.

GEOCHEMICAL SAMPLING AND ANALYTICAL PROCEDURES

During the period January 1981 to March 1983, 105 samples of ground water were collected for geochemical analysis (Lee, 1984). These samples are from wells that probably represent the majority of water-bearing zones in the Southeastern Coastal Plain aquifer system. Wells were selected for sampling on the basis of hydrologic and geologic information. The wells are located approximately along the anticipated ground-water flow paths shown in figure 4, which were deduced from potentiometric maps (Stricker and others, 1985a, b, c). Assignment of a geologic unit for each well was made according to interpretation and definition of the subsurface geology described in WATSTORE. Many of the analyses of the water samples are presented in tables included in the appropriate sections of this report.

Water samples were collected and analyzed by established procedures (Skougstad and others, 1979) in laboratories of the U.S. Geological Survey in Doraville, Ga., Arvada, Colo., and Reston, Va. Temperature, pH, and bicarbonate and carbonate were determined onsite according to methods described by Wood (1976). Values of pH were measured to, and are reported to ±0.02 unit. The ion chromatography method was used to determine major anions (Erdmann and others, 1982). Samples for trace metals were prepared in the field for inductively coupled plasma atomic emission spectroscopy analysis by filtration through 0.45-micrometer (μm) filters and for acidification with ultrapure nitric acid to pH <2.0. Dissolved-gas samples were collected in an evacuated glass tube (fig. 5) for analysis by gas chromatography (Hobba and others, 1977). Stable and radioactive isotope samples and radiochemical samples were collected according to established methods within the U.S. Geological Survey (Busby and others, 1983).

Most of the analytical values reported are in standard units such as milligrams per liter or micrograms per liter. Environmental isotopes of carbon-13, deuterium, oxygen-18, and carbon-14 are reported in values referenced to an internationally recognized standard. For carbon-13, deuterium, and oxygen-18, the reported value was calculated from the following equation (Fritz and Fontes, 1980):

$$\delta x = \left[\frac{Rx}{R_{std}} - 1 \right] \times 10^{3} \qquad (1)$$

where

δx = stable isotope abundance, in per mil;

Rx = isotopic ratio ($^{13}C/^{12}C$, $^{2}H/^{1}H$, or $^{18}O/^{16}O$); and

R_{std} = corresponding isotopic ratio in a standard (R_{std} carbon-13=Pee Dee Belemnite (PDB); R_{std} deuterium and R_{std} oxygen-18=Vienna Standard Mean Ocean Water (V-SMOW)).

The δ-value is expressed in parts per thousand (per mil, ‰). Carbon-14 is expressed in percent of modern atmospheric carbon-14 (before thermonuclear testing). Tritium is expressed in picocuries per liter (pCi/L) or in tritium units (1 T.U.=3.2 pCi/L).

Deuterium and oxygen-18 delta values are plotted in figure 6, along with the meteoric water line, $\delta D = 8\delta^{18}O + 10$ (Craig, 1961).

Carbon-13 ratios of ground water and solid phase samples, all from the Southeastern Coastal Plain aquifer system, are plotted in figure 7; the plot shows the range of values for water samples and pertinent solid phases.

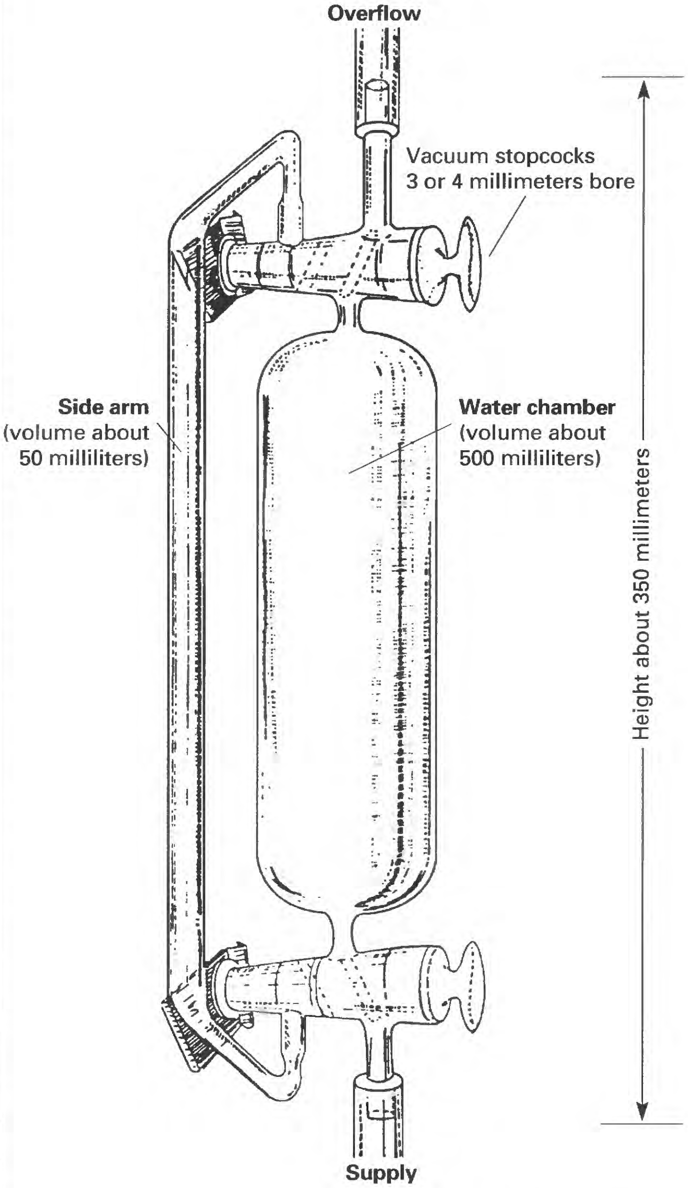


FIGURE 5.—Sampling device used for collecting dissolved gases in water (from Hobba and others, 1977).

CHEMICAL EVOLUTION OF GROUND WATER

As ground water flows from recharge areas to discharge areas, the time in contact with minerals in the aquifer affects the chemical composition of the water. The chemical changes that occur along the flow path are referred to collectively as the chemical evolution of ground water in that aquifer. Piper diagrams (fig. 3) are used to illustrate geochemical evolution of waters. Ground waters evolve from recharge of no dominant facies to either sodium bicarbonate facies or calcium bicarbonate facies in the updip and shallower parts of the aquifers, to sodium chloride facies in the deeper, downgradient parts of the aquifers. This characterization does not reflect all the subtle chemical changes that occur along flow paths, but it does describe the major changes

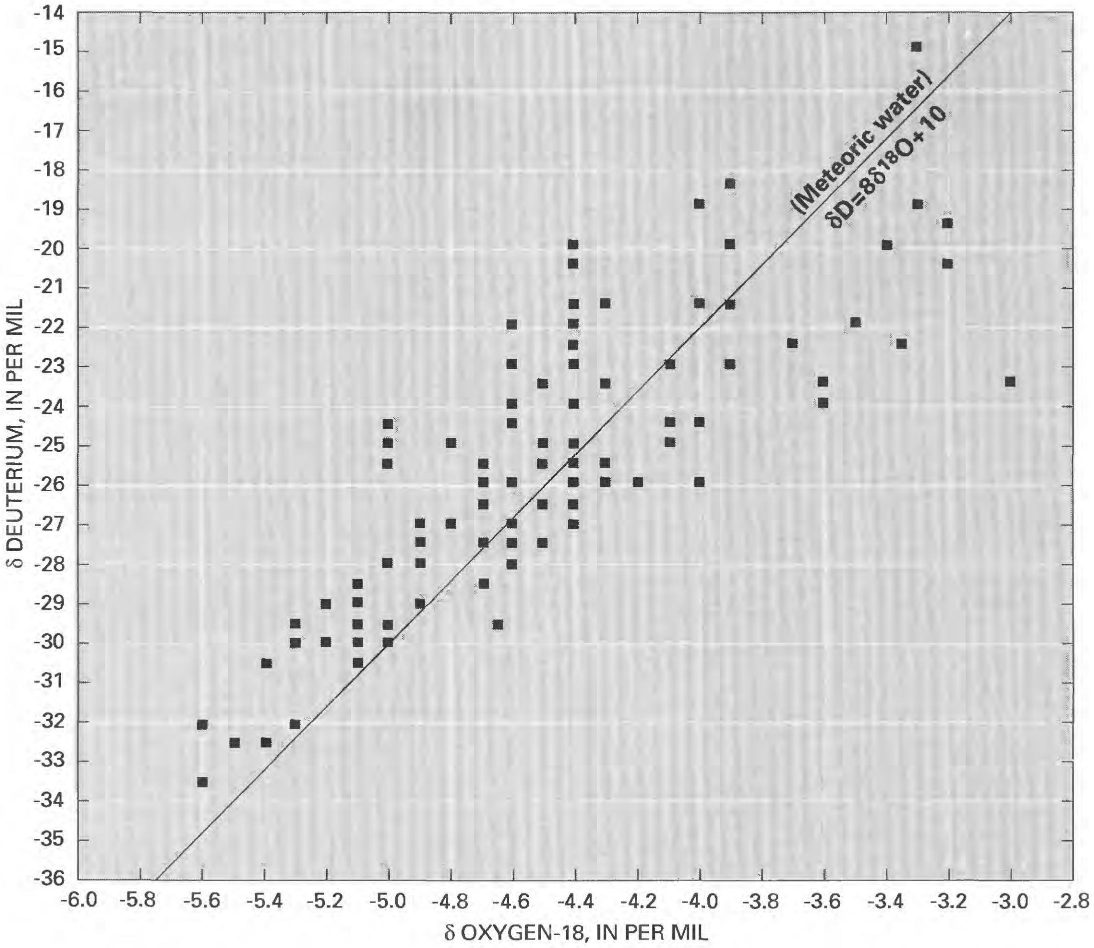


FIGURE 6.—Relation between deuterium (δD) and oxygen-18 ($\delta^{18}O$) in Southeastern Coastal Plain ground waters.

in cation-anion relationships among the ground-water samples.

In describing reaction progress within an aquifer, it is assumed that along a ground-water flow path, chemical changes between two sample sites are indicative of mineral-water interaction or of mixing of waters of different chemical compositions, with the downgradient site representing chemically evolved or mixed ground water. A problem occurs in charting a chemical change against an evolutionary or reaction progress variable. Residence time of water in an aquifer would be an ideal reaction progress variable; however, residence times can only be estimated from hydrologic data or chemical data. Exact length and direction of ground-water flow are more easily and accurately determined. Because recharge of meteoric water to the aquifers occurs in outcrop areas, an approximate representation of reaction progress would be distance downgradient, that is, the horizontal distance along a deduced flow path from the recharge area to the sampled location. Distance downgradient was measured on land surface using the outcrop of the base of the formation as the point of recharge, or zero distance along flow paths to each well site.

MINERAL EQUILIBRIUM

Mineral-water relationships for the water samples analyzed were interpreted using the computer program WATEQ2 (Ball and others, 1980). WATEQ2 calculates mineral saturation states for an aqueous solution using the chemical analysis of the solution and the thermodynamic data for minerals and aqueous species. Selected thermodynamic data for mineral phases used in this report are reported in table 1. The saturation state for a mineral or other participating substance is expressed as saturation index (SI),

$$SI = \log Iap/K(T)$$

where

Iap = ionic activity product; and

$K(T)$ = mineral equilibrium constant at a specified temperature.

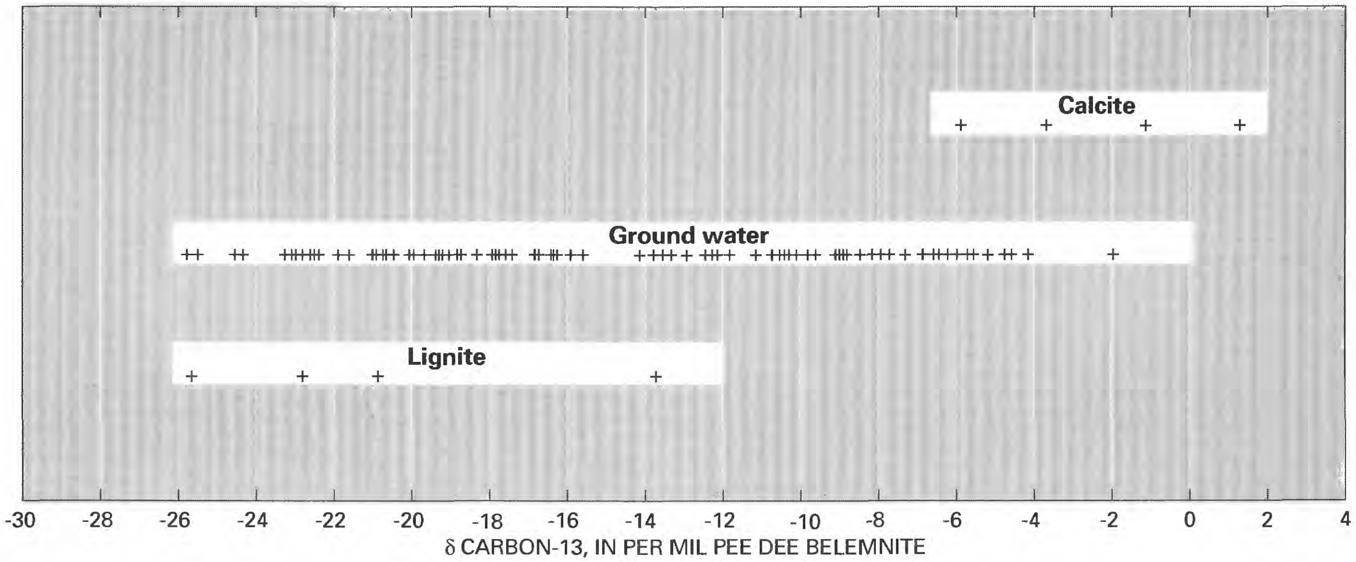


FIGURE 7.—Carbon-13 relationships of sand aquifers in Tertiary and Cretaceous rocks of the Southeastern Coastal Plain.

In general, when SI>0.1, the specific mineral is oversaturated and precipitation is possible; when SI=±0.1, the specific mineral is saturated and precipitation or dissolution is possible; when SI<−0.1, the specific mineral is undersaturated and dissolution is possible. Because mineral stoichiometries are variable, saturation states for some minerals may also vary as much as ±1.0.

TABLE 1.—*Selected thermodynamic data used in WATEQ2 calculations of saturation indices*

[H, enthalpy; K, mineral equilibrium constant; kcal/mol, kilocalories per mole; T, temperature. Dots indicate ditto]

Mineral name	ΔH (kcal/mol)	Log K (T=25 °C)	References
Albite...........	25.896	−18.002	WATEQ, Truesdell and Jones, 1974.
Analcime	18.206	−12.701	WATEQ, ...
Aragonite........	−2.615	−8.36	WATEQ2, Ball and others, 1980.
Calcite...........	−2.585	−8.475	WATEQ2, ...
Chalcedony	4.615	−3.523	WATEQ, Truesdell and Jones, 1974.
Dolomite.........	−8.290	−17.00	WATEQ, ...
Gibbsite	−22.8	8.77	WATEQ2, Ball and others, 1980.
Goethite	−14.48	.5	WATEQ2, ...
Gypsum..........	0.261	−4.848	WATEQ, Truesdell and Jones, 1974.
Kaolinite.........	49.150	−36.921	WATEQ, ...
Na-Montmorillonite.	58.373	−45.027	WATEQ, ...
Pyrite	11.300	−18.479	WATEQ, ...
Siderite..........	−5.328	−10.550	WATEQ, ...
Quartz...........	6.220	−4.006	WATEQ, ...

Saturation indices for minerals commonly found in the Southeastern Coastal Plain aquifer system are shown, by aquifer sampled, in tables 6, 12, 17, 23, and 28. These indices show possible chemical reactions that may control water chemistry. Plausible mineral-water reactions and other pertinent geochemical processes are shown in table 2.

Sodium and potassium feldspars, present in the aquifers, are generally unstable in freshwater systems. Because sodium feldspar is generally much more reactive than potassium feldspar (Drever, 1982), it, and not potassium feldspar, is considered in the chemical reactions and subsequent models. Aluminosilicate phases present some problems. Because the aluminum data obtained from the water samples are generally poor, it is reasonable not to emphasize the calculated saturation states of the aluminosilicate minerals, especially the smectite clays known to be present in the aquifers. Furthermore, calculation of the Gibbs free energy of formation (ΔG_f) for the clays is quite uncertain (Drever, 1982). Difficulties in laboratory measurements and the effect of ionic substitutions in the smectite lattice may produce variable values of ΔG_f, severely restricting interpretation of smectite saturation states. Thus, the discussions dealing with aluminosilicates, especially smectite clay, represented in this report as sodium beidellite, should be considered cautiously.

TABLE 2.—*Mineral phases, reaction stoichiometries, and chemistry of seawater*

[PDB, Pee Dee Belemnite]

Dissolution-precipitation reactions

$CO_2(g)(SOIL) + H_2O = H_2CO_3$

$2NaAlSi_3O_8 + 11H_2O + 2CO_2 = Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$

Albite Kaolinite

$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$

Calcite

$FeCO_3 + H^+ = Fe^{2+} + HCO_3^-$

Siderite

$Fe^{2+} + 2HS^- = FeS_2 + 2H^+$

Pyrite

$CaSO_4{\cdot}2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$

Gypsum

$Ca^{2+} + Na_2\text{-Sediment} = 2Na^+ + Ca\text{-Sediment}$

Cation exchange

Oxidation–reduction reactions

$2CH_2O + O_2 \rightarrow 2CO_2 + H_2O$

Lignite

$CH_2O + 8H^+ + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 11H_2O + CO_2$

Lignite

$2CH_2O + SO_4^{2-} + H^+ \rightarrow HS^- + 2H_2O + 2CO_2$

Lignite

$2CH_2O + CO_2 \rightarrow CH_4 + 2CO_2$

Lignite

***Seawater chemistry**

Total inorganic carbon= 2.14
Na=485.42
K= 10.58
Cl=566.75
SO_4= 29.26
Ca= 10.66
Mg= 55.08
(estimated) $\delta^{13}C$= 0.00 ‰ (PDB)

*Principal ions only, in millimoles

MASS BALANCE

Mass-balance calculations by means of the computer program BALANCE (Parkhurst and others, 1982) use selected phases as sources or sinks of cations and anions to the aqueous solution. In redox processes, electrons are transferred, that is, electrons leave an oxidized species and go to a reduced species. Consideration is given the total number of electrons, or electron balance, by mass balance on the valence of oxidized and reduced species and minerals. The mass of an oxidized or reduced species multiplied by its valence represents the redox state (Plummer and others, 1983). The net sum of oxidized and reduced species for a solution represents the total redox state for that solution. Changes in the redox state of ground water as a result of interaction with aquifer materials constitute an electron balance constraint; this constraint must be considered if redox reactions are occurring. In addition to the chemical balances and electron balance, the change in value of $\delta^{13}C$ in total CO_2 in solution from recharge areas to downgradient areas of the aquifers constrains mass balance of the carbon-bearing phases within the geochemical system.

The minerals selected for mass-balance calculations and the reaction coefficients resulting from the calculations are shown in tables 7, 13, 18, 24, and 29. The calculations are for intervals between consecutive wells in the same aquifer along the same flow path. Consideration of local geochemical environments, laboratory analytical errors, and estimates of mineral isotope ratios ($\delta^{13}C$) and mineral stoichiometry indicate sensitivity of about ±0.5 millimole per kilogram (mmol/kg) of water. However, many results are reported to the nearest 0.01 mmol/kg to account for all important phases. In addition to mass balance of the chemical system, electron balance (oxidation-reduction) and $\delta^{13}C$ distribution between the ground water and solid phases were used to constrain the number of solutions to the mass balance.

The values in the tables of mass balance for flow paths in the aquifers represent reaction coefficients of the mineral phases; they are used to designate these phases as either potential sources or potential sinks of solutes in the aquifers. Positive values indicate dissolution of the phases, and negative values indicate precipitation of the phases. The reaction of calcium-for-sodium cation exchange is written as positive for release of sodium from aquifer minerals to the solution, and as negative for net uptake of sodium from ground water to aquifer materials. In the mass-balance equations, the upgradient ground-water chemistry, plus phases dissolving, minus phases precipitating or degassing, equals the downgradient ground-water chemistry.

Although the results of the mass-balance calculations suggest that the reaction paths for the various aquifers are similar, it is widely recognized that mass balance alone does not provide unique solutions to mass transfer. Other reaction models, such as the mixing of waters of different chemical composition or the presence of minerals with substitutions of cations or anions within the crystal lattices, may also provide plausible mass-balance solutions. However, combining the results of the mass-balance calculations with the thermodynamic constraints of WATEQ2 and with other available mineralogic and chemical data for the various mineral phases within the aquifers limits the plausible solutions to manageable numbers. The best solutions are presented in each of the sections describing the geochemistry of the aquifers.

Descriptions of the geochemical evolution along flow paths at various distances from recharge zones toward downgradient zones are summarized in table 3.

TABLE 3.—*Reaction sequence by geochemical zone*

RECHARGE ZONE:	Rainfall–input chemistry, atmospheric CO_2 plus soil CO_2 plus dissolved O_2.
ZONE A:	Calcite dissolution Sodium feldspar hydrolysis to kaolinite Oxidation of sedimentary organic material, lignite (CH_2O), by dissolved O_2
ZONE B:	Calcite dissolution Sodium feldspar hydrolysis to kaolinite Ferric iron reduction to ferrous iron to saturation with siderite Oxidation of sedimentary organic material, lignite Silica precipitation
ZONE C:	Calcite dissolution Sodium feldspar hydrolysis to kaolinite Siderite precipitation Ferric iron reduction Oxidation of sedimentary organic material, lignite Silica precipitation
ZONE D:	Smectite precipitation Calcite dissolution Na–Ca cation exchange Gypsum dissolution Sulfate reduction FeS_2 precipitation Ferric iron reduction Oxidation of sedimentary organic material, lignite; methanogenesis Silica dissolution
ZONE E:	Mixing with saline water

MODELS OF GEOCHEMICAL ZONES

Using PHREEQE (Parkhurst and others, 1980), a computer program that simulates mass transfer, a generalized reaction model was developed for mass transfer in the geochemical reaction zones (zones A through D) summarized in table 3. Differences in aquifer lithology, such as the presence or absence of calcite in aquifer material or variations in CO_2 input at recharge or from other sources, result in slightly different water chemistries in the aquifers. Models representing the various chemical evolutions within aquifers should be useful for areas for which few data are available and for areas where sampling of ground water along flow paths for mass-balance calculations is not possible.

The plausible chemical reactions and mass balance are shown in table 2. Postulated reaction sequences are supported by the results of PHREEQE calculations using theoretical saturation limits of minerals and approximations of observed mass balance. Mass-transfer coefficients calculated in the models are listed in the appendix. The variables of pH and ΣCO_2 (mmol/kg) ($\Sigma CO_2 = a_{H_2CO_3} + a_{HCO_3^-} + a_{CO_3^=}$; a=activity) along a flow path are compared with pH and ΣCO_2 from PHREEQE calculations which simulate the various zones of specific chemical reactions and the reaction sequences. The models were designed to closely match concentrations of major observed chemical constituents. The reaction sequences are shown in table 3.

The following discussion describes the general sequence of chemical reactions in the aquifers. Recharge water is modeled as pure water plus a quantity of CO_2 in the recharge area. Input CO_2 values of 60, 70, and 80 mg/L, a plausible range of CO_2 gas in the soil environment at 15.0 °C, produce three different simulation models (models 1 through 3, containing the following partial pressures of CO_2: $10^{-3.0}$, $10^{-2.5}$, and $10^{-2.0}$ atmospheres, respectively (see appendix)). Differences in CO_2 input to a particular aquifer affect the outcome of the reaction model.

In zone A (the most upgradient area), the CO_2- and O_2-charged waters react with a fixed proportion of the albite, quartz, and other silica polymorphs, with traces of calcite, and with lignite. The amount of CO_2 produced in this zone should correspond to the amount of O_2 consumed.

The next aqueous environment, zone B (downgradient from zone A), is anoxic, and reduction of ferric iron occurs. Iron reduction, and perhaps some dissolution of reduced iron phases, occur until saturation with siderite ($FeCO_3$) is attained. Calcite, albite, and lignite continue to react if present, but silica may precipitate as quartz, chalcedony, or overgrowths.

In zone C (farther downgradient from zone A), siderite saturation is achieved, with losses of ΣCO_2 and dissolved iron, and pH increases as much as 2 units. Calcite, albite, and lignite continue to dissolve, silica and kaolinite precipitate, and siderite precipitates as more iron is reduced. Zone C ends when calcite saturation is attained.

In zone D (downgradient from zone C), pH increases slightly with very large increases in ΣCO_2. Iron (as ferric iron) is reduced, and lignite is oxidized; however, siderite is probably not the precipitating mineral determining the amount of dissolved iron in waters of this zone. Small amounts of dissolved sulfate are reduced to bisulfide ion (HS^-), which is detected in many of the waters, and thus pyrite (FeS_2) precipitation probably controls dissolved iron concentrations.

Cation exchange (sodium for calcium), which causes undersaturation in solution with respect to calcite, and subsequent calcite dissolution dominate the chemistry of water in zone D. This process continues with CO_2 production from lignite and possible formation of a sodium smectite (Hanor and Helton, Louisiana State University, written commun., 1986). The primary result is a sodium-bicarbonate water of higher dissolved solids which is near or at saturation with calcite. Siliceous phases such as quartz, chalcedony, and amorphous aluminosilicates may be dissolved to form sodium smectite.

Variations of these chemical processes could alter the chemical evolution of the ground water. Although the trends are similar, different amounts of calcite dissolution, silicate hydrolysis, lignite oxidation, or ΣCO_2 at recharge, individually or in combination, produce significant variations in the water chemistry of the aquifers. Several PHREEQE simulations of models 1–3 were run using different concentrations of calcite. Simulations I–III, summarized in the appendix, demonstrate these differences. Ideally, water analyses for the beginning and end of each zone would be available to define the proportions of the major reactions in each aquifer. More information is needed to better quantify the geochemistry, especially ΣCO_2 in recharge areas.

PHREEQE simulation IV differs slightly from the previously discussed geochemistry and applies to flow path 1 shown in figure 4. As ground water flows from well 1 to well 2, pH rises sharply with increases in ΣCO_2. From well 2 to well 3, ΣCO_2 decreases with little change in pH; finally, relatively high pH and high ΣCO_2 are attained at well 4. The PHREEQE model simulates the same chemical results by establishing near saturation of calcite in zone A before the reducing environment is reached. When reduction begins, siderite is already near saturation at the high pH established by calcite dissolution; thus the dissolved ferrous iron remains low in solution, and siderite precipitation proceeds as ferric iron is reduced, with a net loss of ΣCO_2 from the solution phase to the solid phase. Calcite and siderite precipitation is indicated by the model. The water chemistry changes from a calcium-bicarbonate water to a sodium-bicarbonate water in zone D of the PHREEQE models.

PHREEQE simulations II and III represent increasing amounts of calcite dissolution in zones A, B, and C and are designed to match the chemical data from the ground water. The geochemical processes described closely resemble the geochemistry in the Paleocene Aquia Formation in southern Maryland (Chappelle, 1983).

Basically, the four simulations (I–IV) shown in the appendix may be compared as follows: PHREEQE simulation I is characterized by very low reaction coefficients in zones A–C, indicating very low amounts of calcite present in aquifers showing similar chemical evolution. Chemical evolution as shown by simulation II is more common in the Southeastern Coastal Plain aquifers, where ground water in zones A–C reacts with more calcite than used in simulation I. Simulation III is representative of calcareous sand aquifers, although calcite saturation is not achieved in zones A–C. Simulation IV essentially represents flow path 1, shown in figure 4, in a calcareous sand aquifer where calcite saturation is achieved in zone A.

CARBON-14 AGE AND GROUND-WATER FLOW VELOCITY

Most carbon-14 enters aquifers as $^{14}CO_2$ with atmospheric precipitation and from breakdown of plant material and root respiration in the soil zone. Other $^{14}CO_2$ may be derived from oxidizing organic material washed into the unsaturated zone in recharge areas. Increases in carbon-14 in ground water along flow paths in aquifers closed to atmospheric sources are not plausible because natural inorganic and organic sources of carbon should be depleted in carbon-14 content. Because the aquifers are confined and isolated from recharge sources of CO_2 downgradient, the initial carbon-14 at recharge is the only source considered in these calculations. Ground-water age (t) is calculated from the following equation:

$$t = -\frac{t_{1/2}}{0.301}\log\frac{A}{A_{nd}} \qquad (2)$$

where

$t_{1/2}$ = ^{14}C half-life (5,730 years);

A = measured ^{14}C activity at well, in percent modern carbon; and

A_{nd} = ^{14}C activity expected at well in the absence of radioactive decay, in percent modern carbon.

In recharge waters, A_{nd} is assumed equal to 100 percent modern carbon (PM).

Adjustments of the ^{14}C content of ground water along a flow path are based on dilution of the ^{14}C at recharge, with the assumption that there are no inorganic and organic carbon sources containing ^{14}C ("dead" carbon) in the aquifer. Thus, adjusted ages are always younger than unadjusted ages. Addition of "dead" carbon downgradient from aquifer sources dilutes the ^{14}C content of total inorganic carbon (ΣCO_2) at recharge, depending on the amount of "dead" carbon added initially. A mass balance on ^{14}C indicates

$$A_{nd} = \frac{A_r \times \Sigma CO_{2r}}{\Sigma CO_{2r} + \Sigma CO_{2a}} \qquad (3)$$

where

A_r = 100 PM;

ΣCO_{2r} = magnitude of total inorganic carbon in recharge waters; and

ΣCO_{2a} = inorganic carbon added to solution from aquifer sources.

The value of ΣCO_{2r} for most recharge areas within the Southeastern Coastal Plain is estimated at 2.0 millimoles per liter (mmol/L).

For well-to-well increments along a ground-water flow path, A_r becomes the ^{14}C measured at the upgradient well, and A_{nd} becomes the ^{14}C adjusted for aquifer carbon input determined from mass-balance calculations assuming no radioactive decay. In equation 2, A would be the ^{14}C value measured at the downgradient well in the sampled path, and

$$A_{nd}=\frac{A_r(\text{upgradient well})\times\Sigma CO_2(\text{upgradient well})}{\Sigma CO_2(\text{upgradient well})+\Sigma CO_{2a}} \qquad (4)$$

Loss of inorganic carbon from water along a flow path may occur by precipitation of a solid phase such as siderite ($FeCO_3$) or loss of CO_2 gas. Fractionation of $^{14}C/^{12}C$ among these phases has little effect on the percent modern values measured, and corrections from these processes are not considered. However, the amount of inorganic carbon from aquifer sources must be determined from the mass-balance calculations between wells along a flow path, as the dilution of ^{14}C is greater than the difference of ΣCO_2 concentrations between the upgradient and downgradient wells. Calculations of age of water from the upgradient wells near the recharge area are based on no dilution and, therefore, no adjustment; no significant amount of tritium was present in the water. Content of ^{14}C is adjusted for mass balance between well pairs to provide a relative age. An adjusted absolute age of water at a well is the sum of adjusted incremental ages along the flow path to that particular well.

Estimates of the real velocity of ground water (r) along a flow path using carbon-14 ages are determined by

$$r=\frac{\text{horizontal distance downgradient}}{\text{adjusted age of ground water}} \qquad (5)$$

where horizontal distance downgradient was defined earlier as measured from outcrop of the base of the aquifer along a flow path to the specific well.

Owing to uncertainties about actual distance downgradient from recharge, and about estimates of percent modern carbon at recharge, the absolute values of adjusted age and adjusted velocity are less reliable than incremental values calculated and reported on well pairs summarized in tables 8, 14, 19, 25, and 30.

Estimates of ground-water velocity can be determined from a modification of Darcy's equation:

$$Vp=\frac{-K\ \Delta h/\Delta l}{\theta} \qquad (6)$$

where

Vp = pore velocity;
K = hydraulic conductivity;
Δh = potentiometric head change;
Δl = length of flow path;
$\Delta h/\Delta l$ = hydraulic gradient; and
θ = porosity of aquifer material.

From mean values of hydraulic conductivity and potentiometric head gradients simulated by a regional ground-water model of the Southeastern Coastal Plain aquifer system (R.A. Barker, U.S. Geological Survey, written commun., 1986) and an estimate of porosity of sands ($\theta\cong 0.3$, from Freeze and Cherry, 1979, table 2.4), pore velocities have been estimated. Mean pore velocities and the values of hydraulic conductivity and hydraulic gradient for each of the regional aquifers are given in the appropriate section.

GEOCHEMISTRY OF WATER IN THE BLACK WARRIOR RIVER AQUIFER

For discussion of water chemistry, the Black Warrior River aquifer is divided into three water-bearing zones—lower, middle, and upper.

LOWER WATER-BEARING ZONE

The lower water-bearing zone of the Black Warrior River aquifer extends from east of Montgomery, Ala., westward into north-central Mississippi (pl. 2). No chemical data were available for Mississippi near the northern extent of the aquifer.

MINERALOGY AND PETROLOGY

The lower water-bearing zone consists predominantly of clay, sand, and gravel. Thin beds of lignite are also present in some parts of the zone, with carbonaceous material disseminated in the sands. Locally, sands may be partially cemented with calcite or siderite. Pyrite occurs as a secondary mineral in the deeper, downgradient parts of the zone. Albite and orthoclase, which occur throughout the sands, are altered to kaolinite, especially in the shallow, updip parts of the zone. Lignite, bauxite, kaolinite, and some iron ore have been mined from the Cretaceous sediments in Mississippi (Gandl, 1982). Hanor and Helton (Louisiana State University, written commun., 1986) indicate that in the Coker Formation, feldspars are absent west of Noxubee County, Miss., and that smectite is dominant among clays in the sands to the southwest. They further describe authigenic siderite present in the Coker Formation from Lowndes County to Noxubee County, with no pyrite present in the areas sampled and analyzed.

DISSOLVED SOLIDS

Two large areas defined by closed lines of equal concentrations of dissolved solids near the outcrop area of the lower water-bearing zone (100 and 50 mg/L, pl. 2) indicate that dissolved solids increase initially, then decrease farther downgradient, as a result of either chemical precipitation within the water-rock system

(Lee, 1985) or mixing with leakage from overlying water-bearing zones containing lower concentrations of dissolved solids. Pumpage from the lower water-bearing zone may have caused the apparently steeper concentration gradient near Montgomery, Ala. Withdrawal of large volumes of water from the lower water-bearing zone in this area likely has caused water containing higher concentrations of dissolved solids to move toward the pumping center.

DISSOLVED CHLORIDE

In outcrop recharge areas, the lower water-bearing zone contains water having concentrations of dissolved chloride of less than 10 mg/L (pl. 2). Concentrations increase downgradient from recharge areas, with steeper concentration gradients beyond 100 mg/L. Incomplete flushing of brines may be the cause of slightly higher concentrations in wells in Montgomery and Hale Counties, Ala. In Greene County, Ala., concentrations in the lower water-bearing zone are much lower than concentrations in the middle and upper water-bearing zones, indicating that incomplete flushing of seawater in the upper zones is a likely process.

DISSOLVED IRON

The lower water-bearing zone contains concentrations of dissolved iron as high as 16,000 μg/L. The highest concentrations occur in a band a few miles wide that is located near the Fall Line in western Alabama and extends into Lowndes County, Miss. (pl. 3). Concentrations are less than 100 μg/L near the recharge area, but increase downgradient to a "band" of high concentrations. Farther downgradient (southwestward), concentrations decrease to less than 200 μg/L. Few data are available from the deeper, downgradient parts of the zone. Concentrations are less than 800 μg/L eastward toward Montgomery, Ala. Concentrations greater than 1,000 μg/L occur in Tuscaloosa County, Ala., near the Fall Line; the reasons for this occurrence are not clear.

HYDROCHEMICAL FACIES

Hydrochemical facies of the lower water-bearing zone are dominated by calcium bicarbonate in and near recharge areas, sodium bicarbonate in downgradient areas, and sodium chloride in deeper downgradient parts (pl. 3). These areas form sequential bands that are oriented parallel to the outcrop areas of the zone. Although data for downgradient areas are scarce, the transition from sodium bicarbonate to sodium chloride facies is similar to that in the middle and upper water-bearing zones of this aquifer. A narrow band of sodium bicarbonate dominated water extends upgradient toward the Fall Line in Pickens and Tuscaloosa Counties, Ala. A small area containing both sodium bicarbonate and sodium chloride facies occurs upgradient in Lamar, Pickens, and Fayette Counties, Ala. These areas are characterized by low concentrations of dissolved solids and highly variable cation-anion dominances.

TRACE ELEMENTS

Water samples from four wells along a flow path in the lower water-bearing zone (fig. 8) indicate that iron and manganese are the most significant of the trace elements, ranging from 24 to 14,000 μg/L and from 5 to 830 μg/L, respectively (table 4). Measurable amounts of strontium and boron are also present, at concentrations as high as 400 and 200 μg/L, respectively. Concentrations of other trace metals are low, with mercury present in well 4 at a concentration of 0.2 μg/L.

DISSOLVED GASES

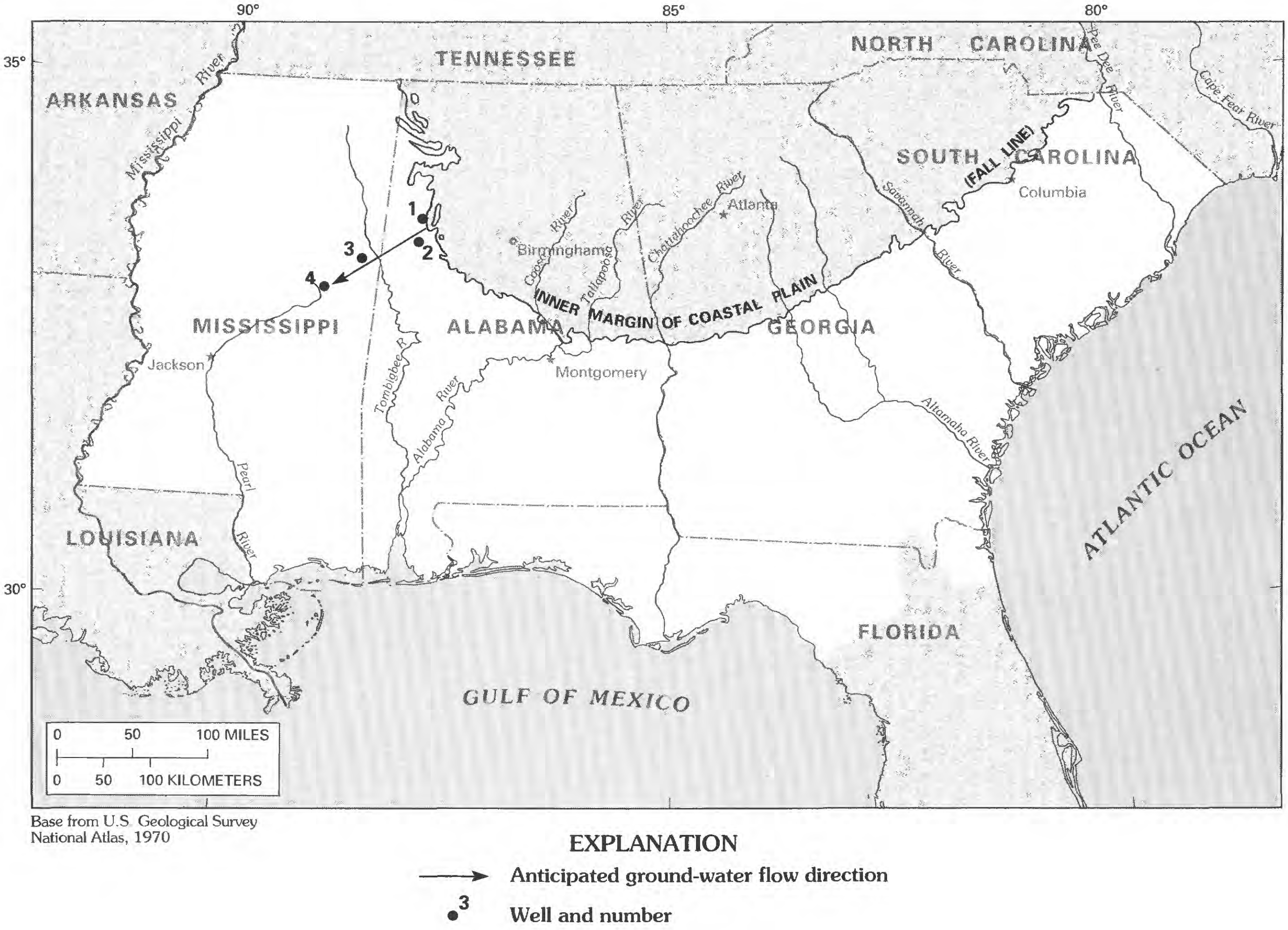
Dissolved gases in water from the four wells in the lower water-bearing zone (fig. 8) demonstrate changes in a downgradient direction. Dissolved oxygen decreases from 10 mg/L at the upgradient well, well 1, to detection limit at well 2 (table 4), indicating that the aquifer system is closed to atmospheric gases and becomes anaerobic downgradient. Dissolved oxygen of 1.8 mg/L at well 3 indicates that some atmospheric contamination occurred during collection or shipping of the water samples. Dissolved carbon dioxide increases from 15 to 36 mg/L from well 1 to well 2, then decreases to 3.6 mg/L at well 4, owing to the increase in pH (table 5). Methane was detected in well 4.

ENVIRONMENTAL ISOTOPES

Analysis of environmental isotopes in water samples from the four wells in the lower water-bearing zone (fig. 8) shows that tritium is present in a significant amount in well 1, 69 pCi/L (table 4). Well 2 contains tritium at 4 pCi/L, indicating that some recent atmospheric recharge may have occurred. Carbon-13 ratios range from −15.9 to −19.6 ‰. Deuterium and oxygen-18 range from −27.5 to −32.5 ‰ and from −4.9 to −5.5 ‰, respectively (fig. 9).

CHEMICAL EVOLUTION

Definite trends in ground-water chemistry (table 5) were observed for waters sampled along the flow path in the lower water-bearing zone (fig. 8). Hydrochemical facies near recharge areas have no major dominant ions, evolve to sodium bicarbonate dominant water downgradient, and to sodium chloride dominant water farther downgradient (fig. 10). Concentrations of dissolved



Base from U.S. Geological Survey National Atlas, 1970

FIGURE 8.—Location of wells sampled for the lower water-bearing zone of the Black Warrior River aquifer.

solids generally increase downgradient (fig. 11*A*), ranging from 33 to 666 mg/L. The increase in concentration of dissolved solids from well 3 to well 4 likely is caused by mixing of potable ground water with more saline ground water. Field-measured pH values also increase with increasing distance downgradient, ranging from 5.38 to 7.83 units (fig. 11*B*). The concentration of dissolved iron is low upgradient (24 μg/L) but increases to 14,000 μg/L in water from well 2 (fig. 11*C*). The concentration of dissolved iron subsequently decreases to as low as 160 μg/L in water from well 3, suggesting precipitation of an iron-bearing phase from aqueous solution. Total inorganic carbon (ΣCO_2; table 4) decreases slightly downgradient, from 1.86 to 1.36 mmol/L, before increasing to 3.30 mmol/L at well 4 (fig. 11*D*). Carbon-13 shows a similar trend (fig. 11*E*), becoming slightly lighter downgradient (from −17.7 to −19.6 ‰) before becoming more positive (−15.9 ‰) at well 4.

MINERAL EQUILIBRIUM

Saturation states for 11 mineral phases in water in the lower water-bearing zone are shown in table 6. Many of the mineral phases are undersaturated. Where shown, albite is undersaturated and kaolinite oversaturated, suggesting the plausibility of albite alteration to kaolinite. Calcite and dolomite are well undersaturated and may be dissolved when encountered by moving ground water. Siderite is slightly undersaturated but approaches saturation at well 4 (fig. 8). Pyrite, where considered, is oversaturated and likely would precipitate from ground water. Chalcedony is near saturation at all wells, indicating that this form of SiO_2 (rather than quartz) is most likely the controlling phase. Sodium beidellite is oversaturated at well 2 and undersaturated at well 4. Owing to the unreliability of thermodynamic data for smectite clay minerals, these results may be misleading and should be interpreted with great caution.

TABLE 4.—*Trace elements, dissolved gases, and environmental isotopes in water from the lower water-bearing zone of the Black Warrior River aquifer*

[In micrograms per liter, unless otherwise specified. pCi/L, picocuries per liter; ‰, per mil; PM, percent modern carbon; mol/kg, moles per kilogram; tr, trace. Dashes indicate no data; negative values for isotopes indicate relatively light content. Location of wells shown in fig. 8]

Well number/name	Al	Ba	B	Cd	Cu	Fe	Pb	Li	Mn	Hg	Sr	Zn	N_2[1]	O_2[1]	CO_2[1]	CH_4[1]	Ar[1]	T (pCi/L)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{18}O$ (‰)	^{14}C (PM)	ΣCO_2 (mol/kg×10^{-3})
1. C. Hubbert	0	30	10	2	81	24	15	<4	5	<0.1	12	41	19	10	15	tr	0.7	69	−17.7	−29.5	−5.3	—	1.86
2. Junkin	10	20	10	5	<10	14,000	18	9	830	<.1	13	9	20	0.08	36	0.01	.79	4	−18.6	−27.5	−4.9	99.5	1.65
3. Black Belt	0	30	10	3	<10	160	20	7	16	<.1	170	<4	26	1.8	1.4	.01	.94	3	−19.6	−29.5	−5.0	38.3	1.36
4. Mashulaville	10	70	200	<1	<10	170	10	22	14	.2	400	4	24	.13	3.6	.26	.95	1	−15.9	−32.5	−5.5	1.5	3.30

[1] Milligrams per liter; errors in laboratory data require interpretation with caution.

TABLE 5.—*Well data and chemical analyses of water from the lower water-bearing zone of the Black Warrior River aquifer*

[In milligrams per liter, unless otherwise specified. ft, feet; mi, miles; µs, microsiemens; ROE, residue on evaporation at 180 °C. Dashes indicate no data. Location of wells shown in fig. 8]

Well number/name	Screened interval (ft)	Distance downgradient (mi)	Specific conductance (µS)	Temperature (°C)	pH (units)	Dissolved solids (ROE)	NH_4	Ca	Mg	Na	K	HCO_3	CO_3	Cl	SO_4	F	SiO_2
1. C. Hubbert	45–46	9.8	46	16.8	5.38	33	<0.01	2.7	0.59	1.6	0.88	10	0	3.09	0.55	0.16	8.5
2. Junkin	—	10.4	90	18.1	6.30	53	.03	1.3	1.7	1.2	4.6	46	0	1.52	4.89	.15	22
3. Black Belt	1,247–1,290	51.3	205	25.0	7.65	95	.01	4.6	.98	26	3.3	80	0	3.4	3.71	.16	12
4. Mashulaville	1,791–1,831	64.2	1,200	31.1	7.83	666	.66	9.0	1.7	260	3.6	198	0	294	0	.41	14

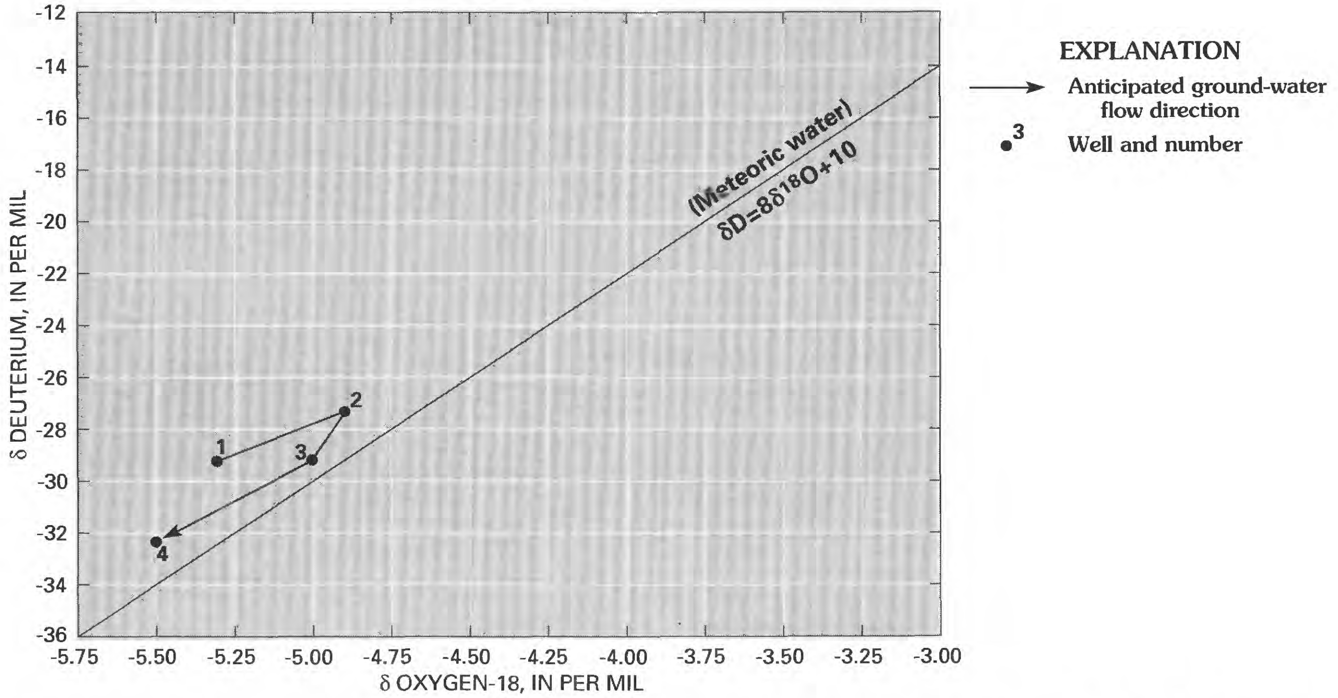


FIGURE 9.—Relation between deuterium (δD) and oxygen-18 ($\delta^{18}O$) in water from the lower water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 8.

MASS BALANCE

Results of mass-balance calculations for water from the lower water-bearing zone of the Black Warrior River aquifer are shown in table 7. Low mass transfer from mineral-water interaction occurs from well 1 to well 2 (fig. 8), with only a slight uptake of chalcedony and a trace amount of cation exchange. The most significant chemical process is oxidation-reduction. Dissolved oxygen is consumed, and a ferric iron source, goethite, yields reduced ferrous iron. This apparently causes near saturation of siderite and, likely, precipitation of siderite. Siderite precipitation continues to occur downgradient (from well 2 to well 3). From well 3 to well 4, bacterial-sulfate reduction occurs, using available organic carbon (lignite) as a nutrient source. Pyrite precipitation appears to occur in the area of well 4 owing to its much lower solubility than siderite. From well 2 to well 3, albite alteration to kaolinite, and a trace of reverse calcium-sodium exchange, are apparent. Mass balance suggests that sodium beidellite forms along the flow path between well 3 and well 4, with substantial amounts of calcium-sodium exchange. Sodium beidellite may form from amorphous aluminosilicate presumed to be available in the aquifer. Well 4 is near an area where saline water is known to be present, and some mixing with brines may have occurred, producing the high chloride content of the ground water. Because the amount and chemistry of the saline water is not known, halite was used in the mass-balance calculations to account for the residual sodium and chloride concentrations from the mixing of freshwater with a small portion of saline water. Elements accessory to sodium and chloride in seawater are insignificant where the proportion of saline water to freshwater is low. Amorphous aluminosilicate could contain a wide variety of ratios of aluminum to silicon. For these calculations, amorphous aluminosilicate is arbitrarily assigned a stoichiometry of 2 Al:2 Si.

REACTION ZONES

Comparison of pH vs. ΣCO_2 of the water samples with pH vs. ΣCO_2 calculated from PHREEQE models shows the approximate distribution of the geochemical reaction zones with respect to the wells along the flow path in the lower water-bearing zone (fig. 12). Considering the approximate nature of the models, well 1 (fig. 8) would be near the transition area from zone A to zone B, well 2 would be near the transition area from zone B to zone C, well 3 would be near the transition area from zone C to zone D, and well 4 would be in zone D. The water in the latter well would evolve farther along the flow path to the chemical characteristics represented by zone E, mixing with saline water.

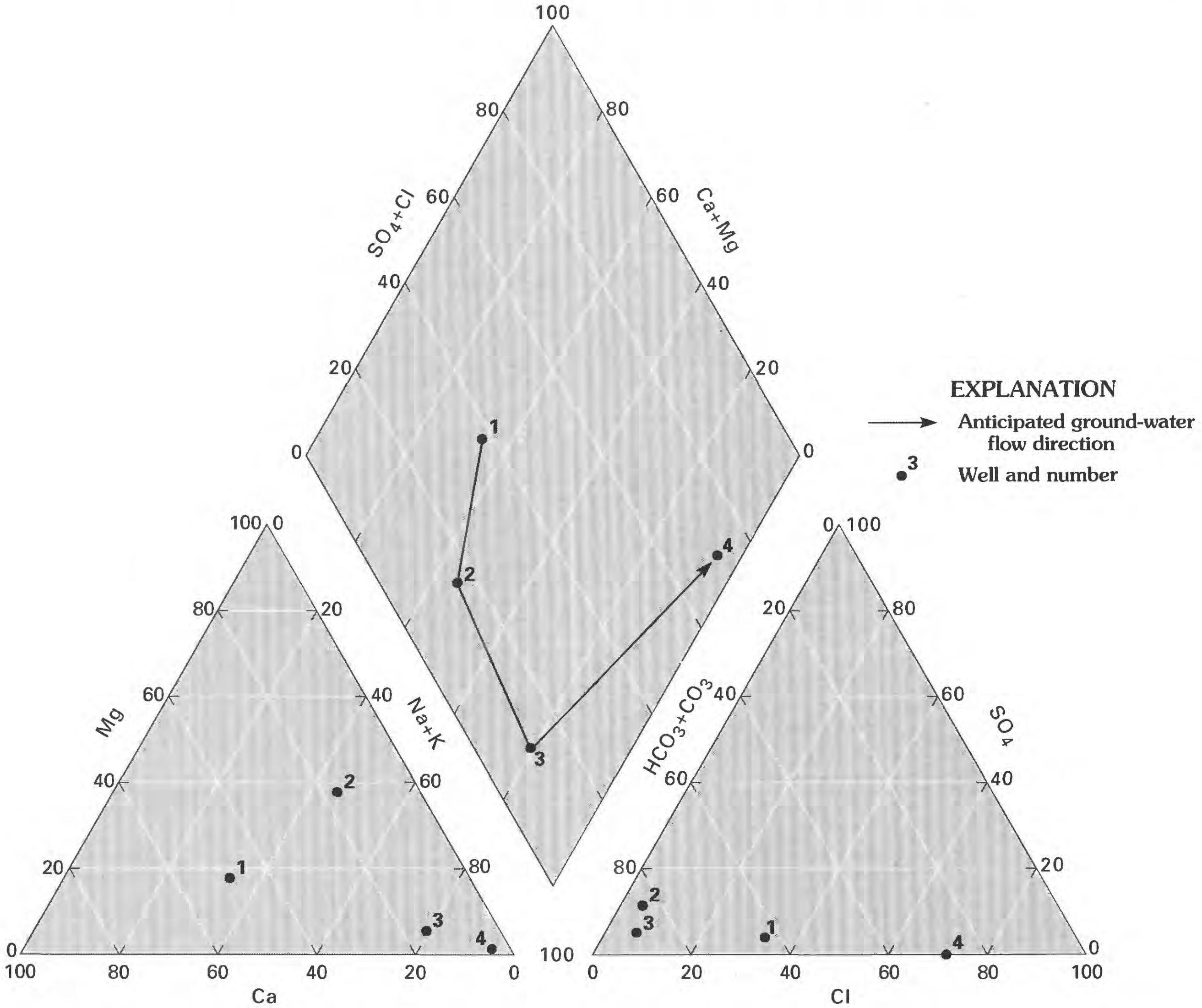


FIGURE 10.—Piper diagram showing evolution of water chemistry in the lower water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 8.

CARBON-14 AGE AND GROUND-WATER FLOW VELOCITY

Table 8 shows unadjusted and adjusted ages of ground water from measurements of carbon-14 at wells along the flow path, as well as estimated velocities of water. Adjusted ages of ground water at wells 3 and 4 (fig. 8) are approximately 7,900 and 28,100 years before present (YBP), respectively. Some recent recharge is present in water from well 1 and, to a lesser extent, in water from well 2; measurable tritium is present in both water samples (table 4). Ground-water velocities, based on measured distance between wells and the adjusted age determined from carbon-14, are estimated to be 27 ft/yr between well 2 and well 3 and 3.6 ft/yr between well 3 and well 4. Regional estimates of flow rates based on hydraulic properties of the Black Warrior River aquifer show velocities ranging from 0.01 to 30 ft/yr and a mean value of 1.9 ft/yr, with the greatest flow rates in central Alabama and eastern Mississippi (R.A. Barker, U.S. Geological Survey, written commun., 1986). Mean ground-water velocity was determined by equation 6, using the following values: mean hydraulic conductivity of 5 ft/d; mean hydraulic gradient of 0.8 ft/mi; and porosity of 0.3.

MIDDLE WATER-BEARING ZONE

The middle water-bearing zone of the Black Warrior River aquifer extends from northern Mississippi eastward to the Atlantic Coast of Georgia and South Carolina (pl. 2). The zone spans the distance between outcrop and subcrops south of the Fall Line to northern Florida and the Gulf Coast of Alabama and Mississippi.

MINERALOGY AND PETROLOGY

The middle water-bearing zone consists predominantly of unconsolidated sand, gravel, and clay, with some lignitic material. The sand and gravel lithology becomes finer and more micaceous in downdip parts of the study area. Core descriptions and mineralogic data from deep wells in South Carolina (table 9) show fine to coarse micaceous sand and clay, with feldspar clasts. Primary minerals present are quartz, potassium feldspar (microcline), albite, and kaolinite, with low to trace levels of smectite, muscovite, and illite. Calcite and pyrite were also detected at low to trace levels in the core samples.

In Mississippi, samples of cuttings from the Gordo Formation show some siderite updip in eastern Lowndes County and pyrite with no siderite in central Noxubee County (Hanor and Helton, Louisiana State University, written commun., 1986). From Lowndes County to eastern Noxubee County, feldspar hydrolysis to kaolinite was reported to be the dominant process. To the south and west, smectite authigenesis was observed and feldspars were presumed to be absent.

DISSOLVED SOLIDS

In the middle water-bearing zone, concentrations of dissolved solids increase in a downgradient direction (pl. 2). The lines representing equal concentrations appear to be farther downgradient by several miles than lines representing the same concentrations in the lower water-bearing zone of the Black Warrior River aquifer in Mississippi and Alabama. In the middle zone, the concentration gradient steepens beyond the 500 mg/L line, where mixing with sodium chloride brines apparently occurs. The steepening is most notable in Lee County, Miss., and Greene County, Ala., where elevated concentrations are near the outcrop area. This alteration of the lines of equal concentration probably is the result of pumping from the middle water-bearing zone in Lee County, Miss., and Montgomery, Ala. Minor disruptions also occur near Noxubee County, Miss., and in Russell County, Ala.; these disruptions may also be related to ground-water withdrawals.

The limited data for Georgia indicate very low concentrations of dissolved solids (less than 50 mg/L) near outcrop areas of the Black Warrior River aquifer. The concentration gradient is not as steep as the gradients in Mississippi and Alabama. Brines are known to exist in the deep, downgradient parts of the aquifer (Brown and others, 1979), but few analyses of these brines were available.

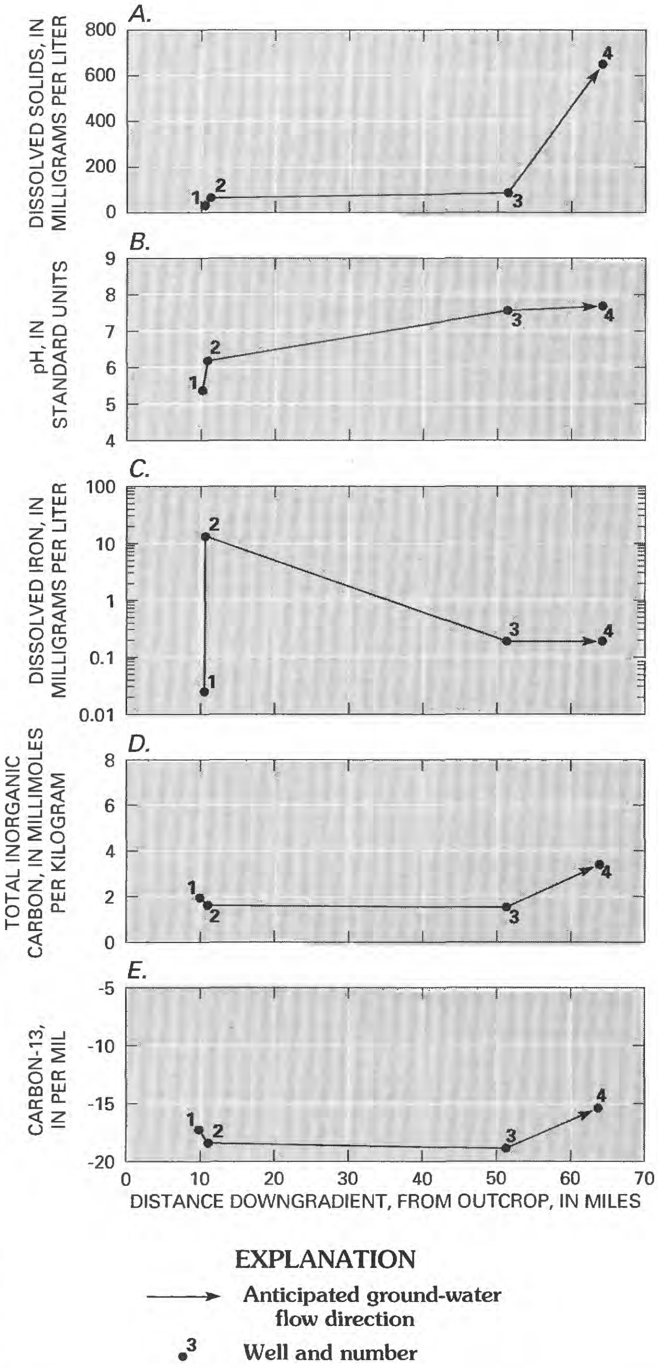


FIGURE 11.—Relation between selected chemical parameters and distance downgradient from outcrop areas for waters from the lower water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 8.

In South Carolina, concentrations of dissolved solids increase in a southeasterly direction, reaching a maximum of 6,400 mg/L at the South Carolina-North Carolina State line near the coast. Although high concentrations of dissolved solids develop in ground waters of the

TABLE 6.—*Selected saturation indices of water from the lower water-bearing zone of the Black Warrior River aquifer*

[Negative numbers indicate undersaturation, and positive numbers indicate oversaturation; dashes indicate mineral saturation index not calculated. Location of wells shown in fig. 8]

Well number/name	Albite	Calcite	Chalcedony	Dolomite	Pyrite	Goethite	Gypsum	Kaolinite	Sodium beidellite	Siderite	Quartz
1. C. Hubbert............	—	−4.65	−0.23	−9.69	—	4.31	−4.64	—	—	−4.79	0.29
2. Junkin..................	−4.31	−3.36	.17	−6.41	—	1.27	−4.09	1.99	1.41	− .45	.68
3. Black Belt.............	—	−1.13	−.15	−2.68	18.0	3.78	−8.59	—	—	−.69	.34
4. Mashulaville...........	−1.78	− .33	−.18	−1.08	18.3	4.57	—	.28	− .33	−.12	.28

TABLE 7.—*Reaction coefficients resulting from mass-balance calculations for water in flow paths between wells in the lower water-bearing zone of the Black Warrior River aquifer*

[In millimoles per kilogram of water. Positive values indicate dissolution, and negative values indicate precipitation; dashes indicate mineral not used in mass balance. Location of wells shown in fig. 8]

Well number/name	Albite	Calcite	Chalcedony	Kaolinite	Amorphous aluminosilicate	Sodium beidellite	Goethite	Siderite	Lignite	Gypsum	Pyrite	Ca−Na exchange	Halite
1. C. Hubbert													
	0.0	0.0	0.2	0.0	—	—	0.7	−0.5	0.2	—	—	0.1	—
2. Junkin													
	1.2	.0	−2.6	−.6	—	—	.0	−.2	.0	—	—	−.1	–
3. Black Belt													
	—	.8	2.0	—	1.8	−1.5	.3	—	1.2	.5	−.3	1.2	8.2
4. Mashulaville													

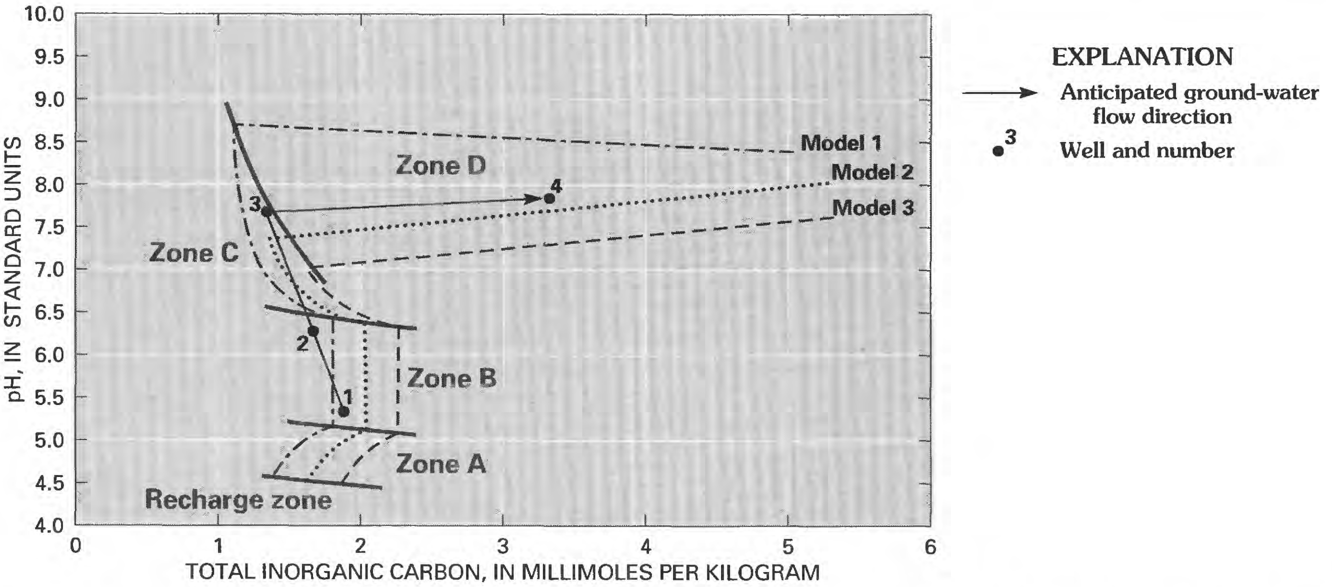


FIGURE 12.—Geochemical models of noncalcareous sand aquifers constructed using chemical data from the lower water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 8.

TABLE 8.—*Radiocarbon ages and flow velocities of ground water in the lower water-bearing zone of the Black Warrior River aquifer*

[YBP, years before present; ft/yr, feet per year. Location of wells shown in fig. 8]

Well number (Flow path)	Unadjusted age (YBP)	Adjusted age (YBP)	Adjusted flow rate (ft/yr)
2	41	41	—
(2→3)	(7,900)	(7,900)	(27.6)
3	7,900	7,900	34.5
(3→4)	(26,800)	(19,300)	(3.6)
4	34,700	28,100	10.2

coastal areas, there are no reported occurrences of sodium chloride brines in the Black Warrior River aquifer in South Carolina.

DISSOLVED CHLORIDE

The distribution of dissolved chloride in the middle water-bearing zone differs slightly from the distribution in the lower water-bearing zone (pl. 2). The concentration gradient appears to steepen in parts of Mississippi

TABLE 9.—*X-ray diffraction mineralogy of selected cores of the Black Warrior River aquifer at U.S. Geological Survey test wells at St. George, Dorchester County, and Britton's Neck, Marion County, S.C.*

[Letters indicate X-ray diffraction relative peak intensity: S, strong; M, medium; L, low; Tr, trace. Dashes indicate mineral not detected]

Depth (ft)	Quartz	Potassium feldspar	Albite	Calcite	Pyrite	Kaolinite	Smectite	Muscovite	Other minerals	Core description
St. George, Dorchester Co., S.C.										
1,717	S	S	L	Tr	—	L	L	Tr	Tr mixed-layer clay	Micaceous sand and clay with coarse feldspar grains, microcline
1,723	S	M	Tr	—	—	L	Tr	Tr	Tr mixed-layer clay	Fine sand and clay w/mica and orthoclase
1,753	S	M	Tr	L	Tr	M	Tr	Tr	Tr dolomite	Sand and clay w/large red and white clasts, rutilated quartz grains, microcline, goethite
1,781	S	L	Tr	Tr	—	L	Tr	Tr	—	Medium sand and clay with large white clasts of microcline
1,798	S	M	L	L	Tr	M	Tr	Tr	Tr illite	Sand, clay, and mica, w/dark mineral, microcline clasts with trace calcite
1,841	S	M	L	Tr	—	L	Tr	Tr	Tr illite	Micaceous sand and clay, microcline
1,861	S	L	Tr	Tr	Tr	L	Tr	Tr	Tr illite	Medium micaceous sand and clay, orthoclase
Britton's Neck, Marion Co., S.C.										
827	S	L	M	Tr	Tr	L	Tr	Tr	Illite	Coarse sand and clay, drilling mud, microcline and plagioclase
1,012	S	M	—	Tr	—	M	L	—	Tr mixed-layer clay	Coarse sand and clay, little or no accessory minerals

and Alabama where concentrations are greater than 50 mg/L, whereas concentrations near outcrop areas are less than 5 mg/L. Ground-water withdrawals at Tupelo and West Point, Miss., may cause upward leakage of saline water toward the pumping centers, resulting in increased chloride in the aquifer. Concentrations exceed 3,000 mg/L in Greene, Hale, and Lowndes Counties, Ala. Ground water in this area is relatively more saline, and the saline water locally may discharge to the Black Warrior River.

Few data are available to describe chloride distribution in the freshwater part of the Black Warrior River aquifer in Georgia. Data from WATSTORE for western Georgia show dissolved-chloride concentrations of less than 10 mg/L. Several water analyses from drill-stem tests of water-bearing zones of the Black Warrior River aquifer in southern Georgia indicate that at least two deep water-bearing zones contain sodium chloride brines (Brown and others, 1979). In this paper, lines of equal concentration of dissolved chloride for the middle water-bearing zone in Georgia were produced from data from the upper water-bearing zone of Brown and others (1979); chloride data for Brown and others' (1979) lower water-bearing zone were not used for contouring. Dissolved-chloride concentrations increase in the middle water-bearing zone of the Black Warrior River aquifer from Beaufort County, S.C., to Horry County, S.C. Concentrations also increase in the Black Warrior River aquifer from outcrop areas seaward.

DISSOLVED IRON

Water in the middle water-bearing zone may contain concentrations of dissolved iron in excess of 20,000 μg/L (pl. 3). An area of elevated concentrations extends from western Alabama to northeastern Mississippi. Concentrations are less than 100 μg/L in outcrop areas, but increase to as much as 20,000 μg/L downgradient. Farther downgradient, concentrations decrease to less than 100 μg/L before increasing again in the deeper, downgradient parts of the zone. Farther southeast, in west-central Alabama, where saline water is present in the middle water-bearing zone, concentrations of dissolved iron are as great as 5,400 μg/L.

Chemical data show concentrations of dissolved iron to be less than 200 μg/L in most of eastern Alabama and Georgia. However, in South Carolina, high concentrations (as great as 5,000 μg/L) occur in the middle water-bearing zone of the Black Warrior River aquifer, with the highest concentrations in Marion and Berkeley Counties.

HYDROCHEMICAL FACIES

The middle water-bearing zone contains water of various hydrochemical facies (pl. 3). Calcium bicarbonate facies is dominant near the areas of outcrop extending from northeastern Mississippi into central Georgia. Downgradient, sodium bicarbonate facies is present in a narrow band in Mississippi and western Alabama and in a broader band in Georgia and South Carolina. Farther downgradient, the deeper waters are dominated by sodium chloride facies, probably as a result of mixing of the fresher waters with the deeper saline waters. In northeastern Mississippi, sodium chloride facies extends eastward to include the area around Lee County, Miss. In Alabama, sodium chloride facies extends as far north as Greene County, probably owing to upward discharge of saline water. Sodium chloride facies also extends inland from the Atlantic Coast into Williamsburg County, S.C.

TRACE ELEMENTS

Water from the middle water-bearing zone generally is low in trace elements (table 10). The greatest concentrations of dissolved iron are in well 2 (fig. 13) in Mississippi (12,000 μg/L) and well 13 in South Carolina (5,500 μg/L). Concentrations of boron are as much as 8,600 μg/L in coastal South Carolina, but generally are less than 100 μg/L in other areas sampled. Strontium was present in measurable amounts in all the water samples from the middle water-bearing zone, with the greatest concentration in water from well 11 in South Carolina (350 μg/L). Mercury was detected in water from well 9 in Georgia and well 13 in South Carolina at 0.2 and 0.3 μg/L, respectively. Cadmium was measured in water from well 5 in Alabama at 20 μg/L.

DISSOLVED GASES

Dissolved gases in water from the 13 wells in the middle water-bearing zone (fig. 13) show distinctive changes from upgradient areas to downgradient areas (table 10). Dissolved oxygen is present in water from upgradient wells 1, 4, and 6 (table 10). Carbon dioxide decreases from concentrations as high as 62 mg/L upgradient to concentrations as low as 0.4 mg/L downgradient. Decreases in concentrations of dissolved oxygen and carbon dioxide in a downgradient direction are typical of chemical evolution in aquifer systems closed to the atmosphere, where oxygen reacts with reduced organic matter and aqueous carbon dioxide reacts with carbonates and silicates. In South Carolina, carbon dioxide increases downgradient from 8.5 mg/L in water from well 10 to 22 mg/L in water from well 11, and from 5.8 mg/L in water from well 12 to 24 mg/L in water from well 13. This suggests either that production of carbon dioxide from reactions between the water and aquifer minerals is fairly rapid, or that the water-bearing zone is open to recharge downgradient. However, methane was detected in waters from well 11 in South Carolina (0.3 mg/L) and well 9 in Georgia (2.3 mg/L), both from deep, downgradient parts of the water-bearing zone. This indicates methanogenic processes, probably bacterially mediated, in the deeper parts of the water-bearing zone.

ENVIRONMENTAL ISOTOPES

Analysis of environmental isotopes in water from the 13 wells penetrating the middle water-bearing zone (fig. 13) shows that tritium is present in a significant amount in water from well 1 (124 pCi/L), but is less than 10 pCi/L in water from other wells (table 10); this indicates that little or no recent waters have recharged the middle water-bearing zone. Carbon-13 ratios range from −6.8 ‰ in waters at wells 10 and 11 to −22.5 ‰ in water from well 6. Carbon-13 isotope ratios appear to be generally more negative in the western part of the middle water-bearing zone than in the eastern part, although a ratio of −19.3 ‰ was measured in water from well 12. The ratios become more positive downgradient from the recharge areas, suggesting more positive carbon-13 ratios in inorganic carbon from sources present in the aquifer. Deuterium and oxygen-18 ratios range from −20 to −32.5 ‰ and from −3.4 to −5.4 ‰, respectively. The flow paths from well 1 to well 3 and from well 6 to well 9 show more negative ratios of deuterium and oxygen-18 in a downgradient direction (fig. 14), indicating that waters present in the deeper, downgradient areas may have entered the aquifer when the climate was colder.

CHEMICAL EVOLUTION

Trends in ground-water chemistry (table 11) are observed for waters sampled along the flow paths in the middle water-bearing zone (fig. 13). Hydrochemical facies range from no dominant facies to calcium bicarbonate facies near recharge areas, but are generally sodium bicarbonate facies in downgradient areas (fig. 15). Farther downgradient, the water increases in chloride content and the dominant facies is sodium-bicarbonate-chloride or sodium-chloride-bicarbonate. Concentrations of dissolved solids generally increase downgradient, ranging from 22 to 2,390 mg/L (fig. 16*A*). A slight decrease in concentrations of dissolved solids in ground water was measured from well 7 to well 8 (157 to 130 mg/L). Field pH measurements range from 4.90 to 9.25. Overall, pH increases downgradient from recharge areas (fig. 16*B*), although slight decreases occur between wells 8 and 9 and between wells 10 and 11. Concentrations of dissolved iron show significant changes in water along the flow paths from well 1 to well 3 and from well 12 to well 13 (fig. 16*C*). Dissolved iron increases from 11 μg/L at well 1 to 12,000 μg/L at well 2 before decreasing to 69 μg/L at well 3, indicating precipitation of an iron-bearing mineral. Dissolved iron increases from 280 μg/L in well 12 to 5,500 μg/L in well 13, correlating with the increase in salinity. Total inorganic carbon (ΣCO_2) increases along

TABLE 10.—*Trace elements, dissolved gases, and environmental isotopes in water from the middle water-bearing zone of the Black Warrior River aquifer*

[In micrograms per liter, unless otherwise specified. pCi/L, picocuries per liter; ‰, per mil; PM, percent modern carbon; mol/kg, moles per kilogram; tr, trace. Dashes indicate no data; negative values for isotopes indicate relatively light content. Location of wells shown in fig. 13]

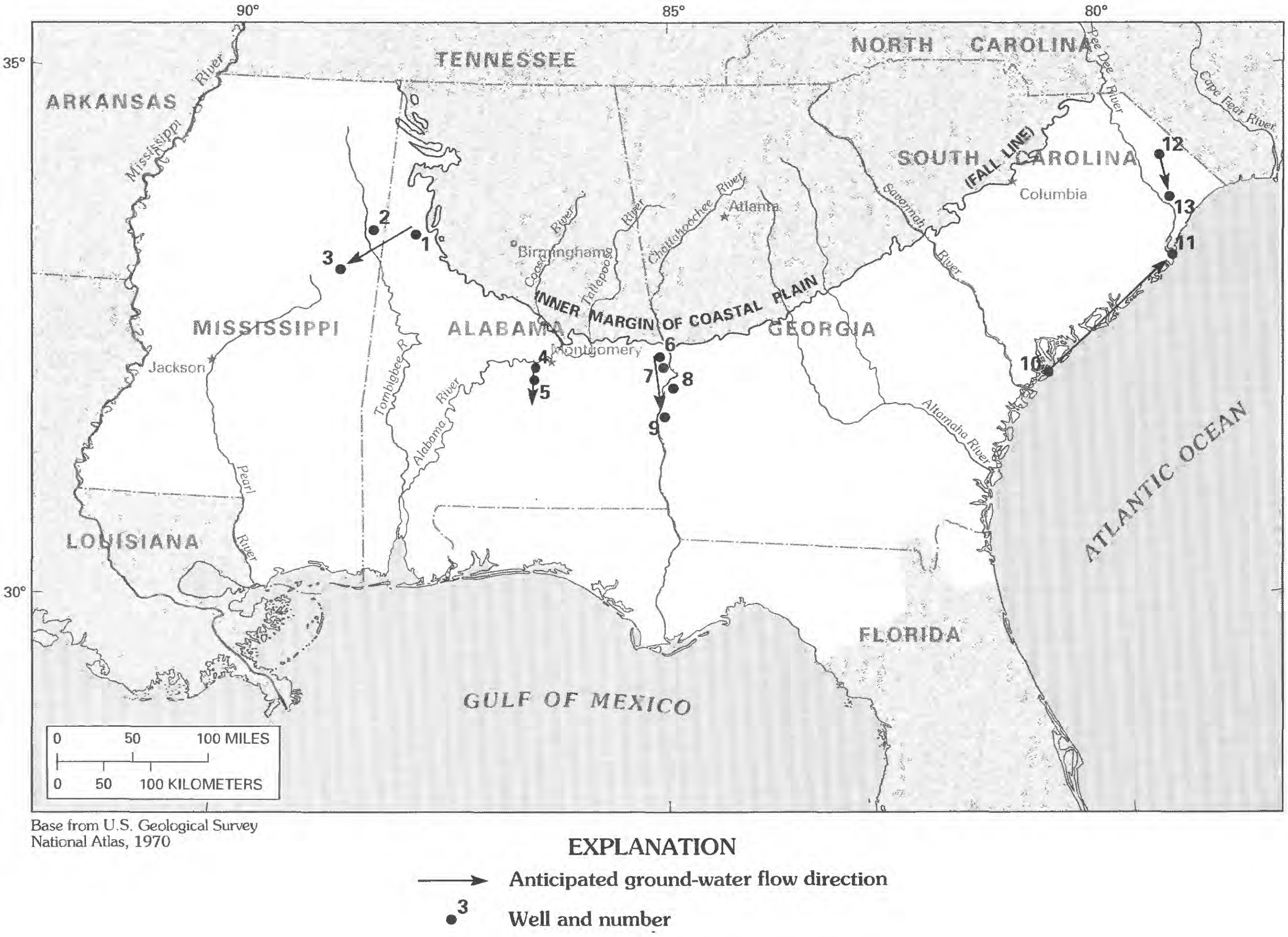
Well number/name	Al	Ba	B	Cd	Cu	Fe	Pb	Li	Mn	Hg	Sr	Zn	N_2[1]	O_2[1]	CO_2[1]	CH_4[1]	Ar[1]	T (pCi/L)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{18}O$ (‰)	^{14}C (PM)	ΣCO_2 (mol/kg×10^{-3})
1. Skelton	0	40	0	3	96	11	27	<4	10	<0.1	13	20	19	10	42	0	0.77	124	−19.2	−27	−4.8	—	2.08
2. Columbus AFB2	0	110	0	5	<10	12,000	20	9	160	<.1	250	<4	23	0.06	35	0.09	.91	3	−18.3	−28	−5	13.3	2.37
3. Brooksville	40	10	40	3	<10	69	15	6	5	<.1	60	<4	24	.29	1.3	.02	.92	2	−17.5	−32.5	−5.4	6.8	2.16
4. Burkville A2	10	9	—	3	<10	36	13	<4	7	—	38	<4	14	4.3	11	0	.65	4	−16.7	−26.5	−4.5	24.5	0.99
5. Hayneville	<10	10	5	20	<10	13	<10	<4	5	<.1	47	<4	24	.8	0.5	.01	.95	<1	−15.6	−26	−4.4	<0.7	2.06
6. Smith	<10	23	<10	<1	<10	11	<10	<4	3	<.1	89	67	22	1.1	62	0	.85	2	−22.5	−22.5	−4.1	60	2.12
7. Ladonia-Crawford	<10	56	10	2	<10	130	<10	<4	40	<.1	290	5	25	<.02	18	0	1	9	−19.3	−25.5	−4.7	9.8	1.50
8. Omaha-1	30	4	80	<1	<10	<3	10	<4	<1	<.1	33	6	24	.12	.4	0	.97	<1	−16.2	−25	−4.8	<.7	1.52
9. Georgetown-1	20	5	360	<1	<10	14	<10	5	4	.2	38	<4	24	.09	.6	2.3	.96	2	−10.4	−25	−5	.7	4.77
10. Hilton Head	30	2	3,800	5	10	51	10	25	3	<.1	160	4	22	.06	8.5	.02	.8	1	−6.8	−28	−4.6	2.3	17.66
11. Estherville	20	220	8,600	5	<10	150	<10	39	1	<.1	350	5	21	.03	22	.3	.83	1	−6.8	−25.5	−4.3	<.55	20.67
12. Marion-1	<100	10	60	1	<10	280	<10	5	16	<.1	43	<4	25	.02	5.8	0	.96	2	−19.3	−20	−3.4	26.7	1.93
13. Britton's Neck-2	10	60	8,000	<1	<10	5,500	<10	21	91	.3	320	110	25	.04	24	tr	.92	2	−12.9	−24.5	−4.05	6	6.26

[1] Milligrams per liter; errors in laboratory data require interpretation with caution.

TABLE 11.—*Well data and chemical analyses of water from the middle water-bearing zone of the Black Warrior River aquifer*

[In milligrams per liter, unless otherwise specified. ft, feet; mi, miles; µs, microsiemens; ROE, residue on evaporation at 180 °C; TD, total depth. Location of wells shown in fig. 13]

Well number/name	Screened interval (ft)	Distance downgradient (mi)	Specific conductance (µS)	Temperature (°C)	pH (units)	Dissolved solids (ROE)	NH_4	Ca	Mg	Na	K	HCO_3	CO_3	Cl	SO_4	F	SiO_2
1. Skelton	98 (TD)	5.5	40	17.8	4.90	22	0.24	0.8	1.0	2.5	0.75	2	0	4.3	0	0	9.2
2. Columbus AFB	400–443	21.1	122	18.8	6.35	58	.04	6.5	2.2	3.9	5.1	71	0	1.8	0.73	0.21	11
3. Brooksville	942 (TD)	41.6	300	25.0	8.30	160	.02	1.2	0.35	57	1.4	130	0	21.2	.72	.16	12
4. Burkville A2	650–742	21.7	88	23.0	6.81	69	.01	2.2	.2	16	1.8	45	0	2.1	2.8	.1	19
5. Hayneville	1,020–1,024	36.0	310	26.9	8.89	186	.21	1.5	0	57	.6	125	4.2	18.9	5.7	.1	14
6. Smith	118–138	6.2	100	19.9	6.02	138	.04	6.6	1.1	6.4	4.9	40.2	0	3.4	4.8	<.01	58
7. Ladonia-Crawford	276–377	12.4	172	19.9	6.83	157	.12	19	.61	11.0	5.1	68.7	0	3	24.4	<.01	53
8. Omaha-1	817–968	17.4	220	24.7	9.25	130	.09	1.9	.06	40	.54	87.8	8.8	7.63	6.9	<.01	15
9. Georgetown-1	1,335–1,365	36.0	510	27.9	9.06	281	.33	1.8	.15	120	.94	276	19.8	8.13	.25	.52	15
10. Hilton Head	2,723–3,035	141.5	1,900	43.5	8.20	1,310	.91	2.6	2.1	520	4.2	1,095	0	230	.77	5.2	20
11. Estherville	1,270–1,296	253.2	3,650	20.1	7.91	2,390	1.1	6	2.7	830	9.9	1,240	0	766	.2	4.2	13
12. Marion-1	351–571	77.6	175	19.3	7.00	133	.08	2.5	.71	33	4.7	92	0	3.59	.2	.34	45
13. Britton's Neck-2	1,011–1,030	99.2	2,880	23.0	7.52	1,700	.42	9.9	2.6	480	6.6	886	0	373	124	.6	32



Base from U.S. Geological Survey National Atlas, 1970

FIGURE 13.—Location of wells sampled for the middle water-bearing zone of the Black Warrior River aquifer.

flow paths (fig. 16*D*), although slight decreases occur between well 2 and well 3 and between wells 6 and 7. Concentrations of total inorganic carbon range from 0.99 mmol/kg in well 4 to 20.67 mmol/kg in well 11. Carbon-13 ratios range from −22.5 to −6.8 ‰ and generally are heavier in water in downgradient areas (fig. 16*E*); exceptions are wells 10 and 11, where no change was measured.

MINERAL EQUILIBRIUM

Saturation states for 11 mineral phases in water in the middle water-bearing zone are shown in table 12. Calcite saturation is attained in ground water along the flow paths from well 8 to well 9 and from well 10 to well 11 (fig. 13). Dolomite is undersaturated in water in most places. Siderite approaches saturation in waters from wells 2 and 3, and is oversaturated in waters from wells 10, 11, and 13. Pyrite, where considered, is oversaturated. Chalcedony is near saturation in waters from all wells, with slight oversaturation in wells 6, 7, 12, and 13, whereas quartz is oversaturated in water from all wells. The clay minerals kaolinite and sodium beidellite and the feldspar albite vary in saturation states, showing no general consistency, probably because of unreliable analytical results for aluminum concentrations among the chemical data.

MASS BALANCE

Mass-balance reaction coefficients for ground waters along various flow paths in the middle water-bearing zone are shown in table 13. The flow path from well 1 to well 3 (fig. 13) shows similar reaction models, with calcite dissolving and kaolinite and chalcedony precipitating at the expense of albite. Although calcium-for-sodium cation exchange is reversed from well 1 to well 2, aqueous calcium is exchanged for sodium in the sediments from well 2 to well 3, as shown by the reaction in table 2. Siderite apparently precipitates between well 2 and well

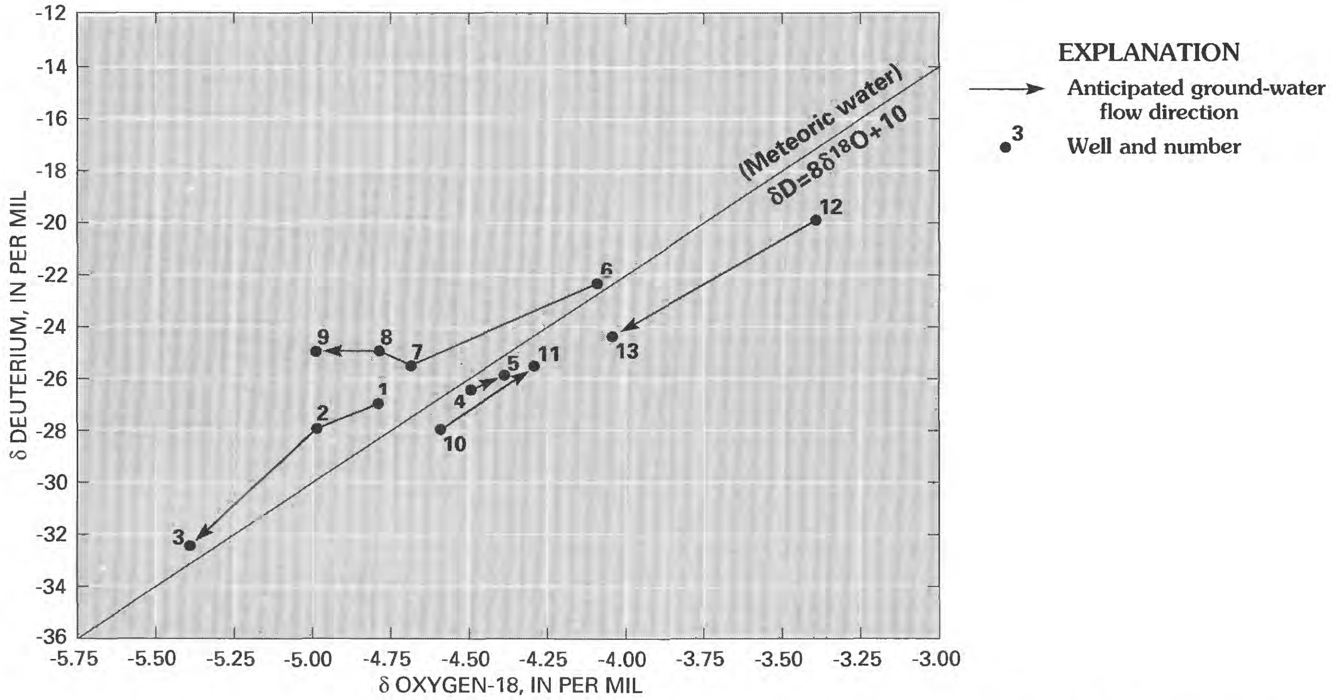


FIGURE 14.—Relation between deuterium (δD) and oxygen-18 ($\delta^{18}O$) in water from the middle water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 13.

3. Water along the flow path from well 4 to well 5 also appears to dissolve calcite, forming sodium beidellite at the expense of chalcedony and amorphous aluminosilicate. More lignite is oxidized to CO_2 from well 4 to well 5, with significant amounts of pyrite precipitating. Either trace amounts of halite dissolve or saline water from fluid inclusions is taken up by ground water, producing the levels of dissolved chloride measured. Cation exchange appears to proceed along a flow path from well 4 to well 5, with a trace of magnesium-for-sodium cation exchange taking place.

The data indicate that the chemical reaction model is different from well 6 to well 7 than from well 7 to well 9 (table 13). From well 6 to well 7, the chemical changes are small, which may magnify analytical errors in the mass-balance results. Calcite is dissolved and lignite is oxidized, with traces of chalcedonyand kaolinite formed authigenically at the expense of albite. Although a slightly undersaturated state for siderite was measured, the chemical reaction model requires precipitation of siderite, suggesting either poor analytical data or insufficient solid phase information for selection of an appropriate reaction model. A small amount of calcium-for-sodium exchange was also calculated. This reaction model is similar to the model used to describe data of water chemistry along the flow path from well 1 to well 3, although with much smaller reaction coefficients. The reaction models for water along the flow path from well 7 to well 9 are similar to those used for water along the flow path from well 4 to well 5. Calcite is dissolved from well 7 to well 9 as lignite is oxidized to CO_2 and calcium-for-sodium cation exchange proceeds. Siderite is precipitated in the reaction model between well 7 and well 8, but pyrite is precipitated between well 8 and well 9. Along the flow path from well 7 to well 9, the reaction models show sodium beidellite forming authigenically at the expense of chalcedony and amorphous aluminosilicate. Some gypsum is dissolved from well 8 to well 9. The reaction coefficients modeled for water from well 8 to well 9 are more than twice the reaction coefficients modeled for water from well 7 to well 8.

The reactions modeled for water from well 10 to well 11 and from well 12 to well 13 are also similar to models of water from well 4 to well 5 and from well 7 to well 9, although models for well 10 to well 11 and well 12 to well 13 have larger coefficients, especially for the silicate phases. The reaction model from well 12 to well 13 requires further mixing with 1.81 percent seawater to account for the increase in salinity. Owing to the unusually large amounts of mass transfer in the reaction model, the model results along this flow path (from well 12 to well 13) should be interpreted with caution. A relatively small amount of magnesium-for-sodium cation exchange also may occur.

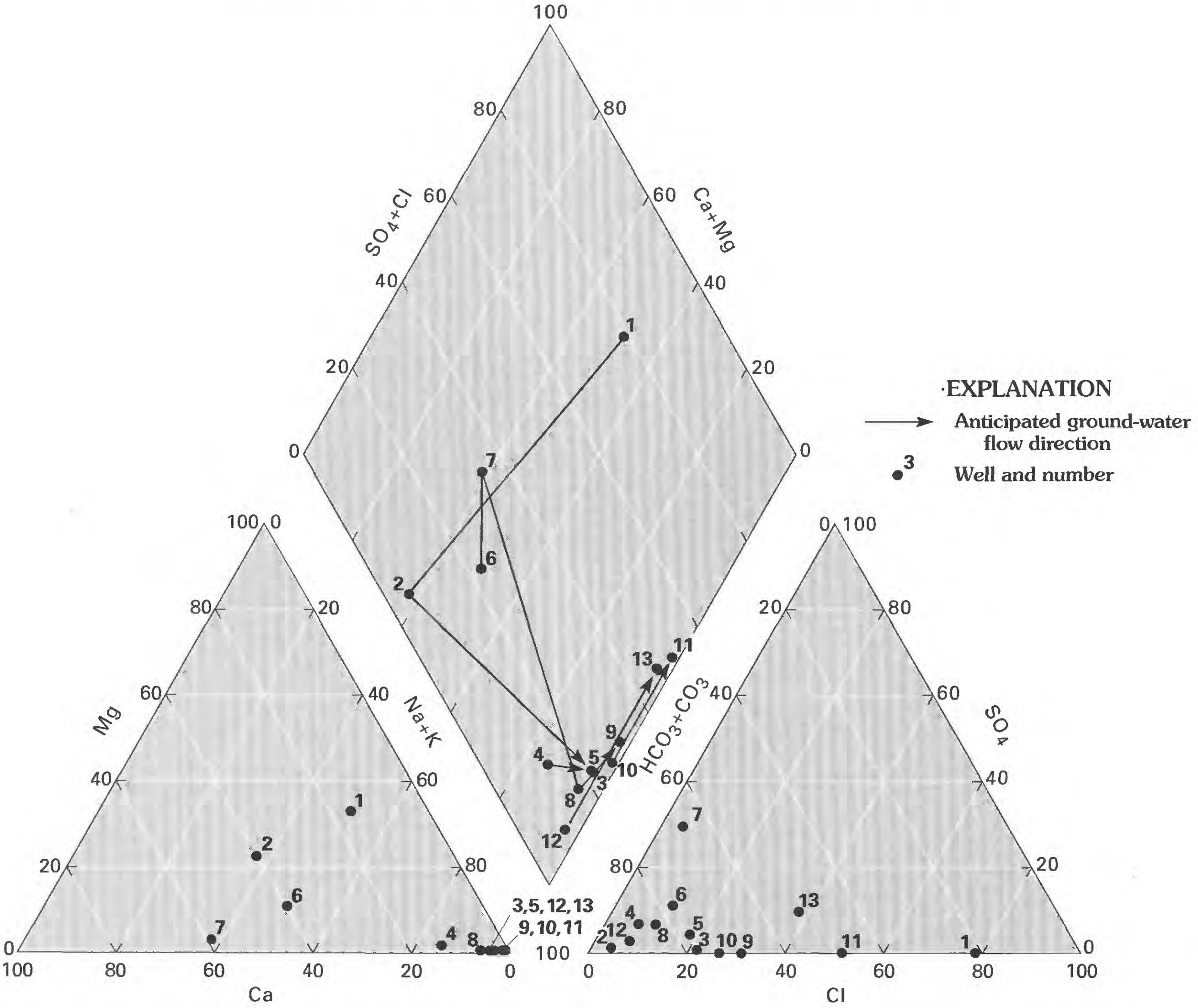


FIGURE 15.—Piper diagram showing evolution of water chemistry in the middle water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 13.

REACTION ZONES

Comparison of chemical data with PHREEQE simulations I and II (appendix) indicates that most of the wells sampled in the middle water-bearing zone are in chemical reaction zones A through C (figs. 17*A*, 17*B*); that is, the predominant processes are oxidation-reduction and feldspar hydrolysis. Data for water from well 10 to well 11 (fig. 13) indicate that chemical evolution has reached its maximum level at well 11, with elevated values of ΣCO_2. Data for water from well 12 to well 13 indicate that well 12 is in zone D, but reaction progress and mixing with saline water causes well 13 to deviate from the models (fig. 17*A*). Data for water from well 8 to well 9 indicate that the water chemistry is transitional from zone C to zone D (fig. 17*B*).

CARBON-14 AGE AND GROUND-WATER FLOW VELOCITY

Table 14 shows that the adjusted age of ground water in the middle water-bearing zone exceeds radiocarbon dating capability in deep, downgradient wells such as well 11 (fig. 13), at greater than 41,600 YBP. Incremental flow velocities along different flow paths range from 1.6 to 22.6 ft/yr. Mean values of hydraulic conductivity of 5 ft/d, hydraulic gradient of 0.8 ft/mi, and an assumed porosity of 0.3, used for the Black Warrior River aquifer, resulted in a mean ground-water velocity of 1.0 ft/yr (R.A. Barker, U.S. Geological Survey, written commun., 1986). Generally, greater flow velocities are observed in the western part than in the eastern part of the study area. Carbon-14 data are questionable for calculating the ground-water flow velocity from well 10

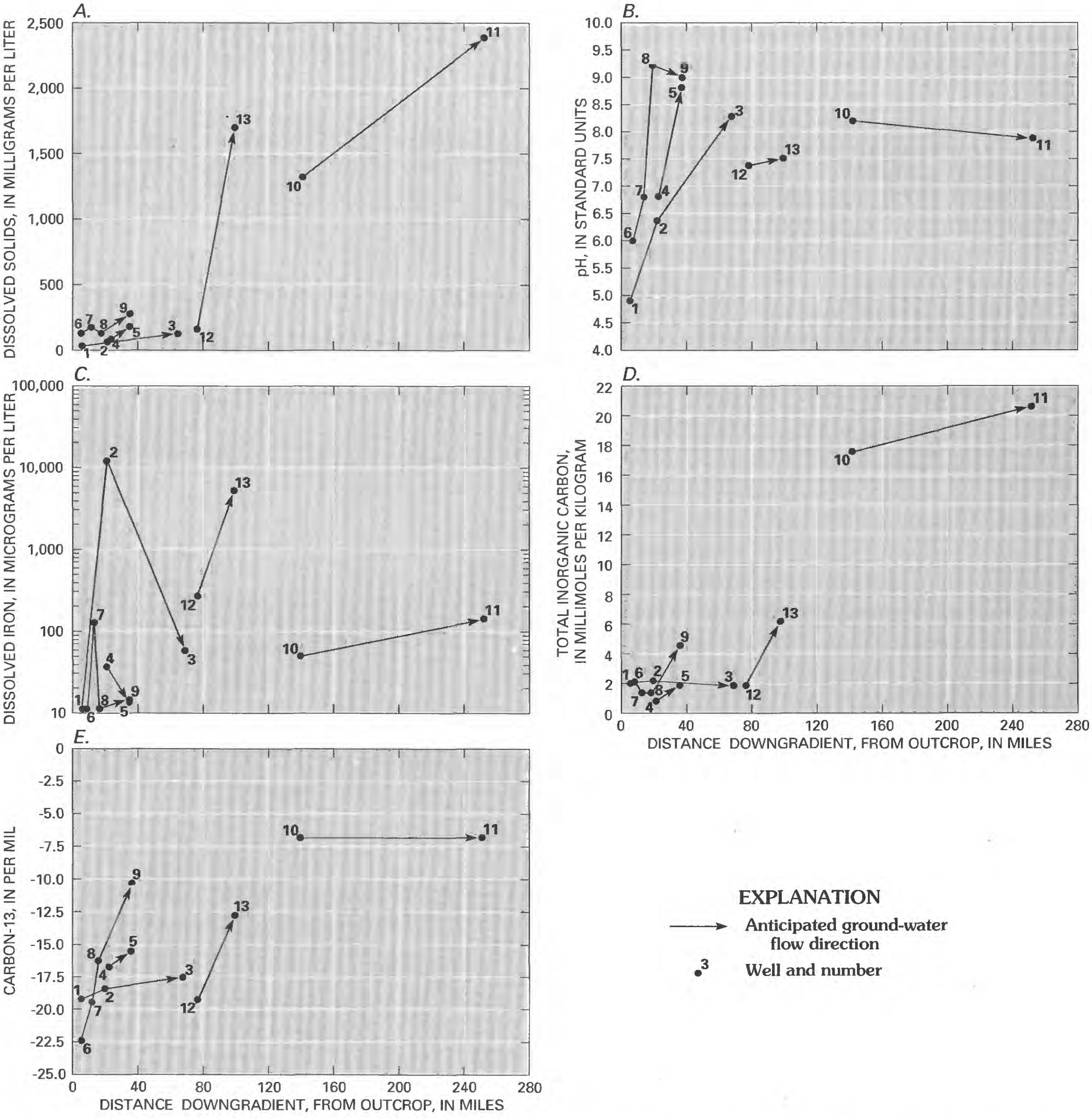


FIGURE 16.—Relation between selected chemical parameters and distance downgradient from outcrop areas for waters from the middle water-bearing zone of the Black Warrior River aquifer.

to well 11 and from well 12 to well 13, owing to possible mixing with younger waters in the wells or sampling error.

UPPER WATER-BEARING ZONE

The upper water-bearing zone of the Black Warrior River aquifer extends eastward from central Mississippi

TABLE 12.—*Selected saturation indices of water from the middle water-bearing zone of the Black Warrior River aquifer*

[Negative numbers indicate undersaturation, and positive numbers indicate oversaturation; dashes indicate mineral saturation index not calculated. Locations of wells shown in fig. 13]

Well number/name	Albite	Calcite	Chalcedony	Dolomite	Pyrite	Goethite	Gypsum	Kaolinite	Sodium beidellite	Siderite	Quartz
1. Skelton	—	−5.99	−0.21	−11.69	—	6.02	—	—	—	−5.98	0.30
2. Columbus AFB	—	−2.43	−.14	−5.12	15.9	1.39	−4.24	—	—	−.28	.37
3. Brooksville	−1.63	−.9	−.19	−2.06	18.9	5.29	−5.02	1.15	0.63	−.26	.30
4. Burkville A2	—	−2.5	.05	−5.9	11.6	.52	−4.1	—	—	−2.4	.54
5. Hayneville	—	−.24	−.18	—	17.0	5.5	−4.1	—	—	−1.3	.30
6. Smith	—	−3.0	.57	−6.5	9.9	−2.6	−3.4	—	—	−3.8	1.1
7. Ladonia-Crawford	—	−1.5	.53	−4.3	14.6	.91	−2.3	—	—	−1.8	1.03
8. Omaha-1	−1.8	.04	−.16	−1.15	—	—	−3.9	−.88	−1.5	—	.32
9. Georgetown-1	−1.6	.26	−.18	−.24	16.5	5.5	−5.5	−1.2	−1.8	−1.4	.29
10. Hilton Head	−1.33	.21	−.17	.69	16.4	5.7	—	.61	−1.5	.56	.24
11. Estherville	−.53	.03	−.08	−.07	—	4.01	—	1.70	1.01	.35	.42
12. Marion-1	.30	−1.89	.41	−4.4	—	2.4	—	4.7	4.9	−1.3	.92
13. Britton's Neck-2	−.9	−.2	.28	−.73	15.9	4.6	—	2.3	2.1	1.5	.77

along outcrop areas west and south of the Fall Line to the Chattahoochee River (pl. 2). The zone extends southward to coastal Mississippi and Alabama.

MINERALOGY AND PETROLOGY

The upper water-bearing zone consists of sediments that vary from massive, calcareous, glauconitic sand to thin, irregular beds of clay and fine- to medium-grained glauconitic sand. Quartz and glauconite are present updip along with sodium and potassium feldspar grains, and kaolinite clay. Downdip, the sand grades to finer grained sediments consisting of quartz, glauconite, and smectite clay minerals. Some siderite cements are present near outcrop areas, whereas pyrite is widely present in the deeper, downgradient parts of the zone. Organic matter and lignite are present throughout the zone. In eastern Mississippi, Hanor and Helton (Louisiana State University, written commun., 1986) report mineralogic evidence of siderite cements downdip from outcrop areas in the lower part of the Eutaw and McShan Formations. Some siderite is present in sediments underlying eastern Noxubee County, Miss., but is generally not present to the west and south in the county. Feldspar and kaolinite are the dominant aluminosilicates updip in eastern Lowndes County, Miss., but to the west and south, including all of Noxubee County, Miss., smectite is the dominant aluminosilicate. Feldspars are reported absent in the Eutaw and McShan Formations throughout most of Noxubee County.

DISSOLVED SOLIDS

The upper water-bearing zone contains water with less than 50 mg/L dissolved-solids concentrations in outcrop areas, but concentrations increase to greater than 5,000 mg/L in deeper, downgradient parts (pl. 2). The concentration gradient appears to steepen beyond the 500 mg/L line of equal concentrations in northern and northeastern Mississippi and western Alabama. The location of the 500 mg/L line for the upper water-bearing zone is slightly west of the 500 mg/L lines for the lower and middle water-bearing zones. Some alteration of the concentration gradient is observed near Tupelo, Miss., and near Montgomery, Ala., probably owing to large groundwater withdrawals from the upper water-bearing zone at these locations. Alteration of the concentration gradient in Noxubee County, Miss., may indicate a local condition of hydraulic separation of the Eutaw and McShan Formations which make up the upper water-bearing zone, resulting in local vertical differences in water chemistry. A large area in Greene and Sumter Counties, Ala., contains water with concentrations of dissolved solids greater than 2,000 mg/L near the outcrop area. This suggests upward leakage of saline water and subsequent discharge to the Black Warrior River.

DISSOLVED CHLORIDE

Concentrations of dissolved chloride in waters in the upper water-bearing zone (pl. 2) are less than 50 mg/L in most outcrop-recharge areas, and many wells produce water with concentrations less than 10 mg/L. Significant increases in concentrations occur in the deeper, downgradient parts of the zone. Gradients increase sharply in Greene, Marengo, Dallas, and Lowndes Counties, Ala., but decrease toward northeastern Mississippi. Lines of equal concentration are altered near Tupelo and West Point, Miss., and west of Montgomery, Ala., owing to pumping from the upper water-bearing zone. In Greene and Sumter Counties, Ala., elevated concentrations occur near the upgradient recharge areas. Upward leakage of water containing elevated concentrations of dissolved chloride through the lower and middle water-

TABLE 13.—*Reaction coefficients resulting from mass-balance calculations for water in flow paths between wells in the middle water-bearing zone of the Black Warrior River aquifer*

[In millimoles per kilogram of water, except as noted. Positive values indicate dissolution, and negative values indicate precipitation; dashes indicate mineral not used in mass balance. Location of wells shown in fig. 13]

Well number/name	Albite	Calcite	Chalcedony	Kaolinite	Amorphous aluminosilicate	Sodium beidellite	Goethite	Siderite	Lignite	Gypsum	Pyrite	Ca-Na exchange	Halite	Mg-Na exchange	Seawater (percent)
1. Skelton															
	0.3	0.1	−0.54	−0.2	—	—	0.1	0.2	0.0	—	—	−0.1	—	—	—
2. Columbus AFB															
	1.1	.2	−2.2	−.5	—	—	.2	−.4	.0	—	—	.4	—	—	—
3. Brooksville															
4. Burkville A2															
	—	.36	1.9	—	1.02	−0.87	.19	—	.71	0.41	−0.19	.79	0.47	0.01	—
5. Hayneville															
6. Smith															
	.002	.19	−.08	−.001	—	—	1.01	−1.01	.20	.20	—	.08	—	—	—
7. Ladonia-Crawford															
	—	.45	2.09	—	2.37	−2.03	1.16	−1.03	.60	—	−.09	.88	.13	.02	—
8. Omaha-1															
	—	2.11	7.57	—	7.57	−5.65	.30	—	1.14	.54	−.30	2.67	.01	—	—
9. Georgetown-1															
10. Hilton Head															
	—	1.85	24.09	—	21.04	−18.06	.42	—	1.58	.05	−.42	2.09	—	—	—
11. Estherville															
12. Marion-2															
	—	5.94	53.39	—	46.52	−39.93	2.13	—	7.66	4.81	−2.04	10.72	—	.90	1.81
13. Britton's Neck-2															

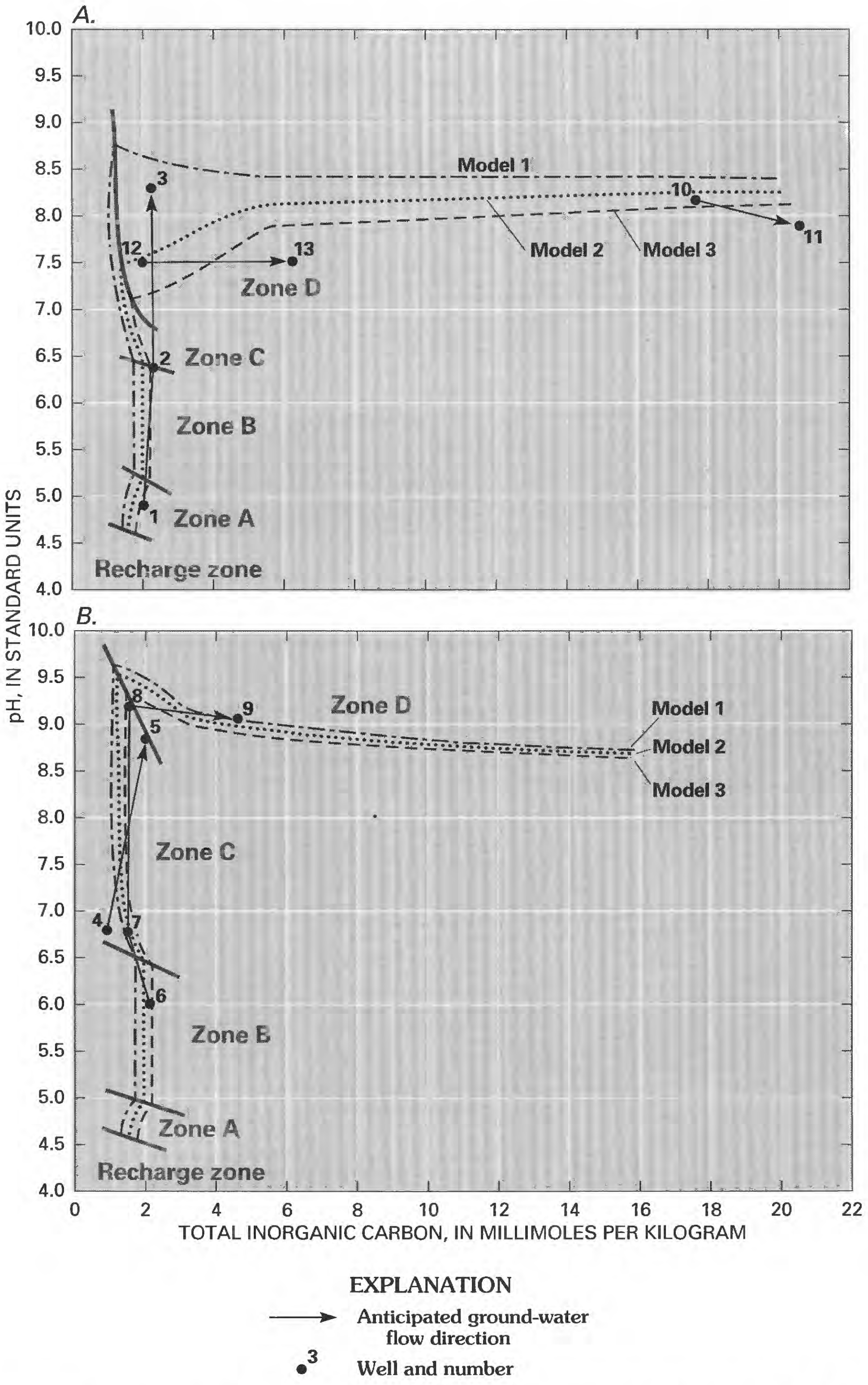


FIGURE 17.—Geochemical models of noncalcareous sand aquifers constructed using chemical data from the middle water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 13.

bearing zones of the Black Warrior River aquifer could be the cause. In northern Lowndes County, Ala., the increased concentrations likely are due to residual saline waters in the upper water-bearing zone, because the deeper, middle, and lower water-bearing zones locally produce waters containing lower concentrations of dissolved chloride.

DISSOLVED IRON

In the upper water-bearing zone, water containing elevated concentrations of dissolved iron occurs in a narrow band extending from Pickens and Lamar Counties, Ala., northwest into northeastern Mississippi (pl. 3). Low concentrations (less than 250 µg/L) occur in water from wells east of Pickens County, Ala. The areal extent of ground water containing high dissolved-iron concentrations shown on plate 3 may be inaccurate because of poor data distribution. Most of the data were obtained from wells in eastern Mississippi. In recharge areas, concentrations generally are less than 100 µg/L. Concentrations increase to greater than 20,000 µg/L downgradient, followed by systematic decreases to concentrations less than 200 µg/L in the deeper, downgradient parts of the zone.

HYDROCHEMICAL FACIES

Three distinct hydrochemical facies of water in the upper water-bearing zone occur in bands nearly parallel to the Fall Line (pl. 3). Calcium bicarbonate is the dominant facies in recharge areas; downgradient, sodium bicarbonate becomes dominant, and farther downgradient, sodium chloride becomes dominant. Sodium chloride facies appears to have displaced sodium bicarbonate facies upgradient in a few areas, for unknown local reasons. Ground-water withdrawals at well fields in Tupelo, Miss., and Montgomery, Ala., may have caused sodium chloride waters to move upward from underlying water-bearing zones. Similarly, in Greene County, Ala., ground water from the upper water-bearing zone discharges to the Sipsey and Black Warrior Rivers. This discharge may have lowered the potentiometric head in that area and caused sodium chloride dominated waters in underlying water-bearing zones to leak upward into the upper water-bearing zone.

TRACE ELEMENTS

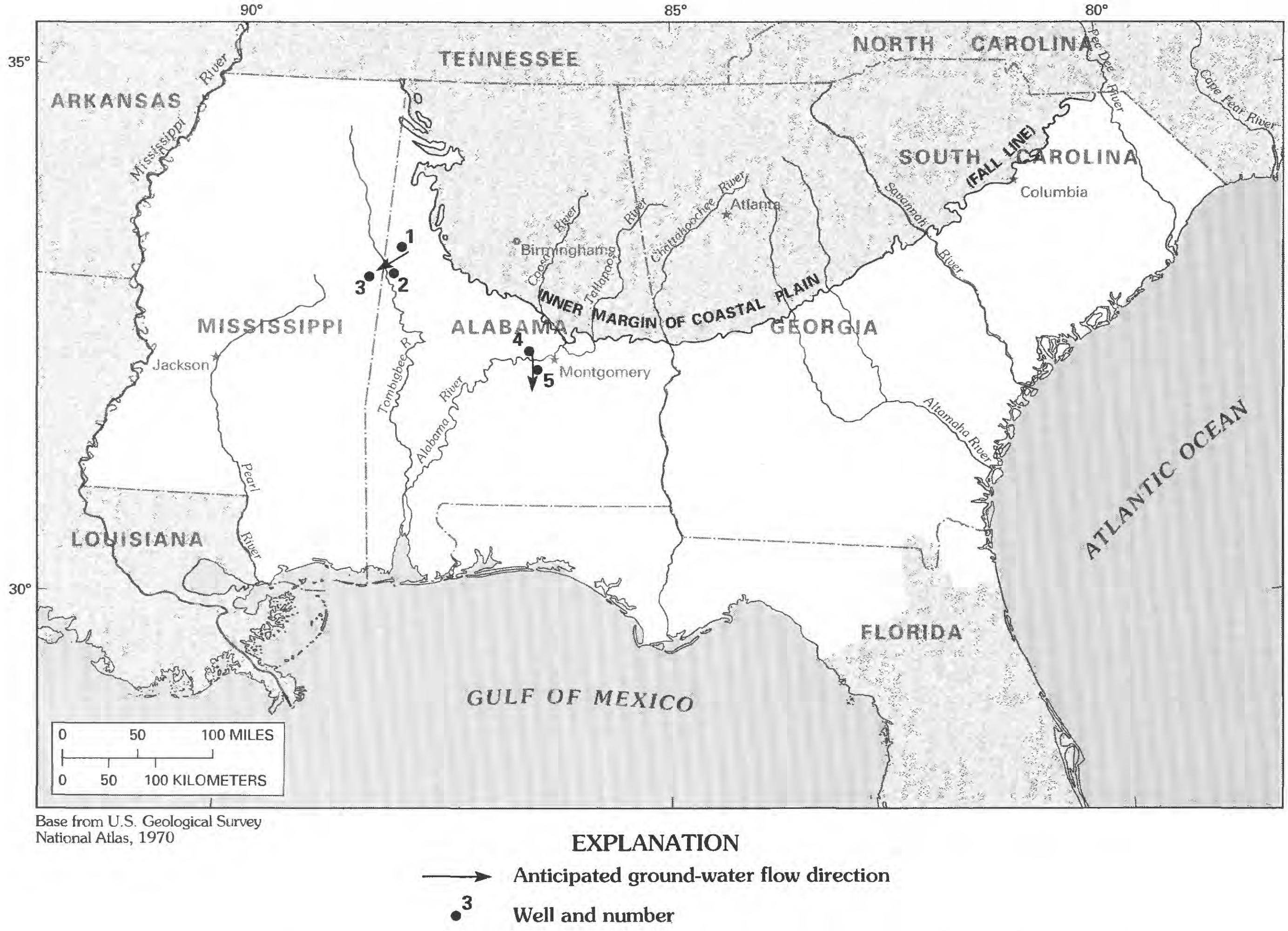
In the upper water-bearing zone, trace elements (table 15) are variable in waters from sampled wells (fig. 18). Concentrations of dissolved iron and manganese in water from well 1 are 5,900 and 430 µg/L, respectively, but diminish downgradient at well 3 to 22 and 3 µg/L, respectively. Strontium is present in significant concentrations, with a maximum of 1,100 µg/L in water from well 5. Boron concentrations are 500 and 490 µg/L in well 3 and well 5, respectively. Measurable amounts of lead are present in water from wells 1, 2, and 3, with a maximum of 22 µg/L in water from well 2. Concentrations of other trace elements in water samples from other wells in the upper water-bearing zone are low or below detection limits.

TABLE 14.—*Radiocarbon ages and flow velocities of ground water in the middle water-bearing zone of the Black Warrior River aquifer*
[YBP, years before present; ft/yr, feet per year. Dashes indicate no data. Location of wells shown in fig. 13]

Well number (Flow path)	Unadjusted age (YBP)	Adjusted age (YBP)	Adjusted flow rate (ft/yr)
2	16,700	15,600	5.2
(2→3)	(5,500)	(4,900)	(22.0)
3	22,200	20,500	9.2
4	11,600	11,600	9.8
(4→5)	(>29,500)	(>23,300)	(3.3)
5	>41,000	>34,900	5.6
6	4,200	4,200	7.9
(6→7)	(15,000)	(13,900)	(2.3)
7	19,200	18,100	3.6
(7→8)	(>21,800)	(17,500)	(1.6)
8	>41,000	>36,700	<2.6
(8→9)	—	—	—
9	>41,000	[projected >95,000]	<2.6
10	31,200	31,200	56.8
(10→11)	(>12,800)	(>10,400)	(<56.8)
11	>44,000	>41,600	<56.8
12	10,900	10,900	37.7
(12→13)	(12,400)	—	—
13	23,300	—	22.6

DISSOLVED GASES

Dissolved gases in water from the five wells in the upper water-bearing zone (fig. 18) show distinct trends from upgradient wells to downgradient wells (table 15). Dissolved carbon dioxide is high in water from both upgradient wells (46 mg/L in well 1 and 31 mg/L in well 4), decreasing downgradient (2.2 mg/L in well 3 and 11 mg/L in well 5) as the pH of the waters increases. Dissolved oxygen is present in trace quantities in wells 1, 2, and 3 but is present in well 4 at a concentration of 5.3 mg/L. Dissolved oxygen of 4.3 mg/L in water from a recently drilled well (well 5) indicates that the sample was contaminated and should not be considered representative of ground water at this location. Methane was detected in water from well 3 at a concentration of 3.7 mg/L.



Base from U.S. Geological Survey National Atlas, 1970

FIGURE 18.—Location of wells sampled for the upper water-bearing zone of the Black Warrior River aquifer.

ENVIRONMENTAL ISOTOPES

Analysis of environmental isotopes in water from the five wells penetrating the upper water-bearing zone (fig. 18) shows trends along flow paths. Tritium is present in well 1 (27 pCi/L), indicating that some recent meteoric water was present in the sample (table 15). Carbon-13 isotope ratios are relatively light in waters from the upgradient wells (−18.9 ‰ in well 1 and −23.2 ‰ in well 4), becoming heavier downgradient (−8.2 ‰ in well 3 and −10.3 ‰ in well 5). Isotope ratios for deuterium and oxygen-18 are typical for meteoric waters (fig. 19). From well 1 to well 3 the water samples show increasingly lighter values of isotope ratios, suggesting slightly cooler mean annual temperatures at the time of recharge for water in wells 2 and 3. Results of measurement of the isotope ratios of deuterium and oxygen-18 from well 4 and well 5 are inconclusive. Carbon-14 decreases downgradient, ranging from 69.7 PM at well 1 to 2.0 PM at well 3, and from 90.5 PM at well 4 to 2.3 PM at well 5.

CHEMICAL EVOLUTION

Analysis of water chemistry (table 16) shows that upgradient wells 1 and 4 are dominated by calcium bicarbonate facies, whereas water samples from wells 3 and 5 farther downgradient are dominated by sodium-bicarbonate-chloride facies (fig. 20). Concentrations of dissolved solids in ground water typically are less than 100 mg/L near outcrop areas and increase downgradient to 1,210 mg/L at well 5 (fig. 21*A*). The pH of ground water consistently increases from upgradient to downgradient (fig. 21*B*), with values ranging from 5.95 in water from well 4 to 8.50 in water from well 3. Concentration gradients of dissolved iron are not consistent along flow paths (fig. 21*C*). Dissolved iron decreases downgradient, from 5,900 μg/L in well 1 to 22 μg/L in well 3, but increases from 12 μg/L in water from well 4 to 250 μg/L in water from well 5. Total inorganic carbon increases substantially downgradient (fig. 21*D*), from 2.18 mmol/kg in well 1 and 1.01 mmol/kg in well 4 in

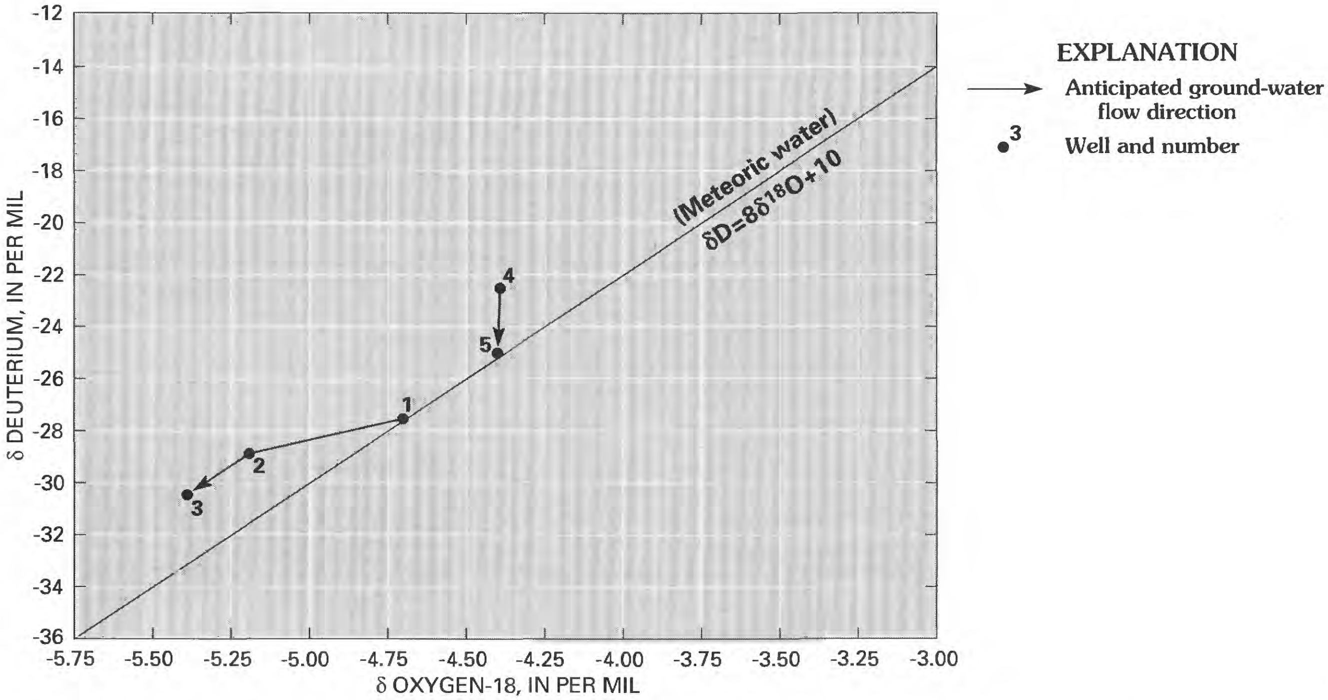


FIGURE 19.—Relation between deuterium (δD) and oxygen-18 ($\delta^{18}O$) in water from the upper water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 18.

recharge areas to 7.64 mmol/kg in well 3 and 10.69 mmol/kg in well 5. However, a slight decrease in ΣCO_2 was observed in water from well 1 to well 2, indicating a loss of carbon from the aqueous phase. Carbon-13 ratios, as discussed previously, become significantly heavier in water downgradient at wells 3 and 5 (fig. 21*E*). The trend in water from well 1 to well 2, where the carbon-13 ratio becomes lighter, indicates that the loss of CO_2 from the aqueous phase is most likely to a solid phase in the aquifer (as a carbonate mineral) rather than to a gas phase.

MINERAL EQUILIBRIUM

Analysis of water from the five wells in the upper water-bearing zone (fig. 18) shows various degrees of saturation for the major mineral phases (table 17). Calcite and dolomite are undersaturated upgradient but approach saturation downgradient, with calcite near or at saturation in most downgradient wells and slightly oversaturated in water from well 5. Albite, where considered, is undersaturated, indicating a propensity to dissolve, whereas chalcedony varies from slightly undersaturated to slightly oversaturated, with quartz oversaturated in all wells. Gypsum, where considered, is undersaturated. Siderite approaches saturation in water from well 3 and is oversaturated in water from well 5.

MASS BALANCE

Mass-balance reaction coefficients for flow paths in the upper water-bearing zone (fig. 18) are shown in table 18. The reaction model for the flow path from well 1 to well 2 is different from the models for the flow paths from well 2 to 3 and from well 4 to well 5. From well 1 to well 2, small amounts of calcite and CO_2 from lignite oxidation are dissolved by ground water. Ferric iron from goethite is reduced to ferrous iron, and siderite may precipitate. Chalcedony and kaolinite also appear to form as albite is weathered along the flow path from well 1 to well 2.

Reactions and reaction coefficients are very similar for reaction models for flow paths from well 2 to well 3 and from well 4 to well 5. Calcite dissolves as more CO_2 is produced from lignite. Calcium-for-sodium cation exchange produces the dissolved-sodium enrichment in the parts of the zone dominated by sodium bicarbonate facies (fig. 20). The areas of sodium-bicarbonate-chloride facies probably result from the mixing of traces of brines in inclusions or, less likely, halite dissolution as indicated in the reaction coefficients used in the chemical reaction model for the flow path from well 4 to well 5. Pyrite precipitates as a consequence of ferric-to-ferrous iron reduction and sulfate reduction. Traces of gypsum dissolve and provide sulfate anions for the sulfate-to-sulfide biogenic reduction reaction. Sodium beidellite may form

TABLE 15.—*Trace elements, dissolved gases, and environmental isotopes in water from the upper water-bearing zone of the Black Warrior River aquifer*

[In micrograms per liter, unless otherwise specified. pCi/L, picocuries per liter; ‰, per mil; PM, percent modern carbon; mol/kg, moles per kilogram. Negative values for isotopes indicate relatively light content. Location of wells shown in fig. 18]

Well number/name	Al	Ba	B	Cd	Cu	Fe	Pb	Li	Mn	Hg	Sr	Zn	N_2[1]	O_2[1]	CO_2[1]	CH_4[1]	Ar[1]	T (pCi/L)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{18}O$ (‰)	^{14}C (PM)	ΣCO_2 (mol/kg×10^{-3})
1. Bain	20	80	0	5	<10	5,900	16	11	430	<0.1	470	6	24	0.09	46.0	0.009	0.87	27	−18.9	−27.5	−4.7	69.7	2.18
2. Hickman	0	50	0	4	<10	130	22	<4	140	<.1	590	<4	25	.54	2.2	.008	.94	2	−19.1	−29	−5.2	9.5	1.62
3. Butler	10	20	500	3	<10	22	20	11	3	.2	230	<4	23	.18	2.2	3.7	.90	3	−8.2	−30.5	−5.4	2	7.64
4. Neighbors	<10	14	10	<1	<10	12	<10	7	<1	<.1	54	44	21	5.3	31.0	.0	.80	3	−23.2	−22.5	−4.4	90.5	1.01
5. Burkville B-2	30	70	490	<1	<10	250	<10	19	13	.9	1,100	<4	14	4.3	11.0	.0	.65	<3	−10.3	−25	−4.4	2.3	10.69

[1] Milligrams per liter; errors in laboratory data require interpretation with caution.

TABLE 16.—*Well data and chemical analyses of water from the upper water-bearing zone of the Black Warrior River aquifer*

[In milligrams per liter, unless otherwise specified. ft, feet; mi, miles; µs, microsiemens; ROE, residue on evaporation at 180 °C; TD, total depth. Location of wells shown in fig. 18]

Well number/name	Screened interval (ft)	Distance downgradient (mi)	Specific conductance (µS)	Temperature (°C)	pH (units)	Dissolved solids (ROE)	NH_4	Ca	Mg	Na	K	HCO_3	CO_3	Cl	SO_4	F	SiO_2
1. Bain	161 (TD)	4.0	140	17.7	6.37	96	0.05	8.9	3.9	4	1.7	66	0	6.19	7.44	0.08	35
2. Hickman	108 (TD)	6.8	170	18.9	7.62	94	.29	8.5	2.5	16	7.1	94	0	1.89	5.62	.09	14
3. Butler	449–709	26.0	1,260	20.3	8.50	700	.77	2.3	0.78	290	3.1	420	4	161	0	2.5	11
4. Neighbors	39–180	9.9	55	19.5	5.95	13	.09	3.3	.85	1.2	3.5	16.9	0	1.31	0.81	<.01	25
5. Burkville B-2	249–518	21.7	2,140	21.9	7.70	1,210	.79	19	3.3	470	3.6	630	0	351	0	3.9	17

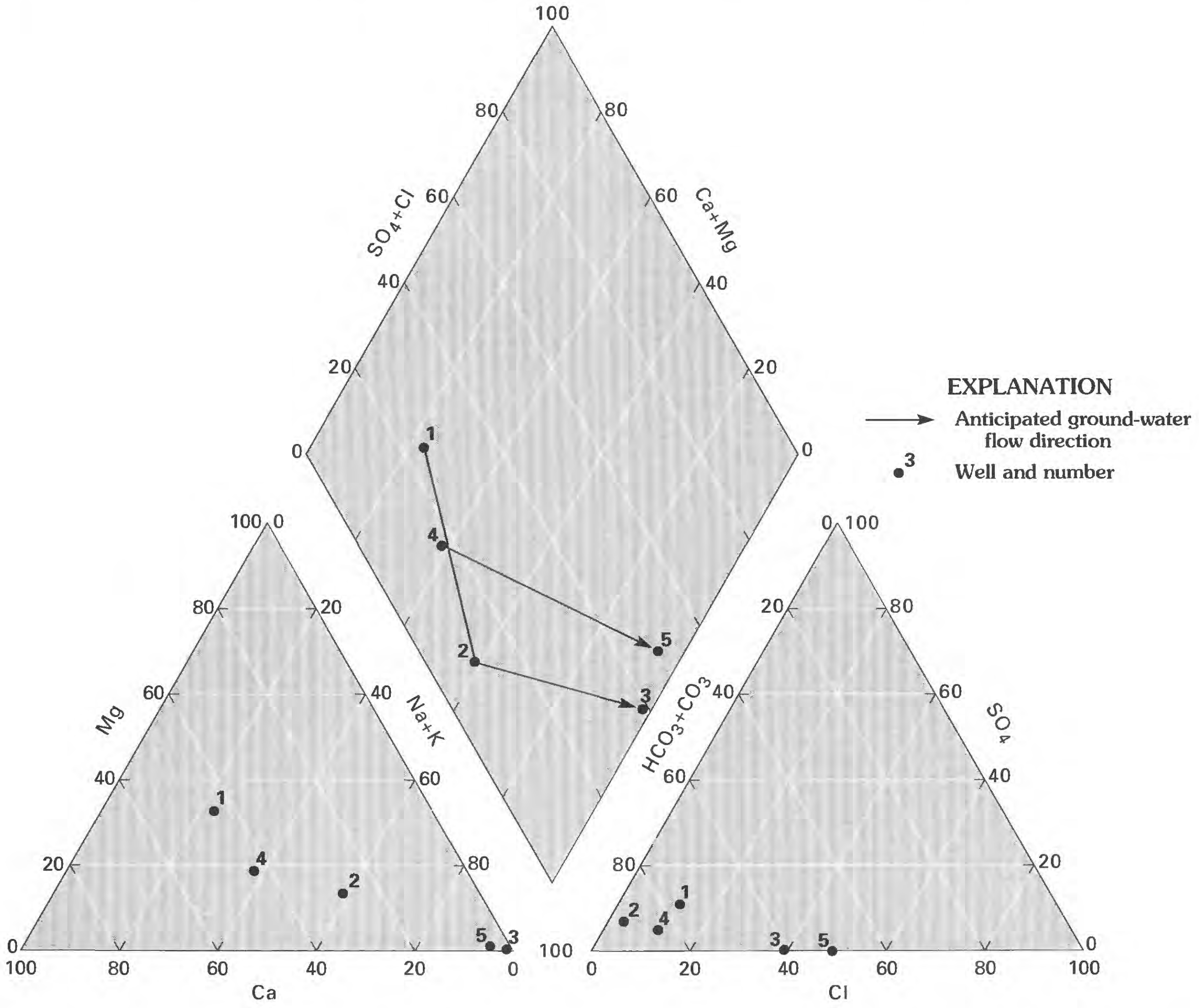


FIGURE 20.—Piper diagram showing evolution of water chemistry in the upper water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 18.

authigenically at the expense of chalcedony and amorphous aluminosilicate in water along flow paths from well 2 to well 3 and from well 4 to well 5.

REACTION ZONES

Comparison of chemical data with PHREEQE simulations indicates that a moderately calcareous aquifer represents the most appropriate chemical model for water in the upper water-bearing zone (fig. 22). The flow path from well 1 to well 3 (fig. 18) extends from zone C for well 1 to zone D for wells 2 and 3. Well 4 is near the recharge zone, but well 5 appears to be in zone D, or possibly zone E. Because of the short distance between wells 4 and 5, it is questionable whether such fast reaction progress actually occurred. The water in well 5 may represent some upward leakage from the underlying water-bearing zone rather than horizontal flow from well 4 to well 5.

CARBON-14 AGE AND GROUND-WATER FLOW VELOCITY

Table 19 gives the age of ground water in the upper water-bearing zone determined from carbon-14 data. Adjusted age and flow velocity could not be calculated for the flow path from well 2 to well 3 (fig. 18) because of an apparent measurement or sampling error at well 3. Based on upgradient flow rates, the carbon-14 at well 3 should be less than the detection limit (0.7 PM), rather than the 2.0 PM reported (table 15). Incremental velocities are relatively low, 1 ft/yr from well 1 to well 2 and 5.2 ft/yr from well 4 to well 5. These values are reason-

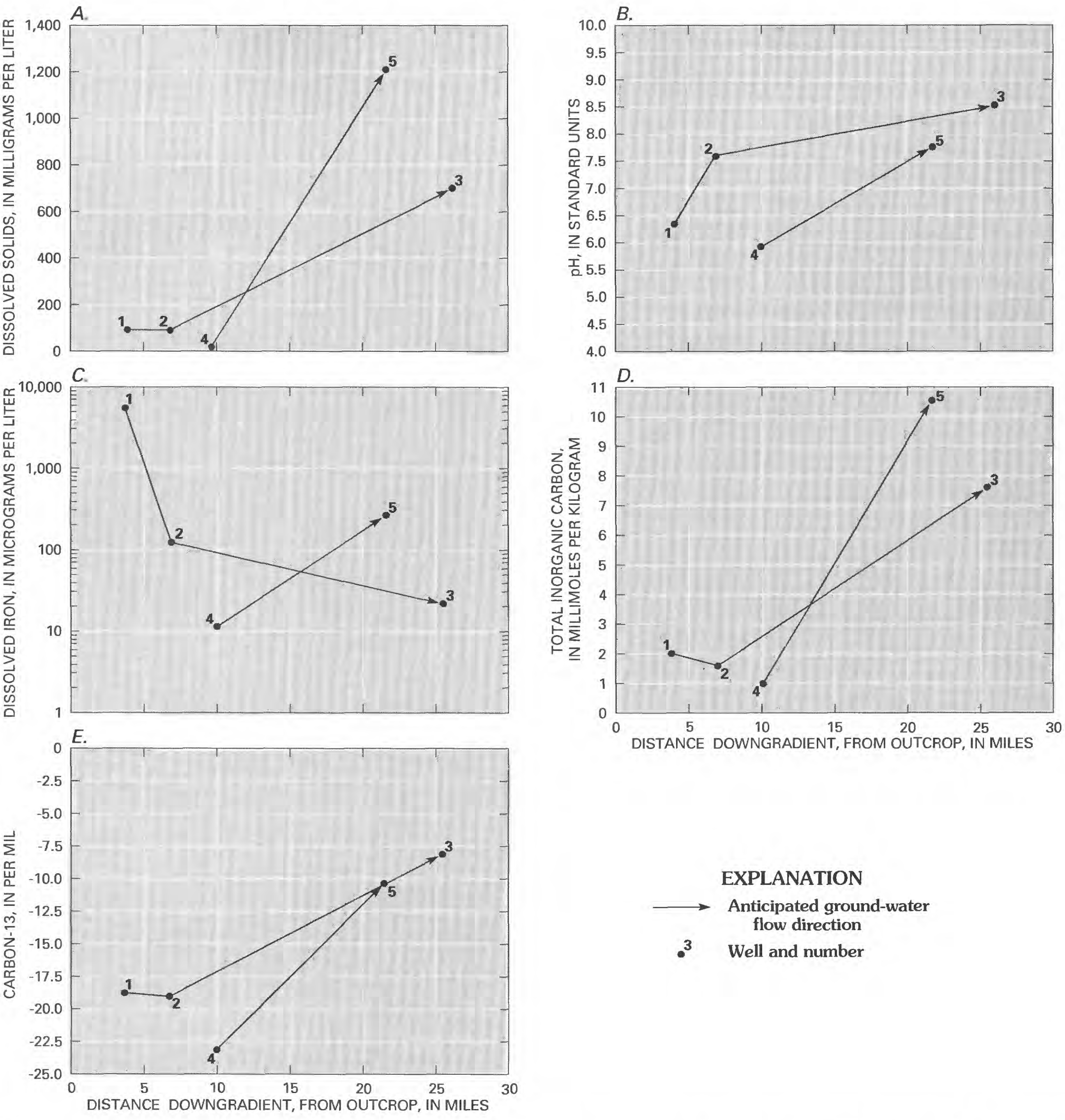


FIGURE 21.—Relation between selected chemical parameters and distance downgradient from outcrop areas for waters from the upper water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 18.

ably close to the mean velocity of about 1 ft/yr calculated using a mean hydraulic conductivity of 5 ft/d, a mean hydraulic gradient of 0.8 ft/mi, and a porosity of 0.3 (R.A. Barker, U.S. Geological Survey, written commun., 1986).

GEOCHEMISTRY OF WATER IN THE CHATTAHOOCHEE RIVER AQUIFER

The Chattahoochee River aquifer is present in two principal segments separated laterally by a chalk facies

TABLE 17.—*Selected saturation indices of water from the upper water-bearing zone of the Black Warrior River aquifer*

[Negative numbers indicate undersaturation, and positive numbers indicate oversaturation; dashes indicate mineral saturation index not calculated. Location of wells shown in fig. 18]

Well number/name	Albite	Calcite	Chalcedony	Dolomite	Pyrite	Goethite	Gypsum	Kaolinite	Sodium beidellite	Siderite	Quartz
1. Bain	−2.75	−2.33	0.37	−4.82	15.7	1.07	−3.11	3.14	3.01	−0.63	0.89
2. Hickman	—	−.93	−.04	−2.19	—	3.23	−3.25	—	—	−.86	.47
3. Butler	−1.41	−.09	−.17	−.41	19.1	4.96	—	−.04	−.56	−.29	.33
4. Neighbors	—	−3.7	.21	−7.7	10.1	−2.7	−4.4	—	—	−4.2	.71
5. Burkville B-2	−.36	.15	.01	−.21	17.6	3.8	—	2.5	2.4	.19	.51

TABLE 18.—*Reaction coefficients resulting from mass-balance calculations for water in flow paths between wells in the upper water-bearing zone of the Black Warrior River aquifer*

[In millimoles per kilogram of water. Positive values indicate dissolution, and negative values indicate precipitation; dashes indicate mineral not used in mass balance. Location of wells shown in fig. 18]

Well number/name	Albite	Calcite	Chalcedony	Kaolinite	Amorphous aluminosilicate	Sodium beidellite	Goethite	Siderite	Lignite	Gypsum	Pyrite	Ca-Na exchange	Halite
1. Bain													
	0.4	0.1	−1.2	−0.2	—	—	0.7	−0.8	0.2	—	—	0.1	—
2. Hickman													
	—	4.7	14.6	—	12.7	−10.9	.4	—	1.4	0.7	−0.4	5.5	—
3. Butler													
4. Neighbors													
	—	5.55	17.04	—	14.70	−12.62	1.05	—	3.94	2.09	−1.05	7.35	9.86
5. Burkville B-2													

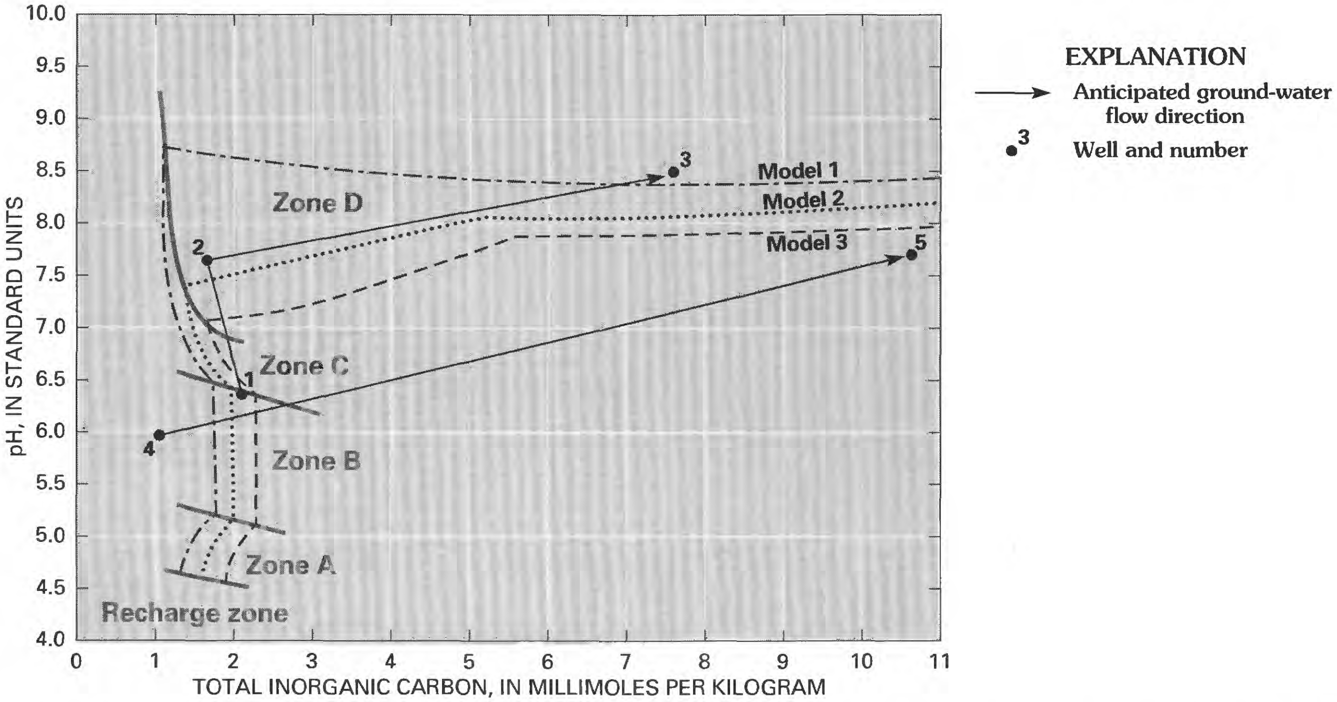


FIGURE 22.—Geochemical models of noncalcareous sand aquifers constructed using chemical data from the upper water-bearing zone of the Black Warrior River aquifer. Location of wells shown in figure 18.

TABLE 19.—*Radiocarbon ages and flow velocities of ground water in the upper water-bearing zone of the Black Warrior River aquifer*
[YBP, years before present; ft/yr, feet per year. Dashes indicate no data. Location of wells shown in fig. 18]

Well number (Flow path)	Unadjusted age (YBP)	Adjusted age (YBP)	Adjusted flow rate (ft/yr)
1	3,000	3,000	6.9
(1→2)	(16,500)	(15,400)	(1.0)
2	19,500	18,400	2.0
(2→3)[1]	(12,800)	—	—
3[1]	32,300	—	—
4	800	800	65.6
(4→5)	(30,400)	(11,000)	(5.2)
5	31,200	11,800	(9.8)

[1] Adjusted ages and flow rates could not be calculated because of an apparent measurement error or sampling error at well 3.

that is not an aquifer. The small western segment, present in northern Mississippi, extends westward from outcrop areas toward the Mississippi River (pl. 4). The larger segment extends from east-central Mississippi and west-central Alabama to the South Carolina-North Carolina State line. The water-bearing zone crops out in Mississippi, Alabama, Georgia, and South Carolina. It extends toward both the Gulf Coast and the Atlantic Coast, as far as the downdip limits of permeability (pl. 4; Renken, 1984). Equivalent aquifers in North Carolina locally are hydraulically and geochemically connected to the Chattahoochee River aquifer but are considered to be part of the Northern Atlantic Coastal Plain aquifer system.

MINERALOGY AND PETROLOGY

The Chattahoochee River aquifer is composed primarily of beds of sand and clay which may contain various amounts of calcareous material. In northern Mississippi, the aquifer contains beds of sand and interbedded limestone. This sedimentary facies thins southeastward and becomes chalk. Sand units reappear in southwestern Alabama and extend eastward toward North Carolina. The sands are predominantly quartz and may contain significant amounts of feldspars, low to moderate amounts of kaolinite and smectite clay minerals, and traces of illite and muscovite. In South Carolina, some fossiliferous sandy limestones are present. Table 20 shows X-ray diffraction mineralogy and describes the lithology of selected cores from test wells at Britton's Neck in Marion County and St. George in Dorchester County, S.C. Most of the calcareous material in these cores is composed of fossil shells. Feldspar clasts are abundant, and some lignitic material is present in the cores.

DISSOLVED SOLIDS

A map showing the areal distribution of dissolved-solids concentrations in the Chattahoochee River aquifer was prepared using values of residue on evaporation at 180 °C, if available, or calculated dissolved solids if no data for residue on evaporation were available (pl. 4). In southern Georgia and parts of South Carolina, ground water in the overlying Floridan aquifer system is plentiful and suitable for most uses. As a result, water wells in this area generally do not penetrate the deeper Chattahoochee River aquifer; thus, chemical data for this aquifer are not available.

A line of equal concentration of 1,000 mg/L of dissolved solids (as sodium chloride) derived from geophysical data of Brown and others (1979) was used to supplement the distribution of dissolved-solids, dissolved-chloride, and hydrochemical facies data on the maps. A similarly derived line of equal concentration produced by Gandl (1982) for the Ripley aquifer in Mississippi was used for that part of the study area.

Concentrations of dissolved solids in ground water generally increase with distance downgradient from the outcrop areas where recharge occurs. Concentrations in recharge areas may be less than 50 mg/L, which is similar to dissolved-solids concentrations in rainfall (Junge and Werby, 1958). Water that contains concentrations greater than 50 mg/L but less than 500 mg/L usually is the result of water-rock chemical interactions. Concentrations greater than 500 mg/L generally are the result of water-rock chemical interaction and mixing with sodium chloride dominated water (Lee, 1985). Exceptions occur in parts of South Carolina where water in the Chattahoochee River aquifer with dissolved-solids concentrations of 1,500 mg/L or more is dominated by sodium and bicarbonate ions (Zack, 1980). Mixing of ground water containing low dissolved solids with saline water containing elevated dissolved solids may result in water containing concentrations of dissolved solids greater than 10,000 mg/L. Sodium and chloride ions dominate waters in the deep, downgradient parts of the Southeastern Coastal Plain aquifer system. In areas such as the Coastal Plain of South Carolina, withdrawals of ground water for industrial or municipal uses may have produced sufficient head decline to cause some landward migration of saline ground water, thus increasing concentrations of dissolved solids in these areas.

In the Chattahoochee River aquifer, water-rock chemical interactions produce concentrations of dissolved solids of 200 mg/L or greater over a large part of the study area. Concentrations that exceed 1,500 mg/L are caused primarily by mixing of fresh ground water with saline water in the aquifer. However, concentrations in northern Mississippi may exceed 500 mg/L owing to dissolu-

TABLE 20.—*X-ray diffraction mineralogy of selected cores of the Chattahoochee River aquifer at U.S. Geological Survey test wells at Britton's Neck, Marion County, and St. George, Dorchester County, S.C.*

[Letters indicate X-ray diffraction relative peak intensity: S, strong; M, medium; L, low; Tr, trace. Dashes indicate mineral not detected; ‰, per mil]

Depth (ft)	Quartz	Potassium feldspar	Albite	Calcite	Pyrite	Kaolinite	Smectite	Muscovite	Other minerals	Core description
Britton's Neck, Marion Co., S.C.										
340	S	Tr	L	S	Tr	—	Tr	—	Tr dolomite	Fine sandy limestone
344	S	Tr	Tr	S	Tr	Tr	Tr	—	Tr dolomite	Fossiliferous sandy limestone; δ^{13}C of fossil shell −5.9 ‰
377	S	—	—	S	—	—	—	—	—	Sandy limestone; δ^{13}C of fossil shell −3.8 ‰
444	S	L	Tr	S	M	—	—	—	—	Fossiliferous, medium sand and clay, calcite δ^{13}C of lignite −13.7 ‰
520	S	L	Tr	L	M	Tr	L	Tr	Apatite? drilling mud	Bit sample, coarse sand, drilling mud; organic material
738	S	M	S	L	Tr	L	Tr	L	Oligoclase	Fine sand and clay, mica
770	S	L	Tr	Tr	M	Tr	Tr	Tr	—	Dark coarse sand with drilling mud, pyrite nugget, feldspars; δ^{13}C of lignite −22.7 ‰
St. George, Dorchester Co., S.C.										
585	S	M	—	M	—	Tr	Tr	Tr	Drilling mud	From cuttings, sand, large grains, micaceous; δ^{13}C of lignite −20.8 ‰
1,331	S	L	Tr	Tr	—	S	Tr	L	Drilling mud	Micaceous sand and silt
1,351	S	—	—	—	—	M	Tr	—	—	Fine sand-silt-clay with dark mineral
1,359	S	L	—	Tr	—	S	Tr	L	—	Micaceous sand and clay with large clasts
1,417	S	L	M	Tr	—	L	L	Tr	—	Fine micaceous sand with feldspar and clay
1,470	S	M	L	L	—	L	L	Tr	—	Slightly cemented quartz sand and clay with large white microcline clasts
1,512	S	S	—	Tr	—	M	Tr	Tr	Tr mixed-layer clay	Coarse micaceous quartz sand with orthoclase clasts and clay
1,524	S	M	S	Tr	—	L	L	Tr	—	Micaceous sand, rutilated quartz, clay, silt
1,530	S	M	L	Tr	—	L	L	Tr	—	Fine micaceous, red-green mottled silty sand and clay with calcite and orthoclase
1,541	S	L	S	Tr	—	Tr	Tr	L	Tr mixed-layer clay	Fine to very fine micaceous sand and clay
1,573	S	S	M	Tr	—	L	Tr	Tr	Tr mixed-layer clay	Fine micaceous sand and clay with BB-size clasts, microcline
1,576	S	S	L	L	Tr	Tr	L	Tr	Drilling mud	Coarse sand with clay, red and green mottles, pink and greenish clasts, orthoclase
1,627	S	S	Tr	Tr	Tr	Tr	M	Tr	Drilling mud	Coarse sand and clay, red and green mottles, pink and greenish clasts, orthoclase
1,681	S	L	Tr	Tr	—	M	L	Tr	Tr mixed-layer clay	Sand and clay with pea-size feldspar clasts; amber, microcline

tion of calcite, which is abundant in the Ripley Formation. The abundance of calcite in the Ripley Formation may also account for the steep dissolved-solids gradient in north-central Mississippi and in western Alabama.

The areal distribution of dissolved solids in water in the Chattahoochee River aquifer may be influenced by regional ground-water discharge to rivers, geochemical variations, and the occurrence and distribution of saline waters in the deeper, downgradient parts of the aquifer. Regional ground-water discharge to the Chattahoochee River along the Alabama-Georgia State line may be responsible for the northward displacement of the 200 mg/L line of equal concentration. Upward leakage from underlying, more saline water-bearing zones, or perhaps the presence of more soluble minerals, may also account for this displacement. A similar situation occurs near the Savannah River along the Georgia-South Carolina State line. Slightly saline waters are intermittently present along the coast of South Carolina, as indicated by the "scalloped" appearance of the lines of equal concentrations in the area, especially the 800 mg/L line. However, this pattern may be due to wells open to different sand units containing vertical variations in water chemistry within the aquifer. Also, ground-water withdrawals in these areas may cause migration of saline water to some wells, although this has not been verified by field data. Farther north, near the South Carolina-North Carolina border, concentrations in some wells exceed 1,000 mg/L.

DISSOLVED CHLORIDE

The distribution of dissolved chloride in the Chattahoochee River aquifer (pl. 4) shows the extent of freshwater flushing of residual brines. Mixing of meteoric ground water with saline water is indicated by pronounced increases in concentrations of dissolved chloride near the downdip limit of the freshwater zone.

Concentrations of dissolved chloride show trends similar to those for concentrations of dissolved solids in excess of 500 mg/L, because most of the increase in dissolved solids above 500 mg/L is in sodium and chloride ions. A line showing concentrations of 1,000 mg/L dissolved solids as sodium chloride has been mapped in Mississippi by Gandl (1982) and in Georgia by Brown and others (1979). Because few chemical data exist for the deeper, downgradient parts of the aquifer, it was useful to add these lines to the map for dissolved chloride (pl. 4).

Concentrations of dissolved chloride are less than 50 mg/L in most of the aquifer area. Concentrations greater than 500 mg/L in Marengo and Wilcox Counties, Ala., indicate either incomplete flushing of relict seawater from sediments of low permeability or upward migration of saline water from the underlying Black Warrior River aquifer. Elevated concentrations in southeastern Wilcox County, Ala., may indicate upward migration of underlying saline water along faults. Concentration gradients steepen beyond the 50 mg/L concentration line.

In South Carolina, the presence of saline water (probably relict seawater or brine) in the aquifer is indicated by steep concentration gradients along the coast. The steep gradient and the high concentrations of dissolved chloride present at the North Carolina-South Carolina State line are indicative of incomplete flushing of seawater from the aquifer.

Two areas in the outcrop area in eastern Alabama where dissolved-chloride concentrations are 50 mg/L or greater may be localized anomalies.

DISSOLVED IRON

Concentrations of dissolved iron exceed 5,000 μg/L in many parts of the Chattahoochee River aquifer. Such elevated concentrations are found in narrow bands near outcrop areas in Georgia and South Carolina (pl. 4). Lee (1985) provided evidence that dissolved iron is removed from ground water by precipitation of iron-bearing solid phases (siderite and pyrite) downgradient from the areas of elevated concentration. This process may account for the decrease in dissolved iron downgradient from the narrow bands. However, concentrations increase farther downgradient as iron solubility increases owing to increasing chloride content of the ground water.

Dissolved-iron data for the aquifer are poorly distributed. Because a relatively large equal-concentration interval was used (100, 500, 1,000, and 5,000 μg/L), estimation of local concentrations of dissolved iron in the aquifer should be made with caution.

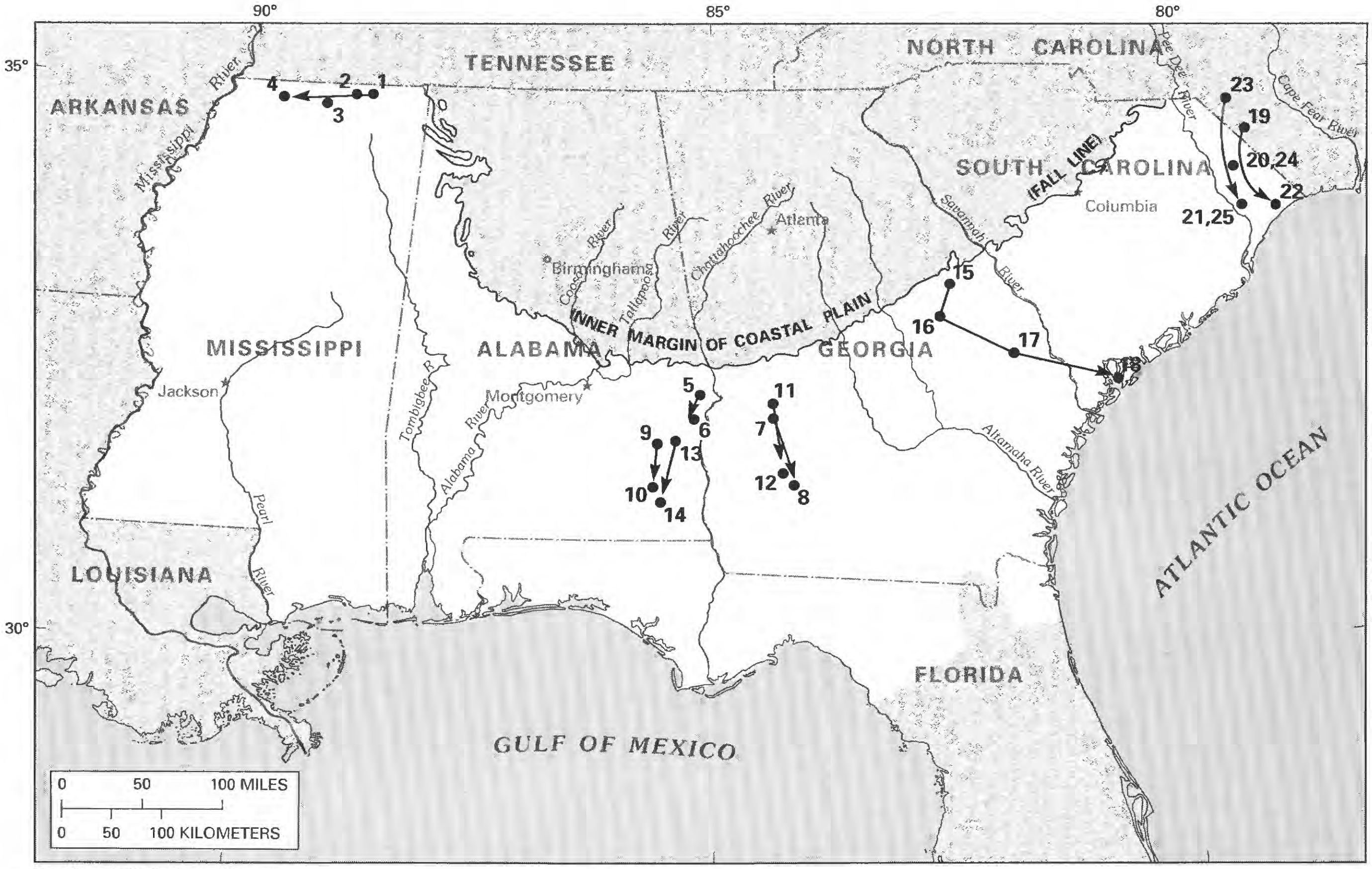
Concentrations of dissolved iron approach 1,000 μg/L in northeastern Mississippi, then decrease farther downgradient. Few data are available for Alabama, and concentrations generally do not exceed 100 μg/L. The elevated concentrations of dissolved iron (up to 5,000 μg/L) that occur near outcrop areas in Georgia and South Carolina decrease to less than 100 μg/L downgradient. Concentrations in recharge areas in Lexington and Richland Counties, S.C., that approach 500 μg/L may be due to high-acidity water from pyrite (FeS_2) oxidation. Substantial concentrations of dissolved sulfate present in water samples from these areas support this hypothesis.

HYDROCHEMICAL FACIES

Three principal hydrochemical facies (pl. 4) occur most commonly in ground water in the Chattahoochee River aquifer: calcium bicarbonate, sodium bicarbonate, and sodium chloride. Near recharge areas, facies may vary owing to low dissolved-solids concentrations. Downgradient, as concentrations of dissolved solids increase, calcium bicarbonate and sodium bicarbonate become the prevalent facies as a result of water-rock chemical interactions (Lee, 1985). Farther downgradient, concentrations of dissolved solids exceed 500 mg/L, and sodium and chloride become the dominant ions in water owing to mixing of freshwater with saline waters known to be present in the downgradient parts of the aquifer.

In northeastern Mississippi, ground water is dominated in recharge areas by calcium bicarbonate facies, but evolves downgradient to sodium bicarbonate facies. Eventually, as the freshwater moves farther downgradient, it mixes with saline water in the deeper, downgradient part of the aquifer and evolves the sodium chloride facies. The large areas of calcium bicarbonate facies in eastern Alabama and western Georgia may be due to water from carbonate aquifers or calcareous sand in overlying aquifers. An area dominated by sodium bicarbonate facies that extends along the Alabama-Georgia State line from Barbour County, Ala., to Early County, Ga., probably is the result of upward movement of sodium bicarbonate dominated ground water in the underlying Black Warrior River aquifer.

In Georgia and South Carolina, sodium chloride-sulfate facies and calcium bicarbonate facies typically are observed near outcrop areas. In coastal South Carolina,



Base from U.S. Geological Survey
National Atlas, 1970

EXPLANATION

→ Anticipated ground-water flow direction

● 3 Well and number

FIGURE 23.—Location of wells sampled for the Chattahoochee River aquifer and for equivalent aquifers in North Carolina.

ground water is sodium bicarbonate dominated, owing to the chemical evolution of high bicarbonate concentrations (Foster, 1950).

Sodium chloride facies occur in the downgradient parts of the aquifer and extend updip approximately to the 1,000 mg/L lines of concentrations of dissolved solids for Georgia reported by Brown and others (1979) and for Mississippi reported by Gandl (1982).

TRACE ELEMENTS

Chemical data for water from 25 wells in the Chattahoochee River aquifer and equivalent aquifers in North Carolina (fig. 23) show that trace element concentrations are low, although some regional variability is apparent (table 21). Among the samples analyzed, concentrations of dissolved iron attain a maximum, 2,200 μg/L, in water from well 7. Dissolved aluminum reached concentrations of 200 μg/L in water from wells 8, 16, and 23. Water from wells 18, 21, 22, and 25 near the Atlantic Coast of South Carolina contained dissolved boron, with concentrations as great as 3,400 μg/L in water from well 18. Also, a boron concentration of 5,600 μg/L was measured in water from well 8 near Albany, Ga. Strontium was present in several water samples from west of central Georgia, with concentrations as great as 460 μg/L in water from well 3. Lead was measured in concentrations as great as 26 μg/L in water from well 2 and 33 μg/L in water from well 23. Mercury was detected in waters from three wells: wells 8, 21, and 25, with concentrations of 0.2, 0.1, and 0.2 μg/L, respectively. Barium, lithium, and zinc were present in measurable concentrations in many of the water samples. Largest concentrations were 140 μg/L of barium in water from well 9, 46 μg/L of lithium in water from well 8, and 170 μg/L of zinc in water from well 9.

TABLE 21.—*Trace elements, dissolved gases, and environmental isotopes in water from the Chattahoochee River aquifer and equivalent aquifers in North Carolina*

[In micrograms per liter, unless otherwise specified. pCi/L, picocuries per liter; ‰, per mil; PM, percent modern carbon; mol/kg, moles per kilogram. Dashes indicate no data; negative values for isotopes indicate relatively light content. Location of wells shown in fig. 23]

Well number/name	Al	Ba	B	Cd	Cu	Fe	Pb	Li	Mn	Hg	Sr	Zn	N_2[1]	O_2[1]	CO_2[1]	CH_4[1]	Ar[1]	T (pCi/L)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{18}O$ (‰)	^{14}C (PM)	ΣCO_2 (mol/kg×10^{-3})
1. Mathis	10	10	0	<1	<10	11	16	4	<1	<0.1	4	<4	20	10	40	0	0.74	43	−19.3	−30	−5	86.1	2.54
2. Walnut Standby	0	40	0	3	<10	660	26	11	19	<.1	220	<4	22	0.37	11	tr	.88	3	−12.4	−29	−5.2	25.8	3.72
3. Ashland	0	50	0	2	<10	280	16	5	22	<.1	460	<4	25	.1	7.6	0	.95	3	−13.2	−30	−5.2	16.7	3.25
4. Byhalia	0	8	440	3	<10	14	22	37	4	<.1	52	<4	26	.37	1.9	.03	1.0	1	−12.1	−32	−5.6	2.4	7.86
5. McArthur	<10	11	<10	<1	<10	7	<10	<4	<1	<.1	20	31	21	11	15	0	.81	89	−21	−24.5	−4.6	54.8	.58
6. Bowden Flowing	<10	5	420	<1	<10	14	<10	13	<1	<.1	240	<4	26	.3	0.5	.02	1.0	<1	−8.5	−26	−4.6	7.1	.87
7. Ellaville	100	37	20	<1	<10	2,200	<10	19	20	<.1	47	52	22	.13	35.0	0	.90	2	−22.3	−21.5	−4.4	35.4	1.07
8. Albany TW-1	200	10	5,600	2	<10	1,600	<10	46	15	.2	410	5	20	.01	12	17	.8	3	−2	−21.5	−3.9	<.7	17.05
9. Green Store	10	140	30	<1	<3	78	<10	<4	22	<.1	370	170	19	4.6	3.9	0	.73	3	−13.2	−21.5	−4.3	8.9	2.60
10. Ozark	20	4	160	<1	<10	7	<10	<4	<1	<.1	160	<4	22	.1	.5	.1	.92	2	−6.5	−23.5	−4.3	.8	2.86
11. Breeland	20	13	10	<1	<10	23	10	<4	6	<.1	13	140	—	—	—	—	—	17	−20.4	−24	−4.4	92.8	.84
12. Albany TW-10	40	<2	260	<1	<10	22	<10	10	<1	<.1	46	<4	20	1.1	.4	.1	.82	2	−4.8	−20.5	−4.4	3.1	3.28
13. Clayton	<10	16	10	<1	<10	9	<10	5	<1	<.1	14	11	20	5.8	45	0	.79	6	−20.0	−24.5	−4.6	84.8	1.45
14. Newton	<10	43	20	<1	<10	100	10	<4	2	<.1	450	11	21	.2	7.4	0	.84	3	−9.5	−19	−4	1.8	3.03
15. Huber-2	100	2	<10	3	16	15	10	4	4	<.1	16	25	22	7.3	41	0	.82	2	−25.7	−29	−5.1	63	1.31
16. Stevens-1A	200	20	10	<1	<10	1,500	10	5	25	<.1	23	5	22	.1	57	0	.85	3	−24.4	−26	−4.6	37.9	1.99
17. King Finishing-1	<10	30	70	2	<10	24	10	4	9	<.1	160	<4	22	.01	1.8	.01	.85	1	−16.4	−27	−4.4	1.65	1.82
18. USMC-1	30	2	3,400	3	10	28	10	31	1	<.1	58	4	([2])	([2])	([2])	([2])	([2])	1	−5.6	−26	−4.5	1.1	17.82
19. Rowland-2	<100	60	20	<1	<10	960	<10	<4	24	<.1	46	<4	25	.04	30.0	0	.95	8	−18.3	−19.5	−3.2	32.6	1.63
20. Marion-1	<100	10	60	1	<10	280	<10	5	16	<.1	43	<4	25	.02	5.8	0	.96	2	−19.3	−20	−3.4	26.7	1.82
21. Britton's Neck-4	20	18	2,000	<1	<10	120	<10	<4	10	.1	51	13	24	.36	5.6	.02	.91	2	−10.25	−24	−4.55	2.5	6.26
22. Conway	20	40	3,100	<1	<10	11	<10	9	4	<.1	64	<4	23	.06	2.1	.02	.90	0	−8.9	−27.5	−4.9	1.7	7.72
23. Laurinburg	200	30	10	<1	<10	2,000	33	<4	24	<.1	11	39	27	.30	40	.0	.88	60	−22.7	−29.5	−5.1	71.5	.91
24. Marion-2	100	10	120	<1	<10	54	<10	<4	13	<.1	18	<4	25	.07	15	.06	.96	3	−16.8	−20.5	−3.2	2.85	1.93
25. Britton's Neck-5	10	31	1,900	<1	<10	44	<10	<4	2	.2	71	<4	22	.07	2.6	.08	.92	0	−7.25	−24	−4.4	2.9	8.15

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[1] Milligrams per liter; errors in laboratory data require interpretation with caution.

[2] Concentrations not shown because sample apparently was contaminated by air.

DISSOLVED GASES

Dissolved gases in water from the 25 wells in the Chattahoochee River aquifer and equivalent aquifers in North Carolina (fig. 23) show trends from upgradient to downgradient similar to trends in the Black Warrior River aquifer (table 21). Concentrations of dissolved carbon dioxide and oxygen are greatest in water from the recharge areas (57 mg/L of carbon dioxide in water from well 16; 11 mg/L of oxygen in water from well 5), but decrease downgradient. Methane gas was present in trace amounts in some downgradient water samples. However, a methane concentration of 17 mg/L was measured in water from well 8. Concentrations of dissolved gases in water from well 18 are not shown in table 21 because the sample from that well apparently was contaminated with air.

ENVIRONMENTAL ISOTOPES

Analysis of environmental isotopes in water from the 25 wells penetrating the Chattahoochee River aquifer and equivalent aquifers in North Carolina (fig. 23) shows trends along flow paths. Elevated tritium concentrations (as great as 89 pCi/L) were measured in waters from wells 1, 5, 11, 13, 19, and 23, which are near recharge areas (table 21). Downgradient, tritium in most places is 3 pCi/L or less. Carbon-13 ratios are relatively light in water from recharge areas, ranging from −18.3 ‰ at well 19 to −25.7 ‰ at well 15. Downgradient, wells produce water with carbon-13 ratios as heavy as −2.0 ‰.

Deuterium and oxygen-18 isotope ratios are typical of meteoric waters (figs. 24*A*, 24*B*). The lightest values are in Mississippi; water from well 4 had a deuterium ratio of−32.0 ‰ and an oxygen-18 ratio of −5.6 ‰. Heaviest values are in North Carolina and South Carolina; water from well 19 had a deuterium ratio of −19.5 ‰ and an oxygen-18 ratio of −3.2 ‰. The differences in deuterium and oxygen-18 ratios may be from effects of higher atmospheric temperatures of precipitation in Mississippi or from overall differences in isotopic abundance in parent storms in these respective areas. Carbon-14 decreased downgradient in water from all wells sampled, from as great as 86.1 PM in water from well 1 to less than 0.7 PM in water from well 8.

CHEMICAL EVOLUTION

Chemical data for water from the Chattahoochee River aquifer and equivalent aquifers in North Carolina (table 22) show typical evolution of water chemistry in the aquifer. Upgradient, near recharge areas, most waters are low in dissolved solids, with variable hydrochemical facies or no dominant facies, except for well 23 (fig. 23). Chemical evolution from recharge areas to deep, downgradient parts of the aquifer range from no dominant facies to sodium bicarbonate facies, followed by trends toward sodium chloride facies (figs. 25*A*, 25*B*). Concentrations of dissolved solids increase from less than 50 mg/L in recharge areas (figs. 26*A*, 26*B*) to as much as 1,620 mg/L downgradient (well 8). A slight decrease in concentration of dissolved solids from well 2 to well 3 was observed, suggesting precipitation of a solid phase in the aquifer.

The pH of ground waters ranges from 4.41 in water from well 23 to 9.40 in water from well 12 (figs. 27*A*, 27*B*). Values of pH increase downgradient except from well 17 to well 18.

Concentrations of dissolved iron generally are low (figs. 28*A*, 28*B*) but range from 7 μg/L in water from wells 5 and 10 to 2,200 μg/L in water from well 7 (table 21). Dissolved-iron concentrations are low (less than 10 μg/L) in water near recharge areas and in wells containing dissolved oxygen, but increase downgradient as reducing conditions in the aquifer are attained, and then decrease to concentrations of less than 100 μg/L in places. A slight decrease in concentration of dissolved iron from well 7 to well 8 (from 2,200 to 1,600 μg/L) was observed. The relatively high concentration of dissolved iron in water from well 8 is due to the increased concentration of dissolved chloride (443 mg/L), which forms a soluble complex with ferrous ion. It is likely that the decrease in concentration of dissolved iron in ground water between wells 7 and 8 would have been larger had it not been for the increase in dissolved chloride. Similarly, concentrations of dissolved iron likely would increase downgradient at well 8 as ground water mixes with saline waters, causing concentrations of dissolved chloride to increase.

Total inorganic carbon increases in a downgradient direction (figs. 29*A*, 29*B*), ranging from as low as 0.58 mmol/kg upgradient in water from well 5 to as great as 17.82 mmol/kg downgradient in water from well 18. The slight loss of total inorganic carbon from well 2 to well 3 indicates that a carbonate solid phase may be precipitating in this part of the aquifer.

Carbon-13 ratios generally increase downgradient (figs. 30*A*, 30*B*). The slightly lighter values of carbon-13 ratios in wells 3 and 20 support the likelihood of mineral carbonate precipitation from well 2 to well 3 and from well 19 to well 20. Overall, heavier carbon-13 ratios indicate that isotopically heavy sources of carbon are predominant in the aquifer.

MINERAL EQUILIBRIUM

Analysis of water from the 25 wells in the Chattahoochee River aquifer and equivalent aquifers in North

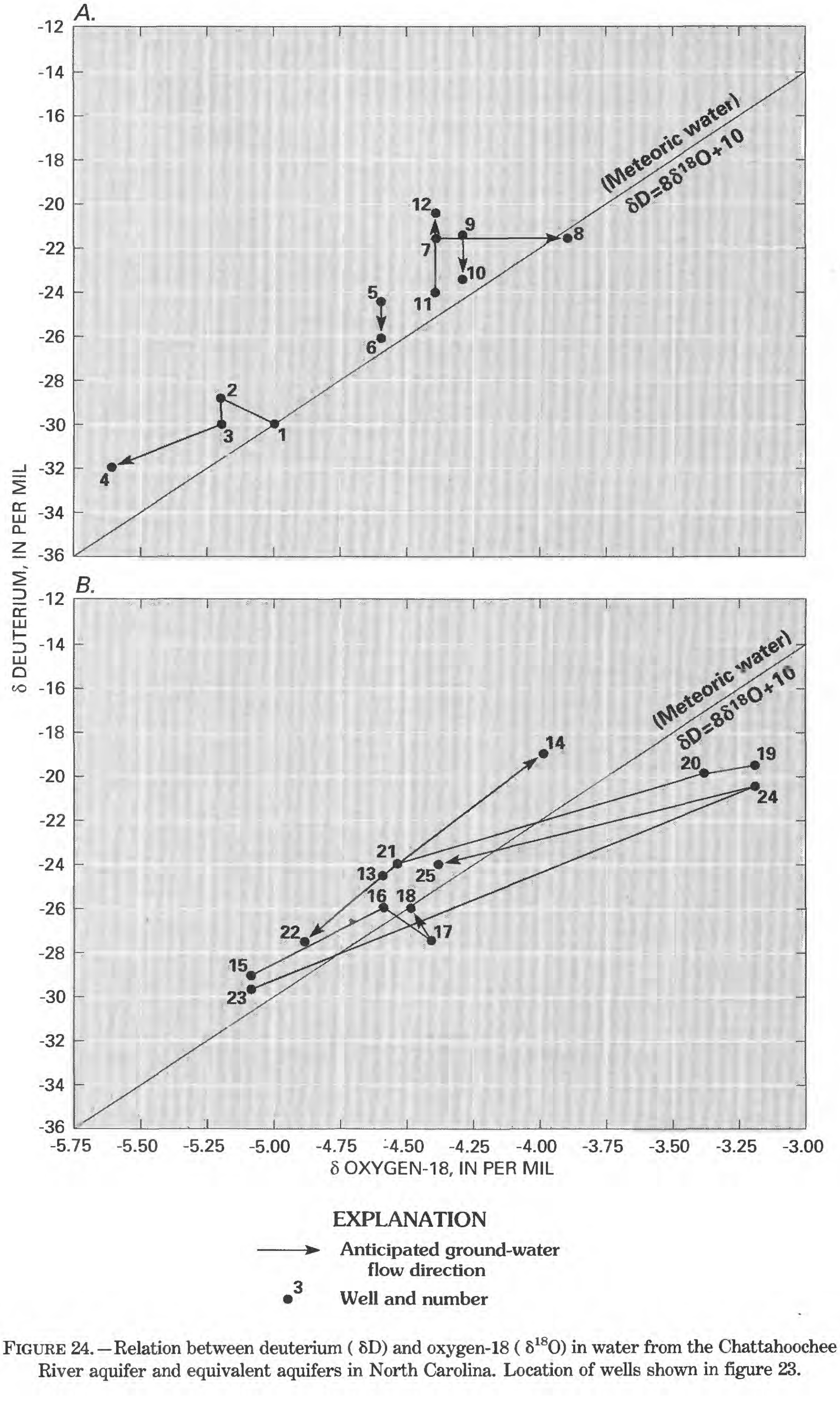


FIGURE 24.—Relation between deuterium (δD) and oxygen-18 ($\delta^{18}O$) in water from the Chattahoochee River aquifer and equivalent aquifers in North Carolina. Location of wells shown in figure 23.

TABLE 22.—*Well data and chemical analyses of water from the Chattahoochee River aquifer and equivalent aquifers in North Carolina*

[In milligrams per liter, unless otherwise specified. ft, feet; mi, miles; µs, microsiemens; ROE, residue on evaporation at 180 °C; TD, total depth. Location of wells shown in fig. 23]

Well number/name	Screened interval (ft)	Distance downgradient (mi)	Specific conductance (µS)	Temperature (°C)	pH (units)	Dissolved solids (ROE)	NH_4	Ca	Mg	Na	K	HCO_3	CO_3	Cl	SO_4	F	SiO_2
1. Mathis	126 (TD)	7.9	40	17.0	5.00	34	0.01	1.3	0.6	2	0.5	6	0	1.90	0	0	16
2. Walnut Standby	118–148	13.2	335	17.5	7.55	200	.01	58	4.9	2.4	1.5	210	0	1.1	5.8	0	24
3. Ashland	741–919	26.0	309	22.1	7.70	180	.22	47	4.8	8.4	1.9	190	0	1.43	8.6	0.2	19
4. Byhalia	1,549–1,641	53.9	760	26.4	8.69	470	.31	1.3	.29	190	1.4	480	8	1.41	5.0	.45	13
5. McArthur	85 (TD)	2.5	30	19.7	5.62	30	.05	1.9	.68	0.9	.97	5.29	0	2.42	<.2	<.01	5.1
6. Bowden Flowing	39–351	19.3	550	20.1	8.70	336	.44	17	.3	93	1.8	52	2.1	54	122	.6	13
7. Ellaville	509–640	9.9	80	21.3	6.16	67	.08	7.8	1.1	1.2	2.7	25.4	0	2.49	9.39	<.06	30
8. Albany TW-1	1,431–1,473	58.4	2,450	21.3	8.13	1,620	1.0	4.6	1.9	610	5.8	1,036	0	443	<.2	4.7	13
9. Green Store	180 (TD)	6.8	270	20.3	7.92	167	.21	29	4.7	13	5	156	0	1.75	6.83	<.01	22
10. Ozark	505–846	42.3	340	23.3	9.00	199	.23	2.6	.9	65	1.4	165	10.4	4.5	8.9	<.01	11
11. Breeland	128 (TD)	4.3	26	19.7	4.88	19	.01	.89	.59	1.3	.2	1.59	0	1.06	<.2	<.01	67
12. Albany TW-10	810–846	64.6	560	22.4	9.40	242	.26	1.3	.17	83	3.6	180	25	2.72	7.41	.56	12
13. Clayton	174–194	8.1	115	19.5	6.20	103	.01	15	.5	2.2	.8	35.9	0	7.1	.6	<.01	16
14. Newton	623–696	41.6	360	23.4	7.66	191	.05	45	6.2	8.6	2.1	178	0	2.4	10	<.01	20
15. Huber-2	200–312	14.8	25	17.7	4.80	27	.01	.5	.3	.2	.09	2	0	1.62	3.03	.08	11
16. Stevens-1A	449–532	25.2	60	21.2	5.40	58	0	5.1	.69	2.3	.48	12	0	2.07	8.52	.07	31
17. King Finishing-1	1,116–1,224	75.6	215	27.2	8.40	131	0	7.5	1.1	27	3.3	111	1	2.76	5.64	.15	15
18. USMC-1	2,612–2,786	148.8	1,675	40.1	8.39	1,040	.8	1.2	1.2	420	3.4	1,076	20	13.3	.65	4.1	19
19. Rowland-2	269–299	56.0	160	17.8	6.35	63	.03	6.2	.84	11	2.5	48	0	2.28	3.1	.1	15
20. Marion-1	351–571	77.6	175	19.3	7.00	133	.08	2.5	.71	33	4.7	92	0	3.59	.2	.34	45
21. Britton's Neck-4	748–768	99.2	765	23.2	8.10	450	.1	1.7	.4	180	2.2	380	0	57.0	13	2.7	24
22. Conway	610–673	105.6	780	23.4	8.55	621	.17	1.7	.53	310	2.8	460	12	91	7.9	3.0	13
23. Laurinburg	79–131	6.4	80	18.0	4.41	43	.03	1.0	.65	8.3	.25	0	0	8.28	12	.09	9.1
24. Marion-2	171–200	46.4	203	20.5	7.48	150	.05	1.1	.18	47	3	111	0	5.29	2.42	.64	40
25. Britton's Neck-5	518–538	68.8	550	21.4	8.57	496	.21	2.3	0	190	3.7	485	11.9	36	<.2	4.7	17

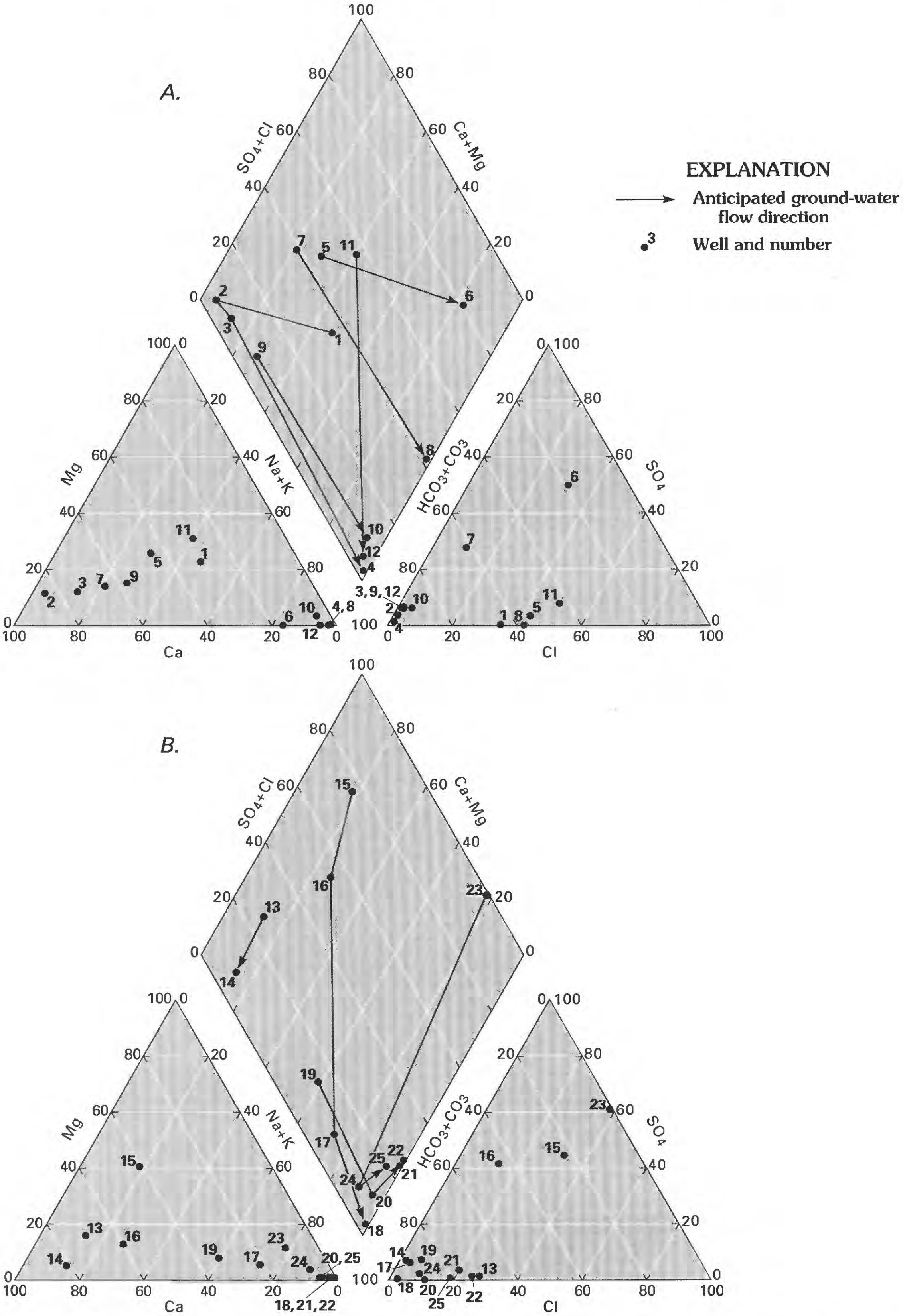


FIGURE 25.—Piper diagrams showing evolution of water chemistry in the Chattahoochee River aquifer and equivalent aquifers in North Carolina. Location of wells shown in figure 23.

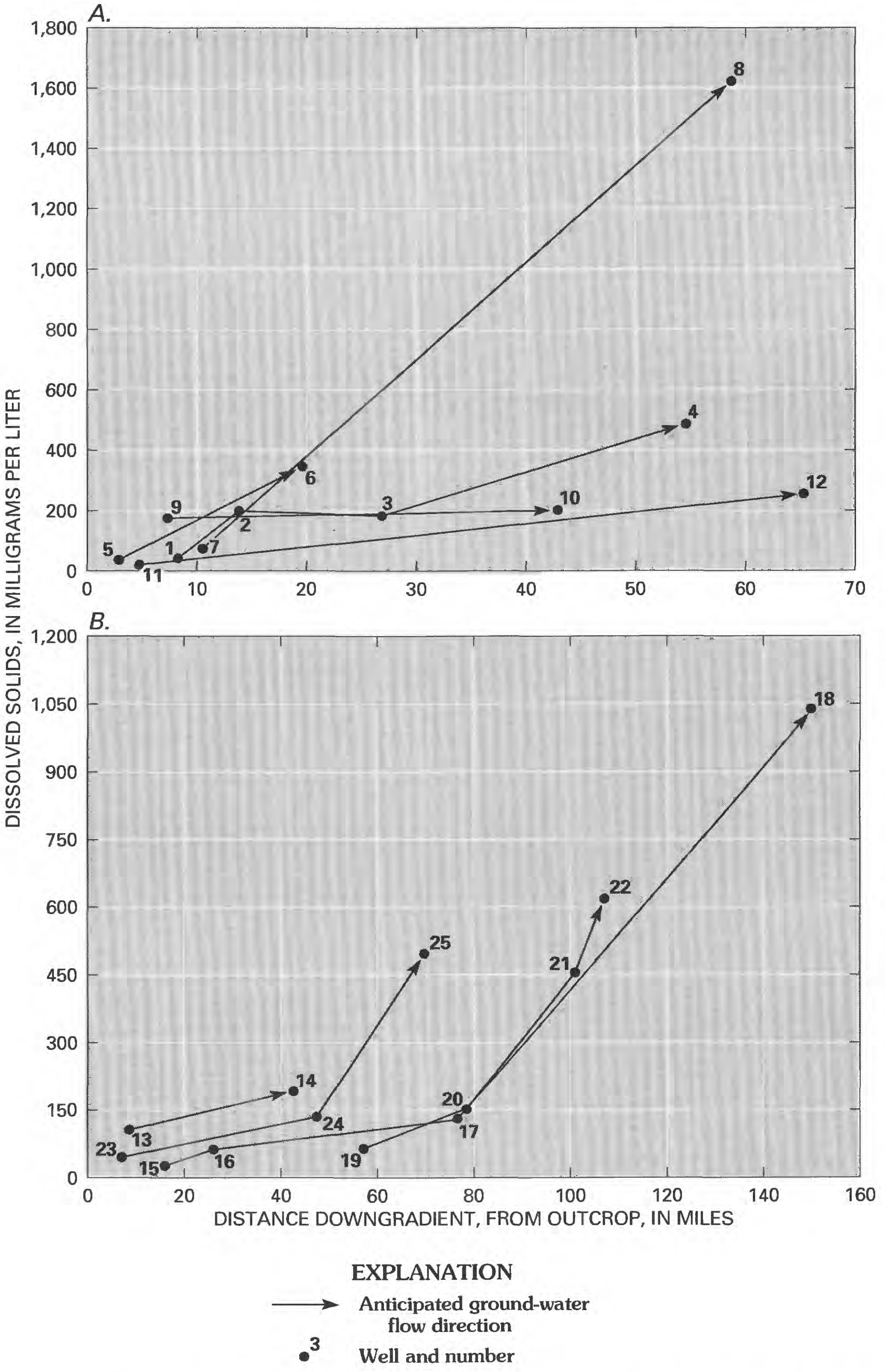


FIGURE 26.—Relation between dissolved solids and distance downgradient from outcrop areas for waters from the Chattahoochee River aquifer and equivalent aquifers in North Carolina. Location of wells shown in figure 23.

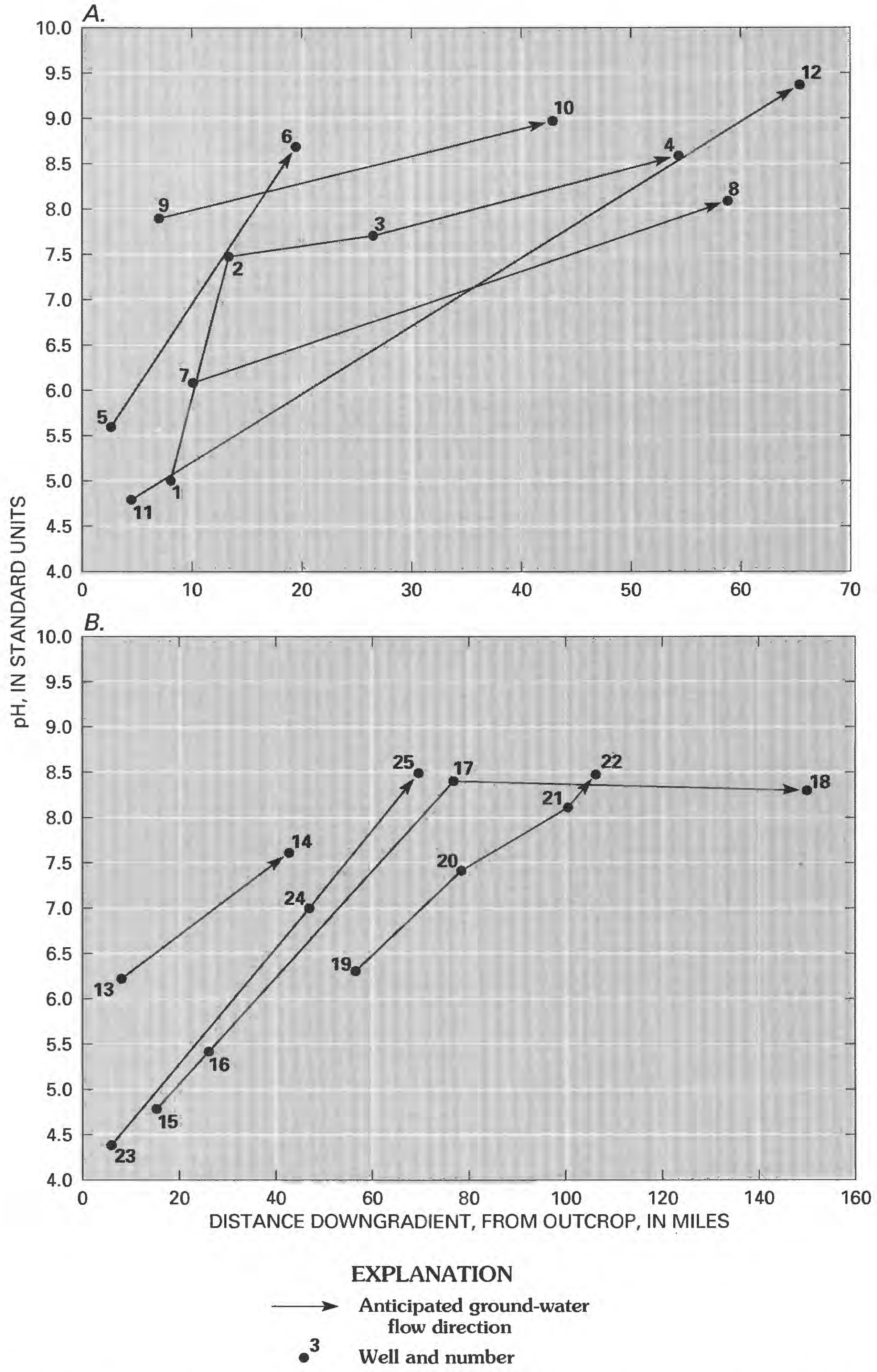


FIGURE 27.—Relation between pH and distance downgradient from outcrop areas for waters from the Chattahoochee River aquifer and equivalent aquifers in North Carolina. Location of wells shown in figure 23.

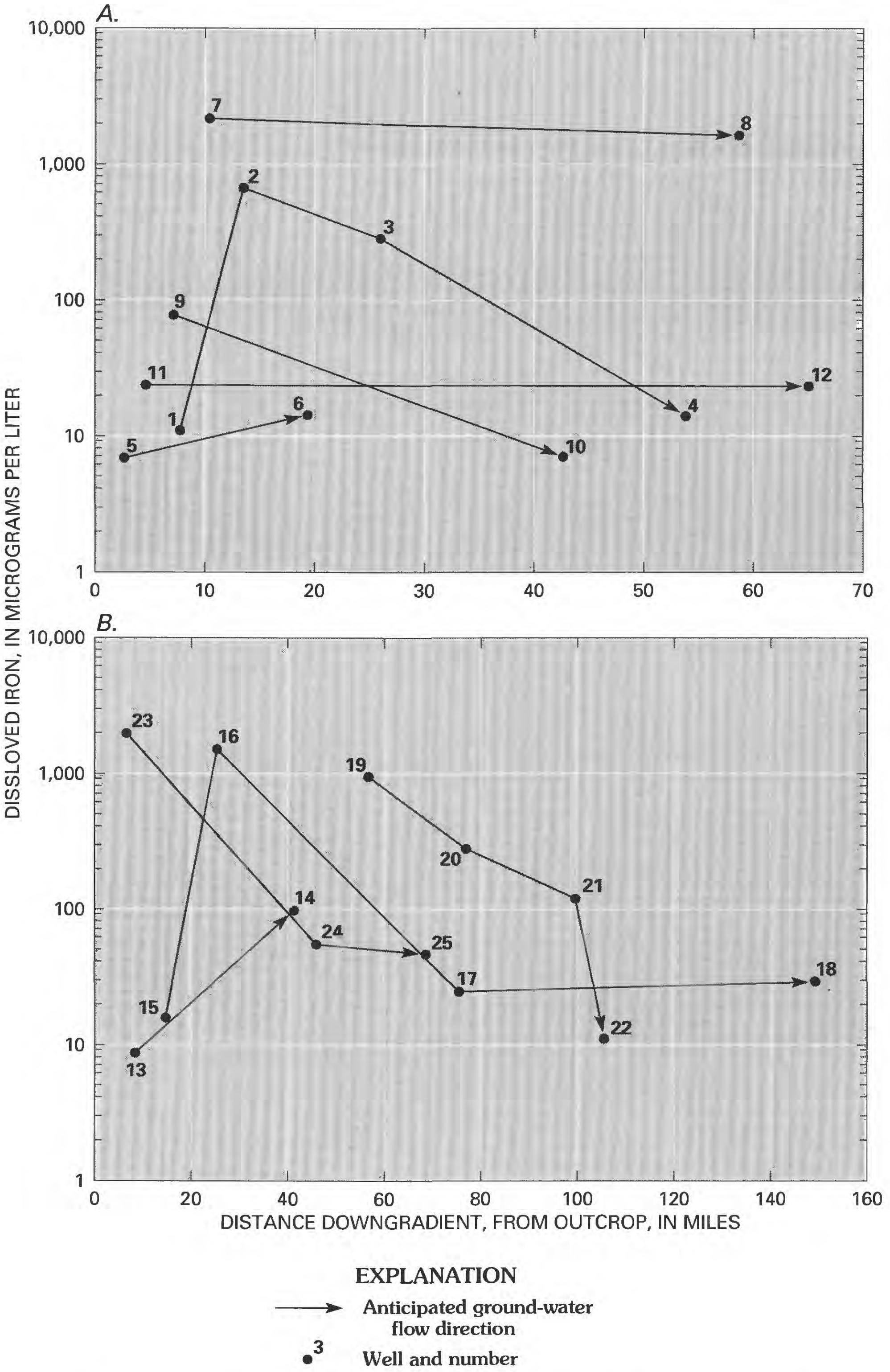


FIGURE 28.—Relation between dissolved iron and distance downgradient from outcrop areas for waters from the Chattahoochee River aquifer and equivalent aquifers in North Carolina. Location of wells shown in figure 23.

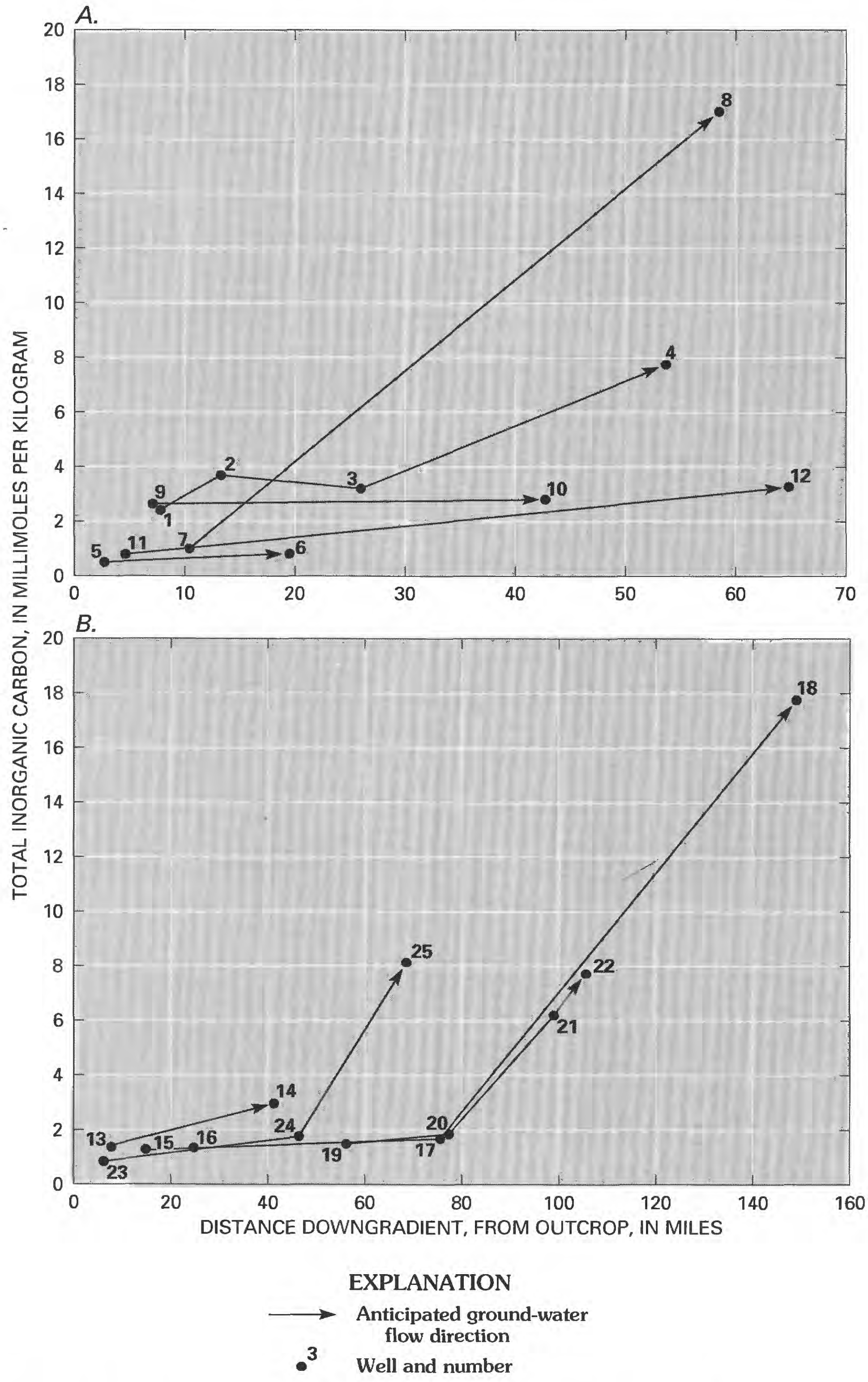


FIGURE 29.—Relation between total inorganic carbon and distance downgradient from outcrop areas for waters from the Chattahoochee River aquifer and equivalent aquifers in North Carolina. Location of wells shown in figure 23.

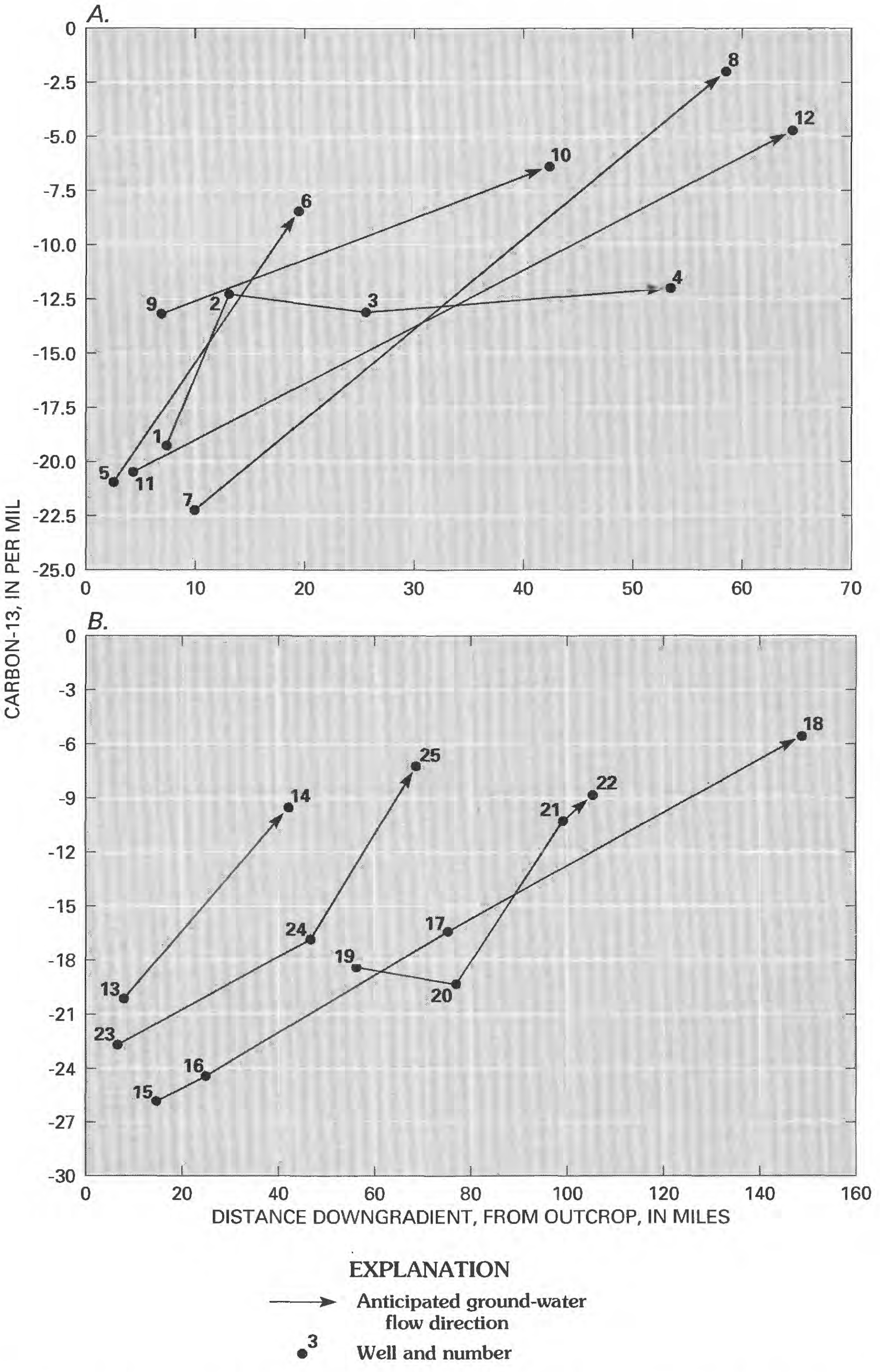


FIGURE 30.—Relation between carbon-13 and distance downgradient from outcrop areas for waters from the Chattahoochee River aquifer and equivalent aquifers in North Carolina. Location of wells shown in figure 23.

TABLE 23.—*Selected saturation indices of water from the Chattahoochee River aquifer and equivalent aquifers in North Carolina*

[Negative numbers indicate undersaturation, and positive numbers indicate oversaturation; dashes indicate mineral saturation index not calculated. Location of wells shown in fig. 23]

Well number/name	Albite	Calcite	Chalcedony	Dolomite	Pyrite	Goethite	Gypsum	Kaolinite	Sodium beidellite	Siderite	Quartz
1. Mathis	−7.02	−5.51	0.04	−11.17	—	−5.76	—	−0.75	−2.45	−5.72	0.56
2. Walnut Standby	—	.10	.21	−.67	—	3.59	−2.54	—	—	.04	.73
3. Ashland	—	.19	.06	−.37	18.1	3.95	−2.45	—	—	.13	.55
4. Byhalia	—	−.05	−.19	−.45	18.2	5.46	−4.36	—	—	.39	.29
5. McArthur	−7.23	−4.75	−.49	−9.72	8.59	−3.93	—	.30	−1.96	−5.29	.02
6. Bowden Flowing	—	.08	−.11	−1.39	17.56	5.17	−1.80	—	—	−1.41	.40
7. Ellaville	−2.86	−2.93	.26	−6.47	12.94	.25	−3.02	4.65	4.42	−1.57	.76
8. Albany TW-1	.33	.10	−.10	.06	18.60	5.80	—	3.25	2.87	1.58	.40
9. Green Store	−1.89	.10	.14	−.37	14.20	3.96	−2.72	1.59	1.33	−.57	.64
10. Ozark	−1.98	.16	−.24	.13	16.68	5.04	−3.66	−.77	−1.71	−1.74	.25
11. Breeland	−8.31	−6.33	−.37	−12.62	6.33	−5.63	—	−1.19	−3.82	−6.03	.14
12. Albany TW-10	−1.60	.20	−.26	−.21	17.88	5.16	−4.13	−.93	−1.85	−2.37	.24
13. Clayton	—	−2.49	.01	−6.23	11.24	−2.13	−3.95	—	—	−3.82	.52
14. Newton	—	.12	.06	−.37	16.52	3.47	−2.41	—	—	−.61	.55
15. Huber-2	−8.10	−6.59	−.13	−13.18	6.58	−6.18	−4.61	−1.41	−3.85	−6.24	.38
16. Stevens-1A	−3.80	−4.19	.28	−9.01	—	−2.19	−3.22	3.67	3.02	−2.81	.78
17. King Finishing−1	—	−.03	−.12	−.61	—	5.26	−3.33	—	—	−.65	.36
18. USMC−1	−1.31	.02	−.17	−.42	17.29	5.86	−5.51	−.67	−1.59	.44	.26
19. Rowland-2	—	−2.62	.004	−5.90	—	.24	−3.60	—	—	−1.55	.52
20. Marion−1	.30	−1.89	.41	−4.36	—	2.43	−4.50	4.65	4.88	−1.33	.92
21. Britton's Neck−4	−.46	−.61	.14	−1.59	17.48	4.81	−3.76	1.70	1.35	.17	.63
22. Conway	−1.06	−.13	−.14	−.50	17.17	4.97	−4.07	.26	−.56	−.49	.35
23. Laurinburg	−8.33	—	−.22	—	—	−5.24	−3.78	−2.42	−5.23	—	.30
24. Marion−2	—	−2.07	.45	−4.46	—	1.78	−5.22	—	—	−1.15	.95
25. Britton's Neck−5	−1.08	.05	.00	—	17.95	5.53	—	.10	−.50	.14	.50

Carolina (fig. 23) shows various degrees of saturation for the major mineral phases where considered (table 23). Calcite and dolomite are well undersaturated in recharge areas. Calcite saturation is attained downgradient in all wells; however, dolomite saturation is attained in waters from wells 8 and 10 only. Siderite saturation is attained in places, although pyrite or some iron sulfide phase, which is well oversaturated where considered, appears to control iron solubility in the deeper, downgradient parts of the aquifer. Quartz is either saturated or oversaturated in all wells, whereas chalcedony varies from undersaturated to slightly oversaturated, indicating that the control of silica solubility varies in the aquifer between chalcedony and quartz. Albite is undersaturated in all wells except wells 8 and 20, where it is slightly oversaturated. Kaolinite and sodium beidellite saturation states vary widely throughout the aquifer and may not be fully representative of mineral dissolution or precipitation, owing to uncertainties in the thermodynamic data of these minerals. Gypsum is undersaturated in all wells.

MASS BALANCE

Mass-balance reaction coefficients for water from wells in the Chattahoochee River aquifer (fig. 23) are shown in table 24. The calculations indicate that calcite, gypsum, and halite, where present, would be dissolved as lignite is consumed in oxidation-reduction processes, although the reaction model indicates that a small amount of calcite should precipitate from well 2 to well 3. Ground water may lose carbon dioxide gas from well 15 to well 16. Siderite and pyrite, where considered, appear to precipitate from solution, although pyrite precipitation is more prominent in the deeper, downgradient parts of the Chattahoochee River aquifer and in water from well 19 to well 22 and from well 23 to well 25 in the North Carolina-South Carolina area. Significant albite weathering to kaolinite is limited to upgradient areas such as from well 19 to well 20. Authigenesis of sodium beidellite at the expense of chalcedony and amorphous aluminosilicates appears to occur downgradient.

The mass-balance model further indicates that carbonic acid dissolution of calcite coupled with sodium-for-

TABLE 24.—*Reaction coefficients resulting from mass-balance calculations for water in flow paths between wells in the Chattahoochee River aquifer and equivalent aquifers in North Carolina*

[In millimoles per kilogram of water. Positive values indicate dissolution, and negative values indicate precipitation; dashes indicate mineral not used in mass balance. Values in parentheses are δ ^{13}C used in mass balance for the respective mineral. Location of wells shown in fig. 23]

Well number/name	Albite	Calcite	Chalcedony	Kaolinite	Amorphous alumino-silicate	Sodium beidellite	Goethite	Siderite	Lignite	Gypsum	Pyrite	Ca-Na exchange	Halite	Mg-Na exchange	Dolomite	CO_2
1. Mathis																
	0.1	1.4(0.0)	0.01	0.0	—	—	0.3	−0.3(−15.0)	0.1(−22.0)	—	—	0.0	—	—	—	—
2. Walnut Standby																
	—	−.1(−12.0)	1.06	—	0.85	−0.73	.53	−.54(−10.0)	.13(−22.0)	0.03	—	.25	0.009	—	—	—
3. Ashland																
	—	2.4(0.0)	6.73	—	5.94	−5.10	.63	—	2.37(−22.0)	1.23	−0.63	4.79	—	—	—	—
4. Byhalia																
5. McArthur																
	—	.62(0.0)	2.18	—	1.78	−1.53	1.65	−1.65(−20.0)	1.28(−22.0)	1.27	—	1.53	1.46	—	—	—
6. Bowden Flowing																
7. Ellaville																
	—	15.87(−.50)	72.45	—	63.24	−54.2	.22	−.18(−15.0)	.23(−22.0)	—	−.05	15.98	12.43	—	—	—
8. Albany TW-1																
9. Green Store																
	—	2.07(0.0)	14.60	—	12.85	−11.03	2.41	−2.41(−12.0)	.60(−22.0)	.02	—	2.75	.08	0.16	—	—
10. Ozark																
11. Breeland																
	—	2.52(0.0)	1.81	—	5.91	−5.07	.10	−.10(−19.0)	.03(−22.0)	.08	—	2.59	.05	—	—	—
12. Albany TW-10																
13. Clayton																
	—	1.20(−1.0)	1.40	—	4.55	−3.91	.11	−.1(−20.0)	.02(−22.0)	.10	—	.78	—	—	−0.23(−1.0)	—
14. Newton																
15. Huber-2																
	.16	.003(0.0)	.008	−.08	—	—	.03	—	.65(−23.0)	.06	—	−.04	.01	—	.02(0.0)	0.65
16. Stevens-1A																
	—	.65(0.0)	.36	—	.53	−.46	.90	−.91(−22.0)	.06(−22.0)	—	−.02	.60	.02	—	—	—
17. King Finishing-1																
	—	12.81(0.0)	49.68	—	43.14	−37.03	.79	—	3.18(−22.0)	1.53	−.79	14.51	.30	—	—	—
18. USMC-1																
19. Rowland-2																
	.63	.01(0.0)	−.77	−.32	—	—	.05	—	.24(−22.0)	.10	−.06	.14	.04	.004(0.0)	—	—
20. Marion-1																
	—	3.12(0.0)	2.85	—	10.95	−9.40	.35	—	1.32(−22.0)	.84	−.35	3.98	1.51	—	—	—
21. Britton's Neck-4																
	—	1.24(0.0)	1.87	—	1.79	−1.54	.09	—	.21(−22.0)	.04	−.09	1.29	3.58	—	—	—
22. Conway																
23. Laurinburg																
	.40	.49(0.0)	−.29	−.20	—	—	.09	—	.53(−22.0)	—	−.12	.27	—	.02	—	—
24. Marion-2																
	—	5.23(0.0)	6.06	—	22.07	−18.95	.32	—	1.19(−22.0)	.62	−.32	5.62	.87	.18	—	—
25. Britton's Neck-5																

calcium cation exchange is apparently the dominant process affecting water chemistry in the Chattahoochee River aquifer. Oxidation of organic carbon to carbon dioxide also appears to drive the process in the deeper, downgradient parts of the aquifer. However, reaction coefficients for water from well 7 to well 8, from well 12 to well 18, and from well 24 to well 25 (table 24) appear to be excessive. The relative lengths of the flow paths may justify such large coefficients. However, it is likely that other chemical processes (such as methanogenesis producing carbon dioxide, which would be relatively heavy in carbon-13 ($\delta^{13}C$ CO_2=0.0 to -4.0 ‰)) are occurring, as reported in a sand aquifer of similar age in Maryland (Chappelle and Knobel, 1985). Further study of this phenomenon is necessary to resolve this issue.

REACTION ZONES

It is clear that the Chattahoochee River aquifer and equivalent aquifers in North Carolina contain a water-bearing zone represented by both calcareous and noncalcareous sand aquifer models (figs. 31*A*–31*C*). The reaction models of water in flow paths from well 1 through well 4, from well 19 through well 22, and from well 23 through well 25 (fig. 23) represent calcareous sand in their respective parts of the Chattahoochee River aquifer, demonstrating the influence of calcite on the aquifer chemistry. Water in flow paths from well 5 to well 6, from well 7 to well 8, from well 9 to well 10, from well 11 to well 12, from well 13 to well 14, and from well 15 through well 18 represent sand aquifers that are noncalcareous or relatively low in calcareous material. Although most of the wells are from reaction zones A through C, wells 8 and 18 probably are from zone D, where the processes of calcite dissolution and sodium-for-calcium cation exchange are extensive, producing the high concentrations of sodium and bicarbonate ions in ground water. Water in zone E is not represented by the well samples, although wells 8 and 18, which contain significant amounts of chloride, could represent a transition from zone D to zone E.

CARBON-14 AGE AND GROUND-WATER FLOW VELOCITY

Table 25 shows adjusted ages of ground water in the Chattahoochee River aquifer and equivalent aquifers in North Carolina as great as 30,400 YBP (well 17, fig. 23). Incremental velocities from well 15 to well 16 and from well 19 to well 20 appear to be excessively high at 78 and 163 ft/yr, respectively, and should not be considered as representative of ground-water flow velocity in the aquifer. Reasonable velocities ranging from 1.6 to 23 ft/yr and averaging about 13 ft/yr were estimated elsewhere. Ground-water velocities in the aquifer calculated from regional ground-water modeling parameters range from 0.01 to 40 ft/yr, with a mean of 10 ft/yr (R.A. Barker, U.S. Geological Survey, written commun., 1986), which compares favorably with the velocities determined by carbon-14 dating. The mean velocity determined by

TABLE 25.—*Radiocarbon ages and flow velocities of ground water in the Chattahoochee River aquifer and equivalent aquifers in North Carolina*

[YBP, years before present; ft/yr, feet per year. Dashes indicate no data. Location of wells shown in fig. 23]

Well number (Flow path)	Unadjusted age (YBP)	Adjusted age (YBP)	Adjusted flow rate (ft/yr)
1	1,200	1,200	34.8
(1→2)	(10,000)	(6,100)	(4.6)
2	11,200	7,300	9.5
(2→3)	(3,600)	(3,300)	(20.7)
3	14,800	10,600	13.1
(3→4)	(16,000)	(8,600)	(17.1)
4	30,800	19,200	14.8
5	5,000	5,000	2.6
(5→6)	(16,900)	(4,900)	(18.0)
6	21,900	9,900	10.2
7	8,600	8,600	6.2
(7→8)	(>32,400)	(>9,500)	(<26.9)
8	>41,000	>18,100	<17.1
9	20,000	20,000	1.8
(9→10)	(20,000)	(14,100)	(13.1)
10	40,000	24,100	9.2
11	600	600	53.2
(11→12)	(28,100)	(16,600)	(19.0)
12	28,700	17,200	19.7
13	1,400	1,400	30.5
(13→14)	(31,800)	(25,500)	(6.9)
14	33,200	26,900	8.2
15	3,800	3,800	20.7
(15→16)	(4,200)	(700)	(78.4)
16	8,000	4,500	29.5
(16→17)	(26,000)	(23,400)	(1.6)
17	34,000	30,400	13.1
(17→18)	—	—	—
18	37,300	—	—
19	9,300	9,300	27.2
(19→20)	(1,600)	(700)	(163.1)
20	10,900	10,000	41.0
(20→21)	(19,600)	(9,400)	(12.1)
21	30,500	19,400	26.9
(21→22)	(3,200)	(1,500)	(22.6)
22	33,700	20,900	24.9
23	2,800	2,800	12.1
(23→24)	(26,500)	(20,400)	(10.5)
24	29,300	23,200	10.5
(24→25)	29,300	—	—
25	—	—	—

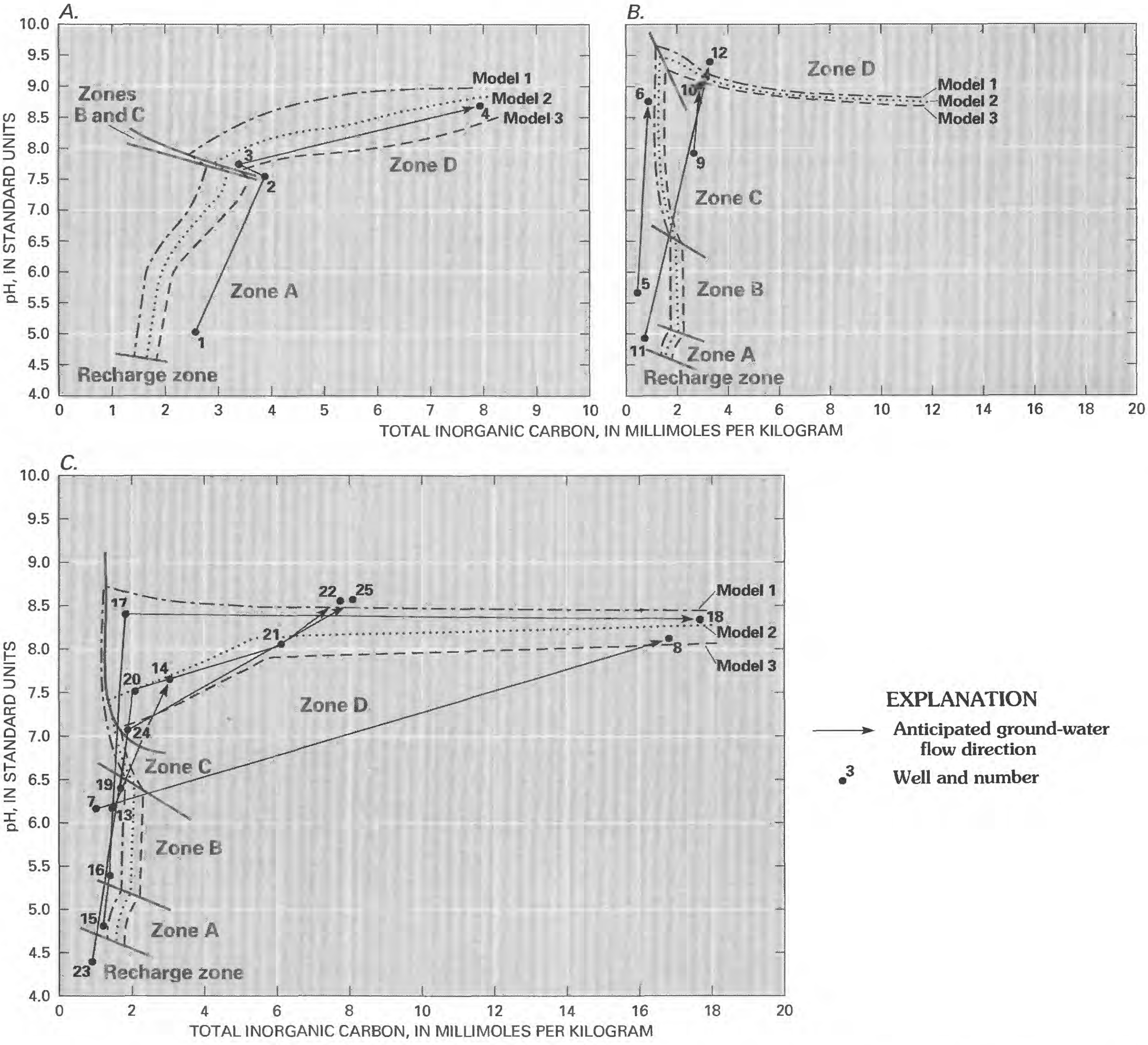


FIGURE 31.—Geochemical models of calcareous and noncalcareous sand aquifers constructed using chemical data from the Chattahoochee River aquifer and equivalent aquifers in North Carolina. Location of wells shown in figure 23.

Barker was calculated assuming a mean hydraulic conductivity of 10 ft/d, a mean hydraulic gradient of 4.3 ft/mi, and a porosity of 0.3.

GEOCHEMISTRY OF WATER IN THE PEARL RIVER AQUIFER

For discussion of water chemistry, the Pearl River aquifer is divided into three water-bearing zones—lower, middle, and upper. The lithology of the lower, middle, and upper water-bearing zones of the Pearl River aquifer varies from fine- to coarse-grained quartz sand, which may be glauconitic and fossiliferous, with thin beds of limestone or lignite in places. The aquifer is predominantly unconsolidated calcareous sand and clay deposited in a shallow marine environment. In parts of South Carolina, the aquifer contains dolomitic limestone. Some feldspar and mica also may be present in the sand.

LOWER WATER-BEARING ZONE

The lower water-bearing zone of the Pearl River aquifer extends westward from outcrops in Mississippi to the Mississippi River and southward to the downdip limit of permeability near the Gulf Coast of Mississippi (Renken, 1984). Some of this water-bearing zone is present in southwest Alabama, extending eastward to the Tombigbee River (pl. 5).

DISSOLVED SOLIDS

Dissolved-solids concentrations in the lower water-bearing zone are less than 100 mg/L near outcrop areas and increase to greater than 100,000 mg/L downgradient (pl. 5). A narrow lobe of slightly elevated concentrations (greater than 200 mg/L) occurs in Montgomery and Choctaw Counties in central Mississippi. An area of low concentrations in southern Choctaw and Winston Counties, Miss., may represent vertical chemical differences in water from different sands. The high concentrations (as much as 100,000 mg/L) in northern Perry County, Miss., probably are related to salt domes in the area. In Mississippi, a line of equal concentration showing the location of 1,000 mg/L dissolved solids as sodium chloride, derived from geophysical data of Gandl (1982), has been used to supplement chemical data.

In southern Georgia and parts of South Carolina, most wells are completed in the Floridan aquifer system and generally do not penetrate the deeper Pearl River aquifer. Consequently, chemical data are not available for water in the Pearl River aquifer in this part of the Southeastern Coastal Plain.

DISSOLVED CHLORIDE

Dissolved-chloride concentrations in waters of the lower water-bearing zone generally are less than 100 mg/L upgradient (pl. 5). Concentrations increase from recharge areas to the west and south, to greater than 100 mg/L in Grenada and Carroll Counties, northern Mississippi, and Wayne County, southeastern Mississippi. An area in Forrest and Perry Counties in southern Mississippi has concentrations that exceed 100,000 mg/L due to salt domes in the area.

DISSOLVED IRON

Dissolved-iron data are sparse but evenly distributed for the lower water-bearing zone in Mississippi (pl. 6). The general downgradient trends of increasing-decreasing-increasing concentrations are similar to those observed in other aquifers. Concentrations increase from less than 100 µg/L near recharge areas to greater than 1,000 µg/L in a band downgradient from, and nearly parallel to, the outcrop area. In Lauderdale County, Miss., dissolved iron was reported in excess of 10,000 µg/L. Concentrations decrease farther downgradient to less than 100 µg/L. Increasing salinity still farther downgradient has produced concentrations of dissolved iron greater than 1,000 µg/L due to chloride complexes of iron. In the salt dome area in Perry County, southeastern Mississippi, where salinities are high (dissolved solids greater than 100,000 mg/L), concentrations of dissolved iron exceed 10,000 µg/L.

HYDROCHEMICAL FACIES

Sodium bicarbonate facies dominates the lower water-bearing zone (pl. 6), except where calcium bicarbonate facies is dominant in recharge areas. Calcium bicarbonate predominance in isolated areas in central Mississippi may be due to leakage from the overlying water-bearing zones of the aquifer into the lower water-bearing zone. The areas of sodium chloride facies in western and southern Mississippi are the result of saline waters present in the lower water-bearing zone, or reflect the influence of salt domes.

MIDDLE WATER-BEARING ZONE

The middle water-bearing zone of the Pearl River aquifer extends from continuous outcrops in Mississippi, Alabama, Georgia, and South Carolina to downdip units defined by the Mississippi River to the west and the downdip limit of permeability to the south and east (Renken, 1984).

DISSOLVED SOLIDS

Dissolved-solids concentrations in the middle water-bearing zone are generally less than 500 mg/L in outcrop areas and increase in a downgradient direction (pl. 5). Concentrations are greater than 1,000 mg/L in Hinds and Rankin Counties, Miss., in Clarke and Marengo Counties, Ala., and in southern South Carolina. Concentrations greater than 1,000 mg/L in Clarke and Marengo Counties, Ala., are representative of water from the lower part of the middle water-bearing zone. Concentrations in Dougherty County, Ga., may have increased because of leakage from the underlying lower water-bearing zone. The slight increase in concentrations in Barnwell and Bamberg Counties, S.C., may have resulted from the occurrence of local vertical chemical variations in discrete sands of the McBean Formation or the Barnwell Formation. The paucity of data for southeastern Georgia required extrapolation of the dissolved-solids contours in order to provide areal descriptions.

DISSOLVED CHLORIDE

Concentrations of dissolved chloride in the middle water-bearing zone generally are less than 100 mg/L (pl. 5). Concentrations exceed 100 mg/L near Jackson, Miss., and in western Wilcox County, Ala. South of Charleston, S.C., concentrations exceed 1,000 mg/L, probably as a result of mixing with saline water in the aquifer. In southeastern Alabama, concentrations that exceed 10,000 mg/L may be due to mixing of freshwater with brines already present in the aquifer or to upward leakage of saline ground water from underlying aquifers.

DISSOLVED IRON

Concentrations of dissolved iron in the middle water-bearing zone generally are less than 100 µg/L near recharge areas (pl. 6). In parts of the zone, concentrations increase downgradient owing to reducing conditions that increase solubility of iron. Concentrations greater than 1,000 µg/L occur in the area from Attala County northward to Panola County in north-central Mississippi, and more locally in east-central Georgia, and in Bamberg and Orangeburg Counties, S.C. Concentrations greater than 1,000 µg/L near Jackson, Miss., likely are due to the higher salinity of the ground water and the formation of aqueous iron chloride complexes. Few data are available for the downgradient parts of Alabama and Georgia, and the 100 µg/L line of equal concentration is inferred over most of this part of the study area.

HYDROCHEMICAL FACIES

In most of the recharge areas of the middle water-bearing zone, ground water is dominated by calcium bicarbonate facies (pl. 6). In eastern Alabama, Georgia, and parts of South Carolina, calcium bicarbonate facies also dominates in downgradient areas. Downgradient from the recharge areas in Mississippi and western Alabama, the deeper waters are dominated by sodium bicarbonate facies. Sodium bicarbonate facies probably also dominates extreme downgradient areas in southern Georgia; however, no data are available to substantiate this assumption. In a small area of Calhoun, Dougherty, and Baker Counties in southwestern Georgia, sodium bicarbonate facies dominates, indicating either upward leakage from the underlying lower water-bearing zone of the Pearl River aquifer of a sodium bicarbonate water, or local differences in the mineralogy of the aquifer sediments. Variable or no dominant facies occurs locally near recharge areas in Mississippi and western South Carolina where concentrations of dissolved solids are low. The occurrence of sodium chloride facies near Charleston, S.C., probably is the result of the presence of residual seawater in this zone.

TRACE ELEMENTS

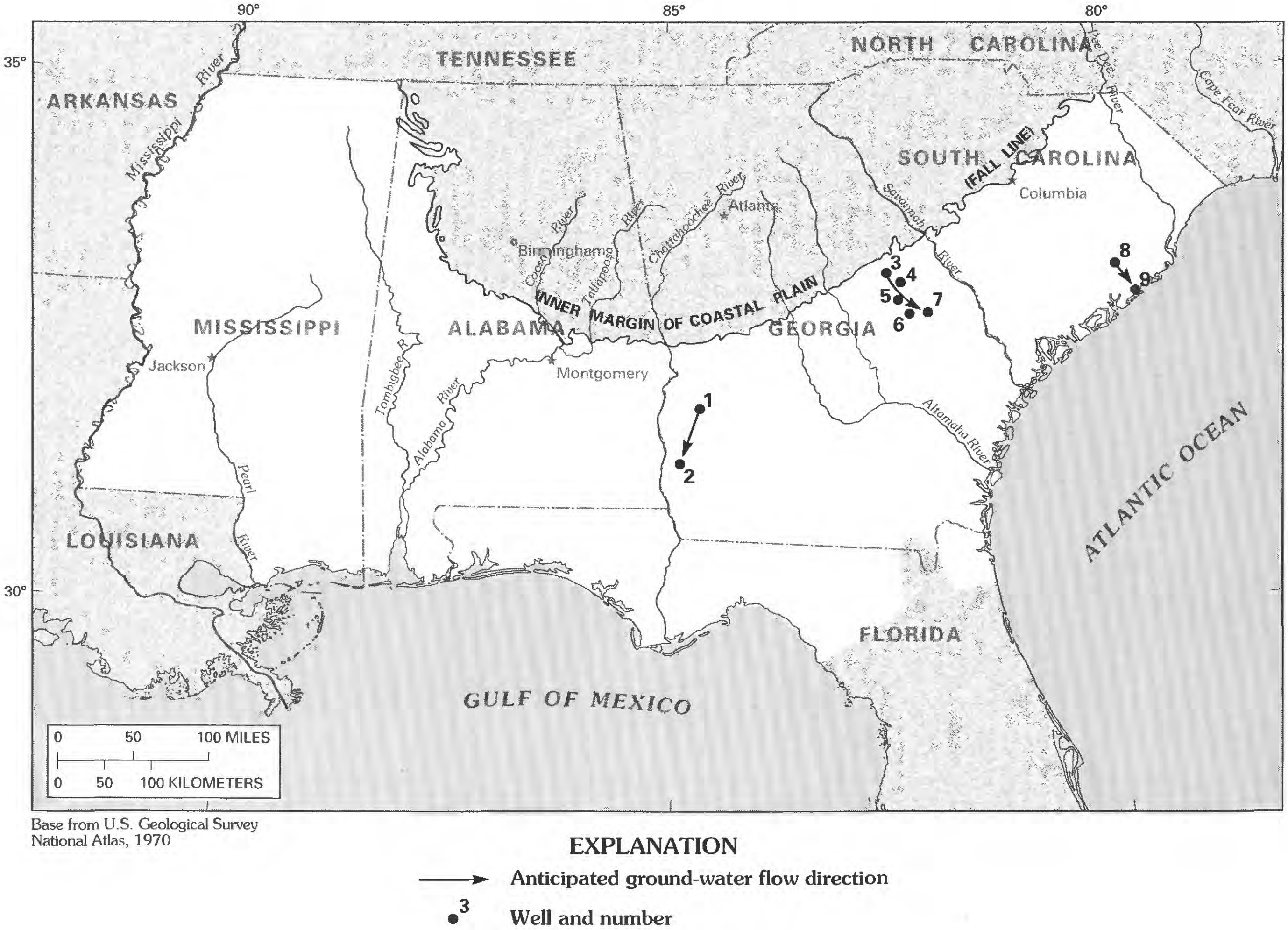
Chemical data for the middle water-bearing zone were collected from nine wells in Georgia and South Carolina (fig. 32); the following discussion is restricted to these two States. In the middle water-bearing zone, trace element concentrations (table 26) generally are low, with some variability. Concentrations of dissolved iron are low in most places, except in water from well 5 (1,200 µg/L) and well 6 (1,900 µg/L). Aluminum concentration is as great as 400 µg/L (well 5), but is 100 µg/L or less in most places. Strontium was detected in water from all wells sampled, with the greatest concentration, 360 µg/L, in well 2. Lead is 10 µg/L or less in all but well 1, which contains water with 20 µg/L of lead. Boron, although present in water samples from wells 8 and 9 in concentrations of 100 and 380 µg/L, respectively, generally is less than 50 µg/L.

DISSOLVED GASES

Dissolved gases in water from the nine wells in the middle water-bearing zone (fig. 32) show typical changes along flow paths (table 26). Dissolved oxygen is measurable in wells 3 and 4 at 9.0 and 3.1 mg/L, respectively, but typically decreases downgradient (see wells 3 through 7, table 26). Carbon dioxide concentrations decrease downgradient from well 1 to well 2 and from well 8 to well 9, but increase from 31 mg/L in well 3 to 44 mg/L in well 4. Concentrations then decrease from well 4 through well 7. Methane was not significant in any of the samples, although 0.06 mg/L was reported in water from well 9.

ENVIRONMENTAL ISOTOPES

Analysis of environmental isotopes in water from the nine wells penetrating the middle water-bearing zone (fig. 32) shows typical trends (table 26). Tritium is highest (280 pCi/L) at well 3 near the outcrop area, but diminishes downgradient. Tritium activities of 20 and 16 pCi/L in water from wells 4 and 8, respectively, indicate them to be near recharge areas. Carbon-13 ratios generally increase downgradient in the aquifer. For example, well 3, a recharge area well, contains water with a carbon-13 ratio of −25.4 ‰, whereas well 9, downgradient, contains water with a carbon-13 ratio of −4.6 ‰. Deuterium ratios range from −27.5 ‰ in well 4 to −15 ‰ in well 9. Oxygen-18 ratios range from −4.6 ‰ in wells 3, 4, and 7 to −3.3 ‰ in wells 8 and 9. The deuterium and oxygen-18 ratios generally plot along the meteoric water line (fig. 33), indicating that the source of recharge is areal precipitation. Carbon-14 values decrease downgradient, from as high as 100 PM in well 3 to as low as 2.05 PM in well 9.



Base from U.S. Geological Survey
National Atlas, 1970

FIGURE 32.—Location of wells sampled for the middle water-bearing zone of the Pearl River aquifer.

CHEMICAL EVOLUTION

Chemical analysis of water from wells in the middle water-bearing zone (fig. 32, table 27) shows trends along flow paths from well 1 to well 2 and from well 8 to well 9 (fig. 34). Near recharge areas, the waters are predominantly calcium bicarbonate hydrochemical facies, as a result of the calcareous nature of the aquifer, but downgradient, the waters evolve to sodium bicarbonate facies. The water evolves from variable or no dominant facies at well 3, to a calcium bicarbonate facies downgradient at well 7, again indicating the calcareous nature of the aquifer. The evolution to a sodium bicarbonate facies observed along other flow paths does not occur at well 7, but might occur farther downgradient.

Chemical constituents show some unusual trends for the middle water-bearing zone of the Pearl River aquifer. Although concentrations of dissolved solids generally increase downgradient, the concentration decreases in water from well 1 to well 2 (fig. 35*A*). However, the calculated concentration of dissolved solids in water from well 2 (180 mg/L) differs from the measured value obtained from residue on evaporation at 180 °C for the water sample from well 2 (170 mg/L), indicating a possible analytical error. The pH increases downgradient (fig. 35*B*), although the increase from well 1 to well 2 is small. Concentrations of dissolved iron are generally low (fig. 35*C*), but increase to greater than 1,000 μg/L in wells 5 and 6 before decreasing to less than 100 μg/L in well 7 farther downgradient. Total inorganic carbon increases in water from wells 3 through 7 and from well 8 to well 9, but decreases slightly from well 1 to well 2 (fig. 35*D*). An overall trend from lighter carbon-13 ratios in water near recharge areas to heavier carbon-13 ratios is observed along all three flow paths (fig. 35*E*). The water from wells 3 through 7 contains lighter carbon-13 ratios than the waters from wells 1, 2, 8, and 9.

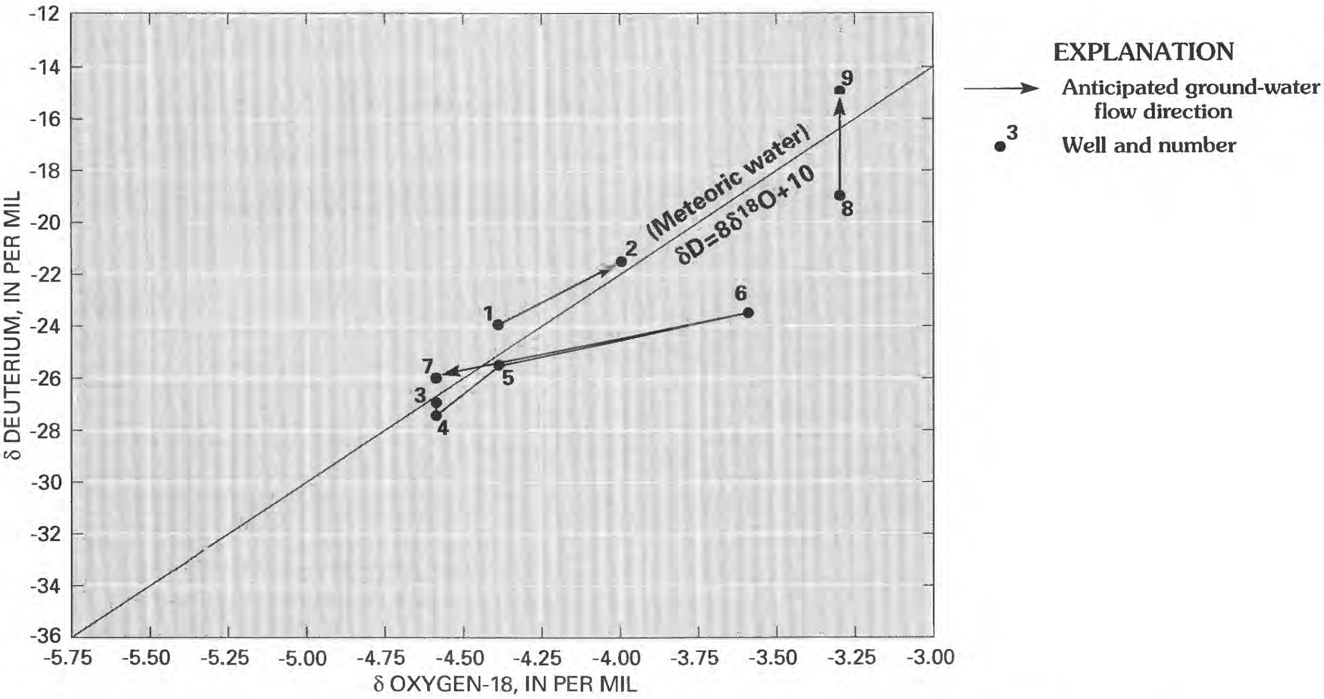


FIGURE 33.—Relation between deuterium (δD) and oxygen-18 ($\delta^{18}O$) in water from the middle water-bearing zone of the Pearl River aquifer. Location of wells shown in figure 32.

MINERAL EQUILIBRIUM

Saturation states of major minerals in water in the nine wells in the middle water-bearing zone (fig. 32) indicate possible mineral phases involved in dissolution and precipitation processes (table 28). Calcite is at saturation in water from wells 1, 2, and 8, but is undersaturated in water in upgradient areas. Water is undersaturated with respect to calcite at well 3 but attains saturation at well 7 downgradient. Although dolomite precipitation is highly unlikely, dolomite is saturated in water from wells 2, 8, and 9. Siderite is undersaturated in all samples, although saturation is approached in wells 2, 6, and 9. Gypsum is well undersaturated, chalcedony is near saturation or slightly oversaturated, and quartz is oversaturated in all wells. Albite, where considered, is undersaturated. Kaolinite and sodium beidellite are generally well oversaturated except for water from well 3, which is undersaturated for all minerals considered, except quartz.

MASS BALANCE

Reaction models for the three flow paths in the middle water-bearing zone (fig. 32) suggest that similarities exist for chemical evolution of water from well 1 to well 2, from well 3 through well 7, and from well 8 to well 9 (table 29). Water in upgradient, recharge parts of the zone dissolves calcite and hydrolyzes albite to kaolinite. From well 6 to well 7, the chemical processes of calcite dissolution and sodium-for-calcium cation exchange occur as siderite precipitates and carbon dioxide is produced from lignite. The latter description also applies to water from well 1 to well 2, although the reaction coefficients are considerably greater. Water from well 8 to well 9, known to be in a dolomitic limestone aquifer, is characterized by incongruent dissolution of dolomite (with calcite precipitation) and some sodium-for-magnesium cation exchange. The chemistry of water from well 8 to well 9 appears to be more closely related to waters in the overlying Floridan aquifer system (Plummer and others, 1983) than to waters in the sands of the Southeastern Coastal Plain aquifers.

REACTION ZONES

Ground-water chemistry from well 3 to well 7 in the middle water-bearing zone (fig. 32) resembles the PHREEQE model for a slightly calcareous sand aquifer (fig. 36). Reaction zones A through C represent chemical evolution of water from well 3 to well 6, with well 7 at the beginning of reaction zone D. Waters from well 1 and well 2 appear to be in reaction zones C and D for a calcareous sand aquifer, although the pH values are much higher in the samples than in the model. The loss of total inorganic carbon from the aqueous phase may be due to degassing of carbon dioxide rather than siderite

TABLE 26.—*Trace elements, dissolved gases, and environmental isotopes of water from the middle water-bearing zone of the Pearl River aquifer*

[In micrograms per liter, unless otherwise specified. pCi/L, picocuries per liter; ‰, per mil; PM, percent modern carbon; negative values for isotopes indicate relatively light content; mol/kg, moles per kilogram. Location of wells shown in fig. 32]

Well number/name	Al	Ba	B	Cd	Cu	Fe	Pb	Li	Mn	Hg	Sr	Zn	N_2[1]	O_2[1]	CO_2[1]	CH_4[1]	Ar[1]	T (pCi/L)	$\delta^{13}C$ (‰)	δD (‰)	$\delta^{18}O$ (‰)	^{14}C (PM)	ΣCO_2 (mol/kg×10^{-3})
1. Weston	20	24	20	1	<10	10	20	6	<1	<0.1	98	28	25	0.09	9.6	0.0	0.94	3	−9.1	−24	−4.4	27.2	3.04
2. Singletary-Bancroft	10	11	50	<1	<10	50	<10	9	5	<.1	360	<4	23	.03	1.4	.01	.91	<1	−6.3	−21.5	−4	4	2.63
3. Gibson-3	100	20	<10	3	<10	130	10	4	19	<.1	9	26	19	9.0	31	.0	.77	280	−25.4	−27	−4.6	100	1.0
4. Thiele	100	10	<10	<1	<10	7	10	4	<1	<.1	63	81	22	3.1	44	.0	.87	20	−19.1	−27.5	−4.6	83	1.47
5. Stevens-4	400	20	10	<1	<10	1,200	<10	8	37	<.1	61	7	22	.2	42	.0	.84	3	−19.1	−25.5	−4.4	33.4	1.66
6. Wadley-1	200	20	20	<1	<10	1,900	<10	5	130	<.1	150	<4	24	.02	18	.01	.92	2	−14.1	−23.5	−3.6	3.8	2.11
7. Midville	<10	8	30	3	<10	39	<10	5	18	<.1	240	<4	24	.2	4.1	.0	.97	0	−10.5	−26	−4.6	2.6	2.44
8. Monck's Corner	20	5	100	3	<10	9	<10	14	<1	<.1	290	5	25	.01	12	.02	.91	16	−7.7	−19	−3.3	3.55	4.43
9. Hodge	20	3	380	8	<10	8	<10	17	<1	.1	68	<4	24	.01	2.2	.06	.92	1	−4.6	−15	−3.3	2.05	4.87

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[1] Milligrams per liter; errors in laboratory data require interpretation with caution.

TABLE 27.—*Well data and chemical analyses of water from the middle water-bearing zone of the Pearl River aquifer*

[In milligrams per liter, unless otherwise specified. ft, feet; mi, miles; μs, microsiemens; ROE, residue on evaporation at 180 °C; TD, total depth. Location of wells shown in fig. 32]

Well number/name	Screened interval (ft)	Distance downgradient (mi)	Specific conductance (μS)	Temperature (°C)	pH (units)	Dissolved solids (ROE)	NH_4	Ca	Mg	Na	K	HCO_3	CO_3	Cl	SO_4	F	SiO_2
1. Weston	240–269	4.3	280	19.4	7.63	178	0.01	56	2.7	1.4	1.1	177	0	2.28	6.1	<0.01	19
2. Singletary-Bancroft	623–768	44.7	285	20.5	8.18	170	.14	19	6.2	29	3	161	0	2.68	9.2	.3	31
3. Gibson-3	203 (TD)	8.8	60	19.3	4.60	47	.05	.6	1.2	2.8	.22	1	0	6.26	.2	.1	9.6
4. Thiele	144–151	12.0	90	18.9	6.03	88	.08	11	.88	.3	.35	28	0	2.61	6.33	.15	32
5. Stevens-4	171–420	26.0	110	20.4	6.28	98	0	16	1.2	1.6	.57	46	0	2.21	6.85	.16	41
6. Wadley-1	371–472	34.8	174	21.0	6.98	148	0	33	2	2.3	1.8	105	0	2.22	6.55	.13	46
7. Midville	200–482	42.3	248	20.6	7.72	183	.04	47	2.7	3.5	2.3	144	0	2.14	8.86	.14	43
8. Monck's Corner	141–161	2.4	440	20.6	7.62	259	.24	32	20	2.7	13	258	0	21.2	3.55	1.19	27
9. Hodge	230–427	19.2	720	21.6	8.41	474	.79	4.5	3.9	160	16	291	5	108	9.36	1.64	34

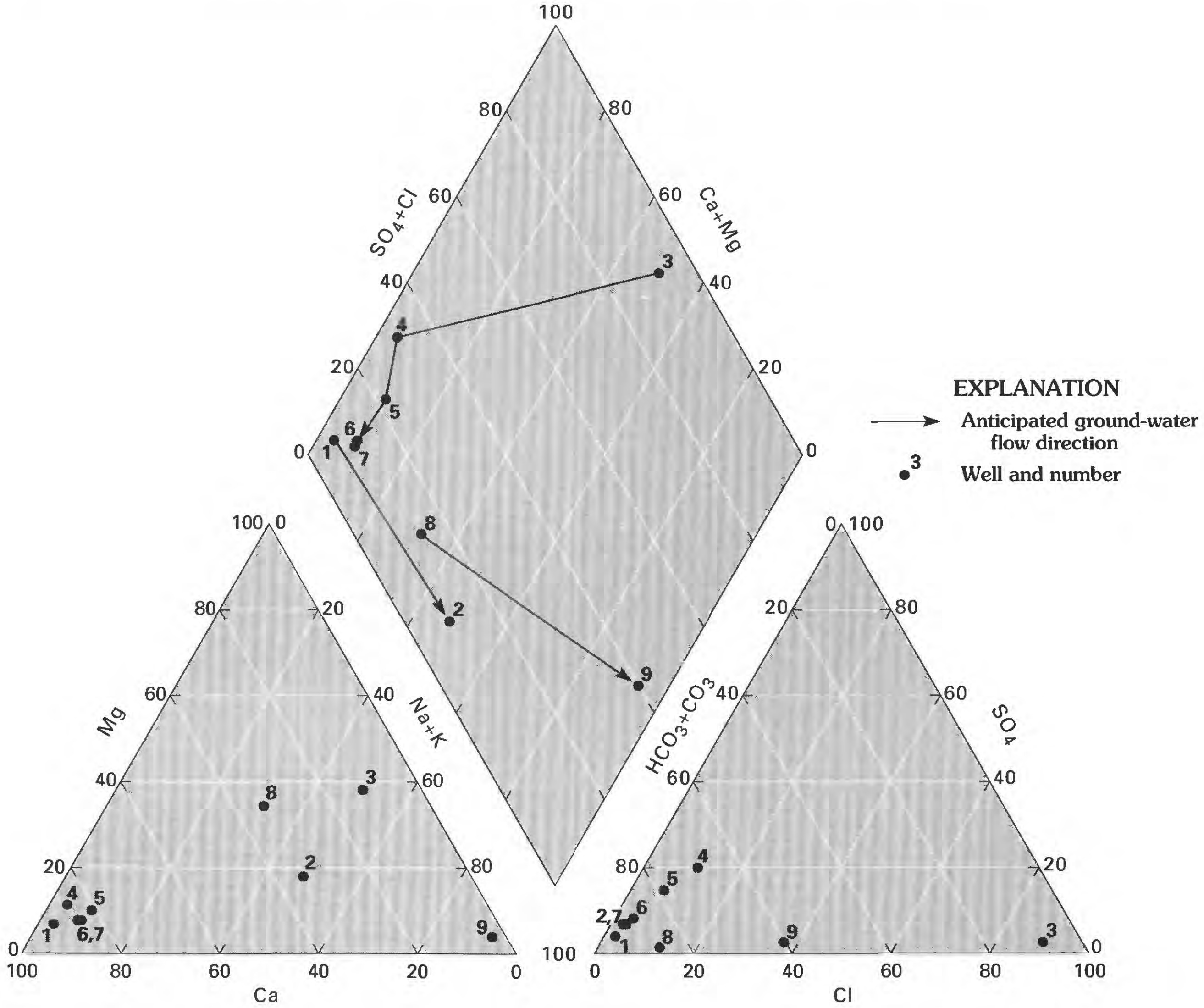

FIGURE 34.—Piper diagram showing evolution of water chemistry in the middle water-bearing zone of the Pearl River aquifer. Location of wells shown in figure 32.

precipitation in the aquifer. More study is needed to verify this observation.

Chemical reactions for water from well 8 to well 9 more closely resemble those in a limestone aquifer than those in a sand aquifer; therefore, they should not be considered typical of chemical evolution of water in the Pearl River aquifer.

CARBON-14 AGE AND GROUND-WATER FLOW VELOCITY

Table 30 shows adjusted ages of ground water in the middle water-bearing zone of up to 25,400 YBP (well 7, fig. 32). Ground-water velocities determined from carbon-14 age dating range from 3 to 34 ft/yr and average about 22 ft/yr. These velocities compare favorably with the velocities of 0.01 to 50 ft/yr and a mean velocity of 15 ft/yr determined from regional simulation of the ground-water flow system (R.A. Barker, U.S. Geological Survey, written commun., 1986). The average velocity was calculated from equation 6 using a mean hydraulic conductivity of 15 ft/d, a mean hydraulic gradient of 4 ft/mi, and a porosity of 0.3.

UPPER WATER-BEARING ZONE

The upper water-bearing zone of the Pearl River aquifer extends from outcrops in Mississippi westward to the Mississippi River and southward to the downdip limit of aquifer permeability (Renken, 1984) near the Gulf Coast. Some of this water-bearing zone is also present in southwest Alabama, extending eastward to the Tombigbee River (pl. 5).

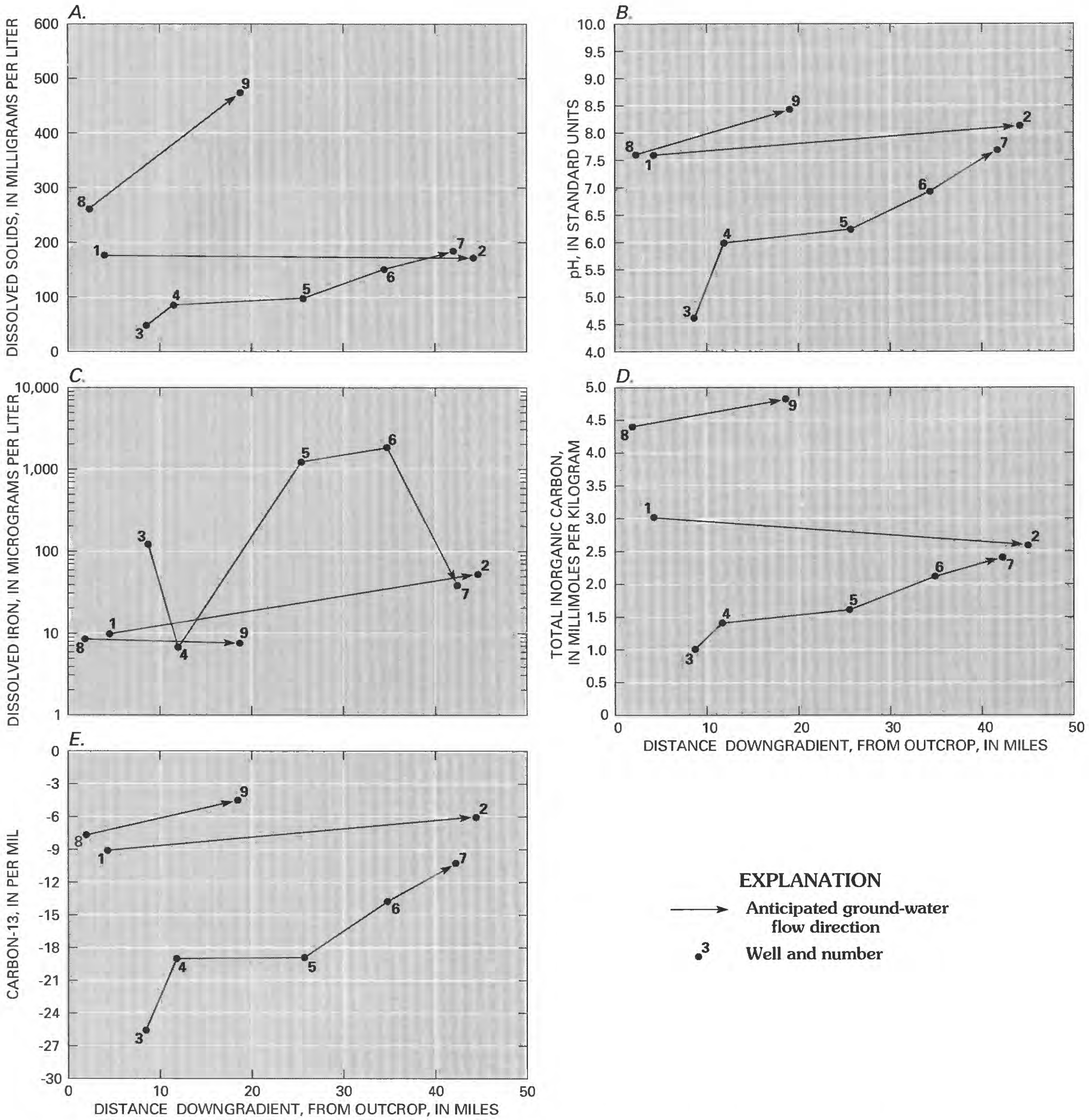

Figure 35.—Relation between selected chemical parameters and distance downgradient from outcrop areas for waters from the middle water-bearing zone of the Pearl River aquifer. Location of wells shown in figure 32.

DISSOLVED SOLIDS

Concentrations of dissolved solids in water in the upper water-bearing zone in Mississippi (pl. 5) increase from recharge areas toward downgradient areas, reaching concentrations of greater than 500 mg/L as a result of dissolution of aquifer minerals (Lee, 1985). An isolated area of low concentrations (less than 100 mg/L) near the city of Jackson, Miss., probably reflects vertical differences in concentrations in the zone, with most of the low values representing wells completed in the Cockfield Formation. Concentrations exceeding 11,000 mg/L occur

TABLE 28.—*Selected saturation indices of water from the middle water-bearing zone of the Pearl River aquifer*

[Negative numbers indicate undersaturation, and positive numbers indicate oversaturation; dashes indicate mineral saturation index not calculated. Location of wells shown in fig. 32]

Well number/name	Albite	Calcite	Chalcedony	Dolomite	Pyrite	Goethite	Gypsum	Kaolinite	Sodium beidellite	Siderite	Quartz
1. Weston	−3.13	0.12	0.09	−0.85	15.32	2.14	−2.50	1.86	1.60	−1.73	0.59
2. Singletary-Bancroft	−1.05	.18	.28	.11	17.54	4.55	−2.80	1.45	1.70	−.51	.78
3. Gibson-3	−8.83	−7.00	−.21	−13.48	—	−5.75	−4.61	−2.95	−5.79	−5.78	.30
4. Thiele	−3.89	−2.90	.32	−6.69	—	−2.79	−3.03	.393	3.61	−4.22	.83
5. Stevens-4	−1.67	−2.27	.41	−5.43	—	.28	−2.88	6.00	6.26	−1.49	.91
6. Wadley-1	−.87	−.92	.45	−2.83	—	2.59	−2.66	5.71	6.27	−.26	.95
7. Midville	—	.08	.43	−.86	—	3.08	−2.42	—	—	−1.11	.93
8. Monck's Corner	−1.12	.02	.23	.07	—	2.12	−3.04	2.74	2.70	−1.62	.73
9. Hodge	−.26	−.01	.30	.16	—	4.42	−3.49	.99	.89	−.88	.80

TABLE 29.—*Reaction coefficients resulting from mass-balance calculations for water in flow paths between wells in the middle water-bearing zone of the Pearl River aquifer*

[In millimoles per kilogram of water. Positive values indicate dissolution, and negative values indicate precipitation; dashes indicate mineral not used in mass balance. Values in parentheses are δ ^{13}C used in mass balance for the respective mineral. Location of wells shown in fig. 32]

Well number/name	Albite	Calcite	Chal-cedony	Kaolinite	Amorphous alumino-silicate	Sodium beidellite	Goethite	Siderite	Lignite	Gypsum	Pyrite	Ca-Na exchange	Halite	Mg-Na exchange	Dolomite	CO_2
1. Weston																
	—	2.07(0.0)	5.49	—	18.12	−15.55	3.68	−3.68(−8.5)	0.92(−22)	0.03	—	3.16	0.01	—	0.14(0.0)	—
2. Singletary-Bancroft																
3. Gibson-3																
	0.014	.19(2.0)	.34	−0.01	—	—	—	—	.02(−22)	.06	—	.01	—	—	—	0.56(−18.0)
4. Thiele																
	.03	.13(0.0)	.08	−.01	—	—	.02	—	.01(−22)	.01	—	.02	—	—	.013(0.0)	.02(−26.0)
5. Stevens-4																
	.07	.37(−1.0)	−.07	−.03	—	—	.01	.003(−15.0)	.01(−22)	.003	—	−.02	.001	—	.033(−1.0)	—
6. Wadley-1																
	—	.44(−2.0)	.19	—	.86	−.74	—	−.03(−12.0)	.0	.02	—	.15	—	—	.029(2.0)	−.14(−20.0)
7. Midville																
8. Monck's Corner																
	—	−1.86(−7.2)	.81	—	2.38	−2.04	—	—	.08(−22.0)	.06	—	.0	2.45	1.77	1.11(0.0)	—
9. Hodge																

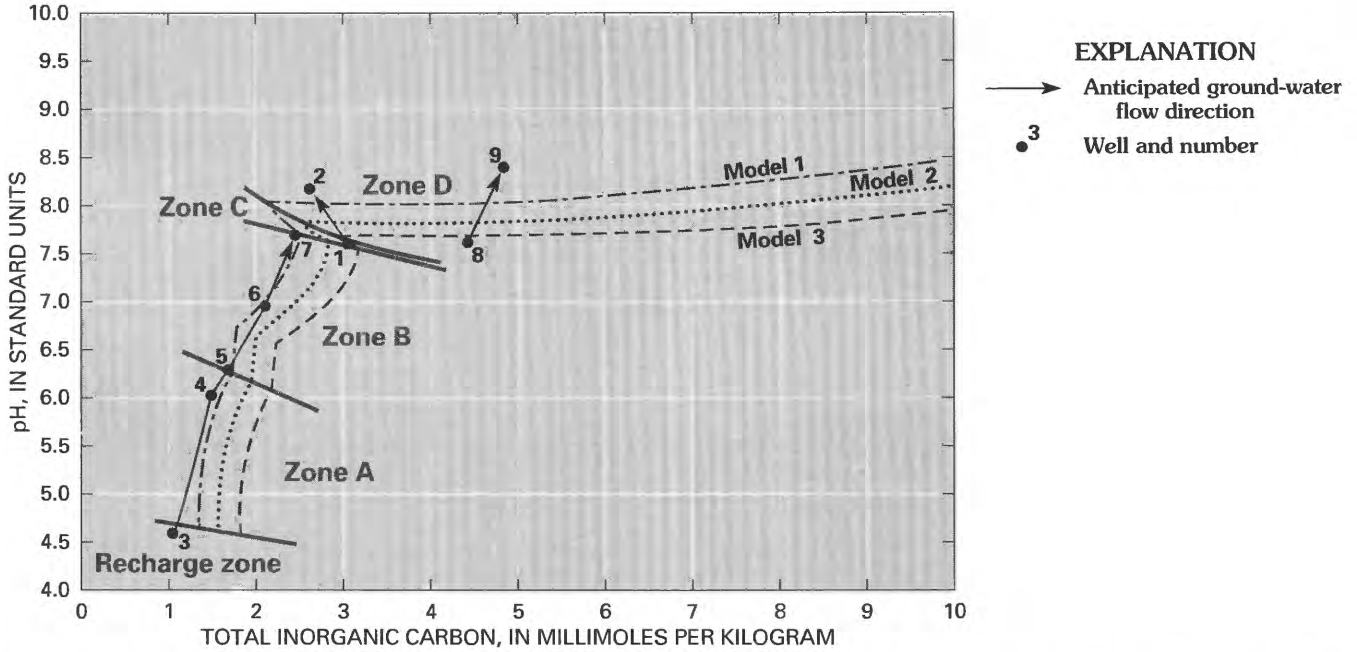

FIGURE 36.—Geochemical models of calcareous sand aquifers constructed using chemical data from the middle water-bearing zone of the Pearl River aquifer. Location of wells shown in figure 32.

TABLE 30.—*Radiocarbon ages and flow velocities of ground water in the middle water-bearing zone of the Pearl River aquifer*

[YBP, years before present; ft/yr, feet per year. Dashes indicate no data. Location of wells shown in fig. 32]

Well number (Flow path)	Unadjusted age (YBP)	Adjusted age (YBP)	Adjusted flow rate (ft/yr)
1	10,800	10,800	2.0
(1→2)	(15,800)	(9,800)	(21.7)
2	26,600	20,600	11.5
3	0	—	—
(3→4)	(1,500)	(1,500)	(11.2)
4	1,500	1,500	4.3
(4→5)	(7,600)	(6,500)	(11.5)
5	9,100	8,000	17.1
(5→6)	(17,900)	(16,000)	(3.0)
6	27,000	24,000	7.5
(6→7)	(3,200)	(1,400)	(26.2)
7	30,200	25,400	8.9
8	21,900	21,900	0.7
(8→9)	10,200	2,600	(34.1)
9	32,100	23,500	4.3

in an area south of Jones and Wayne Counties, Miss. In other parts of southeastern Mississippi, concentrations exceed 100,000 mg/L.

DISSOLVED CHLORIDE

Concentrations of dissolved chloride in water in the upper water-bearing zone (pl. 5) are less than 100 mg/L in most areas and are less than 10 mg/L in many places. Downgradient, concentrations exceed 100 mg/L in southeastern Mississippi and increase to greater than 100,000 mg/L in Perry County, Miss.

DISSOLVED IRON

Concentrations of dissolved iron in water in the upper water-bearing zone are less than 100 μg/L near recharge areas (pl. 6). Just downgradient from recharge areas, concentrations exceed 1,000 μg/L. Farther downgradient, concentrations decrease to less than 100 μg/L. Where dissolved chloride increases in the deeper, downgradient parts of the upper water-bearing zone, concentrations of dissolved iron may exceed 1,000 μg/L in some areas. A band of elevated concentrations of dissolved iron extends from Madison County northward to Panola County, Miss. Moderately high concentrations, exceeding 1,000 μg/L in parts of Hinds and Rankin Counties, Miss., are probably associated with reducing conditions which may develop in the aquifer following local recharge to the upper water-bearing zone. Concentrations greater than 1,000 μg/L in downgradient areas, such as areas near salt domes in southeastern Mississippi, are associated with higher ground-water salinity.

HYDROCHEMICAL FACIES

Hydrochemical facies of the ground water in the upper water-bearing zone (pl. 6) are primarily calcium bicarbonate facies in recharge areas and sodium bicarbonate facies in downgradient areas. However, in southern Mississippi, sodium chloride is the dominant facies. Areas of calcium bicarbonate facies in Madison and Yazoo Counties, Miss., which are encircled by sodium bicarbonate facies, may indicate some meteoric recharge to the upper water-bearing zone.

SUMMARY AND CONCLUSIONS

Regionally extensive sand aquifers in Upper Cretaceous and Tertiary rocks of the Southeastern Coastal Plain have been subdivided vertically in order to delineate distributions of water chemistry. Chemical maps have been prepared for the following aquifers, from lowest units to highest units in the vertical section—Black Warrior River aquifer, Chattahoochee River aquifer, and Pearl River aquifer.

The chemistry of the ground water in these aquifers is shown on maps of dissolved solids, dissolved chloride, dissolved iron, and hydrochemical facies. Concentrations of dissolved solids increase in the downgradient direction of ground-water flow. Water-rock interactions cause the initial increase in concentrations of dissolved solids; sharp increases in concentrations of dissolved solids and dissolved chloride in deep, downgradient parts of the aquifers are in most places the result of mixing with saline waters from brines, salt domes, or relict seawater in the formations.

Concentrations of dissolved iron are greatest in narrow bands just downgradient from, and approximately parallel to, outcrop areas. Lower concentrations of dissolved iron occur in and near outcrop areas, owing to lower solubility of iron in the partially oxygenated water of the shallow aquifers. The concentration of iron in water is controlled by solubility limitations of siderite, and of pyrite farther downgradient. Iron solubility subsequently increases in deeper, downgradient parts of the aquifers as ground water becomes more saline and concentrations of dissolved chloride increase, thus increasing the potential for chloride to form complexes with iron.

Ground-water in and near recharge areas where dissolved-solids concentrations are low varies from no dominant facies to calcium bicarbonate facies. Chemical evolution of water generally proceeds downgradient from recharge areas to calcium bicarbonate facies and then to sodium bicarbonate facies. In the deeper, downgradient parts of the aquifers, mixing of the fresher ground water with saline water in the aquifers produces the sodium chloride facies commonly observed.

Study and interpretation of the geochemical behavior of water along flow paths indicate the likely chemical processes that produce the observed water chemistry. For sandy, low-calcite aquifers, such as the Black Warrior River and Chattahoochee River aquifers, feldspar hydrolysis is interpreted to be a dominant process upgradient, producing relatively low concentrations of dissolved solids (<100 mg/L). Downgradient, more calcite is dissolved, and calcite approaches saturation. Calcium-for-sodium cation exchange, along with carbon dioxide produced from decay of sedimentary organic material (lignite), is thought to be responsible for an increase in calcite dissolution. Further cation exchange results in the sodium bicarbonate facies in the downgradient parts of the aquifers. The amount of calcite present in a given aquifer and the dissolution and precipitation reactions have been simulated by geochemical models of mass transfer.

The occurrence of measurable amounts of carbon-14 in ground waters of the Southeastern Coastal Plain aquifer system provides a means of estimating both the age and the velocity of the ground water. In some instances, ground water contains insufficient carbon-14 for velocity determination, indicating an extreme age of the ground water (>40,000 YBP). Approximate ground-water velocities vary among the Black Warrior River, Chattahoochee River, and Pearl River aquifers. Ground-water velocities generally are lowest in the Black Warrior River aquifer; mean velocities determined by carbon-14 age dating are about 3 ft/yr, compared with 1 ft/yr estimated from ground-water flow model simulations. Ground-water velocities in the Chattahoochee River aquifer are approximately 13 ft/yr determined by carbon-14 age dating, compared with 10 ft/yr estimated from flow model simulations. Velocities generally are highest in the Pearl River aquifer; mean velocities determined from limited carbon-14 data are about 21 ft/yr, compared with 15 ft/yr estimated from flow model simulations.

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APPENDIX: MASS-TRANSFER COEFFICIENTS FROM PHREEQE SIMULATIONS

SIMULATION I.—*Very low calcite*
SIMULATION II.—*Low calcite*
SIMULATION III.—*Moderate calcite*
SIMULATION IV.—*High calcite*

SIMULATION I.—*Very low calcite*

[In millimoles per kilogram of water. Negative sign indicates precipitation of a phase]

Phase	Model 1	Model 2	Model 3
Recharge			
CO_2 (Recharge)	1.363	1.591	1.818
Zone A			
Albite	0.032	0.032	0.032
Dolomite	.008	.008	.008
Chalcedony	.198	.198	.198
Kaolinite	−.016	−.016	−.016
CO_2	.384	.384	.384
Zone B			
Albite	0.383	0.410	0.436
Chalcedony	−.765	−.820	−.871
Goethite	.287	.308	.327
Kaolinite	−.192	−.206	−.218
Zone C			
Albite	0.712	0.712	0.712
Calcite	.013	.013	.016
Chalcedony	−2.032	−2.053	−2.084
Goethite	.534	.534	.534
Kaolinite	−.533	−.533	−.533
Siderite	−.692	−.783	−.848
CO_2	.0	.0	.0
Zone D			
Calcite	18.391	18.391	18.388
Chalcedony	52.925	52.944	52.973
Amorphous aluminosilicate	46.000	46.000	46.000
Ca-Na exchange	36.800	36.800	36.800
Sodium smectite	−39.486	−39.485	−39.485
CO_2	5.120	4.980	4.840
Siderite	−0.129	−0.058	−0.012

SIMULATION II.—*Low calcite*

[In millimoles per kilogram of water. Negative sign indicates precipitation of a phase]

Phase	Model 1	Model 2	Model 3
Recharge			
CO_2 (Recharge)	1.363	1.591	1.818
Zone A			
Albite	0.016	0.016	0.016
Dolomite	.024	.024	.024
Chalcedony	.230	.230	.230
Kaolinite	−.008	−.008	−.008
CO_2	.352	.352	.352
Zone B			
Albite	0.218	0.234	0.248
Chalcedony	−.435	−.467	−.497
Goethite	.327	.351	.373
Kaolinite	−.109	−.117	−.124
Zone C			
Albite	0.534	0.534	0.534
Calcite	.134	.134	.134
Chalcedony	−1.056	−1.067	−1.068
Goethite	.534	.534	.534
Kaolinite	−.267	−.267	−.267
Siderite	−.858	−.852	−.840
CO_2	.053	.053	.053
Zone D			
Calcite	17.030	18.268	18.276
Chalcedony	53.007	53.015	53.012
Amorphous aluminosilicate	46.000	46.000	46.000
Ca-Na exchange	36.800	36.800	36.800
Sodium smectite	−39.484	−39.485	−39.485
CO_2	4.812	4.812	4.812
Siderite	−0.001	−0.032	−0.060

SIMULATION III.—*Moderate calcite*

[In millimoles per kilogram of water. Negative sign indicates precipitation of a phase]

Phase	Model 1	Model 2	Model 3
Recharge			
CO_2 (Recharge)	1.363	1.5907	1.818
Zone A			
Albite	0.012	0.012	0.012
Calcite	.240	.240	.240
Dolomite	.060	.060	.060
Chalcedony	.239	.239	.239
Kaolinite	−.006	−.006	−.006
CO_2	.0	.0	.0
Zone B			
Albite	0.054	0.062	0.069
Chalcedony	−.107	−.123	−.138
Goethite	.161	.185	.208
Kaolinite	−.027	−.031	−.035
Calcite	.054	.062	.069
Zone C			
Albite	0.220	0.220	0.220
Calcite	.660	.660	.660
Chalcedony	−.439	−.440	−.440
Goethite	.022	.022	.022
Kaolinite	−.110	−.110	−.110
Siderite	−.174	−.186	−.196
CO_2	.286	.286	.286
Zone D			
Calcite	16.556	16.551	16.547
Chalcedony	50.906	50.901	50.896
Amorphous aluminosilicate	44.150	44.15	44.150
Ca-Na exchange	35.100	35.100	35.100
Sodium smectite	−37.897	−37.897	−37.897
CO_2	3.455	3.455	3.455
Goethite	0.550	0.550	0.550
Siderite	−.559	−.571	−.583

SIMULATION IV.—*High calcite*

[In millimoles per kilogram of water. Negative sign indicates precipitation of a phase]

Phase	Model 1	Model 2	Model 3
Recharge			
CO_2 (Recharge)	1.363	1.591	1.818
Zone A			
Albite	0.200	0.200	0.200
Calcite	1.070	1.070	1.070
Dolomite	.040	.040	.040
Chalcedony	−.137	−.137	−.137
Kaolinite	−.100	−.100	−.100
CO_2 (from lignite)	.15	.15	.15
Zone B			
Albite	0.002	0.002	0.003
Chalcedony	−.004	−.004	−.005
Goethite	.010	.011	.013
Kaolinite	−.001	−.001	−.001
Calcite	.058	.223	.379
Zone C			
Albite	0.320	0.320	0.320
Calcite	−.294	−.283	−.274
Chalcedony	−.639	−.640	−.640
Goethite	.049	.049	.049
Kaolinite	−.160	−.160	−.160
Siderite	−.051	−.050	−.050
CO_2 (from lignite)	.016	.016	.016
Zone D			
Calcite	18.078	17.904	17.739
Chalcedony	52.319	52.312	52.306
Amorphous aluminosilicate	45.350	45.350	45.350
Ca-Na exchange	37.8	37.8	37.8
Sodium smectite	−38.927	−38.927	−38.927
CO_2 (from lignite)	2.835	2.835	2.835
Siderite	−0.006	−0.009	−0.010