WATER QUALITY IN THE APPALACHIAN VALLEY AND RIDGE, THE BLUE RIDGE, AND THE PIEDMONT PHYSIOGRAPHIC PROVINCES, EASTERN UNITED STATES

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Water Quality in the Appalachian Valley and Ridge, the Blue Ridge, and the Piedmont Physiographic Provinces, Eastern United States

By L. I. BRIEL

REGIONAL AQUIFER-SYSTEM ANALYSIS—
APPALACHIAN VALLEY AND PIEDMONT

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FOREWORD

THE REGIONAL AQUIFER-SYSTEM ANALYSIS PROGRAM

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 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 beginning with Professional Paper 1400.

Gordon P. Eaton

Gordon P. Eaton
Director

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Multiply	By	To obtain
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi2)	2.590	square kilometer

degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) as follows: ° F = 1.8(°C) + 32

Absolute chemical concentrations of major ionic constituents in milligrams per liter (mg/L) can be converted to equivalent concentrations in milliequivalents per liter (meq/L) by multiplying by the following factors:

calcium, mg/L	0.04990	calcium, meq/L
magnesium, mg/L	0.08229	magnesium, meq/L
sodium, mg/L	0.04350	sodium, meq/L
potassium, mg/L	0.02558	potassium, meq/L
chloride, mg/L	0.02821	chloride, meq/L
fluoride, mg/L	0.05264	fluoride, meq/L
sulfate, mg/L	0.02082	sulfate, meq/L
bicarbonate, mg/L	0.01639	bicarbonate, meq/L
nitrate, mg/L as nitrogen	0.07139	nitrate-nitrogen, meq/L
phosphate, mg/L as phosphorus	0.09685	phosphate-phosphorus, meq/L

Abbreviated water-quality units used in this report: Chemical concentrations, water temperature, and specific conductance are given in metric units. Absolute chemical concentration of the most abundant (major) constituents is given in milligrams per liter (mg/L) and, for trace constituents, in micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is the same as for concentrations in parts per million.

For electrically charged solutes (ions), the concentration of charge strongly affects the chemical properties of the water. To compare different ionic constituents on an equal footing, absolute concentrations are converted to equivalent concentrations in milliequivalents per liter (meq/L), by multiplying by the reciprocal of the combining weight. The combining weight of an ion is obtained by dividing the formula weight by the ionic charge. For major ions, the numerical factors used to convert milligrams per liter to milliequivalents per liter are shown in the table.

The relative concentration of a positively charged ion (cation) or a negatively charged ion (anion) is expressed as a percentage of the total milliequivalents per liter of cations or anions. Relative concentration is calculated by use of one the following equations:

percentage of cation = meq of cation / total meq of cations × 100
percentage of anion = meq of anion / total meq of anions × 100

Specific conductance of water is expressed in microsiemens per centimeter at 25 degrees Celsius (µS/cm). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius (µmho/cm), formerly used by the U.S. Geological Survey.

REGIONAL AQUIFER-SYSTEM ANALYSIS—APPALACHIAN VALLEY AND PIEDMONT

WATER QUALITY IN THE APPALACHIAN VALLEY AND RIDGE, THE BLUE RIDGE, AND THE PIEDMONT PHYSIOGRAPHIC PROVINCES, EASTERN UNITED STATES

BY L. I. BRIEL

ABSTRACT

The study area for the Appalachian Valley and Ridge, the Blue Ridge, and the Piedmont Regional Aquifer-System Analysis encompasses approximately 142,000 square miles in 11 eastern states. The principal axis of this area extends for approximately 1,000 miles from the general vicinity of Newark, N.J., to near Birmingham, Ala. The subsurface geology is diverse and ranges from thick sequences of carbonate sediments and shales in the Valley and Ridge Physiographic Province to fractured crystalline rocks mantled with weathered regolith in the Piedmont and the Blue Ridge Physiographic Provinces. Most aquifers consist of local, shallow flow systems whose flow paths are typically less than 20 miles long and within 300 feet of land surface. In all three physiographic provinces, ground water discharges naturally from springs, but almost three-fourths of the sampled springs are in the Valley and Ridge Province. Ground water interacts with stream water in many parts of the study area, and the movement of water between systems is generally complex. Because of these interactions, this study examines the quality and chemical character of ground water, spring water, and surface water in all three physiographic provinces and contrasts geographic trends in a selected set of water-quality properties and constituents.

The principal source of water-quality information in this report is the U.S. Geological Survey's computerized data base, the National Water Information System (NWIS). In some parts of the study area, supplementary data were obtained from reports published by state agencies and universities. The chemical data base used for this study contains a total of 196,852 analyses from 15,263 different sites. Location coordinates (latitude and longitude) for all sites were included in the chemical data base so that a geographic information system (GIS) could be used to display data and facilitate analysis of geographic trends in water quality.

The geographic distribution of water-quality sites in the study area is highly uneven: For ground-water and surface-water sites, the majority of data is for the Piedmont Province, and most of the rest is for the Valley and Ridge Province. For springs, however, these distributions are reversed: the majority of data is for the Valley and Ridge Province, and most of the rest is for the Piedmont. For all three types of sites, the smallest proportion of water-quality data is for the Blue Ridge Province.

In the study area as a whole, typical ground water is not highly mineralized: the median dissolved-solids concentration is 164 milligrams per liter (mg / L). Typical ground water is also nearly neutral (median pH is 6.9) and is classified as moderately hard (median hardness is 82 mg / L as $CaCO_3$).

Chemical quality of ground water in each physiographic province differs substantially: Ground water in the Valley and Ridge Province has the highest median dissolved-solids concentration (226 mg / L), is slightly alkaline (median pH is 7.3), and is classified as hard (median hardness is 149 mg / L as $CaCO_3$). Ground water in this province also tends to have high concentrations of calcium, magnesium, sulfate, bicarbonate, alkalinity, nitrate, and dissolved iron. Ground water in the Piedmont Province, by contrast, has a lower median dissolved-solids concentration (159 mg / L), is slightly acidic (median pH is 6.7), and is classified as moderately hard (median hardness is 65 mg / L as $CaCO_3$). Ground water in this province tends to have high concentrations of sodium, potassium, chloride, silica, ammonia, phosphorus, total iron, and manganese. Ground water in the Blue Ridge Province has the lowest median dissolved-solids concentration (73 mg / L), is slightly acidic (median pH is 6.6), and is classified as soft (median hardness is 29 mg/ L as $CaCO_3$).

Chemical quality of spring water in the study area differs somewhat from ground-water quality. A lower median dissolved-solids concentration (136 mg / L) for spring water indicates that it is typically more dilute than ground water. Higher median values for pH (7.2) and carbonate hardness (120 mg / L as $CaCO_3$) indicate that spring water has a greater degree of exposure to carbonate rock than ground water in the study area as a whole. Spring-water quality generally tends to resemble ground-water quality in the Valley and Ridge Province because most of the sampled springs are in that province.

Chemical quality of surface water in each province is also distinctive and is similar to ground-water quality; surface water, however, is usually more dilute than ground water and commonly more dilute than spring water. Median concentration of dissolved solids in surface water (107 mg / L) indicates that surface water typically contains about 35 percent less dissolved solids than ground water and 21 percent less dissolved solids than spring water. Surface water is slightly alkaline (median pH is 7.2) and is appreciably softer than ground water, although both are classified as moderately hard.

For most water in the study area, the major dissolved ions are calcium, magnesium, and bicarbonate, which are produced by the dissolution of carbonate rocks (limestone and dolostone). Commonly, the order of abundance of major cations is calcium>magnesium>sodium, and for major anions, the order is bicarbonate>sulfate>chloride. In parts of the Valley and Ridge Province, however, the sediments contain significant amounts of gypsum, and sulfate becomes the dominant anion at higher ionic concentrations. Although calcium is usually the dominant cation in most water in the study area, for estuarine streams in the northeastern Piedmont Province, sodium becomes the dominant cation at high ionic concentrations.

A new method for displaying variations in chemical composition of water is described in this report. Shaded-grid trilinear diagrams, which can display general trends in chemical composition for an unlimited number of water samples, are based on the distribution of cell populations in each field of a trilinear diagram. Shaded-grid diagrams are used to show similarities and differences in chemical composition for ground water, surface water, and spring water in each province of the study area.

INTRODUCTION

In 1978, the U.S. Geological Survey (USGS) began a series of Regional Aquifer-System Analysis (RASA) studies to provide information on the hydrogeology and water quality of the Nation's major aquifers (Bennett, 1979). The Appalachian Valley and Ridge, Blue Ridge, and Piedmont RASA (APRASA) is the 22d study in this series. The study area for APRASA consists of approximately 142,000 mi^2 in parts of 11 eastern states and the District of Columbia (pl. 1).

This report describes variations in the chemical quality of shallow ground water, spring water, and surface water in the APRASA area. Although the primary focus of RASA studies is ground water, examination of the quality of water from springs and streams is also useful for areas where data from wells are few or nonexistent. Springs are sites of natural discharge of ground water, and water-quality data for springs represents the final stage in the evolution of ground-water quality. Hydrogeologic interaction of streams and underlying aquifers can be complex. In some locations, the interaction is minimal; in other locations, streambeds are areas of recharge and discharge, depending on the hydraulic gradient. A comparison of quality of stream water and ground water in an area can be a useful means of studying these interactions. The purpose of this report, therefore, is to (1) summarize available data on quality of ground water, spring water, and surface water in the APRASA study area; (2) compare and contrast trends in selected chemical properties and constituents in various parts of this area; and (3) provide a conceptual model that relates variations in ground-water quality to physical, chemical, and hydrogeological processes that occur in aquifers in this area.

DESCRIPTION OF THE STUDY AREA

The study area is oriented northeast-southwest and extends for about 1,000 miles from Newark, N.J. to Birmingham, Al. (pl. 1). Three major regional units based on physiographic province lie parallel to the major axis of the area: (1) the Appalachian Valley and Ridge Province, a belt of about 46,000 mi^2 along the northwestern boundary; (2) the Blue Ridge Province, a shorter and narrower belt of about 20,000 mi^2 in the center of the area and extending about 585 miles from Harrisburg, Pa. to Atlanta, Ga.; and (3) the Piedmont Province, a belt of about 76,000 mi^2 along the southeastern boundary (Swain and others, 1991).

Boundaries between physiographic provinces in this area were originally defined on the basis of differences in geology, lithology, and general topography (Fenneman, 1938). The boundaries shown on plate 1 for the study area and the three provincial units were determined from geographic-information-system (GIS) map coverages of the area produced during this study and are based on digitized versions of state geologic maps and USGS topographic quadrangle maps (Thomas Mesko, U.S. Geological Survey, written commun., 1991). These digital maps can easily incorporate detailed hydrogeologic and water-quality data; hence, the maps are a valuable tool for identifying and relating hydrogeologic units in the study area on the basis of multiple factors (Harlow and Nelms, 1989).

The western and northern boundaries of the study area (pl. 1) correspond to the limit of thrust faults and folds in the carbonate rock, sandstone, and shale sediments of the Valley and Ridge Province. Thickness of sediments in this area ranges from 20,000 to 40,000 ft. The northeastern boundary of the APRASA area is the state border of New Jersey. A 1,000-ft-thick diabase sheet lies at the extreme northern end of the eastern boundary in Hudson and Bergen Counties, N.J.; elsewhere, the eastern and southern boundaries correspond to the Fall Line (pl. 1), which separates the Piedmont Province from the Atlantic Coastal Plain (Fenneman, 1946).

The sedimentary rocks that underlie the Valley and Ridge Province range in age from Cambrian to Pennsylvanian. Regionally, these sediments have been intensely deformed by several mountain-building events interspersed with periods of weathering that have resulted in a region of valleys separated by parallel ridges. The ridges are generally underlain by conglomerate, sandstone, or cherty dolomite, whereas the valleys are underlain by siltstone, shale, limestone, or dolostone that is less resistant to erosion than the rocks forming the ridges. In much of the area, carbonate aquifers contain significant amounts of chert or disseminated quartz sand, but quartzite and sandstone aquifers also are common in the Valley and Ridge Province. Although some of these aquifers are highly permeable locally, few are permeable regionally (areas of hundreds of square miles). Ground-water flow paths, therefore, are typically less than 20 miles long and most of the active flow is within 300 feet of land surface, where permeability is greatest (Seaber and others, 1988).

A large area of paleokarst is present in the lower Ordovician carbonates throughout the southern three-fourths of the Valley and Ridge Province. Ground water in this area discharges from a few large springs at rates of as much as 64.7 million gallons per day (Sun and others, 1963). The discharge is generally concentrated at a few large springs rather than at many small springs because flow is limited to dissolution openings in poorly permeable carbonate rock. A detailed discussion of the hydrogeology of the Valley and Ridge is given in Seaber and others (1988).

The geology of the Piedmont and the Blue Ridge Provinces is more heterogeneous than that of the Valley and Ridge Province. The Piedmont and Blue Ridge Provinces are underlain by igneous, metamorphic, and sedimentary bedrock which has been extensively deformed and broken by a succession of orogenic and metamorphic events that were followed by periods of weathering and erosion. The principal rock types in this area are massive granites and gneisses, foliated phyllites and schists, and consolidated sandstones. Metamorphic and igneous rocks range in composition from felsic to ultramafic and range in age from Middle Proterozoic for granitic rocks in the Blue Ridge to Triassic-Jurassic for the unmetamorphosed dikes and sills of mafic composition that intrude the Piedmont (Swain and others, 1991).

Bedding and foliation within metamorphic bedrock commonly intersect one another in systematic geometric patterns. Bedrock is generally weathered to saprolite; however, the relict structure and directional properties controlling permeability are retained in some places. Although most rocks in the area have been metamorphosed and have strong directional fabrics, igneous intrusives emplaced after the last metamorphic event in the late Paleozoic tend to be massive and less foliated. Most of the rocks were subjected to uplift during the Cenozoic Era; subsequent weathering and erosion widened previously formed fractures or created new ones by stress relief. Fault zones of different types, scales, and orientations are common in the crystalline rocks of the Piedmont and the Blue Ridge Provinces.

In a few places, bedrock is exposed at land surface. Over most of the area, however, fractured bedrock is mantled by unconsolidated material (called regolith), which consists of soil, alluvium, and saprolite. The thickness of regolith can range from 0 to more than 100 feet (Daniel and Payne, 1990),

At isolated locations in the Piedmont Province, sedimentary rocks of Mesozoic age fill a series of rift basins that crop out in a discontinuous belt from northeastern New Jersey to South Carolina. These basins are exposed at land surface in the Piedmont but are covered by as much as several thousand feet of Cretaceous and younger sediments in the adjoining Atlantic Coastal Plain. The basins are generally elongate, down-faulted structures that were formed by continental rifting in the Triassic and Jurassic periods and were subsequently filled with thick sequences of continental sediments eroded from surrounding crystalline highlands. These sediments (the Newark Supergroup) consist predominantly of interbedded red shale, sandstone, and siltstone. In some areas, however, the sediments also contain conglomerate, black mudstone of lacustrine origin, and coal. Coal has been mined in basins near Richmond and Danville, Va., and along the Deep River in North Carolina. Sediment thickness in the largest of the Mesozoic basins has been calculated to exceed 20,000 ft (Szabo and others, 1989). Sedimentation in the basins was accompanied by periods of igneous and volcanic activity, where basaltic and diabase dikes were intruded into the Mesozoic sediments.

The Piedmont and the Blue Ridge Provinces contain no flat-lying or blanket-type formations that have the flow characteristics of sedimentary aquifers. Because of geologic and hydrologic differences, rocks in the Piedmont and the Blue Ridge Provinces have been divided into two groups: crystalline-rock regimes and sedimentary-rock regimes. Fracture-type permeability is typical for most rocks in these provinces, and the degree of fracturing differs little among rock types (LeGrand, 1988, 1989). The mantle of residual soil and soft weathered rock (regolith) that covers the fractured bedrock is an important intergranular medium for the recharge and discharge of ground water. Such a system is complex because ground water circulates through more than one medium between the point of recharge and the point of discharge; thus, permeability and flow paths are especially difficult to determine. Detailed discussion of the hydrogeology of the Piedmont and the Blue Ridge Provinces is given in LeGrand (1988, 1989).

SOURCES OF WATER-QUALITY DATA

All chemical data used to determine water quality in the study area had been collected prior to the APRASA study. Major uncertainties and limitations with the use of previously collected data include the following: (1) sampling sites are not evenly distributed throughout the area, (2) the set of chemical determinations is not uniform for all sites, (3) seasonal data are unavailable for some parts of the hydrologic cycle, and (4) depth horizons at ground-water sites are generally not well represented. These problems make necessary the use of statistical techniques to infer representative values for some parts of the area, and this reliance on statistical techniques limits the interpretation of trends in water quality. Uses and limitations of previously collected data are discussed in Hamilton and others (1993), Alley (1993a, 1993b, 1993c), and Back and others (1993).

Many sources of chemical data were evaluated for incorporation into the data base. Potential sources of data included reports published by Federal, state, and local agencies and universities; the U.S. Environmental Protection Agency's STORET data base; and the U.S. Department of Energy's National Uranium Exploration Project (NURE) data base. Although a large amount of water-quality data was found, data from some sources lack the detailed information about the location of the sampling site or the analytical methodology necessary for inclusion in the APRASA data base.

PREVIOUS STUDIES

Chemical data from previous studies are a valuable source of information on water-quality trends and are cited in this report for comparison. Data from USGS offices in each of 11 states in the APRASA area are published annually in a series of Water Resources Data Reports that provide a continuing synopsis of water quality at selected sites. Trends in these data have been evaluated periodically on a national scale and have been summarized in the USGS "National Water Summary" (U.S. Geological Survey, 1985, 1988, and 1993) and in a series of hydrologic atlases of the United States (Lloyd and Lyke, 1995; Miller, 1990; Trapp and Horn, 1997).

Water-quality data for specific sites and areas within APRASA are also available in reports of hydrologic investigations published by the USGS and other Federal agencies, state and local agencies, and universities. A selected geographical summary of previous studies in the APRASA area that contain tables of water-quality data is given in table 1.

NATIONAL WATER INFORMATION SYSTEM

The principal source of water-quality data used in this study was the USGS National Water Information System (NWIS). Much of the chemical data collected in previous studies in the APRASA area (table 1) can be retrieved from NWIS. For 405 counties in this area, NWIS contains approximately 194,000 measurements of 1,434 different physical, chemical, and biological properties and constituents. Twenty-four properties and constituents were selected for study (Appendix A, table A–2). NWIS data were retrieved from USGS computer files and compiled into a uniform water-quality data base.

For all ground-water sites, selected geophysical properties were also retrieved from the USGS Ground-Water Site Inventory (GWSI) files and merged with the chemical data. GIS data pertaining to the location of hydrogeologic and lithologic units also were incorporated into the water-quality data base so that many kinds of information on sites could be displayed on computer-generated maps and correlated geographically. The APRASA water-quality data base is discussed further in Appendix A.

ADDITIONAL DATA

Chemical data from three additional sources were incorporated into the data base: (1) A file of data from several state agencies in North Carolina (Douglas Harned, U.S. Geological Survey, written commun., 1991). This file contains 2,477 chemical analyses from 1,275 wells in the Piedmont and the Blue Ridge Provinces of that State. (2) A file of data from state agencies in South Carolina (Glenn Patterson, U.S. Geological Survey, written commun., 1991). This file contains 342 chemical analyses from 44 wells in APRASA counties in that State. Some of the sites, however, were outside the study area and had to be excluded. (3) Data from a doctoral dissertation (Leonard, 1962) produced at the Virginia Polytechnic Institute and State University. From this source, 49 analyses from 49 well and stream sites along the western edge of the Blue Ridge Province in Virginia were added to the data base.

TABLE 1.—*Selected references to previous water-quality investigations in the study area, by geographical unit*

MULTIREGIONAL STUDIES		
Davis, 1964	Hallberg and Keeney, 1993	Miller, 1990
Harlow and Nelms, 1989	LeGrand, 1967 and 1988	Trapp and Horn, 1997
Hobba and others, 1977	Lloyd and Lyke, 1995	U.S. Geological Survey, 1970, 1985, 1988, 1993
REGIONAL STUDIES		
Valley and Ridge ...... Seaber and others, 1988		
Blue Ridge .... Hopkins, 1984		
Piedmont............. LeGrand, 1989		
STATE, COUNTY, AND SITE-SPECIFIC STUDIES		
Alabama		
Baker, 1957	Faust and Harkins, 1980	Sanford, 1966
Causey, 1965	Harkins and others, 1980 and 1981	Scott and Lines, 1973
Chandler and Lines, 1974, 1978a, 1978b	Lines and Chandler, 1975	Warman and Causey, 1962
Chandler and Moore, 1987	Lines and Scott, 1972	
Chandler and others, 1972	Moffett and Moser, 1978	
Delaware		
Bachman, 1984	Groot and Rasmussen, 1954	
Barksdale and others, 1958	Rasmussen and others, 1957	
Georgia		
Casteel and Ballew, 1987	Cressler, 1974	Radtke and others, 1986
Clarke, 1989	Cressler and others, 1976	Watson, 1974
Maryland		
Bachman, 1984	Johnston, 1964	Slaughter and Darling, 1962
Bennett, 1946	McFarland, 1989	Trombley and Zynjuk, 1985
Duigon and Dine, 1991	Posner and Zenone, 1983	
Duigon and others, 1989	Richardson, 1982	
New Jersey		
Ayres and Pustay, 1987	Lewis and Spitz, 1987	Puffer and Asemota, 1986
Barksdale and others, 1958	Nemickas, 1976	Szabo and others, 1989
North Carolina		
Bain and Brown, 1981	Daniel and others (in press)	LeGrand, 1958
Crawford, 1985	Harned, 1982 and 1989	Simmons and Heath, 1982
Daniel and others, 1982	Harned and Meyer, 1983	
Pennsylvania		
Barksdale and others, 1958	Longwill and Wood, 1965	Paulachok and others, 1984
Becher and Root, 1981	McGreevy and Sloto, 1977	Poth, 1968, 1972, 1977
Becher and Taylor, 1982	Meisler, 1963	Royer, 1983
Carswell and Lloyd, 1979	Miller and others, 1971	Senior and Vogel, 1989
Carswell and others, 1968	Newport, 1971, 1977	Sloto, 1989
Johnston, 1966	Patterson and Padgett, 1984	Sloto and Davis, 1983
Lloyd and Growitz, 1977	Paulachok, 1991	Stuart and others, 1967

TABLE 1.—*Selected references to previous water-quality investigations in the study area, by geographical unit—Continued*

STATE, COUNTY, AND SITE-SPECIFIC STUDIES—CONTINUED		
Pennsylvania—Continued		
Taylor and others, 1982	Wood, 1980a, 1980b	Wood and others, 1972
Taylor and others, 1983	Wood and Johnston, 1964	
Taylor and Royer, 1981	Wood and MacLachlan, 1978	
South Carolina		
Bradfield, 1992	Donn, 1990	Sun and others, 1963
Clark and Stone, 1989	Speiran and Aucott, 1994	
Tennessee		
Brahana and others, 1986		
Webster and Carmichael, 1993		
Virginia		
Cady, 1936, 1938	Johnston, 1960, 1964	Powell and Hamilton, 1987
Collins and others, 1930	LeGrand, 1960	Subitzky, 1955
Dawson and Davidson, 1979	Leonard, 1962	Waller, 1976
DeBuchananne, 1968	Lynch, 1987	Wright, 1990
Ellison and Masiello, 1979	Posner and Zenone, 1983	Virginia State Water Control Board, 1973
Froelich and Zenone, 1985	Powell and Abe, 1985	
West Virginia		
Bieber, 1961	Doll and others, 1963	Hobba, 1976, 1981, and 1985
Clark and others, 1976	Ferrel, 1987	Hobba and others, 1972

GEOGRAPHIC DISTRIBUTION OF WATER-QUALITY DATA

The water-quality data base compiled during this study contains a total of 196,852 analyses from 15,263 different sites. The geographic distribution of sites is uneven (figs. 1–3): About 54 percent of the well sites are concentrated in four northern states (New Jersey, Pennsylvania, Delaware, and Maryland), another 35 percent are widely scattered over four central states (Virginia, West Virginia, Tennessee, and North Carolina), and 11 percent are in three southern states (South Carolina, Georgia, and Alabama) (fig. 1). The number of analyses and type of chemical data available from wells differ widely from state to state because some wells have been sampled intensively, whereas most wells have been sampled only once or twice for a small set of properties and constituents. The number of water-quality sites and the number of analyses by state and type of site are listed in table 2.

Although fewer in number, stream sites in the area are distributed more evenly (fig. 2) than well sites are (fig. 1), and the central states (especially Virginia and western North Carolina) are better represented in the data base. Moreover, the number of analyses from stream sites (177,149) is nearly 10 times the number of analyses from well sites (18,008). Summary statistics calculated for surface-water-quality data are the more robust indicator of geographic variations in water quality. In this report, therefore, variations in chemical characteristics of water from both types of sites are compared and contrasted and, where possible, the comparisons are used to provide additional information on water-quality variations.

A third type of site is also included in the water-quality data base: Spring water quality represents the final stage in the evolution of ground-water quality. The 608 spring sites in the APRASA area are primarily in the Valley and Ridge and the northern Piedmont Provinces (fig. 3). The data for some chemical properties of spring water is statistically reliable, but the number of analyses for spring sites (1,695) is less than one-tenth the number

TABLE 2.—*Number of water-quality sites and number of available chemical analyses in the study area, by state and type of site*

State	Number of sties			Percentage by type			Number of analyses			Percentage by type		
	well	spring	stream	well	spring	stream	well	spring	stream	well	spring	stream
New Jersey	1,089	3	432	10.3	0.5	10.6	1,727	4	20,228	9.6	0.2	11.4
Pennsylvania	3,638	233	858	34.4	38.3	21.0	6,889	777	41,285	38.3	45.8	23.3
Delaware	31	0	19	0.3	0	.5	36	0	1,999	.2	0	1.1
Maryland	911	108	215	8.6	17.8	5.3	1,621	307	14,555	9.0	18.1	8.2
District of Columbia	0	0	1	0	0	.02	0	0	149	0	0	.1
Virginia	299	67	585	2.8	11.0	14.3	363	111	17,194	2.0	6.6	9.7
West Virginia	481	83	121	4.5	13.6	3.0	611	202	6,869	3.4	11.9	3.9
Tennessee	200	49	558	1.9	8.1	13.6	272	91	14,403	1.5	5.4	8.1
North Carolina	2,682	0	528	25.4	0	12.9	4,173	0	18,071	23.2	0	10.2
South Carolina	353	0	136	3.3	0	3.3	1,026	0	3,012	5.7	0	1.7
Georgia	325	10	440	3.1	1.6	10.8	650	10	32,245	3.6	.6	18.2
Alabama	555	55	198	5.2	9.0	4.8	640	193	7,139	3.5	11.4	4.0
Total	10,564	608	4,091	100	100	100	18,008	1,695	177,149	100	100	100

for well sites. For most properties and constituents, however, the display of data for spring water as values on a county-grid map is not meaningful.

The three physiographic provinces are another basis for grouping the data. The Valley and Ridge Province and the Piedmont Province span the entire length of the area, but the intervening Blue Ridge Province extends only from southern Pennsylvania to northwestern Georgia (pl. 1). The distribution of sites by physiographic province is also uneven: About 66 percent of the well sites are in the Piedmont, 28.5 percent are in the Valley and Ridge, and 5.4 percent are in the Blue Ridge. The provincial distributions of stream and spring sites are different from the distribution of well sites, as shown in table 3.

In some RASA studies, a ground-water flow network was developed to delineate the regional flow of water. A network of this kind also provides a regularly spaced grid for water-quality studies. The APRASA area, however, encompasses a large number of isolated, small-scale aquifer systems, and regional modeling of these systems would not be feasible. Another basis was needed for studying variations in water quality in this area.

The 405 counties represented in the APRASA area (pl. 1) form a continuous, non-overlapping geographic network that covers the area. Although political subdivisions generally are of little hydrologic significance, water-resources investigations are commonly delimited by county boundaries; thus, counties provide a usable grid for describing geographic variations in water quality. In 1970, the Federal Information Processing Standards (FIPS) assigned a unique five-digit number to each county in the United States. The first two digits of this code designate the state, and the last three digits designate the county. NWIS data are indexed by FIPS codes and can easily be retrieved by this means. FIPS codes and county names in the APRASA water-quality data base are listed in Appendix A (table A–1), and the names of the counties are shown on plate 1.

GENERAL CHEMICAL CHARACTERISTICS OF WATER IN THE STUDY AREA

The ionic composition or dominant chemical type of water is usually expressed in terms of the most abundant (major) dissolved ions produced by the dissolution of various minerals. For the APRASA area as a whole, the most abundant cations in ground water, spring water, and surface water are calcium and magnesium, and the most abundant anion is bicarbonate. These ions are produced by the dissolution of sedimentary rock containing calcite and dolomite. In many locations, water contains mixtures of calcium and magnesium bicarbonate and calcium sulfate (gypsum), whereas in other areas, water contains mixtures of calcium and magnesium bicarbonate and sodium and potassium chloride. Most waters in the study area can be represented by mixtures of these three chemical types. A detailed discussion of regional variations in major-ion

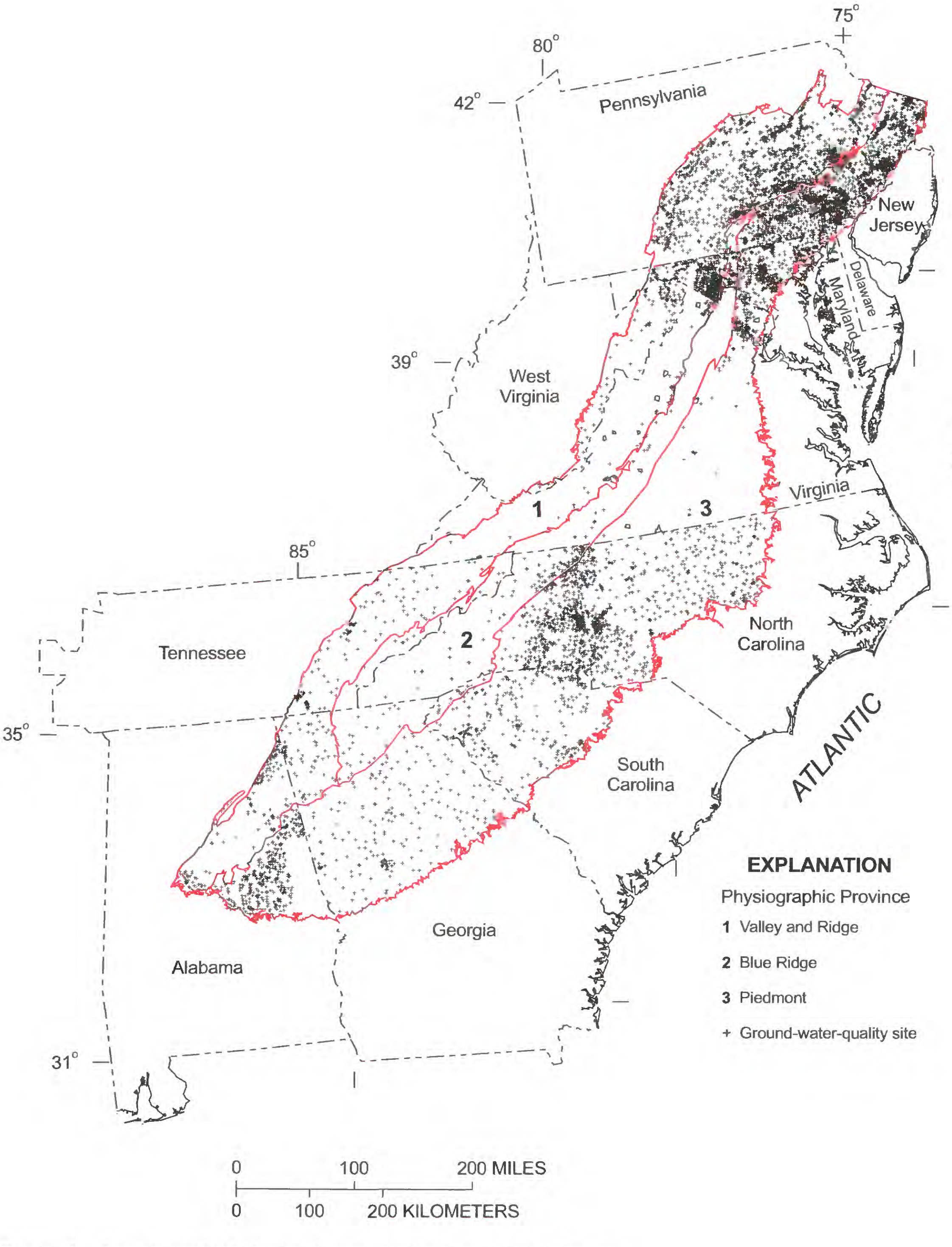


FIGURE 1.—Location of 10,564 ground-water-quality sites in the study area.

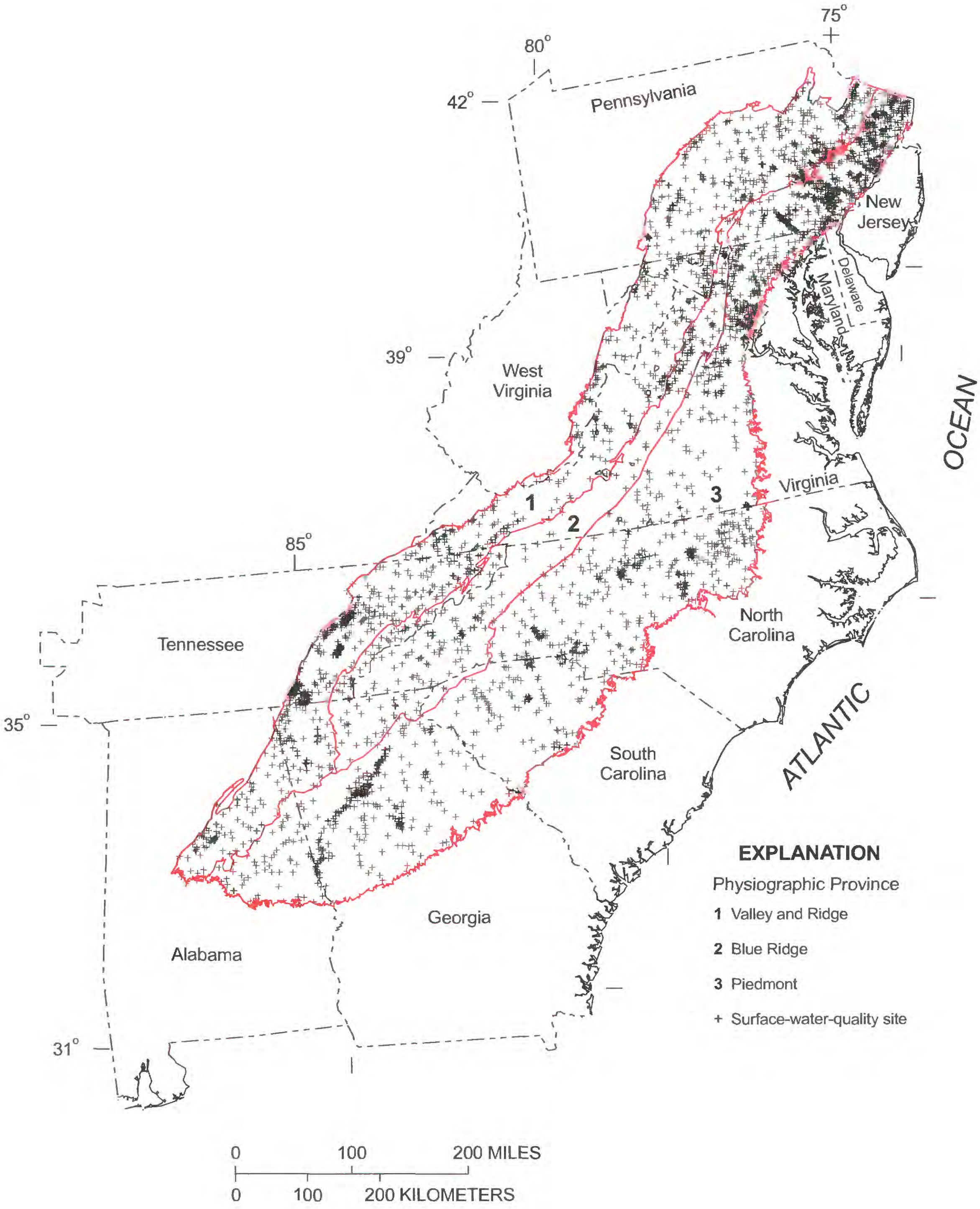


FIGURE 2.—Location of 4,091 surface-water-quality sites in the study area.

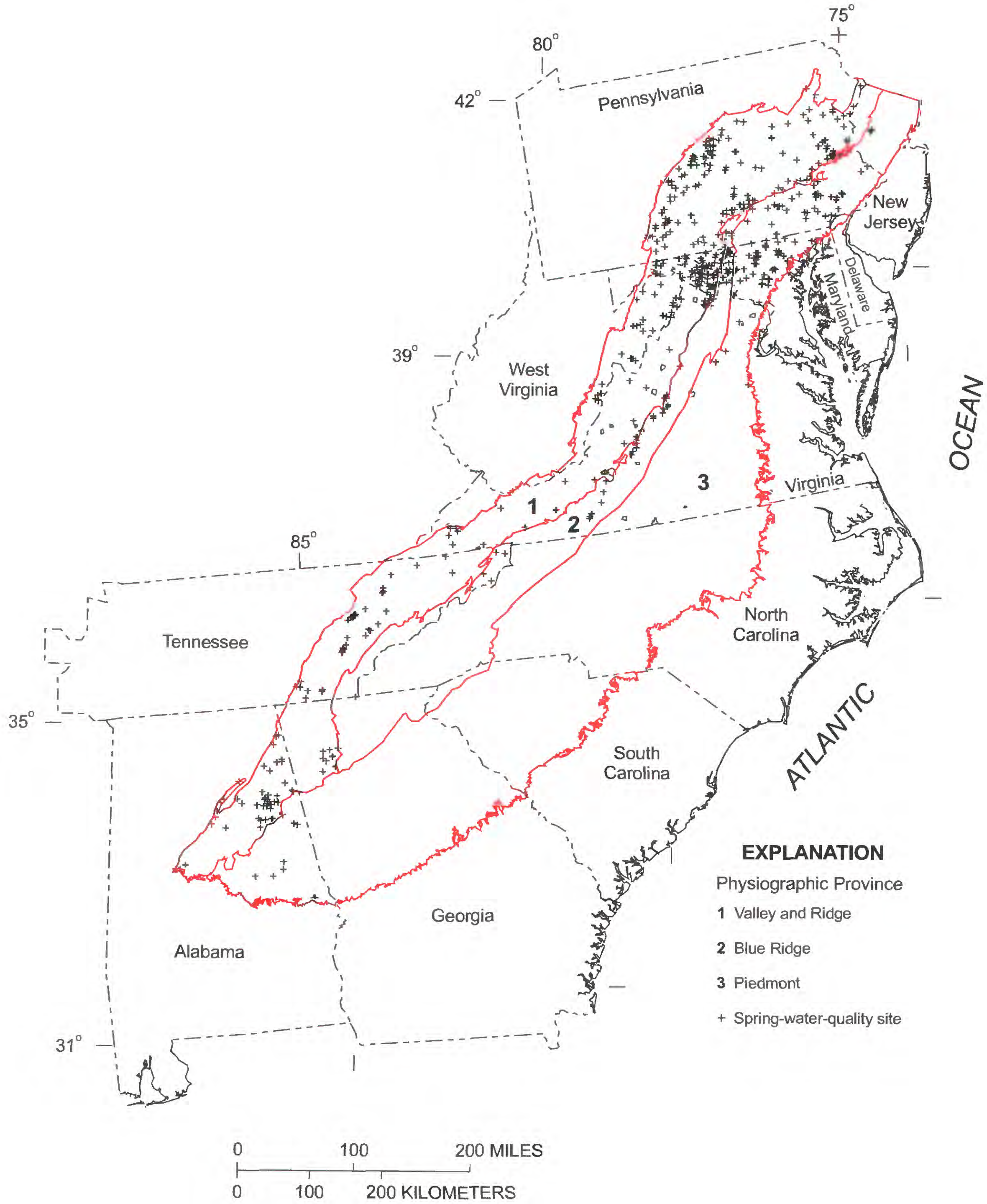


FIGURE 3.—Location of 608 spring-water-quality sites in the study area.

TABLE 3.—*Number of water-quality sites and number of available chemical analyses in the study area, by physiographic province and type of site*

Physiographic province	Number of sites			Percentage of type			Number of analyses			Percentage by type		
	well	spring	stream	well	spring	stream	well	spring	stream	well	spring	stream
Valley and Ridge . .	3,012	428	1,547	28.5	70.4	37.8	3,734	1,011	60,432	20.7	59.7	34.1
Blue Ridge.	571	74	355	5.4	12.2	8.7	776	165	13,126	4.3	9.7	7.4
Piedmont.	6,981	106	2,189	66.1	17.4	53.5	13,498	519	103,591	75.0	30.6	58.5
Total	10,564	608	4,091	100	100	100	18,008	1,695	177,149	100	100	100

composition is presented in a later section of this report ("Variations in Chemical Composition of Water, by Type of Site and Physiographic Province").

In addition to ionic composition, physical and chemical properties commonly used to define water quality include specific electrical conductance, dissolved-solids concentration, acidity, water temperature, dissolved-oxygen concentration, and carbonate hardness. Median values for selected properties and constituents of ground water, spring water, and surface water in the study area are listed by physiographic province in table 4. These values indicate that ground water generally contains a small amount of dissolved minerals, is slightly acidic, and is moderately hard. Spring water is more dilute than ground water but contains a higher percentage of ionic solutes; spring water is slightly alkaline and is much harder than ground water. Surface water is also slightly alkaline but is not as hard as ground water. Surface water is the most dilute water type, with only two-thirds the dissolved-solids concentration of ground water.

Median values for water properties and constituents differ considerably from place to place in the study area. Regional differences in water quality are generally related to the availability of soluble minerals in an area and to the types of hydrologic systems that are there. For ground water, median values for specific conductance and pH and for concentrations of dissolved solids, calcium, magnesium, sulfate, bicarbonate, alkalinity, carbonate hardness, nitrite plus nitrate, dissolved iron, total and dissolved manganese are highest in the Valley and Ridge Province. Median water temperature and concentrations of sodium, potassium, chloride, silica, and total iron are highest in the Piedmont Province. The median for dissolved-oxygen concentration is highest in the Blue Ridge Province. Median concentrations of fluoride, ammonia, total and dissolved phosphorus and total manganese are equal in the Piedmont and the Blue Ridge Provinces.

Ground water in the Valley and Ridge is slightly alkaline and is classified as hard, whereas ground water in the Piedmont generally contains smaller amounts of dissolved solids, is slightly acidic, and is classified as moderately hard. Ground water in the Blue Ridge is lowest in median values for most properties and constituents, and it is classified as soft. Because three-fourths of the available analyses are from wells in the Piedmont Province (table 3), overall median values for ground water in the study area resemble those for the Piedmont Province.

Regional variations among the much larger number of chemical analyses available for surface water are generally similar to those for ground water. Most of the surface-water analyses also are for sites in the Piedmont; thus, many overall median values for surface water strongly resemble medians for the Piedmont Province. The Valley and Ridge Province, however, is better represented in the surface-water data than in the ground-water data, and some overall medians show this difference.

Regional variations for some properties and constituents of spring water are different from those for ground water, because approximately 60 percent of the sampled springs are in the Valley and Ridge Province; thus, overall median values for spring water commonly resemble ground-water medians for that province. The chemical data for spring water shows several unusual features that may be related to regional differences in lithology: (1) An inconsistent relation between specific conductance and dissolved-solids concentration. The regional median for specific conductance of spring water is highest in the Piedmont Province, whereas the median for dissolved-solids concentration is highest in the Valley and Ridge. (2) Water from springs in the Piedmont has an unusually low median pH. These differences in water quality may indicate that springflow in the Piedmont Province is primarily through carbonate-deficient regolith, whereas springflow in the Valley and Ridge is primarily through the carbonate-rich sediments of that region.

TABLE 4.—*Median values for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province*

[µS / cm, microsiemens per centimeter at 25 degrees Celsius; mg / L, milligrams per liter; °C, degrees Celsius; mg / L as $CaCO_3$, milligrams per liter as calcium carbonate; µg / L, micrograms per liter]

Property or constituent and unit	Ground water			Spring water			Surface water		
	Valley and Ridge	Blue Ridge	Piedmont	Valley and Ridge	Blue Ridge	Piedmont	Valley and Ridge	Blue Ridge	Piedmont
Specific conductance, µS / cm	380	103	280	312	75	585	208	45	141
Dissolved solids, residue on evaporation at 180°C, mg / L	226	73	159	160	58	109	134	37	99
pH, standard units	7.3	6.6	6.7	7.4	6.2	6.0	7.4	6.8	7.1
Water temperature, °C	12.8	13.0	14.0	12.5	11.0	11.5	14.5	13.0	16.0
Dissolved oxygen, mg / L	5.4	6.2	4.1	7.7	7.2	8.8	9.1	9.6	8.8
Calcium, mg / L	42	8.3	25	41	6.1	11	26	3.4	12
Magnesium, mg / L	10	2.5	6.6	11	2.3	5.7	7.1	1.1	4
Sodium, mg / L	5.8	5	9.5	2.1	3.1	4.4	5.5	2.6	7.7
Potassium, mg / L	1.1	1.2	1.4	1.2	.8	1.6	1.6	.8	1.9
Bicarbonate, mg / L	150	32	60	140	10	14	64	16	38
Alkalinity, mg / L as $CaCO_3$	122	32	57	137	10	16	55	13	34
Carbonate hardness, mg / L as $CaCO_3$	149	29	65	140	26	48	90	13	49
Sulfate, mg / L	20	5	13	11	5	7.7	22	3.7	16
Chloride, mg / L	6	2.1	7	2.8	3.2	6.6	6.8	2.2	9.6
Fluoride, mg / L	.2	.1	.1	.1	.1	.1	.1	.1	.1
Dissolved silica, mg / L	10	16	17	8.6	13	10	5.7	9	10
Nitrite plus nitrate, total, mg / L as N	3.1	.20	.99	1.5	.54	11	.51	.23	1.1
Ammonia, total, mg / L as N	.03	.05	.05	.02	.01	.03	.07	.05	.15
Phosphorus, dissolved, mg / L as P	.02	.03	.03	.04	.05	.03	.03	.02	.09
Phosphorus, total, mg / L as P	.02	.05	.05	.02	.01	.03	.07	.04	.18
Iron, dissolved, µg / L	100	31	50	20	8	30	40	40	90
Iron, total, µg / L	70	100	200	90	75	110	400	100	440
Manganese, dissolved, µg / L	40	17	38	11	2.5	8	40	11	46
Manganese, total, µg / L	80	50	50	20	15	15	80	50	100

ANALYTICAL AND INTERPRETIVE APPROACH

Systematic variations in properties and constituents of ground water in the study area may result from: geologic and lithologic factors (water-rock interactions), hydrologic factors (recharge, discharge, and mixing of waters), biochemical factors (chemical reactions mediated by living organisms), and physical factors (changes in temperature, pressure, location, and topography); but with previously collected data, systematic variations can also result from the diversity of methods that were used to collect the data. The interpretation of variations in properties and constituents from a large regional data base requires an approach that focuses on comparing representative values for selected groups of data. Statistical techniques based on sorted data (ranked values) provide an unbiased means for obtaining reliable central values (medians), for quantifying the spread of values about the center (interquartile range), and for comparing groups of data (analysis of variance). Statistical techniques based on regression provide a means for fitting a smoothed line to a group of points on a scatterplot. GIS techniques provide a means to display variations in properties and constituents as a function of location (geographic trends). All three methods are used in the following sections of this report.

STATISTICAL TREATMENT OF WATER-QUALITY DATA

Water-quality data commonly contain many values clustered together at the low end of the range and a diminishing number of values scattered across the high end. For this type of skewed distribution, percentile indexes based on the rank of the data values are often used to express: (1) the median (or 50th percentile), a value that represents the center of the group, and (2) the interquartile range (IQR), a value that indicates the degree of uncertainty in the location of the median. The IQR is the difference between the 75th and 25th percentiles and is the middle half of the data. Percentile indexes are comparatively insensitive (or robust) to extreme values and are usually a more reliable description of the data than are the mean and standard deviation.

Seven percentile indexes calculated for selected chemical properties and constituents are listed in table 5 by type of site and physiographic province. Zero and missing values in the data have been excluded from the calculation. Representative values in the lower quartile of each group are shown by the 5th and 10th percentiles; values in the upper quartile are shown by the 90th and 95th percentiles. The arithmetic mean is also listed for comparison.

DISPLAY OF REGIONAL VARIATIONS IN WATER QUALITY

Value-distribution diagrams (boxplots) are a concise way to display the statistical information obtained from percentile indexes. This diagram was introduced by Tukey (1977) and several modifications have been proposed by other researchers (Helsel and Hirsch, 1992; McGill and others, 1978). Most boxplots, however, consist of a few basic elements: a rectangular box that encloses the IQR, a median line that divides the box in half, and a pair of whisker lines that extend outward from the ends of the box to show the lower and upper tails of the distribution. Some features of the diagram have not been standardized: The far ends of whisker lines may extend to: (1) the minimum and maximum data values, (2) specific percentile indexes, or (3) a distance related to the size of the IQR. To emphasize skew, Tukey's boxplots show individual values which lie beyond the ends of the whisker lines (detached values).

Boxplot diagrams are often put side by side to compare and contrast groups of data. In this report, regional variations in water-quality are shown on multiple boxplot diagrams that display nine groups of data for each property or constituent: a group for each type of site (ground water, spring water, and surface water) in each of the three physiographic provinces. Most groups contain detached values, but this report emphasizes differences among the central values for the groups; detached values represent extremes and are not shown. Whisker lines extend to the 10th and 90th percentile indexes and encompass about 80 percent of the data.

DISPLAY OF LOCAL VARIATIONS IN WATER QUALITY

The county grid system for the study area is a useful tool for displaying local variations in water quality because each county can be shown on a map with an intensity of shading that shows the relative magnitude of the property or constituent. The value used to determine the shading for a county is generally the median value for the county. If only one value is available for the county, that value determines the shading. The shading scheme is based on selected percentile indexes calculated from all data shown on the map (see Appendix B, table B–1), and the use of a contrasting color (red) calls attention to counties with unusually high values for a property or constituent. For each shaded map, an inset map shows the location of data sites and emphasizes their uneven geographic distribution.

DISPLAY OF DEPTH VARIATIONS IN GROUND-WATER DATA

Water collected from a network of wells can show water-quality variations as a function of depth. Descriptive statistics for depth of sampled wells are listed by physiographic province in table 6 and summarized graphically in figures 4 and 5. In the APRASA study area, most sampled wells are less than 500 ft deep and half are less than 200 ft deep; only a few wells in the water-quality data base are deeper than 1,000 ft. Median well depths in the Piedmont, the Blue Ridge, and the Valley and Ridge Provinces are 140, 164, and 150 ft, respectively (fig. 4). Nearly twice as many sampled wells are in the Piedmont as are in the Valley and Ridge, and only 4.2 percent are in the Blue Ridge (table 6). Most sampled wells for which depth is known are in New Jersey, Pennsylvania, Maryland, and North Carolina and are less than 200 ft deep (fig. 5). The deepest

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Specific conductance, microsiemens per centimeter at 25 degrees Celsius									
Ground water:									
Valley and Ridge	2,955	604	75	126	220	380	600	817	1,002
Blue Ridge	454	154	29	39	54	103	201	303	440
Piedmont	10,150	387	41	59	115	280	554	780	976
All ground water	13,559	427	44	62	129	295	560	780	970
Spring water:									
Valley and Ridge	803	369	65	168	220	312	535	600	657
Blue Ridge	140	104	16	19	49	75	148	193	332
Piedmont	452	489	78	99	163	585	680	736	772
All spring water	1,395	382	48	77	180	343	580	683	728
Surface water:									
Valley and Ridge	37,406	273	56	80	137	208	298	420	520
Blue Ridge	6,359	76	12	14	20	45	86	145	264
Piedmont	53,795	228	37	47	72	141	249	380	487
All surface water	97,560	235	31	46	80	163	264	392	496
Dissolved solids, residue on evaporation at 180 degrees Celsius, milligrams per liter									
Ground water:									
Valley and Ridge	1,490	369	50	81	130	226	359	499	614
Blue Ridge	393	94	23	32	48	73	125	177	220
Piedmont	5,551	227	37	53	90	159	282	429	554
All ground water	7,434	248	37	52	92	164	292	438	558
Spring water:									
Valley and Ridge	367	187	25	33	112	160	263	370	408
Blue Ridge	110	75	18	20	32	58	106	142	218
Piedmont	79	187	21	30	61	109	216	349	460
All spring water	556	165	22	27	65	136	224	345	404
Surface water:									
Valley and Ridge	14,948	189	46	60	91	134	190	275	378
Blue Ridge	3,553	58	14	17	22	37	60	113	181
Piedmont	25,483	167	36	44	60	99	155	238	304
All surface water	43,984	165	29	40	62	107	165	246	318

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province— Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
pH, standard units									
Ground water:									
Valley and Ridge	2,801	7.2	5.7	6.2	6.9	7.3	7.6	7.9	8.1
Blue Ridge	416	6.6	5.6	5.8	6.1	6.6	7.0	7.6	7.9
Piedmont	8,821	6.7	5.2	5.6	6.1	6.7	7.4	7.8	8.0
All ground water	12,038	6.8	5.3	5.7	6.2	6.9	7.5	7.8	8.1
Spring water:									
Valley and Ridge	749	7.3	6.1	6.5	7.1	7.4	7.7	7.9	8.1
Blue Ridge	154	6.3	5.3	5.5	5.9	6.2	6.6	7.5	7.8
Piedmont	181	6.3	5.4	5.5	5.7	6.0	6.9	7.4	7.6
All spring water	1,084	7.0	5.5	5.7	6.4	7.2	7.6	7.9	8.0
Surface water:									
Valley and Ridge	35,861	7.3	5.0	6.4	7.0	7.4	7.8	8.2	8.4
Blue Ridge	6,345	6.8	6.0	6.2	6.4	6.8	7.2	7.5	7.7
Piedmont	50,701	7.2	6.2	6.4	6.8	7.1	7.5	7.9	8.2
All surface water	92,907	7.2	6.0	6.4	6.8	7.2	7.6	8.0	8.3
Water temperature, degrees Celsius									
Ground water:									
Valley and Ridge	2,025	13.1	9.5	10.3	11.1	12.8	14.5	16.5	17.5
Blue Ridge	327	13.4	9.7	10.0	11.0	13.0	15.5	17.0	18.5
Piedmont	6,991	14.5	10.7	11.5	12.5	14.0	16.5	18.5	19.9
All ground water	9,343	14.2	10.0	11.0	12.0	13.5	16.0	18.0	19.2
Spring water:									
Valley and Ridge	852	13.3	9.5	10.3	11.1	12.5	15.0	17.9	19.0
Blue Ridge	152	11.3	8.0	9.0	10.0	11.0	12.5	14.1	15.0
Piedmont	331	11.5	7.3	9.5	11.0	11.5	12.0	14.0	15.0
All spring water	1,335	12.6	9.0	10.0	11.0	12.0	14.0	16.5	18.0
Surface water:									
Valley and Ridge	43,215	14.3	2.0	4.0	8.5	14.5	20.5	24.0	26.0
Blue Ridge	8,490	12.9	2.0	4.0	8.0	13.0	18.0	21.5	23.2
Piedmont	64,947	15.1	2.0	4.0	9.0	16.0	21.5	25.0	26.5
All surface water	116,652	14.7	2.0	4.0	8.6	15.0	21.0	24.5	26.0

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province—Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Dissolved-oxygen concentration, milligrams per liter									
Ground water:									
Valley and Ridge	359	4.8	0.3	0.5	1.3	5.4	8.1	9.1	9.8
Blue Ridge	14	5.8	.9	1.6	5.4	6.2	7.2	8.1	8.2
Piedmont	2,274	4.4	.2	.2	1.0	4.1	7.3	9.0	9.8
All ground water	2,647	4.5	.2	.2	1.0	4.2	7.4	9.0	9.8
Spring water:									
Valley and Ridge	196	7.5	3.9	4.4	6.0	7.7	8.8	10.0	10.6
Blue Ridge	2	7.2	6.2	6.2	6.2	7.2	8.2	8.2	8.2
Piedmont	92	8.5	4.7	6.2	7.9	8.8	9.5	10.4	11.1
All spring water	290	7.8	4.0	4.9	6.5	8.0	9.0	10.0	10.8
Surface water:									
Valley and Ridge	22,773	9.0	4.4	5.6	7.5	9.1	10.8	12.4	13.4
Blue Ridge	2,043	9.6	6.1	7.0	8.2	9.6	11.0	12.2	13.0
Piedmont	36,911	8.6	2.7	4.6	7.0	8.8	10.7	12.4	13.4
All surface water	61,727	8.8	3.4	5.1	7.2	9.0	10.8	12.4	13.4
Calcium concentration, milligrams per liter									
Ground water:									
Valley and Ridge	2,571	57	4.2	8.9	21	42	78	108	129
Blue Ridge	442	14	1.2	2.2	4.7	8.3	19	32	42
Piedmont	5,098	38	2.2	4.1	9.6	25	50	80	100
All ground water	8,111	43	2.5	4.6	11	30	57	91	110
Spring water:									
Valley and Ridge	579	48	3.1	6.4	26	41	69	93	110
Blue Ridge	149	8.8	.8	1.2	2.5	6.1	12	20	28
Piedmont	110	31	1.5	2.2	5.9	11	49	83	90
All spring water	838	39	1.5	3.2	9.9	32	55	88	97
Surface water:									
Valley and Ridge	14,521	39	6.0	9.4	16	26	38	53	71
Blue Ridge	4,883	6.1	.60	.9	1.6	3.4	5.9	11	26
Piedmont	26,034	16	2.7	3.6	5.7	12	20	32	42
All surface water	45,438	22	2.1	3.2	6	14	26	41	51

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province— Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Magnesium concentration, milligrams per liter									
Ground water:									
Valley and Ridge	2,528	18	1.5	2.6	5.3	10	20	33	42
Blue Ridge	477	3.8	.4	.6	1.2	2.5	4.3	7.8	12
Piedmont	6,344	14	.7	1.2	2.9	6.6	15	25	36
All ground water	9,349	15	.8	1.4	3.1	7.2	16	28	37
Spring water:									
Valley and Ridge	564	12	1.4	2.2	5.3	11	16	22	27
Blue Ridge	149	3.4	.4	.5	1	2.3	4.4	8	11
Piedmont	110	8.7	.9	1.1	3	5.7	11	20	32
All spring water	823	9.8	.8	1.3	3.2	7.6	14	20	25
Surface water:									
Valley and Ridge	14,410	9.6	1.5	2.3	4.2	7.1	12	18	23
Blue Ridge	4,863	1.6	.2	.3	.5	1.1	1.9	2.9	4.6
Piedmont	25,881	6.6	1	1.3	2.1	4	6.7	10	14
All surface water	45,154	7.0	.7	1.1	2.1	4.4	7.9	13	17
Sodium concentration, milligrams per liter									
Ground water:									
Valley and Ridge	2,225	90	.8	1.3	2.7	5.8	12	27	54
Blue Ridge	441	7.1	1.4	2.1	3	5	7.9	12	17
Piedmont	5,888	27	2	2.9	5.3	9.5	17	36	62
All ground water	8,554	42	1.4	2.2	4.3	8.1	16	33	59
Spring water:									
Valley and Ridge	483	4	.5	.6	1.1	2.1	4	8.5	17
Blue Ridge	145	5.6	.9	1.1	2	3.1	7.5	12	18
Piedmont	101	8.7	1.4	2	2.8	4.4	9.1	20	25
All spring water	729	5	.6	.8	1.4	2.6	4.9	11	19
Surface water:									
Valley and Ridge	12,256	18	1.3	1.7	2.9	5.5	11	22	35
Blue Ridge	4,860	6.0	.9	1	1.3	2.6	5.8	14	22
Piedmont	23,497	21	2.5	3.2	4.7	7.7	14	29	44
All surface water	40,613	18	1.3	2	3.5	6.4	13	25	40

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province— Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Potassium concentration, milligrams per liter									
Ground water:									
Valley and Ridge	2,121	16	0.3	0.4	0.6	1.1	2.3	7.3	17
Blue Ridge.............	411	3.3	.3	.4	.7	1.2	1.9	2.8	3.8
Piedmont..............	5,681	2.5	.4	.5	.9	1.4	2.5	4.2	6.1
All ground water	8,213	6.1	.3	.5	.8	1.4	2.4	4.5	7.7
Spring water:									
Valley and Ridge	423	1.4	.4	.5	.8	1.2	1.9	2.5	3.1
Blue Ridge.............	134	.9	.2	.4	.4	.8	1.2	1.6	1.8
Piedmont..............	101	2.2	.5	.6	1	1.6	2.1	3.5	11
All spring water	658	1.4	.4	.5	.7	1.1	1.8	2.4	3.1
Surface water:									
Valley and Ridge	10,542	1.9	.7	.9	1.2	1.6	2.1	3	3.8
Blue Ridge.............	4,732	1	.2	.3	.5	.8	1.3	1.8	2.3
Piedmont..............	22,360	2.7	.8	1	1.4	1.9	2.6	3.8	4.9
All surface water	37,634	2.2	.6	.8	1.2	1.7	2.4	3.4	4.4
Bicarbonate concentration, milligrams per liter									
Ground water:									
Valley and Ridge	1,570	164	14	24	78	150	234	310	351
Blue Ridge.............	349	43	6	9	21	32	54	86	121
Piedmont..............	4,589	89	6	11	28	60	128	196	247
All ground water	6,508	105	8	12	31	72	153	236	297
Spring water:									
Valley and Ridge	383	145	9	12	90	140	199	284	310
Blue Ridge.............	51	13	2	3	6	10	16	34	37
Piedmont..............	93	55	6	7	9	14	61	174	249
All spring water	527	117	6	8	16	124	170	264	302
Surface water:									
Valley and Ridge	11,553	79	6	15	34	64	115	162	190
Blue Ridge.............	4,311	22	4	6	10	16	24	39	66
Piedmont..............	19,735	49	13	16	23	38	60	90	124
All surface water	35,599	55	8	13	22	40	70	123	158

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province—Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
			Total alkalinity, as $CaCO_3$, milligrams per liter						
Ground water:									
Valley and Ridge	1,738	136	11	20	62	122	190	253	290
Blue Ridge	322	45	7	9	18	32	49	98	137
Piedmont	7,634	87	5	10	25	57	123	190	240
All ground water	9,694	94	6	11	28	64	136	208	256
Spring water:									
Valley and Ridge	523	149	8	14	100	137	214	238	250
Blue Ridge	60	24	4	5	6	10	28	83	104
Piedmont	109	55	5	6	7	16	86	198	223
All spring water	692	124	6	7	23	115	206	233	246
Surface water:									
Valley and Ridge	19,342	68	5	11	29	55	95	134	160
Blue Ridge	3,087	18	4	5	7	13	18	34	63
Piedmont	24,242	44	10	13	20	34	55	84	116
All surface water	46,671	52	7	11	20	39	68	112	140
			Carbonate hardness, as $CaCO_3$, milligrams per liter						
Ground water:									
Valley and Ridge	2,931	223	20	37	81	149	274	359	419
Blue Ridge	479	48	6	9.8	16	29	63	102	124
Piedmont	8,268	120	8	12	28	65	160	278	357
All ground water	11,678	143	8.7	14	32	82	184	307	380
Spring water:									
Valley and Ridge	645	161	12	18	103	140	227	298	331
Blue Ridge	151	36	3.8	5	11	26	50	86	114
Piedmont	127	103	7.8	9	23	48	151	262	296
All spring water	923	133	7.3	13	40	120	195	284	321
Surface water:									
Valley and Ridge	22,899	124	24	34	56	90	134	192	249
Blue Ridge	5,286	21	3.2	3.9	6.3	13	23	38	82
Piedmont	30,844	68	11	14	23	49	82	125	167
All surface water	59,029	85	9.3	14	26	60	103	156	198

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province—Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Sulfate concentration, milligrams per liter									
Ground water:									
Valley and Ridge	2,636	62	2	3.2	8.9	20	39	78	164
Blue Ridge.............	471	7.7	.3	.6	2	5	8.2	15	25
Piedmont..............	6,872	35	.8	1.6	5	13	30	64	110
All ground water	9,979	41	.9	1.9	5	14	32	65	120
Spring water:									
Valley and Ridge	604	20	1.5	2.2	4.8	11	23	36	45
Blue Ridge.............	146	6.5	.2	.5	2.1	5	7.5	12	16
Piedmont..............	115	30	.6	1.1	3	7.7	16	29	40
All spring water......	865	19	1	1.9	3.6	8.4	19	34	40
Surface water:									
Valley and Ridge	22,192	58	4.6	7	13	22	46	110	209
Blue Ridge.............	5,102	8.4	.6	.9	2	3.7	8.6	22	33
Piedmont..............	29,942	29	2	3	6.8	16	28	49	77
All surface water	57,236	38	2	3.1	7.4	17	32	67	113
Chloride concentration, milligrams per liter									
Ground water:									
Valley and Ridge	2,993	99	1	1.2	2.5	6	14	33	59
Blue Ridge.............	558	6.4	.7	1	1	2.1	5.9	18	29
Piedmont..............	8,739	25	1.1	1.8	3	7	18	50	88
All ground water	12,290	42	1	1.5	2.8	6.4	17	44	79
Spring water:									
Valley and Ridge	639	6.3	.6	.8	1.4	2.8	7.3	13	23
Blue Ridge.............	150	8.9	.7	.8	1.7	3.2	9.6	25	40
Piedmont..............	127	14	1.6	2	3.3	6.6	13	41	51
All spring water......	916	7.8	.6	.9	1.5	3.5	8.5	17	35
Surface water:									
Valley and Ridge	20,539	34	1.4	2	3.4	6.8	13	25	42
Blue Ridge.............	5,265	6.4	.5	.7	1.1	2.2	5	11	20
Piedmont..............	30,457	85	2	2.7	4.7	9.6	20	42	64
All surface water	56,261	59	1.2	1.9	3.6	7.5	16	34	54

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province— Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
			Fluoride concentration, milligrams per liter						
Ground water:									
Valley and Ridge	1,299	.26	0.1	0.1	0.1	0.2	0.2	0.4	0.6
Blue Ridge	290	.19	.1	.1	.1	.1	.2	.3	.4
Piedmont...............	3,543	.22	.1	.1	.1	.1	.2	.3	.5
All ground water......	5,132	.23	.1	.1	.1	.1	.2	.3	.5
Spring water:									
Valley and Ridge	304	.19	.1	.1	.1	.1	.2	.3	.4
Blue Ridge	15	.13	.1	.1	.1	.1	.1	.24	.3
Piedmont...............	44	.16	.1	.1	.1	.1	.18	.25	.57
All spring water.......	363	.18	.1	.1	.1	.1	.2	.3	.4
Surface water:									
Valley and Ridge	7,175	.19	.1	.1	.1	.1	.2	.3	.4
Blue Ridge	1,863	.19	.1	.1	.1	.1	.2	.2	.3
Piedmont...............	16,185	.24	.1	.1	.1	.1	.2	.3	.5
All surface water	25,223	.23	.1	.1	.1	.1	.2	.3	.4
			Dissolved-silica concentration, milligrams per liter						
Ground water:									
Valley and Ridge	1,704	11	5	6.1	7.9	10	13	18	21
Blue Ridge	443	18	5.8	7.1	10	16	22	29	35
Piedmont...............	5,838	19	5	6.6	11	17	25	32	37
All ground water......	7,985	17	5	6.5	9.3	15	23	30	35
Spring water:									
Valley and Ridge	392	8.6	3.8	5.1	6.8	8.6	10	11	12
Blue Ridge	119	13	5.5	6.1	7.8	13	19	21	23
Piedmont...............	96	13	4.5	5.7	8.7	10	16	24	27
All spring water.......	607	10	4.4	5.5	7.3	8.9	11	18	21
Surface water:									
Valley and Ridge	12,184	6	1.6	2.6	4.1	5.7	7.2	9	11
Blue Ridge	4,859	9.3	4.9	5.8	7.2	9	11	13	15
Piedmont...............	24,076	11	3.5	4.9	7.6	10	14	17	19
All surface water	41,119	9.2	2.6	3.8	5.8	8.5	12	15	17

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province—Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Total nitrite plus nitrate concentration, as nitrogen, milligrams per liter									
Ground water:									
Valley and Ridge	310	5.5	0.03	0.10	0.87	3.1	7.1	14	21
Blue Ridge.............	236	1.1	.01	.02	.05	.2	1.2	3	4.7
Piedmont..............	2,366	4.9	.05	.05	.20	.99	4.3	12	20
All ground water	2,912	4.7	.05	.05	.20	1.0	4.3	12	18
Spring water:									
Valley and Ridge	52	2.8	.10	.17	.84	1.5	4.9	6.2	10
Blue Ridge.............	25	1.1	.08	.11	.25	.54	1.2	4.1	4.7
Piedmont..............	94	8.8	.10	.60	4	11	12	15	18
All spring water	171	5.9	.10	.20	.93	4.3	11	13	16
Surface water:									
Valley and Ridge	11,617	.78	.12	.19	.31	.51	.86	1.5	2.4
Blue Ridge.............	1,077	.37	.03	.06	.12	.23	.48	.82	1.1
Piedmont..............	27,725	2.4	.12	.20	.43	1.1	2.9	5.5	7.6
All surface water	40,419	1.9	.11	.19	.36	.79	2	4.6	6.3
Total-ammonia concentration, as nitrogen, milligrams per liter									
Ground water:									
Valley and Ridge	213	.82	.01	.01	.02	.03	.07	.15	.57
Blue Ridge.............	106	.03	.01	.01	.01	.05	.05	.05	.05
Piedmont..............	1,096	1.4	.01	.02	.04	.05	.09	.25	.57
All ground water	1,415	1.2	.01	.01	.03	.05	.08	.21	.53
Spring water:									
Valley and Ridge	106	.04	.01	.01	.01	.02	.04	.09	.13
Blue Ridge.............	2	.01	0	0	0	.01	.01	.01	.01
Piedmont..............	60	.04	.01	.01	.02	.03	.05	.06	.10
All spring water	168	.04	.01	.01	.01	.02	.04	.08	.11
Surface water:									
Valley and Ridge	11,254	.20	.01	.02	.04	.07	.13	.28	.46
Blue Ridge.............	825	.08	.01	.01	.02	.05	.10	.15	.23
Piedmont..............	26,408	.92	.02	.03	.07	.15	.47	1.40	2.50
All surface water	38,487	.69	.02	.03	.05	.11	.31	1.00	1.90

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province— Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Dissolved-phosphorus concentration, as phosphorus, milligrams per liter									
Ground water:									
Valley and Ridge	36	0.03	0.01	0.01	0.02	0.02	0.04	0.07	0.15
Blue Ridge	15	.05	.02	.02	.02	.03	.08	.11	.14
Piedmont	1,880	.32	.01	.01	.02	.03	.07	.13	.24
All ground water	1,931	.31	.01	.01	.02	.03	.07	.13	.23
Spring water:									
Valley and Ridge	19	.07	.01	.01	.02	.04	.13	.18	.19
Blue Ridge	3	.07	.04	.04	.04	.05	.12	.12	.12
Piedmont	97	.04	.01	.01	.02	.03	.04	.07	.08
All spring water	119	.04	.01	.01	.02	.03	.05	.09	.13
Surface water:									
Valley and Ridge	3,641	.06	.01	.01	.02	.03	.05	.09	.13
Blue Ridge	334	.05	.01	.01	.01	.02	.06	.12	.19
Piedmont	9,919	.34	.01	.01	.03	.09	.24	.62	1.30
All surface water	13,894	.26	.01	.01	.02	.06	.17	.44	.96
Total-phosphorus concentration, as phosphorus, milligrams per liter									
Ground water:									
Valley and Ridge	92	.10	.01	.01	.02	.02	.03	.09	.35
Blue Ridge	134	.06	.01	.02	.04	.05	.06	.11	.16
Piedmont	2,115	.20	.01	.02	.05	.05	.10	.26	.45
All ground water	2,341	.19	.01	.02	.05	.05	.10	.24	.43
Spring water:									
Valley and Ridge	129	.02	0	.01	.02	.02	.03	.03	.04
Blue Ridge	10	.03	.01	.01	.01	.01	.08	.09	.09
Piedmont	87	.06	.01	.01	.02	.03	.05	.07	.17
All spring water	226	.04	.01	.01	.02	.03	.04	.05	.08
Surface water:									
Valley and Ridge	13,981	.17	.01	.02	.03	.07	.14	.28	.45
Blue Ridge	1,065	.12	.01	.01	.02	.04	.11	.31	.52
Piedmont	33,421	.76	.02	.03	.06	.18	.58	2	3.5
All surface water	48,467	.57	.02	.02	.05	.12	.38	1.3	2.7

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province—Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Dissolved-iron concentration, micrograms per liter									
Ground water:									
Valley and Ridge	2,044	2,496	7	10	30	100	400	2,200	7,975
Blue Ridge.............	150	228	4	5	10	31	172	479	1,079
Piedmont..............	3,478	855	4	6	12	50	190	1,200	3,201
All ground water	5,672	1,430	5	7	17	70	270	1,500	4,280
Spring water:									
Valley and Ridge	239	58	3	4	8	20	50	122	200
Blue Ridge.............	64	18	3	4	5	8	15	55	77
Piedmont..............	82	284	4	5	11	30	80	204	756
All spring water	385	100	3	4	7	20	50	121	205
Surface water:									
Valley and Ridge	5,442	4,334	10	10	20	40	100	270	700
Blue Ridge.............	1,181	77	8.7	10	20	40	100	170	240
Piedmont..............	8,532	222	14	20	40	90	200	410	660
All surface water	15,155	1,687	10	15	30	65	160	350	620
Total-iron concentration, micrograms per liter									
Ground water:									
Valley and Ridge	312	3,305	.1	.3	10	70	872	4,270	11,350
Blue Ridge.............	284	443	12	30	90	100	400	1,000	1,637
Piedmont..............	3,109	3,805	17	40	100	200	1,000	5,100	12,000
All ground water	3,705	3,505	10	20	84	170	900	4,600	10,961
Spring water:									
Valley and Ridge	115	1,128	.1	.4	20	90	210	524	988
Blue Ridge.............	24	80	2.1	14	30	75	117	185	190
Piedmont..............	48	416	24	39	50	110	330	1,420	2,595
All spring water	187	811	.2	10	40	90	200	574	1,160
Surface water:									
Valley and Ridge	10,321	3,248	50	100	200	400	920	2,800	6,690
Blue Ridge.............	1,801	698	10	10	30	100	330	790	1,290
Piedmont..............	13,375	1,650	30	60	180	440	1,100	2,500	4,900
All surface water	25,497	2,230	30	60	170	400	980	2,400	5,300

TABLE 5.—*Summary statistics for selected properties and constituents of ground water, spring water, and surface water in the study area, by physiographic province— Continued*

Type of site and physiographic province	Number of analyses	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Dissolved-manganese concentration, micrograms per liter									
Ground water:									
Valley and Ridge	1,463	708	2	5	10	40	190	760	3,000
Blue Ridge	59	62	1	2	4	17	33	280	400
Piedmont	2,869	429	2	3	10	38	170	650	1,400
All ground water......	4,391	517	2	3	10	40	170	660	1,700
Spring water:									
Valley and Ridge	148	38	1	1	2.2	11	38	70	81
Blue Ridge	14	7.7	1	1	1.8	2.5	6.2	36	52
Piedmont	57	142	1	2	3	8	28	91	261
All spring water.......	219	63	1	1	2	9	30	64	110
Surface water:									
Valley and Ridge	4,524	1,173	4	8	20	40	240	1,350	3,000
Blue Ridge	306	25	1	1.4	3	11	24	69	110
Piedmont	5,231	140	6	10	20	46	110	230	410
All surface water......	10,061	601	4	8	20	40	130	486	1,400
Total-manganese concentration, micrograms per liter									
Ground water:									
Valley and Ridge	190	318	.41	10	20	80	242	759	1,345
Blue Ridge	168	254	.15	20	50	50	50	100	256
Piedmont	2,175	1,000	.10	10	50	50	200	1,140	3,958
All ground water......	2,533	900	.10	10	50	50	200	1,000	3,579
Spring water:									
Valley and Ridge	56	1,261	10	10	10	20	37	120	2,500
Blue Ridge	2	15	10	10	10	15	20	20	20
Piedmont	22	48	10	10	10	15	42	208	258
All spring water.......	80	816	10	10	10	20	30	111	256
Surface water:									
Valley and Ridge	7,124	527	20	20	40	80	250	840	2,300
Blue Ridge	608	92	10	20	30	50	80	180	290
Piedmont	6,363	229	20	30	50	100	210	460	720
All surface water......	14,095	374	20	20	50	90	220	580	1,200

TABLE 6.—*Summary statistics for depth of wells sampled in the study area*

Physiographic province	Number of wells	Mean	Percentile values calculated from the data						
			5th	10th	25th	50th	75th	90th	95th
Valley and Ridge	2,195	192	31	51	93	150	243	374	480
Blue Ridge	287	191	39	59	97	164	255	345	403
Piedmont	4,287	187	22	32	75	140	263	400	500
All sampled wells ..	6,769	189	24	38	82	145	250	396	500

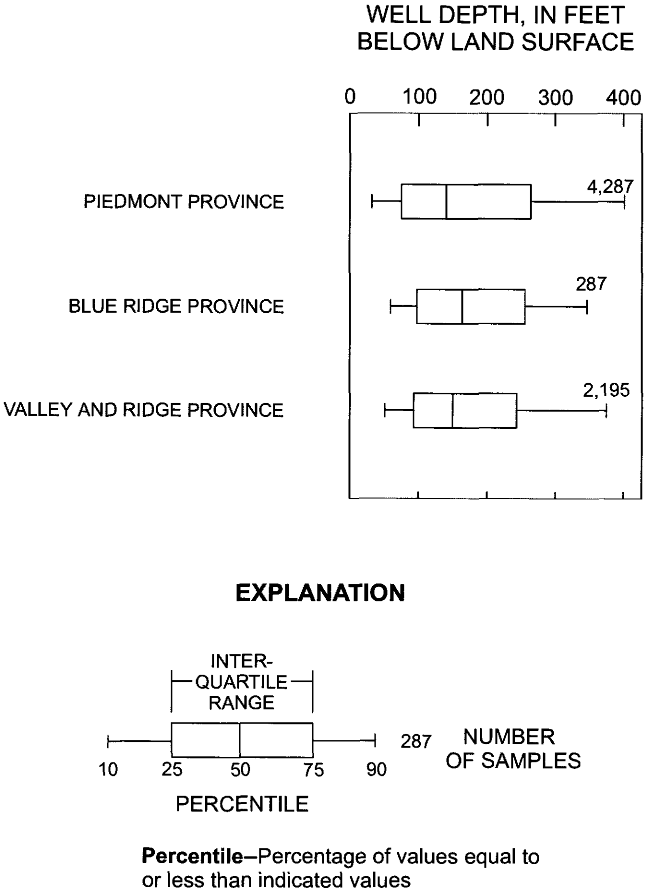


FIGURE 4.—Summary of well depth, by physiographic province.

sampled wells are in the Valley and Ridge Province in Tennessee and Virginia and in the Piedmont Province in Georgia and Virginia (fig. 5).

Depth-related trends calculated for selected chemical constituents are displayed as smoothed curves on X–Y diagrams to show the general effect of increasing well depth on these characteristics. A statistically robust locally weighted least-squares regression technique (called LOWESS) was used to fit a smoothed line to a set of points on a scatterplot. In a regression, the two variables are not mathematically interchangeable; the resulting curve shows the values predicted for the dependent (Y-axis) variable as a function of changes in the independent (X-axis) variable. Details of the LOWESS procedure are given in Cleveland (1979) and in Chambers and others (1983). This method for showing depth-related trends in individual chemical characteristics has also been used to display relations between selected pairs of water-quality characteristics. On all LOWESS plots in this report, the user-selected smoothing fraction is equal to 0.67 and, for clarity, only the smoothed trend line is shown.

VARIATIONS IN SELECTED PROPERTIES AND CONSTITUENTS

Eighteen water properties and constituents were selected from table 5 for individual study. Selection was based on the amount of data available and on the general applicability of a property or constituent to geochemical studies of ground water. Commonly determined properties—such as specific conductance, water temperature, and pH—are represented in the data base by more than 100,000 measurements. Major dissolved constituents—such as solids, major ions, oxygen, silica, and some nutrients—are represented by approximately 40,000 to 70,000 measurements. Other constituents are represented by smaller amounts of data.

In the following sections on individual properties and constituents, the format is the following: (1) The property is described and its geochemical and biological significance is summarized. Unless otherwise cited, the source for this information is Hem (1985). (2) For ground water, spring water, and surface water, the IQR is presented in terms of its lower and upper limits (the 25th and 75th percentiles), and (3) median values for the three physiographic provinces are compared. Analysis of differences in median values among provinces is based on the Kruskal-Wallis and Mann-Whitney tests corrected for the number of pairs involved (Helsel and Hirsch, 1992). A graphical summary of the nine groups of data is shown on a multiple boxplot diagram. (4) For

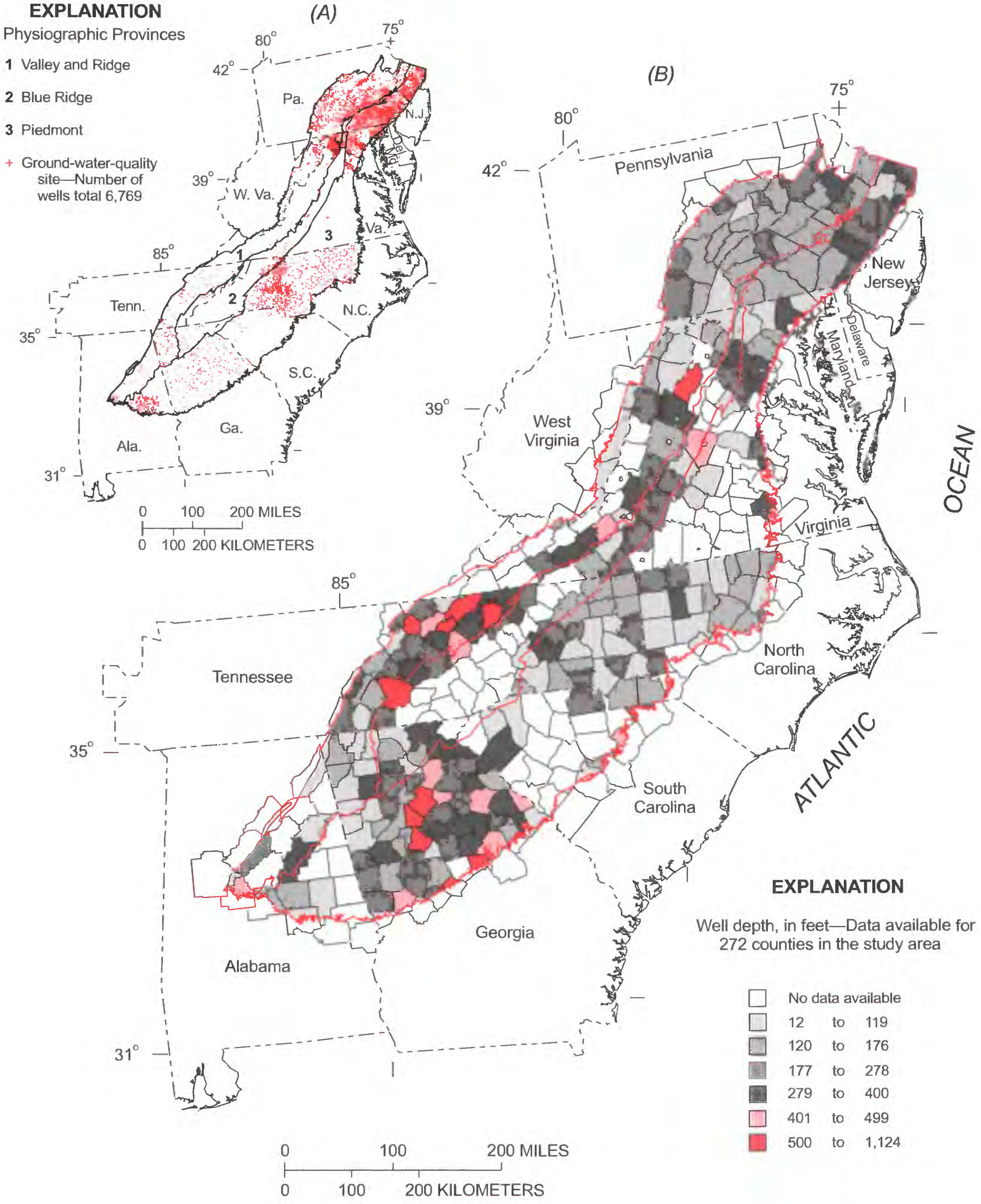


FIGURE 5.—Location of wells in study area where depth is known *(A)*, and geographic variation of median well depth, by county *(B)*.

ground water, the median value is determined for each county where data have been reported and shown on a shaded map.

SPECIFIC CONDUCTANCE

The electrical conductance of water is related to the concentration of dissolved ions. Pure water at 25°C has a specific conductance of only a few hundredths of a microsiemen per centimeter. Natural water, however, usually contains a variety of dissolved minerals and shows a wide range of specific conductance from about 2 µS / cm for melted snow to more than 200,000 µS / cm for deep ground water (brines). Because the conductance of each dissolved ion is related to its mass, charge, and concentration, gross measurements of specific conductance cannot always be used to make accurate estimates of specific ion concentrations or dissolved solids. For dilute freshwater, however, the relation between specific conductance and dissolved solids is commonly well defined; for these waters, specific conductance can be used to extrapolate dissolved-solids concentrations in areas where dissolved-solids data are unavailable (see "Dissolved Solids").

The specific conductance of natural water is one of the most commonly determined properties: in the study area, more than 112,000 measurements have been reported (table 5). The interquartile range (IQR) for specific conductance of ground water is 129 to 560 µS / cm. Although the three regional IQR's overlap (fig. 6), differences in median specific conductance of ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (103, 280, and 380 µS / cm, respectively) are statistically significant at the 0.05 level (significant). The highest median specific conductances for counties are in the Valley and Ridge Province and in widely scattered counties of the Piedmont (fig. 7). A comparison of figures 7 and 5 indicates that wells in several counties in northeastern Tennessee and along the eastern edge of the Valley and Ridge Province in Virginia are not only deep but also produce water high in specific conductance. Most of the high values, however, are based on data for only one or two wells in the county, and data are too sparse to make the correlation on a local basis.

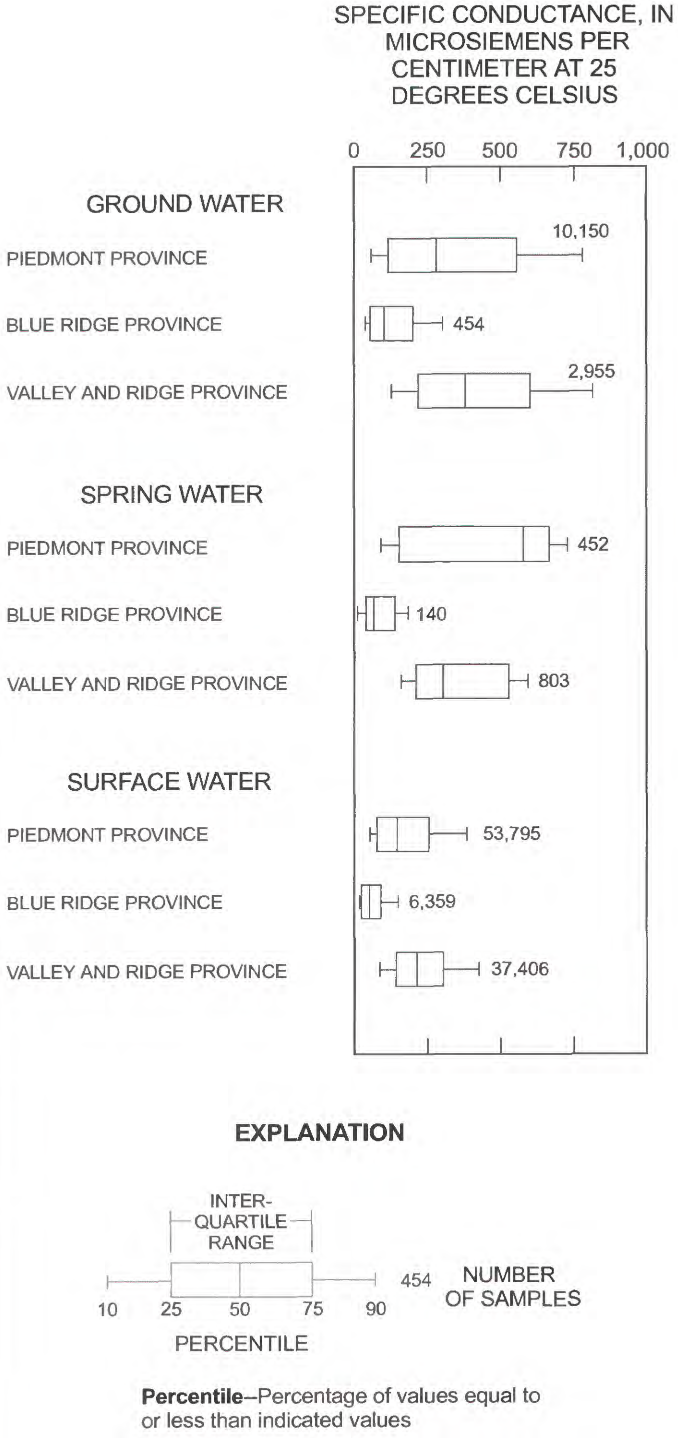


FIGURE 6.—Summary of specific conductance, by type of site and physiographic province.

The statistical variation of specific conductance as a function of well depth by physiographic province for the set of data in which both values are known is shown in figure 8. For the Piedmont Province, specific conductance increases with well depth; for the Blue Ridge and the Valley and Ridge Provinces, however, this relation is poorly defined. In all three provinces, the curve inflects sharply near the median depth; thus, about one-half the data lie on each side of the inflection.

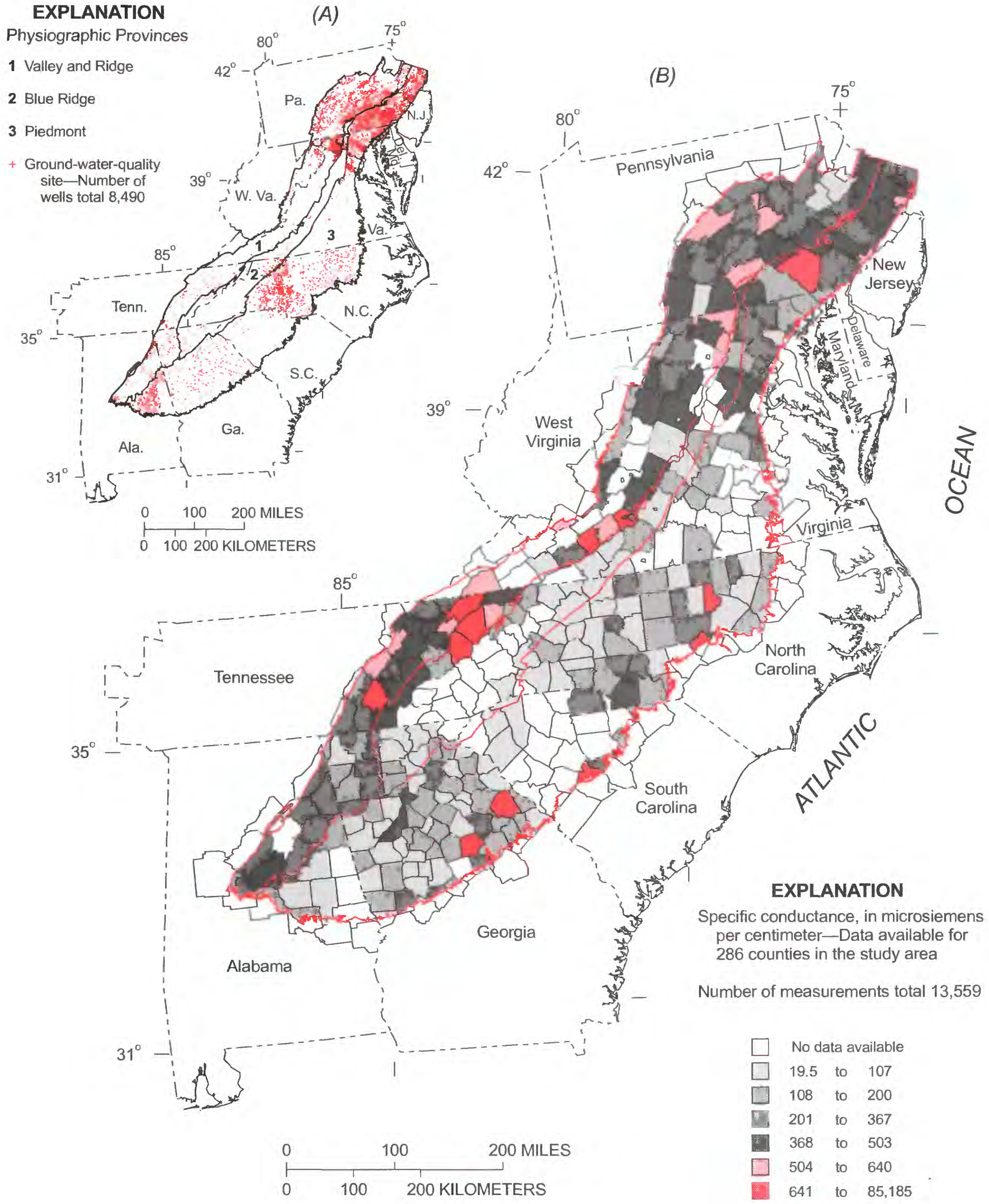


FIGURE 7.—Location of wells in study area where specific conductance is known *(A)*, and geographic variation of median specific conductance of ground water, by county *(B)*.

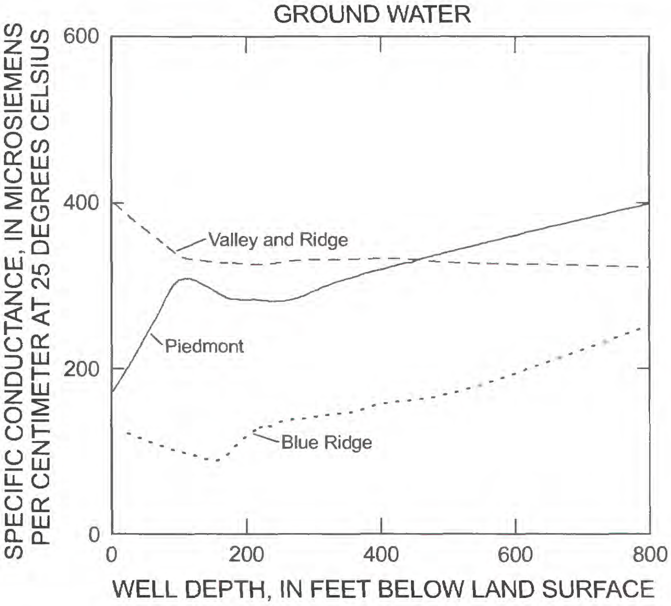


FIGURE 8.—Variation of specific conductance of ground water as a function of well depth, by physiographic province.

The IQR for specific conductance of spring water is 180 to 580 µS / cm. Differences in median specific conductances of spring water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (75, 312, 585 µS / cm, respectively) are significant. The regional pattern for spring water is different from that for ground water: the highest median specific conductance and largest IQR are in the Piedmont Province. In the Valley and Ridge and the Blue Ridge Provinces, spring water has about the same specific conductance as ground water. Whereas in the Piedmont, median specific conductance of spring water is twice that of ground water (fig. 6), which indicates that in this area spring water from is distinctly different from ground water.

The IQR for specific conductance of surface water is 80 to 264 µS / cm. Differences in median specific conductances of surface water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (45, 141, and 208 µS / cm, respectively) are significant. The regional pattern for surface water is similar to that for ground water, except that values are about one-half as large (fig. 6). For surface water, geographic variation of median specific conductances for counties in the study area (fig. 9) is similar to that for ground water (fig. 7). The highest conductances are in the central part of the Valley and Ridge Province and in the northeastern part of the Piedmont. In estuarine areas of New Jersey and Pennsylvania, high specific conductance at some stream sites is affected by brackish water.

DISSOLVED SOLIDS

Dissolved-solids concentration is the total quantity of dissolved minerals in water and is usually determined from the weight of dry residue left after evaporation of the water. Different methods used to dry the sample can lead to different weights of residue, because some volatile constituents may be evaporated with the water. Dissolved-solids concentration can also be estimated by summing the concentrations of dissolved constituents in a complete analysis. The method selected for determination of dissolved solids, therefore, can depend on the specific objectives of the investigation. In this report, concentrations of dissolved solids are reported as residue on evaporation at 180°C.

The interquartile range (IQR) for dissolved-solids concentration in ground water is 92 to 292 mg / L. Concentrations in 7 percent of ground-water samples exceed the secondary maximum contaminant level (SMCL) recommended for domestic use (500 mg / L, U.S. Environmental Protection Agency, 1995). Regional differences in median dissolved-solids concentrations in ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (73, 159, and 226 mg / L, respectively) are significant (fig. 10). The geographic pattern of median concentrations in ground water by county (fig. 11) is similar to that for specific conductance (fig. 7). The highest median dissolved-solids concentrations in ground water are in the Valley and Ridge and the northeastern Piedmont Provinces, and the lowest median concentrations are in the Blue Ridge Province.

The IQR for dissolved-solids concentration in spring water is 65 to 224 mg / L. Median concentration in spring water is about 83 percent that in ground water; however, concentrations in only 3 spring-water samples exceed the SMCL. Differences in median concentrations in spring water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (58, 109, and 160 mg / L, respectively) are significant (fig. 10), and the regional pattern of median concentrations in spring water is similar to that in ground water. For springs in the Piedmont, dissolved-solids concentration is lower than would be expected from specific-conductance data.

The IQR for dissolved-solids concentration in surface water is 62 to 165 mg / L. Median concentration in surface water is 65 percent that in ground water. Dissolved-solids concentrations in 2 percent of surface-water samples exceed the SMCL. Differences in median dissolved-solids concentrations in surface water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (37, 99, 134 mg / L, respectively) are significant. The regional pattern of median concentrations in surface water is similar to that in ground water. A

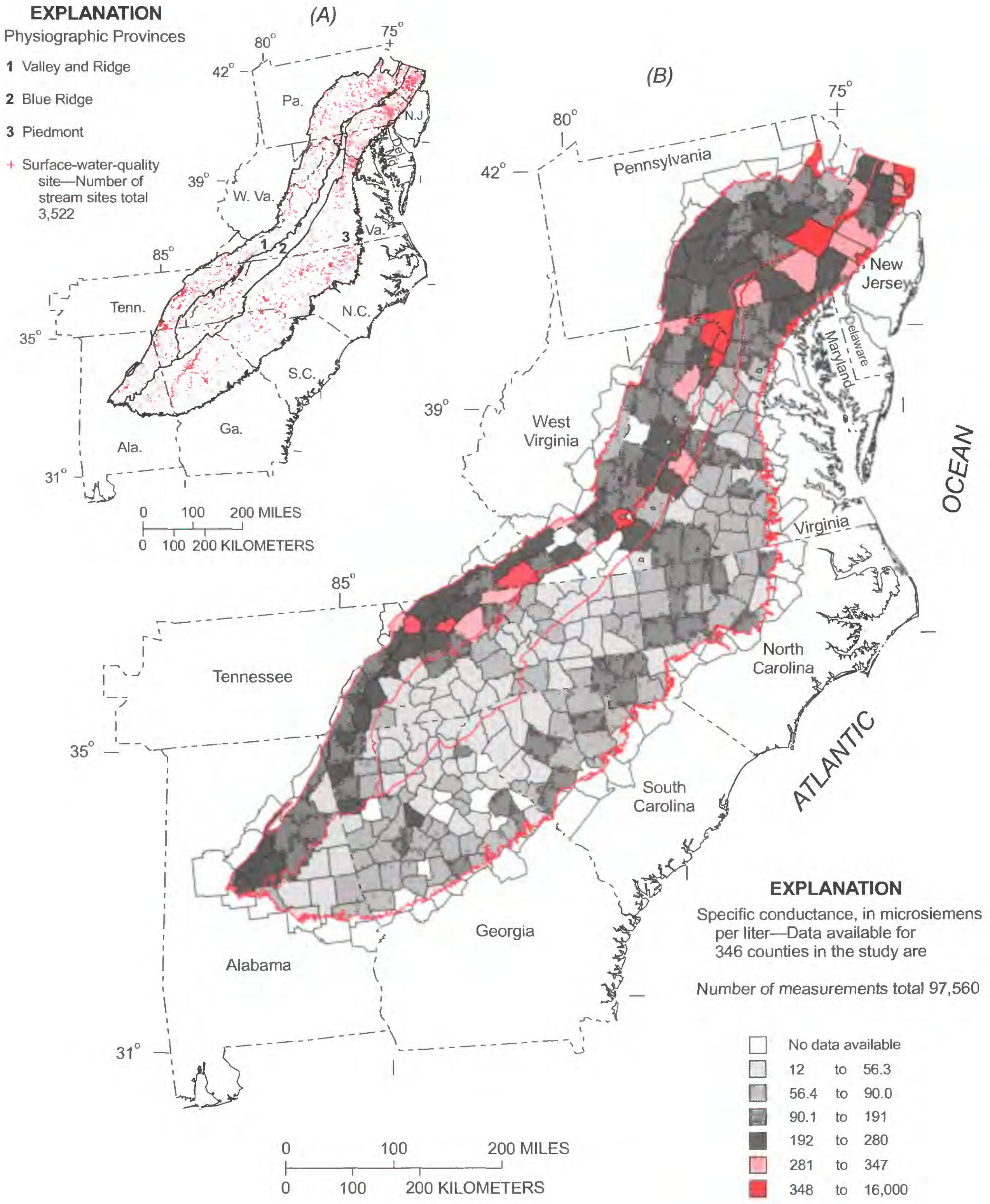


FIGURE 9.—Location of stream sites in study area where specific conductance is known *(A)*, and geographic variation of median specific conductance of surface water, by county *(B)*.

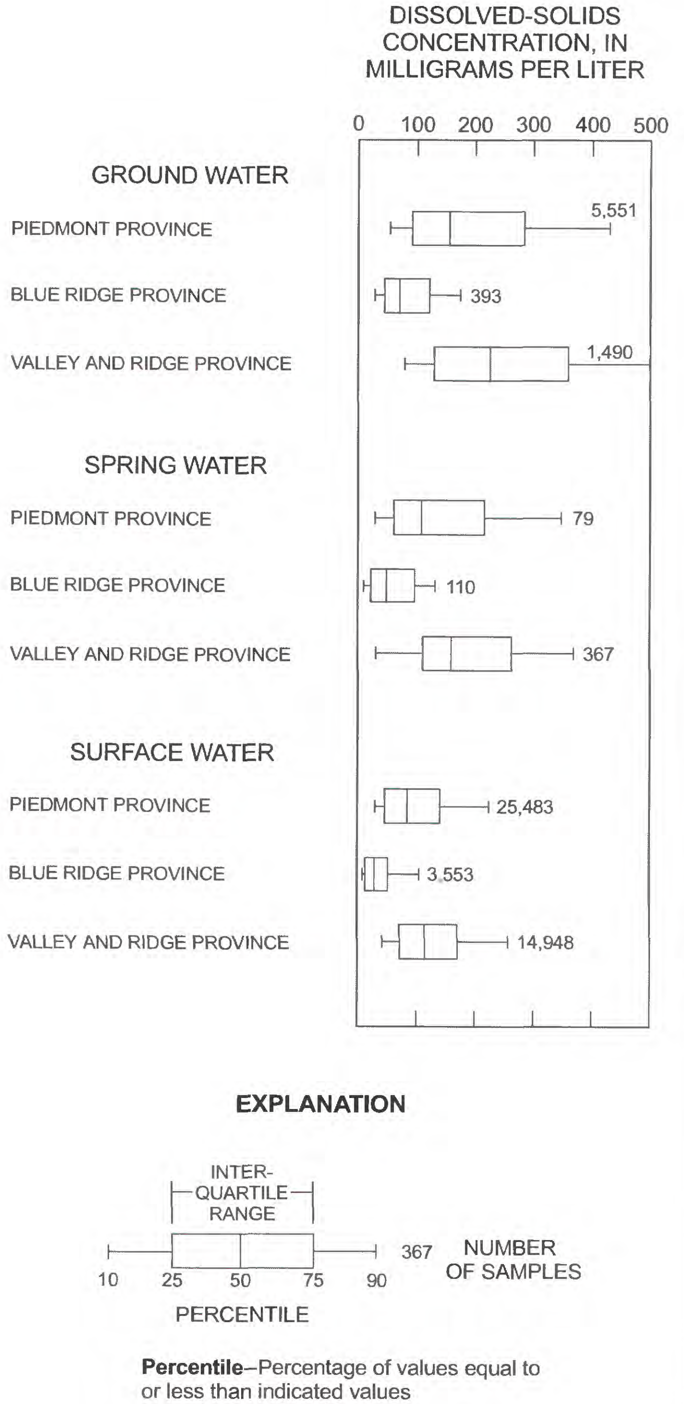


FIGURE 10.—Summary of dissolved-solids concentration, by type of site and physiographic province.

smaller IQR for surface water indicates less variability of dissolved-solids concentrations in surface water than in ground water (fig. 10).

Dissolved-solids data for surface water includes 43 more counties than for ground water, primarily in Virginia and Tennessee. The geographic variation of median concentrations by county for surface water (fig. 12), however, is similar to that for ground water (fig. 11): the highest concentrations are in the Valley and Ridge and the northeastern Piedmont Provinces, and the lowest concentrations are in the Blue Ridge Province. Surface-water data, therefore, can be used to estimate dissolved-solids concentration in ground water in counties where ground-water data are unavailable.

Specific conductance also can be used to estimate dissolved-solids concentration if the mathematical relation between them is suitable. The most commonly applied relation is a linear proportionality, as in the following equation:

$$\text{dissolved solids} = A \times \text{specific conductance},$$

where A is a constant that represents the slope of the line. Natural waters are not simple solutions, however, and a linear relation between dissolved solids and specific conductance is not accurate over a wide range of concentrations and ionic compositions. For the slope of the line, Hem (1985) reported a range of values from 0.54 to 0.96, most of them between 0.55 and 0.75. The highest values of A were associated with high concentrations of sulfate ion.

A series of LOWESS plots for the relation between dissolved solids and specific conductance for each type of site and physiographic province is shown in figure 13. Median values for the slope of the lines shown in figure 13 are listed in table 7; the values range from 0.58 to 0.81. Although the slope for the study area as a whole is 0.65, unusually high values for the Blue Ridge (0.80) indicate that water in this province contains a higher fraction of nonionic solutes than water elsewhere in the study area.

pH

The hydrogen-ion concentration of pure water at 25°C is very low (1×10^{-7} moles per liter) and is most conveniently expressed in logarithmic units. The abbreviation "pH" represents the negative base-10 log of the effective concentration of the hydrogen ion in moles per liter. The pH of natural water is a useful index of the status of chemical reactions that produce or consume hydrogen ions (acid-base reactions). The pH of pure water at 25°C is 7.0; acidic water has a pH less than 7.0, and alkaline water has a pH greater than 7.0. For most ground water in the United States, the range of pH is 6.0 to 8.5. For river water in areas not influenced by pollution, the range is typically 6.5 to 8.5; pH values outside these ranges are unusual but not unknown. The dissolution of many minerals is controlled by pH, and the

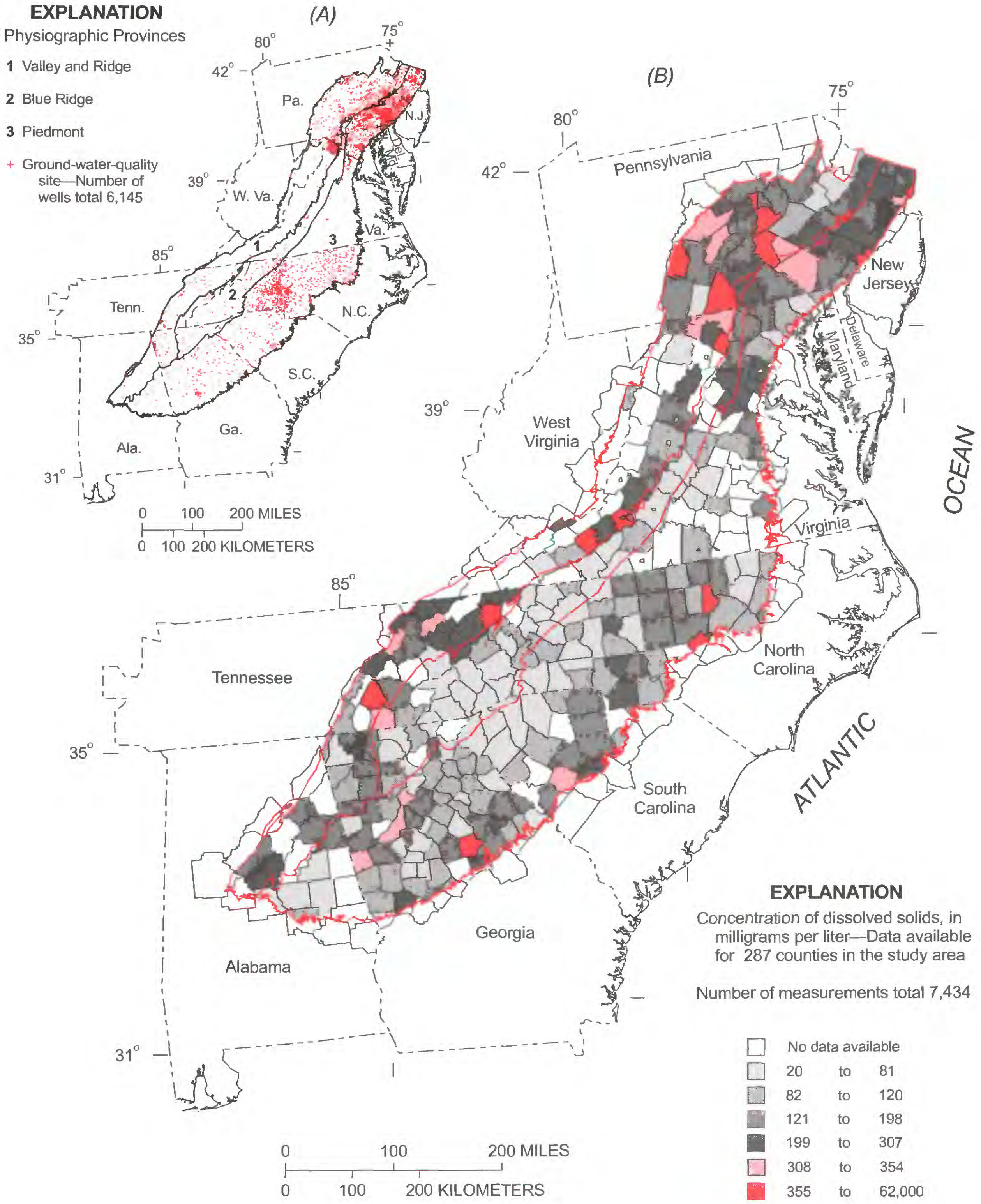


FIGURE 11.—Location of wells in study area where dissolved-solids concentration is known *(A)*, and geographic variation of median dissolved-solids concentration in ground water, by county *(B)*.

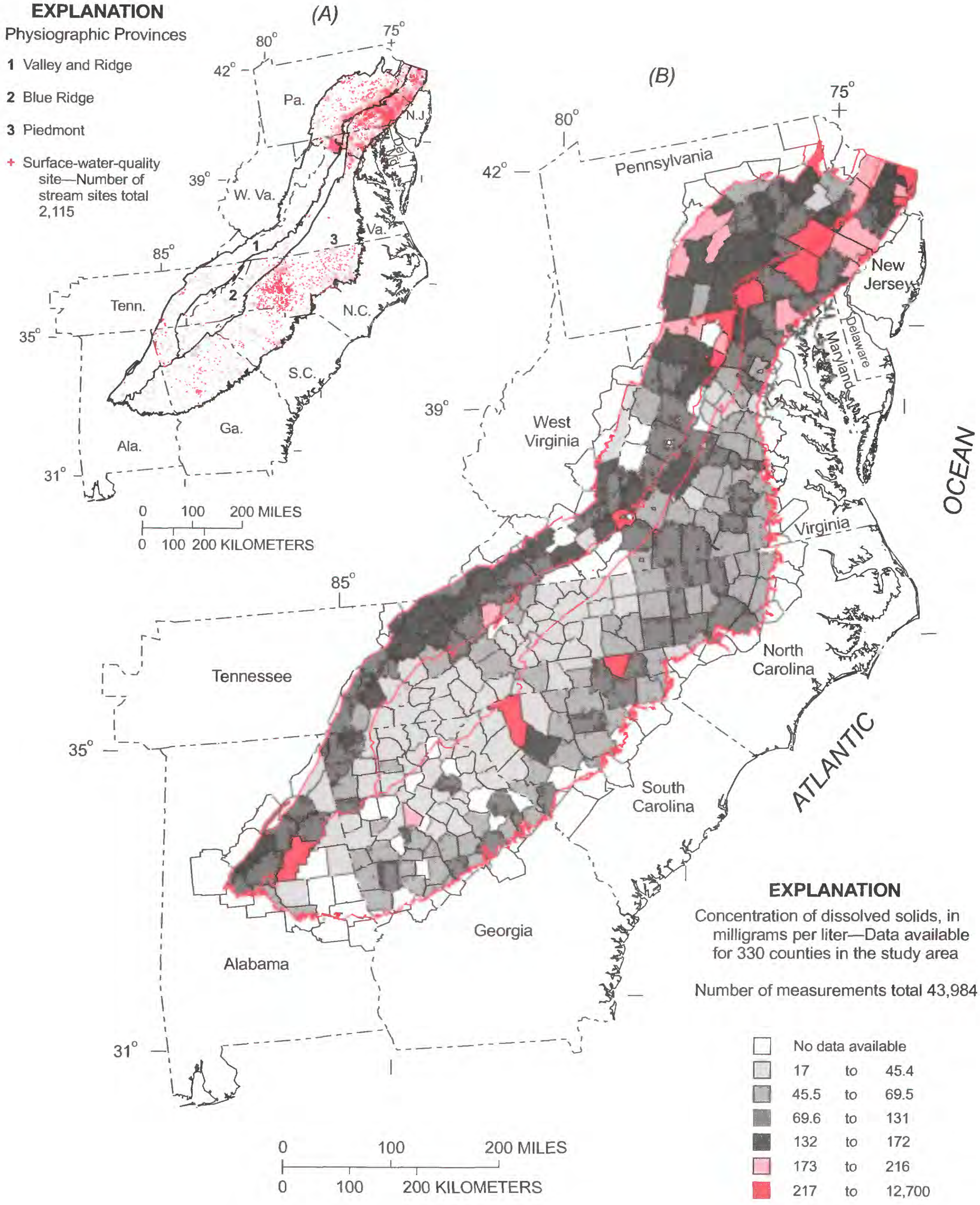


FIGURE 12.—Location of stream sites in study area where dissolved-solids concentration is known *(A)*, and geographic variation of median dissolved-solids concentration in surface water, by county *(B)*.

TABLE 7.—*Median values for relation between dissolved-solids concentration and specific conductance, by type of site and physiographic province*

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; ds, dissolved-solids concentration; sc, specific conductance]

Type of site and physiographic province	Number of analyses	Median dissolved solids (mg/L)	Median specific conductance (µS/cm)	Median value for *A* (ds/sc)
		Ground water		
Valley and Ridge	1,199	236	392	0.61
Blue Ridge	248	80	99	.74
Piedmont	4,680	168	254	.66
All ground water	6,127	173	270	.65
		Spring water		
Valley and Ridge	303	167	290	.58
Blue Ridge	93	56	72	.78
Piedmont	53	126	190	.63
All spring water	449	150	245	.60
		Surface water		
Valley and Ridge	13,542	138	230	.60
Blue Ridge	3,393	37	45	.81
Piedmont	22,679	99	154	.66
All surface water	39,614	107	171	.64

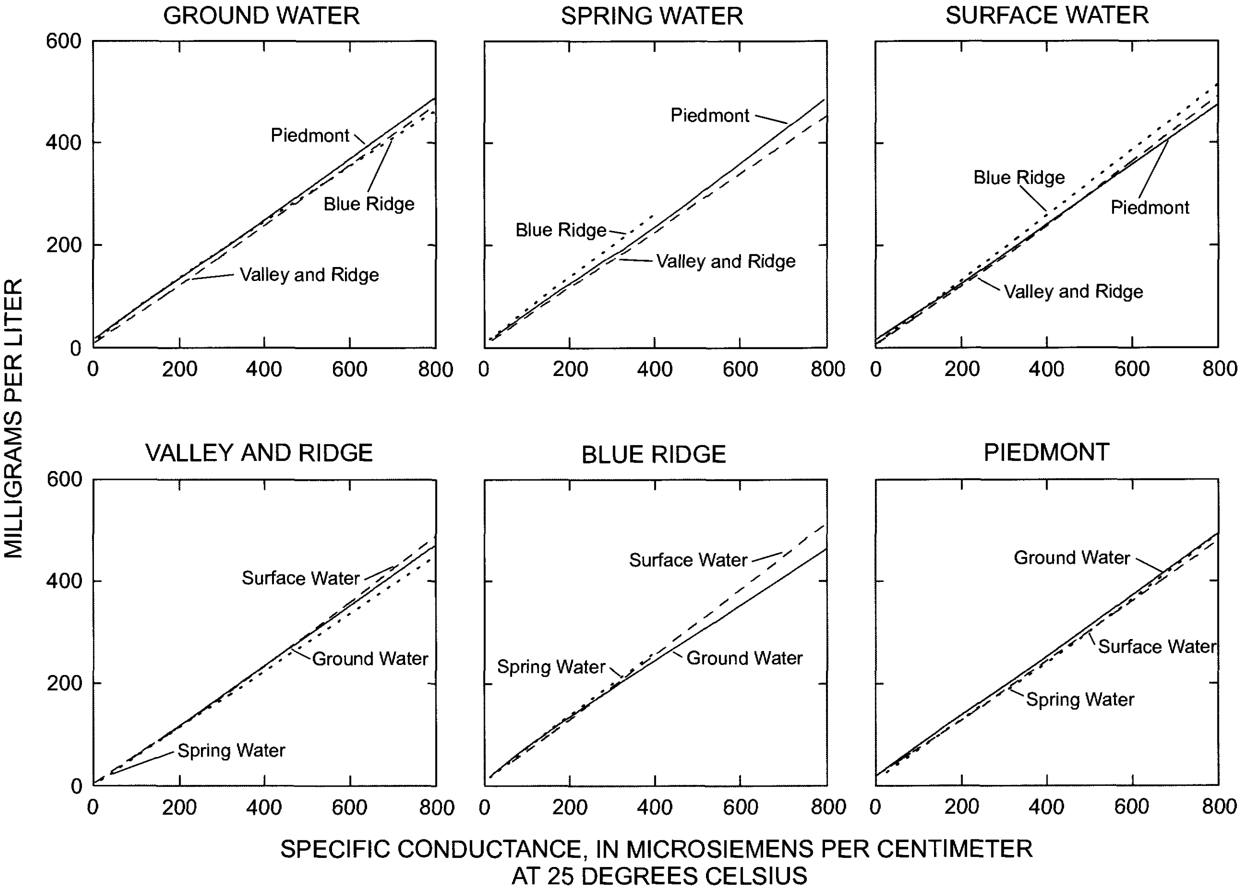


FIGURE 13.—Variation of dissolved-solids concentration as a function of specific conductance, by type of site and physiographic province.

presence of some dissolved ions (called "buffers")—particularly carbonate and bicarbonate—can effectively control pH.

The pH of water is a commonly determined property: in the study area, more than 106,000 measurements have been reported (table 5). The interquartile range (IQR) for the pH of ground water is 6.2 to 7.5. The pH range recommended for domestic use is 6.5 to 8.5 (U.S. Environmental Protection Agency, 1995). For 33 percent of sampled wells, measured pH is less than the lower limit, and for 1 percent of sampled wells, measured pH is greater than the upper limit. Differences in median pH's of ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (6.6, 6.7, and 7.3, respectively) are significant (fig. 14); however, the difference in median pH of ground water in the Piedmont and the Blue Ridge Provinces is within the analytical uncertainty in the measurement of pH. With some exceptions, ground water in much of the Piedmont and the Blue Ridge Provinces is slightly acidic. In these areas, the buffering capacity of crystalline rock is comparatively low. Ground water in the Valley and Ridge Province, however, is generally alkaline, because carbonate sediments in this region effectively control pH (fig. 15). In some counties in the Piedmont Province where the median pH of ground water exceeds 7.0, wells may tap carbonate rock; data for lithology in these counties are inconclusive.

The IQR for pH of spring water is 6.4 to 7.6. For 27 percent of spring-water samples, pH is less than the lower SMCL; for 1 sample, pH is greater than the upper SMCL. Regional median pH's of springs in the Piedmont, the Blue Ridge, and the Valley and Ridge Provinces are 6.0, 6.2, 7.4, respectively. Differences in median pH's of springs in the Valley and Ridge Province and in the other two provinces are significant; whereas, the difference in median pH's of springs in the Piedmont and the Blue Ridge Provinces is not significant (fig. 14). The regional patterns for spring water and ground water are different. In the Piedmont Province, spring water is significantly more acidic than ground water; in the Blue Ridge Province, this difference is smaller, and in the Valley and Ridge Province, median pH's of spring water and ground water are about equal. Variability of pH in water from springs in the Piedmont Province is also greater than that in spring water elsewhere in the study area (fig. 14). In the Piedmont Province, spring water generally comes from shallow regolith that has low buffering capacity; whereas in the Valley and Ridge Province, spring water and ground water are from carbonate rock and have about the same median pH.

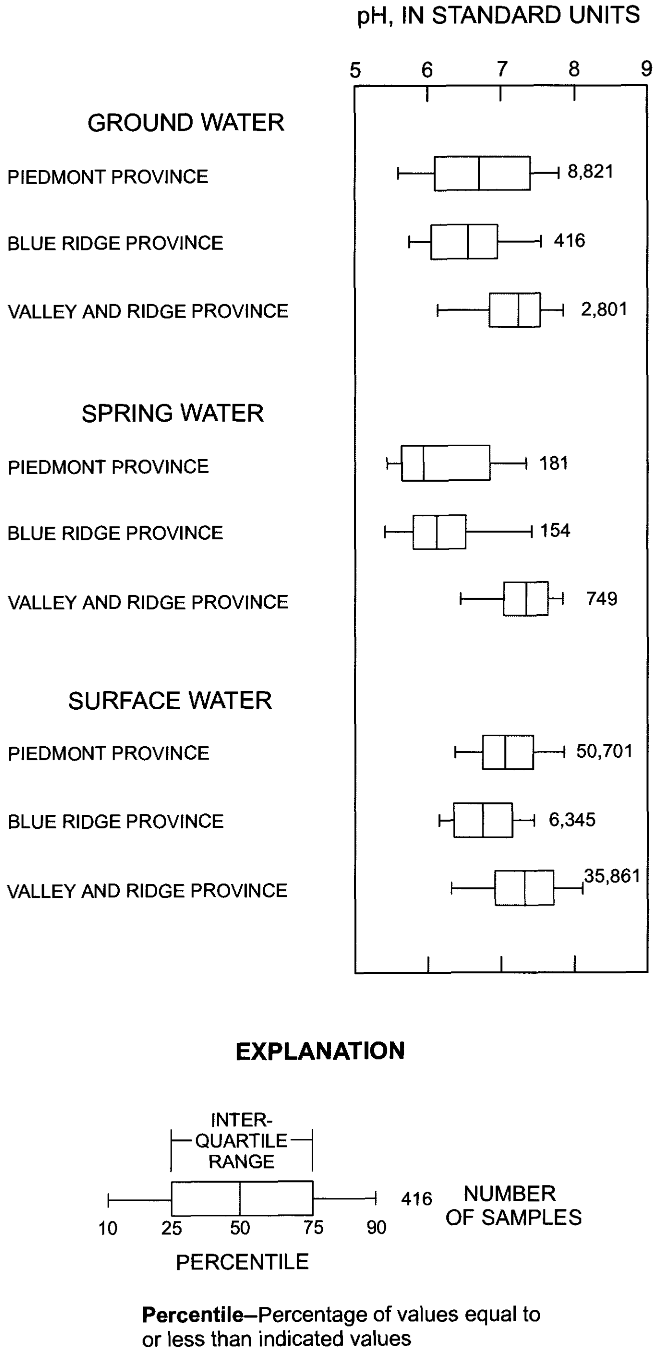


FIGURE 14.—Summary of pH, by type of site and physiographic province.

The IQR for pH of surface water is 6.8 to 7.6. For 11 percent of the surface-water samples, measured pH is less than the lower SMCL; for 2.5 percent of these samples, pH is greater than the upper SMCL. Differences in median pH's of surface water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (6.8, 7.1, 7.4, respectively) are significant. Geographic variation of median pH's by county for surface water is similar to that for ground water (fig. 15), except that pH's of surface water are somewhat higher than those of ground water (fig. 14).

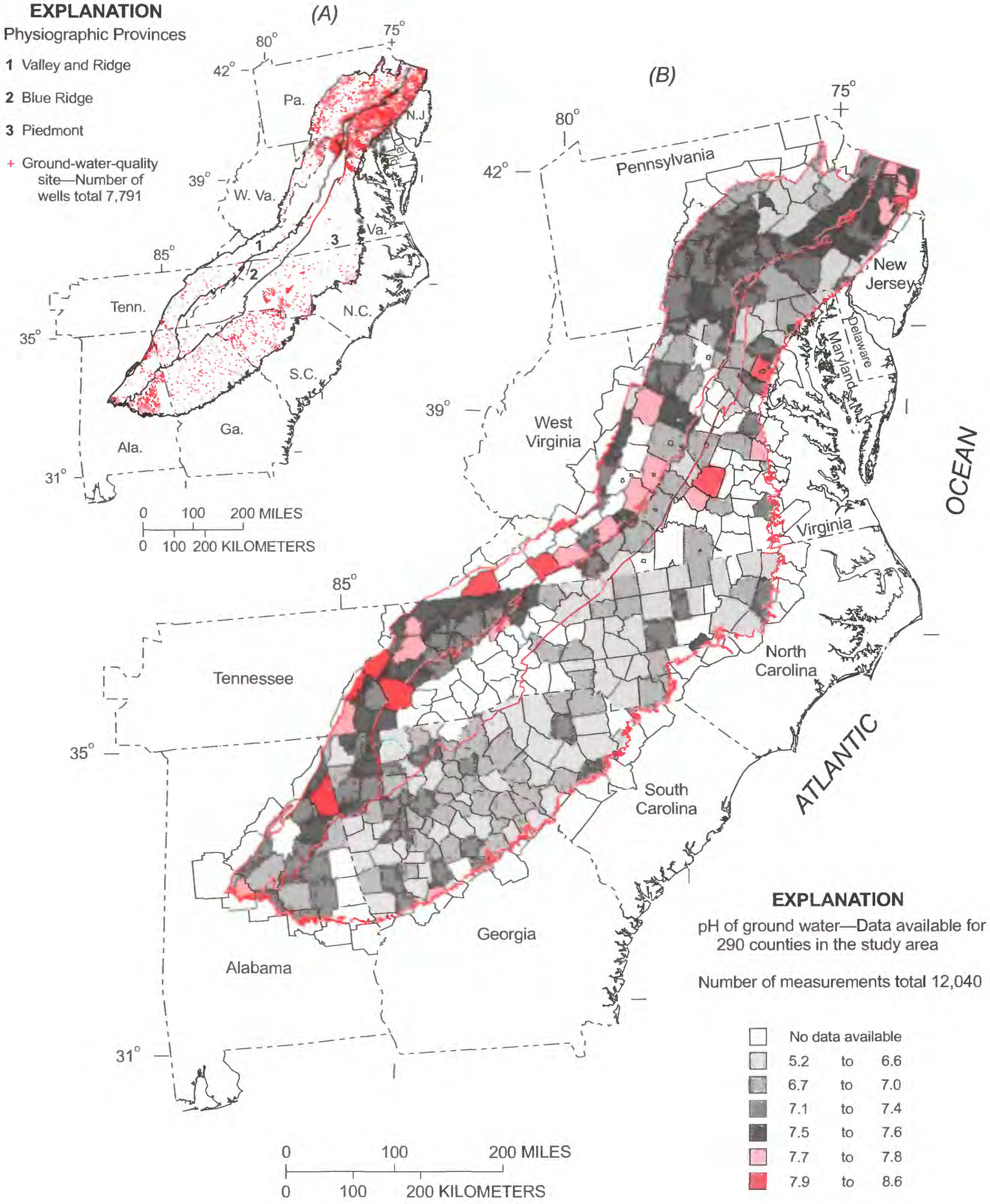


FIGURE 15.—Location of wells in study area where pH is known *(A)*, and geographic variation of median pH of ground water by county *(B)*.

WATER TEMPERATURE

Temperature affects many other characteristics of water, for example, specific conductance, pH, and the solubility of most dissolved constituents. Temperature also affects the rate of chemical reactions among dissolved constituents; water temperature, therefore, is routinely measured whenever most other water-quality characteristics and constituents are determined. In the study area, more than 127,000 measurements of water temperature have been reported (table 5).

The interquartile range (IQR) for temperature of ground water is 12.0 to 16.0°C. Median ground-water temperatures in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces are 12.8, 13.0, and 14.0°C, respectively. Differences in median temperatures in the Piedmont Province and in the other two provinces are significant; whereas, the difference in median temperature of ground water in the Blue Ridge and the Valley and Ridge Provinces is not significant (fig. 16). The warmest ground water is generally in the Piedmont Province. With some exceptions, median temperatures of ground water by county increase gradually from north to south (fig. 17). Unusually warm ground water in two Virginia counties is from wells open to depths greater than 300 ft.

The IQR for temperature of spring water in the study area is 11.0 to 14.0°C. Regional medians for the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces are 11.0, 11.5, and 12.5°C, respectively. Differences in the median temperature of spring water in the Valley and Ridge Province and in the other two provinces are significant; whereas, the difference in median temperatures of spring water in the Piedmont and the Blue Ridge Provinces is not significant (fig. 16). The warmest spring water is generally in Valley and Ridge Province, where median temperatures of spring water and ground water are about equal (fig. 16); elsewhere, spring water is colder than ground water, probably because of a shallow origin for springs in the Piedmont and the Blue Ridge Provinces.

The IQR for temperature of surface water in the study area is 8.6 to 21.0°C. Median surface-water temperatures in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces are 13.0, 14.5, and 16.0°C, respectively. Overlap of the regional IQR's is almost complete (fig. 16), but differences in median temperatures of surface water in the three provinces are significant. Surface water is typically coldest in the Blue Ridge Province (highest land-surface elevation) and warmest in the Piedmont Province. Median temperature of surface water is about 2°C warmer than that of ground water, except in the Blue Ridge Province, where the two medians are equal. Variability of temperature of surface water is almost three times that of ground water (fig. 16).

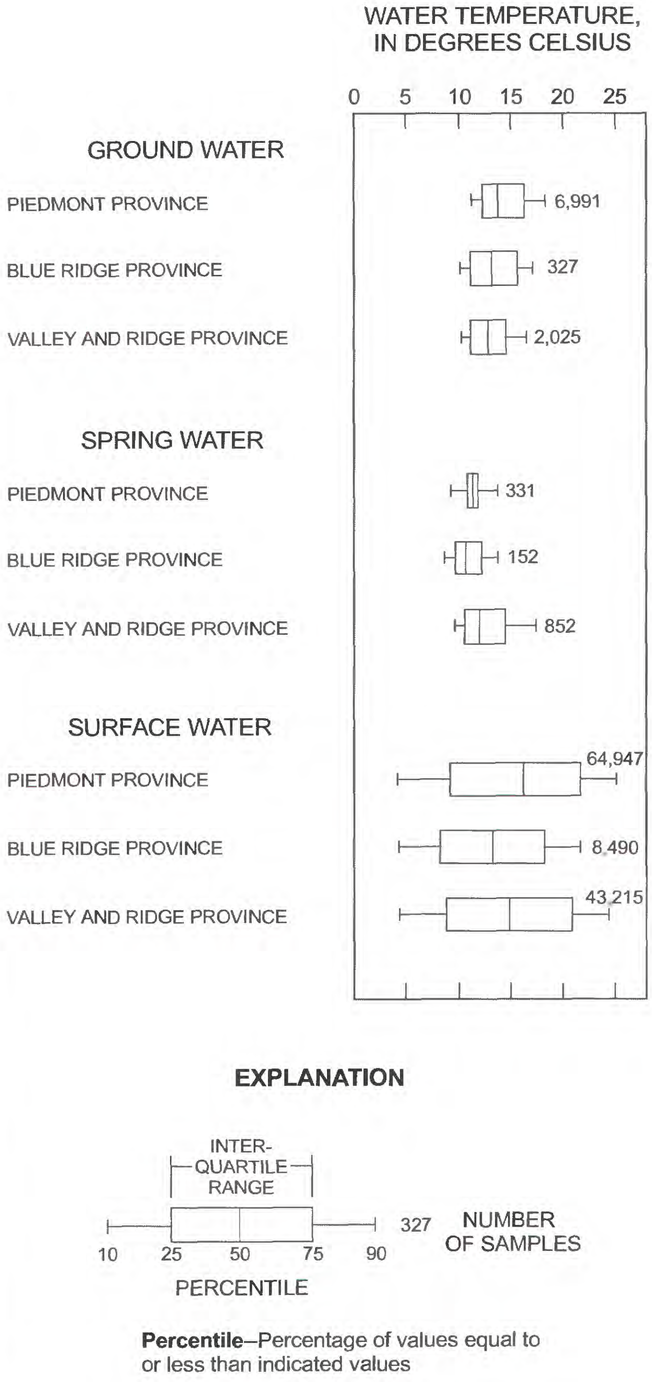


FIGURE 16.—Summary of water temperature, by type of site and physiographic province.

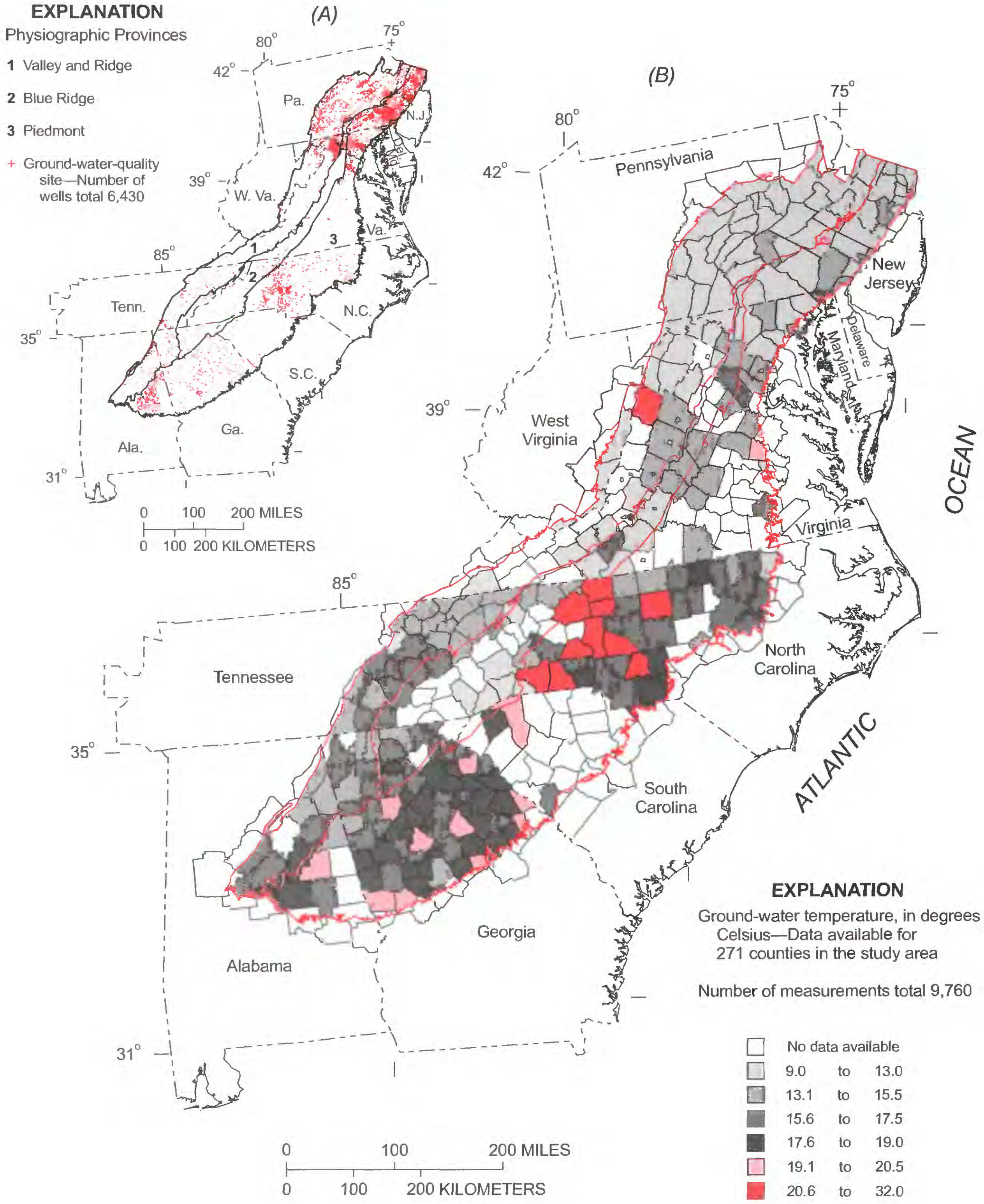


FIGURE 17.—Location of wells in study area where water temperature is known *(A)*, and geographic variation of median ground-water temperature, by county *(B)*.

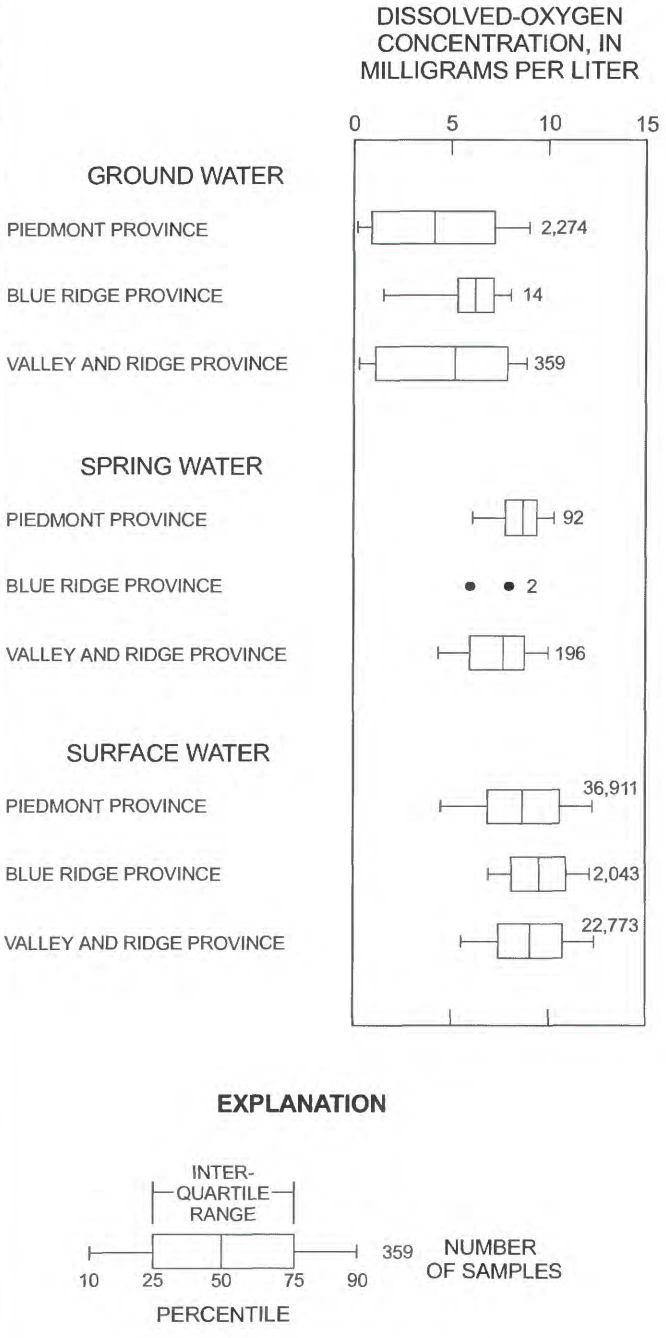
DISSOLVED OXYGEN

Oxygen is the most abundant chemical element in the crust of the Earth. Oxygen comprises about 46 percent of the crustal weight and 94 percent of the crustal volume. As a whole, the crust is a virtual packing of oxygen atoms, bonded by silicon and the ions of six common metals. Chemically bound oxygen in rock and water is difficult to liberate, but oxygen also makes up about 21 percent of the Earth's atmosphere. At normal pressure, the solubility of oxygen gas in water is 7.54 mg / L at 30°C and is highly sensitive to changes in temperature (12.74 mg / L at 5°C). Dissolved oxygen plays an important role in many geochemical and biological processes.

The concentration of dissolved oxygen (DO) in ground water is an indication of the electrochemical redox potential of the system, which is the chemical tendency for various dissolved substances to be oxidized or reduced. DO generally decreases as water passes through organic-rich layers in the soil zone and moves downgradient into an aquifer. In recharge areas where soil contains a large fraction of sand or gravel, or in cavernous limestones, DO in shallow ground water commonly exceeds 0.1 mg / L; whereas in recharge areas where soil contains a large fraction of silt or clay, DO may be undetectable. In areas of fractured rock without a soil mantle, dissolved oxygen can permeate the entire ground-water flow system (Freeze and Cherry, 1979).

The interquartile range (IQR) for DO in ground water is 1.0 to 7.4 mg / L. Regional median DO's in ground water in the Piedmont, the Valley and Ridge, and the Blue Ridge Provinces are 4.1, 5.4, and 6.2 mg / L, respectively. Differences in median DO's in the Piedmont and the Valley and Ridge Provinces are significant; elsewhere, however, these differences are not significant (fig. 18). DO is not commonly determined in ground-water-quality investigations in the study area; data are available for only 50 counties, primarily in New Jersey, Pennsylvania, and Maryland. Among these counties, the highest DO's tend to be in the Valley and Ridge Province (fig. 19), but ground-water data are too sparse to determine a regional trend.

The IQR for DO in spring water is 6.5 to 9.0 mg / L. The median DO in spring water is about twice that in ground water. Median DO's in spring water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces are 7.2, 7.7, and 8.8 mg / L, respectively (table 5). Differences in median DO's in the Piedmont and the Valley and Ridge Provinces are significant; elsewhere, however, these differences are not significant (fig. 18). For spring water, the order of median DO's is the opposite of that for water temperatures (fig. 16): DO is generally higher in the Piedmont Province (colder water)



● ● **Data Values**–Boxplot diagrams are not statistically significant for distributions that contain fewer than 10 data values. These distributions are shown as individual values

Percentile–Percentage of values equal to or less than indicated values

FIGURE 18.—Summary of dissolved-oxygen concentration, by type of site and physiographic province.

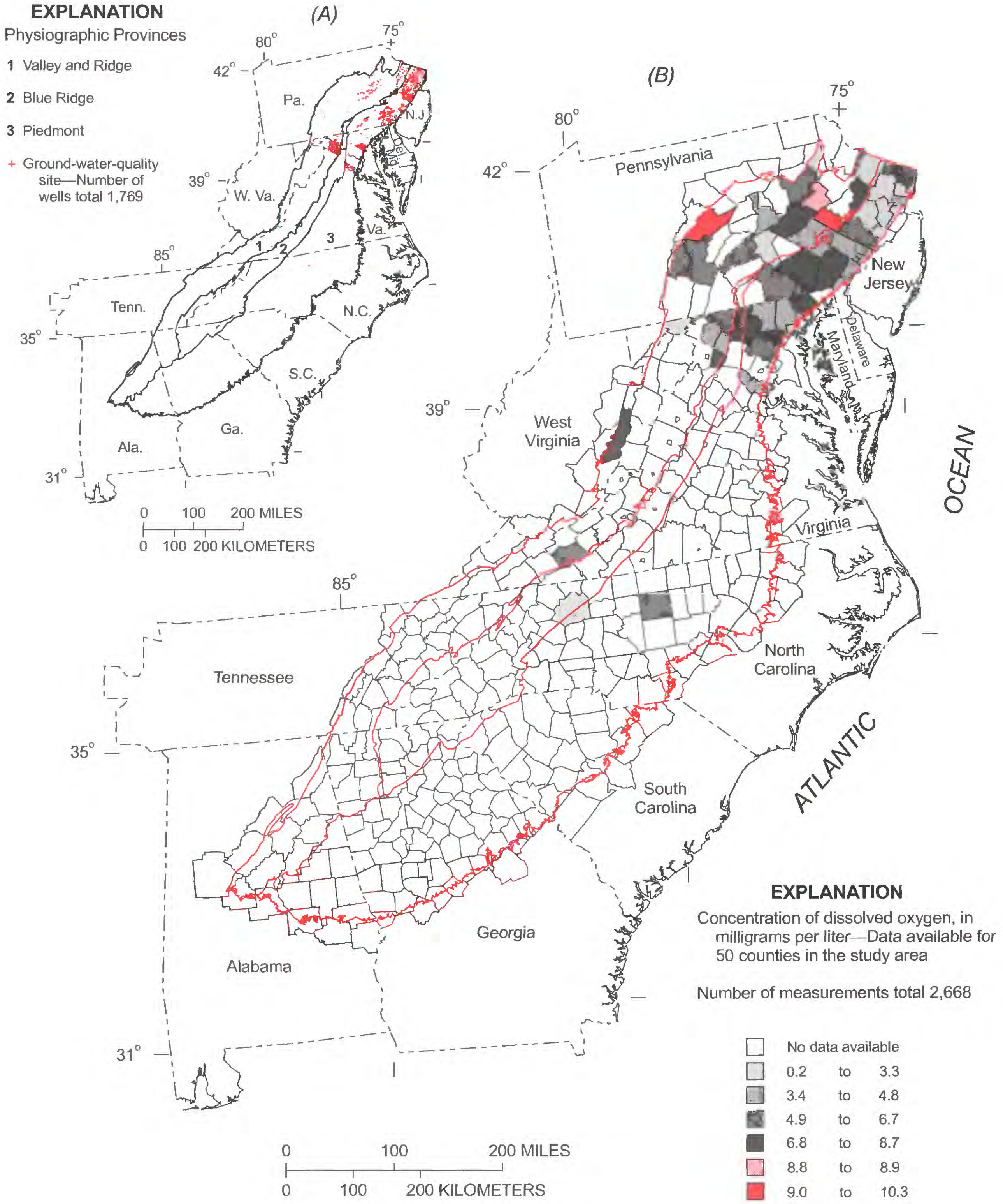


FIGURE 19.—Location of wells in study area where dissolved-oxygen concentration is known *(A)*, and geographic variation of median dissolved-oxygen concentration in ground-water, by county *(B)*.

than in the Valley and Ridge Province (warmer water). A median DO in spring water in the Blue Ridge Province is not shown in figure 18 because this group contains fewer than 10 measurements; these data are shown as individual points.

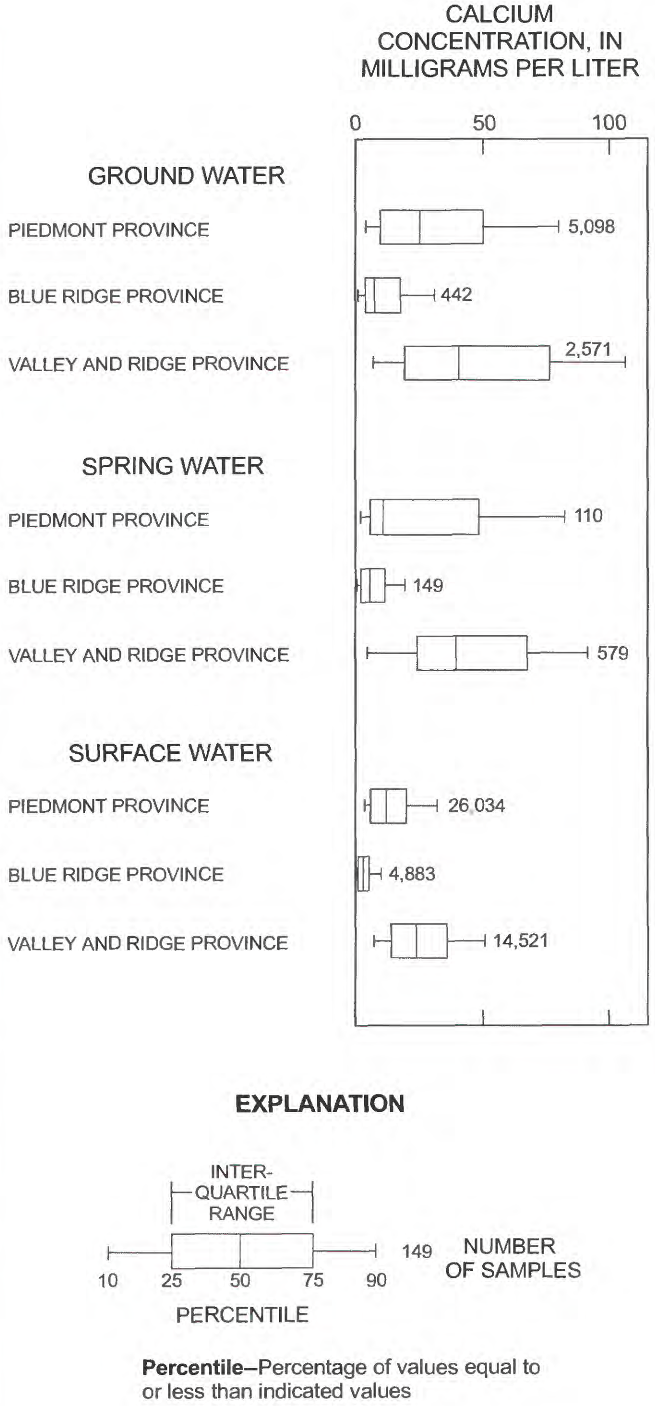
DO is important to biota and is determined routinely in surface-water-quality investigations. More than 61,000 measurements of DO have been reported for surface water in the study area (table 5). The IQR for DO in surface water is 7.2 to 10.8 mg / L; median DO in surface water is about twice that in ground water. The regional IQR's for DO in surface water completely overlap, but differences in median DO's in surface water in the Piedmont, the Valley and Ridge, and the Blue Ridge Provinces (8.8, 9.1, and 9.6 mg / L, respectively) are significant (fig. 18). Although the regional pattern for surface water is similar to that for ground water, extrapolation of DO in ground water from the surface-water data is not justified because surface water is in constant contact with the atmosphere.

CALCIUM

Calcium is the third most abundant metal in rocks at the Earth's surface and is a major constituent of all three classes of common rock minerals—particularly the silicates and the carbonates. Calcium is an essential element for plants and animals and is a major dissolved constituent in most natural water.

Calcium is the dominant cation in most water in the study area. The interquartile range (IQR) for calcium concentration in ground water is 11 to 57 mg / L. The regional IQR's overlap, but differences in median concentrations in ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (8.3, 25, and 42 mg / L, respectively) are significant (fig. 20). The highest calcium concentrations and the greatest variability of concentration in ground water are in the Valley and Ridge Province, where aquifer sediments are enriched in calcite and gypsum. For ground water, the geographic pattern of median calcium concentrations by county (fig. 21) is similar to those for specific conductance and dissolved-solids concentration (figs. 7 and 11). Regional variations in concentrations of calcium and other major ions as a function of well depth are discussed later in this report ("Variations in Chemical Ratios").

The IQR for calcium concentration in spring water is 9.9 to 55 mg / L. Differences in median concentrations in spring water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (6.1, 11, and 41 mg / L, respectively) are significant (fig. 20). The regional pattern for spring water is similar to that for ground water, except that concentrations are lower. In the Valley and Ridge Province, median calcium concentrations in spring water and ground water are about equal. In the Piedmont, however, spring water is deficient in calcium: median concentration is less than half that for ground water. Variability of calcium concentration in



Percentile–Percentage of values equal to or less than indicated values

FIGURE 20.—Summary of calcium concentration, by type of site and physiographic province.

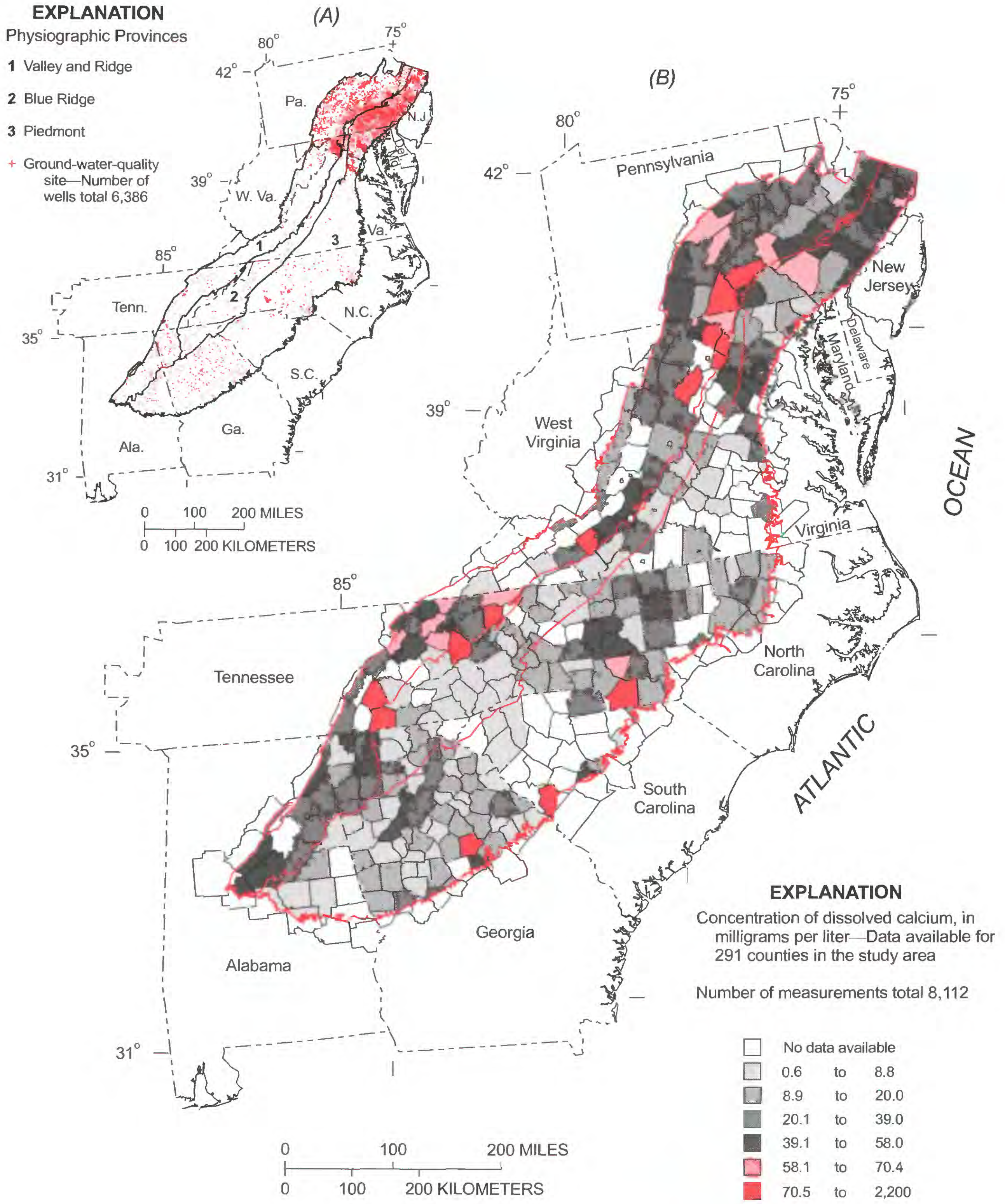


FIGURE 21.—Location of wells in study area where calcium concentration is known *(A)*, and geographic variation of median calcium concentration in ground water, by county *(B)*.

Piedmont springs is large, but the asymmetry of the IQR shows that an unusually large number of these springs produce waters having low calcium concentrations. In the Blue Ridge, spring water is also deficient in calcium, compared with ground water, but the deficiency is smaller. These differences indicate that spring water in the Piedmont and the Blue Ridge Provinces originates in rock that is low in calcium (weathered regolith).

The IQR for calcium concentration in surface water is 6 to 26 mg / L. Differences in median calcium concentrations in surface water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (3.4, 12, and 26 mg / L, respectively) are significant (fig. 20). The regional pattern of median calcium concentrations for surface water is similar to that for ground water, except that concentrations are about half as large. In all three provinces, surface water is generally less mineralized and contains smaller amounts of dissolved calcium than ground water.

MAGNESIUM

Magnesium is the sixth most abundant metal in surface rocks and is a major constituent of common minerals found in igneous, metamorphic, and sedimentary rocks, for example, olivine, pyroxene, mica, chlorite, serpentine, and dolomite. Like calcium, magnesium is an essential element for plants and animals and a major dissolved constituent in natural water. The aqueous geochemistry of magnesium, however, is substantially different from that of calcium.

Magnesium is commonly the second most abundant cation in water in the study area. The interquartile range (IQR) for magnesium concentration in ground water is 3.1 to 16 mg / L. The regional IQR's overlap, but differences in median concentrations in ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (2.5, 6.6, and 10 mg / L, respectively) are significant (fig. 22). The highest magnesium concentrations and greatest variability of concentration in ground water are in the Valley and Ridge Province, where aquifer sediments contain dolomite. A low median concentration in ground water in the Blue Ridge Province indicates that rocks in this area do not provide a major source of soluble magnesium. The geographic pattern of median magnesium concentrations in ground water by county (fig. 23) is generally similar to that for calcium (fig. 21), except that median magnesium concentrations are also high in a few counties in the northeastern Piedmont and along the Fall Line (pl. 1) in North Carolina and South Carolina.

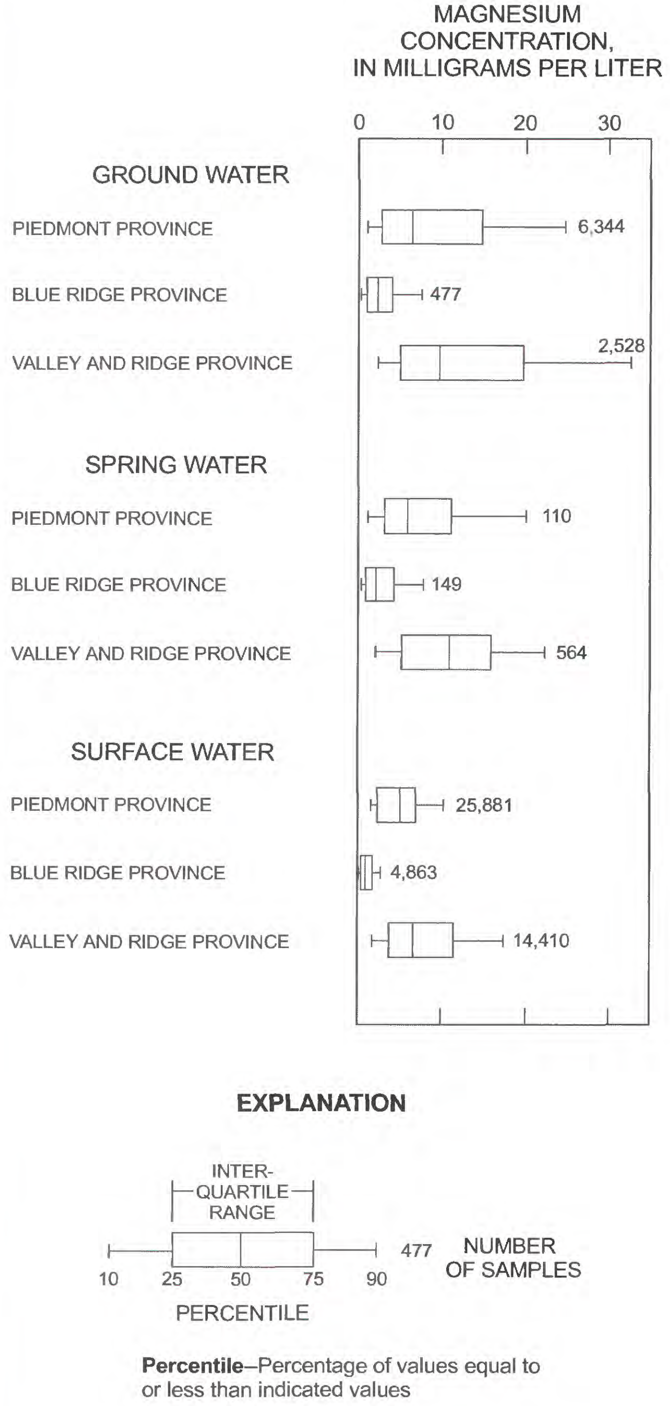


FIGURE 22.—Summary of magnesium concentration, by type of site and physiographic province.

The IQR for magnesium concentration in spring water is 3.2 to 14 mg / L. Differences in median concentrations in spring water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (2.3, 5.7, and 11 mg / L, respectively) are significant (fig. 22). The regional pattern of median magnesium concentrations

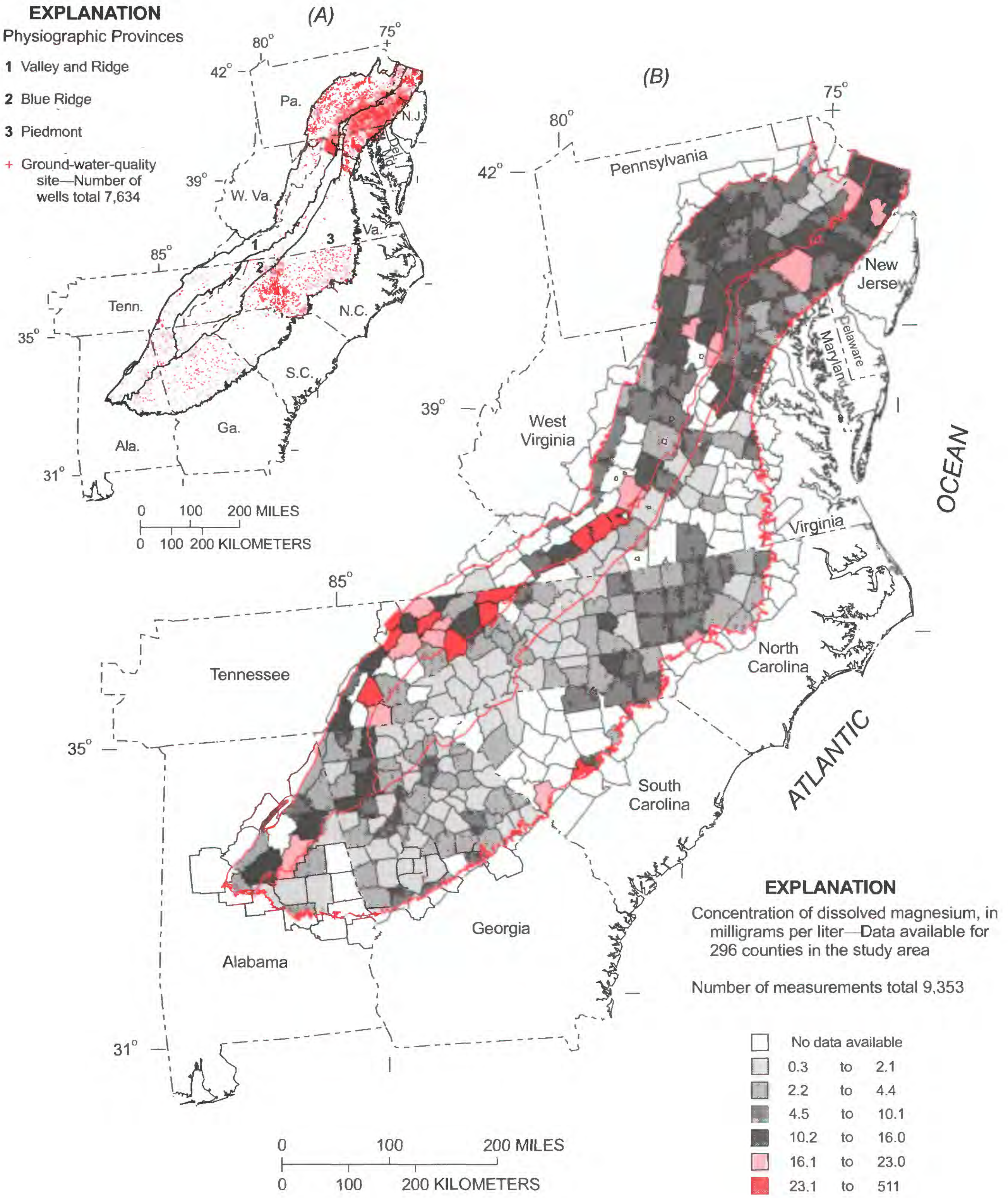


FIGURE 23.—Location of wells in study area where magnesium concentration is known *(A)*, and geographic variation of median magnesium concentration in ground water, by county *(B)*.

for spring water is similar to that for ground water (fig. 22). In the Valley and Ridge and the Blue Ridge Provinces, median magnesium concentrations in spring water and ground water are about equal. In the Piedmont Province, spring water is slightly deficient in magnesium, compared with ground water. The deficiency, however, is not as large as that for calcium.

The IQR for magnesium concentration in surface water is 2.1 to 7.9 mg / L. Differences in median concentrations in surface water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (1.1, 4, and 7.1 mg / L, respectively) are significant (fig. 22). The regional pattern of median magnesium concentrations for surface water is similar to that for ground water (fig. 22), except that concentrations are about half as large (fig. 22).

SODIUM

Sodium is the fourth most abundant metal in surface rocks and is a constituent of minerals found in some igneous and sedimentary rocks (feldspars, clays, and evaporites). Because most sodium salts are highly soluble, a large amount of sodium is dissolved in natural water, particularly in the ocean and in deep ground water. No important precipitation reactions maintain low concentrations of sodium in water in the way that carbonate precipitation controls calcium concentration. Sodium concentration can be controlled, however, by the processes of osmosis and adsorption, which are mechanisms most commonly associated with plants and animals.

Sodium is commonly the third most abundant cation in water in the study area, although some samples contain a dominant fraction of sodium. The interquartile range (IQR) for sodium concentration in ground water is 4.3 to 16 mg / L. The regional IQR's overlap, but differences in median concentrations in ground water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (5.0, 5.8, and 9.5 mg / L, respectively) are significant (fig. 24). The highest sodium concentrations and greatest variability of concentration in ground water are in the Piedmont Province, where the dominant lithology consists of sodium-rich rocks (gneisses, schists, and granites). The geographic pattern of median sodium concentrations in ground water by county (fig. 25) is generally the opposite of those for calcium and magnesium (figs. 21 and 23); in counties where sodium concentration is high, calcium and magnesium concentrations are low, and vice versa. Some counties where sodium concentrations are high are in the Valley and Ridge Province (fig. 25). Because most wells in the study area tap shallow ground water (fig. 4), the principal source of sodium in ground water in the Valley and Ridge Province may be interbedded shales; a few wells in this area tap deep brines.

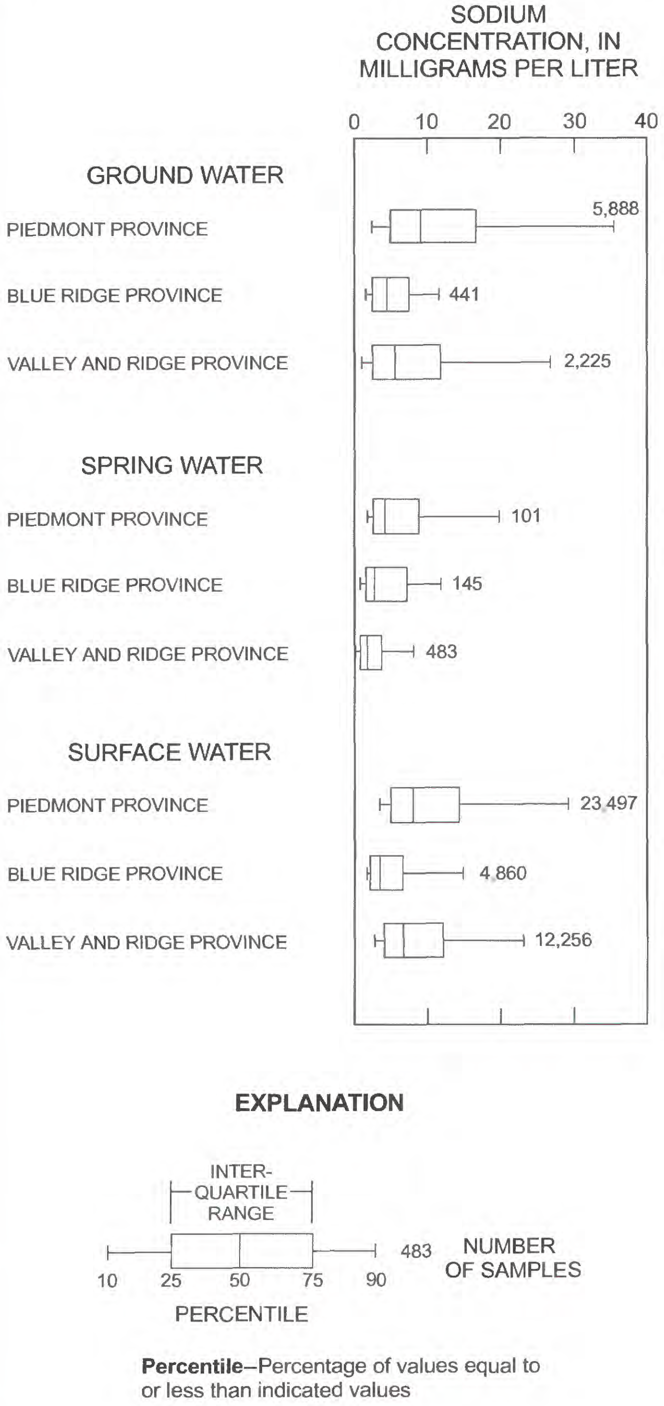


FIGURE 24.—Summary of sodium concentration, by type of site and physiographic province.

The IQR for sodium concentration in spring water is 1.4 to 4.9 mg / L; median sodium concentration of spring water is about one-third that of ground water.

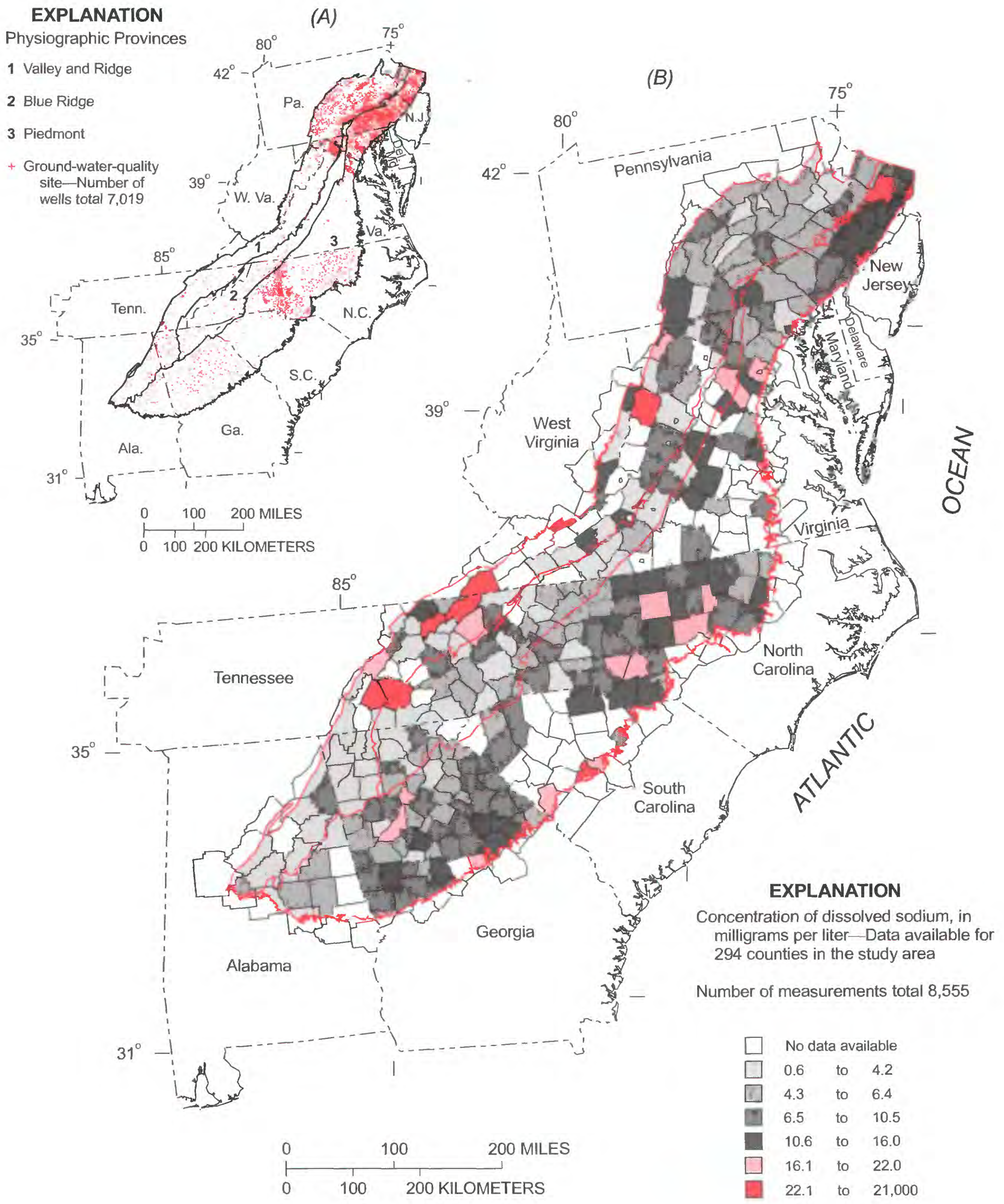


FIGURE 25.—Location of wells in study area where sodium concentration is known *(A)*, and geographic variation of median sodium concentration in ground water, by county *(B)*.

Differences in median concentrations in spring water in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces (2.1, 3.1, and 4.4 mg / L, respectively) are significant (fig. 24). The regional patterns of median sodium concentrations in spring water and ground water are different: in spring water, sodium concentrations and variability of concentration increase gradually from west to east (the Valley and Ridge Province to the Piedmont Province).

The IQR for sodium concentration in surface water is 3.5 to 13 mg / L. Differences in median concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (2.6, 5.5, and 7.7 mg / L, respectively) are significant (fig. 24). The regional pattern of median sodium concentrations for surface water is similar to that for ground water, except that sodium concentrations and variability of concentration are smaller (fig. 24).

POTASSIUM

Potassium is the fifth most abundant metal in surface rocks and is a constituent of feldspars and micas, found in some igneous rocks, and of clays and evaporites, found in many sedimentary rocks. Potassium is slightly less abundant than sodium in igneous rocks but more abundant in sedimentary rocks. The chemical properties of potassium are similar to those of sodium, except that potassium is not as easily dissolved from silicate minerals and is easily reincorporated into clay minerals. Like sodium, potassium is an essential element for plants and animals, but potassium is concentrated by plants, whereas sodium is not. In most natural water—including the ocean—the concentration of potassium is substantially lower than the concentration of sodium.

Potassium is typically the least abundant of four major cations in water in the study area. The interquartile range (IQR) for potassium concentration in ground water is 0.8 to 2.4 mg / L. Median concentrations in ground water in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces are 1.1, 1.2, and 1.4 mg / L, respectively. Differences in median concentrations in ground water in the Piedmont Province and in the other two provinces are significant; whereas, the difference in median concentrations in the Blue Ridge and the Valley and Ridge Provinces is not significant (fig. 26). The highest potassium concentrations in ground water are in the Valley and Ridge Province. Relative differences in regional medians for potassium concentration are smaller than those for sodium concentration (table 5), which indicates that in ground water, potassium is less variable than sodium. The geographic pattern of median potassium concentrations in ground water by county (fig. 27) is similar to that for sodium (fig. 25). Most of the highest concentrations of potassium in ground water are in counties in the southern and central parts of the Piedmont Province.

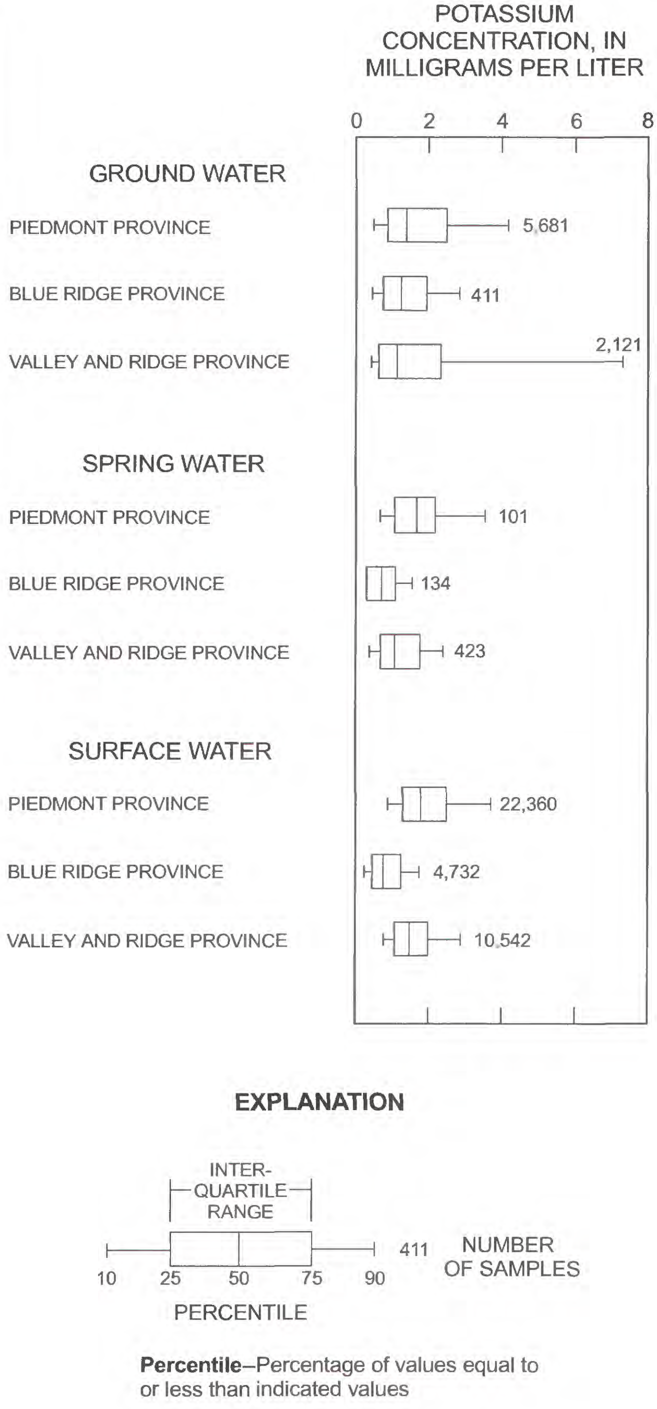


FIGURE 26.—Summary of potassium concentration, by type of site and physiographic province.

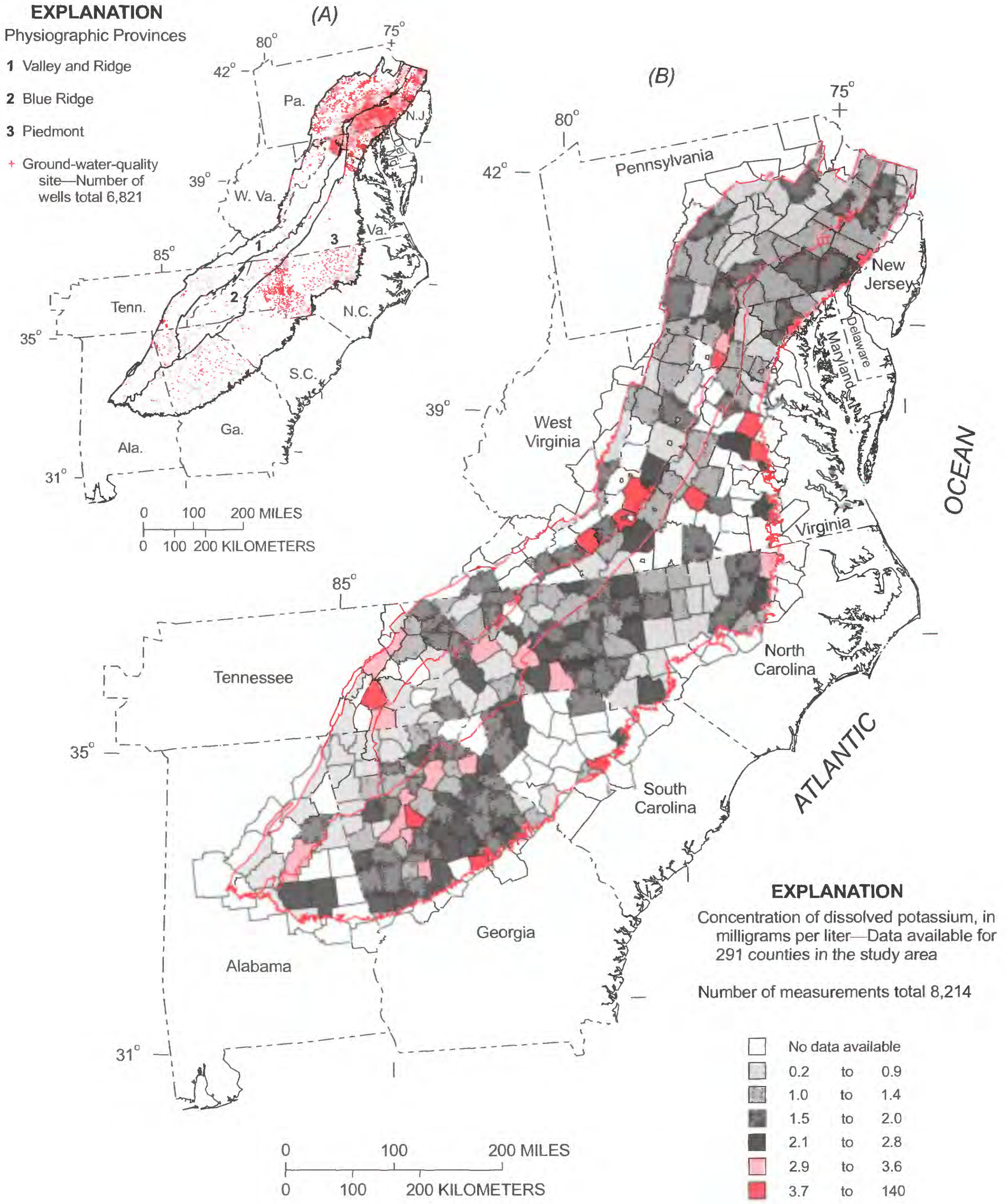


FIGURE 27.—Location of wells in study area where potassium concentration is known *(A)*, and geographic variation of median potassium concentration in ground water, by county *(B)*.

The IQR for potassium concentration in spring water is 0.7 to 1.8 mg / L; median potassium concentration in spring water is approximately three-fourths that in ground water. Differences in median potassium concentrations in spring water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (0.8, 1.2, and 1.6 mg / L, respectively) are significant (fig. 26). The regional patterns of median potassium concentrations in spring water and ground water are different: in the Piedmont, potassium concentration in spring water exceeds that in ground water; in the Blue Ridge, the opposite is true; and in the Valley and Ridge, the concentrations are about equal (fig. 26).

The IQR for potassium concentration in surface water is 1.2 to 2.4 mg / L; median potassium concentration in surface water is slightly larger than that in ground water. Differences in median potassium concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (0.8, 1.6, and 1.9 mg / L, respectively) are significant. The regional patterns of median potassium concentrations in surface water and spring water are similar, except that surface-water concentrations are larger (fig. 26).

BICARBONATE

For major dissolved anions, the crustal abundance of principal nonmetallic elements does not adequately indicate the importance of the anion in the geochemistry of natural water. Carbon is only the 16th most abundant element in surface rocks, but bicarbonate is the dominant anion in most freshwater. Over time, geological, chemical, and biological processes have concentrated carbon in several natural reservoirs, primarily the atmosphere, the ocean, and sedimentary rocks; carbonate sediments are the largest of these reservoirs. Carbon cycles between reservoirs by a number of complex pathways. An extended discussion of this topic is given in Stumm and Morgan (1981). Green plants require carbon dioxide for photosynthesis, and the respiration of all living cells (plants and animals) converts organic forms of carbon (food) back to carbon dioxide.

Chemical equilibria involving the principal forms of dissolved inorganic carbon (carbonate, bicarbonate, and carbon dioxide) control pH and the concentrations of dissolved constituents, especially calcium, magnesium, and iron. These equilibria also control the concentration of bicarbonate in natural water. Hem (1985) reported that bicarbonate concentrations generally range from less than 10 mg / L for rainwater to more than 1,000 mg / L for ground water low in calcium and magnesium; most surface water contains less than 200 mg / L.

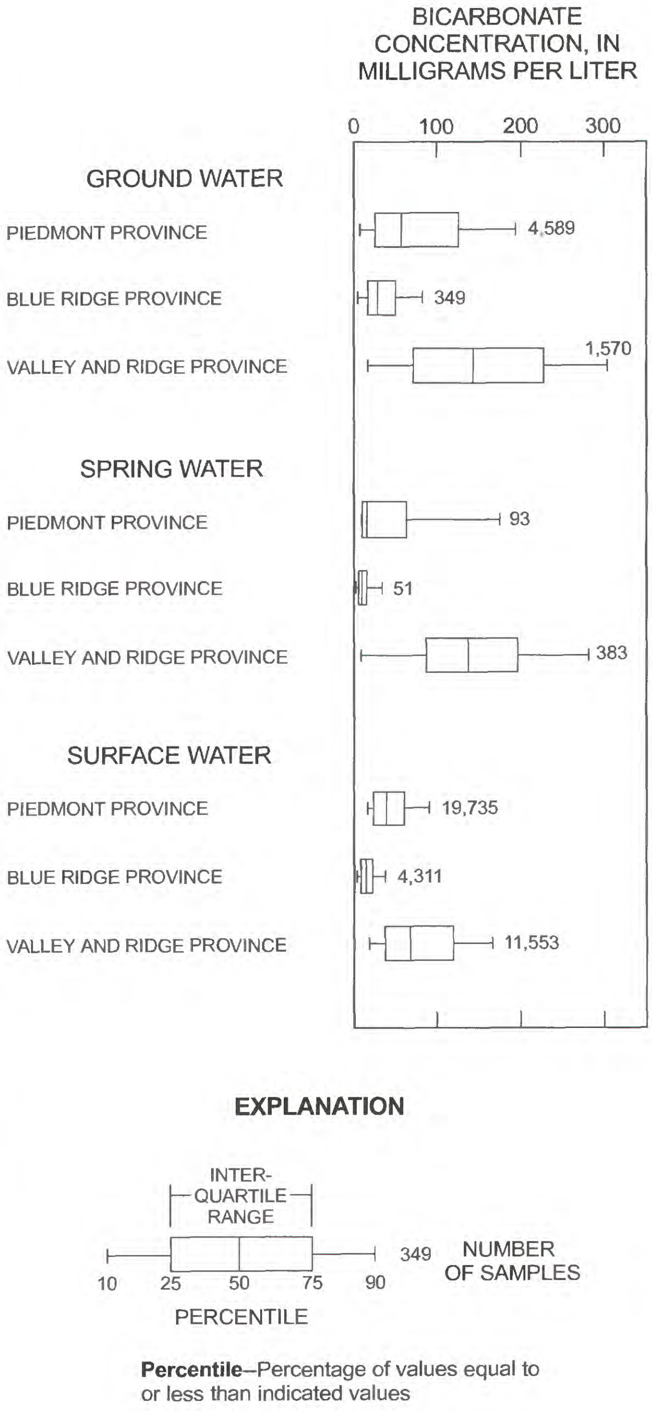


FIGURE 28.—Summary of bicarbonate concentration, by type of site and physiographic province.

Bicarbonate is the dominant anion in most water in the study area. The interquartile range (IQR) for bicarbonate concentration in ground water is 31 to 153 mg / L. The regional IQR's overlap, but differences in median concentrations for ground water in the Blue

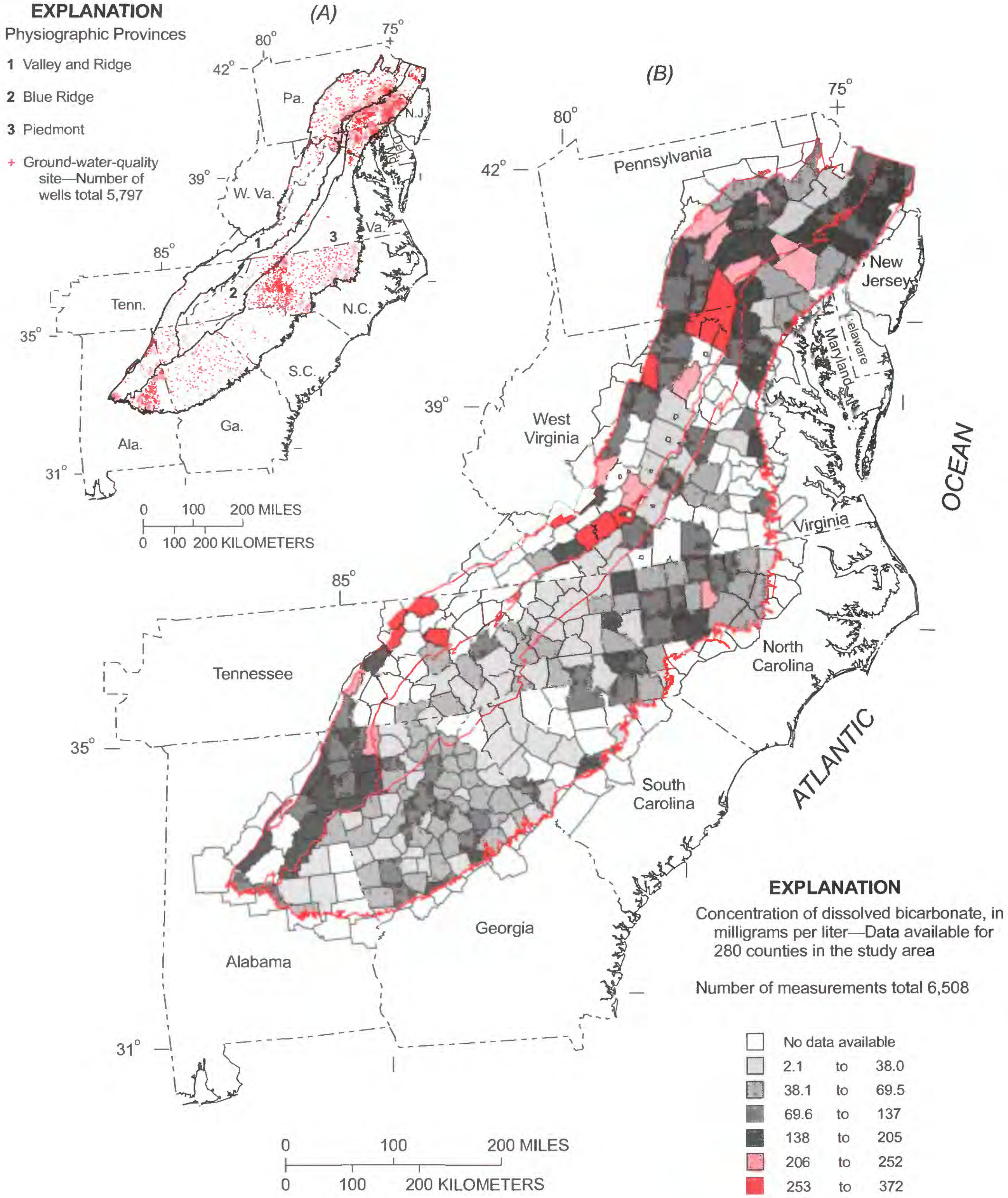


FIGURE 29.—Location of wells in study area where bicarbonate concentration is known *(A)*, and geographic variation of median bicarbonate concentration in ground water, by county *(B)*.

Ridge, the Piedmont, and the Valley and Ridge Provinces (32, 60, and 150 mg / L, respectively) are significant (fig. 28). The highest bicarbonate concentrations and greatest variability of concentration in ground water are in the Valley and Ridge Province, where carbonate sediments are the dominant lithology. The geographic pattern of median bicarbonate concentrations in ground water by county (fig. 29) is similar to those for calcium and magnesium (figs. 21 and 23). In counties where bicarbonate concentration is high, calcium and magnesium concentrations are also high, which indicates the importance of carbonate rocks to chemical composition of ground water.

The IQR for bicarbonate concentration in spring water is 16 to 170 mg / L; median bicarbonate concentration in spring water is almost twice that in ground water. Differences in median bicarbonate concentrations in spring water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (10, 14, and 140 mg / L, respectively) are significant (fig. 28). The regional patterns of median bicarbonate concentrations in spring water and ground water are similar. In the Valley and Ridge Province, bicarbonate concentration in spring water and ground water are about the same; elsewhere, spring water is deficient in bicarbonate.

The IQR for bicarbonate concentration in surface water is 22 to 70 mg / L; median bicarbonate concentration in surface water is about half that in ground water. Differences in median bicarbonate concentrations in surface water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (16, 38, and 64 mg / L, respectively) are significant. The regional patterns of median bicarbonate concentrations in surface water and ground water are similar (fig. 26).

ALKALINITY

The chemical property of alkalinity (or basicity) is the ability of a water to neutralize acids. For most freshwater, alkalinity can be assigned to the dissolved carbonate and bicarbonate species in the sample (Matthess, 1982). Alkalinity is generally reported in milligrams per liter as calcium carbonate (mg / L as $CaCO_3$), where 1 milliequivalent per liter of alkalinity is equal to 1 / 50 times milligrams of $CaCO_3$ per liter.

Direct determination of the concentrations of carbonate and bicarbonate in a water sample is difficult, because chemical reactions involving these ions are highly sensitive to pH and can lead to the formation of carbon dioxide gas that escapes into the atmosphere. In most USGS water analyses performed before 1980, the total concentration of carbonate and bicarbonate in a sample (carbonate alkalinity) was determined in the laboratory by a fixed-endpoint titration to pH 4.5. After 1985, carbonate alkalinity was determined in the field by a different method that indicates the equilibrium endpoint for all basic ions in the sample. Although alkalinity titrations do not determine the concentrations of

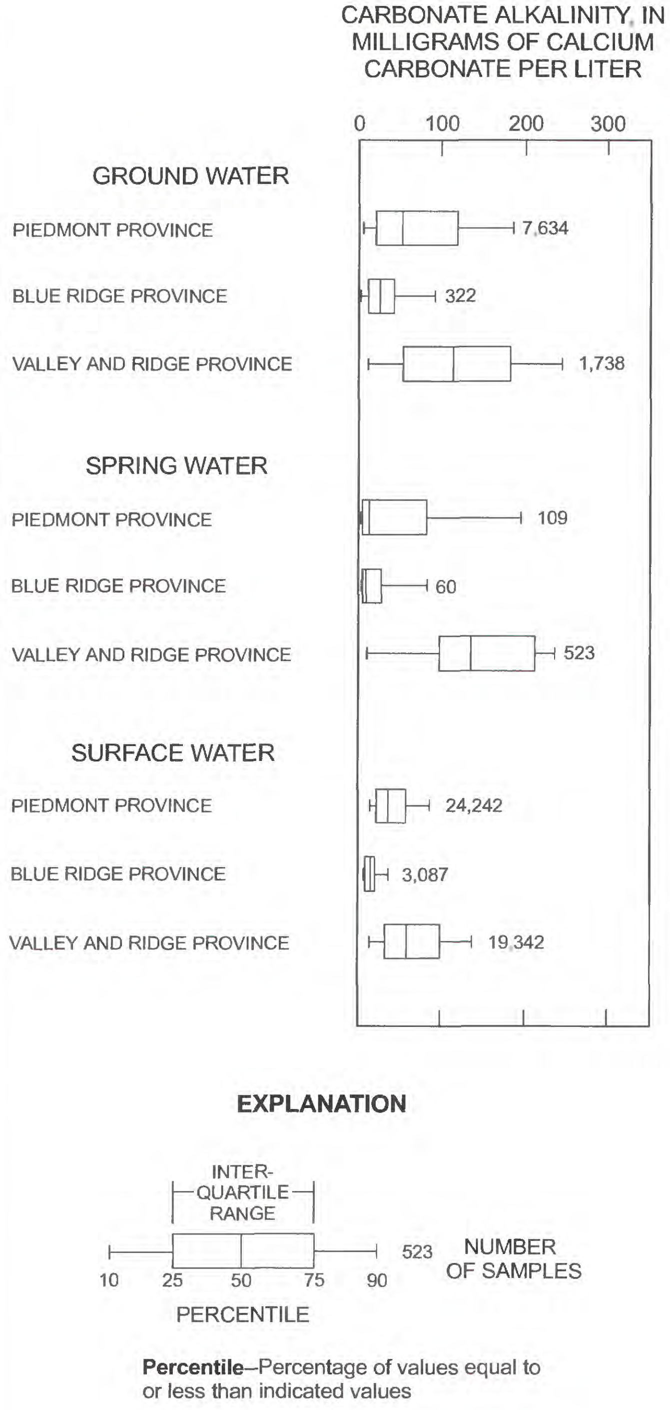


FIGURE 30.—Summary of carbonate alkalinity, by type of site and physiographic province.

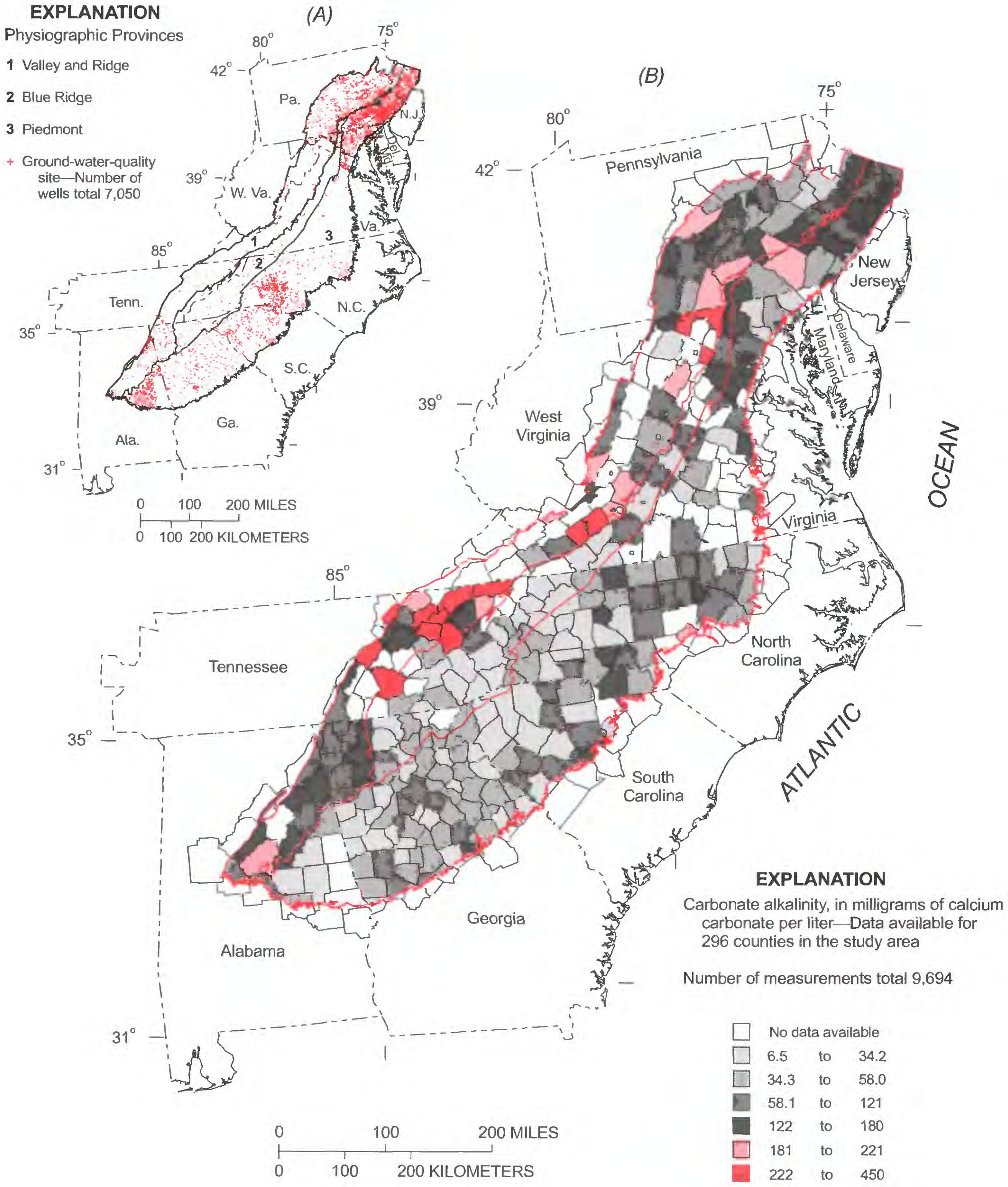


FIGURE 31.—Location of wells in study area where carbonate alkalinity is known *(A)*, and geographic variation of median carbonate alkalinity in ground water, by county *(B)*.

individual ions, for most freshwater at pH's less than 7.3, bicarbonate commonly makes up more than 99 percent of this total (Hem, 1985).

The interquartile range (IQR) for carbonate alkalinity of ground water is 28 to 136 mg / L as $CaCO_3$. The regional IQR's overlap, but differences in median alkalinities of ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (32, 57, and 122 mg / L as $CaCO_3$, respectively) are significant (fig. 30). Regional medians for alkalinity are consistent with those for bicarbonate concentration (fig. 28). For ground water, the highest alkalinities and greatest variability of alkalinity are in the Valley and Ridge Province, where carbonate rocks are abundant; the lowest alkalinities are in the carbonate-deficient rocks of the Blue Ridge Province. The map of median carbonate alkalinities of ground water by county (fig. 31) covers more of the study area than the map of bicarbonate concentrations (fig. 29), but the geographic patterns shown on both maps are virtually the same. These patterns are also similar to those for calcium and magnesium (figs. 21 and 23): in counties where alkalinity and bicarbonate concentration are high, calcium and magnesium concentrations are also high.

The IQR for carbonate alkalinity of spring water is 23 to 206 mg / L as $CaCO_3$; median alkalinity of spring water is almost twice that of ground water. Median alkalinities of spring water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces are 10, 16, and 137 mg / L as $CaCO_3$, respectively. Differences in median alkalinities of spring water in the Valley and Ridge Province and in the other two provinces are significant; whereas, the difference in median alkalinities in the Piedmont and Blue Ridge Provinces is not significant (fig. 30). The regional patterns of median alkalinities of spring water and ground water are similar. In the Valley and Ridge Province, median alkalinities of spring water and ground water are nearly the same; elsewhere, spring water is highly deficient in alkalinity (table 5).

The IQR for carbonate alkalinity of surface water is 20 to 68 mg / L as $CaCO_3$; median alkalinity of surface water is about two-thirds that of ground water. Differences in median alkalinities of surface water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (13, 34, and 55 mg / L as $CaCO_3$, respectively) are significant. The regional patterns of median alkalinities of surface water and ground water are similar (fig. 30), except that variability of alkalinity is generally smaller for surface water than for ground water.

SULFATE

Sulfur is the 14th most abundant element in surface rocks and is widely distributed in igneous, metamorphic, and sedimentary rocks as pyrite and other metallic sulfides (reduced sulfur). When sulfide minerals undergo weathering in contact with aerated water, sulfur is oxidized to sulfate, which dissolves in water and is transported by the hydrologic system. Sulfate is a common constituent of natural water. Oxidation of sulfide minerals produces large quantities of hydrogen ions, and these reactions are controlled jointly by pH and electrochemical potential (Eh). Extended discussions of this topic are given in Garrels and Christ (1965) and Stumm and Morgan (1981).

Like carbon, sulfur cycles between natural reservoirs, which include freshwater, atmosphere, biosphere, ocean water, sediments, and igneous and metamorphic rock. Estimates of the distribution of sulfur among the reservoirs indicate that about half the total is in igneous and metamorphic rock, 7 percent is in solution in the ocean, and most of the remainder is in the sediments. The fraction in other reservoirs is less than 0.1 percent of the total.

Sulfate is commonly the second most abundant anion in water in the study area, although some samples contain a dominant fraction of sulfate. The interquartile range (IQR) for sulfate concentration in ground water is 5 to 32 mg / L. Sulfate concentrations in 2.5 percent of ground-water samples exceed the SMCL (250 mg / L, U.S. Environmental Protection Agency, 1995). The regional IQR's overlap, but differences in median concentrations in ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (5, 13, and 20 mg / L, respectively) are significant (fig. 32). The highest sulfate concentrations and greatest variability of concentration in ground water are in the Valley and Ridge Province, where pyrite and gypsum are common in shales. The geographic pattern of median sulfate concentrations in ground water by county (fig. 33) is similar to that for calcium (fig. 21). In counties where sulfate concentration is high, calcium concentration is also high, an indication that some dissolved sulfate is derived from rocks containing gypsum.

The IQR for sulfate concentration in spring water is 3.6 to 19 mg / L; median sulfate concentration in spring water is about half that in ground water. Sulfate concentrations in less than 0.5 percent of spring-water samples exceed the SMCL. Differences in median sulfate concentrations in spring water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (5, 7.7, and 11 mg / L, respectively) are significant (fig. 32). The regional patterns of median sulfate concentrations in spring water and ground water are similar. In the Blue

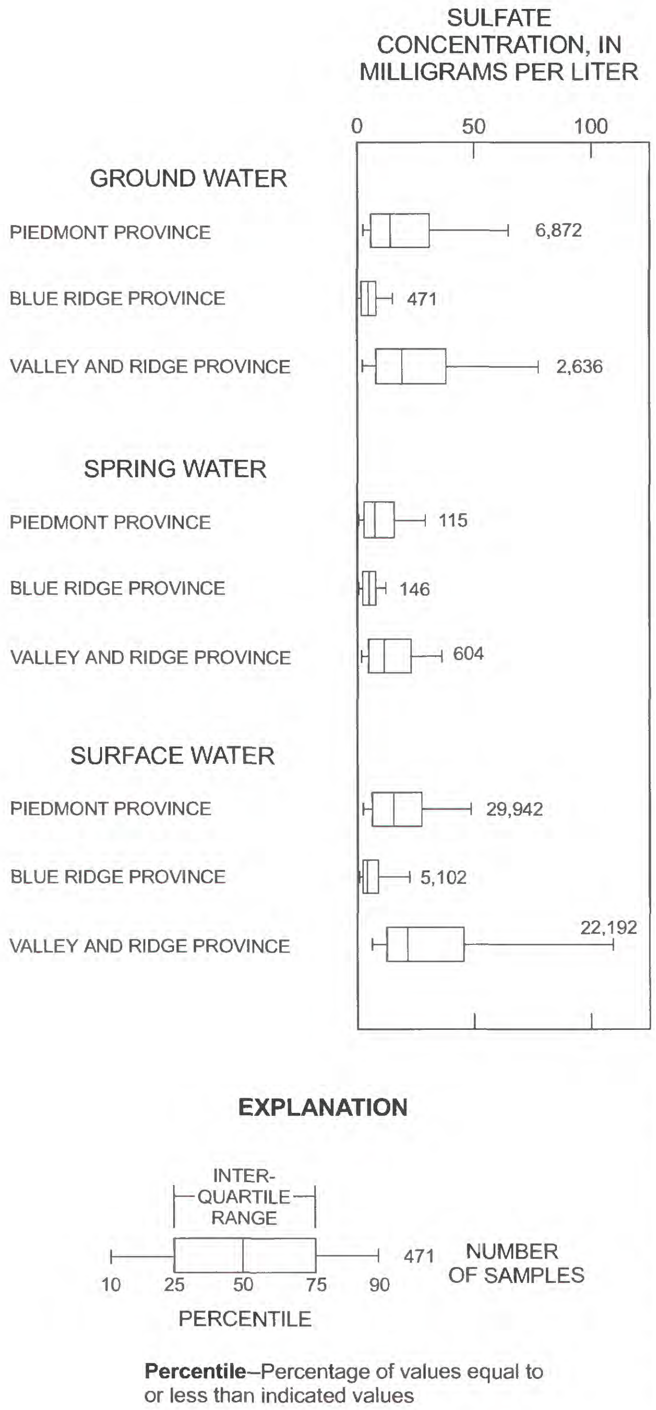


FIGURE 32.—Summary of sulfate concentration, by type of site and physiographic province.

Ridge Province, median sulfate concentrations for spring water and ground water are the same; elsewhere, spring water is deficient in sulfate (table 5).

The IQR for sulfate concentration in surface water is 7.4 to 32 mg / L; median sulfate concentration in surface water is slightly larger than that in ground water. Sulfate concentrations in 18 percent of surface-water samples exceed the SMCL. Many of these streams are in coal mining areas in the Valley and Ridge Province, where oxidized pyrite is the major source of sulfate. Differences in median sulfate concentrations in surface water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (3.7, 16, and 22 mg / L, respectively) are significant. The regional patterns of median sulfate concentrations in surface water and ground water are similar (fig. 32).

CHLORIDE

Chlorine is the 17th most abundant element in surface rocks. Of the several oxidation states for chlorine, only the reduced form (chloride) is significant in aqueous geochemistry. Chloride is present in variable amounts in most natural water: rain and snow contain chloride in concentrations less than 1 mg / L from marine salts entrained in the atmosphere. Surface water contains chloride from various sources including runoff, ground water, and ocean tides. In some areas, spring water contains chloride in concentrations greater than 500 mg / L from zones of highly mineralized ground water. A salty taste is usually detectable at concentrations greater than 250 mg / L, the SMCL recommended for domestic use (U.S. Environmental Protection Agency, 1995). The ocean and deep zones of ground water contain chloride in concentrations greater than 30,000 mg / L. More than 75 percent of the total chlorine present in the crust, atmosphere, and hydrosphere is in solution in the ocean. Marine sediments and submerged rock become impregnated with marine salts, and pore water commonly contains extremely high concentrations of sodium chloride (brines).

Chloride is commonly the third most abundant anion in water in the study area, although some samples contain a dominant fraction of chloride. The interquartile range (IQR) for chloride concentration in ground water is 2.8 to 17 mg / L, an indication that deep ground water is not generally involved in the flow system. Chloride concentrations in less than 1 percent of ground-water samples exceed the SMCL. The regional IQR's overlap, but differences in median concentrations in ground water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (2.1, 6, and 7 mg / L, respectively) are significant (fig. 34). The difference between medians for the Valley and Ridge and the Piedmont Provinces, however, is within the analytical uncertainty in the determination of chloride concentration. The greatest variability of chloride concentration in ground water is in the Piedmont Province. The geographic pattern of median chloride concentrations in

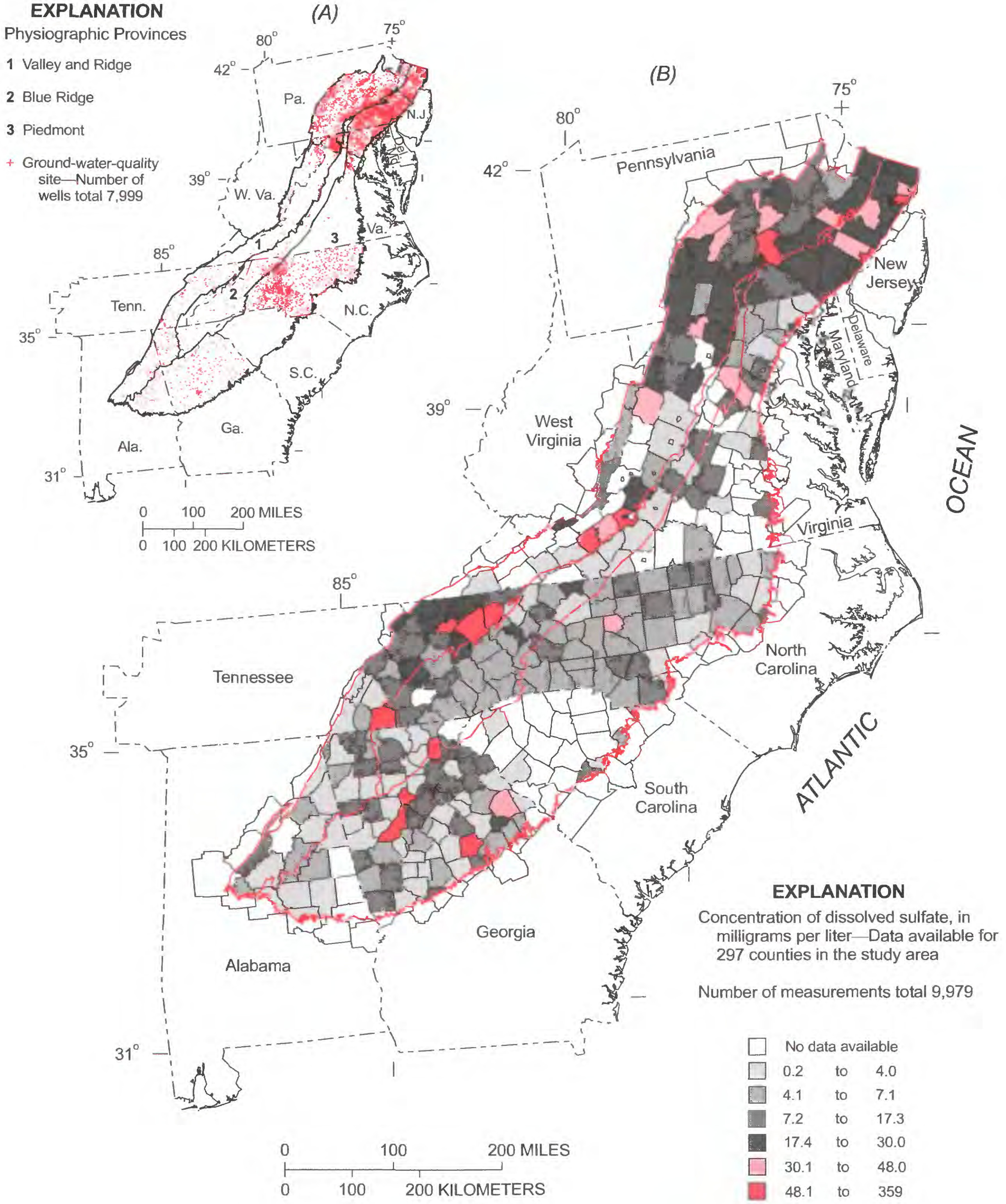


FIGURE 33.—Location of wells in study area where sulfate concentration is known *(A)*, and geographic variation of median sulfate concentration in ground water, by county *(B)*.

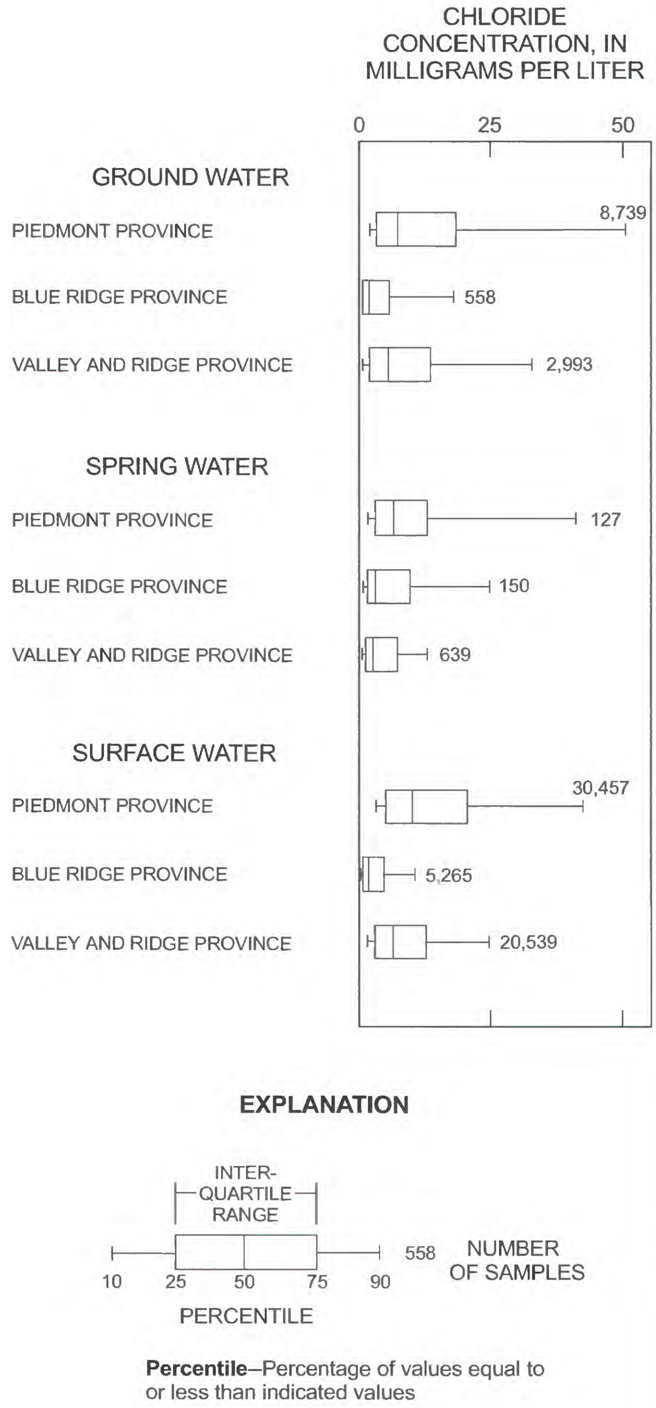


FIGURE 34.—Summary of chloride concentration, by type of site and physiographic province.

ground water by county (fig. 35) is similar to that for sodium (fig. 25). In counties where chloride concentration is high, sodium concentration is also high. Most of these counties are in the Piedmont Province, but chloride concentrations are also high in a few counties in the Valley and Ridge Province. Wells in these counties may tap deep ground water.

The IQR for chloride concentration in spring water is 1.5 to 8.5 mg / L; median chloride concentration in spring water is about half that in ground water. Chloride concentrations in spring-water samples do not exceed the SMCL. Median chloride concentrations in spring water in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces are 2.8, 3.2, and 6.6 mg / L, respectively. Differences in median concentrations in spring water in the Piedmont Province and in the other two provinces are significant; whereas, the difference in median concentrations in the Blue Ridge and the Valley and Ridge Provinces is not significant (fig. 34). The regional patterns of median chloride concentrations in spring water and ground water are different: in spring water, chloride concentrations and variability of concentration increase gradually from west to east (fig. 34).

The IQR for chloride concentration in surface water is 3.6 to 16 mg / L; median chloride concentration in surface water is slightly larger than that in ground water. Chloride concentrations in about 1 percent of surface-water samples exceed the SMCL. Differences in median chloride concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (2.2, 6.8, and 9.6 mg / L, respectively) are significant. The highest chloride concentrations and greatest variability of concentration are in the Piedmont Province. The regional patterns of median chloride concentrations in surface water and ground water are similar (fig. 34). In the Blue Ridge and the Valley and Ridge Provinces, median chloride concentrations in ground water and surface water are about equal. In the Piedmont Province, however, surface water contains more chloride than ground water, an indication of the effect of seawater on streams in the northeastern section of the study area.

SILICA

Silicon is the second most abundant element in the Earth's crust and is the principal constituent of most igneous and metamorphic rocks. Silica (or SiO_2) is present in some form in most rocks and soils and is a common constituent of natural water. The term "silica" refers to all forms of dissolved silicates. In water, dissolved silica results primarily from the weathering of felspars, micas, and other silicate minerals. Although silica is abundant in most rocks, nearly all ground water is greatly undersaturated with respect to dissolved silica (Freeze and Cherry, 1979).

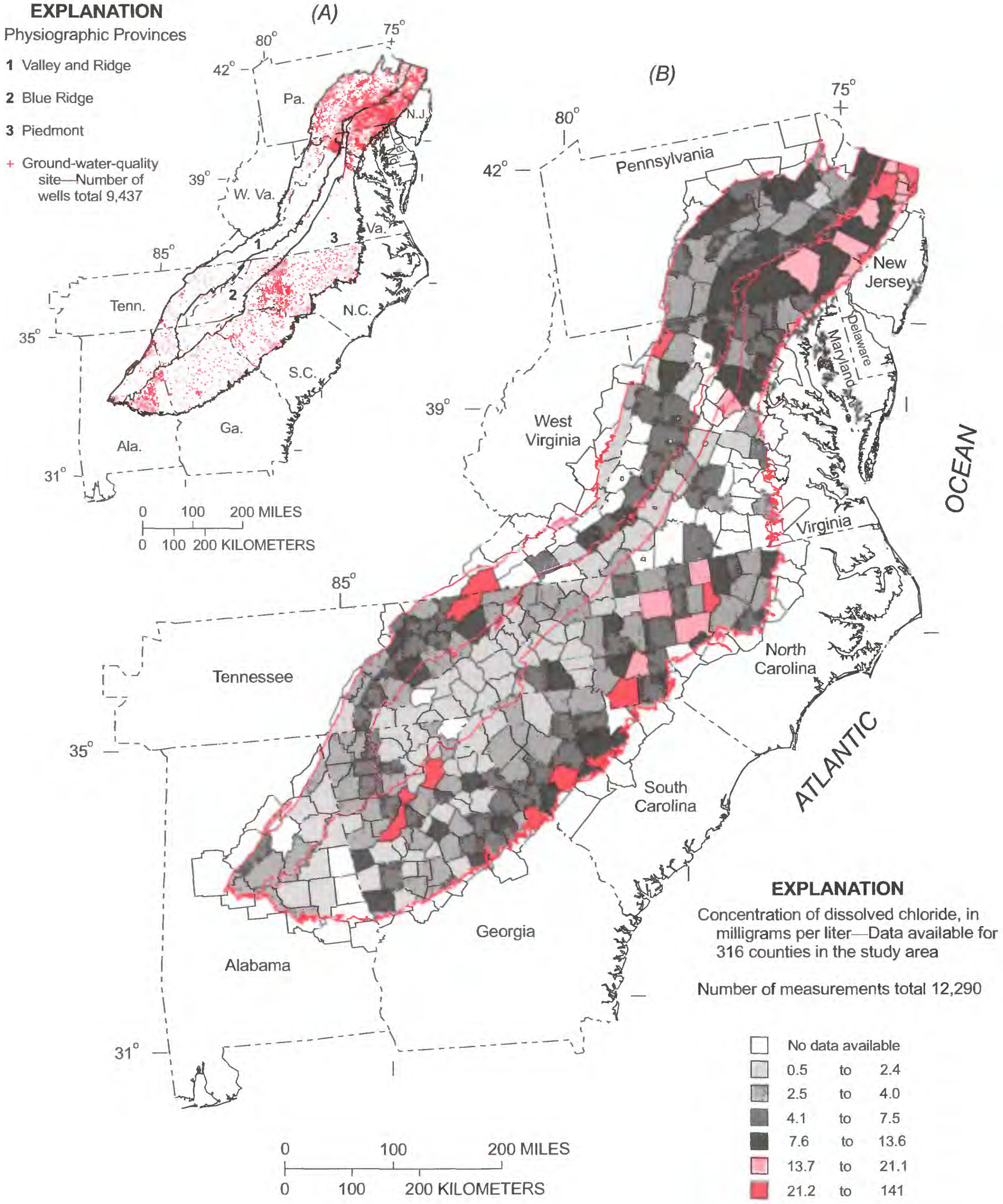


FIGURE 35.—Location of wells in study area where chloride concentration is known *(A)*, and geographic variation of median chloride concentration in ground water, by county *(B)*.

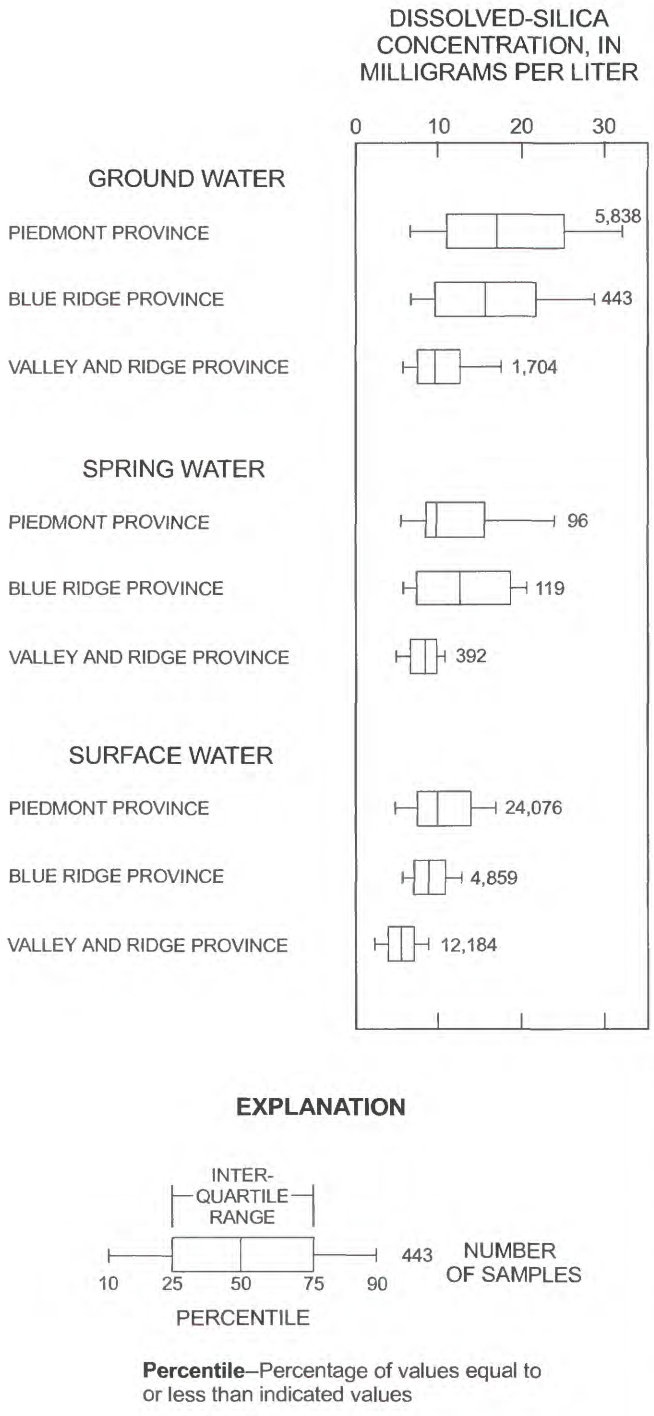


FIGURE 36.—Summary of dissolved-silica concentration, by type of site and physiographic province.

The interquartile range (IQR) for silica concentration in ground water is 9.3 to 23 mg / L; median silica concentration is close to that reported by Davis (1964). The regional IQR's overlap, but differences in median concentrations in ground water in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces (10, 16, and 17 mg / L, respectively) are significant (fig. 36). The difference between medians for the Blue Ridge and the Piedmont Provinces, however, is within the analytical uncertainty in the determination of silica concentration. The highest silica concentrations and greatest variability of concentration are in the Piedmont Province, where silica-rich rocks are common. The geographic pattern of median silica concentrations in ground water by county (fig. 37) is similar to that for sodium (fig. 25). In counties where silica concentration is high, sodium concentration is also high. Most of these counties are in the southern Piedmont Province, particularly in Georgia and Alabama. This pattern is an indication of the abundance of high-silica rocks (gneisses and granites) in the Piedmont and the Blue Ridge Provinces.

For wells less than the median depth, the relation between silica concentration and well depth by province (fig. 38) is strongest in the Piedmont Province and virtually nonexistent in the Valley and Ridge Province. In the Blue Ridge Province, a weak relation between silica concentration and well depth extends to about twice the median depth (table 6).

The IQR for silica concentration in spring water is 7.3 to 11 mg / L; median silica concentration in spring water is about half that in ground water. Median silica concentrations in spring water in the Valley and Ridge, the Piedmont, and the Blue Ridge Provinces are 8.6, 10, and 13 mg / L, respectively. Differences in median concentrations in spring water in the Valley and Ridge Province and in the other two provinces are significant; whereas, the difference in median concentrations in the Piedmont and the Blue Ridge Provinces is not significant (fig. 36). The regional patterns of median silica concentrations in spring water and ground water are different: in spring water, the highest silica concentrations and greatest variability of concentration are in the Blue Ridge Province (fig. 36).

The IQR for silica concentration in surface water is 5.8 to 12 mg / L. Median silica concentration in surface water in the study area is about half that in ground water and lower than the median concentration reported by Davis (1964). Differences in median silica concentrations in surface water in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces (5.7, 9, and 10 mg / L, respectively) are significant (fig. 36); however, the difference between medians for the Blue Ridge and the Piedmont Provinces is within the analytical uncertainty in the determination of silica concentration. The highest silica concentrations and greatest variability of concentration are in the Piedmont Province. The regional patterns of median silica concentrations in surface water and ground water are similar (fig. 34), except that surface-water concentrations are lower.

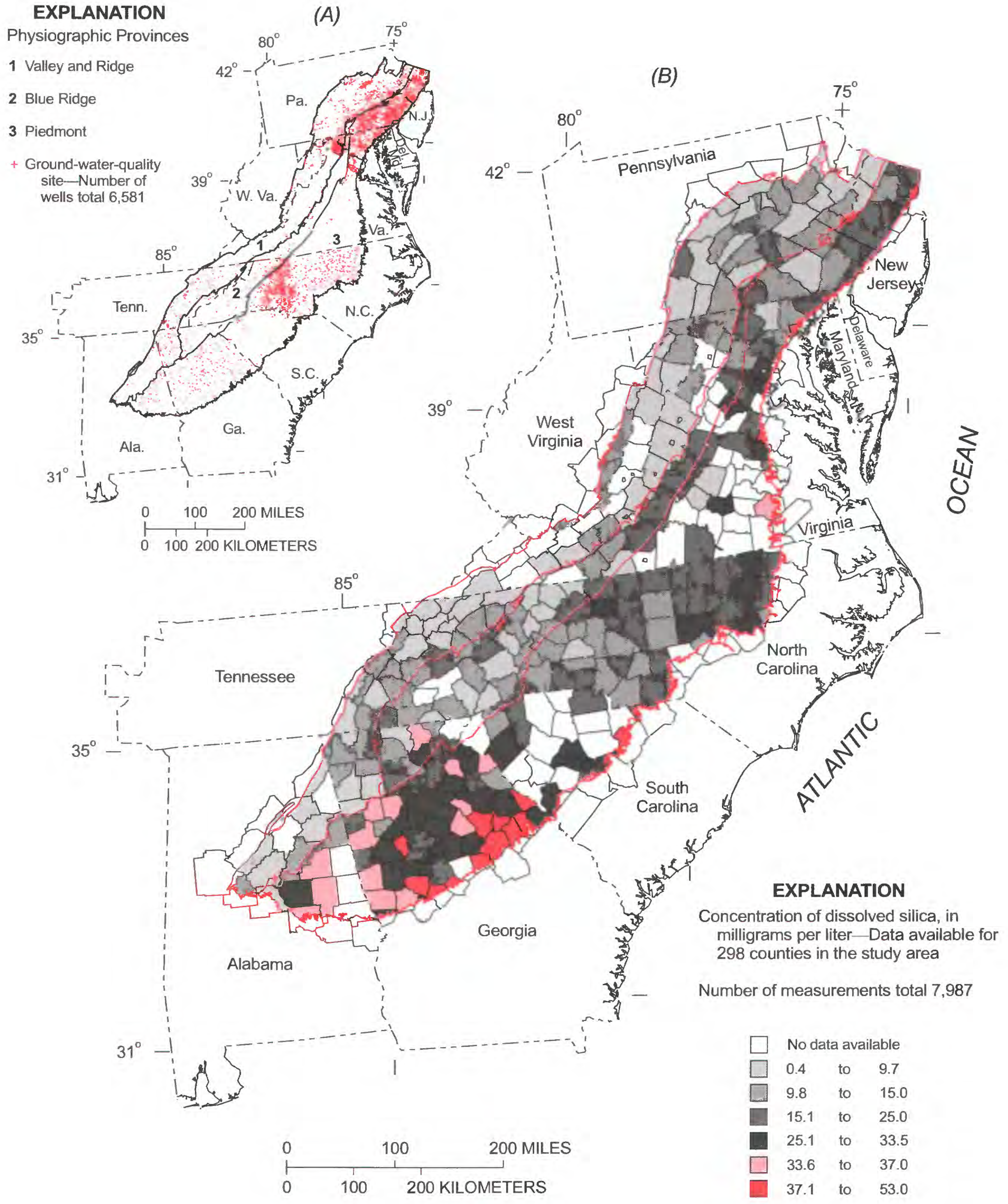


FIGURE 37.—Location of wells in study area where dissolved-silica concentration is known *(A)*, and geographic variation of median dissolved-silica concentration in ground water, by county *(B)*.

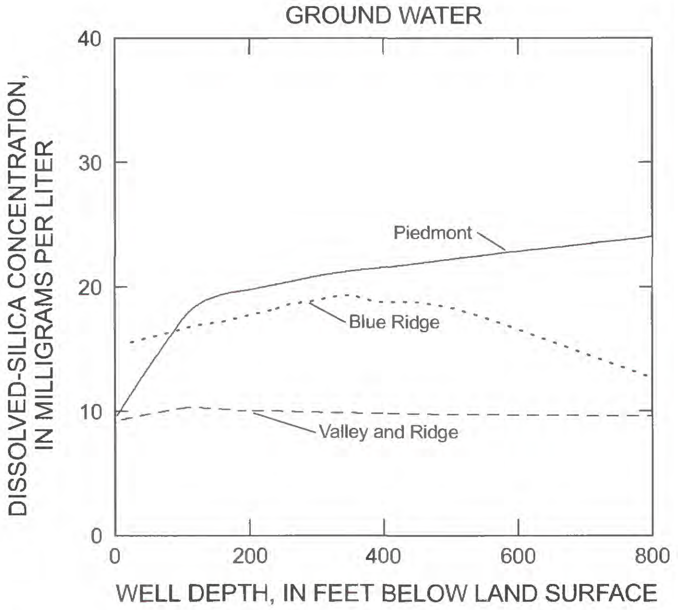


FIGURE 38.—Variation of dissolved-silica concentration in ground water as a function of well depth, by physiographic province.

NITROGEN

Nitrogen is the 28th most abundant element in surface rocks, which contain about one-fourth of the total amount of nitrogen at the Earth's surface. Three-fourths of the total is in the atmosphere, where molecular nitrogen makes up approximately 78 percent of the volume. Conversion of atmospheric nitrogen to dissolved forms (fixation) is an important function of all ecosystems because dissolved inorganic nitrogen is required for plant growth. Organic nitrogen is a constituent of all proteins. Soluble forms of nitrogen are highly mobile in the subsurface environment and are easily leached through the soil zone into underlying aquifers by infiltrating water. Nitrogen, therefore, is perhaps the most widespread contaminant in ground water (Freeze and Cherry, 1979; Hallberg and Keeney, 1993).

Dissolved inorganic nitrogen occurs in several oxidation states: the common forms include ammonia (−1), nitrite (+3), and nitrate (+5). In most natural waters, dissolved nitrogen is easily oxidized and is generally found in the high oxidation states. USGS water analyses generally determine the total concentration of nitrite and nitrate (nitrite plus nitrate) in a sample. To simplify comparison among different forms of dissolved nitrogen (nitrite plus nitrate and ammonia), analytical concentrations are reported in milligrams of nitrogen per liter (mg / L as N). In the study area, median concentrations of nitrite plus nitrate in ground water are 10 to 200 times those of ammonia (table 5). Data for ammonia concentrations in ground water are sparse and discussion of regional variations in ammonia concentrations is not meaningful. Therefore, discussion of dissolved-nitrogen concentrations is in terms of the dominant forms, nitrite plus nitrate.

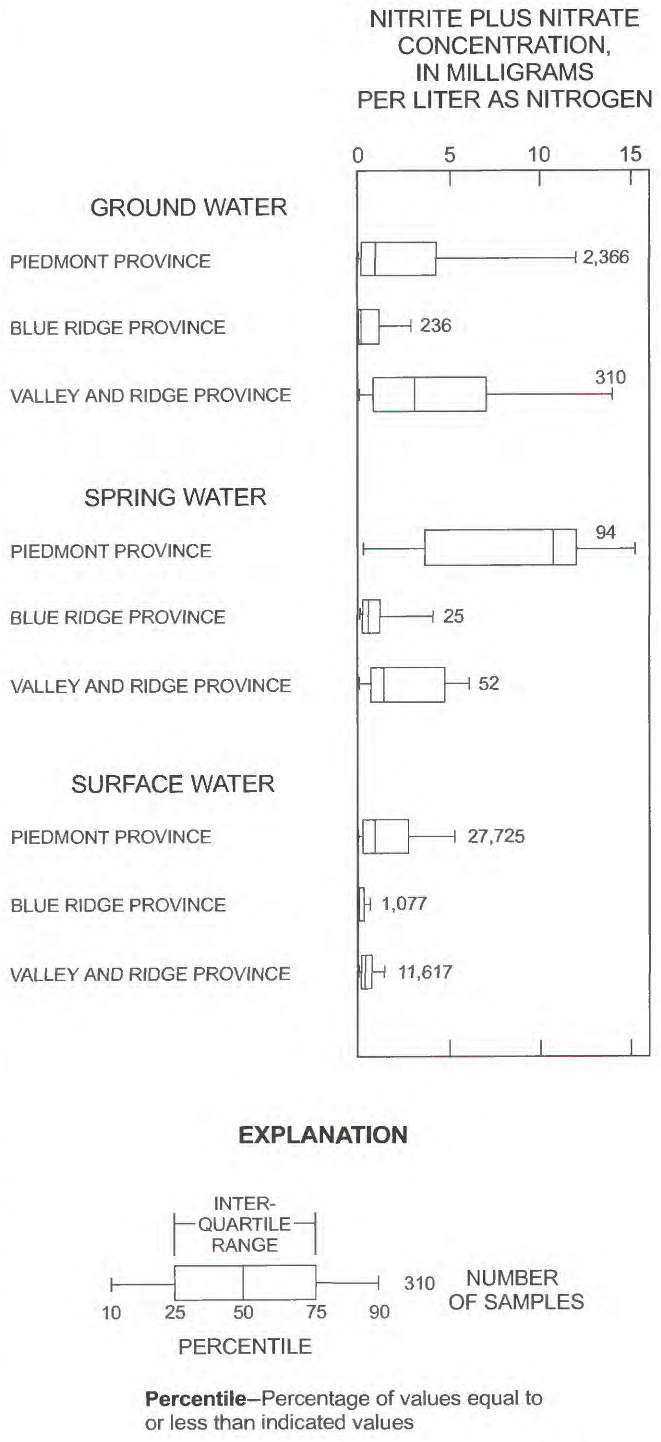


FIGURE 39.—Summary of nitrite plus nitrate concentration, by type of site and physiograhic province.

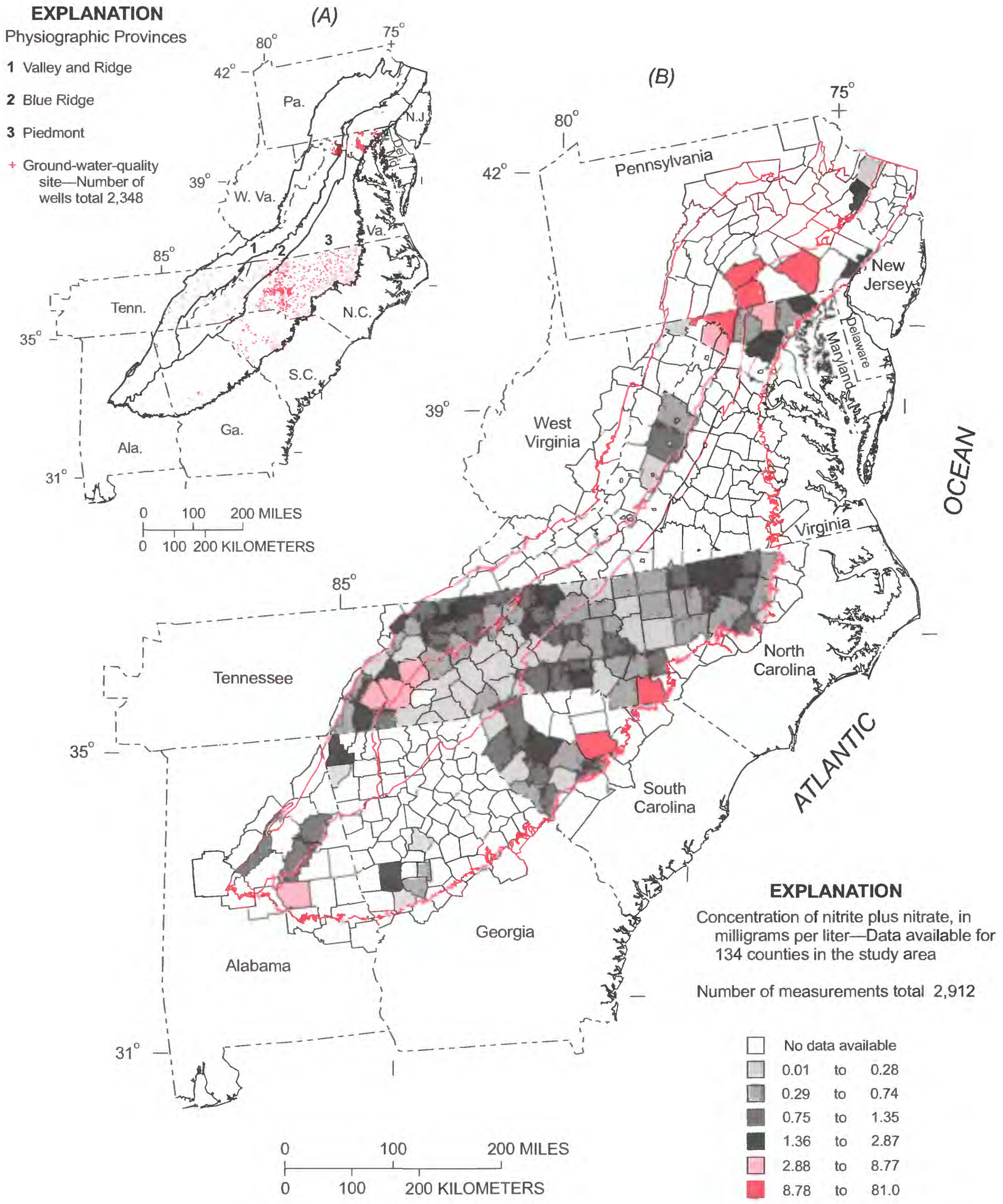


FIGURE 40.—Location of wells in study area where nitrite plus nitrate concentration is known *(A)*, and geographic variation of median nitrite plus nitrate concentration in ground water, by county *(B)*.

Nitrate from natural sources is rarely found in ground water in concentrations greater than 3 mg / L as N; larger concentrations are usually the result of human activity (Bachman, 1984). The interquartile range (IQR) for nitrite plus nitrate concentration in ground water is 0.2 to 4.3 mg / L as N. Concentrations in 13 percent of ground-water samples exceed the maximum contaminant level (MCL) for drinking water (10 mg / L, U.S. Environmental Protection Agency, 1995); 86 percent of these wells are in the Piedmont Province. Regional IQR's overlap, but differences in median concentrations in ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (0.2, 0.99, and 3.1 mg / L as N, respectively) are significant (fig. 39). The difference between medians for the Blue Ridge and the Piedmont Provinces, however, is within the analytical uncertainty in the determination of nitrite plus nitrate concentration. Although most of the high concentrations are in the Piedmont Province, the greatest variability of concentration in ground water is in the Valley and Ridge Province (fig. 39). The 95th percentiles for concentrations in the Piedmont and the Valley and Ridge Provinces are about equal (table 5) and are typical of concentrations reported in previous studies (Bachman, 1984; Duigon and Dine, 1991; Froelich and Zenone, 1985; Hallberg and Keeney, 1993; Johnston, 1964; Patterson and Padgett, 1984; and Poth, 1968 and 1972).

Most of the data for nitrogen concentration in ground water in the study area were collected in North Carolina, South Carolina, Tennessee, and Maryland. The geographic pattern of median nitrite plus nitrate concentrations in ground water by county (fig. 40) is sparse and is not readily compared with those for other major constituents. Where nitrogen data are available for ground water, county concentrations are typically higher in the Valley and Ridge and the Piedmont Provinces than in the Blue Ridge Province. Some of the highest county concentrations, however, are based on data for only one or two wells in the county.

Regional variations in nitrite plus nitrate concentration in ground water as a function of well depth (fig. 41) indicate that in the Valley and Ridge and the Blue Ridge Provinces, nitrogen concentrations decrease rapidly to depths near 200 ft, then become relatively constant. In the Piedmont Province, nitrogen concentration increases rapidly to depths near 200 ft, begins to decrease, then becomes relatively constant. For each of these curves, the principal inflection point is near median well depth.

The IQR for nitrite plus nitrate concentration in spring water is 0.93 to 11 mg / L as N. Median concentration in spring water is about four times that in ground water, probably because of a shallow origin for springs in the Piedmont Province. Nitrite plus nitrate concentrations in 30 percent of spring-water samples in the study area exceed the MCL; 96 percent of these springs are in the Piedmont Province. Differences in median concentrations in spring water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (0.54, 1.5, and 11 mg / L as N, respectively) are significant (fig. 39). The highest nitrite plus nitrate concentrations and greatest variability of concentration in spring water are in the Piedmont Province, where concentrations are high enough to indicate contamination. In the Valley and Ridge Province, median concentration of nitrite plus nitrate in spring water is about half that in ground water (fig. 39).

The IQR for nitrite plus nitrate concentration in surface water is 0.36 to 2 mg / L as N; median concentration in surface water is 79 percent that in ground water. Nitrite plus nitrate concentrations in only 2 percent of surface-water samples exceed the MCL, and more than 99 percent of these samples are in the Piedmont Province. Differences in median concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (0.23, 0.51, and 1.1 mg / L as N, respectively) are significant (fig. 39). The regional patterns of median nitrite plus nitrate concentrations in surface water and ground water are similar, except that the highest concentrations and greatest variability of concentration in surface water are in the Piedmont Province (fig. 39).

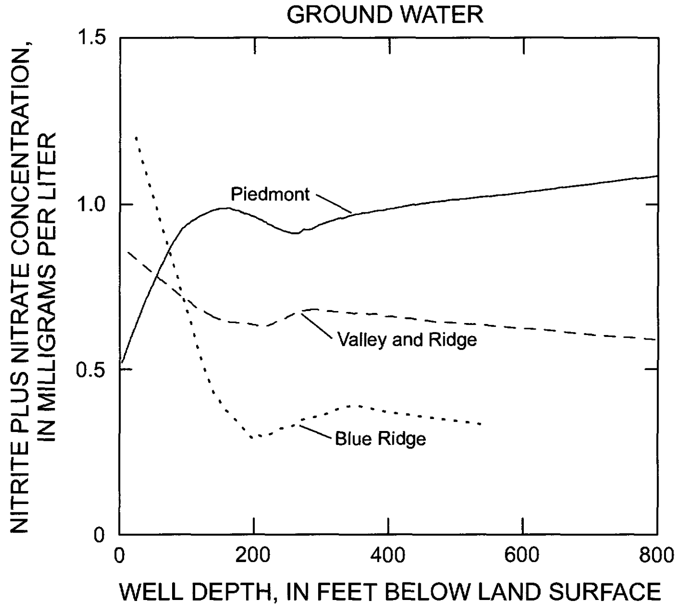


FIGURE 41.—Variation of nitrite plus nitrate concentration in ground water as a function of well depth, by physiographic province.

PHOSPHORUS

Phosphorus is the 10th most abundant element in surface rocks and is a common constituent of many igneous and sedimentary rocks. Phosphorus is important in agriculture as a nutrient required for plant growth. In water containing appreciable concentrations of calcium, the solubility of inorganic forms of phosphorus is low; thus, natural concentrations of dissolved phosphorus seldom exceed 0.5 mg / L. Phosphorus is a waste product of animal metabolism and is common in sewage effluent. In surface water, phosphorus concentrations significantly above background levels can be a cause of eutrophication.

Like nitrogen, phosphorus occurs in several oxidation states. The most common form of inorganic phosphorus is orthophosphate (+5), but some biogenic materials suspended in water contain mixtures of organic phosphorus in lower oxidation states. Depending on the needs of an investigation, water samples collected for the determination of phosphorus concentration can be filtered to determine dissolved phosphorus, or analyzed unfiltered to determine total phosphorus. To simplify comparison among different forms of phosphorus, analytical concentrations are reported in milligrams of phosphorus per liter (mg / L as P). A summary of the data available for dissolved and total phosphorus is listed in table 5. The interpretation of variations in major-ion composition presented in a later section of this report ("Variations in Chemical Composition of Water, by Type of Site and Physiographic Province") is based on dissolved-phosphorus concentrations; data for total-phosphorus concentrations are viewed as an upper limit on dissolved phosphorus.

DISSOLVED-PHOSPHORUS CONCENTRATIONS

The interquartile range (IQR) for dissolved-phosphorus concentration in ground water is 0.02 to 0.07 mg / L as P. Median concentrations in ground water in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces are 0.02, 0.03, and 0.03 mg / L as P, respectively. Differences in median concentrations in the Piedmont and the Valley and Ridge Provinces are significant (fig. 42), but the two medians are virtually the same within the analytical uncertainty in the determination of dissolved-phosphorus concentration. The highest concentrations are in the Piedmont Province, but the greatest variability of concentration is in the Blue Ridge. Dissolved-phosphorus concentrations in ground water in the study area are generally low; the 95th percentile is consistent with typical concentrations reported by Becher and Root (1981), Johnston (1964), Nemickas (1976), Paulachok (1991), and Sloto (1989).

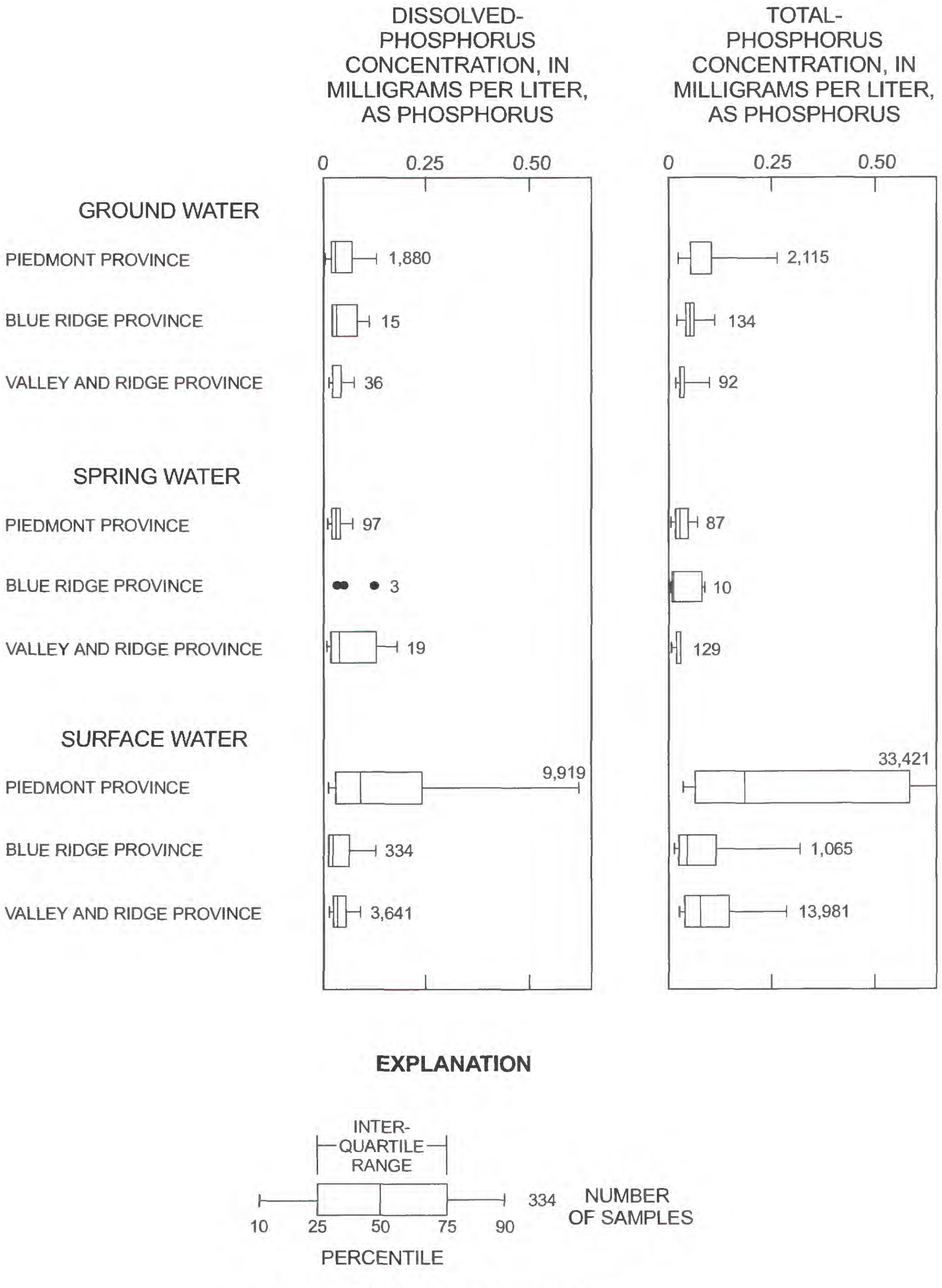
Dissolved-phosphorus concentration is not commonly determined in ground-water-quality investigations in the study area; data are available for only 34 counties, primarily in the Piedmont of New Jersey, Pennsylvania, and Maryland. About 3 percent of the well sites where dissolved-phosphorus data are available are scattered across the central and southern parts of the area. The geographic pattern of median dissolved-phosphorus concentrations in ground water by county (fig. 43) indicates that most of the highest concentrations are in the northeast part of the Piedmont Province. This pattern, however, may be a result of the skewed distribution of sites and may not accurately represent the distribution of dissolved-phosphorus concentrations in the study area as a whole.

The IQR for dissolved-phosphorus concentration in spring water is 0.02 to 0.05 mg / L as P. Median concentrations in spring water and ground water are equal and are consistent with typical concentrations reported by Chandler and Moore (1987) and Hobba and others (1977). Differences in median concentrations in spring water in the Piedmont, the Valley and Ridge, and the Blue Ridge Provinces (0.03, 0.04, and 0.05 mg / L as P, respectively) are not significant (fig. 42). For the Blue Ridge Province, a median value is not shown because this group contains fewer than 10 measurements; the data are shown as individual points, two of which are coincident. For spring water, the highest dissolved-phosphorus concentrations and greatest variability of concentration are in the Valley and Ridge Province.

Dissolved-phosphorus concentration is commonly determined in surface-water-quality investigations. The IQR for dissolved-phosphorus concentration in surface water is 0.02 to 0.17 mg / L as P; median concentration in surface water is twice that in ground water. Differences in median concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (0.02, 0.03, and 0.09 mg / L as P, respectively) are significant (fig. 42). The difference between medians for the Blue Ridge and the Valley and Ridge Provinces, however, is within the analytical uncertainty in the determination of dissolved-phosphorus concentration. In the Piedmont Province, the median concentration of dissolved phosphorus in surface water is about three times that in ground water; elsewhere in the study area, these concentrations are about equal (table 5).

TOTAL-PHOSPHORUS CONCENTRATIONS

Total-phosphorus concentrations in ground water in the study area are generally about twice those of dissolved phosphorus. The interquartile range (IQR) for total-phosphorus concentration in ground water is 0.05 to 0.10 mg / L as P. Median concentrations in ground



● ● **Data Values**–Boxplot diagrams are not statistically significant for distributions that contain fewer than 10 data values. These distributions are shown as individual values

Percentile–Percentage of values equal to or less than indicated values

FIGURE 42.—Summaries of dissolved-phosphorus concentration and total-phosphorus concentration, by type of site and physiographic province.

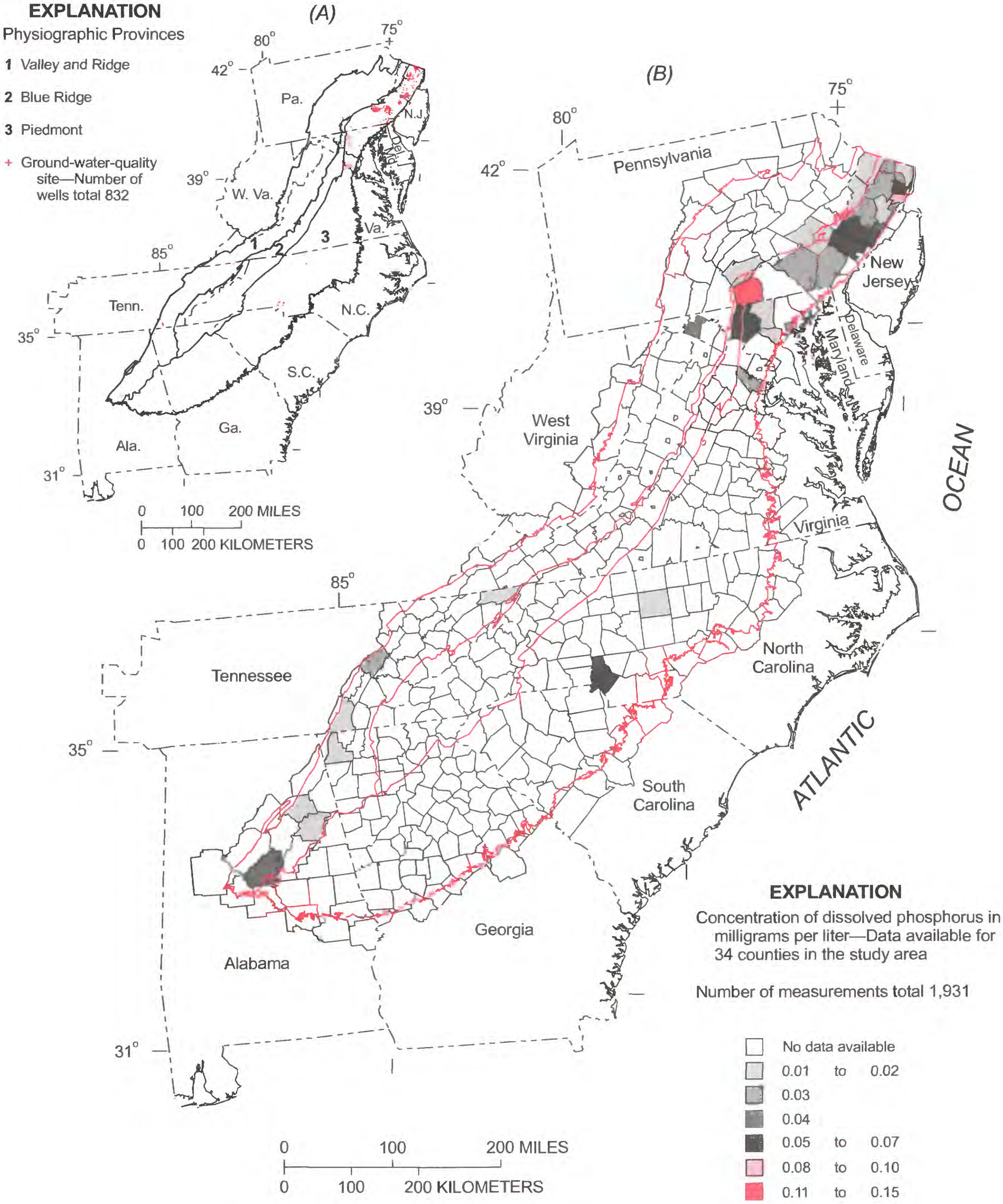


FIGURE 43.—Location of wells in study area where dissolved-phosphorus concentration is known *(A)*, and geographic variation of median dissolved-phosphorus concentration in ground water, by county *(B)*.

water in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces are 0.02, 0.05, and 0.05 mg / L as P, respectively; regional differences in median concentrations, however, are not significant (fig. 42). In ground water, concentrations of total phosphorus and dissolved phosphorus are highest in the Piedmont Province, which is probably the result of locally intensive agricultural activity.

Total-phosphorus concentrations in spring water in the study area are generally the same as those of dissolved phosphorus (table 5). The interquartile range for total-phosphorus concentration in spring water is 0.02 to 0.04 mg / L as P. Median concentrations in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces are 0.01, 0.02, and 0.03 mg / L as P, respectively. Differences in median concentrations in the Blue Ridge Province and elsewhere in the study area are statistically significant; these differences, however, are within the analytical uncertainty in the determination of total-phosphorus concentration. The difference in median concentrations in the Piedmont and the Valley and Ridge Provinces is not statistically significant (fig. 42). Median total-phosphorus concentrations in spring water in the study area are about half those in ground water.

Total-phosphorus concentrations in surface water in the study area are generally about twice those of dissolved phosphorus. The interquartile range for total-phosphorus concentration in surface water is 0.05 to 0.38 mg / L as P. Differences in median concentrations in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (0.04, 0.07, and 0.18 mg / L as P, respectively) are significant (fig. 42). For both total and dissolved phosphorus, the highest concentrations in surface water and greatest variability of concentration are in the Piedmont Province, where calcium-deficient stream sediments do not effectively control phosphorus concentrations. Total-phosphorus concentrations in surface water are generally about twice those in ground water (table 5).

IRON

Iron is the second most abundant metal in surface rock and is a common constituent of silicates and sulfides found in igneous and metamorphic rocks. To a lesser extent, iron (in the form of oxyhydroxides) is also a constituent of some sedimentary rocks. Like phosphorus, iron is an essential element in the metabolism of animals and plants, but natural concentrations of iron in water are generally low. Where concentration exceeds 0.3 mg / L, iron becomes an objectionable impurity in domestic and industrial water supplies because a reddish-brown oxide stain is deposited on porcelain and fabrics.

The aqueous geochemistry of iron has been studied extensively: reviews are given in Garrels and Christ (1965) and Stumm and Morgan (1981). The solubility of iron in water is highly dependent on the acidity (pH) and electrochemical potential (Eh) of the water. For dissolved iron, two oxidation states are common: ferrous (+2) and ferric (+3); in ground water, ferrous iron is the more common form. Igneous rocks provide the most common source of dissolved iron, particularly in water derived from shales. Hobba (1985) reported iron concentrations in ground water as high as 18 mg / L in areas of West Virginia rich in pyrite shales. For limestone aquifers in West Virginia, Bieber (1961) reported iron concentration in ground water is typically less than 0.3 mg / L. Because concentrations of dissolved iron (and other heavy metals) are commonly less than 1 mg / L, these concentrations are reported in units of micrograms per liter (μg / L), where 1 milligram per liter is equal to 1,000 micrograms per liter.

DISSOLVED-IRON CONCENTRATIONS

The interquartile range (IQR) for dissolved-iron concentration in ground water is 17 to 270 μg / L. Dissolved-iron concentrations in 23 percent of ground-water samples exceed the SMCL (300 μg / L, U.S. Environmental Protection Agency, 1995). Median concentrations in ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces are 31, 50, and 100 μg / L, respectively, and are generally consistent with concentrations reported by Bain and Brown (1981), Baker (1957), Hobba (1985), Johnston (1964), and Poth (1968). For ground water, regional differences in median dissolved-iron concentrations in the Valley and Ridge Province and in the other two provinces are significant; whereas, the difference between median concentrations for the Blue Ridge and the Piedmont Provinces is not significant (fig. 44). Although the highest concentrations and greatest variability of concentration are in the Valley and Ridge Province, where pyrite shales are abundant, the distribution of iron concentrations in the Piedmont Province is also skewed at the upper end of the range.

The geographic pattern of median dissolved-iron concentrations in ground water by county (fig. 45) indicates that most of the highest concentrations are in the Valley and Ridge Province, although some high concentrations are in the Piedmont and the Blue Ridge Provinces. The geographical distribution of sites is concentrated in the northern end of the study area: 87 per-

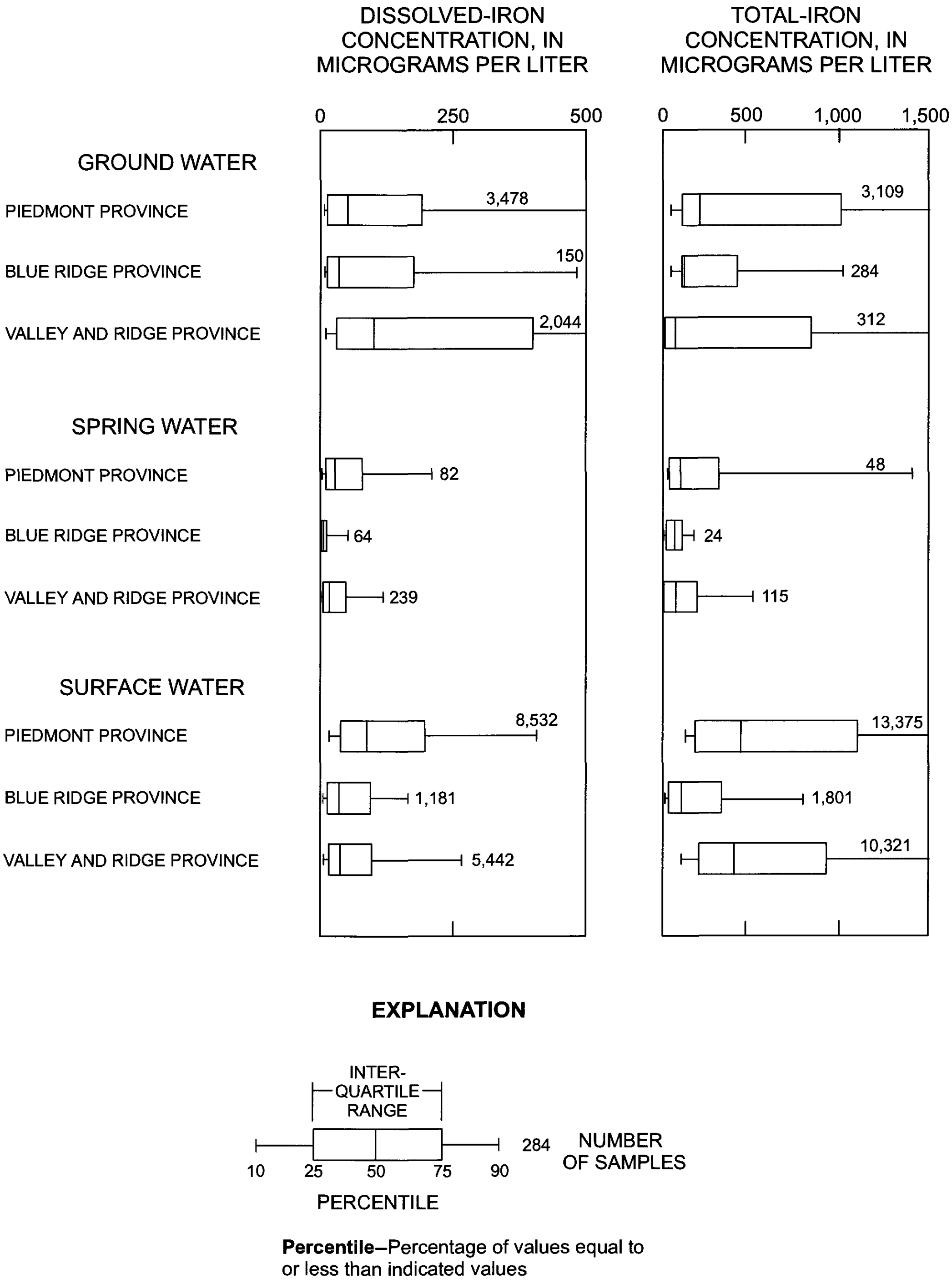


FIGURE 44.—Summaries of dissolved-iron concentration and total-iron concentration, by type of site and physiographic province.

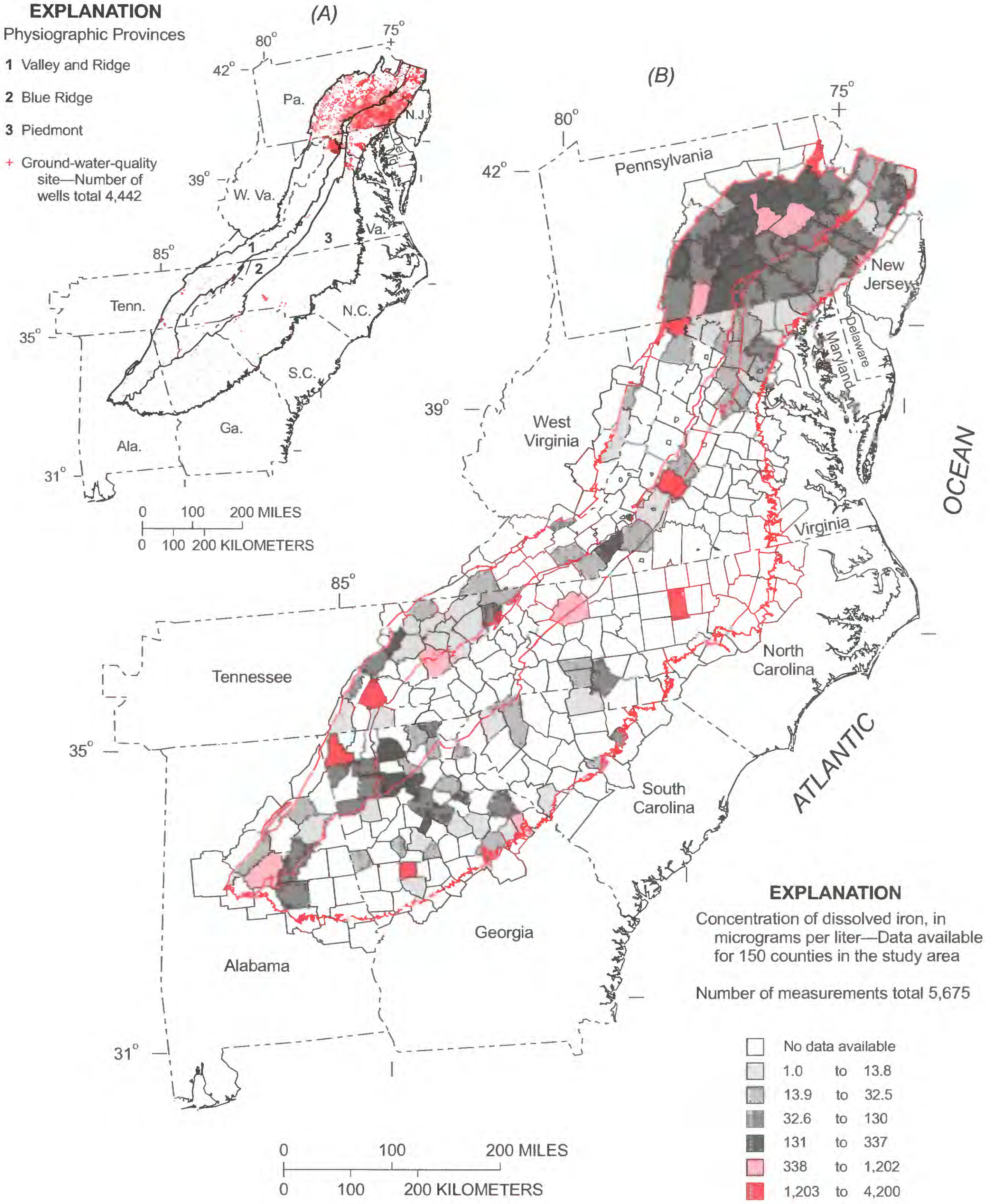


FIGURE 45.—Location of wells in study area where dissolved-iron concentration is known *(A)* and geographic variation of median dissolved-iron concentration in ground water, by county *(B)*.

cent of the wells are in four northern states, 11 percent are in four central states, and the remainder are in three southern states (fig. 45).

The IQR for dissolved-iron concentration in spring water is 7 to 50 µg / L. Median concentration in spring water is about one-fourth that in ground water, an indication that spring water is not generally in contact with iron-rich rock. Dissolved-iron concentrations in 3 percent of spring-water samples exceed the SMCL. Median concentrations in spring water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces are 8, 20, and 30 µg / L, respectively. For spring water, differences in median dissolved-iron concentrations in the Blue Ridge Province and in the other two provinces are significant; whereas, the difference between median concentrations for the Piedmont and Valley and Ridge Provinces is not significant. The regional patterns for spring water and ground water are different: springs in the Piedmont, which are typically acidic, also have the highest dissolved-iron concentrations and greatest variability of concentration (fig. 44).

The IQR for dissolved-iron concentration in surface water is 30 to 160 µg / L. Median concentrations in surface water and ground water are about equal; however, concentrations in only 12 percent of surface-water samples exceed the SMCL. Median concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces are 40, 40, and 90 µg / L, respectively. For surface water, differences in median dissolved-iron concentrations in the Piedmont Province and in the other two provinces are significant; median concentrations for the Blue Ridge and the Valley and Ridge Provinces are equal. The regional patterns for surface water and ground water are different: the highest dissolved-iron concentrations and greatest variability of concentration in surface water are in the Piedmont Province (fig. 44). In the Blue Ridge, median concentrations for surface water and ground water are about equal and generally are the lowest dissolved-iron concentrations found in the study area (fig. 44). The higher percentiles indicate that dissolved-iron data for ground water and surface water are skewed differently; surface-water samples include a smaller fraction of extreme concentrations than ground-water samples (table 5).

TOTAL-IRON CONCENTRATIONS

Total-iron concentrations in ground water in the study area are generally higher than those of dissolved iron. The interquartile range (IQR) for total-iron concentration is 84 to 900 µg / L; median total-iron concentration is more than twice that of dissolved iron. Total-iron concentrations in 38 percent of ground-water samples exceed the SMCL. Data for total-iron concentration in ground water are highly skewed at the upper end of the range and include a complex pattern of regional variations as a function of concentration. Differences in median concentrations in ground water in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces (70, 100, and 200 µg / L, respectively) are significant (fig. 44). The largest total-iron concentrations in ground water are in the Piedmont Province; the smallest total-iron concentrations, however, are not consistent over the range of data (table 5).

The IQR for total-iron concentration in spring water is 40 to 200 µg / L. Median concentration in spring water is about one-half that in ground water. In 19 percent of spring-water samples, total-iron concentrations exceed the SMCL. Differences in median concentrations in spring water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (75, 90, and 110 µg / L, respectively) are not significant. The regional patterns for spring water and ground water are similar: the highest total-iron concentrations and greatest variability of concentration are in the Piedmont Province (fig. 44).

The IQR for total-iron concentration in surface water is 170 to 980 µg / L. Median concentration in surface water is more than twice that in ground water. Total-iron concentrations in 58 percent of surface-water samples in the study area exceed the SMCL. Regional median concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces are 100, 400, and 440 µg / L, respectively. For surface water, differences in median total-iron concentrations in the Blue Ridge Province and in the other two provinces are significant; however, the difference between median concentrations for the Piedmont and the Valley and Ridge Provinces is not significant. The regional patterns for surface water and ground water are similar: the highest total-iron concentrations and greatest variability of concentration are in the Piedmont Province (fig. 44).

MANGANESE

Manganese is the eighth most abundant metal in surface rock and is about one-fiftieth as abundant as iron in the Earth's crust. Minerals found in many igneous and metamorphic rocks—primarily silicates, such as basalt and olivine—and in some sedimentary rocks—such as calcite and dolomite—contain manganese in significant amounts. Like iron, manganese is an essential element in the metabolism of plants and animals, but natural concentrations in water are mostly low. If present in water supplies at concentrations greater than 50 µg / L, dissolved manganese is an undesirable impurity because a black oxide stain is deposited on plumbing fixtures and fabrics.

The aqueous geochemistry of manganese is more complex than that of iron because manganese ions are found in three oxidation states (+2, +3, and +4), and manganese forms a variety of mixed-valence oxides (Garrels and Christ, 1965). For manganese dissolved in ground water, the manganous ion (Mn^{+2}) is the predominant form. This versatile ion can substitute for iron, magnesium, or calcium in many common minerals.

DISSOLVED-MANGANESE CONCENTRATIONS

The interquartile range (IQR) for dissolved-manganese concentration in ground water is 10 to 170 µg / L (table 5). Dissolved-manganese concentrations in 43 percent of ground-water samples exceed the SMCL (50 µg / L, U.S. Environmental Protection Agency, 1995). The regional IQR's overlap, but differences in median concentrations in ground water in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (17, 38, and 40 µg / L, respectively) are significant (fig. 46). The difference between medians for the Piedmont and the Valley and Ridge Provinces, however, is within the analytical uncertainty in the determination of manganese concentration. The ground-water data for dissolved-manganese concentrations are highly skewed at the upper end of the range. The highest concentrations and greatest variability of concentration are in the Valley and Ridge Province (fig. 46). The geographic pattern of median dissolved-manganese concentrations in ground water by county (fig. 47) indicates that most of the highest county concentrations are in the Valley and Ridge Province, but a few high concentrations are also in the Piedmont and the Blue Ridge Provinces. The geographical distribution of wells sampled for manganese concentration is skewed in the northern end of the area: 87 percent of the wells are in four northern states, 10.5 percent are in four central states, and the remainder are in three southern states (fig. 47).

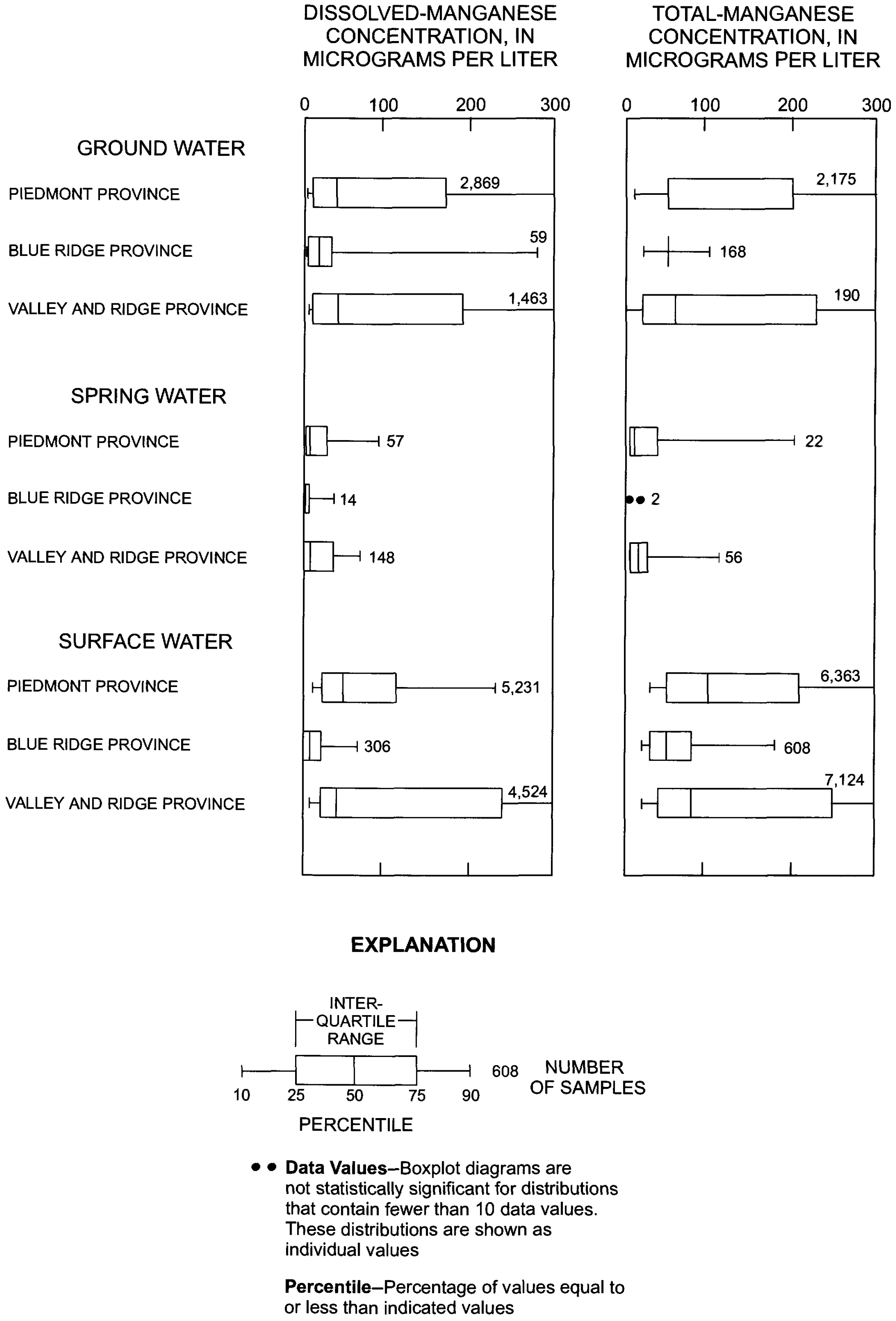
The IQR for dissolved-manganese concentration in spring water is 2 to 30 µg / L. Median concentration in spring water is about one-fourth that in ground water, an indication that dissolved manganese is a minor constituent of spring water in the study area. Dissolved-manganese concentrations in 1 percent of spring-water samples exceed the SMCL. Differences in median concentrations for springs in the Blue Ridge, the Piedmont, and the Valley and Ridge Provinces (2.5, 8, and 11 µg / L, respectively) are not significant (fig. 46). The regional patterns for spring water and ground water are similar, except that spring-water concentrations are lower. For spring water, the highest dissolved-manganese concentrations and greatest variability of concentration are in the Valley and Ridge Province (fig. 46).

The IQR for dissolved-manganese concentration in surface water is 20 to 130 µg / L. Median dissolved-manganese concentrations in surface water and ground water are equal; concentrations in 44 percent of surface-water samples exceed the SMCL. Differences in median concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (11, 40, and 46 µg / L, respectively) are significant (fig. 46). The difference between medians for the Piedmont and the Valley and Ridge Provinces, however, is within the analytical uncertainty in the determination of manganese concentration. The regional patterns for surface water and ground water are similar: the highest dissolved-manganese concentrations and greatest variability of concentration are in the Valley and Ridge Province (fig. 46).

TOTAL-MANGANESE CONCENTRATIONS

Total-manganese concentrations in ground water in the study area are generally higher than those of dissolved manganese. The interquartile range (IQR) for total-manganese concentration in ground water is 50 to 200 µg / L; however, median concentration of total manganese is only slightly higher than that of dissolved manganese. The ground-water data for total-manganese concentration are highly skewed at the upper end of the range. At the 95th percentile, total-manganese concentrations are about twice those of dissolved manganese. Total-manganese concentrations in 47 percent of ground-water samples exceed the SMCL. Median concentrations in ground water in the Piedmont, the Blue Ridge, and the Valley and Ridge Provinces are 50, 50, and 80 µg / L, respectively. Differences in median concentrations in ground water in the Valley and Ridge Province and in the other two provinces are not significant (fig. 46). The highest total-manganese concentrations in ground water are in the Piedmont Province; the lowest total-manganese concentrations, however, are not consistent over the range of data. This trend is similar to that for total-iron concentrations in ground water (table 5).

The IQR for total-manganese concentration in spring water is 10 to 30 µg / L. Median concentration in spring water is about one-half that in ground water. In 15 percent of spring-water samples, total-manganese concentrations exceed the SMCL. Differences in median concentrations in spring water in the Piedmont, the Blue Ridge, and the Valley and Ridge Provinces (15, 15, and 20 µg / L, respectively) are not significant. The regional patterns for spring water and ground water are



● ● **Data Values**–Boxplot diagrams are not statistically significant for distributions that contain fewer than 10 data values. These distributions are shown as individual values

Percentile–Percentage of values equal to or less than indicated values

FIGURE 46.—Summaries of dissolved-manganese concentration and total-manganese concentration, by type of site and physiographic province.

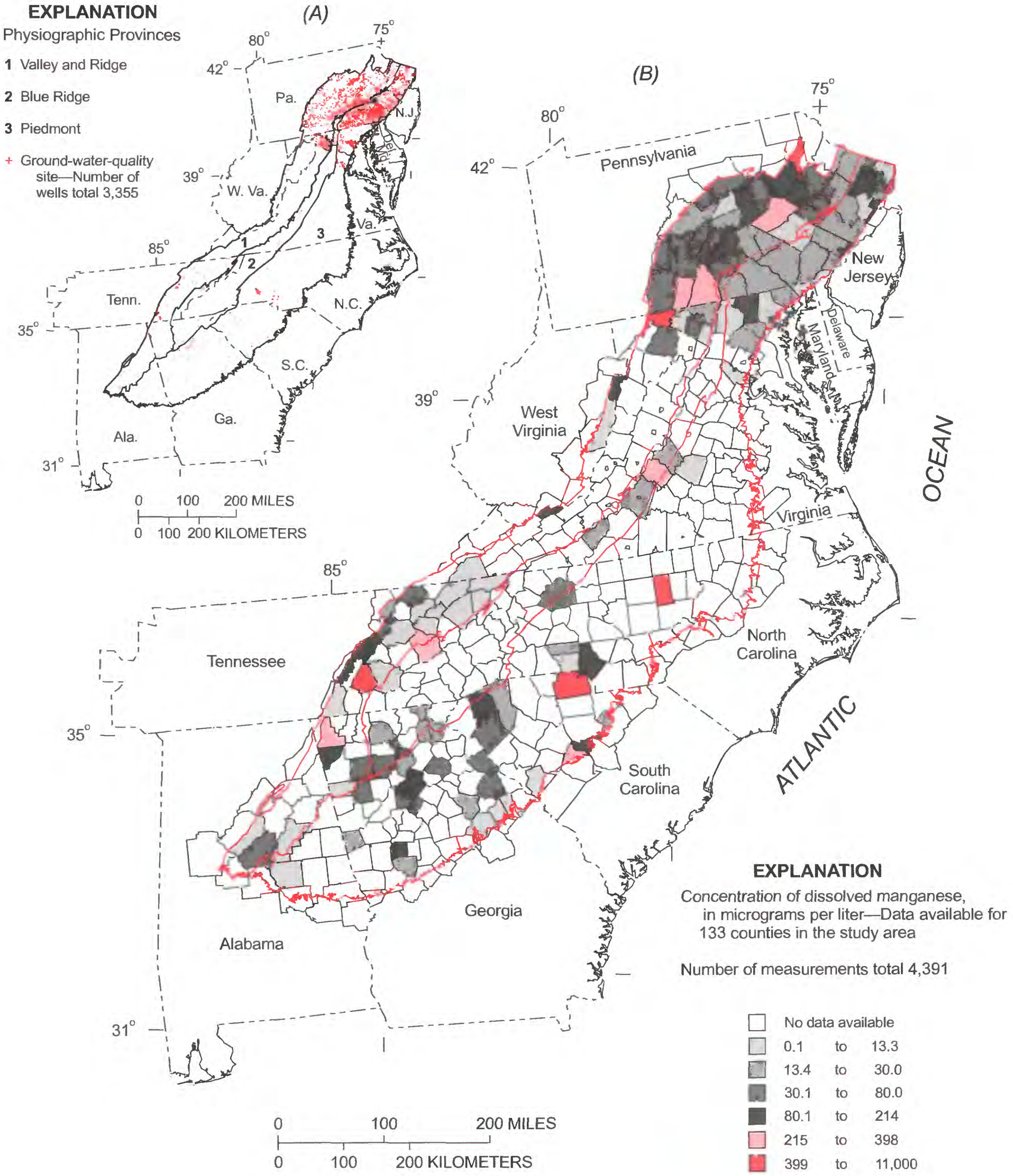


FIGURE 47.—Location of wells in study area where dissolved-manganese concentration is known *(A)*, and geographic variation of median dissolved-manganese concentration in ground water, by county *(B)*.

similar, except that spring-water concentrations are lower. The highest total-manganese concentrations and greatest variability of concentration are in the Valley and Ridge Province (fig. 46).

The IQR for total-manganese concentration in surface water is 50 to 220 µg / L. Median concentration in surface water is about twice that in ground water. Total-manganese concentrations in 66 percent of surface-water samples exceed the SMCL. Differences in median concentrations in surface water in the Blue Ridge, the Valley and Ridge, and the Piedmont Provinces (50, 80, and 100 µg / L, respectively) are significant. The regional patterns for surface water and ground water are different: for surface water, the highest total-manganese concentrations and greatest variability of concentration are in the Valley and Ridge Province (fig. 46).

VARIATIONS IN CHEMICAL RATIOS

Systematic variations in the relative concentrations of major ions can be used to identify various minerals from which these ions are derived. If a mineral dissolves without chemical reaction, the water acquires the ratio of ionic constituents of the mineral; but because most natural waters contain more than one mineral in solution, binary ratios among the major ions often exhibit a complex nonlinear pattern. Ion ratios are unitless numbers, but ion concentrations used in the calculation of these ratios are usually expressed in milliequivalents per liter (meq / L) so that ratios can be related to the chemical formulas of dissolved minerals. Ion concentration in milliequivalents per liter is obtained by multiplying absolute concentration in milligrams per liter by the reciprocal of the combining weight. The combining weight of an ion is the ratio of the formula weight to the ionic charge. A list of conversion factors for major ions is given in the conversion-factors table at the beginning of this report.

For freshwater, the major cations are calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^{+}), and potassium (K^{+}), and the major anions are bicarbonate (HCO_3^{-}), carbonate ($CO_3^{=}$), sulfate ($SO_4^{=}$), and chloride (Cl^{-}). For most water in the APRASA study area, concentrations of potassium and carbonate are small compared with concentrations of other major ions; potassium and carbonate, therefore, are not considered independently in the following discussion. Milliequivalents of potassium are combined with milliequivalents of sodium, and milliequivalents of carbonate are combined with milliequivalents of bicarbonate, as is commonly done on trilinear diagrams (see "Variations in Chemical Composition of Water, by Type of Site and Physiographic Province").

MAJOR-ION RATIOS OF DISSOLVED MINERALS

Although there are no fixed rules for the selection of the most significant ratios among major ions, the most common mineral species containing these ions are calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), gypsum ($CaSO_4$), and halite ($NaCl$). The magnesium-to-calcium ratio is useful in identifying water from limestone and dolostone terranes, the sulfate-to-calcium ratio is useful in detecting gypsum, and the sodium-to-chloride ratio is useful in tracing encroachment of marine water in an aquifer. LOWESS trends for these ratios in different waters in the study area are shown in figures 48 to 50.

MAGNESIUM-TO-CALCIUM RATIO

Calcium carbonate (from calcite) is the most common dissolved mineral in water in the study area, and magnesium carbonate (from dolomite) is also present in many samples. The ratio of magnesium to calcium ranges from zero for dolomite-free water to unity for water derived entirely from dissolved dolomite. Ratios greater than unity are comparatively rare and are possibly due to additional sources of dissolved magnesium. Curved lines for the LOWESS relation between magnesium and calcium concentrations in milliequivalents per liter (fig. 48) indicate that the magnesium-to-calcium ratio is not constant, but varies by region and type of site and with increasing concentration of calcium. For all water in the Valley and Ridge Province and for spring water in the Piedmont Province, the general shape and position of the LOWESS curves are similar. At low concentrations, the ratio is approximately 1:2, which indicates roughly equal proportions of calcite and dolomite. At higher calcium concentrations, the concentration of magnesium rapidly approaches a limit near 1.3 meq / L. Beyond this point, there is no relation between the concentrations of magnesium and calcium. This pattern indicates that saturation with respect to dolomite may effectively limit magnesium concentrations in these waters. For all water in the Blue Ridge Province and for ground water and surface water in the Piedmont Province, the magnesium-to-calcium ratio ranges from approximately 1:2 to 1:4, and there is no limiting value for the concentration of magnesium.

SULFATE-TO-CALCIUM RATIO

Gypsum is present in many parts of the study area. The ratio of sulfate to calcium ranges from zero for sulfate-free water to unity for water derived entirely from the dissolution of gypsum. In freshwater, ratios greater than unity are rare and generally indicate supersaturation with respect to gypsum. High ratios indicate additional sources of dissolved sulfate, such as brine.

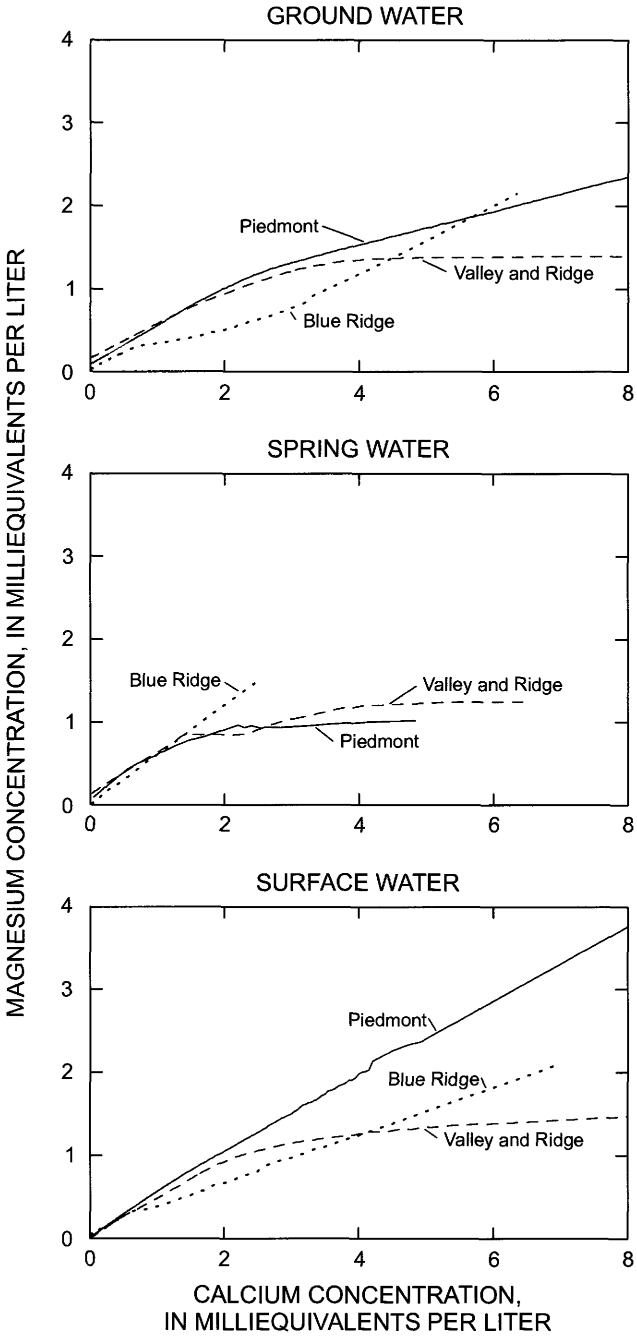


FIGURE 48.—Variation of magnesium concentration as a function of calcium concentration, by type of site and physiographic province.

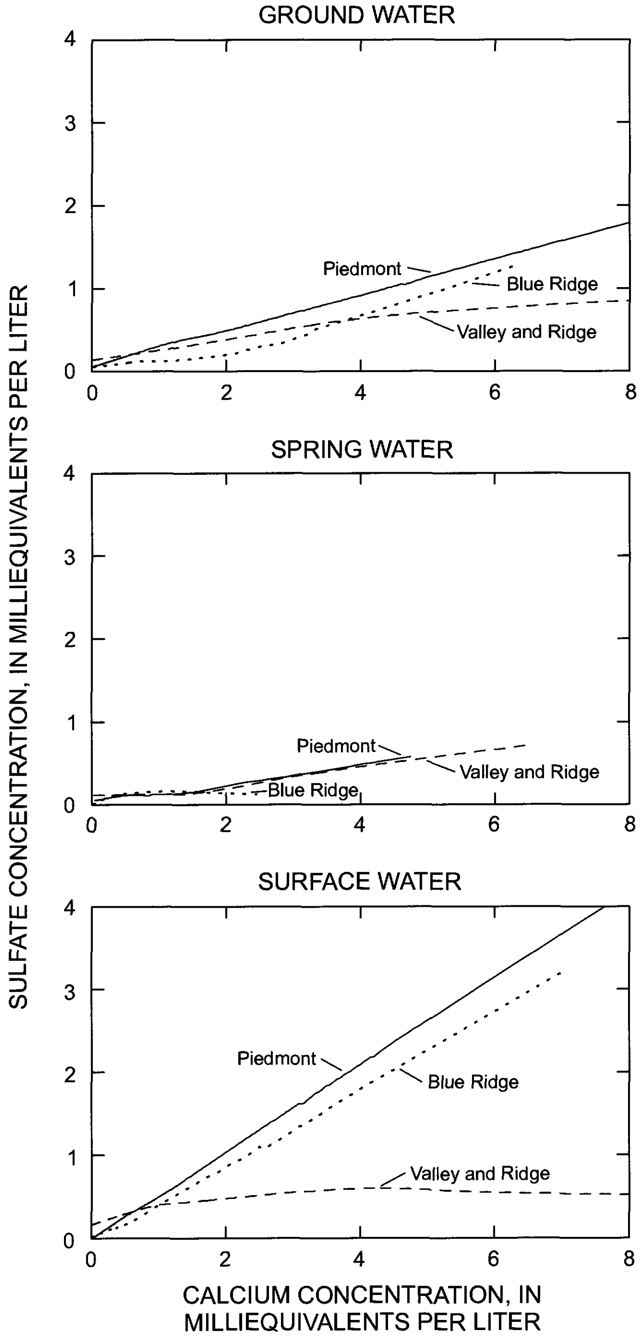


FIGURE 49.—Variation of sulfate concentration as a function of calcium concentration, by type of site and physiographic province.

Curved lines for the LOWESS relation between sulfate and calcium concentrations in milliequivalents per liter (fig. 49) show that the sulfate-to-calcium ratio varies by region and type of site and with increasing concentration of calcium. The general shape and the position of these curves are similar to the corresponding curves in figure 48, although regional variations in the sulfate-to-calcium ratio are not as well defined. This weaker relation indicates competing chemical equilibria involving the calcium ion, possibly between calcite, dolomite, and gypsum. The upward slope of the curves also indicates that gypsum is widespread in the study area.

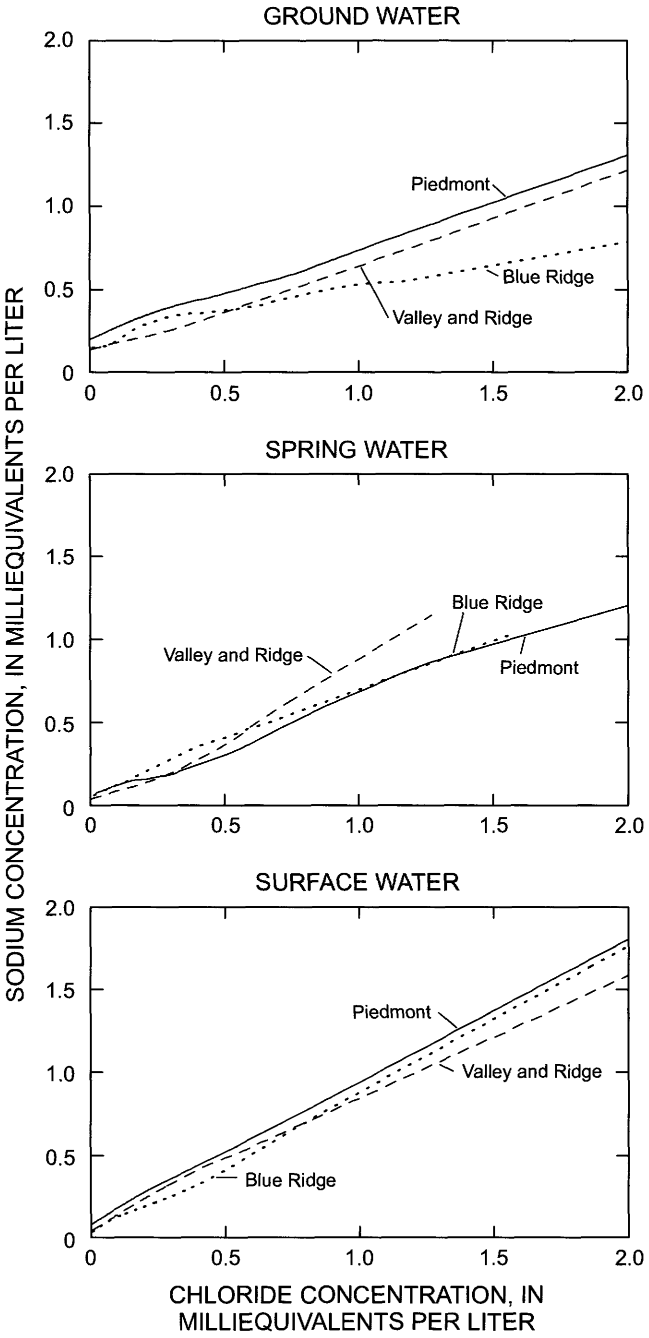


FIGURE 50.—Variation of sodium concentration as a function of chloride concentration, by type of site and physiographic province.

SODIUM-TO-CHLORIDE RATIO

Sodium and chloride ions are common in water in some parts of the study area. The ratio of sodium to chloride in milliequivalents per liter can indicate whether the source of these ions is the highly soluble mineral halite or whether these ions originated from independent sources and subsequently mixed. Ratios that are near unity indicate a common origin. For surface water in the study area and spring water in the Valley and Ridge Province, the ratio of sodium to chloride is near unity and a common source for these ions is likely (fig. 50). For ground water in the study area and spring water in the Piedmont and the Blue Ridge Provinces, however, the ratio is generally less than unity. For ground water in the Blue Ridge Province, the weak relation indicates that sodium and chloride ions probably originate from independent sources.

RELATIVE ABUNDANCE OF MAJOR IONS

The relative abundance of an ion is the ratio of its concentration in milliequivalents per liter to total concentration of all ions of like charge (cations or anions). Ion-abundance ratios are commonly expressed in percent. Variations in relative abundances of major ions indicate changes in chemical composition of water and are clues to the dominant minerals in solution. The relative abundance of individual ions can range from near zero, for low concentrations, to near 100 percent, for high concentrations. Variations in relative abundance of individual ions with changes in total ionic concentration generally mean that ion concentrations are controlled by more than one chemical equilibrium. Distributions of relative-abundance ratios of calcium, magnesium, and sodium to total cations are shown in figure 51 by physiographic province and type of site. LOWESS trends for these cations are shown in figures 52 and 53.

CATIONS

Calcium is the dominant cation in most water in the study area. Median abundances of calcium range from 40 to 66 percent; a typical abundance in ground water is 50 percent (fig. 51). In the Valley and Ridge Province, the median calcium-to-cations ratio exceeds 56 percent for the three types of sites. Differences in median abundances of calcium in water in the Valley and Ridge Province and water in the other two provinces are significant; however, differences in median abundances of calcium in water in the Piedmont and the Blue Ridge Provinces are not significant.

Magnesium is commonly the second most abundant cation in water in the study area; however, samples containing a dominant fraction of magnesium are rare. Median abundances of magnesium range from 20 to 31 percent; a typical abundance in ground water is 26 percent (fig. 51). Variations in the relative abundance of magnesium are much smaller than those for calcium, an indication that magnesium concentration may be less sensitive than calcium concentration to competing

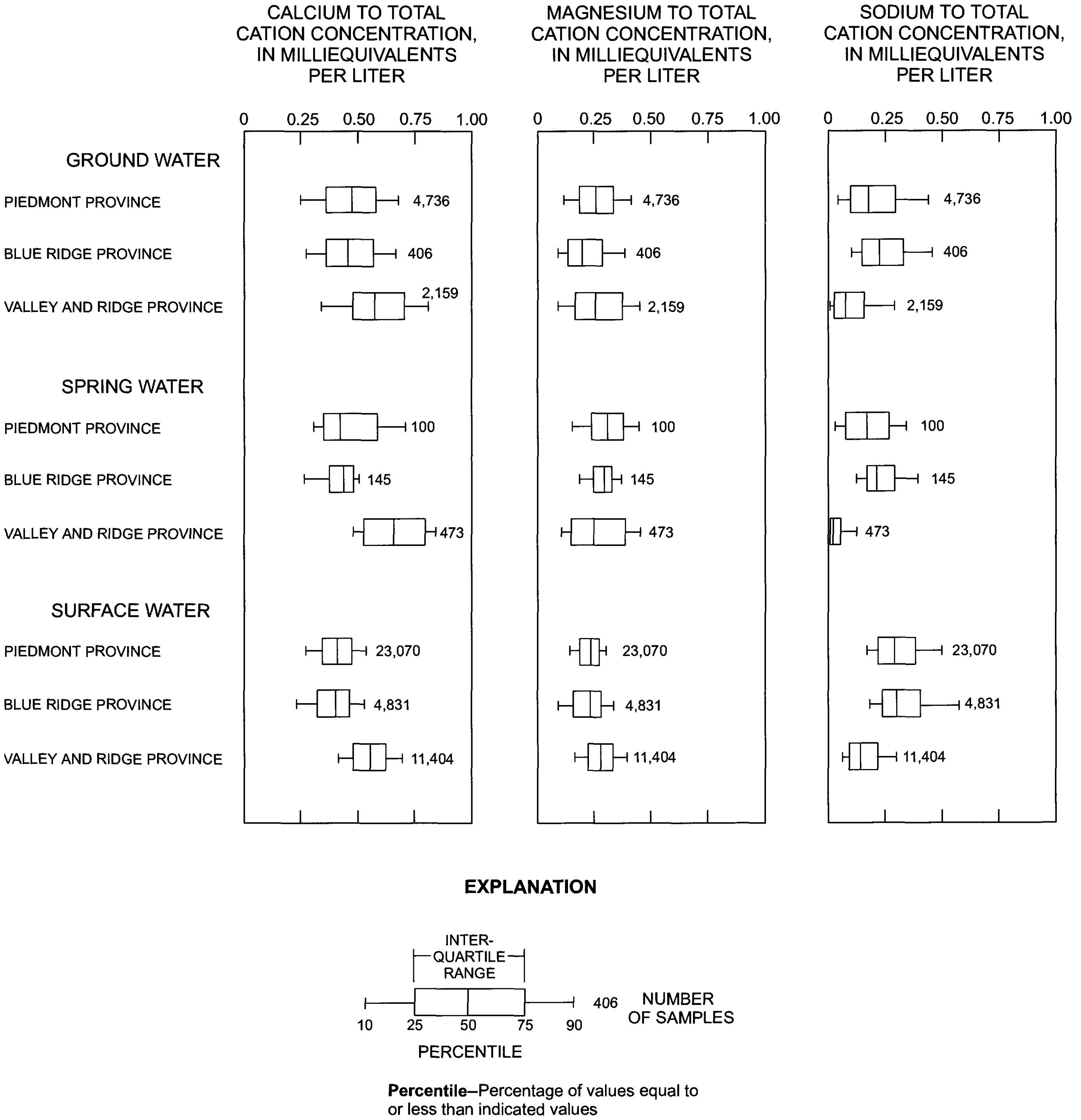


FIGURE 51.—Summaries of the relative abundances of calcium, magnesium, and sodium ions, by type of site and physiographic province.

chemical-mineral equilibria. In the crystalline rocks of the Blue Ridge Province, the median abundance of magnesium in ground water is significantly lower than it is elsewhere in the study area; differences in median abundances of magnesium in ground water in the other two provinces are not significant. Regional differences in median abundances of magnesium in spring water are also not significant. For surface water, however, these differences are significant: the lowest abundances of magnesium in surface water are in the Piedmont Province and the highest abundances are in the Valley and Ridge Province.

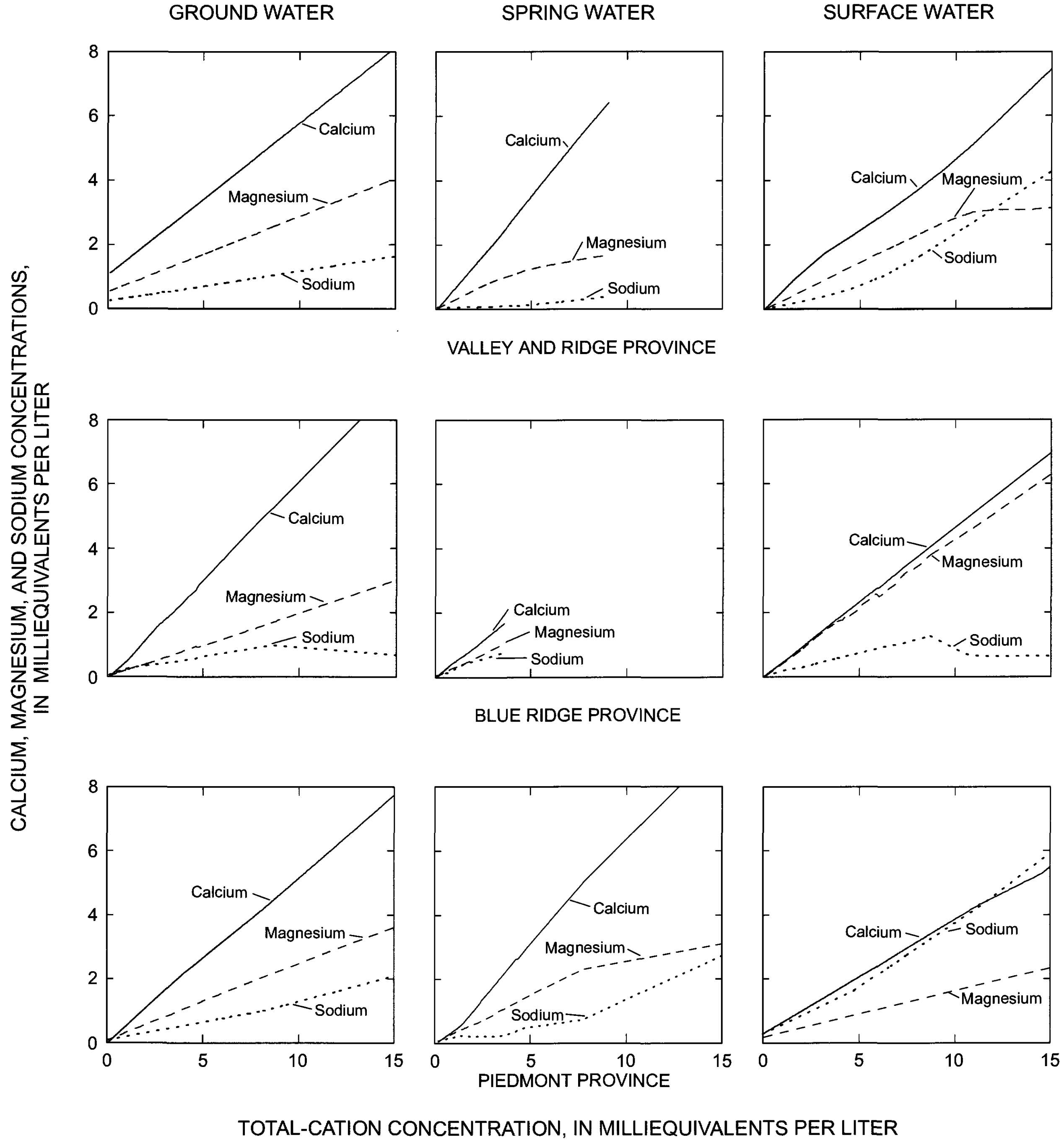


FIGURE 52.—Variation of ionic concentrations of calcium, magnesium, and sodium as a function of total-cation concentration, by type of site and physiographic province.

Sodium is commonly the third most abundant cation in water in the study area, although some samples contain a dominant fraction of sodium. Median abundances of sodium range from 3 to 29 percent; a typical abundance in ground water is 16 percent (fig. 51). For the three types of sites, regional differences in median abundances of sodium are significant, and the three patterns are similar. Median abundance of sodium is highest in the Blue Ridge Province and lowest in the Valley and Ridge Province; the median for the Piedmont Province is near that for the Blue Ridge Province. The consistency of regional patterns indicates that sodium-rich rocks in the Blue Ridge and the Piedmont Provinces strongly affect water quality.

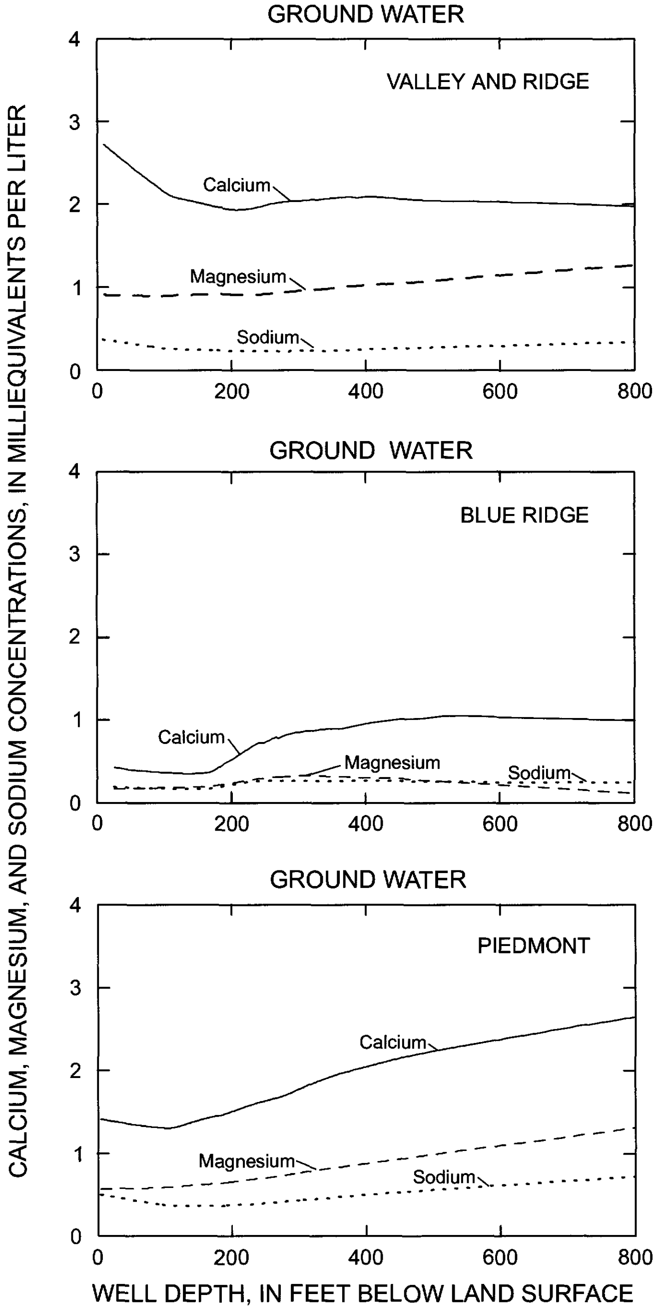


FIGURE 53.—Variation of ionic concentrations of calcium, magnesium, and sodium in ground water as a function of well depth, by physiographic province.

For most water in the study area, the order of abundance of major cations is calcium>magnesium>sodium (fig. 51). This relation is also indicated by the positions of the three LOWESS curves in figure 52. For ground water and spring water, this order applies at all concentrations; for surface water, however, the fraction of sodium increases at high concentrations of cations. Calcium remains the most abundant cation in surface water in the Valley and Ridge and the Blue Ridge Provinces, but in the Piedmont Province, sodium becomes dominant at high concentrations of cations.

Regional variations in relative concentrations of major cations in ground water as a function of well depth indicate that calcium concentrations change, whereas magnesium and sodium concentrations remain constant (fig. 53). In the Valley and Ridge Province, the concentration of calcium in ground water as a function of well depth decreases rapidly to depths near 200 ft, then remains constant. In the Blue Ridge Province, calcium concentrations increase at depths between 160 ft and 250 ft, then remain constant. In the Piedmont Province, calcium concentrations increase continually at depths greater than 150 ft. For each of the regional curves, the principal inflection point is near median well depth.

ANIONS

Bicarbonate is the dominant anion in most water in the study area. Median abundances of bicarbonate range from 54 to 87 percent; a typical abundance in ground water is 70 percent (fig. 54). In the Valley and Ridge Province, the median bicarbonate-to-anions ratio exceeds 62 percent for the three types of sites. The median abundance of bicarbonate in ground water in the Piedmont Province is significantly lower than it is elsewhere in the study area. Differences in median abundances of bicarbonate in ground water in the other two provinces are not significant; for spring water and surface water, however, the regional differences are significant. For the three types of sites, the highest abundances of bicarbonate in water are in the Valley and Ridge Province and the lowest are in the Piedmont Province. The LOWESS trends for anions are shown in figures 55 and 56.

Sulfate is commonly the second most abundant anion in water in the study area, although some samples contain a dominant fraction of sulfate. Median abundances of sulfate range from 8 to 23 percent; a typical abundance in ground water is 13 percent (fig. 54). The median abundance of sulfate in ground water in the Blue Ridge Province is significantly lower than it is elsewhere in the study area; differences in median abundances of sulfate in ground water in the other two provinces are not significant. For spring water, the median abundance of sulfate in the Piedmont Province is significantly higher than it is elsewhere in the study area; differences in median abundances of sulfate in the other two provinces are not significant. Sulfate is generally more abundant in surface water than in ground water; a typical abundance in surface water is 22

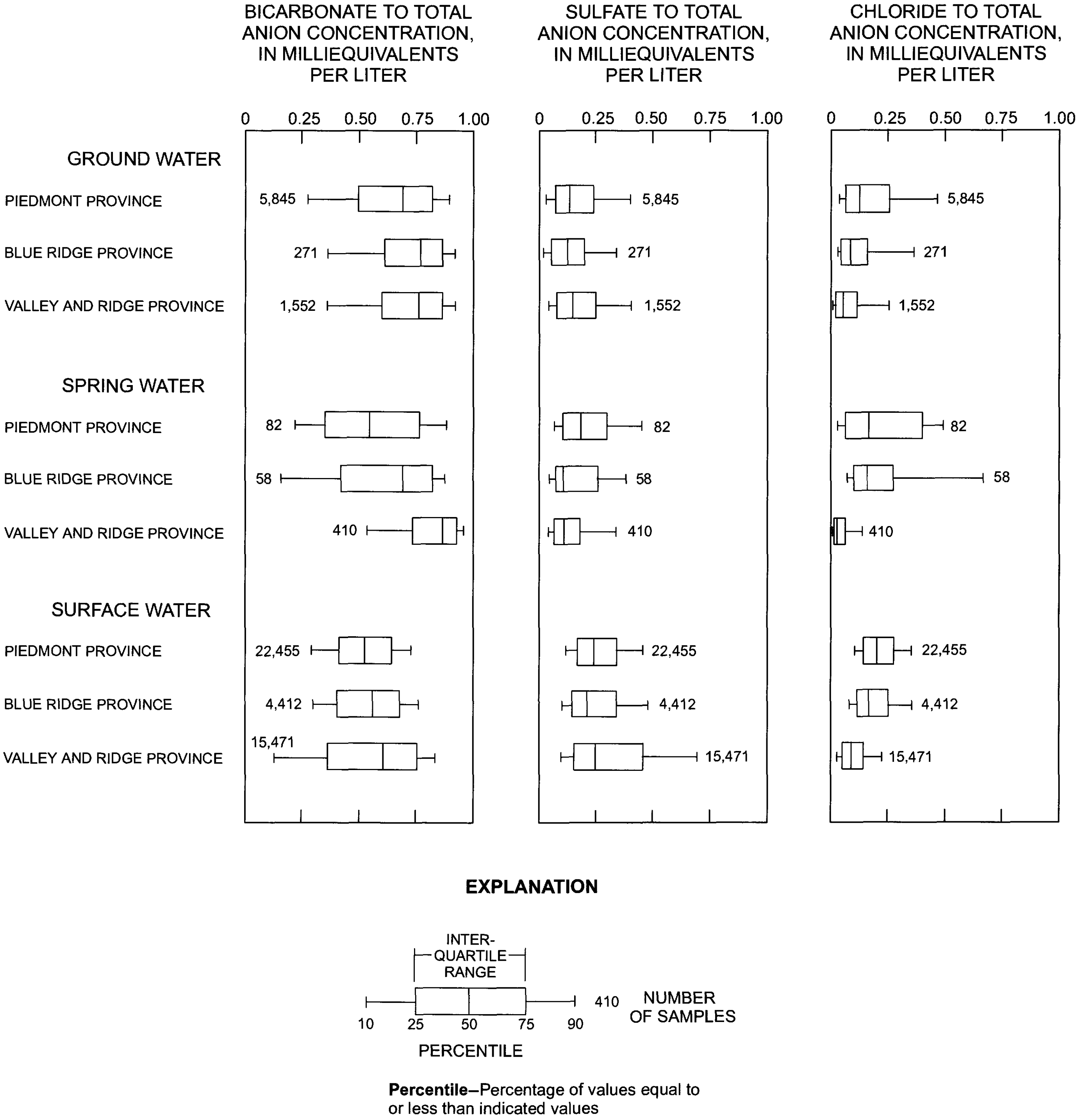


FIGURE 54.—Summaries of the relative abundances of bicarbonate, sulfate, and chloride ions, by type of site and physiographic province.

percent. Regional differences in the abundance of sulfate in surface water are significant: median abundance of sulfate is highest in the Valley and Ridge Province and lowest in the Blue Ridge Province.

Chloride is commonly the third most abundant anion in water in the study area, although some samples contain a dominant fraction of chloride. Median abundances of chloride range from 3 to 20 percent; a typical abundance in ground water is 10 percent (fig. 54). For ground water and surface water, regional differences in median abundances of chloride are significant. For spring water, the median abundance of

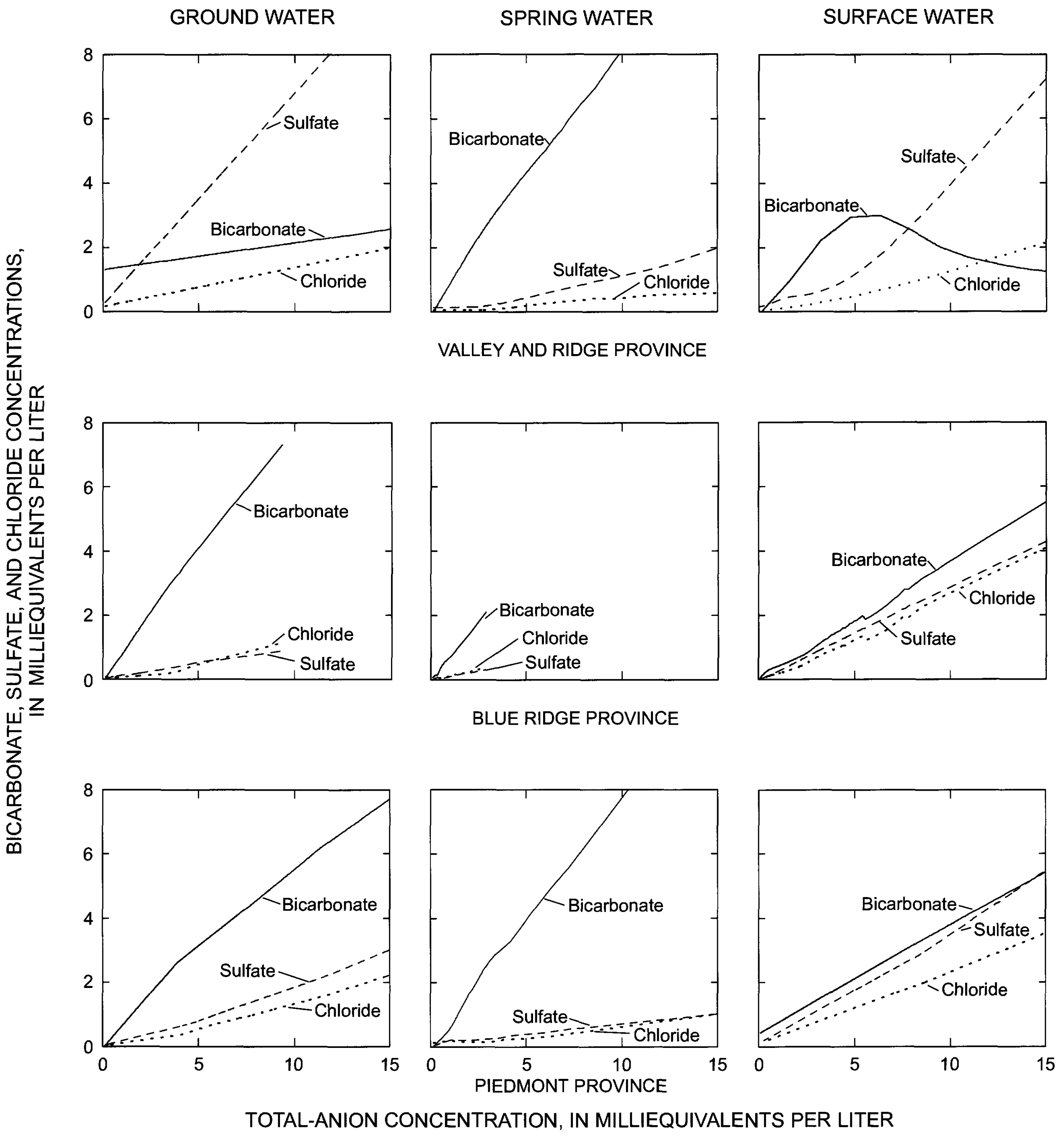


FIGURE 55.—Variation of ionic concentrations of bicarbonate, sulfate, and chloride as a function of total-anion concentration, by type of site and physiographic province.

chloride in the Valley and Ridge Province is significantly lower than it is in the other two provinces; however, differences in median abundances of chloride in the Piedmont and the Blue Ridge Provinces are not significant. The three regional patterns for the abundance of chloride in water are similar: chloride abundances are highest in the Piedmont Province and lowest in the Valley and Ridge Province. The median for the Blue Ridge Province is near that for the Piedmont Province. Regional patterns for chloride abundance are similar to those for sodium (fig. 51), an indication that rocks in the Piedmont and the Blue Ridge Provinces are also a better source of chloride than rocks in the Valley and Ridge Province.

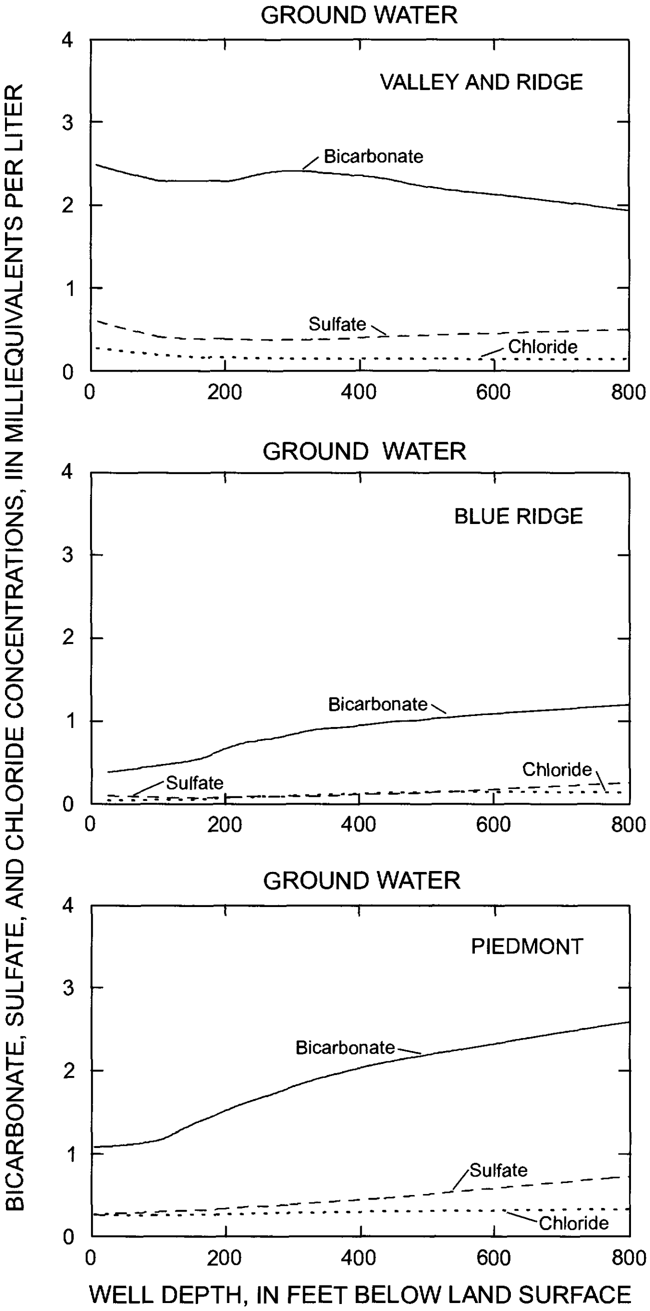


FIGURE 56.—Variation of ionic concentrations of bicarbonate, sulfate, and chloride in ground water as a function of well depth, by physiographic province.

For most water in the study area at anion concentrations less than 2 meq / L, the order of abundance of major anions is bicarbonate>sulfate>chloride (fig. 55). Complex variations in this order can be related to type of site, region, and anion concentration. For ground water in the Piedmont Province, spring water in the Valley and Ridge Province, and surface water in the Blue Ridge Province, this order applies at all anion concentrations (fig. 55). For ground water and spring water in the Blue Ridge Province, bicarbonate is the dominant anion, but chloride and sulfate become equally abundant as anion concentration increases. For ground water and surface water in the Valley and Ridge Province and for surface water in the Piedmont Province, sulfate becomes dominant as anion concentration increases (fig. 55).

Regional variations in relative concentrations of major anions in ground water as a function of well depth indicate that anion concentrations are generally insensitive to depth, except for bicarbonate concentrations in the Piedmont and Blue Ridge Provinces, where these concentrations increase continually at depths greater than 150 ft (fig. 56). These variations of bicarbonate concentration are similar to those for calcium (fig. 53) and indicate a possible relation between the two ions.

RATIO OF DISSOLVED SILICA TO DISSOLVED SOLIDS

Most natural waters contain dissolved constituents that are not ionic. Common igneous and metamorphic rocks contain polysilicate minerals that weather to silica (SiO_2), a neutral compound that is sparingly soluble in mildly alkaline water. The relation between dissolved-silica concentration and dissolved-solids concentration is an aid in identifying waters containing silicate minerals. Hem (1985) reported that specific types of polysilicate minerals can be indentified by ratios among the major cations.

For water in the study area, variations in the relation between dissolved-silica concentration and dissolved-solids concentration (determined as residue on evaporation at 180°C) are shown in figure 57 by type of site and physiographic province. The relation is strongest in the Blue Ridge and the Piedmont Provinces and virtually nonexistent in the Valley and Ridge Province. For ground water and spring water in the Blue Ridge and the Piedmont Provinces, the relation is linear at low to moderate dissolved-solids concentrations but becomes nonexistent as silica concentrations approach 18 mg / L. Upper limits for silica concentrations in spring water in the Piedmont Province and surface water in the Blue Ridge Province are 13 and 10 mg / L, respectively. The consistent shape of the three curves for the Blue Ridge Province is an indication that chemical composition of water in this region is strongly affected by the weathering of silicate rocks.

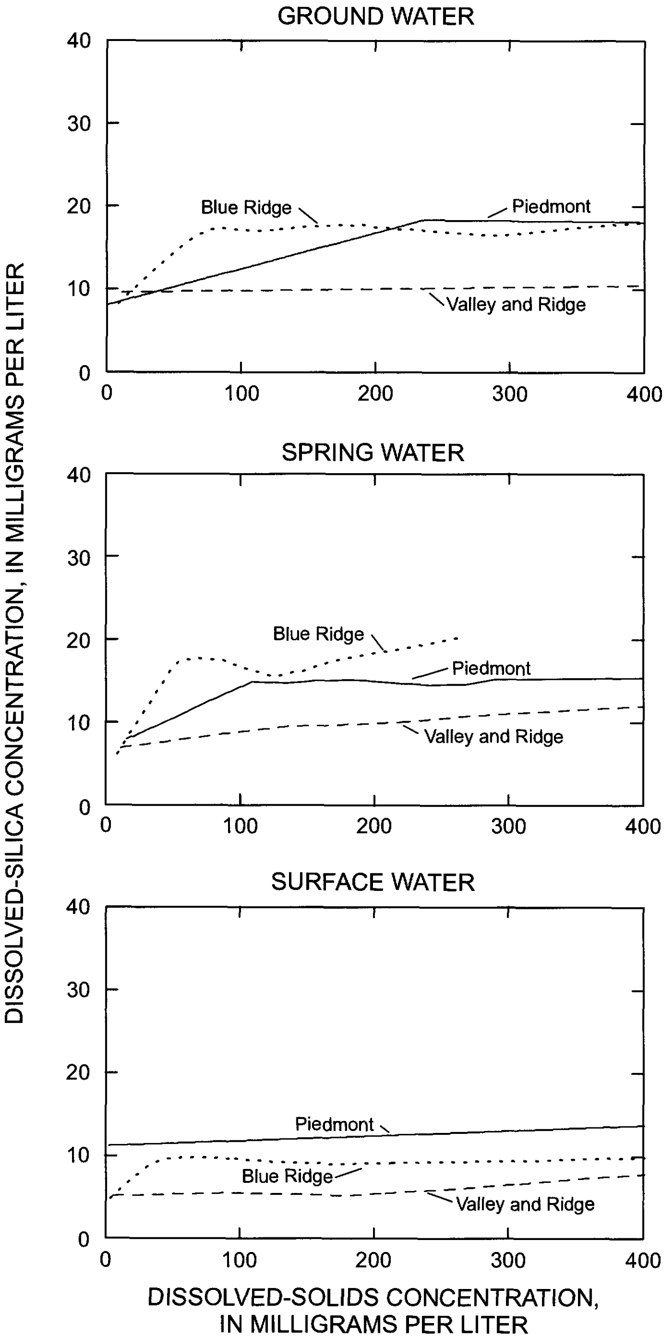


FIGURE 57.—Variation of dissolved-silica concentration as a function of dissolved-solids concentration, by type of site and physiographic province.

VARIATIONS IN CHEMICAL COMPOSITION OF WATER, BY TYPE OF SITE AND PHYSIOGRAPHIC PROVINCE

Systematic variations in the relative concentrations of major ions can also be used to establish similarities and differences in chemical composition among different waters in an area. Classification schemes for grouping waters that are chemically similar extend the concept of binary ratios between pairs of ions to express the proportion of all major ions within the total concentration of solutes (Hem, 1985). A trilinear diagram introduced by Piper (1944) is an aid in determining similarity in chemical composition of water. Piper's diagram contains three distinct fields for showing major-ion constituents: one for cations, another for anions, and a third for showing the resulting chemical type. The diagram requires data for at least three cations (calcium, magnesium, and sodium) and three anions (bicarbonate, sulfate, and chloride). A scheme for grouping chemically similar ions (sodium plus potassium, bicarbonate plus carbonate, chloride plus nitrate) provides for a more comprehensive display of data when needed. Each field of the diagram shows relative abundances of cation and anion constituents in percent of total milliequivalents per liter, and the sum of abundances in each field is always equal to 100 percent. Electrical neutrality is assumed for individual water samples, but the diagram can display the ionic composition of any analysis that contains all the required data. Piper's trilinear diagram is commonly used (1) to display relative abundances of cations and anions in water and to show the resulting chemical composition, (2) to analyze conservative-ion mixtures of water from two or three different compositions, and (3) to show changes in chemical composition of water caused by mineral-water interactions. Detailed discussions of the first two uses are given in Piper (1944), Freeze and Cherry (1979), Matthess (1982), and Briel (1993); the third use was proposed by Hanshaw and Back (1979).

EVOLUTION OF GROUND-WATER QUALITY

Hanshaw and Back (1979) proposed a conceptual model that uses the trilinear diagram to show the evolution of ground-water quality in the development of a carbonate aquifer. This model relates specific changes in water-quality constituents to physical and chemical processes that occur in carbonate aquifers including dissolution and precipitation of minerals, cementation, dolomitization, and mixing of waters having different chemical compositions. For ground water in the Piedmont and Blue Ridge Provinces, the conceptual model was extended to include additional processes that occur in crystalline-rock aquifers that are interbedded with significant amounts of carbonate minerals, primarily water softening by cation exchange on clay sediments (Back, 1966; Chapelle and Knobel, 1983) and the displacement of soft water by mineralized water in a confined aquifer. Seven dominant processes (reaction paths) are shown in figure 58. Reaction path 1 shows the change in chemical composition from seawater to recharge water where rainwater begins to flush saline pore water from the aquifer. Along path 1, dissolved-solids concentration decreases by two to three orders of magnitude. Chemical composition of the water changes from a sodium chloride magnesium sulfate brine to a calcium bicarbonate freshwater. As mildly acidic rainwater percolates through the recharge area, the dominant processes involve selective dissolution and recrystallization of carbonate minerals in the aquifer, which results in cementation and dolomitization (Brahana and others, 1988; Hanshaw and Back, 1979).

Reaction path 2 (fig. 58) shows the reverse change in chemical composition—from freshwater to seawater—where marine water recharges an aquifer close to the coast. Along path 2, dissolved-solids concentration increases, and chemical composition changes from a calcium bicarbonate freshwater to a sodium chloride magnesium sulfate brine. The dominant process along this path involves conservative mixing of pore water and seawater, although selective dissolution of minerals can also occur in the zone of dispersion.

Reaction path 3 (fig. 58) shows an evolutionary change in chemical composition of water that results from downgradient flow in recharge areas to areas of confined flow. Along path 3, dissolved-solids concentration increases slightly, and chemical composition changes from a calcium bicarbonate water to a mixed water containing calcium magnesium bicarbonate and calcium sulfate. The dominant processes along this path involve the dissolution of dolomite and gypsum. Magnesium and sulfate concentrations increase, whereas calcium and bicarbonate concentrations remain constant.

Reaction path 4 (fig. 58) shows the change in chemical composition that results from encroachment of seawater in the deep parts of coastal aquifers. Along path 4, dissolved-solids concentration increases by two orders of magnitude, and chemical composition changes from a calcium magnesium bicarbonate water to a sodium potassium chloride water. Dolomitization is also possible along this path.

Reaction path 5 (fig. 58) shows the change in chemical composition that results from the dissolution of large amounts of evaporite minerals in aquifer sediments. Along path 5, dissolved-solids concentration increases by as much as three orders of magnitude to the concentration of brines. Chemical composition changes from a calcium magnesium bicarbonate water to a sodium and potassium chloride brine.

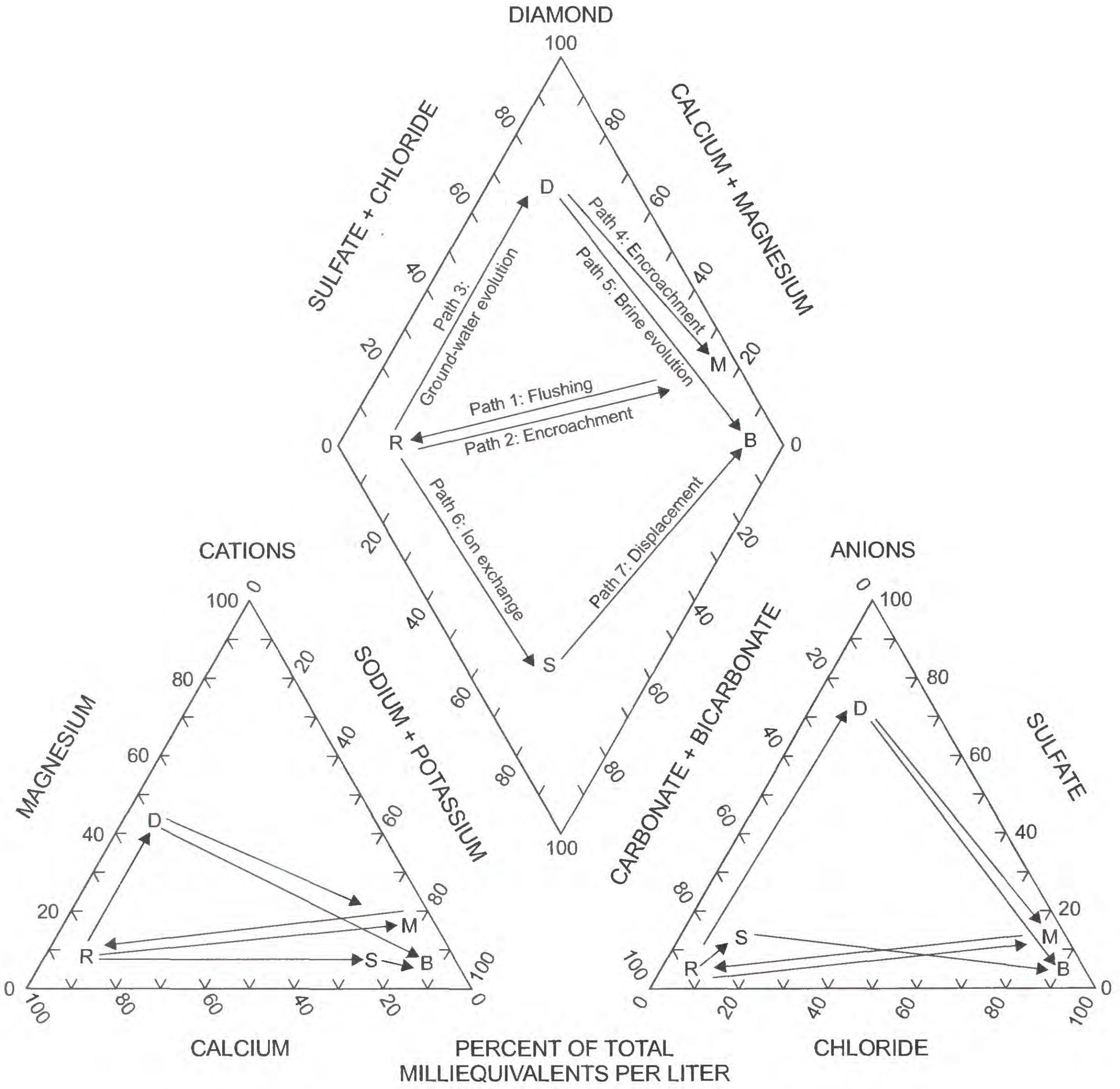
Reaction path 6 (fig. 58) shows the change in chemical composition that results from the replacement of calcium and magnesium ions in ground water by sodium ions loosely bound to clay minerals in the aquifer (called "softening"). Along path 6, dissolved-solids concentration increases slightly, and chemical composition changes from a calcium magnesium bicarbonate (hard) water to a sodium bicarbonate (soft) water.

Reaction path 7 (fig. 58) shows the reverse change in chemical composition from soft water to seawater as the result of displacement by mineralized water in a confined aquifer. Along path 7, dissolved-solids concentration increases by two to three orders of magnitude, and chemical composition changes from a soft freshwater to a brine.

WATER-QUALITY PATTERNS IN THE STUDY AREA

Although there is no theoretical limit to the number of water samples that can be shown on a trilinear diagram, resolution of individual samples becomes difficult as the number of adjacent samples increases. A Piper diagram of all samples in the study area would be unreadable. Even if samples were grouped by type of site and physiographic province, too many points would be clustered together to show systematic variations in chemical composition.

As an alternative to the standard Piper diagram, a shaded-grid trilinear diagram was developed to summarize chemical composition for an unlimited number of water samples. The basis for the shaded-grid trilinear diagram is the relative abundance of samples in each grid cell compared with the total number of samples shown in the diagram. Ranked statistical indexes for the number of samples in each field are a convenient basis for shading individual cells to show relative differences in cell populations across the field. Cells that contain large numbers of samples are filled with the most intense shading, and cells that contain small numbers of samples are filled with light shading; unoccupied cells are not shaded. Because individual sample points are not shown, there is no loss due to inadequate resolution of large numbers of adjacent samples. In fact, as the number of samples per cell increases, the relative error in cell rankings decreases, and the general pattern of chemical compositions becomes increasingly distinct. The dark cells in the diagram aid in the determination of a typical composition (or mode) for a set of samples. Multiple modes in different areas of a field indicate the presence of multiple chemical types, and the pattern of modes may indicate an evolutionary sequence for the set. The method for constructing shaded-grid trilinear diagrams is given in Appendix B.



EXPLANATION

CHEMICAL COMPOSITION	
M	MARINE WATER
R	RECHARGE WATER
S	SOFT WATER
D	DOWNGRADIENT WATER
B	BRINE

REACTION PATHS	DOMINANT PROCESS
PATH 1 M → R	Recrystalization of aragonite to calcite. Selective dissolution of aragonite. Inversion of calcite from high-magnesium to low-magnesium. Cementation
PATH 2 R → M	Simple mixing. Dissolution in dispersion zone
PATH 3 R → D	Dissolution of dolomite and gypsum. Dedolomitization
PATH 4 D → M	Dolomitization
PATH 5 D → B	Dissolution of halite
PATH 6 R → S	Ion exchange on clay sediments. Replacement of calcium and magnesium ions by sodium ions
PATH 7 S → B	Displacement of soft water by mineralized water within a confined aquifer

FIGURE 58.—Reaction paths for evolution of chemical composition of ground water in the study area. (Modified from Hanshaw and Back, 1979.)

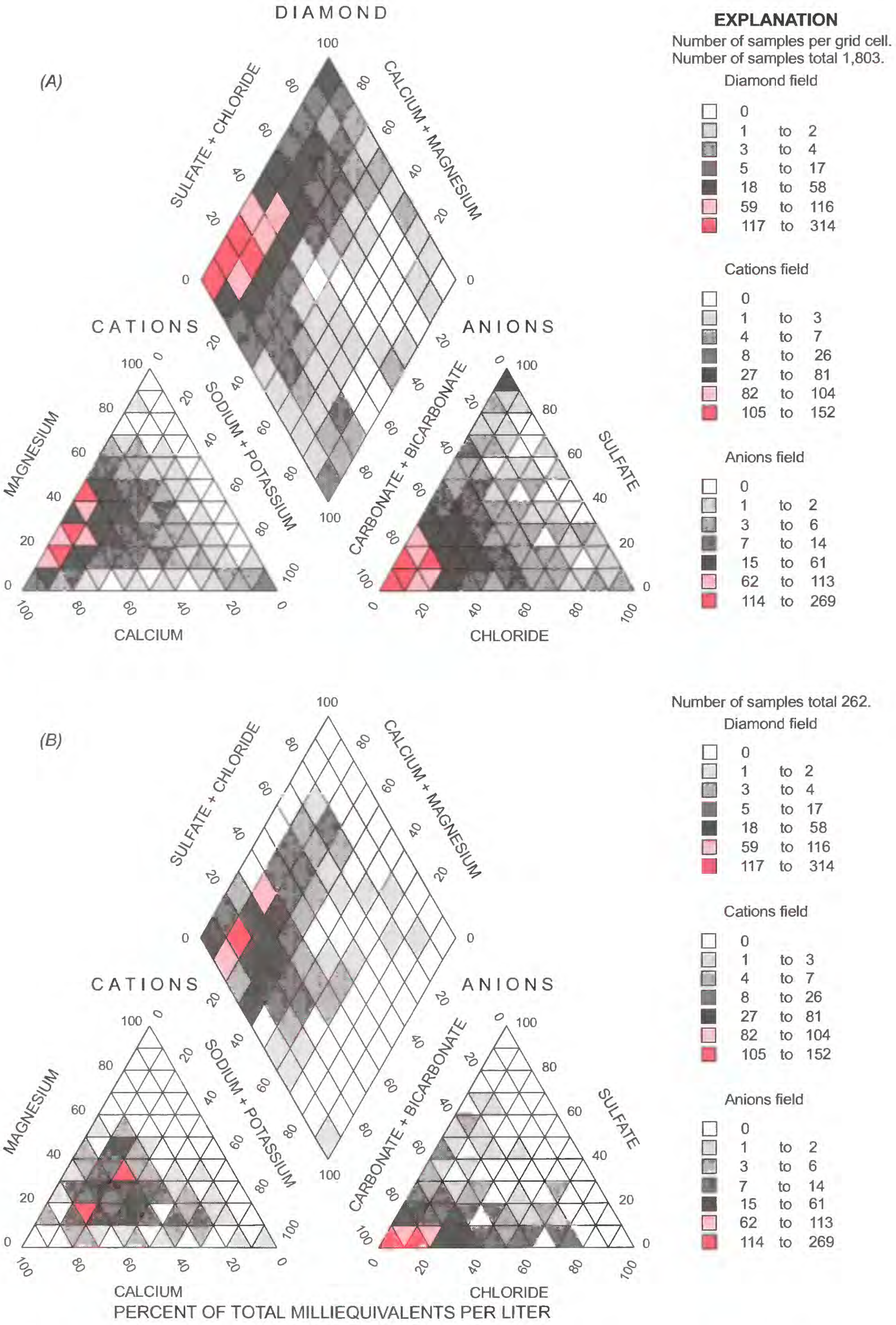


FIGURE 59.—General chemical composition of ground water in (*A*) the Valley and Ridge, (*B*) the Blue Ridge, and *(C)* the Piedmont Provinces.

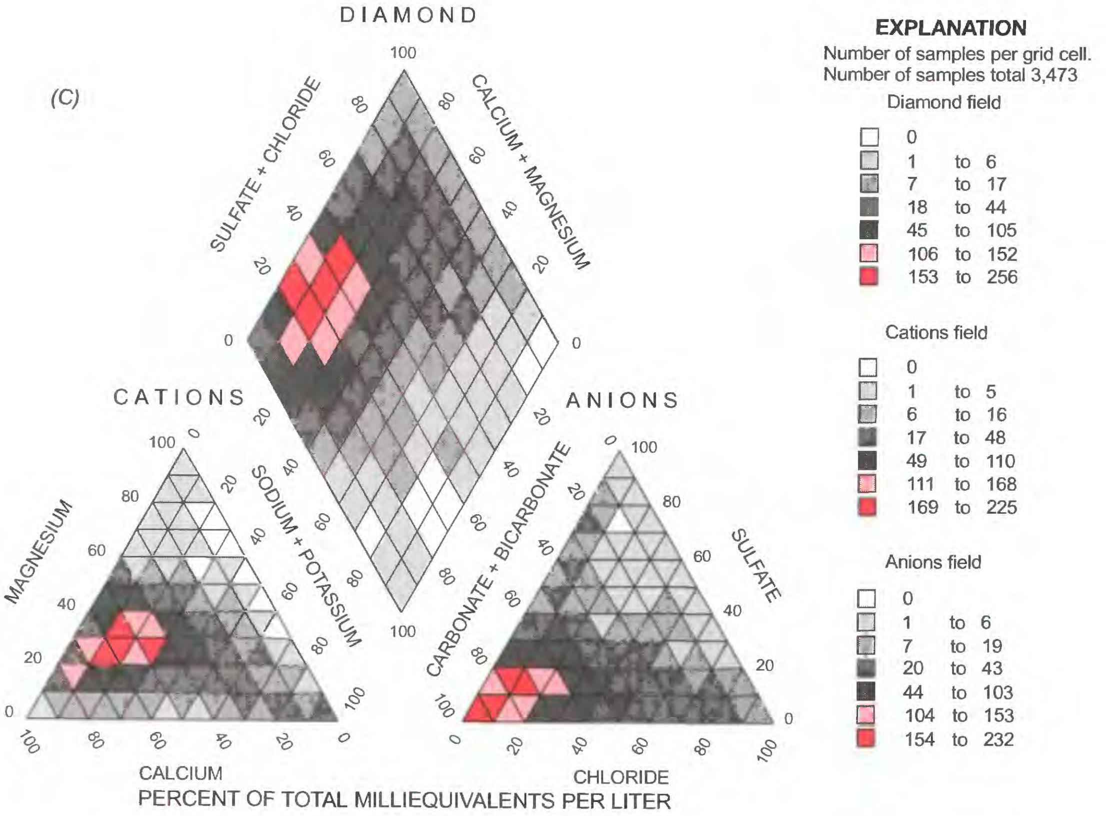


FIGURE 59.—General chemical composition of ground water in (*A*) the Valley and Ridge, (*B*) the Blue Ridge, *(C)* and Piedmont Provinces—Continued.

Shaded-grid trilinear diagrams for selected ground-water, surface-water, and spring-water samples in the Valley and Ridge, the Blue Ridge, and the Piedmont Provinces are shown in figures 59–61. The only test used to select samples for display was a 10 percent limit for ion balance: if the difference in total concentrations of cations and anions was greater than 10 percent, the sample was not displayed.

GROUND WATER

For 1,803 ground-water samples in the Valley and Ridge Province (fig. 59*A*), the dominant cations are calcium and magnesium, and the Ca:Mg ratio ranges from about 4:1 (primarily calcite) to 1:1 (dolomite). Typical proportions for the major cations are 70:20:10 (Ca:Mg:Na). The dominant anion is bicarbonate, but sulfate and chloride are also found in some samples. Typical proportions for the major anions are 85:08:07 (HCO_3:SO_4:Cl). A representative composition for these samples is a water containing 80 percent calcium magnesium bicarbonate and 20 percent calcium sulfate. Alignment of chemical compositions in the diagram indicates that the dominant process affecting ground-water quality in this area is downgradient flow from recharge areas to areas of confined flow (fig. 58, reaction path 3).

The pattern of chemical compositions for 262 ground-water samples from the Blue Ridge Province (fig. 59*B*) is different from the pattern for ground water in the Valley and Ridge Province (fig. 59*A*), primarily because of an increase in the relative abundances of sodium and chloride. Typical proportions for cations in ground water in the Blue Ridge Province are 50:25:25, and for anions, 80:04:16. The dominant anion is bicarbonate; chloride (plus nitrate) makes up most of the remainder, and sulfate abundance is low. The dominant chemical type is a mixed water containing calcium magnesium bicarbonate and sodium chloride. In the diamond-shaped field, alignment of chemical compositions along reaction path 3 is indicated, but this trend is not as strong as it is for ground water in the Valley and Ridge Province. A secondary alignment of chemical compositions along reaction path 6 indicates the effect of higher abundances of sodium and chloride in ground water in the Blue Ridge Province compared with the Valley and Ridge Province.

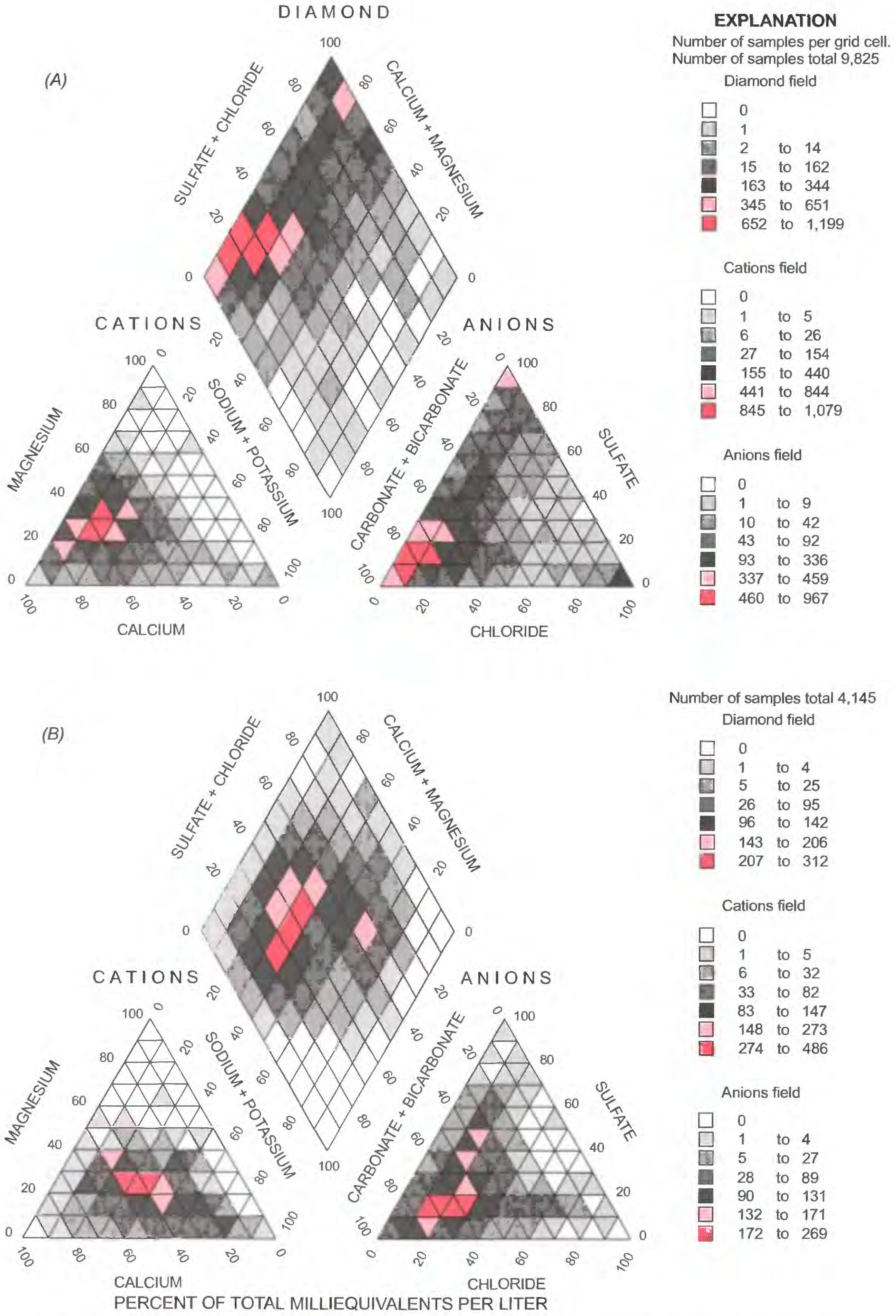


FIGURE 60.—General chemical composition of surface water in (*A*) the Valley and Ridge, (*B*) the Blue Ridge, and *(C)* the Piedmont Provinces.

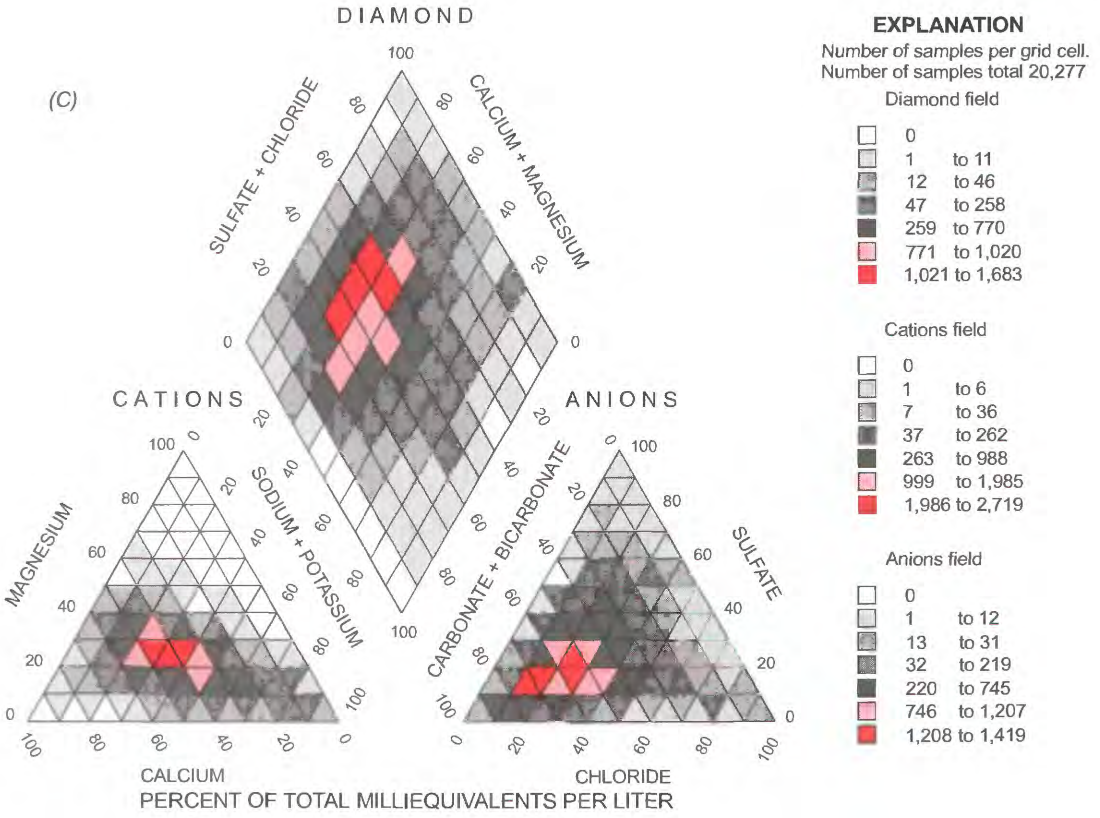


FIGURE 60.—General chemical composition of surface water in (*A*) the Valley and Ridge, (*B*) the Blue Ridge, and *(C)* the Piedmont Provinces—Continued.

The pattern of chemical compositions for 3,473 ground-water samples from the Piedmont Province (fig. 59*C*) shows the effects of distinctly smaller percentages of the dominant ions (calcium and bicarbonate) and larger percentages of magnesium, sodium, and chloride, compared with ground water in the Valley and Ridge Province (fig. 59*A*). Typical proportions for cations in ground water in the Piedmont Province show a mode near 50:30:20, and for anions, near 80:08:12. The set of samples for the Piedmont Province is statistically more robust than the smaller set for the Blue Ridge Province. Proportions of cations and of anions for these two sets, however, are so similar that differences between them may not be significant. Significance testing was not performed on compositions determined from the shaded-grid trilinear diagrams. For ground water in the Piedmont Province, the dominant chemical type is a mixed water containing 60 percent calcium magnesium bicarbonate, 30 percent sodium chloride, and 10 percent calcium sulfate. Different alignments of chemical compositions in this diagram indicate the effects of competing processes. In the diamond-shaped field, major alignments along reaction paths 2, 3 and 6 are indicated and in the cations and anions fields, paths 2 and 6 are prominent. For these samples, increased mineralization (path 4) is most likely related to greater abundances of chloride in rocks in the Piedmont Province than in rocks in the Valley and Ridge Province.

SURFACE WATER

In the Valley and Ridge Province, the pattern of chemical compositions for 9,825 surface-water samples (fig. 60*A*) is generally similar to the pattern for ground-water samples (fig. 59*A*), an indication that lithology in this region is an important factor in the determination of chemical composition of water. Similarities in these patterns indicate that interactions between ground water and surface water may be common in the Valley and Ridge Province. Differences in the patterns indicate that (1) sulfate is much more abundant in surface water than in ground water and (2) the abundance of chloride in surface water is low. Typical proportions for cations in surface water in the Valley and Ridge Province are 60:25:15, and for anions, 75:20:05. Within the range of dominant compositions of surface water in the Valley and Ridge Province are two distinct modes, one for water containing calcium magnesium bicarbonate, and another for water containing calcium sulfate (fig. 60*A*).

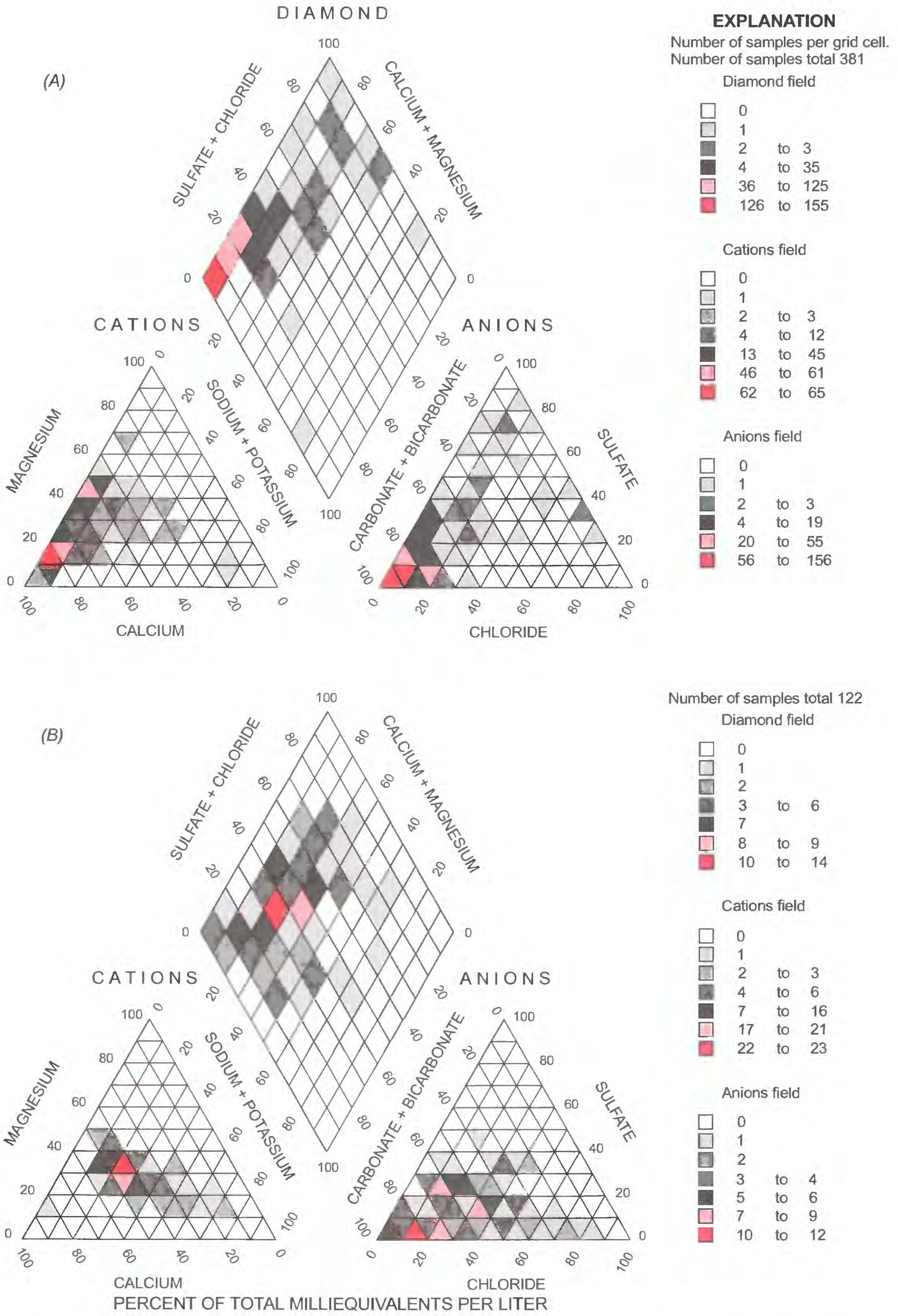


FIGURE 61.—General chemical composition of spring water in (*A*) the Valley and Ridge and (*B*) the Blue Ridge Provinces.

Alignment of compositions between these modes indicates a diversity of mixed waters containing these minerals.

In the Blue Ridge Province, the pattern of chemical compositions for 4,145 surface-water samples (fig. 60*B*) is different from the pattern for ground-water samples (fig. 59*B*). Modal compositions of surface-water samples spread over a larger range and are nearer to centers of the three fields than those of ground water, an indication that chemical composition of surface water in the Blue Ridge Province is generally more diverse than that of ground water. Distinctive features of the surface-water pattern include large relative abundances of sodium, chloride, and sulfate. No cation is dominant: typical proportions are 40:20:40. Bicarbonate is the dominant anion (60:20:20), but major alignments of compositions toward the sulfate and the chloride apexes are evident (fig. 60*B*). In the Blue Ridge Province, surface water is typically a mixed chemical type containing calcium magnesium bicarbonate, sodium chloride, and calcium sulfate in various amounts.

In the Piedmont Province, the pattern of chemical compositions for 20,277 surface-water samples (fig. 60*C*) is distinctly different from the pattern for ground water (fig. 59*C*), but similar to the pattern for surface water in the Blue Ridge Province (fig. 60*B*). Ranges of modal compositions of surface water in the Piedmont and the Blue Ridge Provinces are about equal and indicate a diversity of mixed chemical types is present in both provinces. For surface water in the Piedmont Province, calcium is the dominant cation (43:23:34), and bicarbonate is the dominant anion (55:15:30). Sodium and chloride fractions are about equal, which indicates a possible relation between these ions. Sulfate abundance is slightly lower in the Piedmont Province than in the Blue Ridge Province, but the difference may not be significant. In the Piedmont Province, surface water is typically a mixed water containing calcium magnesium bicarbonate, sodium chloride, and calcium sulfate in various amounts.

SPRING WATER

Because fewer analyses are available for spring water in the study area, regional trends in chemical composition are harder to define and are generally less statistically robust than those for ground water and for surface water. The pattern of chemical compositions for 381 spring-water samples in the Valley and Ridge Province (fig. 61*A*) is similar to the pattern for ground-water samples (fig. 59*A*), except that the range of compositions for spring water is smaller than the range for ground water. For both types of sites, the dominant cation is calcium and the dominant anion is bicarbonate. Typical proportions for cations in spring water in the Valley and Ridge Province are 75:15:10, and for anions, 85:08:07. Relative abundances of sodium, chloride, and sulfate in spring water are low. The dominant chemical type is water containing calcium magnesium bicarbonate.

In the Blue Ridge Province, the pattern of chemical compositions for 122 spring-water samples (fig. 61*B*) is similar to that for ground-water samples (fig. 59*B*), except that spring water is slightly more diverse than ground water with respect to anion compositions. Modal compositions of spring-water samples in the Blue Ridge and the Valley and Ridge Provinces are different (fig. 61), an indication that spring-water composition is generally more diverse in the Blue Ridge than in the Valley and Ridge. Typical proportions for cations in spring water in the Blue Ridge Province are 45:30:25. For anions, several scattered modes in the lower half of the field range from 85:05:10 to 54:13:33. Sodium and chloride abundances are similar, although chloride abundance is highly variable. Sulfate abundance in these samples is generally low. Typical chemical composition of spring water in the Blue Ridge Province is a mixed water containing calcium magnesium bicarbonate and sodium chloride in various amounts.

In the Piedmont Province, the pattern of chemical compositions for 56 spring-water samples (fig. 62*A*) indicates that most of the samples are mixed waters containing bicarbonate and chloride with no dominant cation. Typical proportions of cations are 37:37:26, and of anions, 80:05:15. In the Piedmont Province, ranges in compositions of spring water and of ground water are about the same, except that the ground-water range is better defined. Alignments of cation and anion compositions in the two groups are similar, although the ionic proportions are different. These differences may be due to differences in lithology near the springs, or they could be due to the small number of analyses available.

The summary of trends in chemical composition displayed on a shaded-grid trilinear diagram is more reliable for larger numbers of samples. For fewer than 100 samples, display of the individual compositions may provide more useful information than display of the relative populations of grid cells. A standard Piper diagram for the 56 spring-water samples in the Piedmont Province (fig. 62*B*) shows that about half the samples are predominantly calcium magnesium bicarbonate water, and the rest are mixed-cation water that contains a significant fraction of chloride. Although the same information is displayed on both diagrams, figure 62*B* shows the proximity of samples to cell boundaries and

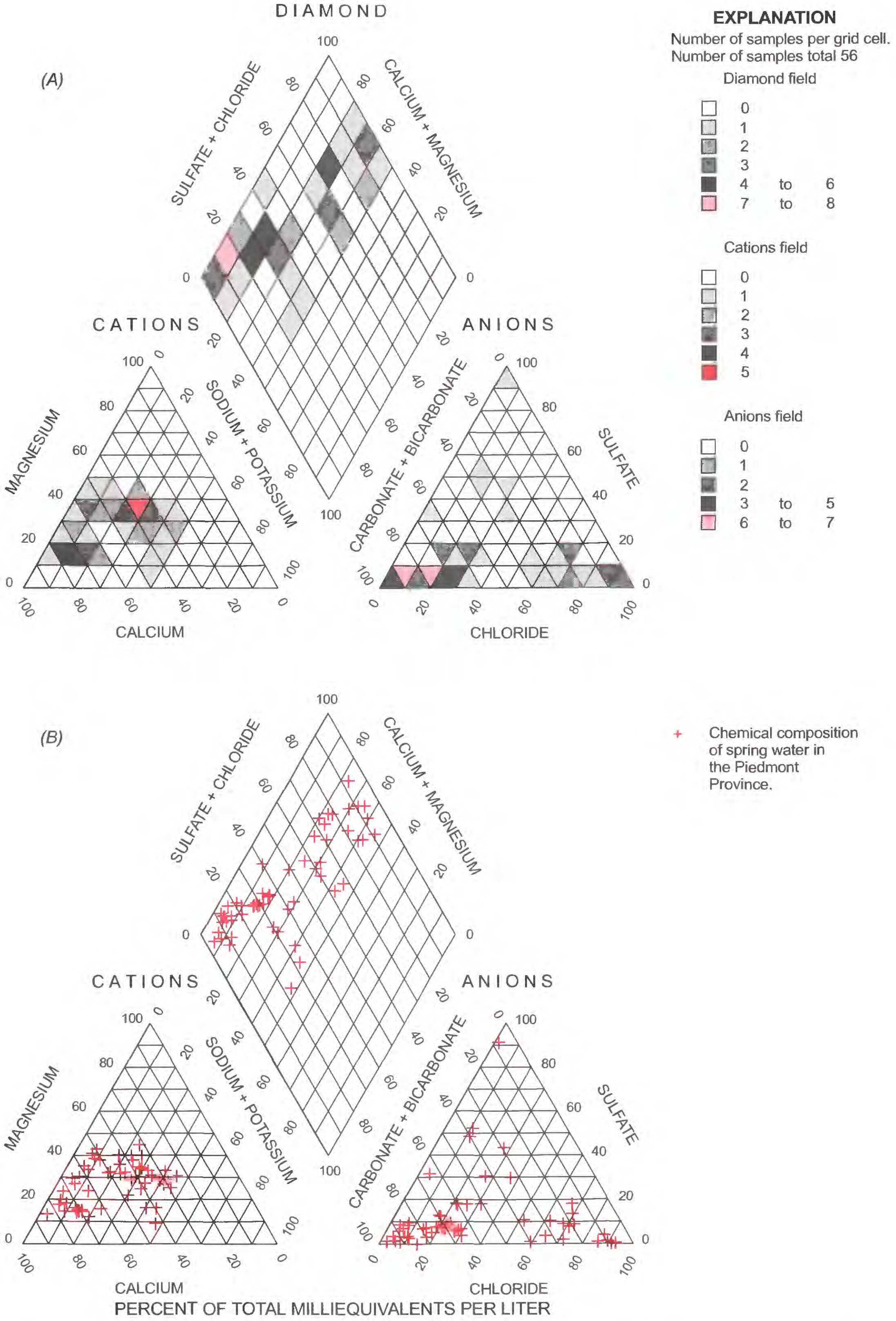


FIGURE 62.—Variations in chemical composition of spring water in the Piedmont Province shown on (*A*) a shaded-grid trilinear diagram, and (*B*) a Piper diagram.

groups of points that are arbitrarily separated by the grid. The standard diagram is preferable where sample resolution is not a problem.

SUMMARY AND CONCLUSIONS

Regional and local variations in water quality in the Appalachian Valley and Ridge, the Blue Ridge, and the Piedmont Regional-Aquifer System Analysis (APRASA) study area are due to differences in geologic and hydrologic factors. Geologic factors include dominant lithology and availability of soluble minerals; the principal hydrologic factor is the degree of exposure of rock to water. Concentrations of many dissolved minerals indicate that water-rock interactions are strongest in ground water, intermediate in spring water, and weakest in surface water. Most ground water in the study area, however, is not highly mineralized. Ground water is moderately hard and slightly acidic; spring water is harder than ground water and slightly alkaline; surface water is softer than ground water and also slightly alkaline.

For the three types of water, variations in many properties and constituents show regional patterns. In the Valley and Ridge Province, median values of specific conductance, pH, carbonate hardness, and concentrations of dissolved solids, calcium, magnesium, sulfate, bicarbonate, alkalinity, nitrate, and dissolved iron are generally the highest in the study area. In the Piedmont Province, median concentrations of sodium, potassium, chloride, silica, ammonia, phosphorus, total iron, and manganese are the highest in the study area. Water in the Blue Ridge Province typically is the least mineralized and has low median values for most of the properties and constituents studied. The exception is dissolved oxygen: median concentrations in ground water and surface water are highest in the Blue Ridge Province.

Major-ion composition of most water in the study area can be represented by various mixtures of four dissolved minerals: calcite, dolomite, gypsum, and halite. Ionic constituents of the first two minerals account for the predominant chemical composition in most of the area: calcium magnesium bicarbonate water. Ionic constituents of the second pair of minerals represent secondary chemical compositions in locally varying amounts. Ground water contains sulfate throughout the study area, but especially in the Valley and Ridge Province, where sulfate is the dominant anion at total-anion concentrations greater than 2 meq / L. Ground water also contains chloride throughout the study area, but primarily in the Piedmont Province and in a few deep wells in the Valley and Ridge Province that tap brines.

For ground water, regional variations in concentrations of other dissolved constituents—such as silica and iron—appear to be related to differences in dominant lithology. Median concentrations of dissolved silica are highest in the Piedmont and the Blue Ridge Provinces, where the dominant rocks are generally rich in silica (weathered gneisses, granites, and schists), and lowest in the Valley and Ridge Province, where the dominant rocks are carbonates and shales. The reverse is true for dissolved iron: median concentration is the highest in the Valley and Ridge Province, where pyritic shales are locally abundant, and lowest in the Blue Ridge Province, where weathered igneous and metamorphic rocks are not a ready source of soluble iron.

Trends in chemical composition for various groups of water samples were displayed on trilinear diagrams. Because the large number of samples in each group made it impossible to discern patterns on a conventional Piper diagram, a shaded-grid trilinear diagram was developed to summarize general chemical composition of waters in the study area. The shading pattern indicates modes in chemical composition without loss of resolution from large numbers of adjacent samples. On these diagrams trends are shown by major alignments of the composition of samples between modes.

Analyses of dominant chemical compositions for nine groups of water samples yield the following results: For ground water in the Valley and Ridge Province, typical proportions for major cations are 70:20:10 (Ca:Mg:Na), and for major anions, 85:08:07 (HCO_3:SO_4:Cl). The dominant chemical type is a mixed water containing calcium magnesium bicarbonate and calcium sulfate. A major alignment of chemical compositions may be related to downgradient flow in recharge areas.

For ground water in the Blue Ridge Province, typical proportions for major cations are 50:25:25, and for major anions, 80:04:16. The dominant chemical type is a mixed water containing calcium magnesium bicarbonate and sodium chloride; abundance of sulfate in ground water in the Blue Ridge Province is low. The major alignments of chemical compositions of ground water in the Blue Ridge and the Valley and Ridge Provinces are similar, except that alignments are not as well defined for Blue Ridge samples. A secondary alignment of chemical compositions indicates the effect of higher abundances of sodium and chloride in ground water in the Blue Ridge Province compared with the Valley and Ridge Province.

For ground water in the Piedmont Province, typical proportions for major cations are 50:30:20, and for major anions, 80:08:12. These proportions are similar to those for ground water in the Blue Ridge Province, and differences between them may not be statistically significant. The dominant chemical type a mixed water containing calcium magnesium bicarbonate, sodium chloride, and a small amount of calcium sulfate. Like ground water in the Blue Ridge Province, the major alignment of chemical compositions of ground water in the Piedmont Province indicates an increase in mineralization that is probably due to the greater abundance of chloride in rocks in this area compared with rocks in the Valley and Ridge Province.

Variability in chemical composition of surface water in the study area is greater than that of ground water, an indication that surface water is more likely than ground water to be represented by mixtures of several chemical types. For surface water in the Valley and Ridge Province, typical proportions for major cations are 60:25:15, and for major anions, 75:20:05. Calcium and bicarbonate are the dominant ions, but an alignment of anion compositions toward sulfate is evident. For surface water in the Valley and Ridge Province, a typical composition is a mixed water containing a large fraction of calcium magnesium bicarbonate and smaller fractions of calcium sulfate and sodium bicarbonate. Abundance of chloride in surface water is low in this province.

For surface water in the Blue Ridge Province, typical proportions for major cations are 40:20:40, and for major anions, 60:20:20. A distinctive feature of this water is an increase in the relative abundances of sodium, chloride, and sulfate compared with ground water. No cation is dominant, and the sodium fraction is about equal to the calcium fraction. Bicarbonate is the dominant anion, but the chloride and sulfate fractions are also equal. A typical composition for surface water in the Blue Ridge Province is a mixed water containing calcium bicarbonate, sodium chloride, and calcium sulfate in various amounts.

For surface water in the Piedmont Province, typical proportions for major cations are 43:23:34, and for anions, 55:15:30. These proportions are similar to corresponding proportions for surface water in the Blue Ridge Province. Bicarbonate is the dominant anion, and the chloride fraction is twice that of sulfate. Sodium and chloride fractions are about equal, which indicates a possible relation between these ions. A typical chemical composition for surface water in the Piedmont Province is a mixed water containing calcium magnesium bicarbonate, and sodium chloride. In some samples, calcium sulfate is also present in small amounts.

Most of the sampled springs in the study area are in the Valley and Ridge Province. For spring water in this province, typical proportions for major cations are 75:15:10, and for major anions, 85:08:07. Calcium and bicarbonate are the dominant ions in this water; however, a second mode is evident for cations with proportions of 50:45:05, an indication that magnesium is also present in spring water in significant amounts. In the Valley and Ridge Province, chemical compositions of spring water and ground water are almost identical: calcium is slightly more abundant in spring water, and magnesium is more abundant in ground water.

For spring water in the Blue Ridge Province, typical proportions for major cations are 45:30:25. For anions, several scattered compositional modes range from 85:05:10 to 54:13:33. A typical chemical composition for spring water in the Blue Ridge Province is a mixed water containing a dominant fraction of calcium magnesium bicarbonate and a smaller fraction of sodium chloride; abundance of sulfate in spring water in the Blue Ridge Province is low.

The APRASA data base has only 56 analyses for spring water in the Piedmont Province. For these samples, typical proportions for major cations are 37:37:26, and for major anions, 80:05:15. Bicarbonate is the dominant anion, but no cation is dominant. A typical chemical composition for these samples is a mixed water containing a large fraction of bicarbonate and a smaller fraction of chloride. Some of these samples also contain small amounts of sulfate. Spring water in the Piedmont Province is unusual with respect to several properties and constituents. Water-quality patterns indicate a different lithology of origin (weathered regolith) for Piedmont springs than for springs elsewhere in the study area.

REFERENCES

Alley, W.M., 1993a, General design considerations, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 3–21.

———1993b, Establishing a conceptual framework, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 23–60.

———1993c, Ground-water-quality surveys, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 63–85.

Aucott, W.R., and Speiran, G.K., 1985, Geohydrology and water quality of the Coastal Plain aquifers of South Carolina, *in* McGill, H.J., and Stone, P.A., eds., Symposium on Ground Water and Environmental Hydrogeology in South Carolina: South Carolina State Department of Health and Environmental Control, Columbia, South Carolina, October 1–2, 1985, Proceedings, p. 26–50.

Ayres, M.A., and Pustay, E.A., 1987, New Jersey ground water quality: U.S. Geological Survey Open-File Report 87–740, 8 p.

Bachman, L.J., 1984, Nitrate in the Columbia aquifer, central Delmarva Peninsula, Maryland: U.S. Geological Survey Water-Resources Investigations Report 84–4322, 51 p.

Back, William, 1961, Techniques for mapping of hydrochemical facies: U.S. Geological Survey Professional Paper 424–D, p. D380–D382.

Back, William, 1966, Hydrochemical facies and ground-water flow patterns in northern part of Atlantic Coastal Plain: U.S. Geological Survey Professional Paper 498–A, 42 p.

Back, William, Baedecker, M.J., and Wood, W.W., 1993, Scales in chemical hydrogeology—a historical perspective, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 111–129.

Back, William, and Hanshaw, B.B., 1970, Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan: Journal of Hydrology, v. 10, p. 330–368.

Bain, G.L., and Brown, C.E., 1981, Evaluation of the Durham Triassic Basin of North Carolina and techniques used to characterize its waste-storage potential: U.S. Geological Survey Open-File Report 80–1295, 132 p.

Baker, Jack, 1957, Geology and ground water of the Piedmont area of Alabama—a reconnaissance report: Geological Survey of Alabama Special Report 23, 99 p.

Barker, J.L., 1984, Compilation of ground-water-quality data: U.S. Geological Survey Open-File Report 84–706, 102 p.

Barksdale, H.C., Greenman, D.W., Lang, S.M., Hilton, G.S., and Outlaw, D.E., 1958, Ground-water resources in the tri-state region adjacent to the lower Delaware River: New Jersey Department of Conservation and Economic Development Special Report 13, 190 p.

Becher, A.E., and Root, S.I., 1981, Groundwater and geology of the Cumberland Valley, Cumberland County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 50, p. 40–48, 74–95.

Becher, A.E., and Taylor, L.E., 1982, Groundwater resources in the Cumberland and contiguous valleys of Franklin County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 53, p. 35–42, 48–67.

Bennett, G.D., 1979, Regional ground-water systems analysis: Water Spectrum, Fall 1979, p. 36–42.

Bennett, R.R., 1946, Water resources of Carroll and Frederick Counties, in The physical features of Carroll County and Frederick County: Maryland Department of Geology, Mines, and Water Resources, p. 165–187.

Bieber, P.P., 1961, Ground-water features of Berkeley and Jefferson Counties, West Virginia: West Virginia Geological Survey Bulletin 21, 81 p.

Bradfield, A.D., 1992, Hydrology of the Cave Springs area near Chattanooga, Hamilton County, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 92–4018, p. 20–26.

Brahana, J.V., Mulderink, Dolores, Macy, J.A., and Bradley, M.W., 1986, Preliminary delineation and description of the regional aquifers of Tennessee—The east Tennessee aquifer system: U.S. Geological Survey Water-Resources Investigations Report 82–4091, 30 p.

Brahana, J.V., Thrailkill, John, Freeman, Tom, and Ward, W.C., 1988, Carbonate rocks, *in* Back, William, Rosenshein, J.S., and Seaber, P.R., eds., Hydrogeology: Boulder, Colo., Geological Society of America, The Geology of North America, v. O–2, p. 333–352.

Briel, L.I., 1993, Documentation of a multiple-technique computer program for plotting major-ion composition of natural waters: U.S. Geological Survey Open-File Report 93–74, 88 p.

Cady, R.C., 1936, Ground-water resources of the Shenandoah Valley, Virginia: Virginia Geological Survey Bulletin 45, 137 p.

———1938, Ground-water resources of northern Virginia: Virginia Geological Survey Bulletin 50, 200 p.

Carswell, L.D., Hollowell, J.R., and Platt, L.B., 1968, Geology and hydrology of the Martinsburg Formation in Dauphin County, Pennsylvania: Pennsylvania Geological Survey Ground Water Report Bulletin W 24, p. 35–43, 53–54.

Carswell, L.D., and Lloyd, O.B., Jr., 1979, Geology and ground-water resources of Monroe County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 47, p. 29–35, 48–61.

Casteel, C.A. and Ballew, M.D., 1987, Water-resources activities, Georgia, District, 1986: U.S. Geological Survey Open-File Report 87–381, 59 p.

Causey, L.V., 1965, Availability of ground water in Talladega County, Alabama—a reconnaissance: Geological Survey of Alabama Bulletin 81, 63 p.

Chambers, J.M., Cleveland, W.S., Kiner, Beat, and Tukey, P.A., 1983, Graphical methods for data analysis: Pacific Grove, Calif., Wadsworth and Brooks / Cole Publishing Company, 395 p.

Chandler, R.V., and Lines, G.C., 1974, Water availability, Chambers County, Alabama: Geological Survey of Alabama Map 133, 29 p.

———1978a, Water availability, Cleburne County, Alabama: Geological Survey of Alabama Map 143, 29 p.

———1978b, Water availability, Tallapoosa County, Alabama: Geological Survey of Alabama Map 142, 27 p.

Chandler, R.V., Lines, G.C. and Scott, J.C., 1972, Water availability, Clay County, Alabama: Geological Survey of Alabama Map 103, 22 p.

Chandler, R.V., and Moore, J.D., 1987, Springs in Alabama: Geological Survey of Alabama Circular 134, 95 p.

Chapelle, F.H. and Knobel, L.L., 1983, Aqueous geochemistry and the exchangeable cation composition of glauconite in the Aquia Aquifer, Maryland: Ground Water, v. 21, no. 3, p. 343–352.

Clark, S.L., and Stone, P.A., 1989, Ground-water mineralization in the Carolina slate belt near Chapin, South, Carolina, *in* Daniel, C.C., III, White, R.K., and Stone, P.A., eds., Ground water in the Piedmont: Clemson, S.C., Clemson University, p. 455–474.

Clark, W.E., Chisholm, J.L., and Frye, P.M., 1976, Water resources of the upper New River basin, West Virginia: West Virginia Geological and Economic Survey River Basin Bulletin 4, p. 52–85.

Clarke, J.S., 1989, Geohydrologic evaluation of spring sites at Social Circle, Georgia, December 5–8, 1988: U.S. Geological Survey Open-File Report 89–236, 18 p.

Cleveland, W.S., 1979, Robust locally weighted regression and smoothing scatterplots: Journal of the American Statistical Association, v. 74, no. 368, p. 829–836.

Collins, W.D., Foster, M.D., Reeves, Frank, and Meacham, R.P., 1930, Springs of Virginia—a report on the discharge, temperature and chemical character of springs in the southern part of the Great Valley: Virginia Division of Water Resources and Power Bulletin 1, 55 p.

Crawford, J. Kent, 1985, Water-quality characteristics for selected sites on the Cape Fear River, North Carolina, 1955–80, variability, loads, and trends of selected constituents: U.S. Geological Survey Professional Paper 2185–F, 44 p.

Cressler, C.W., 1974, Geology and ground-water resources of Gordon, Whitfield, and Murray Counties, Georgia: Georgia Department of Natural Resources Information Circular 47, 56 p.

Cressler, C.W., Franklin, M.A., and Hester, W.G., 1976, Availability of water supplies in northwest Georgia: Georgia Department of Nautral Resources Bulletin 91, 140 p.

Daniel, C.C., III, Eimers, J.L., and Smith, D.G., in press, Hydrogeology and simulation of ground-water flow in the thick regolith-fractured crystalline rock aquifer system of the Indian Creek Basin, North Carolina: U.S. Geological Survey Water-Supply Paper 2341–C, 137 p.

Daniel, C.C., III, and Payne, R.A., 1990, Hydrogeologic unit map of the Piedmont and Blue Ridge Provinces of North Carolina: U.S. Geological Survey Water-Resources Investigations Report 90–4035, 1 sheet, scale 1:500,000.

Daniel, C.C., III, Wilder, H.B., and Weiner, M.S., 1982, Water quality of the French Broad River, North Carolina—an analysis of data collected at Marshall, 1958–77: U.S. Geological Survey Water-Supply Paper 2185–C, 28 p.

Davis, S.N., 1964, Silica in streams and ground water: American Journal of Science, v. 262, p. 870–891.

Dawson, J.W., and Davidson, C.B., 1979, Groundwater resources of Henry County, Virginia: Virginia State Water Control Board Planning Bulletin 312, p. 59–65, B1–B7.

DeBuchananne, G.D., 1968, Ground-water resources of the James, York, and Rappahannock River basins of Virginia, west of the fall line: U.S. Geological Survey Hydrologic Investigations Atlas HA–283, 1 sheet, scale 1:500,000.

Doll, W.L., Meyer, Gerald, and Archer, R.J., 1963, Water resources of West Virginia: West Virginia Department of Natural Resources, 134 p.

Donn, T.F., 1990, South Carolina ambient ground-water quality monitoring network: South Carolina Department of Health and Environmental Control Report, 62 p.

Duigon, M.T., and Dine, J.R., 1991, Water resources of Washington County, Maryland: Maryland Geological Survey Bulletin 36, p. 26–44, 67–79.

Duigon, M.T., Dine, J.R., and Tompkins, M.D., 1989, Ground-water and surface-water data for Washington County, Maryland: Maryland Geological Survey Basic Data Report 18, 273 p.

Ellison, R.P., III, and Masiello, R.A., 1979, Groundwater resources of Hanover County, Virginia: Virginia State Water Control Board Planning Bulletin 314, 169 p.

Faust, R.J., and Harkins, J.R., 1980, Water availability of Blount County, Alabama: Geological Survey of Alabama Map 141, 19 p.

Federal Information Processing Standards Publication 5–1, 1970, States and outlying areas of the United States, *in* WATSTORE User's Guide, Appendix: U.S. Geological Survey, Open-File Report 79–1336–I, p. B3.

Federal Information Processing Standards Publication 6–3, 1970, Counties and county equivalents to the states of the United States and the District of Columbia, *in* WATSTORE User's Guide: U.S. Geological Survey, Open-File Report 79–1336–I, p. C1–C14.

Fenneman, N.M., 1938, Physiography of eastern United States: New York, McGraw-Hill, 714 p

———1946, Physical divisions of the United States: U.S. Geological Survey special map, 1 sheet, scale 1:7,000,000.

Ferrel, G.M., 1987, West Virginia ground-water quality: U.S. Geological Survey Open-File Report 87–761, 9 p.

Freeze, R.A. and Cherry, J.A., 1979, Groundwater: Englewood Cliffs, N.J., Prentice-Hall, 604 p.

Froelich, A.J., and Zenone, Chester, 1985, The relation of water quality to geology and land use changes in Fairfax County and vicinity, Virginia: U.S. Geological Survey Miscellaneous Investigations Series map I–1561, 1 sheet, scale 1:48,000.

Garrels, R.M. and Christ, C.L., 1965, Solutions, minerals, and equilibria: New York, Harper and Row, 450 p.

Groot, J.J., and Rasmussen W.C., 1954, Geology and ground-water resources of the Newark area, Delaware: Delaware Geological Survey Bulletin 2, 133 p.

Grubb, H.F., 1986, Gulf Coast Regional Aquifer-System Analysis—a Mississippi perspective: U.S. Geological Survey Water-Resources Investigations Report 86–4162, 22 p.

Grubb, H.F., Carrillo R., J.J., 1988, Region 23, Gulf of Mexico Coastal Plain, *in* Back, William, Rosenshein, J.S., and Seaber, P.R., eds., Hydrogeology: Boulder, Colo., Geological Society of America, The Geology of North America, v. O–2, p. 219–228.

Hack, J.T., 1982, Physiographic divisions and differential uplift in the Piedmont and Blue Ridge: U.S. Geological Survey Professional Paper 1265, 49 p.

Hallberg, G.R., and Keeney, D.R., 1993, Nitrate, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 297–322.

Hamilton, P.A., Welch, A.H., Christenson, S.C., and Alley, W.M., 1993, Uses and limitations of existing ground-water-quality data, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 613–622.

Hanshaw, B.B., and Back, William, 1979, Major geochemical processes in the evolution of carbonate-aquifer systems: Journal of Hydrology, v. 43, p. 287–312.

Hanshaw, B.B., Back, William, and Deike, R.G., 1971, A geochemical hypothesis for dolomitization by ground water: Economic Geology, v. 66, 710–724.

Harkins, J.R., and others, 1980, Hydrologic assessment, Eastern Coal Province Area 23, Alabama: U.S. Geological Survey Water-Resources Investigations Open-File Report 80–683, 76 p.

———1981, Hydrology of Area 22, Eastern Coal Province, Alabama: U.S. Geological Survey Water-Resources Investigations Open-File Report 81–135, 72 p.

Harlow, G.E. and Nelms, D.L., 1989, Use of a geographic information system to identify hydrogeologic units in the Piedmont and Blue Ridge Physiographic Provinces, Virginia to New Jersey, *in* Daniel, C.C., III, White, R.K., and Stone, P.A., eds., Ground water in the Piedmont: Clemson, S.C., Clemson University, p. 312–316.

Harned, D.A., 1982, Water quality of the Neuse River, North Carolina—variability, pollution loads, and long-term trends: U.S. Geological Survey Water-Supply Paper 2185–D, 44 p.

———1989, The hydrogeologic framework and a reconnaissance of ground-water quality in the Piedmont Province of North Carolina, with a design for future study: U.S. Geological Survey Water-Resources Investigations Report 88–4130, 55 p.

Harned, D.A., and Meyer, Dann, 1983, Water quality of the Yadkin-Pee Dee River system, North Carolina—Variability, pollution loads, and long-term trends: U.S. Geological Survey Professional Paper 2185–E, 71 p.

Helsel, D.R. and Hirsch, R.M., 1992, Statistical methods in water resources: Amsterdam, Netherlands, Elsevier, 522 p.

Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, 263 p.

Hobba, W.A., Jr., 1976, Ground-water hydrology of Berkeley County, West Virginia: West Virginia Geological and Economic Survey and the Berkeley County Court, 21 p.

———1981, Ground-water hydrology of Jefferson County, West Virginia: West Virginia Geological and Economic Survey Environmental Geology Bulletin EGB–16, 21 p.

———1985, Water in Hardy, Hampshire, and western Morgan Counties, West Virginia: West Virginia Geological and Economic Survey Environmental Geology Bulletin EGB–19, 91 p.

Hobba, W.A., Jr., Chemerys, J.C., Fisher, D.W., and Pearson, F.J., Jr., 1977, Geochemical and hydrologic data for wells and springs in thermal-spring areas of the Appalachians: U.S. Geological Survey Water-Resources Investigations Report 77–25, 36 p.

Hobba, W.A., Jr., Friel, E.A., and Chisholm, J.L., 1972, Water resources of the Potomac River basin, West Virginia: West Virginia Geological and Economic Survey River Basin Bulletin 3, p. 77–102.

Hollyday, E.F., and Hileman, G.E., 1996, Hydrogeologic terranes and potential yield of water to wells in the Valley and Ridge Physiographic Province in the eastern and southeastern United States: U.S. Geological Survey Professional Paper 1422–C, 31 p.

Hollyday, E.F., Knopman, D.S., Smith, M.A., and Hileman, G.E., 1992, Statistical analysis of well records for classifying and mapping hydrogeologic terranes in the Valley and Ridge province, *in* Hotchkiss, W.R., and Johnson, A.I., eds., Regional Aquifer Systems of the United States—Aquifers of the Southern and Eastern States, American Water Resources Association, Monograph Series no. 17, p 75–92.

Hollyday, E.F., and Smith, M.A., 1990, Large springs in the Valley and Ridge Province in Tennessee: U.S. Geological Survey Water-Resources Investigations Report 89–4205, 9 p.

Hopkins, H.T., 1984, Ground-water availability along the Blue Ridge Parkway, Virginia: U.S. Geological Survey Water-Resources Investigations Report 84–4168, p. 17–29.

Jacobson, R.L., and Langmuir, Donald, 1970, The chemical history of some spring waters in carbonate rocks: Ground Water, v. 8, no.2, p. 5–9.

Johnston, H.E., 1966, Hydrology of the New Oxford Formation in Lancaster County, Pennsylvania: Pennsylvania Geological Survey Ground Water Report Bulletin W 23, p. 38–46, 52–77.

Johnston, P.M., 1960, Ground-water supplies in shale and sandstone in Fairfax, Loudon, and Prince William Counties, Virginia: U.S. Geological Survey Circular 424, 7 p.

———1964, Geology and ground-water resources of Washington, D.C., and vicinity: U.S. Geological Survey Water-Supply Paper 1776, p. 67–83.

Knobel, L.L., 1985, Ground-water-quality data for the Atlantic Coastal Plain, New Jersey, Delaware, Maryland, Virginia, and North Carolina: U.S. Geological Survey Open-File Report 85–154, 84 p.

Knobel, L.L., Chapelle, F.H., and Phillips, S.W., 1987, Overview of geochemical processes controlling the chemistry of ground water in the Aquia and Magothy aquifers, Northern Atlantic Coastal Plain, Maryland, *in* Vecchioli, John, and Johnson, A.I., eds., Regional Aquifer Systems of the United States, Aquifers of the Atlantic and Gulf Coastal Plain: American Water Resources Association Monograph Series, no. 9, p. 25–37.

Knobel, L.L., and Phillips, Scott, 1988, Aqueous geochemistry of the Magothy aquifer, Maryland: U.S. Geological Survey Water-Supply Paper 2323, 28 p.

Knopman, D.S., 1991, Factors related to the water-yielding potential of rocks in the Piedmont and Valley and Ridge Provinces of Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 90–4174, 52 p.

Lee, R.W., 1984, Ground-water quality data from the Southeastern Coastal Plain, Mississippi, Alabama, Georgia, South Carolina and North Carolina: U.S. Geological Survey Open-File Report 84–237, 20 p.

———1985, Water-quality maps for selected Upper Cretaceous water-bearing zones in the Southeastern Coastal Plain: U.S. Geological Survey Water-Resources Investigations Report 85–4193, 2 sheets, scale 1:2,000,000.

———1988, Water-quality maps for the Upper Cretaceous and Lower Tertiary aquifer in the Southeastern Coastal Plain of Mississippi, Alabama, Georgia, South Carolina and southeastern North Carolina: U.S. Geological Survey Water-Resources Investigations Report 86–4116, 2 sheets, scale 1:2,000,000.

———1988, Water-quality maps for the Middle Tertiary aquifer in the Southeastern Coastal Plain of Mississippi, Alabama, Georgia, and South Carolina: U.S. Geological Survey Water-Resources Investigations Report 86–4117, 2 sheets, scale 1:2,000,000.

———1993, Geochemistry of ground water in the Southeastern Coastal Plain aquifer system in parts of Mississippi, Alabama, Georgia, and South Carolina: U.S. Geological Survey Professional Paper 1410–D, 72 p.

Lee, R.W., DeJarnette, S.S., and Barker, R.A., 1986, Distribution and altitude of the top of saline ground water in the Southeastern Coastal Plain: U.S. Geological Survey Water-Resources Investigations Report 85–4109, 1 sheet, scale 1:2,000,000.

Lee, R.W., and Strickland, D.J., 1988, Geochemistry of groundwater in Tertiary and Cretaceous sediments of the Southeastern Coastal Plain in eastern Georgia, South Carolina, and southeastern North Carolina: Water Resources Research, v. 24, no. 12 p. 291–303.

LeGrand, H.E., 1958, Chemical character of rocks in the igneous and metamorphic rocks of North Carolina: Economic Geology, v. 53, p. 178–189.

———1960, Geology and ground-water resources of Pittsylvania and Halifax Counties: Virginia Division of Mineral Resources Bulletin 75, 86 p.

———1967, Ground water of the Piedmont and Blue Ridge Provinces in the southeastern United States: U.S. Geological Survey Circular 538, 11 p.

———1988, Region 21, Piedmont and Blue Ridge, *in* Back, William, Rosenshein, J.S., and Seaber, P.R., eds., Hydrogeology: Boulder, Colo., Geological Society of America, The Geology of North America, v. O–2, p. 201–208.

———1989, A conceptual model of ground water settings in the Piedmont region, *in* Daniel, C.C., III, White, R.K., and Stone, P.A., eds., Ground water in the Piedmont: Clemson, S.C., Clemson University, p. 317–327.

Leonard, R.B., 1962, Ground-water geology along the northwest foot of the Blue Ridge between Arnold Valley and Elkton, Virginia: Blacksburg, Va., Virginia Polytechnic Institute and State University, unpublished Ph.D. dissertation, p. 186–201.

Lewis, J.C., and Spitz, F.J., 1987, Hydrogeology, ground-water quality, and the possible effects of a hypothetical radioactive-water spill, Plainsboro Township, New Jersey: U.S. Geological Survey Water-Resources Investigations Report 87–4092, p. 30–33.

Lines, G.C., and Chandler, R.V., 1975, Water availability, Randolph County, Alabama: Geological Survey of Alabama Map 137, 29 p.

Lines, G.C., and Scott, J.C., 1972, Water availability, Coosa County, Alabama: Geological Survey of Alabama Map 111, 28 p.

Lloyd, O.B., Jr., and Growitz, D.J., 1977, Ground-water resources of central and southern York County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 42, p. 50–64, 72–93.

Lloyd, O.B., Jr., and Lyke, W.L., 1995, Ground water atlas of the United States—segment 10 Illinois, Indiana, Kentucky, Ohio, Tennessee: U.S. Geological Survey Hydrologic Investigations Atlas 730–K, 30 p.

Longwill, S.M., and Wood, C.R., 1965, Ground-water resources of the Brunswick Formation in Montgomery and Berks Counties, Pennsylvania: Pennsylvania Geological Survey Ground Water Report Bulletin W 22, p. 26–36, 40–43.

Lynch, D.D., 1987, Hydrologic conditions and trends in Shenandoah National Park, Virginia, 1983–84: U.S. Geological Survey Water-Resources Investigations Report 87–4131, 115 p.

Matthess, Georg, 1982, The properties of groundwater: New York, John Wiley and Sons, 406 p.

McFarland, E.R., 1989, Ground-water hydrology, geochemistry, and nitrogen transport in a saprolite-fractured schist aquifer under agricultural land in the Piedmont Physiographic Province of Maryland, *in* Daniel, C.C., III, White, R.K., and Stone, P.A., eds., Ground water in the Piedmont: Clemson, S.C., Clemson University, p. 442–454.

McGill, R., Tukey, J.W., and Larsen, W.A., 1978, Variations of box plots: The American Statistician, v. 32, no. 1, p. 12–16.

McGreevy, L.J., and Sloto, R.A., 1977, Ground-water resources of Chester County, Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 77–67, p. 44–58

Meisler, Harold, 1963, Hydrology of the carbonate rocks in Lebanon Valley, Pennsylvania: Pennsylvania Geological Survey Ground Water Report Bulletin W 18, p. 38–50, 79–81.

———1989, The occurrence and geochemistry of salty ground water in the Northern Atlantic Coastal Plain: U.S. Geological Survey Professional Paper 1404–D, 51 p.

Meisler, Harold, Miller, J.A., Knobel, L.L., and Waite, R.L., 1988, Region 22, Atlantic and Eastern Gulf Coastal Plain, *in* Back, William, Rosenshein, J.S., and Seaber, P.R., eds., Hydrogeology: Boulder, Colo., Geological Society of America, The Geology of North America, v. O–2, p. 209–218.

Mesko, T.O., 1990, Geohydrology and water quality of Cenozoic and Mesozoic units in southeast Missouri: U.S. Geological Survey Hydrologic Investigations Atlas HA–719, 2 sheets, scale 1:1,000,000.

Miller, J.A., 1990, Ground water atlas of the United States—segment 6 Alabama, Florida, Georgia, South Carolina: U.S. Geological Survey Hydrologic Investigations Atlas 730–G, 28 p.

Miller, R.A., Troxell, John, and Leopold, L.B., 1971, Hydrology of two small river basins in Pennsylvania before urbanization: U.S. Geological Survey Professional Paper 701–A, 57 p.

Moffett, T.B., and Moser, P.H., 1978, Ground-water resources of the Birmingham and Cahaba Valleys, Jefferson County, Alabama: Geological Survey of Alabama Circular 103, 78 p.

Nemickas, Bronius, 1976, Geology and ground-water resources of Union County, New Jersey: U.S. Geological Survey Water-Resources Investigations Report 76–73, 103 p.

Newport, T.G., 1971, Ground-water resources of Montgomery County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report Bulletin W 29, 83 p.

———1977, Summary ground-water resources of Luzerne County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 40, 63 p.

Nutter, L.J., 1973, Hydrogeology of the carbonate rocks, Frederick and Hagerstown Valleys, Maryland: U.S. Geological Survey Report of Investigations 19, p. 34–44.

———1977, Ground-water resources of Harford County, Maryland: Maryland Geological Survey Bulletin 32, p. 25–35.

Patterson, G.G., and Padgett, G.G., 1984, Quality of water from bedrock aquifers in the South Carolina Piedmont: U.S. Geological Survey Water-Resources Investigations Report 84–4028, 24 p.

Paulachok, G.N., 1991, Geohydrology and ground-water resources of Philadelphia, Pennsylvania: U.S. Geological Survey Water-Supply Paper 2346, p. 47–68.

Paulachok, G.N., Wood, C.R., and Norton, L.J., 1984, Hydrologic data for aquifers in Philadelphia, Pennsylvania: U.S. Geological Survey Open-File Report 83–149, 104 p.

Pettijohn, R.A., 1986, Processing water-chemistry data, Gulf Coast aquifer systems, south-central United States, with summary of dissolved-solids concentrations and water types: U.S. Geological Survey Water-Resources Investigations Report 86–4186, 42 p.

———1996, Geochemistry of ground water in the Gulf Coast aquifer systems, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 96–4107, 158 p.

Pettijohn, R.A., Busby, J.F., and Beckman, J.D., 1992, Properties and chemical constituents in ground water from the Mississippi River Valley alluvial aquifer and permeable zone A (Holocene-upper Pleistocene deposits), south-central United States: U.S. Geological Survey Water-Resources Investigations Report 91–4149, 5 sheets, scale 1:3,500,000.

———1993, Properties and chemical constituents in ground water from permeable zone D (middle Miocene deposits), coastal lowlands aquifer system, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 92–4105, 5 sheets, scale 1:3,500,000.

———1993, Properties and chemical constituents in ground water from the middle Wilcox aquifer, Gulf Coast regional aquifer systems, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 93–4070, 5 sheets, scale 1:3,500,000.

———1993, Properties and chemical constituents in ground water from the lower Wilcox aquifer, Mississippi embayment aquifer system, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 93–4071, 5 sheets, scale 1:3,500,000.

Pettijohn, R.A., Busby, J.F., and Cervantes, M.A., 1993, Properties and chemical constituents in ground water from permeable zone C (lower Pliocene-upper Miocene deposits), coastal lowlands aquifer system, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 91–4151, 5 sheets, scale 1:3,500,000.

———1993, Properties and chemical constituents in ground water from the lower Claiborne-upper Wilcox aquifer, Gulf Coast regional aquifer systems, south- central United States: U.S. Geological Survey Water-Resources Investigations Report 92–4102, 5 sheets, scale 1:3,500,000.

———1993, Properties and chemical constituents in ground water from the middle Claiborne aquifer, Gulf Coast regional aquifer systems, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 92–4104, 5 sheets, scale 1:3,500,000.

Pettijohn, R.A., Busby, J.F., and Layman, T.B., 1993, Properties and chemical constituents in ground water from the upper Claiborne aquifer, Gulf Coast regional aquifer systems, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 91–4150, 5 sheets, scale 1: 3,500,000.

———1993, Properties and chemical constituents in ground water from permeable zone B (lower Pleistocene-upper Pliocene deposits), coastal lowlands aquifer system, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 91–4152, 5 sheets, scale 1:3,500,000.

———1993, Properties and chemical constituents in ground water from permeable zone E (lower Miocene-upper Oligocene deposits), coastal lowlands aquifer system, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 92–4103, 5 sheets, scale 1:3,500,000.

Pettijohn, R.A., Weiss, J.S., and Williamson, A.K., 1988, Distribution of dissolved-solids concentrations and temperature in ground water of the Gulf Coast aquifer systems, south-central United States: U.S. Geological Survey Water-Resources Investigations Report 88–4082, 5 sheets, scale 1:3,500,000.

Piper, A.M., 1944, A graphic procedure in the geochemical interpretation of water analyses: American Geophysical Union Transactions, v. 25, p. 914–923.

Posner, Alex, and Zenone, Chester, 1983, Chemical quality of ground water in the Culpeper Basin, Virginia and Maryland: U.S. Geological Survey Miscellaneous Investigations Series map I–1313–D, 1 sheet, scale 1:250,000.

Poth, C.W., 1968, Hydrology of the metamorphic and igneous rocks of central Chester County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 25, 84 p.

———1972, Hydrology of the Martinsburg Formation in Lehigh and Northhampton Counties, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 30, p. 19–50.

———1977, Summary ground-water resources of Lancaster County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 43, 80 p.

Powell, J.D., and Abe, J.M., 1985, Availability and quality of ground water in the Piedmont Province of Virginia: U.S. Geological Survey Water-Resources Investigations Report 85–4235, 32 p.

Powell, J.D., and Hamilton, P.A., 1987, Virginia ground-water quality: U.S. Geological Survey Open-File Report 87–759, 7 p.

Puffer, J.H., and Asemota, Isaac, 1986, Sulfide mineral distribution of northern New Jersey rock formations and their surface drainage induced acid generating capacity: New Brunswick, N.J., Rutgers University Center for Coastal and Environmental Studies, Division of Water Resources, 33 p.

Radtke, D.B., Cressler, C.W., Perlman, H.A., Blanchard, H.E., Jr., McFadden, K.W., and Brooks, Rebekah, 1986, Occurrence and availability of ground water in the Athens region, northeastern Georgia: U.S. Geological Survey Water-Resources Investigations Report 86–4075, p. 34–41.

Rasmussen W.C., Groot, J.J., Martin, R.O.R., McCarren, E.F., Behn, V.C., and others, 1957, The water resources of northern Delaware, Delaware Geological Survey Bulletin 6, v. 1, 223 p.

Richardson, C.A., 1982, Ground water in the Piedmont upland of central Maryland: U.S. Geological Survey Water-Supply Paper 2077, 42 p.

Royer, D.W., 1983, Summary groundwater resources of Lebanon County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 55, p. 37–49, 56–84.

Runnells, D.D., 1993, Inorganic chemical processes and reactions, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 131–153.

Rutledge, A.T., and Mesko, T.O., 1996, Estimated hydrologic characteristics of shallow aquifer systems in the Valley and Ridge, the Blue Ridge, and the Piedmont Physiographic Provinces based on analysis of streamflow recession and base flow: U.S. Geological Survey Professional Paper 1422–B, 58 p.

Saad, D.A., and Hippe, D.J., 1990, Large springs in the Valley and Ridge Physiographic Province in Pennsylvania: U.S. Geological Survey Open-File Report 90–164, 17 p.

Sanford, T.H., Jr., 1966, Ground water in Marshall County, Alabama—a reconnaissance: Geological Survey of Alabama Bulletin 85, 66 p.

Scott, J.C., and Lines, G.C., 1973, Water availability, Lee County, Alabama: Geological Survey of Alabama Map 131, 29 p.

Seaber, P.R., Brahana, J.V., and Hollyday, E.F., 1988, Region 20, Appalachian Plateaus and Valley and Ridge, *in* Back, William, Rosenshein, J.S., and Seaber, P.R., eds., Hydrogeology: Boulder, Colo., Geological Society of America, The Geology of North America, v. O-2, p. 189–200.

Senior, L.A., and Vogel, K.L., 1989, Geochemistry of radium-226 and radium-228, and radon-222 in ground water in the Chickies Quartzite, southeastern Pennsylvania, *in* Daniel, C.C., III, White, R.K., and Stone, P.A., eds., Ground water in the Piedmont: Clemson, S.C., Clemson University, p. 547–565.

Shedlock, R.J., Hamilton, P.A., Denver, J.M., and Phillips, P.J., 1993, Multiscale approach to regional ground-water-quality assessment of the Delmarva Peninsula, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 563–587.

Simmons, C.E., and Heath, R.C., 1982, Water-quality characteristics of streams in forested and rural areas of North Carolina: U.S. Geological Survey Water-Supply Paper 2185–B, 33 p.

Slaughter, T.H., and Darling, J.M., 1962, The water resources of Allegany and Washington Counties: Maryland Department of Geology, Mines, and Water Resources Bulletin 24, p. 1–244.

Sloto, R.A., 1989, Selected ground-water data, Chester County, Pennsylvania: U.S. Geological Survey Open-File Report 87–217, 198 p.

Sloto, R.A., and Davis, D.K., 1983, Effect of urbanization on the water resources of Warminster Township, Bucks County, Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 82–4020, 72 p.

Speiran, G.K., and Aucott, W.A., 1994, Effects of sediment depositional environment and ground-water flow on the quality and geochemistry of water in aquifers in sediments of Cretaceous age in the Coastal Plain of South Carolina: U.S. Geological Survey Water-Supply Paper 2416, 53 p.

Stuart, W.T., Schneider, W.J., and Crooks, J.W., 1967, Swatara Creek basin of southeastern Pennsylvania—an evaluation of its hydrologic system: U.S. Geological Survey Water-Supply Paper 1829, 79 p.

Stumm, Werner, and Morgan, J.J., 1981, Aquatic chemistry—an introduction emphasizing chemical equilibria in natural waters (2d ed.): New York, Wiley-Interscience, 780 p.

Subitzky, Seymour, 1955, Summary of geology and ground-water conditions in the Fredericksburg District, eastern Spotsylvania County, Virginia: Virginia Division of Geology Mineral Resources Circular 4, 32 p.

Sun, P-C., Criner, J.H., and Poole, J.L., 1963, Large springs of east Tennessee: U.S. Geological Survey Water-Supply Paper 1755, 52 p.

Sun, R.J., and Weeks, J.B., 1991, Bibliography of Regional Aquifer-System Analysis Program of the U.S. Geological Survey, 1978–91: U.S. Geological Survey Water-Resources Investigations Report 91–4122, 92 p.

Swain, L.A., Hollyday, E.F., Daniel, C.C., III, and Mesko, T.O., 1992, An overview of the Appalachian Valleys-Piedmont Regional Aquifer-System Analysis, *in* Hotchkiss, W.R., and Johnson, A.I., eds., Regional Aquifer Systems of the United States, Aquifers of the Southern and Eastern States: American Water Resources Association Monograph Series, no. 17, p. 43–57.

Swain, L.A., Hollyday, E.F., Daniel, C.C., III, and Zapecza, O.S., 1991, Plan of study for the regional aquifer-system analysis of the Appalachian Valley and Ridge, Piedmont, and Blue Ridge Physiographic Provinces of the eastern and southeastern United States, with a description of study-area geology and hydrogeology: U.S. Geological Survey Water-Resources Investigations Report 91–4066, 44 p.

Szabo, Zoltan, Zapecza, O.S., and Nawyn, J.P., 1989, Effects of ground-water geochemistry on the distribution of dissolved uranium and radium-226 in the Newark basin, New Jersey, *in* Daniel, C.C., III, White, R.K., and Stone, P.A., eds., Ground water in the Piedmont: Clemson, S.C., Clemson University, p. 566–586.

Taylor, L.E., and Royer, D.W., 1981, Summary ground-water resources of Adams County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 52, p. 19–26, 34–50.

Taylor, L.E., Werkheiser, W.H., duPont, N.S., and Kriz, M.L., 1982, Groundwater resources of the Juniata River basin, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 54, p. 30–43, 84–129.

Taylor, L.E., Werkheiser, W.H., and Kriz, M.L., 1983, Groundwater resources of the west branch of the Susquehanna River basin, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 56, p. 31–44, 86–141.

Trapp, Henry, Jr., and Horn, M.A., 1997, Ground water atlas of the United States—segment 11 Delaware, Maryland, New Jersey, North Carolina, Pennsylvania, Virginia, West Virginia: U.S. Geological Survey Hydrologic Investigations Atlas 730–L, 24p.

Trombley, T.J., and Zynjuk, L.D., 1985, Hydrology and water quality of the Catoctin Mountain National Park, Frederick County, Maryland: U.S. Geological Survey Water-Resources Investigations Report 85–4241, p. 24–37.

Tukey, J.W., 1977, Exploratory data analysis: Reading, Mass., Addison-Wesley, 688 p.

U.S. Environmental Protection Agency, 1995, Drinking water regulations and health advisories: Washington, D.C., Office of Water, 11 p.

U.S. Geological Survey, 1970, National atlas of the United States of America: U.S. Geological Survey, 417 p.

———1985, National Water Summary, 1984—Hydrologic events, selected water-quality trends, and ground-water resources: U.S. Geological Survey Water-Supply Paper 2275, 467 p.

———1988, National Water Summary, 1986—Hydrologic events and ground-water quality: U.S. Geological Survey Water-Supply Paper 2325, 560 p.

———1993, National Water Summary, 1990–91—Hydrologic events and stream water quality: U.S. Geological Survey Water-Supply Paper 2400, 590 p.

U.S. Geological Survey and U.S. Bureau of Mines, 1968, Mineral resources of the Appalachian region: U.S. Geological Survey Professional Paper 580, 492 p.

Virginia State Water Control Board, 1973, Ground water in Virginia—quality and withdrawals: Virginia State Water Control Board Basic Data Bulletin 38, 177 p.

Waller, J.O., 1976, Geohydrology of the upper Roanoke River basin, Virginia: Virginia State Water Control Board Planning Bulletin 302, p. 17, C1–C11.

Warman, J.C., and Causey, L.V., 1962, Geology and ground water resources of Calhoun County, Alabama: Alabama Geological Survey County Report 7, p. 66–71.

Watson, T.W., 1974, Hydrogeology of Greene, Morgan, and Putnam Counties: Georgia Department of Natural Resources Information Circular 60, p. 10.

Webster, D.A., and Carmichael, J.K., 1993, Ground-water hydrology of the lower Wolftever Creek basin, with emphasis on the Carson Spring area, Hamilton County, Tennessee: U.S. Geological Survey Water-Resources Investigations Report 91–4190, p. 31–44.

White, W.B., 1993, Analysis of karst aquifers, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 471–489.

Wood, C.R., 1980a, Groundwater resources of the Gettysburg and Hammer Creek Formations, southeastern Pennsylvania: Pennsylvania Geological Survey Water Resource Report 49, p. 36–54, 60–87.

———1980b, Summary groundwater resources of Centre County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 48, p. 13–14, 48–60.

Wood, C.R., Flippo, H.N., Jr., Lescinsky, J.B., and Barker, J.L., 1972, Water resources of Lehigh County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 31, 263 p.

Wood, C.R., and MacLachlan, D.B., 1978, Geology and groundwater resources of northern Berks County, Pennsylvania: Pennsylvania Geological Survey Water Resource Report 44, p. 54–91.

Wood, P.R., and Johnston, H.E., 1964, Hydrology of the New Oxford Formation in Adams and York Counties, Pennsylvania: Pennsylvania Geological Survey Ground Water Report Bulletin W 21, p. 31–37, 62–66.

Wright, W.G., 1990, Ground-water hydrology and quality in the Valley and Ridge and Blue Ridge Physiographic Provinces of Clarke County, Virginia: U.S. Geological Survey Water-Resources Investigations Report 90–4134, 61 p.

APPENDIXES

APPENDIX A.—NATIONAL WATER INFORMATION SYSTEM WATER-QUALITY DATA BASE FOR THE APPALACHIAN VALLEY AND RIDGE, THE BLUE RIDGE, AND THE PIEDMONT REGIONAL-AQUIFER SYSTEM ANALYSIS STUDY AREA

CONTENTS

TABLES

Introduction

The principal source of water-quality data used in this study is the U.S. Geological Survey's computerized data base, the National Water Information System (NWIS). For the study area, the NWIS contains approximately 194,000 records from 13,935 sites. Each record contains one or more water-quality measurements made at specific site on a specific date. Chemical data were retrieved from NWIS files at USGS offices in 10 states and were compiled into a unified data base. The only selection criteria used for retrieval from the NWIS were (1) a list of Federal Information Processing Standards (FIPS) identification codes for counties and independent cities[1] in the study area (table A–1), and (2) a list of parameter codes for water properties and constituents (table A–2). Both lists were compiled at the beginning of the study and were revised periodically.

Types of Sites

Because no other restrictions were placed on data selection, data were retrieved for the period of record for all types of data-collection sites in the study area. The chemical data base, therefore, contains data for ground water, surface water, springs, and several minor categories of data-collection sites that are not included in this report. In the assembled data base, type of site is identified to permit isolation of data and facilitate study.

Site-location Information

Information pertaining to the location of sites in the data base includes latitude and longitude (in degrees, minutes, and seconds), the FIPS code, and the physiographic province, which were obtained from geographic-information-system (GIS) coverages produced during the study (Thomas Mesko, U.S. Geological Survey, written commun., 1991).

Codes for Water Properties and Constituents

To identify properties and constituents in the data base, the NWIS uses a five-digit parameter code system developed by the U.S. Environmental Protection Agency for its STORET Database. Each parameter code defines a specific set of attributes for the constituent including the chemical species, reporting form, reporting units, sampling matrix, filter size, and analysis recovery (total, dissolved, recoverable). A weakness of the five-digit parameter code system is that the analytical method used to determine the data is not identified. To provide this information, codes indicating the method, precision, and quality-assurance data were added to the NWIS in 1983. For most of the 194,000 analyses retrieved from the NWIS, however, this information is not available.

Use of the NWIS data base for regional studies is comparatively recent, although many state-level projects have used NWIS data from adjoining states. The main problem with the use of the NWIS on a regional scale is the diversity of parameter codes represented in the data base. A preliminary survey of the number of codes used by 10 USGS offices in the study area produced a total of 1,434 different codes. From this list, 24 properties and constituents were selected for retrieval from all 10 offices (table A–2).

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[1] In Virginia, independent cities are not part of adjacent counties and have individual FIPS codes.

TABLE A–1.—*Federal Information Processing Standards identification codes for counties and independent cities in the study area*

County name	Code	County name	Code	County name	Code
ALABAMA					
Bibb	01007	Coosa	01037	Russell	01113
Blount	01009	De Kalb	01049	Saint Clair	01115
Calhoun	01015	Elmore	01051	Shelby	01117
Chambers	01017	Etowah	01055	Talladega	01121
Cherokee	01019	Jefferson	01073	Tallapoosa	01123
Chilton	01021	Lee	01081	Tuscaloosa	01125
Clay	01027	Macon	01087		
Cleburne	01029	Randolph	01111		
DELAWARE					
New Castle	10003				
DISTRICT OF COLUMBIA					
Washington	11001				
GEORGIA					
Baldwin	13009	Gilmer	13123	Oconee	13219
Banks	13011	Glascock	13125	Oglethorpe	13221
Barrow	13013	Gordon	13129	Paulding	13223
Bartow	13015	Greene	13133	Pickens	13227
Bibb	13021	Gwinnett	13135	Pike	13231
Butts	13035	Habersham	13137	Polk	13233
Carroll	13045	Hall	13139	Putnam	13237
Catoosa	13047	Hancock	13141	Rabun	13241
Chattooga	13055	Haralson	13143	Richmond	13245
Cherokee	13057	Harris	13145	Rockdale	13247
Clarke	13059	Hart	13147	Spalding	13255
Clayton	13063	Heard	13149	Stephens	13257
Cobb	13067	Henry	13151	Talbot	13263
Columbia	13073	Jackson	13157	Taliaferro	13265
Coweta	13077	Jasper	13159	Taylor	13269
Crawford	13079	Jones	13169	Towns	13281
Dade	13083	Lamar	13171	Troup	13285
Dawson	13085	Lincoln	13181	Union	13291
De Kalb	13089	Lumpkin	13187	Upson	13293
Douglas	13097	McDuffie	13189	Walker	13295
Elbert	13105	Madison	13195	Walton	13297
Fannin	13111	Meriwether	13199	Warren	13301
Fayette	13113	Monroe	13207	Washington	13303
Floyd	13115	Morgan	13211	White	13311
Forsyth	13117	Murray	13213	Whitfield	13313
Franklin	13119	Muscogee	13215	Wilkes	13317
Fulton	13121	Newton	13217		

TABLE A–1.—*Federal Information Processing Standards identification codes for counties and independent cities in the study area—Continued*

County name	Code	County name	Code	County name	Code
MARYLAND					
Allegany	24001	Cecil	24015	Montgomery	24031
Baltimore	24005	Frederick	24021	Prince Georges	24033
Baltimore City	24510	Harford	24025	Washington	24043
Carroll	24013	Howard	24027		
NEW JERSEY					
Bergen	34003	Mercer	34021	Somerset	34035
Essex	34013	Middlesex	34023	Sussex	34037
Hudson	34017	Morris	34027	Union	34039
Hunterdon	34019	Passaic	34031	Warren	34041
NORTH CAROLINA					
Alamance	37001	Gaston	37071	Orange	37135
Alexander	37003	Graham	37075	Person	37145
Alleghany	37005	Granville	37077	Polk	37149
Anson	37007	Guilford	37081	Randolph	37151
Ashe	37009	Halifax	37083	Richmond	37153
Avery	37011	Harnett	37085	Rockingham	37157
Buncombe	37021	Haywood	37087	Rowan	37159
Burke	37023	Henderson	37089	Rutherford	37161
Cabarrus	37025	Iredell	37097	Stanly	37167
Caldwell	37027	Jackson	37099	Stokes	37169
Caswell	37033	Johnston	37101	Surry	37171
Catawba	37035	Lee	37105	Swain	37173
Chatham	37037	Lincoln	37109	Transylvania	37175
Cherokee	37039	McDowell	37111	Union	37179
Clay	37043	Macon	37113	Vance	37181
Cleveland	37045	Madison	37115	Wake	37183
Davidson	37057	Mecklenburg	37119	Warren	37185
Davie	37059	Mitchell	37121	Watauga	37189
Durham	37063	Montgomery	37123	Wilkes	37193
Edgecombe	37065	Moore	37125	Wilson	37195
Forsyth	37067	Nash	37127	Yadkin	37197
Franklin	37069	Northampton	37131	Yancey	37199
PENNSYLVANIA					
Adams	42001	Clinton	42035	Juniata	42067
Bedford	42009	Columbia	42037	Lackawanna	42069
Berks	42011	Cumberland	42041	Lancaster	42071
Blair	42013	Dauphin	42043	Lebanon	42075
Bucks	42017	Delaware	42045	Lehigh	42077
Carbon	42025	Franklin	42055	Luzerne	42079
Centre	42027	Fulton	42057	Lycoming	42081
Chester	42029	Huntingdon	42061	Mifflin	42087

TABLE A–1.—*Federal Information Processing Standards identification codes for counties and independent cities in the study area — Continued*

County name	Code	County name	Code	County name	Code
		PENNSYLVANIA—CONTINUED			
Monroe	42089	Philadelphia	42101	Susquehanna	42115
Montgomery	42091	Pike	42103	Union	42119
Montour	42093	Schuylkill	42107	Wayne	42127
Northampton	42095	Snyder	42109	York	42133
Northumberland	42097	Somerset	42111		
Perry	42099	Sullivan	42113		
		SOUTH CAROLINA			
Abbeville	45001	Greenville	45045	Newberry	45071
Aiken	45003	Greenwood	45047	Oconee	45073
Anderson	45007	Kershaw	45055	Pickens	45077
Cherokee	45021	Lancaster	45057	Richland	45079
Chester	45023	Laurens	45059	Saluda	45081
Chesterfield	45025	Lexington	45063	Spartanburg	45083
Edgefield	45037	McCormick	45065	Union	45087
Fairfield	45039	Marlboro	45069	York	45091
		TENNESSEE			
Anderson	47001	Hamilton	47065	Monroe	47123
Blount	47009	Hancock	47067	Morgan	47129
Bradley	47011	Hawkins	47073	Polk	47139
Campbell	47013	Jefferson	47089	Rhea	47143
Carter	47019	Johnson	47091	Roane	47145
Claiborne	47025	Knox	47093	Sevier	47155
Cocke	47029	Loudon	47105	Sullivan	47163
Grainger	47057	McMinn	47107	Unicoi	47171
Greene	47059	Marion	47115	Union	47173
Hamblen	47063	Meigs	47121	Washington	47179
		VIRGINIA			
Albemarle	51003	Campbell	51031	Franklin	51067
Alleghany	51005	Caroline	51033	Frederick	51069
Amelia	51007	Carroll	51035	Giles	51071
Amherst	51009	Charlotte	51037	Goochland	51075
Appomattox	51011	Chesterfield	51041	Grayson	51077
Arlington	51013	Clarke	51043	Greene	51079
Augusta	51015	Craig	51045	Greensville	51081
Bath	51017	Culpeper	51047	Halifax	51083
Bedford	51019	Cumberland	51049	Hanover	51085
Bland	51021	Dinwiddie	51053	Henrico	51087
Botetourt	51023	Fairfax	51059	Henry	51089
Brunswick	51025	Fauquier	51061	Highland	51091
Buchanan	51027	Floyd	51063	Lee	51105
Buckingham	51029	Fluvanna	51065	Loudoun	51107

TABLE A–1.—*Federal Information Processing Standards identification codes for counties and independent cities in the study area — Continued*

County name	Code	County name	Code	County name	Code
VIRGINIA—CONTINUED					
Louisa	51109	Powhatan	51145	Smyth	51173
Lunenburg	51111	Prince Edward	51147	Spotsylvania	51177
Madison	51113	Prince William	51153	Stafford	51179
Mecklenburg	51117	Pulaski	51155	Sussex	51183
Montgomery	51121	Rappahannock	51157	Tazewell	51185
Nelson	51125	Roanoke	51161	Warren	51187
Nottoway	51135	Rockbridge	51163	Washington	51191
Orange	51137	Rockingham	51165	Wise	51195
Page	51139	Russell	51167	Wythe	51197
Patrick	51141	Scott	51169		
Pittsylvania	51143	Shenandoah	51171		
VIRGINIA (INDEPENDENT CITIES)—CONTINUED					
Alexandria	51510	Fairfax	51600	Norton	51720
Bedford	51515	Falls Church	51610	Petersburg	51730
Bristol	51520	Fredericksburg	51630	Radford	51750
Buena Vista	51530	Galax	51640	Richmond	51760
Charlottesville	51540	Harrisonburg	51660	Roanoke	51770
Clifton Forge	51560	Lexington	51678	Salem	51775
Colonial Heights	51570	Lynchburg	51680	South Boston	51780
Covington	51580	Manassas	51683	Staunton	51790
Danville	51590	Manassas Park	51685	Waynesboro	51820
Emporia	51595	Martinsville	51690	Winchester	51840
WEST VIRGINIA					
Berkeley	54003	Jefferson	54037	Morgan	54065
Grant	54023	McDowell	54047	Pendleton	54071
Greenbrier	54025	Mercer	54055	Pocahontas	54075
Hampshire	54027	Mineral	54057	Randolph	54083
Hardy	54031	Monroe	54063	Tucker	54093

TABLE A–2.—*National Water Information System parameter codes for selected water properties and constituents*

Code	Water-quality characteristic and unit
00095	Specific conductance, field measurement, microsiemens per centimeter at 25 degrees Celsius
70300	Dissolved solids, residue on evaporation at 180^0 Celsius, milligrams per liter
00400	pH, field measurement, standard units
00010	Water temperature, degrees Celsius
00300	Dissolved-oxygen concentration, milligrams per liter
00915	Calcium concentration, milligrams per liter
00925	Magnesium concentration, milligrams per liter
00930	Sodium concentration, milligrams per liter
00935	Potassium concentration, milligrams per liter
00440	Bicarbonate concentration, field measurement, fixed-endpoint titration, milligrams per liter
00410	Total alkalinity, as calcium carbonate, field measurement, fixed-endpoint titration, milligrams per liter
00900	Carbonate hardness, as calcium carbonate, milligrams per liter
00945	Sulfate concentration, milligrams per liter
00940	Chloride concentration, milligrams per liter
00950	Fluoride concentration, milligrams per liter
00955	Dissolved-silica concentration, as SiO_2, milligrams per liter
00630	Total nitrite plus nitrate concentration, as nitrogen, milligrams per liter
00610	Total-ammonia concentration, as nitrogen, milligrams per liter
00666	Dissolved-phosphorus concentration, as phosphorus, milligrams per liter
00665	Total-phosphorus concentration, as phosphorus, milligrams per liter
01046	Dissolved-iron concentration, micrograms per liter
01045	Total-iron concentration, micrograms per liter
01056	Dissolved-manganese concentration, micrograms per liter
01055	Total-manganese concentration, micrograms per liter

APPENDIX B.—SHADED-GRID TRILINEAR DIAGRAMS—A METHOD FOR SHOWING VARIATIONS IN CHEMICAL COMPOSITION FOR UNLIMITED NUMBERS OF WATER SAMPLES

CONTENTS

FIGURES

TABLES

Introduction

The water-quality data base for the Appalachian Valley and Ridge, the Blue Ridge, and the Piedmont Regional-Aquifer System Analysis (APRASA) study area contains 52,372 samples that have enough information to display chemical composition on a Piper diagram. Although there is no theoretical limit to the number of samples that can be shown on this type of figure, resolution of individual samples becomes difficult as the number of adjacent samples increases. A Piper diagram containing 52,372 samples would be unreadable. Even if these samples are grouped by type of site and physiographic province, similarities in chemical composition produce too many points clustered together to discern systematic variations as a function of the group. On these diagrams, trends in chemical composition are apparent (fig. B–1*A*), but they are difficult to isolate because a general scatter of points fills most of the area.

Approach

A modified trilinear diagram was developed to show general chemical composition of an unlimited number of water samples. On this diagram, the location of individual sample points is not shown directly. Instead, samples of similar chemical composition are shown as a group. The overlay of a 10-by-10 grid on the diamond-shaped field of a Piper diagram divides this area into 100 diamond-shaped cells of equal size. Similarly, the overlay of a 10-by-10-by-10 grid on the triangular fields divides each of these areas into 100 triangular cells of equal size; the triangular cells are half the size of the diamond-shaped cells. All sample compositions are located within specific cells (fig. B–1*A*), and the population of each cell can be determined (fig. B–1*B*). Each field of the new diagram is a numerical summary of the distribution of samples across the grid, without loss of resolution due to large numbers of adjacent samples.

The presentation of cell populations across the grid can be further simplified by dividing the 100 cells in each field into seven categories that range from unpopulated cells to densely populated cells. Each cell population can be ranked according to its position in the distribution of cell populations for the field, and ranks can be grouped into ranges that are displayed on the grided diagram with a common shading (fig. B–1*C*). Cells that contain large numbers of samples are filled with the most intense shading, and cells that contain small numbers of samples are filled with light shading; unoccupied cells are not shaded. Percentiles for the distribution of 100 cell populations in each field are a convenient basis for defining range limits (table B–1); however, range limits and the number of categories can be adjusted to suit individual applications.

TABLE B–1.—*Method used to assign cell color on shaded-grid trilinear diagrams*

Category	Cell count		Cell color and shade
	Lower limit	Upper limit	
1	0	0	Not shaded
2	1	25th percentile	Light gray
3	25th percentile + 1	50th percentile	Medium gray
4	50th percentile + 1	75th percentile	Dark gray
5	75th percentile + 1	90th percentile	Black
6	90th percentile + 1	95th percentile	Light red
7	95th percentile + 1	Maximum count	Bright red

Advantages of the shaded-grid trilinear diagram are the following: (1) The format is similar to that of a conventional Piper diagram, but the shaded-grid diagram does not become cluttered as the number of samples increases. For large numbers of samples, the shaded-grid diagram is a clearer generalization of the data than is the standard Piper diagram. (2) Densely populated cells indicate dominant chemical compositions (modes) in a set of samples, and modal compositions can be easily determined from the grid. (3) The shaded-grid diagram can also show multiple modes and trends in chemical composition across the grid. (4) Sparsely populated cells around modes indicate limits for dominant compositions. (5) For different groups of samples, modes and trends in composition can be quickly compared and contrasted.

Limitations of the shaded-grid trilinear diagram are the following: (1) Special emphasis is given to boundaries of grid cells because adjacent samples across cell boundaries are separated, whereas samples in the same cell are combined. Small differences in the major-ion data can shift the sample point and affect the cell count. A 5-by-5 grid, which divides each field into 400 cells, provides a finer mesh for displaying the data, but—for a fixed number of samples—the cell populations are reduced. For a grid of any size, the relative error in the determination of cell populations decreases as the number of samples increases. (2) For small numbers of samples, the conventional Piper diagram provides useful information about the distribution of individual compositions that is not shown on the generalized diagram.

Use of a Geographic Information System

The shaded-grid trilinear diagrams shown in this report were produced by a special application of ARC / INFO geographic-information-system (GIS) software. To assign individual sample compositions to specific grid cells, a point coverage for each group of samples was overlain on a master polygon coverage containing the grid system for the trilinear diagram. The GIS software automatically resolves the problem of points located at cell boundaries. Cell populations were determined, and ARCPLOT software was used to produce the shaded-grid diagrams.

Summary

Shaded-grid trilinear diagrams were developed to display general chemical compositions of an unlimited number of water samples, without the loss of resolution that is common on a conventional Piper plot. Shaded-grid diagrams have been useful in interpreting variations in chemical composition for groups of samples in the APRASA study area, and they should prove useful in other investigations that involve analysis of large numbers of samples.

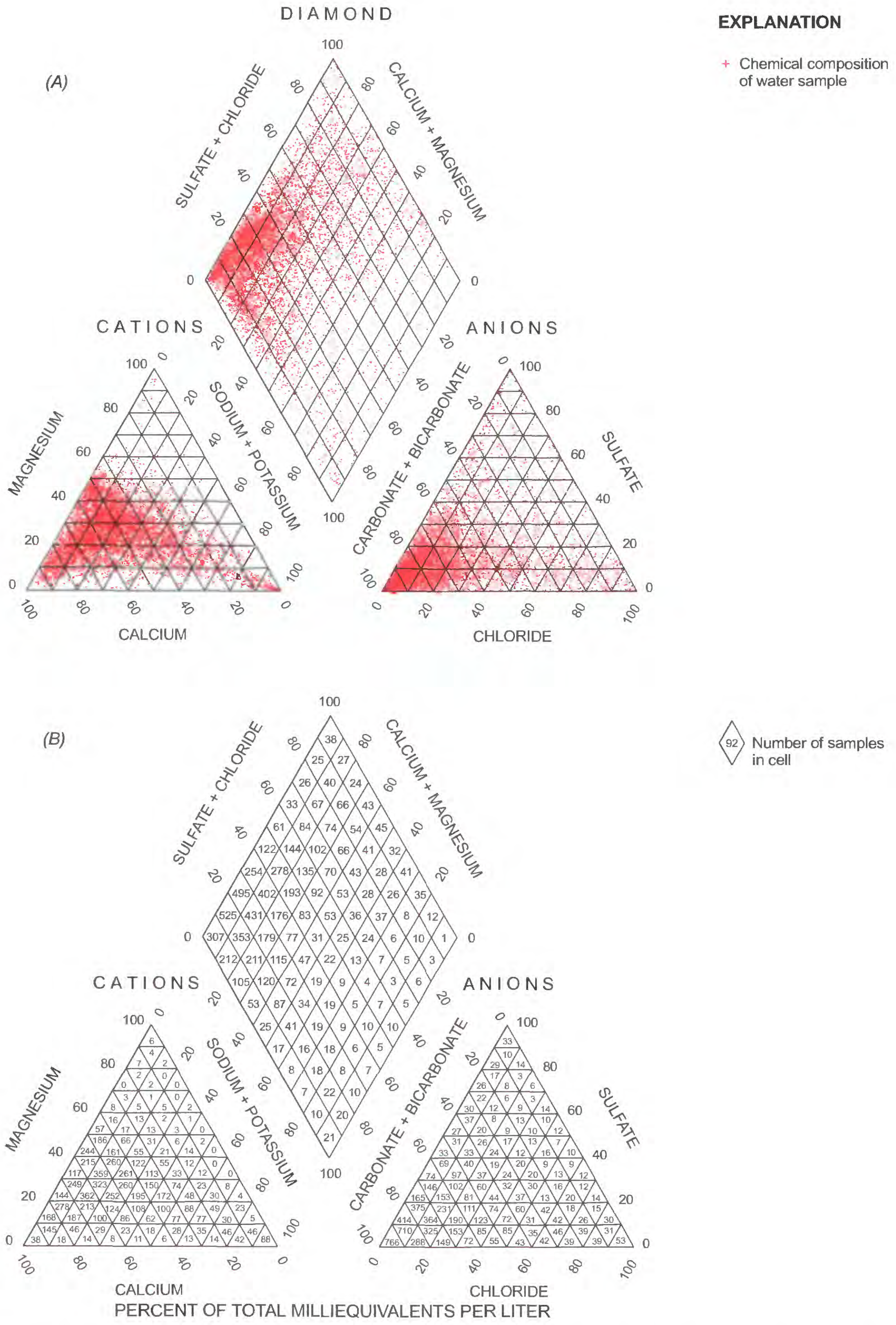

FIGURE B-1—Chemical composition of 7,251 water samples *(A)*, the number of samples in each grid cell *(B)*, and the general chemical composition of these samples *(C)*.

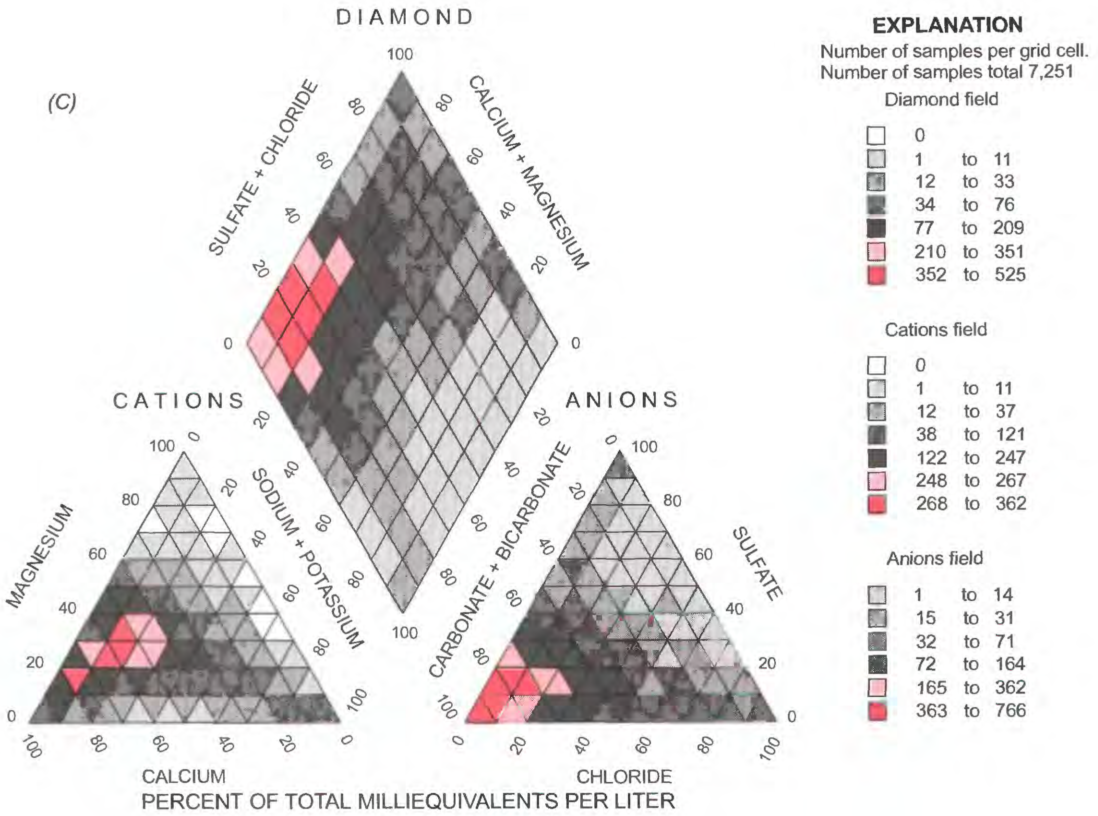

FIGURE B-1—Chemical composition of 7,251 water samples *(A)*, the number of samples in each grid cell *(B)*, and the general chemical composition of these samples *(C)*—Continued.

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