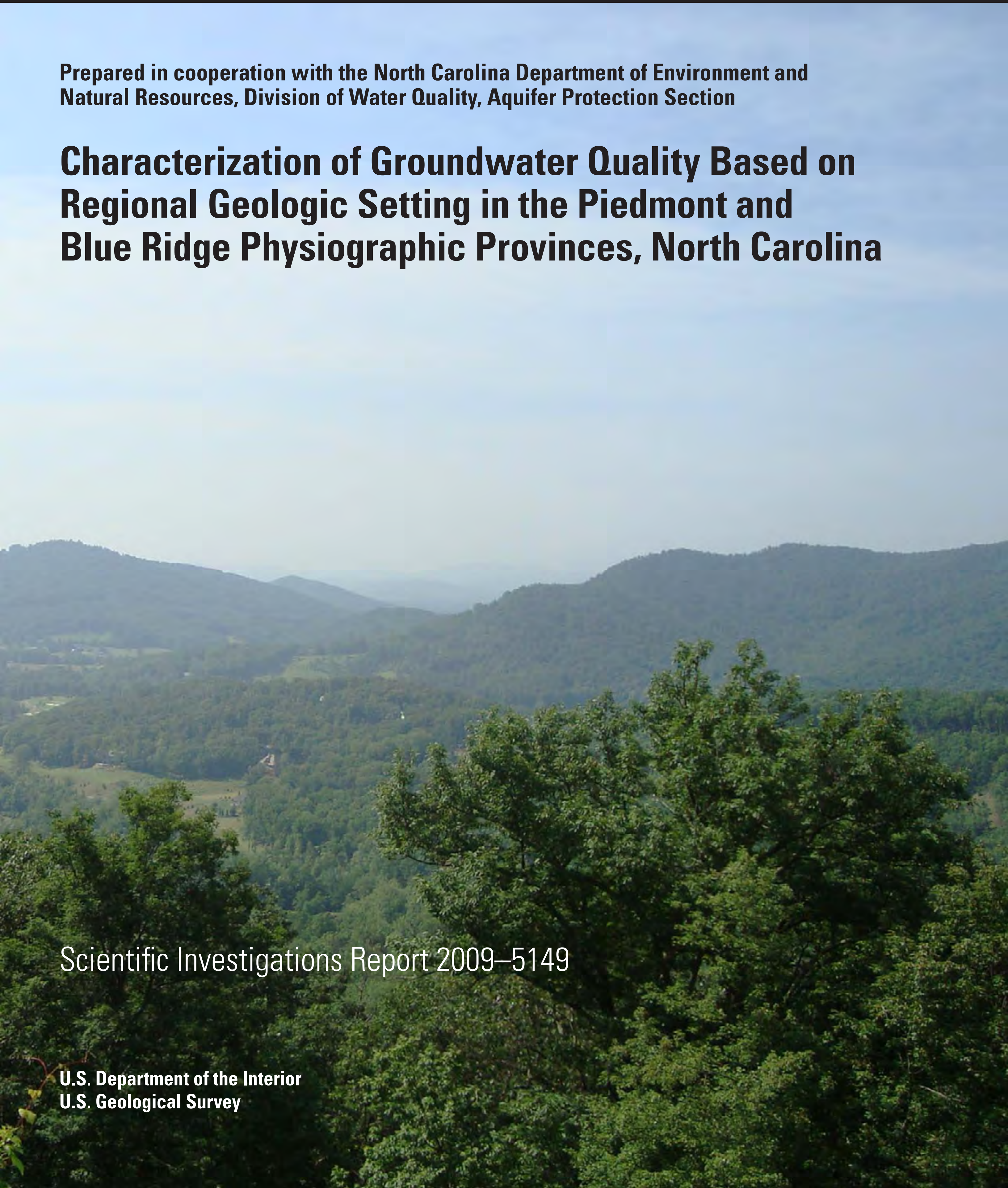
Prepared in cooperation with the North Carolina Department of Environment and
Natural Resources, Division of Water Quality, Aquifer Protection Section

Characterization of Groundwater Quality Based on Regional Geologic Setting in the Piedmont and Blue Ridge Physiographic Provinces, North Carolina



Scientific Investigations Report 2009–5149

U.S. Department of the Interior
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Front-cover photograph. Walnut Cove Overlook at mile marker 396 along the Blue Ridge Parkway, Buncombe County, North Carolina. Photograph by Jung-Jun Lin, Engineer, Tainan Hydraulics Laboratory, National Cheng Kung University, Taiwan. Used with permission.

Back-cover photograph. Groundwater monitoring well cluster at the North Carolina Zoological Park Research Station, Randolph County, North Carolina. Photograph by Kristin McSwain, U.S. Geological Survey.

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By Stephen L. Harden, Melinda J. Chapman, and Douglas A. Harned

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Contents

Note: Appendixes are available for download as Microsoft® Excel files from http://pubs.usgs.gov/sir/2009/5149/

Figures

Tables

Conversion Factors, Datums, and Abbreviated Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Radioactivity	
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Acronyms and Abbreviations

AMCL	alternative MCL
ANOVA	analysis of variance
APRASA	Appalachian Valley and Ridge, Blue Ridge, and Piedmont regional aquifer-system analysis
APS	Aquifer Protection Section of the NCDENR DWQ
AWRS	Allison Woods research station
BAT^3	Bedrock-Aquifer Transportable Testing Tool
BCRS	Bent Creek research station
DO	dissolved oxygen
DWQ	Division of Water Quality of the NCDENR
E	estimated
LPRS	Langtree Peninsula research station
LWRS	Lake Wheeler research station
MCL	maximum contaminant level
MDL	method detection limit
MMM	multimedia mitigation program
N	nitrogen
NAWQA	National Water-Quality Assessment Program
NCDENR	North Carolina Department of Environment and Natural Resources
NWQL	National Water Quality Laboratory
PAS	Piedmont Aquifer System
PMREP	Piedmont and Mountains Resource Evaluation Program
RHRS	Raleigh hydrogeologic research station
RL	reporting levels
ROS	regression on order statistics
SMCL	secondary maximum contaminant level
THRS	Tater Hill research station
UPRS	Upper Piedmont research station
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
ZPRS	Zoological Park research station

Characterization of Groundwater Quality Based on Regional Geologic Setting in the Piedmont and Blue Ridge Physiographic Provinces, North Carolina

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Abstract

A compilation of groundwater-quality data collected as part of two U.S. Geological Survey studies provides a basis for understanding the ambient geochemistry related to geologic setting in the Piedmont and Blue Ridge Physiographic Provinces (hereafter referred to as Piedmont and Mountains Provinces) of North Carolina. Although the geology is complex, a grouping of the sampled wells into assemblages of geologic units described as "geozones" provides a basis for comparison across the region. Analyses of these two data sets provide a description of water-quality conditions in bedrock aquifers of the Piedmont and Mountains Provinces of North Carolina. Analyzed data were collected between 1997 and 2008 from a network of 79 wells representing 8 regional geozones distributed throughout the Piedmont and Mountains Provinces. This area has experienced high rates of population growth and an increased demand for water resources. Groundwater was used by about 34 percent of the population in the 65 counties of this region in 2005. An improved understanding of the quality and quantity of available groundwater resources is needed to plan effectively for future growth and development. The use of regional geologic setting to characterize groundwater-quality conditions in the Piedmont and Mountains Provinces is the focus of this investigation.

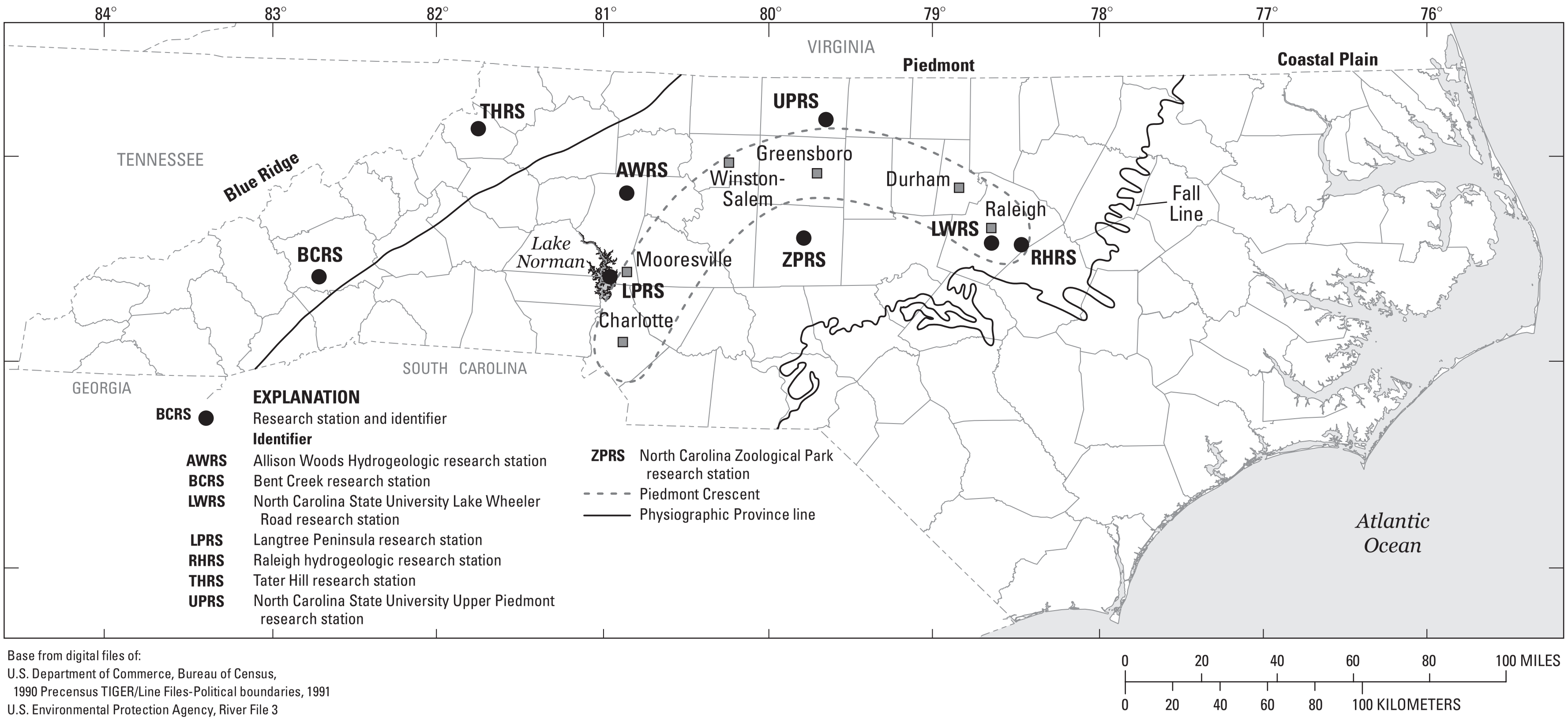
Data evaluation included an examination of selected properties and the ionic composition of groundwater in the geozones. No major differences in overall ionic chemistry of groundwater among the geozones were evident with the data examined. Variability in the cationic and anionic composition of groundwater within a particular geozone appeared to reflect local differences in lithologic setting, hydrologic and geochemical conditions, and(or) land-use effects. The most common exceedances of the drinking-water criteria (in accordance with Federal and State water-quality standards) occurred for radon, pH, manganese, iron, and zinc. Radon had the most exceedances, with groundwater from 61 of the 69 sampled wells having activities higher than the U.S. Environmental Protection Agency's proposed maximum contaminant level of 300 picocuries per liter. Overall, the Milton and the Raleigh and Charlotte geozones had the greatest number, eight each, of water-quality properties or constituents that exceeded applicable drinking-water criteria in at least one well. The Eastern Blue Ridge and Felsic intrusive geozones each had seven properties or constituents that exceeded criteria, and the Carolina slate geozone had six.

Based on limited data, initial results of statistical comparison tests identified statistically significant differences in concentrations of some groundwater constituents among the geozones. Statistically significant differences in median values of specific conductance and median concentrations of calcium, potassium, sodium, bicarbonate, chloride, silica, ammonia, aluminum, antimony, cadmium, and uranium were identified between one or more geozone pairs. Overall, the groundwater constituents appear to be influenced most significantly by the Inner Piedmont, Carolina slate, and Felsic intrusive geozones. The study data indicate that grouping and evaluating analytical data on the basis of regional geozone setting can be useful for characterizing water-quality conditions in bedrock aquifers of the Piedmont and Blue Ridge Provinces of North Carolina.

Introduction

Population in the Piedmont and Blue Ridge Physiographic Provinces (hereafter referred to as Piedmont and Mountains Provinces) of North Carolina, including all or part of 65 counties, has grown from about 2.66 million people in 1940 to 6.11 million people in 2000 (Daniel and Dahlen, 2002). In 2005, the estimated population of the region was 6.66 million people, an increase of about 9 percent from 2000 (U.S. Census Bureau, 2005). Associated with this high rate of population growth is an increased demand for water resources.

The percentage of the total population in the Piedmont and Mountains Provinces supplied by groundwater was about 47 percent between 1960 and 1980 and then decreased to about 32 percent in 1990 (Daniel and Dahlen, 2002). The percentage of the population in the region served by groundwater was about 41 percent in 2000 (U.S. Geological Survey, 2003) and about 34 percent in 2005 (U.S. Geological Survey, 2008a). These decreases are attributed primarily to the high rates of population growth associated with the five metropolitan areas of Raleigh, Durham, Greensboro, Winston-Salem, and Charlotte, known collectively as the "Piedmont Crescent" (fig. 1; Pippin and others, 2008) that are served primarily by



Base from digital files of:
U.S. Department of Commerce, Bureau of Census,
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Figure 1. Study area and locations of groundwater research stations used in the Piedmont Mountains Resource Evaluation Program in North Carolina.

surface-water based municipal supplies. The potential for future development of surface water may become limited to meet increased demands associated with population growth (Harned, 1989; Daniel and Dahlen, 2002). Consequently, the development of groundwater as a source of supply may become more important for meeting future demands in metropolitan areas of the Piedmont, and remains an important source of water supply for more than 2.25 million persons in the region. Because future drinking-water supplies are a primary concern in the Piedmont and Mountains Provinces, an improved understanding of the quality and quantity of available groundwater resources is needed by State and local agencies to plan effectively for growth and development.

Previous Studies

Groundwater quality in the crystalline igneous and metamorphic rock aquifers of the Piedmont and Mountains Provinces has been examined through various local and regional studies. Studies of ambient groundwater quality in bedrock wells associated with different rock types have varied in geographic extent, covering areas ranging from one or more counties to the physiographic-province scale.

LeGrand (1958) examined the chemical composition of water from various wells located in igneous and metamorphic rocks of the North Carolina Piedmont province. He noted chemical differences in groundwater between two rock groups, felsic rocks (granite, granite gneiss, mica schist, slate, and rhyolite flows and tuffs) and mafic rocks (diorite, gabbro, hornblende gneiss, and andesite flows and tuffs). Groundwater associated with the felsic rocks had low concentrations of dissolved solids, low hardness, a pH less than 7, and about equal amounts of sodium and calcium. The mafic rocks yielded groundwater that had higher concentrations of dissolved solids, greater hardness, a pH greater than 7, and a greater amount of calcium than sodium.

Similar results are noted for a groundwater study in Orange County, North Carolina, that examined water-quality results of groundwater samples from 51 domestic bedrock wells that were grouped into felsic rocks and mafic rocks (Cunningham and Daniel, 2001). The observed median values of dissolved solids (122 milligrams per liter (mg/L)), pH (6.66), bicarbonate (100 mg/L), calcium (18 mg/L), magnesium (3.9 mg/L), and sodium (8.4 mg/L) for groundwater in the felsic rocks generally were lower than median values of dissolved solids (176 mg/L), pH (7.10), bicarbonate (161 mg/L), calcium (34 mg/L), magnesium (5.6 mg/L), and sodium (8.1 mg/L) for groundwater in the mafic rocks. Although these results are consistent with the findings of LeGrand (1958), a statistical evaluation of the Orange County data indicated no significant differences in median concentrations for any of the sampled water-quality constituents (including common anions and cations, metals and trace elements, nutrients, and radon) between the felsic and mafic rock groups (Cunningham and Daniel, 2001).

Several previous investigations have assessed the distribution of naturally occurring contaminants, such as arsenic and radon, in groundwater in the Piedmont and Mountains Provinces (Loomis and others, 1987; Pippin, 2005; Campbell, 2006, 2008; Vinson and others, 2009). Arsenic and radon are known to pose a risk to human health. Natural occurrences of these contaminants in groundwater associated with bedrock aquifers, therefore, is an important environmental issue for more than 2.25 million people in the Piedmont and Mountains region who use groundwater as a source of water supply.

Pippin (2005) performed a spatial analysis of total arsenic in groundwater from wells located throughout the North Carolina Piedmont and found that wells in rock bodies of the Carolina Slate Belt in the area around Stanly and Union Counties had the greatest probability of containing elevated levels of arsenic above a concentration of 0.001 mg/L. Wells in some areas of the Kings Mountain Belt, Charlotte Belt, and Inner Piedmont Belt also had a relatively high probability of containing elevated arsenic concentrations. Rocks of volcanic or volcaniclastic origin associated with the high probability areas have the greatest potential for hosting wells with elevated arsenic concentrations (Pippin, 2005).

Concentrations of naturally occurring radon in groundwater of the Piedmont and Mountains Provinces generally are higher in metaigneous rocks than in metasedimentary rocks (Loomis and others, 1987; Campbell, 2006, 2008; Vinson and others, 2009). Loomis and others (1987) examined data from 96 public water-supply wells and found that groundwater radon levels were highest in granites and gneisses within the Blue Ridge, Inner Piedmont, and Raleigh Belt regions; lower levels were observed for mafic and metavolcanic rocks.

Similar results were observed in multicounty studies by Campbell (2006 and 2008) where groundwater radon concentrations were higher for wells in metaigneous rocks than for wells in metasedimentary rocks. Groundwater samples from 103 private supply wells in Buncombe, Henderson, and Transylvania Counties (Campbell, 2006) had a median radon concentration of 7,480 picocuries per liter (pCi/L) for wells in metaigneous rocks (including Henderson gneiss, Toxaway gneiss, meta-granodiorite, Caesar’s Head granite, and amphibolite) compared to a median radon concentration of 4,040 pCi/L for wells in metasedimentary rocks (including migmatitic biotite gneiss, garnet-mica schist, metagraywacke, biotite gneiss, muscovite-biotite gneiss, and rocks of the Brevard Fault zone). Groundwater samples from 87 private supply wells in 11 western North Carolina counties (Campbell, 2008) had a median radon concentration of 1,810 pCi/L for wells in metaigneous rocks (including Caeser’s Head granite, Cherryville granite, granitic gneiss, Henderson gneiss, porphyroblastic gneiss, and amphibolite) compared to a median radon concentration of 1,390 pCi/L for wells in metasedimentary rocks (including schists, para-gneisses, metagraywacke, and rocks of the Brevard Fault zone). In an investigation of 117 private supply wells in fractured crystalline rock in Wake County, Vinson and others (2009) noted that groundwater radon activities for wells in the Rolesville granite (monzogranite, granite, granodiorite, and pegmatite in places) were an order of magnitude higher compared to wells in the Raleigh gneiss (sedimentary and granitic components) and wells in metasedimentary and metavolcanic rocks (felsic gneiss, felsic schist, phyllite, meta-tuff, and some ultramafic rocks).

As part of the Appalachian Valley and Ridge, Blue Ridge, and Piedmont regional aquifer-system analysis (APRASA), Briel (1997) compiled and examined available groundwater-quality data spanning 11 eastern states from Alabama to New Jersey. A total of 10,564 wells with water-quality data were used to characterize the study area, with 25 percent of the wells (2,682) located in the Piedmont and Mountains Provinces of North Carolina (Briel, 1997). Regional and local variations in groundwater quality were observed among the physiographic provinces throughout the study area and reflected differences in geologic and hydrologic factors, such as lithology, the availability of soluble materials, and the degree of exposure of rock to water.

In a large-scale water-quality investigation of the bedrock aquifers of the Piedmont Physiographic Province of the eastern United States, Lindsey and others (2006) subdivided the Piedmont Aquifer System (PAS) on the basis of the general rock type of the aquifers into three areas for study, including crystalline, siliciclastic, and carbonate aquifers. The rocks in the Piedmont of North Carolina are primarily igneous and metamorphic and were considered as part of the crystalline aquifer system. Overall, constituent concentrations of nitrate, pesticides, and volatile organic compounds were related to land-use factors. The subgrouping of the three aquifer types based on the general rock lithology was not considered appropriate for analysis of radon where activities varied on the basis of variations in mineralogy (Lindsey and others, 2006). In general, radon activities were greater in the crystalline rock aquifer having felsic mineralogy than in the crystalline rock aquifer having mafic mineralogy. As part of their work, Lindsey and others (2006) indicated that further study of explanatory factors, including such things as spatial density of well networks, different land-use conditions, and aquifer rock lithologies, was needed for characterizing water-quality conditions in the PAS.

In 1999, the North Carolina Department of Environment and Natural Resources Division of Water Quality (NCDENR DWQ) Groundwater Section implemented the Piedmont and Mountains Resource Evaluation Program (PMREP) to evaluate groundwater resources in the crystalline bedrock aquifers of the Piedmont and Mountains Provinces (Daniel and Dahlen, 2002). The program is supported through a cooperative study, which began in 1999 between the NCDENR DWQ Aquifer Protection Section (APS), formerly known as the Groundwater Section, and the U.S. Geological Survey (USGS) North Carolina Water Science Center. The PMREP supports NCDENR DWQ's mission of preserving and protecting North Carolina's groundwater and surface-water resources by characterizing groundwater flow in a variety of hydrogeologic settings, as well as documenting the occurrence and mobility of both naturally occurring and land-use related contaminants (Daniel and Dahlen, 2002).

During the first part of the PMREP from 2000 through 2008, intensive field data collection and interpretive data analyses were conducted at research stations established in regionally representative hydrogeologic settings of the Piedmont and Mountains Provinces (Chapman and others, 2005, 2007; Huffman and others, 2006; Pippin and others, 2008). The research stations are located in areas having a range of geologic, hydrologic, and land-use characteristics where hydrogeologic processes and water-quality conditions have been described in diverse geologic regions of the Piedmont and Mountains Provinces (fig. 1). In this study, results of investigations conducted at selected PMREP research stations were combined with data from studies conducted as part of the USGS National Water-Quality Assessment (NAWQA) Program (Hughes and others, 2000; Kozar and others, 2001; Lindsey and others, 2006) to characterize water-quality conditions based on regional geologic settings in the Piedmont and Mountains Provinces of North Carolina.

Purpose and Scope

This report presents the results of an evaluation to determine whether grouping groundwater-quality data based on regional geologic setting may be a useful approach for characterizing ambient water-quality conditions in bedrock aquifers of the Piedmont and Mountains region in North Carolina. Water-quality data obtained from bedrock wells sampled as part of the PMREP and as part of USGS NAWQA studies were grouped into eight regional geologic zones, or "geozones" (as identified later in this report), distributed throughout the Piedmont and Mountains Provinces of North Carolina. Water-quality data (primarily inorganic constituents, including major ions, nutrients, metals, and radiochemical isotopes) are compiled and described for each geozone. Differences in water-quality constituents among the geozones were examined statistically. Study results can be used to characterize the influence of hydrogeologic setting on ambient groundwater quality in the North Carolina Piedmont and Mountains.

Description of the Study Area

The study area covers approximately 27,500 square miles (mi^2) and includes the Piedmont and Mountains Provinces of North Carolina (fig. 1). Groundwater in the Piedmont and Mountains Provinces flows in hydrogeologic settings composed primarily of metamorphic and igneous rocks that range in composition from felsic to ultramafic. Rocks in these regions have undergone several episodes of intense metamorphism, folding, faulting, and igneous intrusion. Weathered regolith, composed of soil, residuum, saprolite, alluvium, and colluvium, overlies the fractured bedrock (Heath, 1980).

Groundwater flow is complex, consisting of an interconnected but distinct two-component groundwater system, with the regolith providing storage to underlying fractures in the bedrock (Heath, 1980). A third component, the transition zone, commonly is present between the regolith and bedrock (Harned and Daniel, 1992). The transition zone generally is considered to be the most transmissive part of the groundwater-flow system and likely is susceptible to contamination. Because the shallow regolith and underlying bedrock fractures are connected, the aquifer systems of the Piedmont and Mountains Provinces are considered to be unconfined, although local confinement may occur where overlain by thick regolith (Chapman and others, 2005). Additionally, because the aquifers in these provinces are shallow, they are susceptible to contamination from activities on land surface (Daniel and Dahlen, 2002).

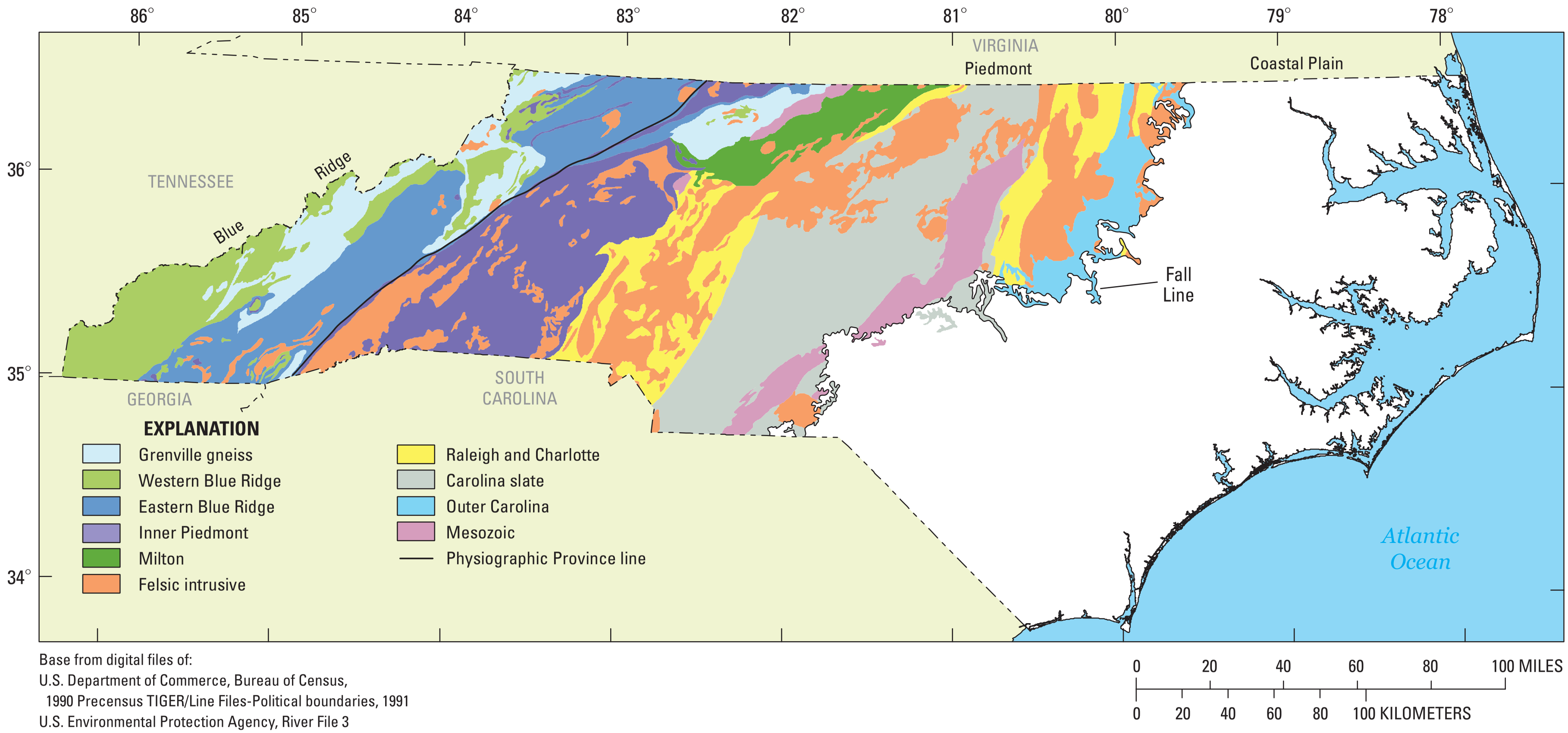
Geozones

In the Piedmont and Mountains Provinces, the metamorphic and igneous rocks have been historically grouped and described as a series of northeast-trending geologic belts (North Carolina Geological Survey, 1985). Studies during the last two decades indicate that the geology is more complicated, and that these belts do not adequately distinguish among lithostratigraphic, structural, and metamorphic features (see discussion in Horton and Zullo, 1991). Hibbard and others (2006) present a modern interpretation of the regional geology with groupings based on lithology and tectonic history. As part of ongoing studies, USGS investigators (Wright Horton and Bruce Lindsey, U.S. Geological Survey, written commun., 2008) have modified the lithotectonic units of Hibbard and others (2006) into regional "geozones" for use in evaluating water-quality characteristics throughout the Piedmont and Mountains aquifer system in the eastern United States. The resulting geozones for the Piedmont and Mountains Provinces are presented in figure 2. The distribution of geozones from west to east, with some deviation based on age, includes the Grenville gneiss, Western Blue Ridge, Eastern Blue Ridge, Inner Piedmont, Milton, Felsic intrusive, Raleigh and Charlotte, Carolina slate, Outer Carolina, and Mesozoic geozones (fig. 2). Descriptions of the geozones in relation to lithotectonic units of Hibbard and others (2006) as well as geologic belts based on the Geologic Map of North Carolina (North Carolina Geological Survey, 1985) are provided in table 1.

Table 1. Regional geozones in the Piedmont and Mountains Provinces of North Carolina (modified from North Carolina Geological Survey [1985] and Hibbard and others [2006]).

[mi^2, square miles; NCGS, North Carolina Geological Survey]

Geozone	Areal extent (mi^2)	Percent of total	Description
Mesozoic	1,424	5.2	Mesozoic rift basins. Hibbard and others (2006) unit 38a. Mainly alluvial and lacustrine clastic sedimentary rocks with local diabase dikes and sills. NCGS (1985): Triassic basins.
Outer Carolina	975	3.5	Unseparated magmatic and clastic metasedimentary sequences. Hibbard and others (2006) unit 14c. NCGS (1985): Eastern slate belt.
Carolina slate	5,012	18.3	Magmatic-arc rocks east of the Central Piedmont suture, low metamorphic grade. Hibbard and others (2006) units 14a and 14b; NCGS (1985): Carolina Slate Belt.
Raleigh and Charlotte	2,194	8.0	Infrastructural magmatic-arc/oceanic rocks. Hibbard and others (2006) unit 15: gneiss, schist, metavolcanic rocks, and amphibolites, with local mélange and ultramafic bodies. NCGS (1985): Raleigh belt.
Felsic intrusive	5,654	20.6	Plutonic (igneous intrusive) rocks of felsic to intermediate composition throughout the Piedmont and Mountains. Hibbard and others (2006) unit 37 and parts of 8b, 14, 25, 15, and 34.
Milton	932	3.4	Magmatic-arc and associated rocks east of the Central Piedmont suture. Hibbard and others (2006) units 8a and 9. Mainly lower to middle (8a) Ordovician metamagmatic rocks and associated metaclastic rocks of the Chopawamsic volcanic arc; (9) Neoproterozoic to Lower Paleozoic mainly clastic metasedimentary rocks, schist, and gneiss locally associated with amphibolite and meta-ultramafic rocks. NCGS (1985): Milton belt.
Inner Piedmont	3,601	13.1	Inner Piedmont composite terrane including Smith River allochthon. Hibbard and others (2006) units 7a, 9, and 10.
Eastern Blue Ridge	3,298	12.0	Western Piedmont accretionary complex of Potomac composite terrane. Hibbard and others (2006) unit 7: Neoproterozoic to lower Paleozoic mainly clastic metasedimentary rocks, schist, and gneiss containing metaclastic mélanges and subordinate amphibolites, and meta-ultramafic rocks. NCGS (1985) part of Blue Ridge belt.
Western Blue Ridge	2,483	9.0	Neoproterozoic to Cambrian mainly clastic metasedimentary rocks filling rift basins and associated magmatism relate to Iapetan rifting. Locally contains fragments of oceanic crust. Hibbard and others (2006) units 2, 3, and 4. NCGS (1985): part of Blue Ridge belt.
Grenville gneiss	1,901	6.9	Ancestral North American basement and associated rocks of the Blue Ridge Province and Sauratown Mountains window. Hibbard and others (2006) unit 1: gneiss, schist, and plutonic rocks affected by the Grenville orogeny and associated post-orogenic granitoid bodies. NCGS (1985): part of Blue Ridge and Inner Piedmont belts.
Total	27,474	100	



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1990 Precensus TIGER/Line Files-Political boundaries, 1991
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Figure 2. Regional geozones in the Piedmont and Mountains Provinces of North Carolina.

Methods

This section provides a discussion of the network of well sites and sample collection methods used to generate the water-quality data set used in this study. Methods used for compiling and analyzing the data for use in evaluating water-quality characteristics within and between the geozones also are presented.

Well Network

The groundwater-quality data examined in this report were collected between 1997 and 2008. The well network consists of 79 wells located in different regional geozones distributed throughout the North Carolina Piedmont and Mountain study area (fig. 3). Data for this study were obtained from PMREP research stations and the NAWQA Program.

Groundwater-quality data were compiled for 30 bedrock wells sampled at 8 PMREP research stations (table 2; fig. 3), each of which included several individual wells. Six of the research stations (AWRS, LPRS, LWRS, RHRS, UPRS, and ZPRS) are located in the Piedmont, and two research stations are located in the Mountains (BCRS and THRS). The research station wells are located in 7 of the 10 regional geozones (fig. 3; table 2).

The research stations generally consist of transects of monitoring wells located parallel to an assumed flow path within a conceptual “slope-aquifer” system (LeGrand, 2004) from recharge areas to discharge areas. Well clusters installed at the research stations are designed to monitor separate zones in the groundwater system, including the shallow regolith, transition zone, and deep bedrock (Chapman and others, 2005). In this study, water-quality data were compiled only from bedrock wells located at the PMREP research stations, in accordance with the purpose of this investigation. In addition to the PMREP well sites, water-quality data also were obtained from 49 domestic-supply bedrock wells within the North Carolina Piedmont and Mountain provinces that were sampled as part of NAWQA studies in North Carolina, South Carolina, and West Virginia. The NAWQA wells are located in 8 of the 10 regional geozones (fig. 3; table 3).

Groundwater Sampling

From 2001 to 2008, both the USGS and the NCDENR DWQ collected groundwater-quality samples from the PMREP research station well sites (table 2) for analysis by their respective laboratories. Multiple rounds of sampling typically were conducted at each of the PMREP well sites although the specific number of samples collected per well varied. The NAWQA wells (table 3) generally had one round of groundwater samples collected for laboratory analyses. Groundwater samples were collected from the NAWQA–NC, NAWQA–SC, and NAWQA–WV well sites in 2007, 1998, and 1997, respectively.

Groundwater sampling conducted by the USGS at PMREP and NAWQA well sites followed established, documented protocols for collecting and processing samples for chemical analyses (Koterba and others, 1995; U.S. Geological Survey, variously dated; U.S. Geological Survey, written commun., 2008). The NCDENR DWQ also followed established protocols for collecting groundwater samples at the PMREP research stations (North Carolina Division of Water Quality, 2008a). Sampling methods included the use of submersible pumps and peristaltic pumps. Wells were purged until measured physical properties stabilized. Physical properties were measured by using a multiparameter water-quality instrument and flow-through chamber to record dissolved oxygen (DO), pH, temperature, and specific conductance. Incremental alkalinity titrations were conducted in the field. Additional details of groundwater-sampling methods used at PMREP research stations are provided by Huffman and others (2006).

Groundwater samples collected by the USGS were analyzed by the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado, and their contract laboratories. Samples collected by the NCDENR DWQ were analyzed by the DWQ Laboratory Section in Raleigh, North Carolina. Information on the analytical program and services of each laboratory can be accessed on the Internet (U.S. Geological Survey, 2008b; North Carolina Division of Water Quality, 2008b). The laboratory results for common ions, nutrients, metals, and radiochemical isotopes analyzed in samples collected from the PMREP and NAWQA wells were compiled and evaluated to characterize water-quality conditions in the geozones of the Piedmont and Mountains study area. The complete analytical data set, grouped by geozone, is provided as Appendix 1. The nitrate-concentration values presented in this report were measured as nitrite plus nitrate, in milligrams per liter as nitrogen (N). Because nitrite typically represents a small fraction of the total concentration, the reported values are presented and discussed as nitrate.

The following discussion notes differences in the analytical results of samples collected and analyzed by the USGS and the NCDENR DWQ for PMREP well sites (Appendix 1). The number of samples analyzed by the USGS and NCDENR for a given PMREP well often varied because of differences in sampling frequency between the two agencies. Filtered samples collected by the USGS were analyzed by the NWQL for dissolved concentrations of major ions, nutrients, and trace elements. Most NCDENR samples were unfiltered and analyzed by the DWQ laboratory for total concentrations of major ions, nutrients, and metals. The analytical reporting levels (RL) for constituent concentrations reported by the USGS NWQL tend to be lower than those reported by the DWQ laboratory. For example, dissolved arsenic concentrations reported by the NWQL generally have an RL of 1 or 2 micrograms per liter (μg/L), and total arsenic concentrations reported by the DWQ laboratory generally have an RL of 5 or 10 μg/L (Appendix 1). Because of these differences, an intercomparison of analytical results between the USGS NWQL and the DWQ laboratory for the PMREP well samples was considered beyond the scope of this study.

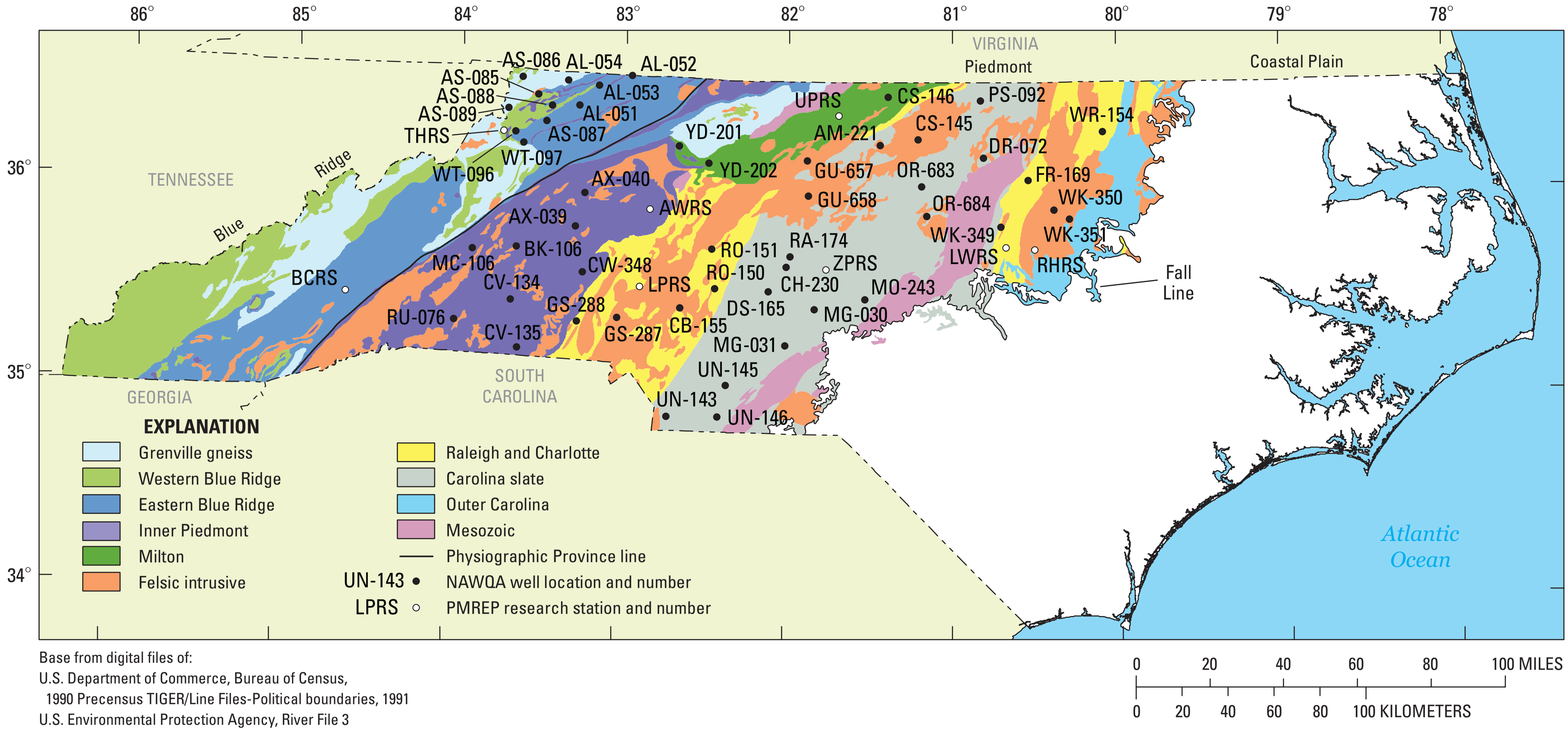

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Figure 3. Distribution of Piedmont and Mountains Resource Evaluation Program research stations and National Water-Quality Assessment Program well sites in regional geozones of the Piedmont and Mountains Provinces of North Carolina.

Table 2. Well information for the North Carolina Department of Environment and Natural Resources, Division of Water Quality, Piedmont and Mountains Resource Evaluation Program research stations.

[USGS, U.S. Geological Survey; ddmmss.s, degrees, minutes, seconds; bls, below land surface; NAVD 88, North American Vertical Datum of 1988]

Local field name	USGS site number	USGS station name	County	Latitude ddmmss.s	Longitude ddmmss.s	Well depth (feet bls)	Land-surface altitude (feet above NAVD 88)	Regional geozone designation
Allison Woods research station (AWRS)								
IR-163	355429080492303	IR-163 Allison Woods RS MW-1D Bed nr Turnersburg	Iredell	355429.7	804923.2	400	900	Inner Piedmont
IR-164	355429080492304	IR-164 Allison Woods RS CH-1 nr Turnersburg	Iredell	355430.3	804923.6	100	900	Inner Piedmont
IR-167	355428080493003	IR-167 Allison Woods RS MW-2D Bed nr Turnersburg	Iredell	355428.3	804930.2	400	870	Inner Piedmont
IR-176	355427080493704	IR-164 Allison Woods RS CH-4 nr Turnersburg	Iredell	355427.9	804936.9	100	830	Inner Piedmont
Bent Creek research station (BCRS)								
BU-070	352840082381003	BU-070 Bent Creek RS MW-1D (bedrock well)	Buncombe	352841	823812	221	2,202	Eastern Blue Ridge
BU-082	352810082383503	BU-082 Bent Creek RS MW-5D (bedrock well)	Buncombe	352810	823835	300	2,305	Eastern Blue Ridge
BU-103	352919082383802	BU-103 Bent Creek RS MW-6D (bedrock well)	Buncombe	352919	823839	190	2,420	Eastern Blue Ridge
Langtree Peninsula research station (LPRS)								
IR-132	353135080524203	IR-132 Langtree RS MW-2D nr Mt Mourne, NC	Iredell	353136	805242	400	803	Raleigh and Charlotte
IR-147	353141080524703	IR-147 Langtree RS MW-1D (bedrock well)	Iredell	353141	805247	602	813	Raleigh and Charlotte
IR-153	353145080524703	IR-153 Langtree RS MW-4D (bedrock well)	Iredell	353145	805247	400	802	Raleigh and Charlotte
Lake Wheeler research station (LWRS)								
WK-279	354356078403503	WK-279 Lake Wheeler RS MW-1D (bedrock well)	Wake	354356	784034	302	339	Raleigh and Charlotte
WK-286	354404078403103	WK-286 Lake Wheeler RS MW-3D (bedrock well)	Wake	354405	784031	301	376	Raleigh and Charlotte
WK-287	354401078403401	WK-287 Lake Wheeler RS PW-1	Wake	354401	784034	302	358	Raleigh and Charlotte
Raleigh Hydrogeologic research station (RHRS)								
WK-331	354328078295704	WK-331 Raleigh Hydrogeologic RS WC-1CH (bedrock)	Wake	354329	782957	90	165	Felsic intrusive
WK-334	354315078300103	WK-334 Raleigh RS WC-2D nr Garner, NC (bedrock)	Wake	354315	783002	460	188	Felsic intrusive
WK-335	354315078300104	WK-335 Raleigh RS WC-2CH nr Garner, NC (bedrock)	Wake	354316	782959	85	199	Felsic intrusive
WK-338	354305078295803	WK-338 Raleigh Hydrogeologic RS WC-3D (bedrock)	Wake	354306	782958	300	210	Felsic intrusive

Table 2. Well information for the North Carolina Department of Environment and Natural Resources, Division of Water Quality, Piedmont and Mountains Resource Evaluation Program research stations.—Continued

[USGS, U.S. Geological Survey; ddmmss.s, degrees, minutes, seconds; bls, below land surface; NAVD 88, North American Vertical Datum of 1988]

Local field name	USGS site number	USGS station name	County	Latitude ddmmss.s	Longitude ddmmss.s	Well depth (feet bls)	Land-surface altitude (feet above NAVD 88)	Regional geozone designation
Tater Hill research station (THRS)								
WT-098	361646081433001	WT-098 Tater Hill RS ASU-1D (bedrock) nr Boone, NC	Watauga	361646	814303	345	4,060	Western Blue Ridge
WT-099	361646081430402	WT-099 Tater Hill RS ASU-2D bedrock nr Boone, NC	Watauga	361645.9	814303.7	350	4,060	Western Blue Ridge
Upper Piedmont research station (UPRS)								
RK-229	362334079421603	RK-229 Upper Piedmont RS MW-N1D	Rockingham	362335	794217	300	673	Milton
RK-232	362331079421603	RK-232 Upper Piedmont RS MW-N2D	Rockingham	362332	794217	300	672	Milton
RK-234	362328079421702	RK-234 Upper Piedmont RS MW-N3D	Rockingham	362328	794217	260	770	Milton
RK-236	362323079421202	RK-236 Upper Piedmont RS MW-N4D	Rockingham	362323	794213	300	840	Milton
RK-238	362240079411802	RK-238 Upper Piedmont RS MW-S1D	Rockingham	362241	794119	301	803	Milton
RK-242	362231079310804	RK-242 Upper Piedmont RS MW-S3D	Rockingham	362232	794108	438	705	Milton
RK-245	362226079410103	RK-245 Upper Piedmont RS MW-S4D	Rockingham	362226	794101	380	660	Milton
Zoological Park research station (ZPRS)								
RA-164	353704079451204	RA-164 NC Zoo RS MW-1D (bedrock)	Randolph	353704.1	794511.9	300	598	Carolina slate
RA-167	353708079452103	RA-167 NC Zoo RS MW-2D (bedrock)	Randolph	353707.7	794520.6	260	639	Carolina slate
RA-170	353712079452703	RA-170 NC Zoo RS MW-3D (bedrock)	Randolph	353711.8	794527.3	180	665	Carolina slate
RA-172	353708079452104	RA-172 NC Zoo RS CH-2 (corehole)	Randolph	353708	794521	98	636	Carolina slate

Table 3. Well information for U.S. Geological Survey National Water-Quality Assessment Program sites used in this study.

[USGS, U.S. Geological Survey; ddmmss.s, degrees, minutes, seconds; bls, below land surface; NAVD 88, North American Vertical Datum of 1988]

Local field name (see fig. 3)	USGS site number	USGS station name	County	Latitude ddmmss.s	Longitude ddmmss.s	Well depth (feet bls)	Land-surface altitude (feet above NAVD 88)	Regional geozone designation
Wells sampled by NAWQA Study Unit in North Carolina								
AM-221	361355079261601	AM-221 Piedmont MAS 18	Alamance	361355	792616	240	244	Felsic intrusive
CB-155	352529080380801	CB-155 Piedmont MAS 24	Cabarrus	352529	803808	305	680	Felsic intrusive
CH-230	353756079295501	CH-230 Piedmont MAS 46	Chatham	353756	795955	263	544	Carolina slate
CS-145	361540079123001	CS-145 Piedmont MAS 17	Caswell	361540	791230	182	215	Felsic intrusive
CS-146	362817079231601	CS-146 Piedmont MAS 35	Caswell	362817	792316	322	138	Milton
DR-072	361020078484801	DR-072 Piedmont MAS 42	Durham	361020	784848	125	446	Carolina slate
DS-165	353040080062101	DS-165 Piedmont MAS 47	Davidson	353040	800621	105	162	Carolina slate
FR-169	360345078323201	FR-169 Piedmont MAS 9	Franklin	360345.4	783231.7	125	148	Raleigh and Charlotte
GU-657	360923079524201	GU-657 Piedmont MAS 19	Guilford	360923.1	795241.6	165	261	Felsic intrusive
GU-658	355900079521101	GU-658 Piedmont MAS 20	Guilford	355900	795211	400	275	Felsic intrusive
MG-030	352512079494501	MG-030 Piedmont Major Aquifer Study Site 50	Montgomery	352512	794945	245	530	Carolina slate
MG-031	351440080000601	MG-031 Piedmont Major Aquifer Study Site 52	Montgomery	351440	800006	230	415	Carolina slate
MO-243	352828079313501	MO-243 Piedmont Major Aquifer Study Site 49	Moore	352828	793135	308	412	Carolina slate
OR-683	360152079110301	OR-683 Piedmont MAS 43	Orange	360151.8	791102.5	160	649	Carolina slate
OR-684	355302079091201	OR-684 Piedmont MAS 44	Orange	355302.3	790912.2	300	173	Carolina slate
PS-092	362707078495301	PS-092 Piedmont MAS 41	Person	362707	784953	142	—	Carolina slate
RA-174	354054079583201	RA-174 Piedmont MAS 45	Randolph	354054	795832	325	143	Carolina slate
RO-150	353127080253401	RO-150 Piedmont MAS 13	Rowan	353127	802534	145	227	Raleigh and Charlotte
RO-151	354307080265501	RO-151 Piedmont MAS 22	Rowan	354307	802655	165	255	Felsic intrusive
UN-145	350251080212301	UN-145 Piedmont Major Aquifer Study Site 53	Union	350251	802123	255	508	Carolina slate
UN-146	345327080241601	UN-146 Piedmont Major Aquifer Study Site 54	Union	345327	802416	250	501	Carolina slate
WK-349	354954078421301	WK-349 Piedmont MAS 12	Wake	354953.6	784213	185	177	Felsic intrusive
WK-350	355448078225901	WK-350 Piedmont MAS 23	Wake	355447.9	782259.3	240	102	Felsic intrusive
WK-351	355212078173501	WK-351 Piedmont MAS 21	Wake	355211.6	781734.7	125	91	Felsic intrusive
WR-154	361805078051001	WR-154 Piedmont MAS 8	Warren	361804.5	780510.3	300	85	Raleigh and Charlotte
YD-201	361322080391801	YD-201 Piedmont MAS 37	Yadkin	361322	803918	422	993	Milton
YD-202	360819080281501	YD-202 Piedmont MAS 38	Yadkin	360819	802815	222	877	Milton

Table 3. Well information for U.S. Geological Survey National Water-Quality Assessment Program sites used in this study.—Continued

[USGS, U.S. Geological Survey; ddmmss.s, degrees, minutes, seconds; bls, below land surface; NAVD 88, North American Vertical Datum of 1988]

Local field name (see fig. 3)	USGS site number	USGS station name	County	Latitude ddmmss.s	Longitude ddmmss.s	Well depth (feet bls)	Land-surface altitude (feet above NAVD 88)	Regional geozone designation
Wells sampled by NAWQA Study Unit in South Carolina								
AX- 039	354911081161401	AX- 39	Alexander	354910.62	811614.26	155	1,060	Inner Piedmont
AX- 040	355856081130501	AX- 40	Alexander	355857.96	811308.01	80	1,330	Inner Piedmont
BK-106	354252081372501	BK- 106	Burke	354251.84	813725.43	830	1,700	Felsic intrusive
CV-134	352703081391601	CV- 134	Cleveland	352703	813916	205	960	Inner Piedmont
CV-135	351252081363401	CV- 135	Cleveland	351252	813634	300	750	Inner Piedmont
CW-348	353535081133401	CW- 348	Catawba	353535	811334	165	890	Inner Piedmont
GS-287	352222081005001	GS- 287	Gaston	352222	810050	205	830	Felsic intrusive
GS-288	352106081152601	GS- 288	Gaston	352106	811526	80	910	Raleigh and Charlotte
MC-106	354154081532201	MC- 106	McDowell	354154	815322	305	1,340	Inner Piedmont
RU- 076	352050081593201	RU- 76	Rutherford	352050	815932	450	1,010	Inner Piedmont
UN-143	345323080423701	UN- 143	Union	345323	804237	160	635	Carolina slate
Wells sampled by NAWQA Study Unit in West Virginia								
AL-051	362445081154701	AL-051	Alleghany	362445	811547	700	2,750	Eastern Blue Ridge
AL-052	363345080564001	AL-052	Alleghany	363345	805640	146	2,735	Eastern Blue Ridge
AL-053	363053081084101	AL-053	Alleghany	363053	810841	273	3,020	Eastern Blue Ridge
AL-054	363208081195801	AL-054	Alleghany	363208	811958	500	2,780	Grenville gneiss
AS-085	362739081305001	AS-085	Ashe	362739	813050	205	2,680	Eastern Blue Ridge
AS-086	363254081364201	AS-086	Ashe	363254	813642	125	3,480	Western Blue Ridge
AS-087	361957081273001	AS-087	Ashe	361957	812730	135	3,040	Eastern Blue Ridge
AS-088	362436081254101	AS-088	Ashe	362436	812541	95	2,720	Eastern Blue Ridge
AS-089	362339081412601	AS-089	Ashe	362339	814126	144	3,080	Grenville gneiss
WT-096	361638081384401	WT-096	Watauga	361638	813844	305	3275	Eastern Blue Ridge
WT-097	361327081354601	WT-097	Watauga	361327	813546	150	3230	Eastern Blue Ridge

The following discussion notes differences between the data sets compiled from the PMREP and NAWQA wells (fig. 3; tables 2, 3) to characterize groundwater quality in the regional geozones. The PMREP well set consists of stations that are somewhat limited in geographic range but have many wells present at each station. The NAWQA well set consists of single wells that are spatially diverse throughout the study area. In addition, many groundwater samples typically were collected and analyzed for the PMREP wells, which are used solely for monitoring and are pumped only during sampling events. Only one sample, typically, was collected and analyzed for the NAWQA wells, which are used for domestic supply and are pumped regularly. The data from both programs were combined for data analysis to examine water-quality conditions in 8 of the 10 geozones located in the study area. In this study, no wells were present in the Mesozoic or Outer Carolina geozones (fig. 3); hence, these geozones are not discussed further. Analytical data were available for only two wells (AL-054 and AS-089) in the Grenville gneiss geozone and three wells (AS-086, WT-098, and WT-099) in the Western Blue Ridge geozone (fig. 3; tables 2, 3).

Statistical Analysis of Water-Quality Data

Evaluation of the chemical data was accomplished in several ways to characterize water-quality conditions in regional geozones within the Piedmont and Mountains Provinces (fig. 2). Piper diagrams, analysis of variance (ANOVA), and box plots were used to analyze the statistical and geochemical variability in the water-quality data for the regional geozones.

Within each geozone, water-quality analyses were examined using Piper diagrams (Piper, 1944), which display overall information on the primary ionic composition of water in each geozone. In addition, the analytical results within each geozone were compared to available State (North Carolina Department of Environment and Natural Resources, 2006) and Federal (U.S. Environmental Protection Agency, 2003) maximum contaminant levels (MCLs) for drinking-water standards to determine if the chemical constituents in samples exceeded drinking-water criteria. The analytical results also were compared to the U.S. Environmental Protection Agency (USEPA) secondary maximum contaminant levels (SMCLs; U.S. Environmental Protection Agency, 2003), which typically are used for examining constituents that have an aesthetic effect on drinking water.

A Kruskal-Wallis one-way ANOVA test (Helsel and Hirsch, 1992) on ranked data was used to examine the relation between regional geozones and groundwater constituents. The test is used for a given constituent to determine if all geozones have the same median concentration of the constituent or whether at least one median is different. The null hypothesis for the Kruskal-Wallis test is that the median concentrations of each geozone are identical. The alternate hypothesis is that the median concentration in at least one geozone differs from the other geozones. The null hypothesis is rejected if the p-value computed from the test is smaller than or equal to the significance level of $\alpha = 0.05$, indicating that the geologic setting, or geozone, has a significant influence on the constituent concentrations. If the p-value is greater than $\alpha = 0.05$, the null hypothesis is not rejected. Note that the lack of significance does not mean that for a given constituent, concentrations do not differ among the geozones; it only means that a significant difference in medians between the geozones, if any, was not large enough to be detected with the given sample size.

The Kruskal-Wallis test results for a given constituent may indicate that the null hypothesis is rejected and that a statistically significant difference in median concentrations of the constituent exists among the geozones; however, it does not specify which geozones are different. In these cases, a Tukey multiple-comparison test (Helsel and Hirsch, 1992) was used to pinpoint differences among the geozones for a particular constituent. The Tukey multiple-comparison test compares all possible pairs of the geozones and determines which comparisons are significantly different at $\alpha = 0.05$.

Box plots were used to provide statistical summaries of those chemical constituents noted as having significant differences among the geozones. Outlier data that were less than the 10th percentile or greater than the 90th percentile were excluded from the box plots. For many constituents examined in the data set, individual results often were reported as a left-censored value (less than [<] the RL), which complicates the process for statistically summarizing the data, and hence, obtaining necessary data for constructing the box plots. Often times, researchers may substitute the censored result, or nondetect, with an arbitrary value that is equal to zero, the RL, or one-half of the RL; however, this approach can potentially bias the data set and lead to false conclusions (Bonn, 2008).

For constituents having left-censored data with one or more reporting levels, summary statistics were estimated using regression on order statistics (ROS) methods (Helsel and Cohn, 1988; Helsel and Hirsch, 1992). Some of the censored data analyzed with ROS contained constituent values that were reported by the laboratory as estimated (E), which means analytes are considered to be present in the sample at concentrations above the long-term method detection limit (MDL) but less than the RL. A conservative approach was used in handling E values. In preparing censored data for analysis with ROS, the E values were replaced with the RL such that these values with high uncertainty were not compared to one another, but rather, were ranked equally in the analysis (Bonn, 2008). Similarly, the Tukey multiple-range test, which is used to test for geozone differences for a given constituent, often was performed on a constituent data set having “less than” censored values, usually with one or more RLs. In these cases, the censored data were set to the highest RL such that all reported censored values that were less than the RL were ranked equally prior to analysis with the Tukey multiple-range test. Additional information on various approaches and methods used for understanding and interpreting low-level concentration data reported by the USGS NWQL is presented by Bonn (2008). Statistical summaries were not estimated with

ROS for a given constituent data set when the percentage of censored values exceeded 80 percent, there were fewer than three uncensored observations, or the uncensored observations were all equal. Box plots for constituents having censored data were plotted using the percentiles estimated with ROS.

Bedrock Groundwater Quality within Regional Geozones

Characterization of the chemical properties of groundwater within the geozones is necessary for a better understanding of the quality of water contained in the fractured bedrock aquifers and the suitability of the water for various uses. The quantities and types of dissolved chemical constituents and the physical and chemical properties of groundwater are a result of the bedrock mineralogy and processes of the hydrogeologic environment. Various factors influence groundwater quality in bedrock aquifers (Briel, 1997; Daniel and Dahlen, 2002; Lindsey and others, 2006; McMahon and Chapelle, 2008; Vinson and others, 2009), including (1) the chemical characteristics of the water from recharge areas; (2) lithologic composition of the crystalline bedrock and overlying regolith materials, which contain soluble parent minerals; (3) the rate of flow, which controls the residence time between the moving water and the aquifer materials; and (4) redox conditions, which influence the distribution of natural and anthropogenic contaminants along groundwater-flow paths. Identification of the physical properties and chemical constituents in groundwater, therefore, reveals information about the aquifer materials that contain the water as well as whether the water contains contaminants, such as radon or nitrate, which are derived from natural rock sources and anthropogenic surface sources, respectively. Changes in water quality through time within an aquifer are often indicative of human activities and are caused either by changes in population and land use or changes in pumping for water supplies (Daniel and Dahlen, 2002). Changes in quality also can occur naturally over time from other factors, such as groundwater circulation and geochemical reactions.

Ionic Composition

Overview: The general ionic composition, or water type, of groundwater within the geozones was examined by using a Piper diagram (fig. 4). The water type(s) present in the geozones were classified based on the predominant cations and anions dissolved in the bedrock groundwater samples (Appendix 1). In determining water type using a Piper diagram (fig. 4), the analytical results are plotted on the central quadrilinear diagram. To determine the specific primary cations, the plotted data point is projected to the lower left-side trilinear diagram, which shows the percentage of cations in water composition. The anions are determined the same way on the right-side trilinear diagram. In the middle of the quadrilinear part of the Piper diagram, mixed ionic composition is indicated where no cation or anion is dominant. The chemical analyses from the PMREP and NAWQA wells in each geozone included for analysis with the Piper diagram were limited to those samples where the ion balance, or cation and anion sums, were determined to be within 10 percent of each other. Only dissolved cations (calcium, magnesium, sodium, and potassium) and anions (bicarbonate, sulfate, chloride, and nitrate) having concentrations detected above the RL were included in the analyses. The water type determined for individual well samples plotted for each geozone in figure 4 is provided in Appendix 1.

The limited samples available for evaluation of the ionic composition of groundwater for the Grenville gneiss (two wells) and Western Blue Ridge (three wells) geozones indicate a calcium/bicarbonate to calcium-sodium/bicarbonate water type (Appendix 1; fig. 4). Water quality in these geozone wells appears to reflect ambient conditions with no noticeable influence from local land use.

The ionic composition of groundwater in the Eastern Blue Ridge, Inner Piedmont, Milton, Felsic intrusive, Raleigh and Charlotte, and Carolina slate geozones is variable with no dominant water type (fig. 4). No major differences in overall ionic chemistry among these geozones were evident with the data examined. The basic ionic compositions of most groundwater samples in these geozones generally are either a calcium-sodium/bicarbonate or a calcium-magnesium/bicarbonate water type where calcium is the dominant cation, followed by either magnesium or sodium, and bicarbonate is the dominant anion (fig. 4; Appendix 1). The more notable changes in water type occurred in the anionic composition of the groundwater in response to anthropogenic effects, such as nutrient inputs from local land use that increased groundwater nitrate concentrations.

Observed variability in the cationic and anionic composition of groundwater within a particular geozone appears to reflect local differences in lithologic setting, groundwater-flow paths, geochemical conditions, and(or) land use. Data from the Milton and Felsic intrusive geozones is used to describe some of the factors that influence bedrock groundwater chemistry at local scales.

Milton Geozone: The ionic compositions of groundwater samples from seven PMREP wells at the Upper Piedmont research station (UPRS) and three spatially separated NAWQA wells were evaluated for the Milton geozone (fig. 5*A*; Appendix 1). The UPRS is located on an agricultural research farm owned and operated by North Carolina State University and the North Carolina Department of Agriculture; consequently, groundwater quality at some well locations has been influenced by nutrients, potentially including animal manure and inorganic fertilizers. The overall ionic composition for samples from the Milton geozone is variable, including a calcium-magnesium/bicarbonate type for well RK-232, a calcium-sodium-magnesium/nitrate-bicarbonate type for well RK-242, and a calcium-sodium/sulfate-bicarbonate type for well RK-245. Wells RK-242 and RK-245 are located about

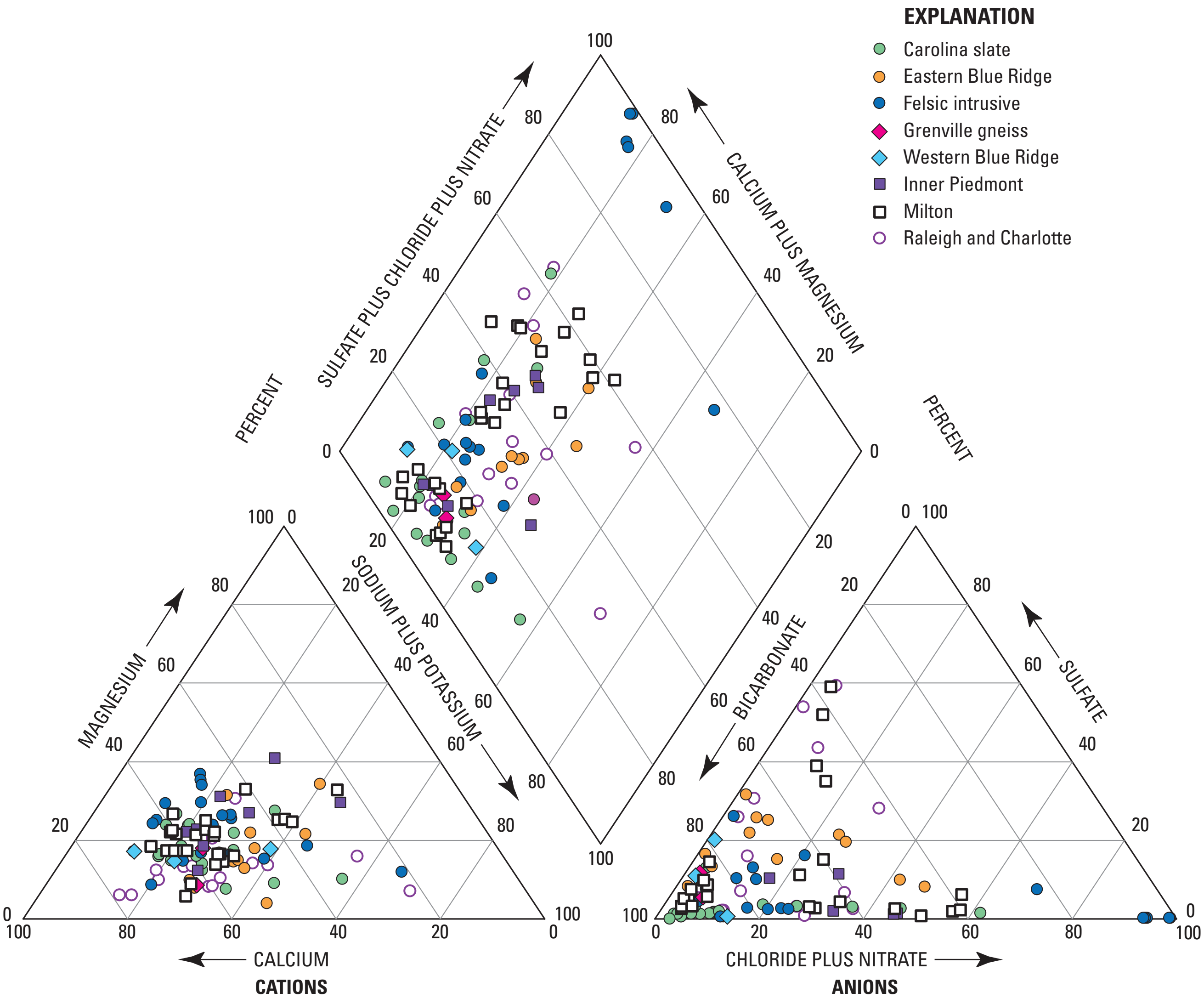

Figure 4. Piper diagram showing ionic composition of groundwater samples within eight geozones in the Piedmont and Mountains Provinces of North Carolina.

825 feet (ft) apart along a transect in the southern part of the UPRS all within a felsic gneiss rock type (Huffman and others, 2006). Well RK-232 is located about 1.6 miles (mi) away in the northern part of the UPRS and taps a mica gneiss and schist rock type.

Groundwater samples from wells RK-232, RK-242, and RK-245 (with borehole depths ranging from 300 to 438 ft) typically were collected by lowering a pump down the open borehole of the well to target a fracture zone at a depth of about 130–160 ft. These "open-hole" samples are considered to be a composite of the entire well because water may have been pulled from fractures located above and below the targeted zone. In 2004, a multifunction Bedrock-Aquifer Transportable Testing Tool (BAT^3; Shapiro, 2001) was used to collect groundwater-quality samples from wells RK-232, RK-242, and RK-245. The BAT^3 allows discrete intervals of a borehole to be isolated hydraulically for water-quality sampling by using two inflatable packers that seal against the borehole wall and isolate the fracture zone to be sampled.

The groundwater ionic composition differs among wells RK-232, RK-242, and RK-245 for both the open-hole samples and the individual fracture-zone samples (fig. 5*B*; Appendix 1), most likely because of variable rock types tapped by the wells at the local scale and effects from local agricultural practices. A subtle transition in groundwater cationic composition occurs with depth at these well sites. Calcium is the dominant cation for these well samples at all depths (fig. 5*B*; Appendix 1). After calcium, the relative proportion of magnesium tends to decrease with fracture depth as the proportion of sodium increases. The proportion of calcium to both magnesium and sodium also tends to increase with depth. This shift in cationic composition likely reflects differences in the amount of ion exchange between the groundwater and rock materials where a greater proportion of calcium has dissolved

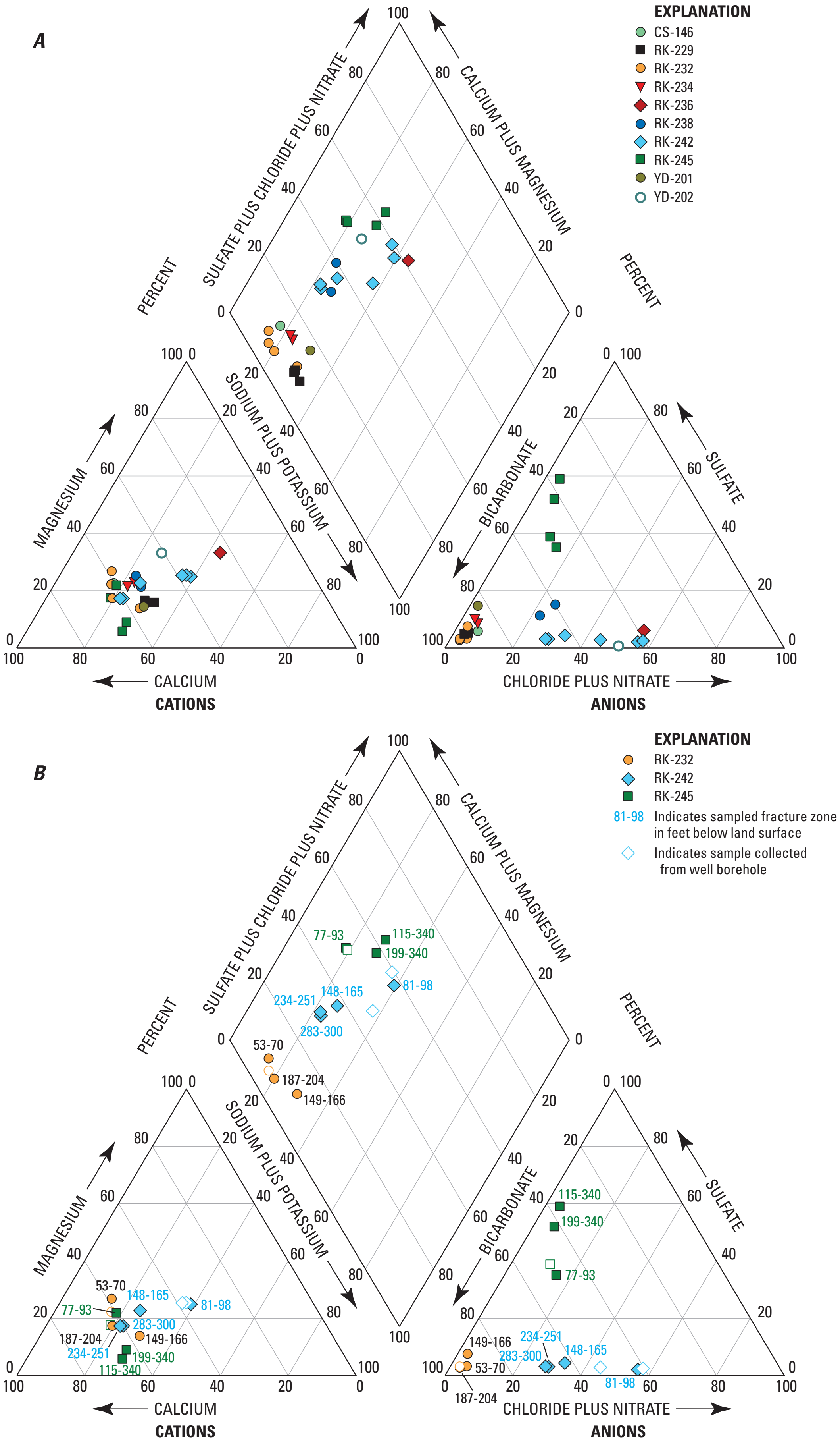

Figure 5. Piper diagram showing ionic composition of (*A*) all samples from the Milton geozone, and (*B*) open-hole samples and individual fracture-zone samples for wells RK-232, RK-242, and RK-245 in the Milton geozone in the Piedmont and Mountains Provinces of North Carolina.

into older groundwater with longer residence times and flow paths that occur in the deeper fractures. Water composition for well RK-232 shifts from calcium-magnesium/bicarbonate at fracture interval 53–70 ft, to calcium-sodium/bicarbonate at fracture interval 149–166 ft, to calcium/bicarbonate at fracture interval 187–204 ft. The open-hole sample for well RK-232 is classified as a calcium-magnesium/bicarbonate type that appears to be influenced primarily by groundwater derived from the shallow fracture at 53–70 ft.

Dissolved nitrate concentrations for all RK-232 samples plotted in figure 5*B* were less than the RL of 0.06 mg/L (Appendix 1). Dissolved chloride and dissolved sulfate concentrations in the same samples were less than 5 mg/L and 8 mg/L, respectively. The absence of nitrate in well RK-232 possibly reflects denitrification processes occurring along the groundwater-flow path and potential dilution from surface-water interaction. Well RK-232 is located in a flood plain near the groundwater-discharge zone at the stream, downgradient from agricultural land use in upgradient recharge areas of the groundwater-flow path (Huffman and others, 2006). Conditions that generally promote denitrification in groundwater occur when nitrate is present, DO concentrations are low—less than 0.2 mg/L, and electron donors (such as carbon) are present (Korom, 1992; Seitzinger and others, 2006; McMahon and Chapelle, 2008). In general, dissolved oxygen is consumed along groundwater-flow paths from recharge areas to discharge areas as microorganisms use DO as an electron acceptor during microbial degradation of organic carbon. As DO is depleted along the groundwater-flow path, nitrate, if present, becomes the next most favorable electron acceptor used by microorganisms (Korom, 1992; McMahon and Chapelle, 2008). The presence of anoxic redox conditions, as indicated by the low DO concentrations of about 0.2 mg/L, in older groundwater moving along deeper flow paths at well RK-232 suggest that any nitrate that may have been present from upgradient areas of the flow path likely has been reduced through denitrification processes.

A more pronounced difference is noted in the anionic composition of samples from wells RK-242 and RK-245 as compared to RK-232. At well RK-242, the principal anions include bicarbonate and nitrate, with a slight shift occurring at depth as the relative proportion of bicarbonate to nitrate increases. The occurrence of nitrate in groundwater at well RK-242 (fig. 5*B*; Appendix 1) likely reflects surface inputs of nitrogen associated with agricultural activities at the site. This well is located in a recharge area with downward gradients from the shallow regolith to the bedrock. Additionally, hydraulic heads measured during sampling of the four bedrock-fracture zones were all similar, within 0.5 ft of each other, indicating that the fractures may be interconnected and have similar transmissivities; thereby, allowing groundwater nitrate from surface sources to migrate downward into deeper bedrock fractures. Dissolved chloride concentrations were detected at fairly uniform concentrations in the four fracture zones, ranging from 5.44 to 5.96 mg/L. The decrease in concentrations of both DO and nitrate with depth in the fracture-zone samples at 81–98 ft (DO = 7.0 mg/L, nitrate = 9.46 mg/L), 148–165 ft (DO = 2.8 mg/L, nitrate = 8.17 mg/L), 234–251 ft (DO = 0.6 mg/L, nitrate = 8.16 mg/L), and 283–300 ft (DO = 0.3 mg/L, nitrate = 7.71 mg/L) indicates that some denitrification of nitrate may be occurring in deeper parts of the bedrock aquifer at well RK-242.

A difference in anionic composition also is observed for the open-hole and fracture-zone samples from well RK-245, ranging from a calcium-magnesium/bicarbonate-sulfate type in fracture interval 77–93 ft to a calcium/sulfate-bicarbonate type in fracture zone 199–340 ft (fig. 5*B*; Appendix 1). At this well, the relative proportion of sulfate to bicarbonate increases with depth. In contrast to well RK-242, groundwater redox conditions at well RK-245 appear more favorable for enabling nitrate reduction through denitrification. Well RK-245, located downgradient from well RK-242 in a discharge area next to a stream, has an upward vertical hydraulic gradient. Dissolved nitrate concentrations for all RK-245 samples plotted in figure 5*B* were less than the RL of 0.06 mg/L (Appendix 1). The anoxic redox conditions present in groundwater at well RK-245, as indicated by the low DO concentrations of about 0.1 mg/L, suggest that any groundwater nitrate moving along deep flow paths from upgradient sources likely has been reduced through denitrification processes. Dissolved sulfate concentrations are higher in the RK-245 samples (range of 46.2–96.3 mg/L) as compared to concentrations in samples from wells RK-232 and RK-242, which are less than 8 mg/L. Although local mineralogy and redox processes cannot be excluded, the drilling fluids used during well construction are the suspected source of the elevated sulfate levels in this well. The borehole of well RK-245 is highly fractured, and the drilling mud may not have been completely flushed from the fractures during well development, thus, representing a potential source of sulfate to groundwater in this well.

Felsic Intrusive Geozone: The ionic composition of most samples from the 14 wells in the Felsic intrusive geozone (fig. 6; Appendix 1) cluster around a calcium-sodium/bicarbonate to calcium-magnesium/bicarbonate water type. A noticeable shift in ionic composition, however, occurs for several sites (WK-331, WK-335, and WK-338) where nitrate replaces bicarbonate as the dominant anion. These three wells are located at the Raleigh hydrogeologic research station (RHRS; fig. 3) where past field applications of municipal biosolids from a wastewater treatment plant have resulted in nitrate contamination of shallow groundwater in the regolith and transition zones (McSwain and others, 2009). Wells WK-338 (depth = 300 ft) and WK-335 (depth = 85 ft) are located in recharge areas of the groundwater-flow path, and well WK-331 (depth = 90 ft) is located by the discharge area near the receiving river. The vertical hydraulic gradients in the open borehole of deep well WK-338 and shallow wells WK-335 and WK-338 are downward such that surface-derived nitrate in shallow groundwater flows downward into deeper parts of the bedrock aquifer. Dissolved nitrate and dissolved chloride concentrations in these wells commonly exceed 50 mg/L and 12 mg/L, respectively (Appendix 1).

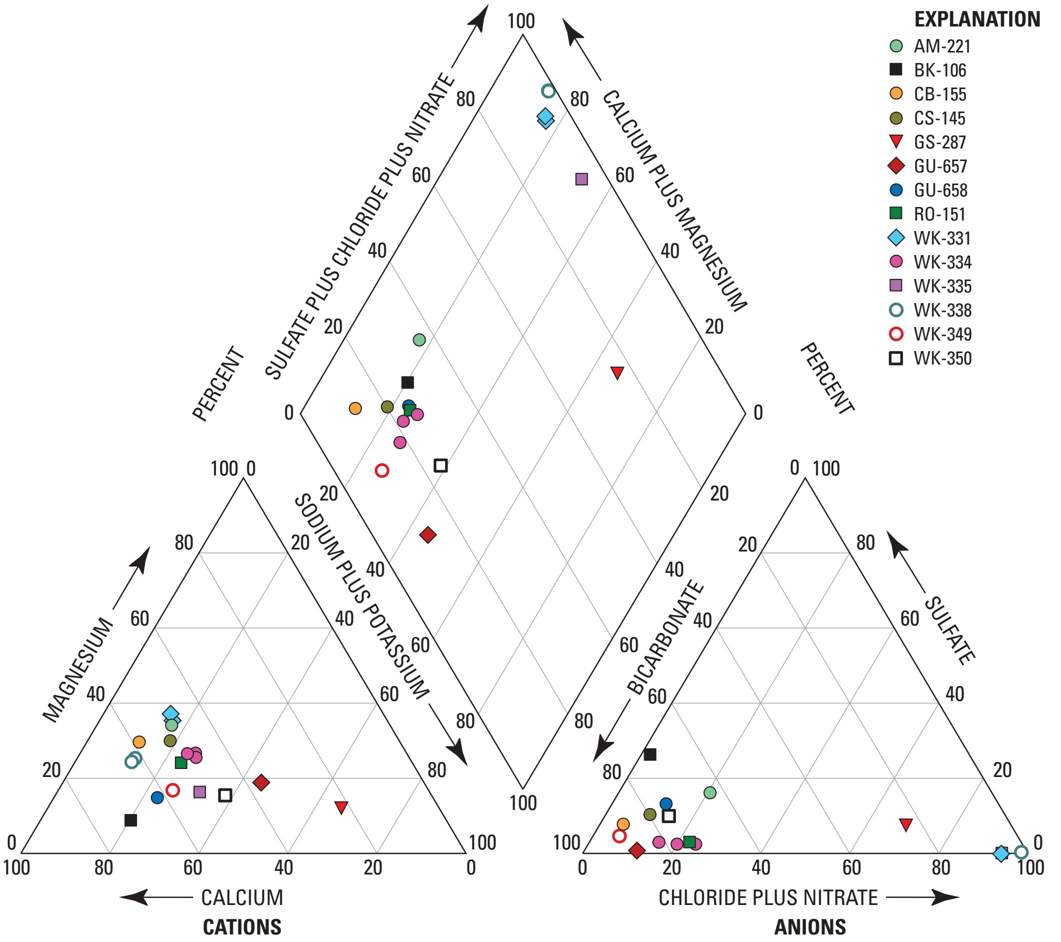

Figure 6. Piper diagram showing ionic composition of samples from the Felsic intrusive geozone in the Piedmont and Mountains Provinces of North Carolina.

DO concentrations in these wells range from 4.8 to 6.3 mg/L, indicating oxic conditions where the potential for nitrate reduction from denitrification is low.

Interestingly, in well WK-334, also located at the RHRS waste application fields, the mean dissolved nitrate concentration (5.6 mg/L) and mean dissolved chloride concentration (4.2 mg/L) for the three samples are noticeably lower than those observed for wells WK-331, WK-335, and WK-338. Well WK-334 is located near WK-335 and is the deepest well (depth = 460 ft) along the flow path. DO concentrations (range of 0.3–1.0 mg/L) indicate suboxic to anoxic conditions at well WK-334. The lower nitrate concentrations at well WK-334 may reflect geochemical conditions that promote the reduction of nitrate through denitrification. Additionally, well WK-334 has an upward vertical hydraulic gradient within the borehole (from higher head in the deeper fractures), which may result in a dilution of nitrate concentrations in shallow fractures with older groundwater in deeper fractures, having little or no nitrate. These data illustrate how hydrogeologic, geochemical, and land-use factors can have a substantial influence on groundwater quality at the local scale. The complex nature of the fractured bedrock system can allow contaminants at one site to be confined to shallow parts of the aquifer (less than 100 ft in depth), whereas a well located hundreds of feet away may have interconnected fractures that allow the contaminants to migrate hundreds of feet down into the bedrock where vertical hydraulic gradients are downward.

Comparison with Water-Quality Standards

Another approach used to characterize water-quality conditions in the regional geozones was comparison of the sample analytical results with applicable State and Federal water-quality standards to determine if sample constituents in the geozones exceeded drinking-water criteria. All of the groundwater samples collected at the PMREP research station wells (table 2) and the NAWQA wells (table 3) were included in the comparison with the water-quality standards. A list of water-quality constituents (that have applicable water-quality standards) measured in the groundwater samples is provided in table 4. Both dissolved and total constituent concentrations in

Table 4. Water-quality standards applicable to constituents or properties measured in groundwater samples.

[MCL, maximum contaminant level; USEPA, U.S. Environmental Protection Agency; SMCL, secondary maximum contaminant level; —, not applicable; mg/L, milligram per liter]

Chemical constituent	North Carolina MCL (mg/L)[a]	USEPA MCL (mg/L)[b]	USEPA SMCL (mg/L)[b]
Aluminum	—	—	0.05–0.2
Antimony	—	0.006	—
Arsenic	0.05	0.010[c]	—
Barium	2.0	2.0	—
Beryllium	—	0.004	—
Boron	0.315	—	—
Cadmium	0.00175	0.005	—
Chloride	250	—	250
Chromium	0.05	0.1	—
Copper	1.0	1.3[d]	1.0
Fluoride	2.0	4.0	2.0
Iron	0.3	—	0.3
Lead	0.015	0.015[d]	—
Manganese	0.05	—	0.05
Mercury	0.00105	0.002	—
Nickel	0.1	—	—
Nitrate (as nitrogen)	10.0	10.0	—
pH	6.5–8.5[e]	—	6.5–8.5[e]
Selenium	0.05	0.05	—
Silver	0.0175	—	0.10
Sulfate	250	—	250
Thallium	—	0.002	—
Uranium	—	0.030[f]	—
Zinc	1.05	—	5

[a] North Carolina Department of Environment and Natural Resources (2006); standard represents maximum allowable total concentration of constituent in groundwater used as a source of drinking-water supply.

[b] U.S. Environmental Protection Agency (2003); standard represents maximum allowable concentration of constituent in finished drinking water delivered to any user of a public water system. Finished drinking water typically has undergone filtration as part of treatment process.

[c] As of January 23, 2006.

[d] Copper and lead regulated by a treatment technique that requires water suppliers to control the corrosiveness of their water. Water systems must take additional steps if 10 percent of tap samples exceed the 1.3-mg/L action level for copper or 0.015-mg/L action level for lead.

[e] Reported in standard pH units.

[f] As of December 8, 2003.

samples measured by the USGS NWQL and(or) the NCDENR DWQ laboratory were compared with the standards. The radionuclide radon is not listed in table 4 because no official MCL has been finalized for this constituent; however, the USEPA has proposed an MCL of 300 pCi/L for radon in drinking water provided by community water systems if no state or local multimedia mitigation (MMM) program is in place or an alternative MCL (AMCL) of 4,000 pCi/L if a USEPA-approved MMM program exists (U.S. Environmental Protection Agency, 2007). Radon results for the groundwater samples are compared to both proposed standards. The analytical data for all groundwater samples used in this study are provided in Appendix 1.

To compare the analytical results with the drinking-water standards, the data were summarized by chemical constituent (total and dissolved) to reflect the number of wells (not the number of samples) in a geozone that exceeded a particular standard. This approach was used to normalize the data set because the number of samples (both filtered and unfiltered) collected at the PMREP wells varied and only one sample (filtered) typically was collected at each NAWQA well site. This method ensures that a well is counted only once if an exceedance for a constituent is observed, regardless of whether the constituent exceeded the standard in one sample or all the samples from the well. Additional information on exceedances for each well sample can be found with the analytical data provided for all the samples in Appendix 1.

For each geozone, the number of wells sampled and the number of wells exceeding a drinking-water standard were summarized by constituent (table 5). Approximately half of the constituents measured in all geozone wells had total or dissolved concentrations less than the applicable Federal and State MCLs (tables 4, 5). The constituents with no exceedances for any geozone include antimony, barium, beryllium, boron, cadmium, chloride, chromium, copper, mercury, nickel, selenium, silver, and sulfate. Those constituents or properties that exceeded drinking-water standards for at least one geozone well include aluminum, arsenic, fluoride, iron, lead, manganese, nitrate, pH, uranium, and zinc (table 5). Radon activities exceeded the proposed MCL of 300 pCi/L in 61 of the 69 geozone wells sampled for radon. The proposed AMCL of 4,000 pCi/L was exceeded in 18 of the 69 wells.

Few exceedances were noted for the three wells sampled in the Western Blue Ridge geozone and the two wells sampled in the Grenville gneiss geozone, likely reflecting the small sample size. The pH value for one well in the Western Blue Ridge geozone was outside the pH range of 6.5–8.5 standard pH units. Radon also exceeded the AMCL of 4,000 pCi/L for the one well sampled for that constituent in the Western Blue Ridge geozone. Both wells in the Grenville gneiss geozone had radon measurements exceeding the MCL of 300 pCi/L.

A limited number of geozone wells had exceedances of arsenic, lead, nitrate, and uranium (table 5). The USEPA MCL of 0.010 mg/L for arsenic was exceeded in 2 of 7 wells sampled in the Milton geozone and 4 of 17 wells sampled in the Carolina slate geozone. For the Milton geozone, exceedances

Table 5. Summary of wells within geozones in the Piedmont and Mountains Provinces in North Carolina having chemical constituents in groundwater exceeding North Carolina and U.S. Environmental Protection Agency drinking-water standards.

[#, number; diss., dissolved; N, nitrogen; >, greater than; pCi/L, picocuries per liter]

Chemical constituent or property	Grenville gneiss		Western Blue Ridge		Eastern Blue Ridge		Inner Piedmont	
	# wells sampled	# wells exceeded	# wells sampled	# wells exceeded	# wells sampled	# wells exceeded	# wells sampled	# wells exceeded
Aluminum, total	0	0	2	0	3	1	4	2
Aluminum, diss.	2	0	3	0	11	0	11	0
Antimony, diss.	2	0	3	0	10	0	8	0
Arsenic, total	0	0	2	0	3	0	4	0
Arsenic, diss.	2	0	3	0	11	0	11	0
Barium, total	0	0	2	0	3	0	4	0
Barium, diss.	2	0	3	0	11	0	11	0
Beryllium, diss.	2	0	3	0	10	0	8	0
Boron, diss.	0	0	2	0	2	0	1	0
Cadmium, total	0	0	2	0	3	0	4	0
Cadmium, diss.	2	0	3	0	11	0	11	0
Chloride, total	0	0	2	0	3	0	4	0
Chloride, diss.	2	0	3	0	10	0	8	0
Chromium, total	0	0	2	0	3	0	4	0
Chromium, diss.	2	0	3	0	11	0	11	0
Copper, total	0	0	2	0	3	0	4	0
Copper, diss.	2	0	3	0	11	0	11	0
Fluoride, total	0	0	2	0	3	0	4	0
Fluoride, diss.	2	0	3	0	10	0	8	0
Iron, total	0	0	2	0	3	3	4	2
Iron, diss.	2	0	3	0	11	2	11	2
Lead, total	0	0	2	0	3	1	0	0
Lead, diss.	2	0	3	0	11	0	8	0
Manganese, total	0	0	2	0	3	2	4	1
Manganese, diss.	2	0	3	0	11	2	11	1
Mercury, total	0	0	0	0	3	0	0	0
Mercury, diss.	0	0	0	0	3	0	0	0
Nickel, total	0	0	2	0	3	0	4	0
Nickel, diss.	2	0	3	0	11	0	11	0
Nitrate+nitrite (as N), total	0	0	2	0	3	0	4	0
Nitrate+nitrite (as N), diss.	2	0	3	0	10	0	9	0
pH	2	0	3	1	11	7	11	6
Radon-222, total								
(>300 pCi/L)	2	2	1	1	10	9	9	9
(>4,000 pCi/L)	2	0	1	1	10	3	9	0
Selenium, total	0	0	2	0	3	0	3	0
Selenium, diss.	2	0	3	0	11	0	10	0
Silver, total	0	0	2	0	3	0	4	0
Silver, diss.	2	0	3	0	11	0	11	0
Sulfate, total	0	0	2	0	3	0	4	0
Sulfate, diss.	2	0	3	0	10	0	8	0
Uranium, diss.	2	0	3	0	10	0	9	0
Zinc, total	0	0	2	0	3	1	4	0
Zinc, diss.	2	0	3	0	11	1	11	0

Table 5. Summary of wells within geozones in the Piedmont and Mountains Provinces in North Carolina having chemical constituents in groundwater exceeding North Carolina and U.S. Environmental Protection Agency drinking-water standards.—Continued

[#, number; diss., dissolved; N, nitrogen; >, greater than; pCi/L, picocuries per liter]

Chemical constituent or property	Milton		Felsic intrusive		Raleigh and Charlotte		Carolina slate	
	# wells sampled	# wells exceeded	# wells sampled	# wells exceeded	# wells sampled	# wells exceeded	# wells sampled	# wells exceeded
Aluminum, total	7	2	4	0	4	1	3	0
Aluminum, diss.	10	0	11	0	8	0	17	0
Antimony, diss.	10	0	11	0	9	0	16	0
Arsenic, total	7	2	4	0	5	0	3	0
Arsenic, diss.	10	2	14	0	9	0	17	4
Barium, total	8	0	4	0	5	0	3	0
Barium, diss.	10	0	11	0	9	0	16	0
Beryllium, diss.	10	0	11	0	9	0	16	0
Boron, diss.	10	0	12	0	8	0	15	0
Cadmium, total	7	0	4	0	4	0	3	0
Cadmium, diss.	10	0	11	0	9	0	17	0
Chloride, total	7	0	4	0	5	0	3	0
Chloride, diss.	10	0	15	0	9	0	16	0
Chromium, total	7	0	4	0	4	0	3	0
Chromium, diss.	10	0	11	0	9	0	17	0
Copper, total	7	0	4	0	4	0	3	0
Copper, diss.	10	0	11	0	9	0	17	0
Fluoride, total	7	2	4	0	5	0	3	0
Fluoride, diss.	10	2	15	0	9	1	16	0
Iron, total	7	4	4	3	5	1	3	0
Iron, diss.	10	3	15	0	9	0	17	3
Lead, total	7	0	4	0	4	0	3	0
Lead, diss.	10	0	11	0	9	0	17	0
Manganese, total	7	5	4	1	5	2	3	2
Manganese, diss.	10	5	15	4	9	1	17	8
Mercury, total	0	0	4	0	2	0	0	0
Mercury, diss.	0	0	0	0	3	0	0	0
Nickel, total	7	0	4	0	4	0	3	0
Nickel, diss.	10	0	11	0	9	0	17	0
Nitrate+nitrite (as N), total	7	0	4	4	2	0	3	0
Nitrate+nitrite (as N), diss.	10	0	15	4	9	0	16	0
pH	10	6	15	9	10	6	17	6
Radon-222, total								
(>300 pCi/L)	10	10	14	13	9	6	14	11
(>4,000 pCi/L)	10	3	14	7	9	3	14	1
Selenium, total	7	0	4	0	4	0	3	0
Selenium, diss.	10	0	11	0	9	0	17	0
Silver, total	7	0	4	0	4	0	3	0
Silver, diss.	10	0	11	0	9	0	17	0
Sulfate, total	7	0	4	0	5	0	3	0
Sulfate, diss.	10	0	15	0	9	0	16	0
Uranium, diss.	10	0	11	1	9	1	16	0
Zinc, total	7	5	4	1	4	1	3	2
Zinc, diss.	10	4	11	1	9	0	17	2

of total and dissolved arsenic were confined to wells RK-229 (maximum total concentration of 0.025 mg/L) and RK-234 (maximum total concentration of 0.014 mg/L) located at the UPRS (Appendix 1). Exceedances of dissolved arsenic for the Carolina slate geozone occurred in four NAWQA wells, with concentrations ranging from 0.0106 to 0.0383 mg/L in wells MG-031, RA-174, UN-145, and UN-146 located in the central and southern parts of the geozone (fig. 3). This observed distribution of arsenic exceedances is in agreement with the study by Pippin (2005) that identified a zone trending northeast from Union to Person Counties where groundwater has a high probability of containing ambient concentrations of arsenic above the USEPA MCL of 0.010 mg/L, especially in association with rocks of the Carolina Slate Belt.

The concentration of total lead measured in one of three wells from the Eastern Blue Ridge geozone exceeded the MCL of 0.015 mg/L. Concentrations of dissolved lead measured in all 11 wells from the Eastern Blue Ridge geozone were less than the MCL of 0.015 mg/L. Both total and dissolved concentrations of nitrate exceeded the MCL of 10 mg/L in four wells for the Felsic intrusive geozone. These four wells are WK-331, WK-334, WK-335, WK-338, and they are located at the RHRS (Appendix 1) where past over-applications of municipal biosolids have elevated nitrate concentrations in groundwater. No other PMREP wells or NAWQA wells sampled for any of the geozones had nitrate concentrations exceeding 10 mg/L. Concentrations of dissolved uranium, a naturally occurring radionuclide, exceeded the USEPA MCL of 0.030 mg/L in 2 wells, 1 each from the Felsic intrusive (total of 11 wells) and Raleigh and Charlotte (total of 9 wells) geozones.

The most common exceedances of the drinking-water criteria occurred for radon, pH, manganese, iron, and zinc (table 5). Radon activity levels exceeding the proposed MCL of 300 pCi/L occurred in all geozones. Radon occurs naturally in groundwater of the Piedmont and Mountains Provinces with the highest levels often associated with metaigneous rocks of felsic composition (Loomis and others, 1987; Campbell, 2006 and 2008; Vinson and others, 2009), such as those in the Felsic intrusive geozone, which had the largest proportion of wells (7 of 14) with radon activities that exceeded the proposed AMCL of 4,000 pCi/L (table 5; Appendix 1). The Eastern Blue Ridge, Milton, and Raleigh and Charlotte geozones also had several wells with radon activities greater than 4,000 pCi/L. All nine wells in the Inner Piedmont geozone had radon activities higher than 300 pCi/L but less than 4,000 pCi/L. All geozones, with the exception of the Grenville gneiss geozone, had multiple wells with pH values outside the range of 6.5–8.5, most of which were less than 6.5. Manganese exceeded the MCL of 0.05 mg/L for wells in six geozones, with the highest proportion of exceedances occurring in the Milton and Carolina slate geozones. Exceedances of iron and zinc occurred in over half the geozones, and most commonly for the Milton or Carolina slate geozones. All exceedances of zinc occurred solely for samples collected from wells constructed with galvanized steel casing, suggesting that the high zinc concentrations may be related to leaching from well-casing material and not ambient groundwater conditions in the geozones.

Overall, the Milton and the Raleigh and Charlotte geozones had the greatest number of constituents, eight each, that exceeded applicable drinking-water criteria in at least one well (table 5). The Eastern Blue Ridge and Felsic intrusive geozones followed with seven constituents each and the Carolina slate geozone with six constituents that exceeded drinking-water criteria. With the exception of nitrate and zinc, constituents with concentrations exceeding drinking-water criteria appeared to reflect ambient groundwater conditions in the geozones. Exceedances of nitrate and zinc are considered to reflect contamination from local land use and well-casing materials, respectively. Radon was the most commonly exceeded constituent, with 61 of the 69 sampled wells having activities higher than the proposed MCL of 300 pCi/L. The presence of radon in groundwater used for public supply is of particular environmental concern because of the potential human exposure to radon in groundwater through ingestion (drinking) or inhalation (showering), which increases the risk of developing cancer (U.S. Environmental Protection Agency, 2007). The trace elements iron, manganese, and zinc were the other most common constituents that exceeded drinking-water criteria, but the concern with these analytes in drinking water generally is associated with aesthetic effects.

Comparison of Bedrock Groundwater-Quality Characteristics by Regional Geozone

The relation between regional geozones and groundwater constituents was evaluated to determine whether potential differences in groundwater-constituent concentrations were discernible among the geozone groupings used to represent the different regional geologic settings in the Piedmont and Mountains Provinces. This type of information is important because it can be used to identify potential areas or type settings that may be suitable for withdrawing groundwater as a source of drinking-water supply or for avoiding areas where naturally occurring constituents may be present at concentrations that are hard to remove or treat for water-supply purposes. The results of this evaluation are considered to be preliminary because of the limited number of wells (2–14) analyzed per geozone.

Several steps were taken in compiling the data used in statistical comparisons of the constituent concentrations among the geozones. The primary steps were aimed at reducing potential bias within the geozones between the PMREP research station data (locally concentrated wells with multiple samples) and the NAWQA data (spatially separated wells with single samples). A median constituent concentration was used for each PMREP station, derived from the all samples and wells at each station (Appendix 1). These data were combined with the NAWQA well data for each geozone. PMREP wells deemed to be influenced significantly with nitrate derived from land-use activities at the PMREP stations were excluded from the evaluation. In addition, the samples collected from the NAWQA wells were analyzed by the USGS laboratory; hence, only USGS laboratory data from the PMREP wells were considered in the evaluation. This process of elimination produced a more uniform data set but also reduced the statistical power of the data by lowering the overall number of values for a given constituent in each geozone. The compiled data set used for the geozone statistical comparisons and additional details on the processing steps are provided in Appendix 2.

Two statistical methods were used to test for statistical differences in median concentrations of constituents among the geozones. Results of the Kruskal-Wallis test and Tukey comparison test performed on the analytical data presented in Appendix 2 are summarized in table 6. The Kruskal-Wallis test results indicated that the median concentrations of some constituents were significantly different (where the p-value is less than $\alpha = 0.05$) for some geozones. The water-quality properties and constituents noted to be influenced by the geologic setting, or geozone, include specific conductance, total hardness, calcium, magnesium, potassium, sodium, bicarbonate, chloride, silica, ammonia, aluminum, antimony, cadmium, selenium, and uranium. These properties and constituents were analyzed further using the Tukey multiple comparison test to identify the geozone pairs where the median concentrations were different.

With some exceptions, the Tukey test identified one or more geozone pairs for each constituent or property having a statistical difference in median concentration at the 0.05 significance level (table 6). The Kruskal-Wallis test indicated a significant difference in median concentration for total hardness, magnesium, and selenium (p-value of about 0.03). Conversely, the pair-wise comparison with the Tukey test did not identify any geozone pairs with significant differences for total hardness, magnesium, or selenium, thus reflecting possible limitations of the method for examining data sets where the sample size is small and variability is high.

Box plots are provided in figure 7 as a visual reference for examining those geozone pairs in table 6 having statistically significant differences in median values for specific conductance and concentrations of calcium, potassium, sodium, bicarbonate, chloride, silica, ammonia, aluminum, and uranium. The geozone concentrations for antimony and cadmium are not displayed in the box plots because most noncensored detections above the analytical RL for each constituent occurred in one geozone (Appendix 2). The concentration percentiles displayed in each box plot for each geozone constituent, along with the number of censored values and levels, are provided as Appendix 3. For a given constituent with censored data, the box plots include the maximum censoring level observed for all the geozones. For example, the maximum RL for ammonia was 0.04 mg/L as N (fig. 7); however, a given geozone may not have censored data or there may be more than one RL (Appendix 3).

In most cases, the geozones with statistically significant differences in median values of a property (specific conductance) or concentrations of a particular constituent were limited to one geozone pair, or the median concentration of a constituent in one geozone was significantly different when compared with several other geozones (table 6). For example, significant differences in specific conductance were identified between the Carolina slate and Inner Piedmont geozones. The median specific conductance of 278 microsiemens per centimeter at 25 degrees Celsius (μS/cm) for the Carolina slate geozone is significantly greater than the median of 86 μS/cm for the Inner Piedmont geozone (fig. 7). For the remaining six geozones, the overall range in specific-conductance values may vary among the geozones; however, no other statistically significant differences in median values of specific conductance were identified based on the Tukey test (table 6). This finding does not mean that specific-conductance values do not differ among the geozones in the Piedmont and Mountains Provinces; it only means that a significant difference in medians between the geozones, if any, was not large enough to be detected with the given sample size.

Potassium is an example of a constituent where the median concentration in one geozone is significantly different from several other geozones (table 6). The median potassium concentration of 0.56 mg/L in the Carolina slate geozone is significantly lower than the median concentrations in the Grenville gneiss (3.82 mg/L), Eastern Blue Ridge (1.70 mg/L), Inner Piedmont (1.62 mg/L), Milton (2.62 mg/L), and Felsic intrusive (2.51 mg/L) geozones (table 6; fig. 7). Of all the constituents, sodium had the most diverse combination of geozone pairs identified as having statistically significant differences in median concentrations (table 6).

Overall, the Inner Piedmont, Carolina slate, and Felsic intrusive geozones had the most significant variations in median concentrations of groundwater constituents. The Inner Piedmont geozone had 10 constituents with median concentrations significantly different compared with one or more of the other geozones (table 6). The Carolina slate and Felsic intrusive geozones followed with eight constituents each with significantly different median concentrations. Although the results of this preliminary examination are based on a data set with a limited number of wells and many constituent concentrations near to or less than analytical RLs, the results suggest that evaluating analytical data on the basis of geozone setting may be a useful approach for characterizing water-quality conditions in bedrock aquifers of the Piedmont and Mountains Provinces of North Carolina. Further evaluation of a more comprehensive data set would be needed to more fully characterize similarities and differences in water quality, as well as causal effects, among the geozones. Additional data needed include local lithologic information at each site, additional well sampling sites in each geozone, and wells in locations considered to represent ambient groundwater conditions.

Table 6. Summary results of Kruskal-Wallis test and Tukey comparison test of water-quality constituent or property and geozone in the Piedmont and Mountain Provinces of North Carolina.

[diss., dissolved; NS, no significant differences between geozones based on Tukey test; *, indicates significance at $\alpha = 0.05$; <, less than]

Chemical constituent or property	Kruskal-Wallis test	Tukey comparison test
	p-value	Geozone comparisons significant at $\alpha = 0.05$
Oxygen, diss.	0.2756	NS
pH	0.4843	NS
Specific conductance	0.0135*	Carolina slate - Inner Piedmont
Hardness, total	0.0295*	NS
Calcium, diss.	0.0138*	Carolina slate - Inner Piedmont
Magnesium, diss.	0.0308*	NS
Potassium, diss.	<0.0001*	Carolina slate - Grenville gneiss Carolina slate - Eastern Blue Ridge Carolina slate - Inner Piedmont Carolina slate - Milton Carolina slate - Felsic intrusive
Sodium, diss.	<0.0001*	Inner Piedmont - Milton Felsic intrusive - Western Blue Ridge Felsic intrusive - Inner Piedmont Carolina slate - Western Blue Ridge Carolina slate - Eastern Blue Ridge Carolina slate - Inner Piedmont
Bicarbonate, diss.	0.0104*	Carolina slate - Eastern Blue Ridge
Chloride, diss.	0.0073*	Carolina slate - Western Blue Ridge
Fluoride, diss.	0.1374	NS
Silica, diss.	0.0010*	Felsic intrusive - Western Blue Ridge Felsic intrusive - Eastern Blue Ridge Felsic intrusive - Inner Piedmont
Sulfate, diss.	0.4126	NS
Ammonia, diss.	0.0027*	Inner Piedmont - Eastern Blue Ridge Inner Piedmont - Milton Inner Piedmont - Felsic intrusive Inner Piedmont - Raleigh and Charlotte
Nitrite+nitrate, diss.	0.5960	NS
Orthophosphate, diss.	0.0861	NS
Phosphorus, diss.	0.0786	NS

Table 6. Summary results of Kruskal-Wallis test and Tukey comparison test of water-quality constituent or property and geozone in the Piedmont and Mountain Provinces of North Carolina.—Continued

[diss., dissolved; NS, no significant differences between geozones based on Tukey test; *, indicates significance at α = 0.05; <, less than]

Chemical constituent or property	Kruskal-Wallis test	Tukey comparison test
	p-value	Geozone comparisons significant at α = 0.05
Aluminum, diss.	0.0002*	Inner Piedmont - Milton Inner Piedmont - Felsic intrusive Inner Piedmont - Carolina slate
Antimony, diss.	0.0022*	Carolina slate - Eastern Blue Ridge Carolina slate - Inner Piedmont Carolina slate - Felsic intrusive Carolina slate - Raleigh and Charlotte
Arsenic, diss.	0.0962	NS
Barium, diss.	0.0551	NS
Beryllium, diss.	0.1693	NS
Boron, diss.	0.1370	NS
Cadmium, diss.	0.0037*	Raleigh and Charlotte - Eastern Blue Ridge Raleigh and Charlotte - Inner Piedmont Raleigh and Charlotte - Milton Raleigh and Charlotte - Felsic intrusive Raleigh and Charlotte - Carolina slate
Chromium, diss.	0.1261	NS
Cobalt, diss.	0.1898	NS
Copper, diss.	0.7724	NS
Iron, diss.	0.3128	NS
Lead, diss.	0.0617	NS
Manganese, diss.	0.8692	NS
Molybdenum, diss.	0.5540	NS
Nickel, diss.	0.4116	NS
Selenium, diss.	0.0322*	NS
Zinc, diss.	0.5082	NS
Radon-222, total	0.1101	NS
Uranium, diss.	0.0034*	Felsic intrusive - Eastern Blue Ridge Felsic intrusive - Inner Piedmont

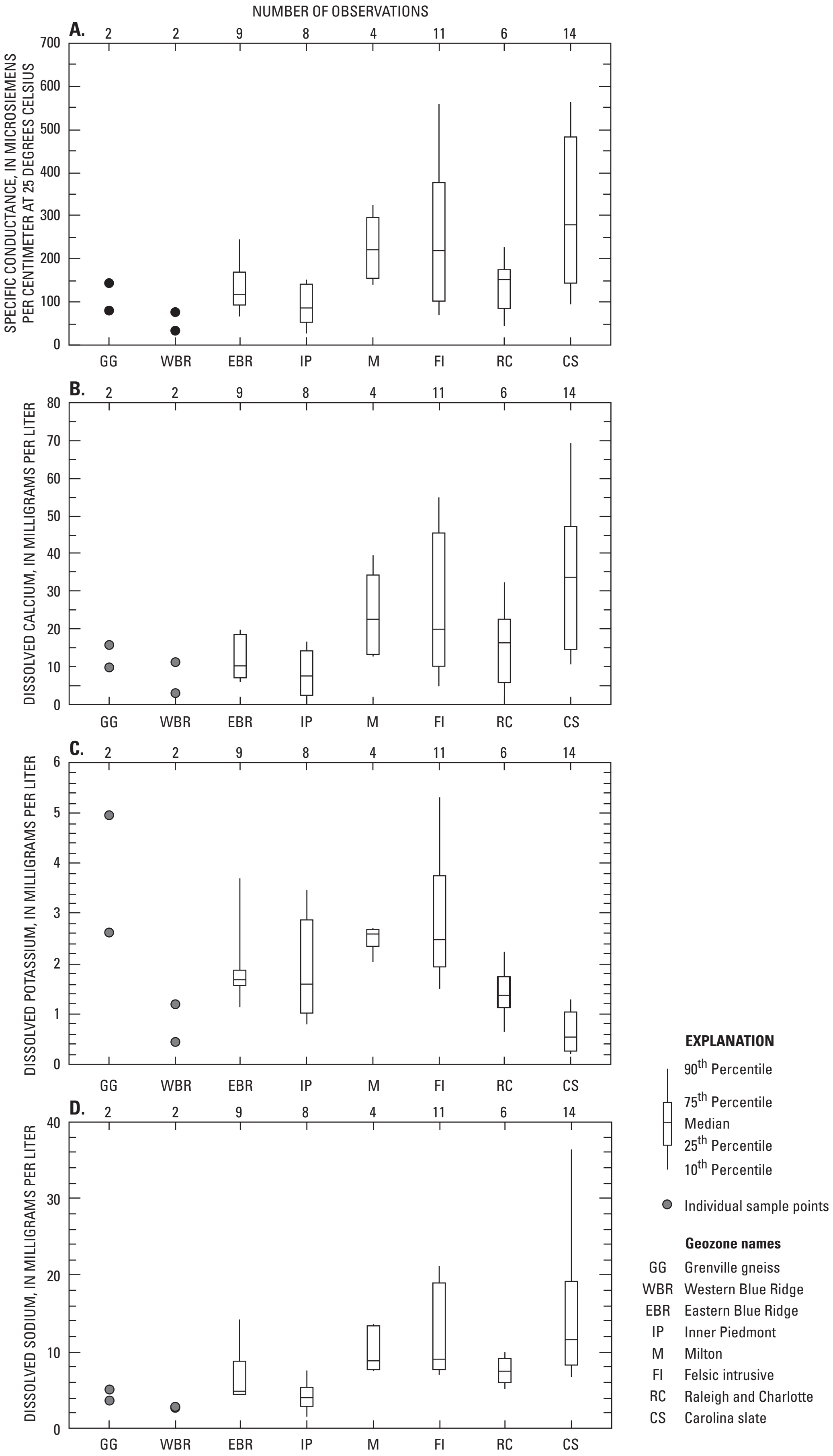

Figure 7. Distributions of values of (*A*) specific conductance and concentrations of (*B*) calcium, (*C*) potassium, (*D*) sodium, (*E*) bicarbonate, (*F*) chloride, (*G*) silica, (*H*) ammonia, (*I*) aluminum, and (*J*) uranium for geozones in the Piedmont and Mountains Provinces of North Carolina.

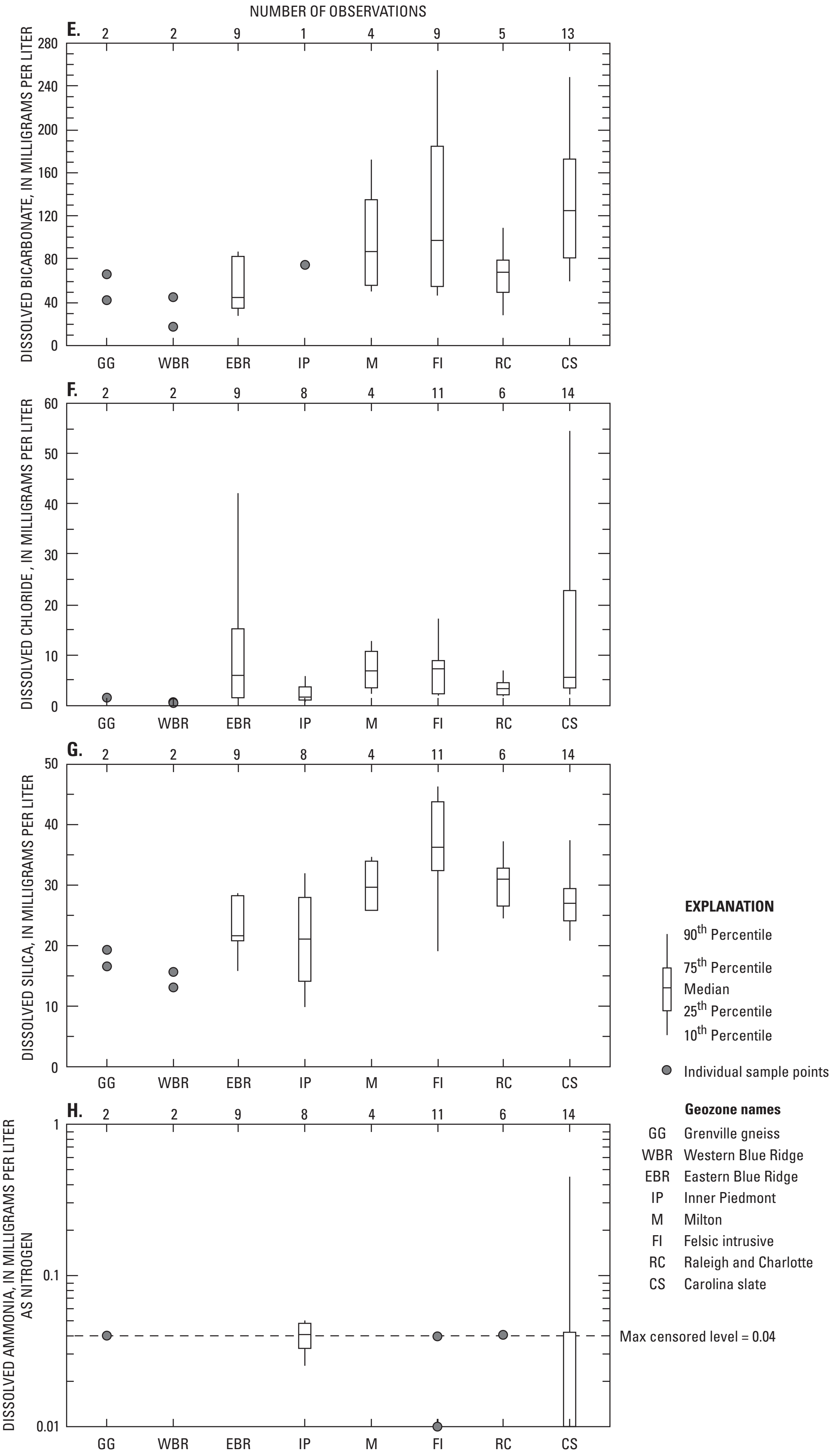

Figure 7. Distributions of values of (*A*) specific conductance and concentrations of (*B*) calcium, (*C*) potassium, (*D*) sodium, (*E*) bicarbonate, (*F*) chloride, (*G*) silica, (*H*) ammonia, (*I*) aluminum, and (*J*) uranium for geozones in the Piedmont and Mountains Provinces of North Carolina.—Continued

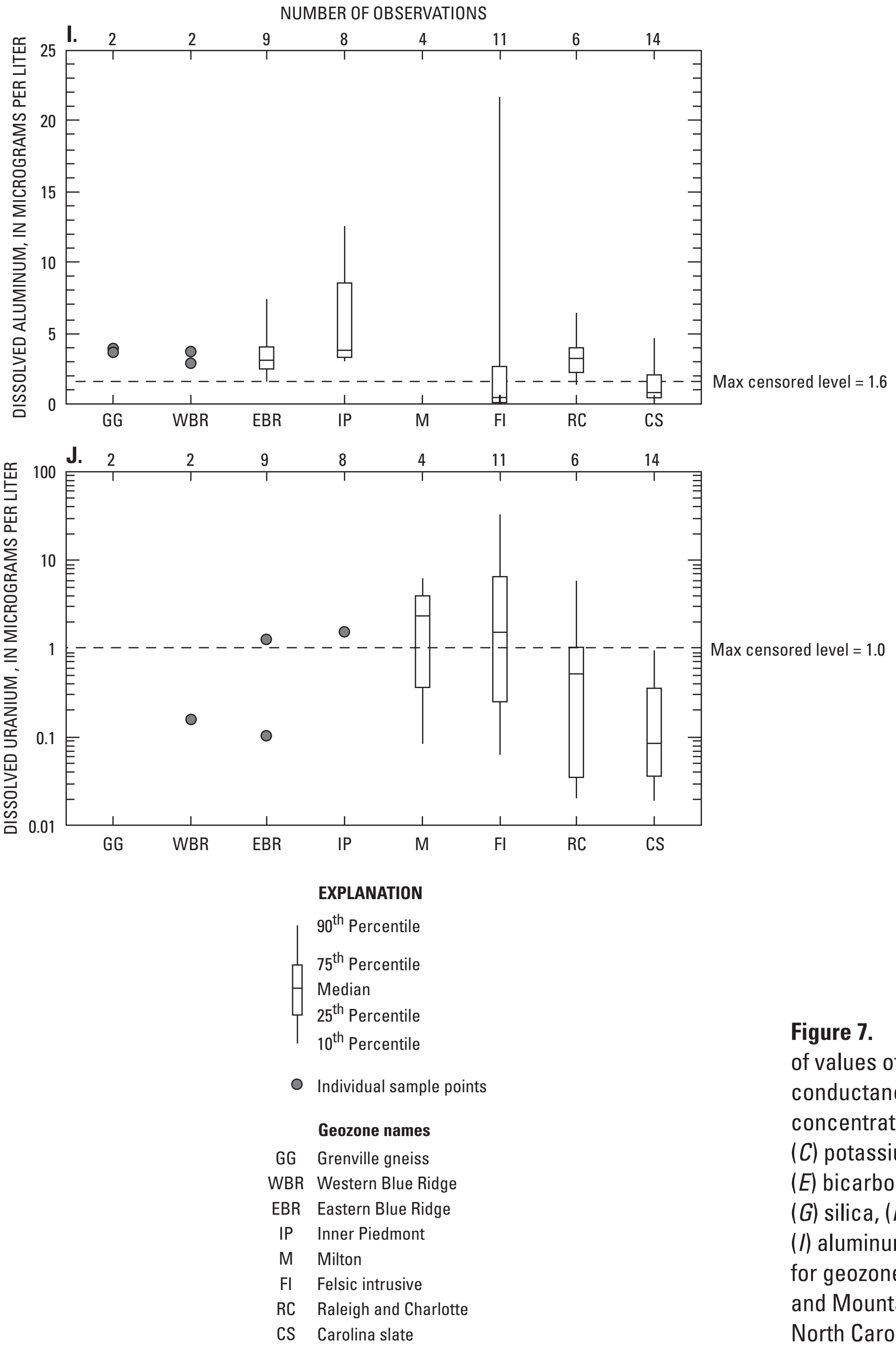

Figure 7. Distributions of values of (*A*) specific conductance and concentrations of (*B*) calcium, (*C*) potassium, (*D*) sodium, (*E*) bicarbonate, (*F*) chloride, (*G*) silica, (*H*) ammonia, (*I*) aluminum, and (*J*) uranium for geozones in the Piedmont and Mountains Provinces of North Carolina.—Continued

Summary and Conclusions

In this report, grouping and evaluating analytical data based on regional geozone setting provided useful information for characterizing the quality of groundwater in bedrock aquifers in the North Carolina Piedmont and Blue Ridge Physiographic Provinces (Piedmont and Mountains Provinces). Analytical data were evaluated from 79 wells representing 8 of 10 different regional geozones distributed throughout the North Carolina Piedmont and Mountains Provinces. Data evaluation included an examination of the ionic composition of groundwater in the geozones, a comparison of groundwater constituent concentrations to applicable State and Federal drinking-water standards, and statistical comparisons to identify significant differences in constituent concentrations among the geozones.

The general ionic composition, or water type, in the geozones combined with other chemical and hydrologic data provide insight into some of the factors that influence groundwater quality in the bedrock aquifers. The basic ionic compositions of bedrock groundwater in the geozones generally were classified as a calcium-sodium/bicarbonate or calcium-magnesium/bicarbonate water type. No major differences in overall ionic chemistry among the geozones were evident based on the data examined. Variability in the cationic and anionic composition of groundwater within a particular geozone appeared to reflect local differences in lithologic setting, geochemical conditions, groundwater-flow paths, and(or) land-use effects. At many of the geozone well sites, a subtle transition in groundwater cationic composition occurred with depth. The shift in cationic composition appeared to reflect differences in the amount of ion exchange between the groundwater and rock materials, where a greater proportion of calcium was dissolved into older groundwater with longer flow paths deeper in bedrock. In some cases, hydrologic factors, such as vertical hydraulic gradients and the degree of fracture interconnectivity, as well as land use, were found to have a significant influence on groundwater quality at the local scale. At some sites, surface-derived contaminants were localized to shallow portions of the bedrock aquifer or were present in multiple fracture zones distributed over hundreds of feet within the bedrock well. The more noticeable changes in water type occurred in the anionic composition of the groundwater in response to anthropogenic effects, such as nutrient inputs from local land use that increased groundwater concentrations of nitrate and chloride.

Analytical results of groundwater samples were compared to applicable State and Federal water-quality standards to determine if sample constituents and properties in the geozones exceeded drinking-water criteria. For all of the geozone wells, concentrations of antimony, barium, beryllium, boron, cadmium, chloride, chromium, copper, mercury, nickel, selenium, silver, and sulfate were less than drinking-water standards. Those constituents and properties that exceeded drinking-water standards for at least one geozone well include aluminum, arsenic, fluoride, iron, lead, manganese, nitrate, pH, uranium, and zinc. The most common exceedances of the drinking-water criteria occurred for radon, pH, manganese, iron, and zinc. Exceedances of nitrate and zinc are considered to reflect contamination from local land use and well-casing materials, respectively. The remaining constituents with concentrations that exceeded drinking-water criteria appeared to reflect ambient groundwater conditions in the geozones. Naturally occurring radon was the most commonly exceeded constituent, with 61 of the 69 sampled wells having activities higher than the USEPA proposed MCL of 300 pCi/L. The Felsic intrusive geozone had the largest proportion of wells (7 of 14) with radon activities that exceeded the USEPA proposed AMCL of 4,000 pCi/L. The presence of radon in groundwater used for public supply is of particular environmental concern because of the potential for human exposure to radon through ingestion or inhalation. Overall, the Milton and the Raleigh and Charlotte geozones had the greatest number, eight each, of water-quality properties or constituents that exceeded applicable drinking-water criteria in at least one well. The Eastern Blue Ridge and Felsic intrusive geozones each had seven properties or constituents that exceeded drinking-water criteria, and the Carolina slate geozone had six.

A preliminary evaluation was conducted to identify statistically significant differences in median concentrations of groundwater constituents among the geozones. Significant differences were identified for several water-quality properties or constituents, including specific conductance, calcium, potassium, sodium, bicarbonate, chloride, silica, ammonia, aluminum, antimony, cadmium, and uranium. In most cases, statistically significant differences in median values of a property or concentrations of a particular constituent were limited to one geozone pair, or the median concentration of a constituent in one geozone was significantly different when compared with several other geozones. Overall, the Inner Piedmont, Carolina slate, and Felsic intrusive geozones had the most significant variations in median concentrations of groundwater constituents.

The preliminary results of the statistical comparison tests among the geozones suggest that evaluation of analytical data based on geozone setting may be a useful approach for characterizing water-quality conditions in bedrock aquifers of the Piedmont and Mountains Provinces. Additional data are needed for a more thorough analysis of groundwater-quality conditions within the different geozone settings to better characterize similarities and differences in bedrock aquifers throughout the North Carolina Piedmont and Mountains Provinces. Enhanced data are needed with wells in areas that best indicate ambient water quality and wells that reflect different land-use effects for the geozones. These types of data could provide a good baseline for understanding natural variability and better ascertaining differences related to land use.

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