

National Water-Quality Assessment Program

**Naturally Occurring Contaminants in the Piedmont and
Blue Ridge Crystalline-Rock Aquifers and Piedmont Early
Mesozoic Basin Siliciclastic-Rock Aquifers, Eastern
United States, 1994–2008**



Scientific Investigations Report 2013–5072

Cover: Photo showing Whiteside tonalite (rock types quartz diorite and granodiorite, lithologic group mafic igneous rocks and their metamorphic equivalents, lithochemical subgroup 41). Photograph by William Burton, U.S. Geological Survey

Naturally Occurring Contaminants in the Piedmont and Blue Ridge Crystalline-Rock Aquifers and Piedmont Early Mesozoic Basin Siliciclastic-Rock Aquifers, Eastern United States, 1994–2008

By Melinda J. Chapman, Charles A. Cravotta III, Zoltan Szabo, and Bruce D. Lindsey

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Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with reliable scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). The NAWQA Program is designed to answer: What is the quality of our Nation's streams and groundwater? How are conditions changing over time? How do natural features and human activities affect the quality of streams and groundwater, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991 to 2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (http://water.usgs.gov/nawqa/studies/study_units.html).

In the second decade of the Program (2001–12), a major focus is on regional assessments of water-quality conditions and trends. These regional assessments are based on major river basins and principal aquifers, which encompass larger regions of the country than the Study Units. Regional assessments extend the findings in the Study Units by filling critical gaps in characterizing the quality of surface water and groundwater, and by determining water-quality status and trends at sites that have been consistently monitored for more than a decade. In addition, the regional assessments continue to build an understanding of how natural features and human activities affect water quality. Many of the regional assessments employ modeling and other scientific tools, developed on the basis of data collected at individual sites, to help extend knowledge of water quality to unmonitored, yet comparable areas within the regions. The models thereby enhance the value of our existing data and our understanding of the hydrologic system. In addition, the models are useful in evaluating various resource-management scenarios and in predicting how our actions, such as reducing or managing nonpoint and point sources of contamination, land conversion, and altering flow and (or) pumping regimes, are likely to affect water conditions within a region.

Other activities planned during the second decade include continuing national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, trace elements, and aquatic ecology; and continuing national topical studies on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on stream ecosystems, and transport of contaminants to public-supply wells.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

William H. Werkheiser
USGS Associate Director for Water

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Conversion Factors, Datums

Inch/Pound to SI

Multiply	By	To obtain
Length		
foot (ft)	0.305	meter
mile (mi)	1.609	kilometer (km)
Area		
square foot (ft ²)	929	square centimeter (cm ²)
square foot (ft ²)	0.093	square meter (m ²)
square mile (mi ²)	259	hectare (ha)
square mile (mi ²)	2.59	square kilometer (km ²)
Volume		
cubic foot (ft ³)	28.32	cubic decimeter (dm ³)
cubic foot (ft ³)	0.028	cubic meter (m ³)
cubic mile (mi ³)	4.168	cubic kilometer (km ³)
acre-foot (acre-ft)	1,233	cubic meter (m ³)
acre-foot (acre-ft)	0.001	cubic hectometer (hm ³)
Flow rate		
acre-foot per day (acre-ft/d)	0.014	cubic meter per second (m ³ /s)
acre-foot per year (acre-ft/yr)	1,233	cubic meter per year (m ³ /yr)
acre-foot per year (acre-ft/yr)	0.001	cubic hectometer per year (hm ³ /yr)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C}=(^{\circ}\text{F}-32)/1.8$$

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

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

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Acronyms and Abbreviations

acfbclusur1	Apalachicola-Chattahoochee Flint River Basin urban land-use study
acfbclusur2	Apalachicola-Chattahoochee Flint River Basin urban land-use study
Al	aluminum
albesus8	Albemarle-Pamlico Drainages major aquifer study
AMCL	alternative maximum contaminant level
ANOVA	analysis-of-variance
Ba	barium
C	carbon
Ca	calcium
Cl	chloride
CLSD	clastic sedimentary rocks
CLSDF	feldspar-rich clastic sedimentary rocks
CLSDLAC	clastic lacustrine/evaporite sedimentary rocks
CLSDMT	metamorphosed clastic sedimentary rocks
CLSDQ	quartz-rich sedimentary rocks
CZmd	Cambrian/Late Proterozoic metamudstone and meta-argillite
CZms	Cambrian/Late Proterozoic mica schist
CZph	Cambrian/Late Proterozoic phyllite and schist
delrsus1	Delaware River Basin major aquifer study
DO	dissolved oxygen
Fe	iron
GEOLEX	USGS National Geologic Map Database Geologic Names Lexicon
GIS	geographic information system
H	hydrogen
HHB	human health benchmark
HBSL	health-based screening level
HFO	hydrous ferric oxide
HCRL	highest common reporting limit
IGMTF	felsic igneous and metamorphic rocks
IGMTI	intermediate igneous or metamorphic rocks
IGMTM	mafic igneous and metamorphic rocks
K	potassium
KANA	Kanawha/New River Basins
Lc	critical level of detection

linjsus3	Long Island/New Jersey Study Unit major aquifer study
Isussus2	Lower Susquehanna River Basin agricultural land-use study
MCL	maximum contaminant level
Mg	magnesium
µg/L	micrograms per liter
mg/L	milligrams per liter
Mn	manganese
MTQ	quartz-rich metamorphic rocks
Na	Sodium
NAD83	North American Datum of 1983
NAVD88	North American Vertical Datum of 1988
NAWQA	U.S. Geological Survey National Water-Quality Assessment Program
NJDEP	New Jersey Department of Environmental Protection
NLCD 1992	National Land Cover Dataset 1992
NURE	U.S. Geological Survey National Uranium Resource Evaluation Program
NWQL	U.S. Geological Survey National Water Quality Laboratory
OHSU	Oregon Health and Science University
O	oxygen
P	phosphorus
PBR	Piedmont and Blue Ridge
PC	principal components
PCA	principal components analysis
Ra	radium
S	sulfur
SC	specific conductance
Si	silica
SI	mineral saturation index
SMCL	secondary maximum contaminant level
SSMDC	sample-specific minimum-detection concentration
TDS	total dissolved solids
ULMAF	ultramafic rocks
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Naturally Occurring Contaminants in the Piedmont and Blue Ridge Crystalline-Rock Aquifers and Piedmont Early Mesozoic Basin Siliciclastic-Rock Aquifers, Eastern United States, 1994–2008

By Melinda J. Chapman, Charles A. Cravotta III, Zoltan Szabo, and Bruce D. Lindsey

Abstract

Groundwater quality and aquifer lithologies in the Piedmont and Blue Ridge Physiographic Provinces in the eastern United States vary widely as a result of complex geologic history. Bedrock composition (mineralogy) and geochemical conditions in the aquifer directly affect the occurrence (presence in rock and groundwater) and distribution (concentration and mobility) of potential naturally occurring contaminants, such as arsenic and radionuclides, in drinking water. To evaluate potential relations between aquifer lithology and the spatial distribution of naturally occurring contaminants, the crystalline-rock aquifers of the Piedmont and Blue Ridge Physiographic Provinces and the siliciclastic-rock aquifers of the Early Mesozoic basin of the Piedmont Physiographic Province were divided into 14 lithologic groups, each having from 1 to 16 lithochemical subgroups, based on primary rock type, mineralogy, and weathering potential. Groundwater-quality data collected by the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program from 1994 through 2008 from 346 wells and springs in various hydrogeologic and land-use settings from Georgia through New Jersey were compiled and analyzed for this study. Analyses for most constituents were for filtered samples, and, thus, the compiled data consist largely of dissolved concentrations. Concentrations were compared to criteria for protection of human health, such as U.S. Environmental Protection Agency (USEPA) drinking water maximum contaminant levels and secondary maximum contaminant levels or health-based screening levels developed by the USGS NAWQA Program in cooperation with the USEPA, the New Jersey Department of Environmental Protection, and Oregon Health & Science University. Correlations among constituent concentrations, pH, and oxidation-reduction (redox) conditions were used to infer geochemical controls on constituent mobility within the aquifers.

Of the 23 trace-element constituents evaluated, arsenic, manganese, and zinc were detected in one or more water

samples at concentrations greater than established human health-based criteria. Arsenic concentrations typically were less than 1 microgram per liter ($\mu\text{g/L}$) in most groundwater samples; however, concentrations of arsenic greater than 1 $\mu\text{g/L}$ frequently were detected in groundwater from clastic lacustrine sedimentary rocks of the Early Mesozoic basin aquifers and from metamorphosed clastic sedimentary rocks of the Piedmont and Blue Ridge crystalline rock aquifers. Groundwater from these rock units had elevated pH compared to other rock units evaluated in this study. Of the nine samples for which arsenic concentration was greater than 10 $\mu\text{g/L}$, six were classified as oxic and three as anoxic, and seven had pH of 7.2 or greater. Manganese concentrations typically were less than 10 $\mu\text{g/L}$ in most samples; however, 8.3 percent of samples from the Piedmont and Blue Ridge crystalline-rock aquifers and 3.0 percent of samples from the Early Mesozoic basin siliciclastic rock aquifers had manganese concentrations greater than the 300- $\mu\text{g/L}$ health-based screening level. The positive correlation of manganese with iron and ammonia and the negative correlation of manganese with dissolved oxygen and nitrate are consistent with the reductive dissolution of manganese oxides in the aquifer. Zinc concentrations typically were less than 10 $\mu\text{g/L}$ in the groundwater samples considered in the study, but 0.4 percent and 5.5 percent of the samples had concentrations greater than the health-based screening level of 2,000 $\mu\text{g/L}$ and one-tenth of the health-based screening level, respectively. The mean rank concentration of zinc in groundwater from the quartz-rich sedimentary rock lithologic group was greater than that for other lithologic groups even after eliminating samples collected from wells constructed with galvanized casing.

Approximately 90 percent of 275 groundwater samples had radon-222 concentrations that were greater than the proposed alternative maximum contaminant level of 300 picocuries per liter. In contrast, only 2.0 percent of 98 samples had combined radium (radium-226 plus radium-228) concentrations greater than the maximum contaminant level of 5.0 picocuries per liter, and 0.6 percent

of 310 samples had uranium concentrations greater than the maximum contaminant level of 30 $\mu\text{g/L}$. Radon concentrations were highest in the Piedmont and Blue Ridge crystalline-rock aquifers, especially in granite, and elevated median concentrations were noted in the Piedmont Early Mesozoic basin aquifers, but without the extreme maximum concentrations found in the crystalline rocks (granites). Although the siliciclastic lithologies had a greater frequency of elevated uranium concentrations, radon and radium were commonly detected in water from both siliciclastic and crystalline lithologies. Uranium concentrations in groundwater from clastic sedimentary and clastic lacustrine/evaporite sedimentary lithologic groups within the Early Mesozoic basin aquifers, which had median concentrations of 3.6 and 3.1 $\mu\text{g/L}$, respectively, generally were higher than concentrations for other siliciclastic lithologic groups, which had median concentrations less than 1 $\mu\text{g/L}$. Although 89 percent of the 260 samples from crystalline-rock aquifers had uranium concentrations less than 1 $\mu\text{g/L}$, 0.8 percent had uranium concentrations greater than the 30- $\mu\text{g/L}$ maximum contaminant level, and 6.5 percent had concentrations greater than 3 $\mu\text{g/L}$.

Introduction

Since its inception in 1991, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program has collected and reported information about water-quality conditions and changes in those conditions over time. From 1991 to 2001 (Cycle I), the NAWQA Program was focused on describing water-quality conditions within 51 major river basins across the United States. Interdisciplinary assessments of water chemistry, hydrology, land use, stream habitat, and aquatic life established a baseline understanding of water-quality conditions within the 51 river basins and aquifers, referred to as study units (Gilliom and others, 1995).

A major focus of the NAWQA Program during its second decade (2002–13, Cycle II) is on regional- and national-scale assessments of groundwater-quality status and trends in about one-third of the 62 principal aquifers identified by the USGS Office of Groundwater (U.S. Geological Survey, 2003; Lapham and others, 2005). A goal of the Cycle II NAWQA Regional Assessments of Principal Aquifers is to address the effects of natural features on water quality of major aquifers, including soil, geology, mineral composition, and geochemistry, especially oxidation-reduction potential (oxygen-reducing, nitrate-reducing, manganese-reducing, and iron-reducing conditions) (Lapham and others, 2005).

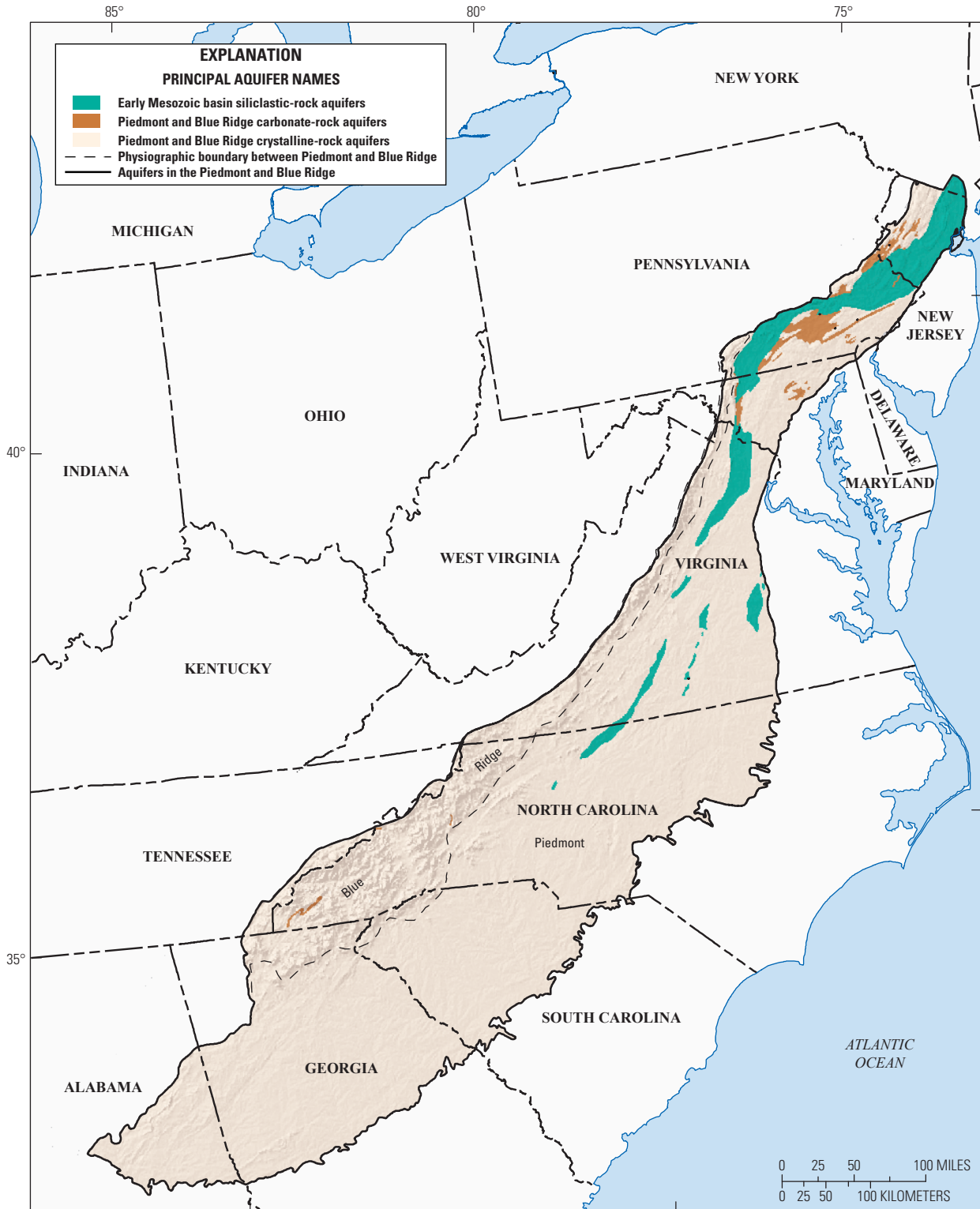
This report focuses on naturally occurring contaminants in groundwater of the Piedmont and Blue Ridge crystalline-rock aquifers and the Early Mesozoic basin siliciclastic-rock aquifers (fig. 1). The Piedmont and Blue Ridge crystalline-rock aquifers are categorized as fractured igneous and metamorphic rock aquifers, and the Early Mesozoic basin aquifers are categorized as fractured sandstone aquifers (U.S. Geological Survey, 2003).

As a precursor to this study, Lindsey and others (2006) combined groundwater-quality analyses from 11 NAWQA Program studies in the Piedmont Physiographic Province to present findings on the occurrence of anthropogenic contaminants and naturally occurring radon. Lindsey and others (2006) categorized the aquifer lithologies into three groups: carbonate rock, crystalline rock, and siliciclastic rock. Compared to the carbonate-rock aquifers, the crystalline-rock and siliciclastic-rock aquifers had higher concentrations of radon and associated characteristics that implied naturally occurring contaminants could be widespread. The current report is a continuation of the effort by Lindsey and others (2006), evaluating the effects of lithologies and geochemical environment on the occurrence and distribution of radon and other naturally occurring contaminants in groundwater from the crystalline-rock and siliciclastic-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces.

Description of Study Area

The Piedmont and Blue Ridge Physiographic Provinces extend from Alabama to New York in the eastern United States (Fenneman, 1938; Fenneman and Johnson, 1946) and have a collective area of 154,000 square miles (mi^2) (fig. 1). This region includes three principal aquifers: (1) the Piedmont and Blue Ridge crystalline-rock aquifers; (2) the Piedmont and Blue Ridge carbonate-rock aquifers; and (3) the Piedmont Early Mesozoic clastic sedimentary rock aquifers, also referred to as “sandstone” aquifers (U.S. Geological Survey, 2003). In the study area, groundwater generally occurs in aquifer units that are local in scale because of complex geologic and topographic controls, but that are similar on a regional scale on the basis of major bedrock type and hydrogeologic properties. The aquifers are affected locally by geologic factors such as lithology and structure, particularly features such as fractures and joints, which provide secondary permeability for water movement within these “fractured-rock” aquifers.

The study area discussed in this report includes parts of 14 NAWQA study units (see “Network Code,” table 1) where groundwater-quality data were collected for major aquifer, land-use, or drinking water studies in the Piedmont and Blue Ridge crystalline-rock and Piedmont Early Mesozoic basin siliciclastic-rock aquifers (table 1 and fig. 2). Regional and national assessments of the effects on water quality from natural environmental factors and human activities are possible because of the application of a consistent study design and uniform methods of data collection and analysis within the NAWQA Program (Gilliom and others, 1995; Lapham and others, 2005). The study area includes several large metropolitan areas (Atlanta, Ga., Charlotte, N.C., Raleigh, N.C., Richmond, Va., Washington, D.C., Baltimore, Md., Philadelphia, Pa., and Trenton, N.J.), rural or forested areas in the southern and mid-Atlantic sections, and agricultural areas in the northeast section (fig. 2). The geologic setting of the area is complex and includes a history of deposition, metamorphism, igneous intrusion, and extensive folding and faulting; a wide



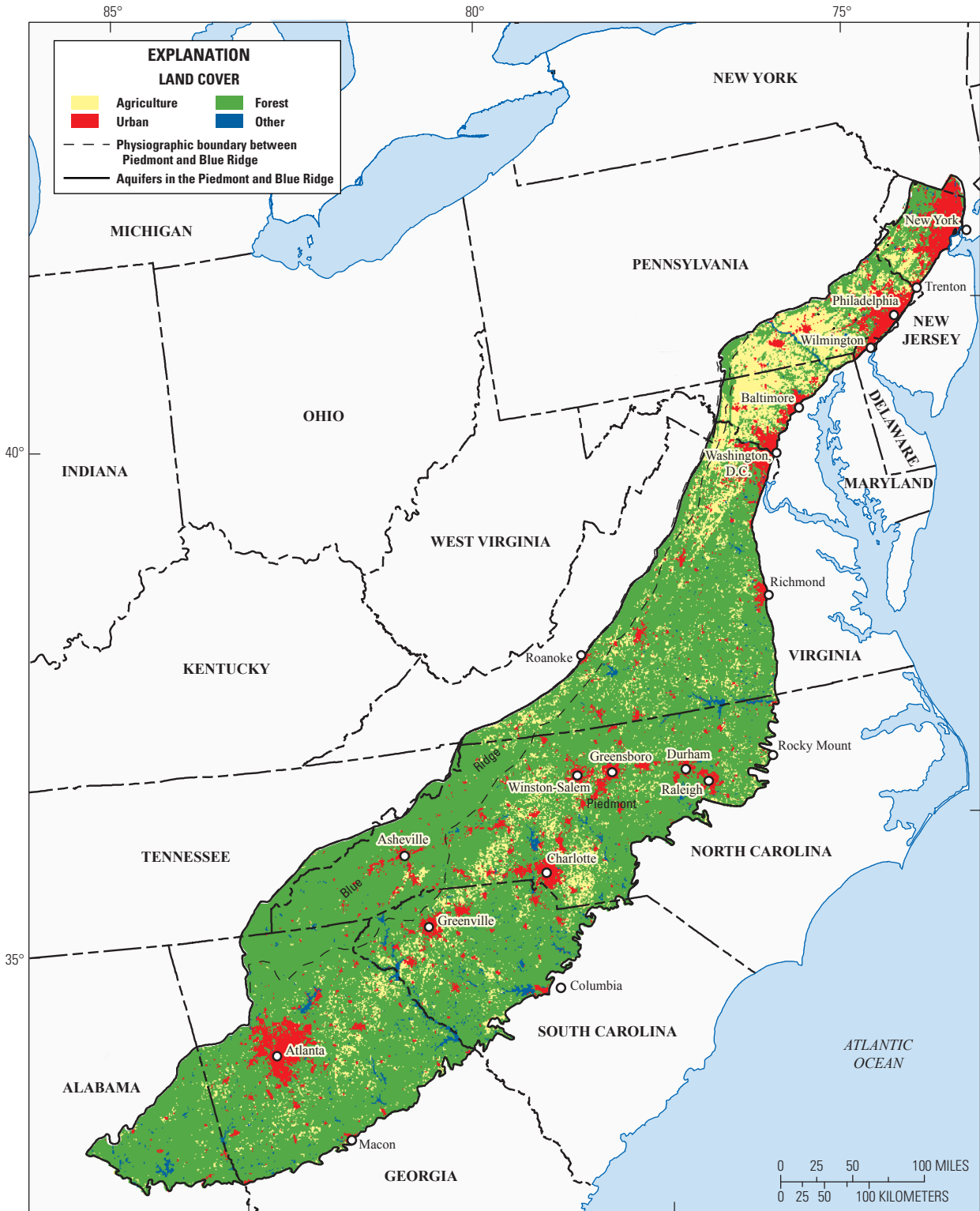
Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 National Elevation Data from U.S. Geological Survey, 1999
 Principal Aquifers from U.S. Geological Survey, 2003

Figure 1. Boundaries for the three principal aquifers within the Piedmont and Blue Ridge Physiographic Provinces.

Table 1. NAWQA study units in the Piedmont and Blue Ridge Physiographic Provinces.

[PIED-CRY, Piedmont Physiographic Province crystalline-rock aquifer; PIED-EMZ, Piedmont Physiographic Province Early Mesozoic rock aquifer; BR-CRY, Blue Ridge Physiographic Province crystalline-rock aquifer]

Study unit name	Study unit code	Network code	Aquifer	Study type	Number of ground water samples	Year(s) sampled	State(s) sampled
Apalachicola-Chattahoochee-Flint River Basin	acfb	acfbtusur1	PIED-CRY	Urban land-use study - shallow regolith wells only	21	1994–1995	Georgia
Apalachicola-Chattahoochee-Flint River Basin	acfb	acfbtusur2	PIED-CRY	Urban land-use study - springs only	19	1994–1995	Georgia
Albemarle-Pamlico Drainages	albe	albesus8	PIED-CRY	Major aquifer study	55	2007	North Carolina; Virginia
Deleware River Basin	delr	delrsus1	PIED-EMZ	Major aquifer study	30	1999	New Jersey; Pennsylvania
Kanawha/New River Basins	kana	kanasus2	BR-CRY	Major aquifer study	30	1997	North Carolina; Virginia
Long-Island/New Jersey Coastal Drainages	linj	linjsus3	PIED-EMZ	Major aquifer study	21	1998	New Jersey
Lower Susquehanna River Basin	lsus	lsususs2	PIED-CRY	Agricultural land-use study	30	1994	Maryland; Pennsylvania
Potomac River Basin and Delmarva Peninsula	podl	podldwgs1	PIED-CRY	Drinking water study	15	2003	Maryland; Virginia
Potomac River Basin and Delmarva Peninsula	podl	podltsur1	PIED-CRY	Urban land-use study - shallow wells only	30	2003	Maryland; Virginia
Potomac River Basin and Delmarva Peninsula	podl	podlreffo2	PIED-CRY	Urban land-use study - reference network shallow wells	2	2003; 2005	Maryland; Virginia
Potomac River Basin	poto	potosus1	PIED-CRY	Major aquifer study	25	1994	Maryland; Virginia
Potomac River Basin	poto	potosus2	PIED-EMZ	Major aquifer study	23	1994	Maryland; Pennsylvania; Virginia
Santee River Basin and Coastal Drainages	sant	santdwgs1	PIED-CRY	Drinking water study	15	2008	South Carolina
Santee River Basin and Coastal Drainages	sant	santsus3	PIED-CRY	Major aquifer study	30	1998	North Carolina; South Carolina
TOTAL					346		



Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 Land cover digital data from Nakagaki and others, 2007

Figure 2. 2007 land-use data for the Piedmont and Blue Ridge Physiographic Provinces and major metropolitan areas.

variety of bedrock lithologies ranging from quartz sandstone to black shale and from felsic-rich granite to ultramafic metamorphic rocks; and many rock types of intermediate composition, such as siltstones, gneisses, and schists. The weathering of minerals within the rock and the geochemical conditions within the aquifer directly affect groundwater quality in this region. Thus, in order to assess conditions in the aquifer and predict areas where specific contaminants may affect drinking water sources, it is important to understand the factors that control the release and transport of naturally occurring contaminants in groundwater.

Purpose and Scope

This report contains the results of an evaluation of the potential occurrence and distribution of naturally occurring contaminants in groundwater in the Piedmont and Blue Ridge crystalline-rock aquifers and the Piedmont Early Mesozoic basin siliciclastic-rock aquifers in the eastern United States (fig. 1). Descriptions of the primary rock type and associated mineral assemblages for mapped bedrock in the region were used to delineate mappable lithologic groups and lithochemical subgroups that could influence groundwater quality. The focus is on trace elements, radionuclides, nutrients, and major ions in groundwater that have potential for human health effects when present at concentrations approaching or exceeding drinking water standards or other human health benchmarks.

Water-quality data collected as part of the NAWQA Program from 1994 through 2008 from 346 wells and springs in various hydrogeologic and land-use settings from Georgia through New Jersey were compiled and analyzed for this regional assessment. The sampled sites are from the following NAWQA study units (table 1): Apalachicola-Chattahoochee Flint River Basins (acflusur1 and acflusur2), Albemarle-Pamlico Drainages (albesus8), Delaware River Basin (delsus1), Long Island/New Jersey Coastal Drainages (linjsus3), Lower Susquehanna River Basin (lsussus2), Potomac River Basin and Delmarva Peninsula (podldwgs1, podllusrc1, podlreffo2, potosus1, and potosus2), and Santee Basin and Coastal Drainages (santsus3 and sandwgs1) (fig. 3 and table 1).

Graphical and statistical techniques were used to compare constituent concentrations in groundwater to human health criteria for drinking water and to compare concentrations among different lithologies. Interactions between groundwater and lithologies in various settings were inferred through comparison of major and trace-ion chemistry. Implications of observations and conclusions for regional mapping of risk for elevated arsenic, radionuclides, and other naturally occurring contaminants on the basis of geologic mapping are discussed. Results and interpretations are compared to those from studies conducted by other Federal and State agencies throughout the Piedmont and Blue Ridge crystalline-rock and Piedmont Early Mesozoic siliciclastic-rock aquifer systems in the eastern United States.

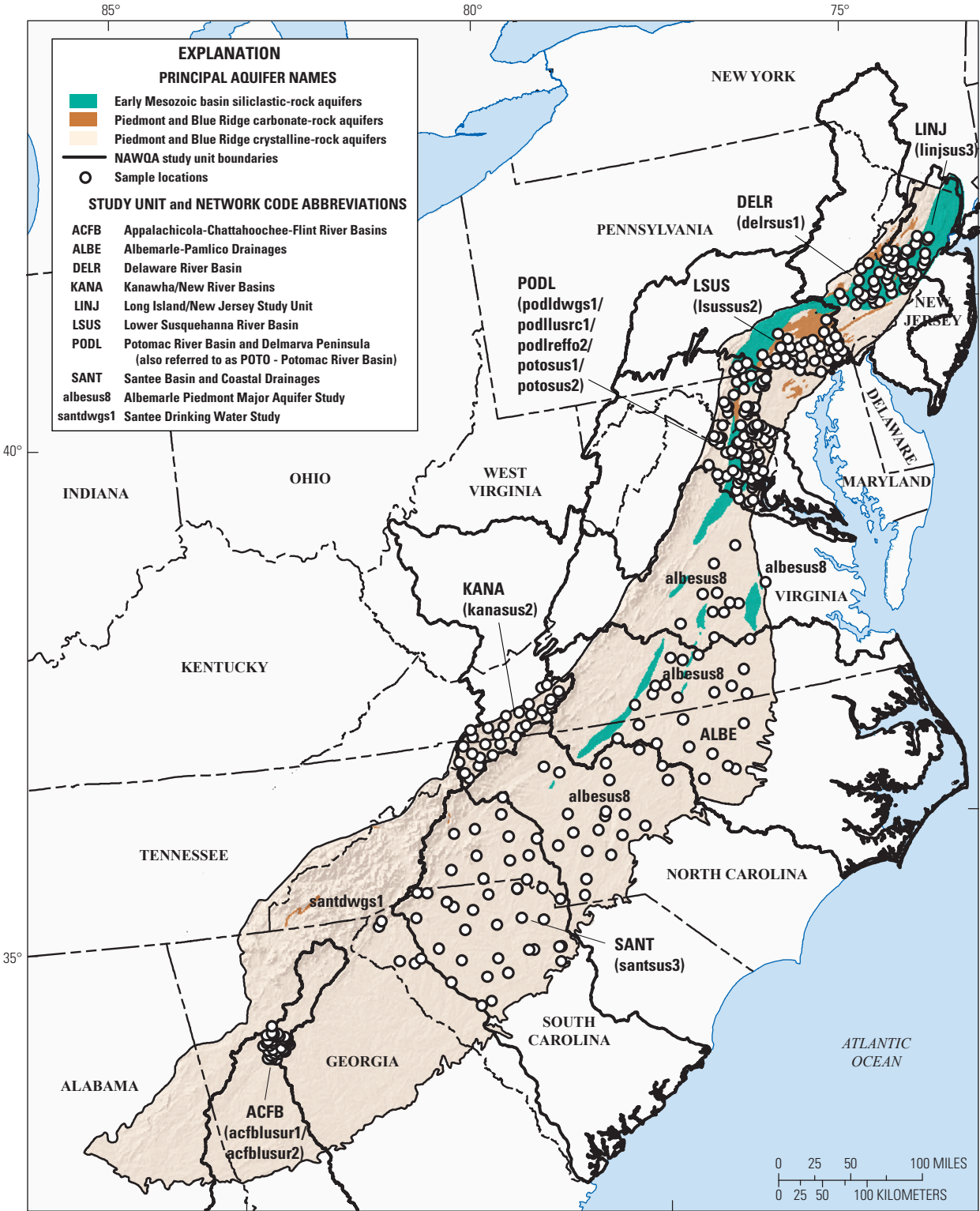
Geologic Setting and Aquifer Descriptions

The geologic setting within the Piedmont and Blue Ridge (PBR) Physiographic Provinces of the eastern United States (fig. 1) is complex as a result of diverse geologic factors including rock type, metamorphic and structural history, and weathering. Bedrock in the study area has undergone multiple periods of metamorphism, deformation, including folding and faulting resulting in superimposed fracturing, and igneous intrusion that has altered mineralogy as well as inherent bedrock fabric (foliation). These mineralogical and structural characteristics directly affect groundwater and surface-water flow, recharge to the aquifer system, and geochemical processes within the aquifer (Cranford and others, 1982).

Regional geologic units in the PBR Physiographic Provinces historically have been grouped into northeast-trending “belts” that described common assemblages of rock types grouped by metamorphic facies and broad structural features (North Carolina Geological Survey, 1985). More recently, Hibbard and others (2006) produced a lithotectonic map of the Appalachian Orogen in the eastern United States, grouping mapped units into “terrane” that better reflect geologic structural history. The geologic setting of the southern Blue Ridge and western Piedmont Physiographic Provinces from Virginia to Alabama is described in Clark (2008). Major rock types are described in terms of their respective geologic history, including depositional setting, metamorphism, and structural characteristics. Geologic structural terranes and rock assemblages typically strike northeast-southwest.

The Blue Ridge Physiographic Province, in the western part of the study area, is characterized by high relief, with mountain peaks rising more than 6,000 feet (ft) above the North American Vertical Datum of 1988 (NAVD 88) with steep slopes, and valleys generally near 2,000 ft in altitude. The Blue Ridge primarily is underlain by metamorphic and igneous crystalline rocks; however, some sedimentary rocks also are present in Maryland, Pennsylvania, Virginia, and North Carolina. The Piedmont Physiographic Province in the eastern part of the study area is characterized by a more subdued topography, with gently rolling hills and valleys and land-surface altitudes ranging from about 300 to 1,500 ft above NAVD 88. The Piedmont can be subdivided topographically into lowland and upland areas, where lowlands generally are underlain by carbonate rocks (Pennsylvania, Maryland, and New Jersey), and by clastic sedimentary rocks in the Early Mesozoic rift basins, as shown in a conceptual diagram (fig. 4).

Trapp and Horn (1997) describe bedrock aquifers in the PBR Physiographic Provinces in North Carolina, Virginia, Maryland, Delaware, Pennsylvania, and New Jersey as being dense and almost impermeable, yielding groundwater primarily from secondary porosity and permeability provided by fractures. Except for the carbonate rocks, which contain solution openings, joints and fractures are the only openings that



Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 National Elevation Data from U.S. Geological Survey, 1999
 Principal Aquifers from U.S. Geological Survey, 2003

Figure 3. U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program study unit boundaries within the Piedmont and Blue Ridge Physiographic Provinces and sample-collection locations for groundwater-quality data collected from 1994–2008.

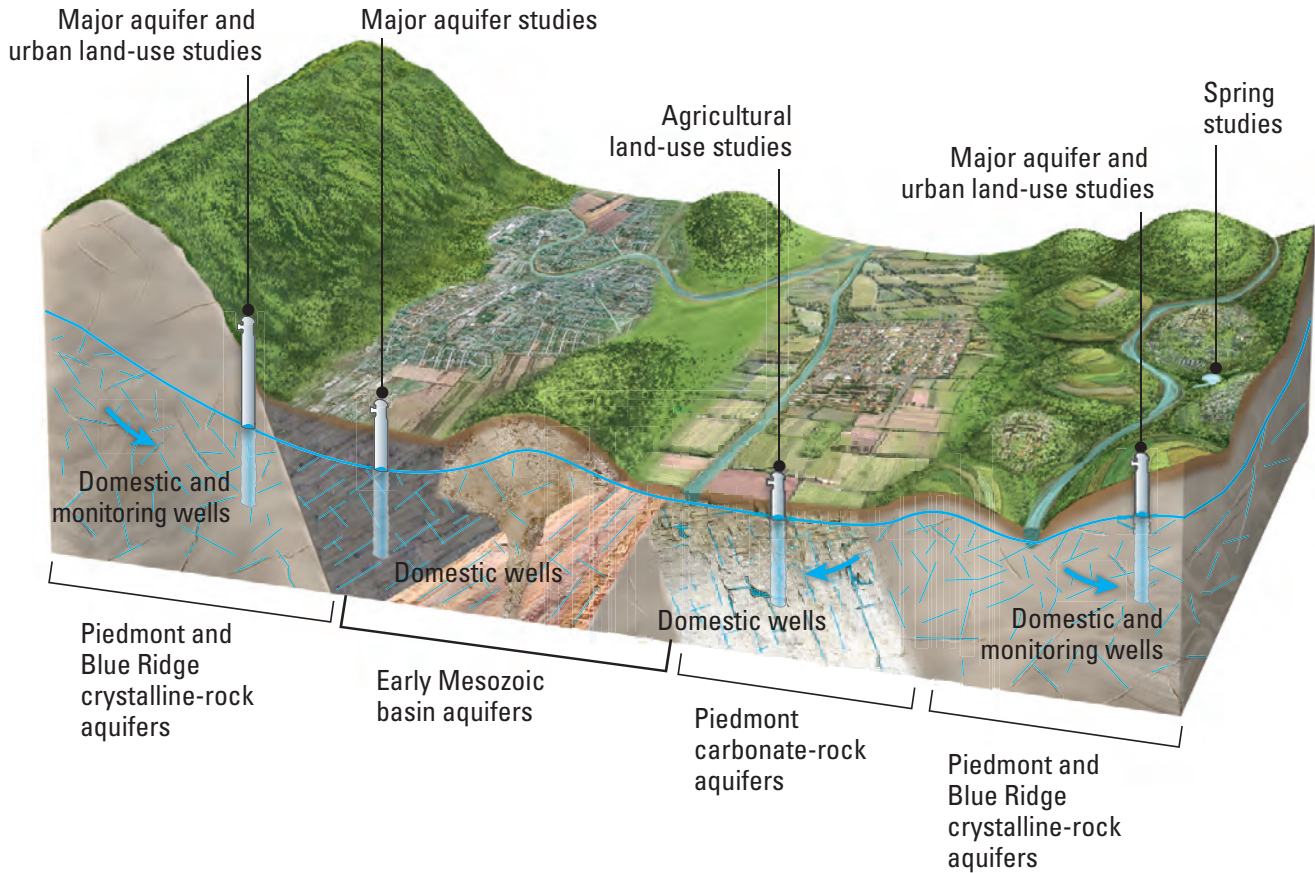


Figure 4. The conceptual groundwater system, aquifers, and typical well types included as part of this study within the Piedmont and Blue Ridge Physiographic Provinces.

store and transmit water. Despite this description, many wells completed in fractured bedrock aquifers of the PBR are sufficiently productive to be the main source of local water supplies. The carbonate rock units of the Piedmont typically are the most productive of the bedrock aquifers but are not widely distributed in the region, occurring primarily in Maryland, Pennsylvania, and New Jersey. The PBR bedrock aquifers in northeastern Pennsylvania and northern New Jersey locally are covered by glacial deposits, which include productive sand and gravel of the surficial aquifer system. Three principal bedrock aquifers underlie the northern PBR Provinces, in order of decreasing area: crystalline-rock and undifferentiated sedimentary-rock aquifers, clastic sedimentary-rock aquifers in Early Mesozoic basins, and carbonate-rock aquifers.

Miller (1990) describes the geologic setting of the PBR as consisting of many different types of metamorphic and igneous rocks that are complexly related. Main rock types are varieties of gneiss and schist and extremely fine-grained rocks such as phyllite and metamorphosed volcanic tuff and ash. Most of the metamorphic rocks were originally sediments

(metasediments), but some were originally igneous or volcanic materials (metagranites, granite gneiss, metavolcanics). The degree of heat and pressure to which the original rocks were subjected during metamorphism, as well as the degree of structural deformation (principally folding, foliation, jointing, and shearing) that they have undergone, has determined the final texture and mineralogy of the rocks. Most of the rocks have undergone several periods of metamorphism. The metamorphic rocks have been intruded by large to small bodies of igneous rock that vary in composition from felsic (light-colored rocks that contain large quantities of silica as quartz and potassium as potassium-feldspar) to mafic (dark-colored rocks that contain large quantities of ferromagnesian minerals such as pyroxene, amphibole, or ferrous phyllosilicate mineral groups). Large igneous intrusions consist of granite, quartz monzonite, and gabbro that occur in plutons that cover many tens of square miles. Smaller igneous intrusions, such as dikes and sills, include felsic and mafic rocks, such as syenite, andesite, diabase, and pegmatite. Rocks in this region are displaced by several major fault zones, some of which extend

for hundreds of miles. Shearing along large fracture zones has produced siliceous, intensely fractured rocks, such as mylonite or phyllonite (Miller, 1990).

Trapp and Horn (1997) describe aquifers in Early Mesozoic basins that primarily are in three major basins—the Newark basin in New Jersey and Pennsylvania is the largest and is the basin from which the most groundwater is withdrawn; the Gettysburg basin of Pennsylvania and Maryland is second largest; and the Culpeper basin of Virginia is third largest. The Richmond basin in Virginia and the Dan River/Danville basin in Virginia and North Carolina are of intermediate size. Nine small early Mesozoic basins are located in Virginia. Sedimentary rocks in the basins consist predominately of interbedded shale, sandstone, and siltstone, all typically red, reddish brown, or maroon, but locally gray or black. Conglomerate, dolomite, lacustrine black mudstone, and coal are present locally. In many places, the sedimentary rocks are interbedded with basalt flows or have been intruded by diabase dikes and sills. Thicknesses of Triassic and Jurassic rocks in the large basins have been calculated to be more than 20,000 ft. Additional basins in North Carolina, including the Durham, Sanford, Wadesboro, and Davie County basins (Lindsey and others, 2006, fig. 10), were not considered to be important aquifers because they are more compact and more tightly cemented than those in the basins to the north and do not yield sufficient quantities of water to be considered principal aquifers.

Physically, the aquifer system in the PBR can be composed of one (bedrock only), two (regolith-bedrock), or three parts (regolith, transition zone, and bedrock), depending upon whether or not weathered material (regolith) overlies the bedrock and if a local transition zone has developed between the shallow regolith and deeper bedrock. In the Blue Ridge Physiographic Province, very little, if any, regolith may be present, and, if present, it is often debris flow, colluvium, or alluvium in stream valleys. In the Piedmont Physiographic Province, generally there is at least a two-part system with the weathered regolith overlying fractured bedrock as described by Heath (1984). The regolith consists of soil, residuum, saprolite, and possibly colluviums, alluvium, and debris flow. Residuum and saprolite are formed from in situ weathering of the bedrock and form a blanket of decomposed or partially decomposed rock that is usually thick and clayey. Saprolite retains the texture and structure of the parent bedrock from which it is derived. A third component, a transition zone between the regolith and bedrock (Harned and Daniel, 1992), has been more commonly delineated in recent years. The regolith is more porous and more permeable than the underlying bedrock everywhere. Because the crystalline bedrock formed under intense heat and pressure during metamorphism and igneous intrusion, the bedrock has few primary pore spaces, and the porosity and permeability of the unweathered and unfractured bedrock is extremely low (Miller, 1990). Groundwater in the bedrock is stored in and moves through secondary fractures and other discontinuities, which form the only effective porosity in the unweathered rock. Because of the absence of

substantial water storage (storativity) in the unweathered rock, a large amount of groundwater is found in the weathered and slightly porous overlying saprolite. Water slowly drains from the saprolite to the fractures in the underlying and hydraulically connected bedrock. Although there are considerable differences in the mineralogy, texture, and structure of the rocks composing the PBR aquifers, the overall hydraulic characteristics of the aquifers are similar in a regional context (Miller, 1990).

Previous Studies

Data on naturally occurring and manmade contaminants in groundwater in the PBR have been collected and reported through the NAWQA Program and other USGS studies, some of which are summarized in this section. Table 2 lists pertinent reports published for these studies, constituents analyzed, and major findings relevant to this study. Results from a few selected studies that are applicable to this report are summarized in this section.

One of the larger NAWQA data compilations for the Piedmont Physiographic Province was reported by Lindsey and others (2006) in a summary of groundwater-quality data collected from 11 of the 14 NAWQA studies listed in table 1 (all except albesus8, kanasus2, and sandtwgs1). Lindsey and others (2006) grouped samples from 225 wells and 19 springs into 3 aquifer types: crystalline, siliciclastic, and carbonate. While the report focused on the detection and occurrence of anthropogenic contaminants, selected naturally occurring contaminants also were evaluated. Concentrations of radon were higher in areas underlain by felsic crystalline rocks and lower in areas underlain by mafic crystalline rocks. Groundwater from adjacent siliciclastic-rock aquifers had concentrations of radon lower than those in samples from felsic crystalline-rock aquifers. Ninety percent of the 205 samples analyzed for radon had concentrations that exceeded the proposed maximum contaminant level (MCL) of 300 picocuries per liter (pCi/L), and 13 percent of samples had concentrations that exceeded the proposed alternative maximum contaminant level (AMCL) of 4,000 pCi/L (Lindsey and others, 2006).

Fifty-five domestic wells in the Piedmont crystalline-rock aquifers were sampled for a major aquifer study in the Albemarle-Pamlico (ALBE) drainages of North Carolina and Virginia in 2007–08 (fig. 3 albesus8, table 1). The data for NAWQA samples were combined with other USGS data collected in the Piedmont and Blue Ridge of North Carolina for comparison of analytical results for 79 groundwater samples within the statewide geologic belt units, or geozones (Harden and others, 2009) (table 2). Results from this study suggest that the cationic and anionic composition of groundwater from within a particular geozone reflected differences in lithologic setting, hydrologic and geochemical conditions, and (or) land-use effects. Exceedances in Federal and State drinking water standards or proposed standards were noted for radon, pH, manganese, iron, and zinc. Radon had the most

Table 2. Published reports from USGS NAWQA studies and other data sources conducted in the Piedmont and Blue Ridge Physiographic Provinces categorized by aquifer and constituents investigated.

[PDX, Piedmont crystalline-rock aquifer; EMZ, Early Mesozoic basin aquifer; BRX, Blue Ridge crystalline-rock aquifer; VOCs, volatile organic compounds; PODL, Potomac River/Delmarva Peninsula; POTO, Potomac River; LSUS, Lower Susquehanna River; LINJ, Long-Island/New Jersey Coastal Drainages; SANT, Santee River Basin and Coastal Drainages; ACFB, Apalachicola-Chattahoochee-Flint River Basin; DELR, Delaware River Basin; KANA, Kanawha-New River Basin; ALBE, Albemarle-Pamlico Drainages; USGS NC WSC, USGS North Carolina Water Science Center; USGS PA WSC, USGS Pennsylvania Water Science Center]

Report	Constituents studied	Aquifers	NAWQA study area	Data sources	Major findings relevant to current study
USGS NAWQA Program					
Ator and Denis (1997)	Nitrate, phosphorus	PDX, EMZ	PODL, POTO	USGS NAWQA	
Ator and others (1998)	Radon, nitrate, pesticides, VOCs	EMZ	POTO, LSUS	USGS NAWQA	Radon from the EMZ rocks are similar in concentration to the PDX rocks
Ayers and others (2000)	Arsenic	EMZ	LINJ	USGS NAWQA	Arsenic higher in Early Mesozoic rocks
Ayotte and others (2007)	Radon, uranium	PDX, OTHERS	LINJ, DELR	USGS NAWQA	Uranium and radon higher in New England crystalline-rock aquifers
Carter and others (2010)	VOCs, pesticides	PDX, OTHERS	SANT, PODL	USGS NAWQA	
Denver and others (2011)	Phosphorus, trace metals	PDX, EMZ	POTO, LSUS, ACFB, DELR, SANT, LINJ	USGS NAWQA	Phosphorus from natural sources reported in crystalline-rock aquifers with alkaline pH or iron-reducing conditions.
Fischer and others (2004)	Nitrate, pesticides, VOCs, radon, trace elements	EMZ, OTHERS	DELR	USGS NAWQA	Arsenic and radon higher in Early Mesozoic rocks relative to other aquifer units
Frick and others (1998)	Pesticides, VOCs	PDX, OTHERS	ACFB	USGS NAWQA	
Hughes and others (2000)	Nitrate, pesticides, VOCs, radon	PDX, OTHERS	SANT (Santee Circular)	USGS NAWQA	Radon higher in crystalline-rock aquifers
Lapham and others (2005)	Radon, uranium, trace elements, VOCs, pesticides	PDX, BRX, OTHERS		USGS NAWQA	Uranium and radon higher in New England crystalline-rock aquifers

Table 2. Published reports from USGS NAWQA studies and other data sources conducted in the Piedmont and Blue Ridge Physiographic Provinces categorized by aquifer and constituents investigated.—Continued

[PDX, Piedmont crystalline-rock aquifer; EMZ, Early Mesozoic basin aquifer; BRX, Blue Ridge crystalline-rock aquifer; VOCs, volatile organic compounds; PODL, Potomac River/Delmarva Peninsula; POTO, Potomac River; LSUS, Lower Susquehanna River; LINJ, Long-Island/New Jersey Coastal Drainages; SANT, Santee River Basin and Coastal Drainages; ACFB, Apalachicola-Chattahoochee-Flint River Basin; DELR, Delaware River Basin; KANA, Kanawha-New River Basin; ALBE, Albemarle-Pamlico Drainages; USGS NC WSC, USGS North Carolina Water Science Center; USGS PA WSC, USGS Pennsylvania Water Science Center]

Report	Constituents studied	Aquifers	NAWQA study area	Data sources	Major findings relevant to current study
USGS NAWQA Program—Continued					
Kozar and others (2002)	Radon	PDX, BRX, OTHERS	KANA	USGS NAWQA	Noted high concentrations of radon in wells near fracture zones of crystalline rocks.
Lindsey and Ator (1996)	Radon	EMZ, PDX, OTHERS	POTO, LSUS	USGS NAWQA	Noted high concentrations of radon in crystalline rocks; differences between concentrations in mafic and felsic lithologies.
Lindsey and others (1997)	Nitrate	PDX, OTHERS	LSUS	USGS NAWQA	
Lindsey and others (2006)	Nitrate, pesticides, VOCs, radon	EMZ, PDX, OTHERS	POTO, LSUS, ACFB, DELR, SANT, LINJ	USGS NAWQA	Radon higher in crystalline-rock aquifers
Paybins and others (2000)	Radon, nitrate, pesticides, VOCs	BRX	KANA	USGS NAWQA	Radon higher in crystalline-rock aquifers
Other data sources					
Campbell (2006)	Radon, radium, uranium, trace elements	BRX, PRX		NC DENR	Radon elevated in meta-igneous rocks (granites and gneisses) compared to meta-sedimentary rocks.
Harden and others (2009)	Radon, uranium, trace elements	PDBRX	ALBE	USGS NAWQA; USGS NCWSC; NC DENR	Correlation of Geozones (geologic belts) with radon, uranium, and trace elements
Pippin (2005)	Arsenic	PDX		NC DENR	Elevated arsenic associate with geologic formations in the Carolina Slate Belt in North Carolina. Rock types including meta-mudstone, meta-argillite, phyllite, schist, and mica schist of volcanic origin were associated with elevated arsenic concentrations in groundwater.
Senior and Vogel (1992)	Radium	PDX		PAWSC	Elevated radium concentrations correlated to pH conditions lower than 4.7.

Table 2. Published reports from USGS NAWQA studies and other data sources conducted in the Piedmont and Blue Ridge Physiographic Provinces categorized by aquifer and constituents investigated.—Continued

[PDX, Piedmont crystalline-rock aquifer; EMZ, Early Mesozoic basin aquifer; BRX, Blue Ridge crystalline-rock aquifer; VOCs, volatile organic compounds; PODL, Potomac River/Delmarva Peninsula; POTO, Potomac River; LSUS, Lower Susquehanna River; LINJ, Long-Island/New Jersey Coastal Drainages; SANT, Santee River Basin and Coastal Drainages; ACFB, Apalachicola-Chattahoochee-Flint River Basin; DELR, Delaware River Basin; KANA, Kanawha-New River Basin; ALBE, Albemarle-Pamlico Drainages; USGS NC WSC, USGS North Carolina Water Science Center; USGS PA WSC, USGS Pennsylvania Water Science Center]

Report	Constituents studied	Aquifers	NAWQA study area	Data sources	Major findings relevant to current study
Other data sources—Continued					
Senior and Sloto (2006)	Arsenic	EMZ	PAWSC	PAWSC	Elevated arsenic correlated to pH conditions higher than 8.
Serfes (2004), Serfes and others (2010)	Arsenic	EMZ	NJGS		Elevated arsenic higher in EMZ black shale members of Lackatong and Passaic formations in New Jersey
Sloto and Senior (1998)	Radon	PDX, EMZ	USGS PAWSC	USGS PAWSC	Radon highest from areas underlain by a schist, phyllite, and quartzite rock types
Sloto (2002)	Radon	PDX, EMZ	USGS PAWSC	USGS PAWSC	Radon lowest in ultramafic serpentinite rocks and higher in the Wissahickon Schist.
Sloto (2000)	Uranium, radium, radon	PDX, EMZ	USGS PAWSC	USGS PAWSC	Radium elevated in the Chickies Quartzite formation. Radon higher in schist and quartzite rock types.

exceedances, with 61 of 69 wells sampled exceeding the U.S. Environmental Protection Agency's (USEPA's) proposed MCL of 300 pCi/L and with 18 of 69 sampled wells exceeding the USEPA's AMCL (requires treatment) of 4,000 pCi/L of radon (U.S. Environmental Protection Agency, 2010). Fifty percent of samples collected from the felsic intrusive rock geozone had radon concentrations greater than the AMCL. Statistically different median concentrations of calcium, silica, ammonia, aluminum, antimony, cadmium, and uranium were delineated between one or more geozone pairs (Harden and others, 2009).

The New England and Appalachian Piedmont region was highlighted for radon occurrence in groundwater by the reconnaissance assessment by the USEPA (U.S. Environmental Protection Agency, 1999). Radon and uranium occurrences in crystalline-rock aquifers in New York and New England were identified as an issue of concern by Lapham and others (2005) and Ayotte and others (2007). Granitic rocks, such as two-mica granites and other high-grade metamorphic rocks, were reported to be a source of uranium that is soluble under predominantly oxic to sub-oxic geochemical conditions. The median value of radon reported was 2,122 pCi/L from the New York and New England crystalline-rock aquifer group, with about 25 percent of samples exceeding the proposed AMCL (Ayotte and others, 2007).

Sloto (2000) presented the results of sampling groundwater from domestic wells in the Piedmont Physiographic Province in southeastern Pennsylvania for naturally occurring radionuclides, including uranium, radium-226, radium-228, and radon-222 (table 2). The results were analyzed according to the underlying bedrock lithology, which included carbonate rock (limestone, dolomite, and marble), crystalline rock (gneiss, phyllite, quartzite, and schist), diabase, sedimentary rock of Paleozoic age (conglomerate, limestone, sandstone, siltstone, and shale), sedimentary rock of Triassic age (conglomerate, sandstone, siltstone, and shale), and unconsolidated sediments (clay, sand, and gravel). Of the more than 250 samples analyzed for radium isotopes, 46 percent of the wells located in the Chickies Quartzite had elevated radium activities that exceeded the USEPA MCL of 5 pCi/L for combined radium (radium-226 and radium-228 combined). Elevated radium values were correlated with water samples having a pH of less than 4.7 (Senior and Vogel, 1992) (table 2). Twenty-three percent of the 170 wells sampled in the Chickies Quartzite also had gross alpha-particle activities in water that exceeded the 15-pCi/L MCL and 46 percent of the wells sampled in the Chickies Quartzite had combined radium concentrations exceeding the 5-pCi/L MCL (Sloto, 2000). Water samples from 33 percent of the wells in the Chickies Quartzite also had gross beta particle activity exceeding the 15-pCi/L MCL. Samples from 13 wells in the Chickies Quartzite and nearby geologic units contained concentrations of radium-224 (a short-lived daughter product of radium-228) up to 265 pCi/L and gross alpha-particle activities up to 1,300 pCi/L (Senior and Sloto, 2000). Radon-222 activities differed among rock types, and of the more than 900 samples analyzed from the study area in southeastern Pennsylvania,

the greatest median values were in the schist (2,500 pCi/L) and quartzite (2,300 pCi/L) rock types (Sloto, 2000). About 89 percent of 534 wells sampled in 38 geologic formations in the Piedmont Physiographic Province in Chester County, southeastern Pennsylvania, had water with radon-222 concentrations greater than the proposed 300-pCi/L MCL that ranged up to 53,000 pCi/L (Senior, 1998).

Sloto (2002) described results from the analyses of 64 well samples collected in the Big Elk Creek Basin in Chester County, Pennsylvania, and Cecil County, Maryland, from 1925 through 1999 (table 2). Samples were categorized based on surface lithologies consisting of the Peters Creek Schist, serpentinite, Wissahickon Schist, pegmatite, and pelitic schist. The groundwater from wells located in the Wissahickon Schist had the lowest median pH of 5.9, while the samples from wells in the serpentinite rock type had the highest values ranging from 7.8 to 8.5. Groundwater from the serpentinite was categorized as magnesium-bicarbonate type, compared to samples from the other lithologies, which had no dominant cation to correspond with the dominant anion, bicarbonate. The three groundwater samples from the serpentinite unit also had the lowest concentrations of radon-222, with a maximum activity of 392 pCi/L, while wells in the other lithologic units were notably higher; samples from the Wissahickon Schist had a median value of 2,500 pCi/L. An assessment of groundwater quality and its relation to lithology and land use based on analyses of water samples from 82 wells in the Red Clay Creek Basin in the Piedmont Physiographic Province of Pennsylvania and Delaware (a hydrogeologic setting similar to that of Elk Creek) also indicated that concentrations of barium, lithium, and radon-222 differed among lithologies; radon-222 activities generally were highest (up to 10,000 pCi/L) in water from felsic gneiss and schist units and lowest in water from mafic gneiss and serpentinite units (Senior, 1996).

Radon concentrations documented by Kozar and others (2001) (table 2) for the Kanawha/New River Basins (KANA) study unit in the Blue Ridge Physiographic Province of Virginia and North Carolina were similar to those reported by Sloto (2000, 2002) for Pennsylvania, Maryland, and Delaware. Kozar and others (2001) noted that radon was detected in concentrations exceeding the proposed USEPA 300-pCi/L MCL for radon in 26 of 30 (87 percent) wells sampled. In 10 of 30 (33 percent) samples, radon exceeded the 4,000-pCi/L proposed AMCL. The median radon concentration detected was 2,080 pCi/L, and the maximum concentration detected was 30,900 pCi/L. Of 10 wells having radon concentrations greater than 4,000 pCi/L, 8 were on or adjacent to faults; this finding suggests that fault zones may be areas of uranium enrichment and that fault zones may allow radon migration upward along the fault (Kozar and others, 2001).

Pippin (2005) (table 2) presented results from a database of more than 10,000 analytical results for arsenic concentrations from groundwater samples collected primarily from domestic wells across North Carolina. A probability analysis using indicator kriging techniques was applied to the georeferenced dataset. Spatial correlation between the zone having

the highest probabilities for elevated arsenic concentrations in groundwater and rocks of the Carolina Slate Belt was evident. Common rock types associated with these areas of elevated arsenic were of volcanic origin, with the highest average arsenic concentrations estimated for the following lithologies: metamudstone and meta-argillite (CZmd; North Carolina Geological Survey, 1985), phyllite and schist (CZph, North Carolina Geological Survey, 1985), and mica schist (CZms, North Carolina Geological Survey, 1985).

Sources, mobilization, and transport of arsenic in groundwater in the Early Mesozoic basin aquifers of the Passaic and Lockatong Formations of the Newark basin, New Jersey, were documented by Serfes (2004) and Serfes and others (2010) (table 2). Elevated arsenic concentrations [greater than 10 micrograms per liter ($\mu\text{g/L}$)] correlated with geochemical conditions, including dissolved oxygen (DO) less than 3 milligrams per liter (mg/L) and pH from 7.5 to 8.0. For concentrations of arsenic greater than 40 $\mu\text{g/L}$, DO was suboxic (less than 1.0 mg/L) or nearly suboxic. The major source of arsenic was determined to be the mineral pyrite (FeS_2) within the black shale members of the Passaic Formation (Serfes, 2004).

An assessment of arsenic, boron, and fluoride in groundwater in the Newark basin in Pennsylvania included a review of available data (Senior and Sloto, 2006). About 10 percent of wells completed in the Early Mesozoic basin aquifers had water with arsenic concentrations greater than the MCL of 10 $\mu\text{g/L}$. For data collected from 46 wells during that study, all groundwater samples with pH values greater than 8 had arsenic concentrations greater than 10 $\mu\text{g/L}$; no samples with pH below 7 had arsenic concentrations greater than 10 $\mu\text{g/L}$.

Geological and Geochemical Framework for Interpretations of Water Quality

Building on previous work linking aquifer lithology to the occurrence of radionuclides, arsenic, and other naturally occurring contaminants in groundwater, the primary purpose of this study was to determine if primary rock type and associated mineral assemblages described for published State geologic maps could be organized into mappable lithologic groups and lithochemical subgroups and related to the occurrence of natural contaminants in the crystalline-rock aquifers of the Piedmont and Blue Ridge Physiographic Provinces and the siliciclastic-rock aquifers in the Piedmont Physiographic Province. For this study, bedrock aquifers were divided into lithologic groups and lithochemical subgroups based on overall bedrock composition with regard to specific mineralogy and the potential for similar weathering characteristics. This classification of bedrock aquifer types follows the organization of lithochemical groups by McCartan and others (1998) and Peper and others (2001) in the Chesapeake Bay region of Maryland, Virginia, and the District of Columbia.

Previous Lithochemical Classifications

McCartan and others (1998) related regional geologic data (rock type and mineralogical characteristics) from geologic maps of Maryland and northern Virginia in the southern Chesapeake Bay watershed to water-quality data from shallow wells and streams collected from the region. The rock types within the region were first grouped with the three primary classes of rock—sedimentary, igneous, and metamorphic—then by acid-neutralizing capacity and weathering characteristics. Interest stemmed from the apparent mitigation of high-acidity surface- and groundwater-quality problems from contact with carbonate rock types and elevated nitrate problems in groundwater and surface water by rocks and sediments high in carbon and sulfur (peat and black shale). McCartan and others (1998) organized regional geologic map data within the southern Chesapeake Bay watershed into four groups: (1) “Sedimentary rocks and their metamorphic equivalents,” which included carbonate-rich rocks, clastic sedimentary rocks, and metamorphosed clastic sedimentary rocks; (2) “Igneous rocks and their metamorphic equivalents,” which included mafic igneous rocks and their metamorphic equivalents, ultramafic rocks, and felsic igneous rocks and their metamorphic equivalents; (3) “Unconsolidated sediments,” such as sands, silts, clays, and organic-rich deposits; and (4) “Iron-rich sediment,” such as greensand, magnetite and ferro-ilmenite beach sand, and bog iron ore. Lithologies in the study area were categorized into 30 lithologic-mineralogic equivalent, or “lithochemical,” units (McCartan and others, 1998).

Peper and others (2001) modified the organization of McCartan and others (1998) to form three main geologic groups by including iron-rich sediments under the “Unconsolidated sediments” group, and then by classifying lithologies on the basis of potential rock-water interaction. Classes of rock types based on water-reactive minerals and their weathering reactions were regrouped by Peper and others (2001) into the following five classes of lithochemical units: (1) carbonate rocks and calcareous rocks and sediments, the most acid-neutralizing; (2) carbonaceous-sulfidic rocks and sediments, likely to be oxygen-depleting and reducing; (3) quartzofeldspathic rocks and siliciclastic sediments, mostly relatively weakly reactive with water; (4) mafic silicate rocks and sediments, likely to be oxygen consuming and high solute-load delivering; and (5) rare calcareous-sulfidic (carbonaceous) rocks that may be neutralizing and reducing.

Lithologic Groups

Fourteen lithologic groups (table 3) were delineated within the study area as an expansion of previous work by McCartan and others (1998) and Peper and others (2001) to southeastern and northeastern areas of the PBR Physiographic Provinces [(appendix 1, table 1-1 (appendix 1 available online at <http://pubs.usgs.gov/sir/2013/5072/>)]. The same principal

Table 3. Lithologic group, major rock types, and lithochemical subgroups for groundwater sites within the siliciclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008.

[Lithologic groups and lithochemical subgroups are described in detail in appendix table 1-1. **Red** font indicates units that lack groundwater-quality data. Na, not applicable]

Rock type	Lithologic group	Site count	Abbreviation	Principal lithologies	Lithochemical subgroup number(s)
Carbonate	Carbonate-rich rocks	0	na	Limestone, dolostone, marble	11, 12, 13
Siliciclastic	Clastic sedimentary rocks	9	CLSD	Mudstone, shale	21, 21c
Siliciclastic	Quartz-rich sedimentary rocks	11	CLSDQ	Conglomerate, sandstone	22, 22c
Siliciclastic	Clastic lacustrine/evaporite sedimentary rocks	51	CLSDLAC	Argillite, fine-grained mixed clastic, mudstone, sandstone, shale, siltstone, arkose	22e
Siliciclastic	Feldspar-rich clastic sedimentary rocks	0	na	Arkose, graywacke	22f
Siliciclastic	Sulfidic clastic sedimentary rocks	0	na	Black shale, coal	23s, 24s
Crystalline	Metamorphosed clastic sedimentary rocks	96	CLSDMT	Slate, mica schist, pelitic schist, phyllite, quartz-feldspar schist, schist, metasedimentary rock, meta-argillite, paragneiss, gneiss, melange	31, 31s, 32a, 32c, 32g, 32m, 32s, 32u, 35, 35a, 35c, 35gn, 35gns, 35ml, 41bs
Crystalline	Quartz-rich metamorphic rocks	17	MTQ	Meta-conglomerate, metasedimentary rock, quartzite	33, 33c, 33my
Crystalline	Felsic igneous rocks and their metamorphic equivalents	71	IGMTF	Granite, quartz monzonite, tonalite, metamorphic rock, felsicmetavolcanic rock, metavolcanic rock, felsic volcanic rock, rhyolite, alkali syenite	61, 61c, 61m, 61mf, 61ml, 61mv, 61v, 62
Crystalline	Intermediate igneous rocks and their metamorphic equivalents	55	IGMTI	Biotite gneiss, gneiss, felsic gneiss	34agn, 34bg, 34f, 34fi, 34i, 34s

Table 3. Lithologic group, major rock types, and lithochemical subgroups for groundwater sites within the siliciclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008.—Continued

[Lithologic groups and lithochemical subgroups are described in detail in appendix table 1-1. Red font indicates units that lack groundwater-quality data. Na, not applicable]

Rock type	Lithologic group	Site count	Abbreviation	Principal lithologies	Lithochemical subgroup number(s)
Crystalline	Mafic Igneous rocks and their Metamorphic equivalents	34	IGMTM	Amphibolite, meta-basalt, intermediate metavolcanic rock, diabase, gabbro, mafic rock, metamorphic rock, norite, quartz diorite, basalt, diabase, mafic gneiss	41, 41c, 41mv, 41v, 42, 43, 43em, 44
Crystalline	Ultramafic rocks	2	ULMAF	Metamorphic rock, serpentinite	50c
Sediment	Unconsolidated sediments	0	na	Sand, silt, clay, gravel, terrace (undifferentiated), alluvium, gravel, sand	71c, 72, 73, 74, 75, 76, 78, 79, 80
Sediment	Iron-Rich sediments	0	na	Greensand, silty in places; magnetite and ferro-ilmenite beach sand; bog iron ore	77
Total number of samples					346

aquifers are covered—the crystalline-rock aquifers of the Piedmont and Blue Ridge and the siliciclastic rocks in the Early Mesozoic aquifers of the Piedmont. As with McCartan and others (1998), the first step for this study was to translate information from each mapped geologic unit within the study area to lithologic-mineralogic equivalents based on descriptions for each State geologic map (see References Cited section and appendix 1, table 1-2). As a new approach for this study, further division of the geologic units under “Sedimentary rocks and their metamorphic equivalents” heading was made within the siliciclastic sedimentary rocks sequence by introducing clastic sedimentary (fine-grained), clastic lacustrine/evaporite sedimentary, feldspar-rich clastic sedimentary, quartz-rich sedimentary, and sulfidic clastic sedimentary as major lithologic groups in the study area (table 3 and appendix 1, table 1-1). The metamorphosed clastic sedimentary sequence was further divided in the study area by introduction of quartz-rich metamorphic and feldspar-rich metamorphic lithologic groups. All other major lithologic groups used for this study followed McCartan and others (1998) (appendix 1, table 1-1). The 14 major lithologic groups delineated for this study and a listing of associated major rock types compiled from State geologic maps (Dicken and others, 2005a, 2005b; Nicholson and others, 2005, 2006) are described in table 3, based on classification schemes presented in appendix table 1-1. Representative geologic formations are listed in appendix table 1-1 and a detailed descriptions of geologic formations (including State abbreviations) are grouped by lithologic group and lithochemical subgroup number in appendix table 1-2. Abbreviations for the lithologic groups used in this report are listed in table 3 to simplify technical discussions and figure/table presentations. For example, the felsic igneous rocks and their metamorphic equivalents group is abbreviated as “IGMTF” (table 3). For more detailed descriptions and formation references, please see appendix 1, tables 1-1 and 1-2.

As a result of the classification of the lithologic groups for the purposes of this report, the metamorphic and igneous lithologic groups are associated primarily with the crystalline-rock aquifers in the PBR Physiographic Provinces, and the sedimentary or siliciclastic-rock groups are associated with the Early Mesozoic basin within the Piedmont Physiographic Province (fig. 1). Additionally, crystalline diabase rocks locally intrude the primary sedimentary rocks in the Early Mesozoic basins. The diabase dikes are mafic rocks with geochemical properties likely similar to rock types such as amphibolite. The carbonate-rich lithologic group is limited to the northeastern area of the Piedmont (fig. 1).

The distributions of lithologic groups, as delineated for this study, are shown in figure 5 along with available USGS NAWQA groundwater-quality sample locations. (Note: sulfidic clastic sedimentary and iron-rich sediments were not delineated in the study area.) For this report, NAWQA groundwater sample data were available for 9 of the 14 lithologic groups; samples were not available for the carbonate-rich group, the feldspar-rich clastic sedimentary group, the

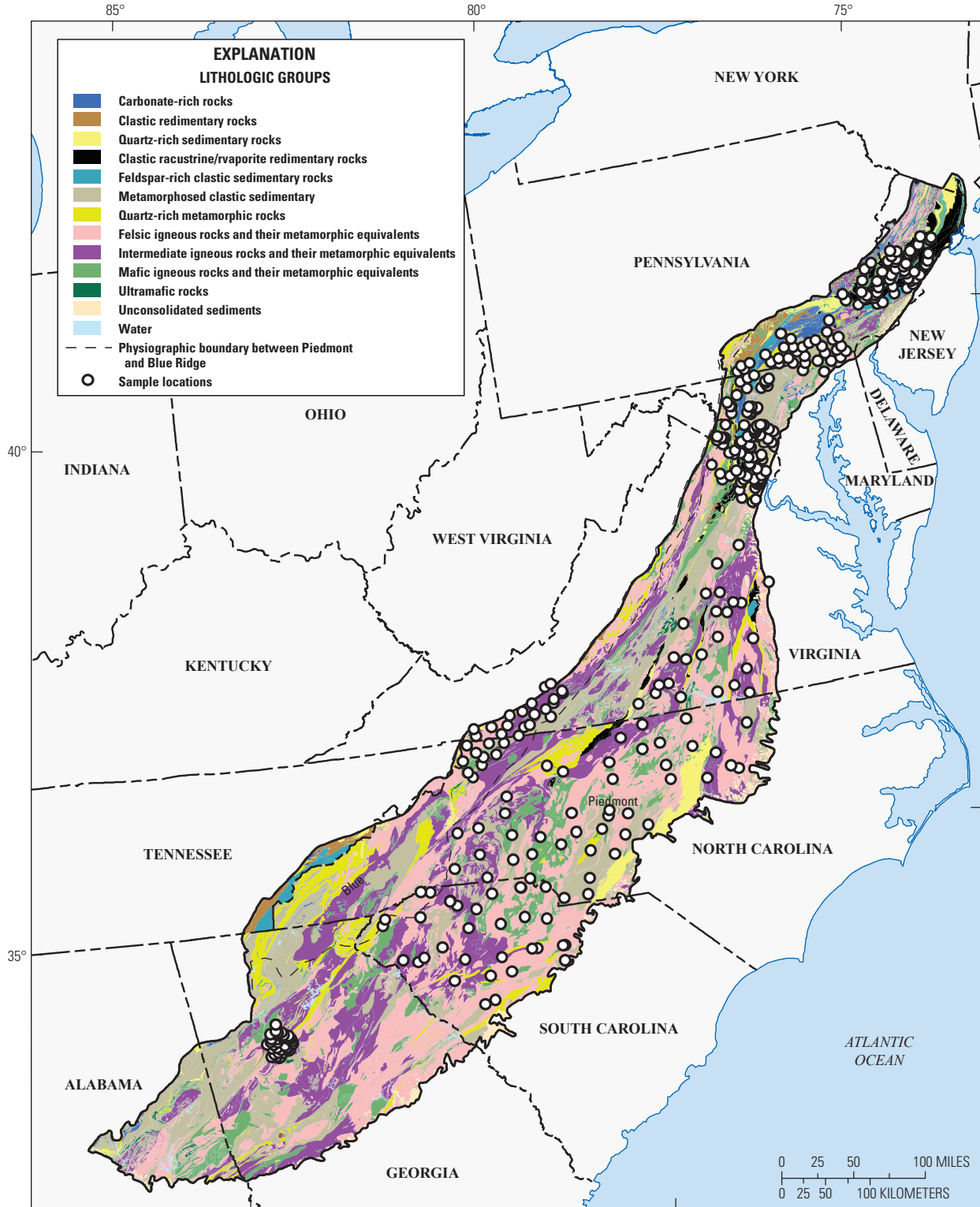
sulfide-rich sedimentary group, unconsolidated sediments, and iron-rich sediments (table 3). To illustrate the physical relations among different lithologic groups, representative lithologic groups within mapped geologic terranes in North Carolina are shown in figure 6.

Lithochemical Subgroups

As a starting point, rock type designations from the geographic information system (GIS) attributes for the State maps (appendix 1, table 1-1 “ROCK_TYPE1”) (Dicken and others, 2005a, 2005b; Nicholson and others, 2005, 2006) were directly assigned to a particular subgroup number as listed in McCartan and others (1998). For example, the use of subgroup 32 (appendix 1, table 1-1) for schist rock types is continued in this study. Because some of the lithologic groups delineated as part of this study are large and contain several variable rock types, such as the metamorphosed clastic sedimentary, the mafic igneous and metamorphic equivalents, and the felsic igneous and metamorphic equivalent groups, the generalized rock types such as gneiss or schist, for example, were further divided to evaluate potential effects of mineralogical distinctions on geochemistry and thereby groundwater quality in the aquifers. Detailed descriptions of geologic units are available in the geographic information system (GIS) attributes for the State maps as compiled by Dicken and others (2005a, 2005b) and Nicholson and others (2005, 2006) (appendix 1, table 1-1). Where formation descriptions did not include mineralogy in the GIS attribute file, the USGS National Geologic Map Database Geologic Names Lexicon “GEOLEX” was used to obtain mineralogical descriptions of the formations (http://ngmdb.usgs.gov/Geolex/geolex_home.html; accessed February 2011). Each lithologic group (with the exception of the unconsolidated sediments group) is categorized with regard to chemical composition as felsic, intermediate, mafic, carbonaceous, or sulfidic (appendix 1, table 1-1).

The metamorphosed clastic sedimentary lithologic group is subdivided into 16 lithochemical subgroups based on the presence of minerals that may affect aquifer geochemistry. For example, sulfidic characteristics [31s and 32s, following McCartan and others (1998)], graphitic content (32g and 35gns), the presence of calcareous minerals or rocks (35c), the presence of aluminous minerals (32al), the presence of mafic minerals (chlorite and hornblende, 32m; biotite, 41bs). The subgroup “u” designation is simply “undifferentiated” because the description of the geologic unit or formation indicated mixed rock types. Other distinctions were made with regard to rock types that have similar geologic origin, structure, or textural characteristics (35gn and 35ml) (appendix 1, table 1-1). Figure 7 shows an example of the further division of lithologic groups into lithochemical subgroups and corresponding geologic formations.

A few lithologic groups have only minor modifications from McCartan and others (1998). The quartz-rich metamorphic group has an additional 33my lithochemical subgroup for mylonitic rocks associated with major fault zones (Brevard



Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 Lithologic group data from Dicken and others, 2005a and
 2005b and Nicholson and others, 2005 and 2006

Figure 5. Distribution of delineated lithologic groups and 1994–2008 sample locations within the study area, Piedmont and Blue Ridge Physiographic Provinces.

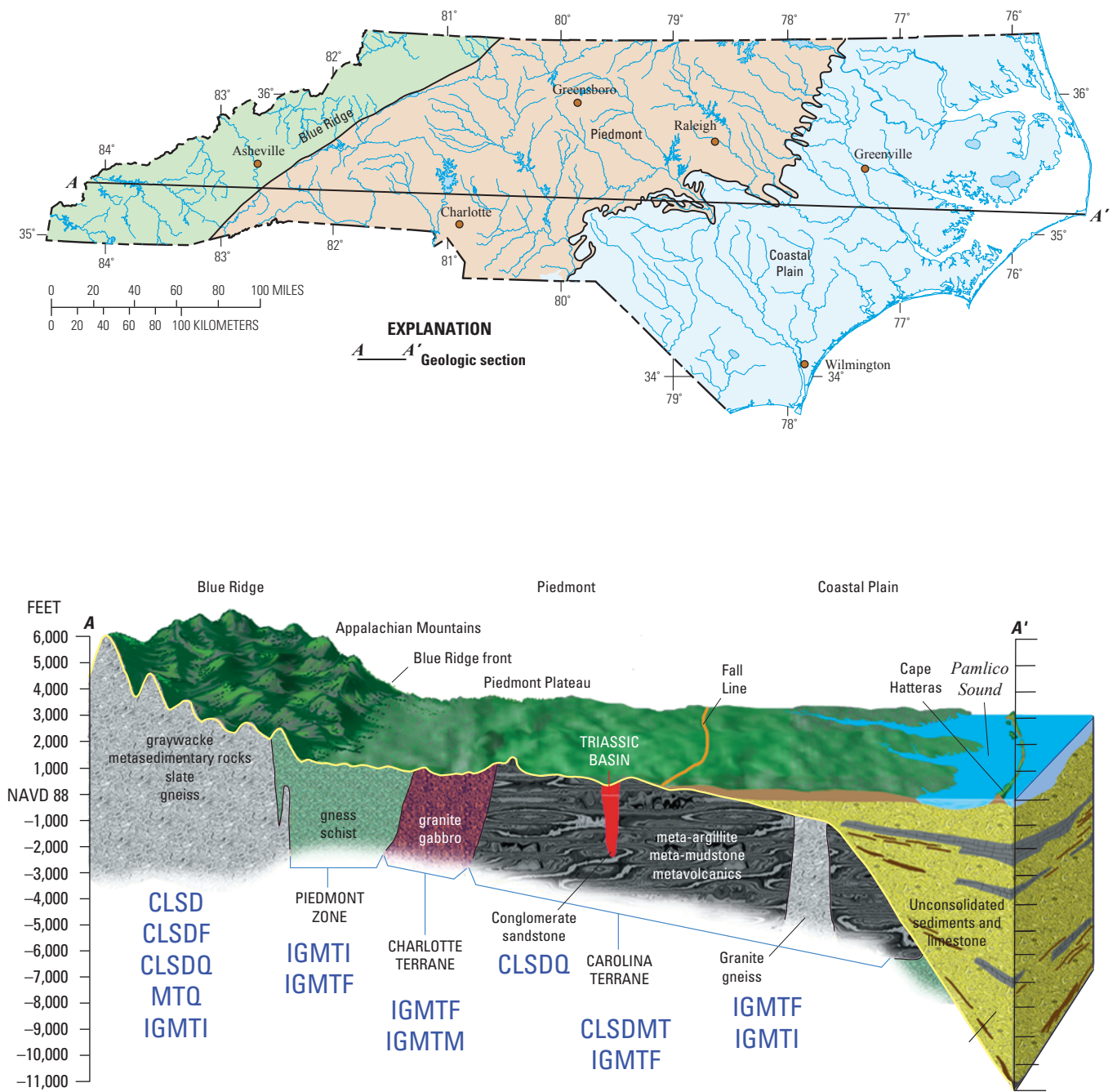


Figure 6. Generalized schematic cross-section diagram across North Carolina physiographic provinces showing generalized geologic terranes and common lithologic groups delineated as part of this study.

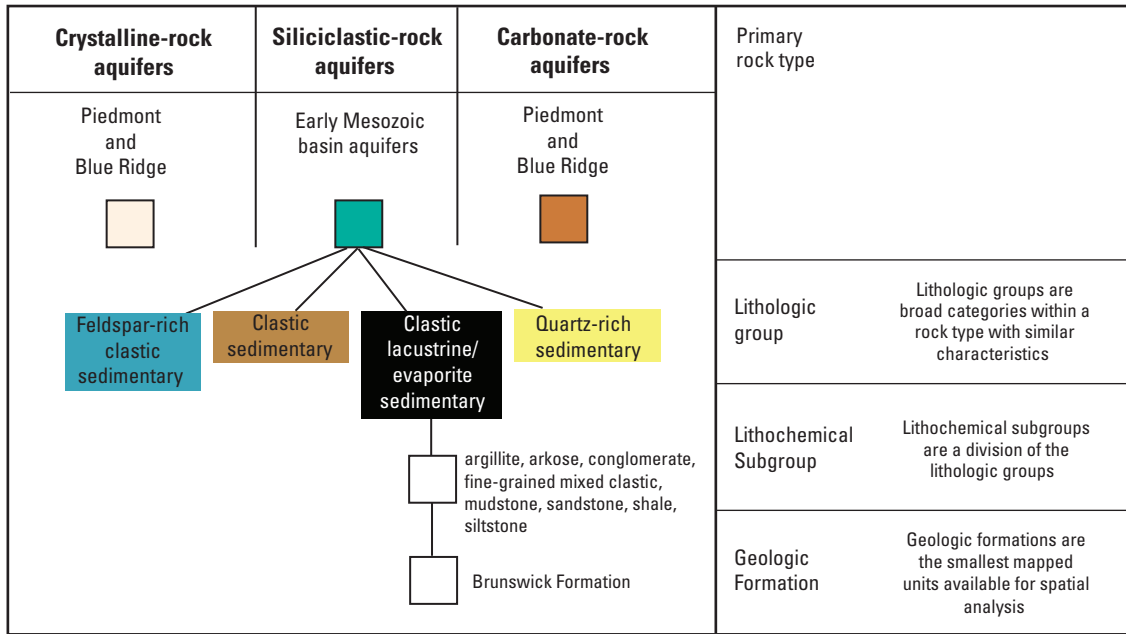


Figure 7. An example division of the aquifers into lithologic groups, lithochemical subgroups, and corresponding geologic formations.

fault zone, appendix 1, table 1-1). The intermediate igneous rocks and their metamorphic equivalents group includes distinctions for the more feldspathic subgroups (34f and 34fl) compared to the more intermediate composition groups (34i). This group also includes some rock type designations, including biotite gneiss (34bg) and augen gneiss (34agn), as well as mineralogical distinctions for sulfidic and graphitic rocks (34s). The mafic igneous and metamorphic equivalent rocks group has seven lithochemical subgroups, most of which follow McCartan and others (1998), with the addition of 41mv and 41v for metavolcanic and volcanic origin, respectively. A subgroup 44 was added for an undifferentiated mafic gneiss rock type. For the ultramafic rocks group, the subgroup 50gs was added to distinguish greenstones that did not contain carbonates. For the felsic igneous and metamorphic equivalent rocks group, the subgroup 61m is used to distinguish metamorphosed intrusive, while 61mf and 61mi distinguish compositional differences of felsic and intermediate, respectively. The subgroup 61v follows McCartan and others (1998) with the addition of 61mv for metavolcanic rocks. Where lithochemical subgroups were important to the interpretation and extrapolation of groundwater-quality data from this study for human health issues, the correlation of formations across State boundaries was reviewed. Geologic formations may be categorized differently based on the available geologic formation data and rock and mineral assemblage descriptions on the State maps (appendix 1, table 1-1, “ROCK_TYPE1”; Dicken and others, 2005a, 2005b; Nicholson and others, 2005, 2006). Also, the USGS National Geologic Map Database, Geologic Names Lexicon “GEOLEX” searchable database was used to

obtain mineralogical descriptions of the formations (http://ngmdb.usgs.gov/Geolex/geolex_home.html; accessed October 2012).

Geochemical Controls on Naturally Occurring Trace Elements and Radionuclides in Groundwater

Dissolved chemicals in groundwater may be derived from rock weathering, biological processes, and anthropogenic sources. Dissolution of minerals in bedrock and overlying geologic materials commonly release naturally occurring constituents to the groundwater. Major cations (positively charged ions such as calcium, magnesium, sodium, and potassium), major anions (negatively charged ions such as sulfate, chloride, fluoride, and bicarbonate), and nonionic solutes (uncharged solutes such as silica and DO typically are present at concentrations greater than 1 mg/L, whereas trace constituents typically are present at concentrations less than 1 mg/L (Hem, 1985). However, dissolved concentrations of trace constituents can range widely depending on their occurrence in the rock or other source, the solubility of the constituent elements and interacting substances, and geochemical conditions such as pH and oxidation-reduction (redox) state that affect element form, mobility, and transport in the aqueous environment.

Groundwater from diverse environments may contain naturally occurring trace elements such as iron, manganese, zinc, lead, copper, nickel, vanadium, molybdenum, arsenic, radium, and uranium (Rose and others, 1979). Descriptions of

the mineral assemblages in mapped geologic units may be useful when identifying potential geologic sources of dissolved constituents, although the mere presence of minerals containing such constituents may not lead to elevated concentrations in the associated groundwater. Elevated concentrations of trace constituents tend to be found locally or are associated with specific aquifer settings, particularly (1) under acidic conditions where the solubilities and mobilities of many element species are increased (Kirby and Cravotta, 2005; Cravotta, 2008a,b) or (2) under reducing conditions where the dissolution of ferric iron [Fe(III)] and manganese [Mn(III,IV)] to more soluble ferrous Fe(II) and dissolved manganese [Mn(II)] can release adsorbed and coprecipitated metals (Langmuir, 1997, p. 294–296; McMahan and Chapelle, 2008).

Although the release of trace elements through mineral weathering is a natural process, accelerated mineral decomposition that accompanies the development of strongly acidic or reducing conditions could be a consequence of human activities. For example, acidification can result from the excavation of sulfide minerals or the release of gaseous emissions containing sulfur or nitrogen oxides, and reduction can result from the disposal of organic wastes or over-fertilization. Furthermore, some constituents may originate from industrial sources, manmade materials, or land applications. Thus, in order to determine constituent concentrations that may have been added to groundwater as a consequence of land-use or waste-disposal practices, natural background concentrations for specific geologic settings need to be established. Additionally, in order to identify geochemical environments where elevated concentrations of constituents may be present, water-quality conditions such as pH and redox state and major ion composition need to be characterized.

Whether a dissolved constituent has originated from the weathering of rocks or from anthropogenic sources, its transport may be affected by its ionic charge, redox state, and tendency to interact with other dissolved elements (ion complexation) and solid surfaces (surface complexation or ion exchange). Redox-sensitive elements that commonly occur in more than one valence state under atmospheric conditions near the surface of the Earth include carbon (−4, +4), sulfur (−2, +6), nitrogen (−3, +3, +5), iron (+2, +3), manganese (+2, +3, +4), arsenic (−3, +3, +5), selenium (−2, +4, +6), chromium (+3, +6), molybdenum (+4, +6), vanadium (+3, +4, +5), and uranium (+3, +4, +5, +6). Although these and many other elements can have a positive valence state or core charge, the predominant aqueous species may be positively or negatively charged ions, depending on the tendency of the charged element to hydrolyze and to form aqueous complexes. Generally, the highly positively charged valences are present as cations form oxyanions and, less commonly, oxycations (Turner and others, 1981; Stumm and Morgan, 1996; Langmuir, 1997; Hodge and others, 1998). For example, in a reducing groundwater environment, chromium in the +3 valence state may be present as a cation (Cr^{+3}), whereas in a strongly oxidizing environment, chromium in the +6 valence state may be present

as the oxyanion chromate (CrO_4^{-2}). Likewise, under oxidizing conditions, arsenic in the +3 or +5 valence states tends to form the oxyanions arsenite (AsO_3^{-3}) or arsenate (AsO_4^{-3}), respectively, and uranium in the +6 valence state tends to form the uranyl (UO_2^{+2}) oxycation. Furthermore, at the typical pH range of natural water, the uranyl ion may interact with carbonate and bicarbonate ions to form negatively charged carbonate complexes (Langmuir, 1997). The formation of such soluble ion complexes can increase the concentrations and transport of dissolved trace elements (Cravotta, 2008a, 2008b).

Concentrations of major cations and anions in natural waters generally are controlled by acid-base and precipitation-dissolution reactions; however, the concentration and mobility of most trace ions generally are controlled by surface-complexation (adsorption) reactions on hydrous Fe(III) oxides, Mn(III,IV) oxides, and aluminum oxides and silicates (Dzombak and Morel, 1990; Bowell, 1994; Stumm and Morgan, 1996; Drever, 1997; Langmuir, 1997). Consequently, the concentrations of trace elements in natural waters typically are far below the values that would be predicted for saturation with respect to a pure mineral phase (Drever, 1997; Cravotta, 2008b). For example, at the acidic pH range (5 to 6.5) of natural groundwater, dissolved oxyanions, such as chromate (CrO_4^{-2}), phosphate (PO_4^{-3}), selenite (SeO_3^{-2}), selenate (SeO_4^{-2}), arsenite (AsO_3^{-3}), and arsenate (AsO_4^{-3}), tend to be weakly sorbed and partly immobilized by hydrous ferric oxide (HFO) minerals (fig. 8, such as goethite (FeOOH) and ferrihydrite [$\text{Fe}(\text{OH})_3$]). However, at the alkaline pH range (7.5 to 9) of natural water, sorption of these anions generally decreases with increasing pH and is accompanied by corresponding increases in their dissolved concentrations (fig. 7). In contrast, dissolved cations, such as chromium (Cr^{+3}), copper (Cu^{+2}), cadmium (Cd^{+2}), nickel (Ni^{+2}), and zinc (Zn^{+2}), tend to be poorly adsorbed and are relatively mobile at acidic pH, whereas at alkaline pH, the cation concentrations tend to be attenuated by adsorption on HFO and other oxide surfaces (fig. 8).

The apparent opposite sorption behavior of the anions and cations (fig. 8) results from a progressive decrease in the effective charge on oxide surfaces from positive (attractive to anions) to negative (attractive to cations) as the pH increases from acidic to alkaline values (Dzombak and Morel, 1990; Stumm and Morgan, 1996; Langmuir, 1997). At alkaline pH values, negatively charged oxide atoms at mineral surfaces attract cations; however, at acidic pH, protons attached to the oxide atoms yield an effective positive charge at the mineral surface and thus attract anions. In addition, the sorbed cations or anions may be displaced by other charged ions such as magnesium (Mg^{+2}), chloride (Cl^-), and sulfate (SO_4^{-2}) through ion exchange or competition for sorption sites. Thus, concentrations of trace elements in solution may increase with concentrations of total dissolved solids, not only because of the release of trace constituents with the major ions dissolved from minerals, but because of the displacement of trace ions from surface sorption sites by the major ions. For the trace

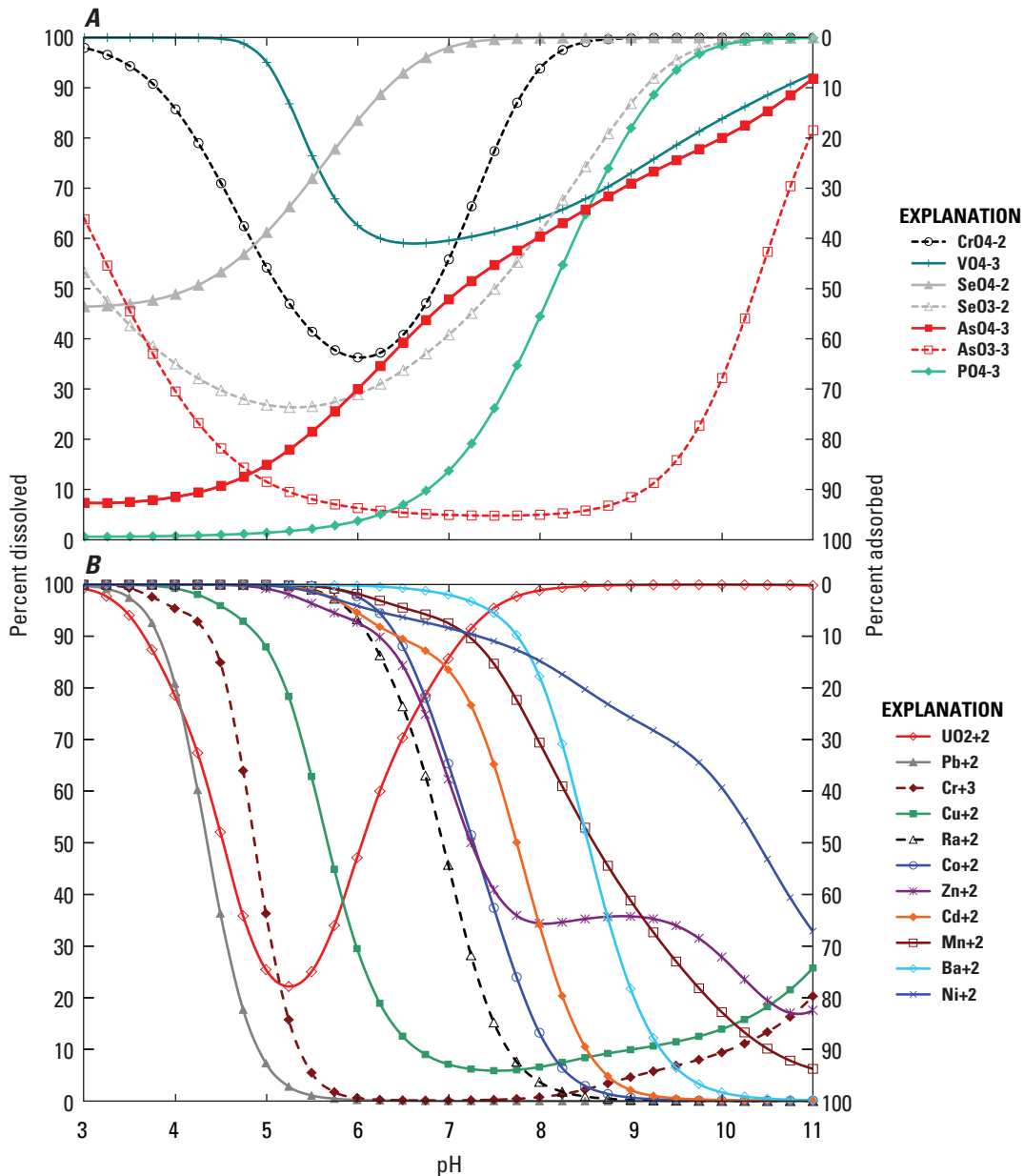


Figure 8. Equilibrium fractions of initial concentrations of ions that may be dissolved or adsorbed on a finite amount of hydrous ferric oxide at 25 degrees Celsius as a function of pH. *A*, anions; *B*, cations.

elements that form aqueous complexes, the increase in soluble major ion concentrations also increases the likelihood of the formation of soluble ion complexes.

Cations and anions that had been adsorbed or coprecipitated with Fe(III) or Mn(III,IV) compounds may be remobilized under anoxic, reducing conditions. The reducing conditions must be sufficient to reduce and dissolve iron and manganese but not to produce sulfide, which tends to form insoluble compounds with many trace cations (Korte, 1991; Welch and others, 2000; Kirk and others, 2004). The reductive dissolution of Fe(III) and Mn(III,IV) oxides typically is coupled with the oxidation of organic compounds after supplies of dissolved oxygen, nitrate (NO₃⁻), and nitrite (NO₂⁻)

have been depleted, but before the development of sulfate-reducing conditions (Ehrlich, 1990; Stumm and Morgan, 1996; Drever, 1997; McMahon and Chapelle, 2008). Under such reducing geochemical conditions, the concentrations of dissolved iron and manganese and associated sorbed trace anions and cations may become elevated. Thus, the presence of dissolved iron, manganese, and sulfate in anoxic groundwater that lacks nitrate and nitrite can be interpreted to indicate reducing geochemical conditions capable of mobilizing trace elements associated with Fe(III) or Mn(III,IV) oxides in the aquifer (McMahon and Chapelle, 2008).

Naturally occurring radionuclides in groundwater include isotopes of uranium (U-238), thorium (Th-232), radium

(Ra-224, Ra-226, Ra-228), and radon (Rn-222). Uranium-238 is the parent of radium-226 and radon-222; thorium-232 is the parent of radium-228 and radium-224 (fig. 9). Uranium, thorium, radium, and other radioisotopes in the decay chains tend to be present as dissolved ions that are affected by different geochemical speciation, solubility, and sorption processes (Ames and others, 1983a, 1983b). Consequently, the presence of uranium, thorium, or radium in groundwater requires a mineral source and geochemical conditions in the aquifer that are conducive to transport of those elements. The presence of radon (of which radon-222 is the most abundant isotope) in groundwater is directly related to the presence of a decay-chain parent, such as uranium, in the aquifer because radon is a highly soluble noble gas that generally is not affected by chemical reactions. In addition, all radon isotopes have short half-lives and generally occur relatively near the parent source in the aquifer.

Water-Quality Data and Methods

Groundwater-quality data collected by the USGS NAWQA Program (Gilliom and others, 1995) from wells in various hydrogeologic and land-use settings from Georgia through New Jersey were compiled to establish a regional database on water quality in the study area. The NAWQA design is discussed in Gilliom and others (1995) and Lapham and others (2005); protocols for collection of water-quality data are presented in Koterba and others (1995). The NAWQA groundwater sampling protocols specified prolonged flushing of the well to remove water stored in the well bore prior to sample collection (Koterba and others, 1995). Furthermore, field measurements of dissolved oxygen, pH, alkalinity, and other unstable constituents were routinely conducted without exposing samples to the atmosphere at the time of sample collection. Thus, the data used for this study are presumed to represent the in situ water-quality characteristics of the aquifer.

This report includes groundwater-quality data collected as part of 14 NAWQA studies across the eastern United States covering the Early Mesozoic basin principal aquifer and a variety of fractured felsic and mafic crystalline-rock aquifers of the Piedmont and Blue Ridge aquifer as described by Lapham and others (2005) (figs. 1 and 3). The compiled data are not distributed evenly throughout the study area and therefore are not spatially representative of all the aquifers. The dataset analyzed consists of 346 samples (appendix 1, tables 1-3 and 1-4) collected as part of land use, major aquifer, and drinking water studies (table 1). Each study involved a network of 20 to 30 wells to document and explain the occurrence and distribution of selected chemical compounds in groundwater in particular settings (Gilliom and others, 2006) (table 1; fig. 3; appendix 1, tables 1-3 and 14). Groundwater data from carbonate rock and glacial aquifers are not included in this study.

Data for physical characteristics and concentrations of dissolved chemical constituents in groundwater were compiled for the 346 sampled wells (appendix 1, tables 1-3 and 1-4). A variety of crystalline and siliciclastic bedrock types with associated lithologies were sampled at these well locations. Most of these data were collected during the late spring through the late summer. Although collected only once per site (from 1994 through 2008; appendix 1, table 1-4), the groundwater-quality data are assumed comparable for the purpose of evaluating spatial patterns in water quality for this study. Selected data from these compilations are presented in this report; all data compiled for this report are accessible on the World Wide Web at <http://infotrek.er.usgs.gov/apex/f?p=NAWQA:HOME:0;> accessed October 2012.

Analytical results for most samples were obtained for major ions, various trace elements (including iron, manganese, aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, lithium, mercury, molybdenum, nickel, selenium, silver, strontium, thallium, vanadium, and zinc), selected nutrients (including phosphorus and nitrogen compounds), dissolved organic carbon, and radionuclides [including radon-222 (hereafter referred to as radon), radium isotopes, uranium, and tritium] as well as temperature, specific conductance (SC), pH, and concentrations of dissolved oxygen (DO). All analyses are for dissolved constituents in water samples that were filtered in the field, unless otherwise specified. The water temperature, SC, pH, and dissolved-oxygen concentrations were measured in the field immediately prior to sample collection. Other chemical analyses were conducted at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado (Patton and Truitt, 1992; Brenton and Arnett, 1993; Fishman, 1993; Werner and others, 1996).

To assess the potential for naturally occurring solutes to contaminate drinking water, the concentrations of chemical constituents are compared to criteria for protection of human health such as USEPA (2009) drinking water maximum contaminant levels (MCLs) and secondary maximum contaminant levels (SMCLs) or health-based screening levels (HBSLs). Because water quality at a given location will vary temporally owing to natural hydrologic processes and seasonality, and because samples were collected only once from each well, constituent concentrations also were compared to a value of one-tenth of the relevant human health criteria. Consideration of this lower threshold level increases the certainty that constituents will be acknowledged that could have human health implications under variable circumstances.

The reported water-quality data were used to compute mineral saturation indices (explained below), hardness, and groundwater redox classes. Hardness was calculated as the sum of calcium and magnesium concentrations and is expressed as calcium carbonate (Fishman, 1993). The redox class was determined on the basis of concentrations of dissolved oxygen, nitrate, manganese, iron, and sulfate using thresholds of McMahon and Chapelle (2008). The redox classifications used in this report were simplified to consider only

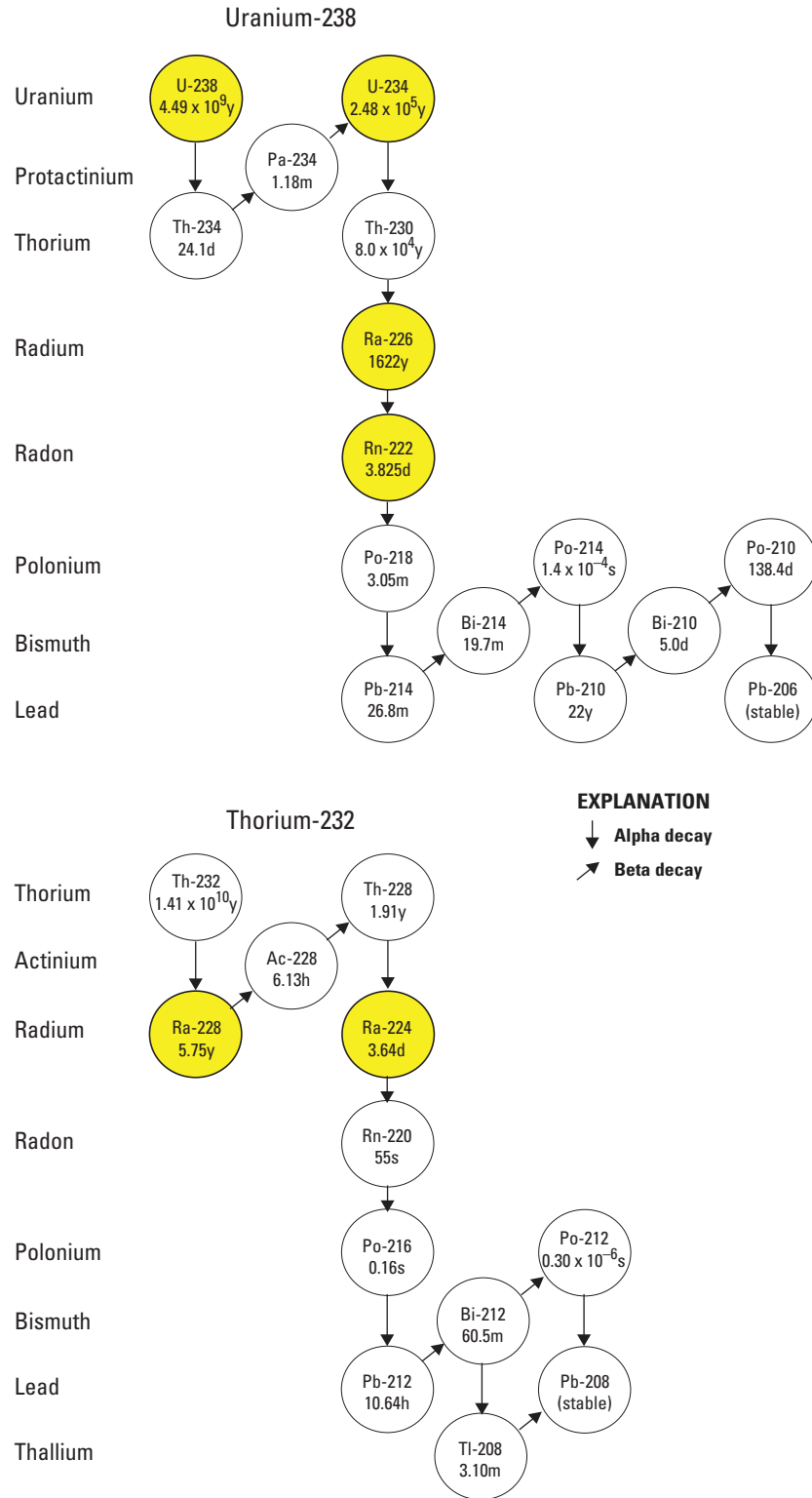


Figure 9. Uranium-238 and thorium-232 decay series.

three major classes: “anoxic” ($\text{DO} < 0.5 \text{ mg/L}$, manganese $\geq 50 \text{ }\mu\text{g/L}$, and iron $\geq 100 \text{ }\mu\text{g/L}$); “mixed” ($\text{DO} \geq 0.5 \text{ mg/L}$ and either manganese $\geq 50 \text{ }\mu\text{g/L}$ or iron $\geq 100 \text{ }\mu\text{g/L}$); and “oxic” ($\text{DO} \geq 0.5 \text{ mg/L}$, manganese $< 50 \text{ }\mu\text{g/L}$, and iron $< 100 \text{ }\mu\text{g/L}$).

Ancillary geospatial data were compiled to describe the physical characteristics of the watersheds within the potential contributing areas of 1,640 ft (NAWQA buffer for ancillary data including land use, census data, nutrient sources, and point sources) of sampled wells. Each groundwater sample site was classified on the basis of the physiographic setting, bedrock type (crystalline or siliciclastic), lithologic group, and lithochemical subgroup (table 3). Land-cover data were compiled and used to compute the percentage of four major land uses (wetland, forested, agricultural, and urban) within 1,640 ft of sampled wells (appendix 1, table 1-3). Generalized land cover was modified from the National Land Cover Database 1992 (NLCD 1992) using historical land-use and land-cover data (Price and others, 2007) (fig. 2).

Graphical and Statistical Analyses

Various graphical and statistical techniques were used in this report to compare water-quality data for different aquifers or geologic settings, to estimate natural and anthropogenic sources of dissolved constituents, and to identify possible factors affecting the occurrence or transport of solutes in the aquifers in the study area. In general, nonparametric, rank-based statistical approaches were used to accommodate non-normally distributed and censored data typical of most environmental samples (Helsel and Hirsch, 2002). Data for individual continuous variables, such as chemical concentrations, were censored to a common level, and censored values were set to a common reporting limit before ranks were computed for use in statistical tests. Relations between continuous variables were evaluated with scatter plots and correlation coefficients (Spearman’s rho); distributions of continuous variables were compared among different groups (such as lithology) using probability plots, boxplots, and rank-sum or rank-transform analysis-of-variance (ANOVA) (Helsel and Hirsch, 2002).

The data reported for trace element concentrations typically included “censored” values that were less than (<) the reporting limit. The reporting limit for a given constituent generally was not uniform for all samples. For example, 157 of 253 samples had censored values for arsenic concentration at five different reporting limits, in micrograms per liter, with count (n) indicated in parentheses: <0.06 (n = 11), <0.12 (n = 15), <0.26 (n = 23), <1.0 (n = 106), or <2.0 (n = 2). However, the other 96 samples had reported trace element concentrations ranging from 0.036 to 57 $\mu\text{g/L}$ (appendix 1, tables 1-4 and 1-5). Only 42 of these reported concentration values were greater than 2.0 $\mu\text{g/L}$, which was the highest common reporting limit (HCRL) for arsenic (appendix 1, tables 1-4 and 1-5). For statistical tests and other computations, the censored data and reported values less than the HCRL were considered equivalent to the HCRL at 0.99 times the HCRL for most

constituents; however, for several constituents (arsenic, zinc, iron, manganese, aluminum), where the HCRL applied to few samples and resulted in excessive censoring, the next highest common reporting limit was considered. In the case of arsenic, the next highest reporting limit is 1.0 $\mu\text{g/L}$, which is one-tenth of the MCL and one-half of USEPA’s health advisory level of 2.0 $\mu\text{g/L}$ (U.S. Environmental Protection Agency, 2001) (appendix 1, tables 1-4 and 1-5).

Probability plots and boxplots are used to illustrate univariate distributions for the different aquifers and associated lithologic groups or redox classes. Horizontal reference lines on the plots indicate the applicable values of drinking water or other human health benchmarks. Probability plots indicate the frequency (x-axis), or the proportion, of samples within the crystalline- and siliciclastic-rock aquifers that exceeded the constituent concentration (y-axis) or other plotted parameter values. For parameters without censored data (where all reported values exceeded the detection limits), the maximum and minimum reported values correspond to the 0.0 and 1.0 probability values, respectively, and the median value corresponds to the 0.5 probability value. Censored values are not displayed, but are counted to estimate the frequency of samples that exceeded the reported values. For parameters with censored data, the minimum plotted value corresponds to the lowest reported value greater than the detection limit. For some constituents, such as fluoride, cobalt, lead, and selenium, the minimum reported value has a frequency of exceedance less than 0.5, which indicates the median is a censored value.

Boxplots were used to show the water-quality concentration distributions for the three lithologic groups of the siliciclastic-rock aquifers and the six lithologic groups of the crystalline-rock aquifers that have water-quality data (table 3). The boxplots show the percentile distributions of samples with concentrations equal to or less than the associated value. All censored values were set to a common reporting limit. Where the median for a group is greater than the common reporting limit, it is displayed as a horizontal line within the box that is defined by the 25th and 75th percentiles for that group; otherwise, the median is displayed at the reporting limit. Along the top of each boxplot, the number of samples in each group is shown above a letter symbol. Groups with a different letter symbol have mean ranks that are significantly different on the basis of the nonparametric Tukey test (Helsel and Hirsch, 2002) (appendix 1, table 1-6). Results were ranked and coded sequentially, with the group with the highest mean rank coded “A,” the group with the next highest mean rank coded “B,” then “C,” and so on; overlapping groups were coded with letters for overlapping groups, “BC,” for example, or “BD,” representing overlap with groups B and C, and B, C, and D, respectively. Only the first and last letters of the range of overlapping groups are listed. The mean ranks of groups with one or more of the same letters are not significantly different. Although the mean ranks of groups may not differ, data

values greater than the 75th percentile are of particular interest because these values may exceed relevant benchmarks.

The frequency and number of samples within specified pH and redox classes are illustrated using a bivariate matrix. These pH-redox matrices are used in this report to indicate relations among aquifer lithology, geochemical environment, and probability of contaminant occurrence. Each matrix considers four general pH classes (x-axis—pH 4.5 to <5.5; 5.5 to <6.5; 6.5 to <7.5; 7.5 to <8.5) and the three simplified redox classes (y-axis—anoxic; mixed; oxic). The pH-redox matrices indicate the frequency of occurrence of the pH-redox classes by lithologic group and the frequency of occurrence of contaminant concentrations in relation to a specified reporting limit or human health benchmark for all the groups combined. The corresponding reporting limit or benchmark value and the total number of samples considered are indicated at the top of the matrix. The number of samples counted within each pH-redox class is color-coded to highlight those pH-redox classes with the greatest frequency of samples exceeding relevant limits.

Principal components analysis (PCA), computed with SAS 9.2 (SAS Institute, Inc., 2008), was used to evaluate multivariate correlations among the elements in the regional groundwater dataset without prior classification. The goal was to identify important hydrochemical processes or master variables that could explain element associations and distributions (Joreskog and others, 1976; Drever, 1997; Thyne and others, 2004). The Spearman-rank correlation coefficient matrix for the groundwater dataset (appendix 1, table 1-7) provided the standardized input for the PCA. Because the PCA model would exclude the entire record for any sample with a missing value, those constituents that were missing or those that were censored in more than 40 percent of the samples, such as dissolved aluminum, fluoride, bromide, organic carbon, and many trace elements, were excluded. The PCA model was optimized with varimax rotation, and only principal components with eigenvalues greater than unity, equivalent to correlations with a probability greater than or equal to 0.999, were retained (Joreskog and others, 1976; Thyne and others, 2004). Loadings for each constituent included in the PCA model are equivalent to the Spearman-rank correlation coefficient between that constituent and the principal component. To aid in interpretations, the scores for each principal component in the PCA model were compiled and then evaluated by correlation or graphical analysis with additional variables that had been excluded from the PCA, such as lithology, land use, well depth, and chemical constituents. For simplification of displayed results, the loading values and Spearman-rank correlation coefficient values are multiplied by 100 and rounded. Significant correlation coefficients for the additional variables are displayed beneath the main PCA model results; only correlation coefficients with probability greater than or equal to 0.999 are considered significant.

Geochemical Modeling

Geochemical equilibrium models were developed to explain the occurrence of solutes in different geochemical environments and the relations among concentrations of dissolved constituents in the groundwater samples. Aqueous speciation computations with WATEQ4F (Ball and Nordstrom, 1991) and PHREEQC (Parkhurst and Appelo, 1999) using the WATEQ4F database were used to evaluate the potential for the concentrations of dissolved constituents to be limited by precipitation-dissolution and (or) adsorption-desorption processes. The computed mineral saturation index (SI) values for various major and trace minerals were used to indicate the potential for mineral dissolution and precipitation. If a mineral phase is undersaturated in groundwater (SI less than 0), that mineral phase (if present) has the potential to be dissolved by the groundwater. Likewise, if a mineral is supersaturated in groundwater (SI greater than 0), that mineral phase feasibly could precipitate, thus limiting the dissolved constituent concentrations. To illustrate potential differences in geochemical properties, the SI values for selected minerals were illustrated as boxplots by lithologic groups.

Adsorption and desorption of anions and cations on hydrous ferric-oxide-coated surfaces were evaluated using a diffuse double-layer modeling approach with PHREEQC (Parkhurst and Appelo, 1999), aqueous speciation data from WATEQ4F (Ball and Nordstrom, 1991), and surface complexation data from Dzombak and Morel (1990). Supplemental thermodynamic data for radium, chromium, cobalt, and vanadium were obtained from the ThermoChimie data base offered with PHREEQC (sit.dat), and surface-complexation constants for radium were estimated using empirical adsorption data presented by Benes and others (1984). For all of the sorption models, to be consistent with Dzombak and Morel (1990), the hydrous ferric oxide was specified as 90 mg/L, with a specific surface area of 600 square meters per gram consisting of 5×10^{-6} moles of strong binding sites and 2×10^{-4} moles of weak binding sites. Aqueous speciation and adsorption distribution for a range of pH values were computed, and the percentage of the total concentration distributed between the solution and sorbent was plotted as a function of pH. The sorption modeling results were illustrated as fractions of initial concentrations of ions that may be dissolved or adsorbed on a finite amount of hydrous ferric oxide at 25 degrees Celsius ($^{\circ}\text{C}$) as a function of pH.

Water-Quality Characteristics of Aquifers, Lithologic Groups, and Lithochemical Subgroups

Descriptions of groundwater quality generally include concentrations of major ions, pH, dissolved oxygen, and other variables. In this report, these characteristics are described in order to explain naturally occurring contaminants in groundwater from different geologic settings and geochemical environments.

The groundwater quality for the PBR crystalline-rock aquifers generally differed from that for the Early Mesozoic siliciclastic-rock aquifers, considering the major ion and other constituent concentrations for the two bedrock types (figs. 10–14). Compared to the crystalline-rock aquifers, the groundwater from siliciclastic-rock aquifers had higher maximum and median concentrations of total dissolved solids, hardness, calcium, alkalinity (calcium carbonate), and sulfate (figs. 10–11). Although the median concentrations of magnesium, sodium, chloride, and nitrate in groundwater from siliciclastic aquifers also were higher than those medians for the crystalline-rock aquifers, the maximum concentrations of these constituents were present in groundwater from the crystalline-rock aquifers (figs. 10–11). Although median concentrations of silica were comparable for the two aquifer rock types, the crystalline-rock aquifers had a larger range for silica concentrations and larger ranges and higher medians for potassium and aluminum concentrations than the siliciclastic-rock aquifers (figs. 10–11).

The PBR crystalline-rock aquifers and the Early Mesozoic siliciclastic-rock aquifers also exhibited differences in the frequency distributions of minor and trace constituents in the groundwater (figs. 12–14). However, as explained previously and in more detail below, spatial and temporal variations in concentrations of these constituents may be attributed to variations in lithology within a particular rock type (lithologic group, lithochemical subgroup) and (or) geochemical environment (pH and redox conditions) within the aquifer (figs. 15–21). For example, the pH of the groundwater samples evaluated for this study ranged from 4.7 to 8.2 (fig. 12A, appendix 1, table 1-4). Although the highest and lowest pH values were recorded for groundwater from the PBR crystalline-rock aquifers, the groundwater from the Early Mesozoic siliciclastic-rock aquifers, particularly the clastic sedimentary (CLSD) and clastic lacustrine/evaporite sediments (CLSD-LAC), generally had higher mean rank pH values than the PBR crystalline-rock aquifers, particularly the felsic or intermediate igneous and metamorphic lithologic units (IGMTI) (fig. 16C). About 70 percent of groundwater samples from the siliciclastic-rock aquifers had pH greater than 7 compared to only about 10 percent from the crystalline-rock aquifers.

Although DO concentrations in the groundwater varied widely, a majority of samples for all the aquifer lithologies could be characterized as oxic, with DO greater than or equal

to 0.5 mg/L (fig. 12B). Seven redox classes were determined on the basis of concentrations of DO, nitrate, manganese, iron, and sulfate by using thresholds of McMahon and Chapelle (2008). Of the 346 groundwater samples evaluated for this study, 65.0 percent were classified as “oxic” (with DO greater than or equal to 0.5 mg/L); 18.2 percent were classified as “mixed” (with DO greater than or equal to 0.5 mg/L and manganese greater than or equal to 50 mg/L or iron greater than or equal to 100 mg/L); 14.2 percent were classified “anoxic” (with DO less than 0.5 mg/L); and the remaining 2.6 percent, which lacked data for DO, were classified as “unknown.” Based on the Tukey analysis, DO concentrations in groundwater did not differ among lithologies (fig. 15). Of the anoxic samples, 3.2 percent were suboxic, 1.7 percent were nitrate-reducing, 1.7 percent were manganese-reducing, 5.8 percent were iron-reducing, and 0.3 percent were methanogenic. Because few samples could be characterized as strongly reducing, the anoxic samples were considered as a single class for evaluation of geochemical environment.

To evaluate the potential for aquifer lithology to affect contaminant concentrations, the water-quality data and saturation indices for selected minerals were considered in relation to the major bedrock type, lithologic groups, and lithochemical subgroups [tables 3 and 4 (table 4 available online at <http://pubs.usgs.gov/sir/2013/5072/>), figs. 10–17]. To evaluate potential for geochemical factors to affect the mobility of contaminants in the aquifer, the saturation indices for minerals that may be present in the aquifers and soil were summarized by lithologic group (figs. 18 and 19), and the frequency of contaminant detections and exceedances of human health benchmarks were evaluated with respect to the groundwater pH and redox characteristics (figs. 20 and 21) that may affect the adsorption and release of trace constituents by iron and manganese oxides.

Exceedances of Drinking Water Criteria

Constituents of potential concern were identified on the basis of drinking water exposure guidelines proposed by the USEPA for sources of public drinking water (U.S. Environmental Protection Agency, 2009, 2010), including MCLs, HBSLs, or other criteria such as SMCLs. HBSLs were developed by the USGS, USEPA, New Jersey Department of Environmental Protection (NJDEP), and Oregon Health and Science University (OHSU) as an interagency pilot effort beginning in 1998 to communicate the potential relevance of the water-quality findings of the USGS NAWQA Program in a human-health context (Toccalino and others, 2012).

Provisionally promulgated drinking water standards for radium (U.S. Environmental Protection Agency, 1976) became final with the Radionuclide Rule of 2000 (U.S. Environmental Protection Agency, 2000) when the other proposed standards for radionuclides were also finalized, or in the case of uranium, newly promulgated. Uranium, radium, and radon are radioactive elements that can increase human cancer risk

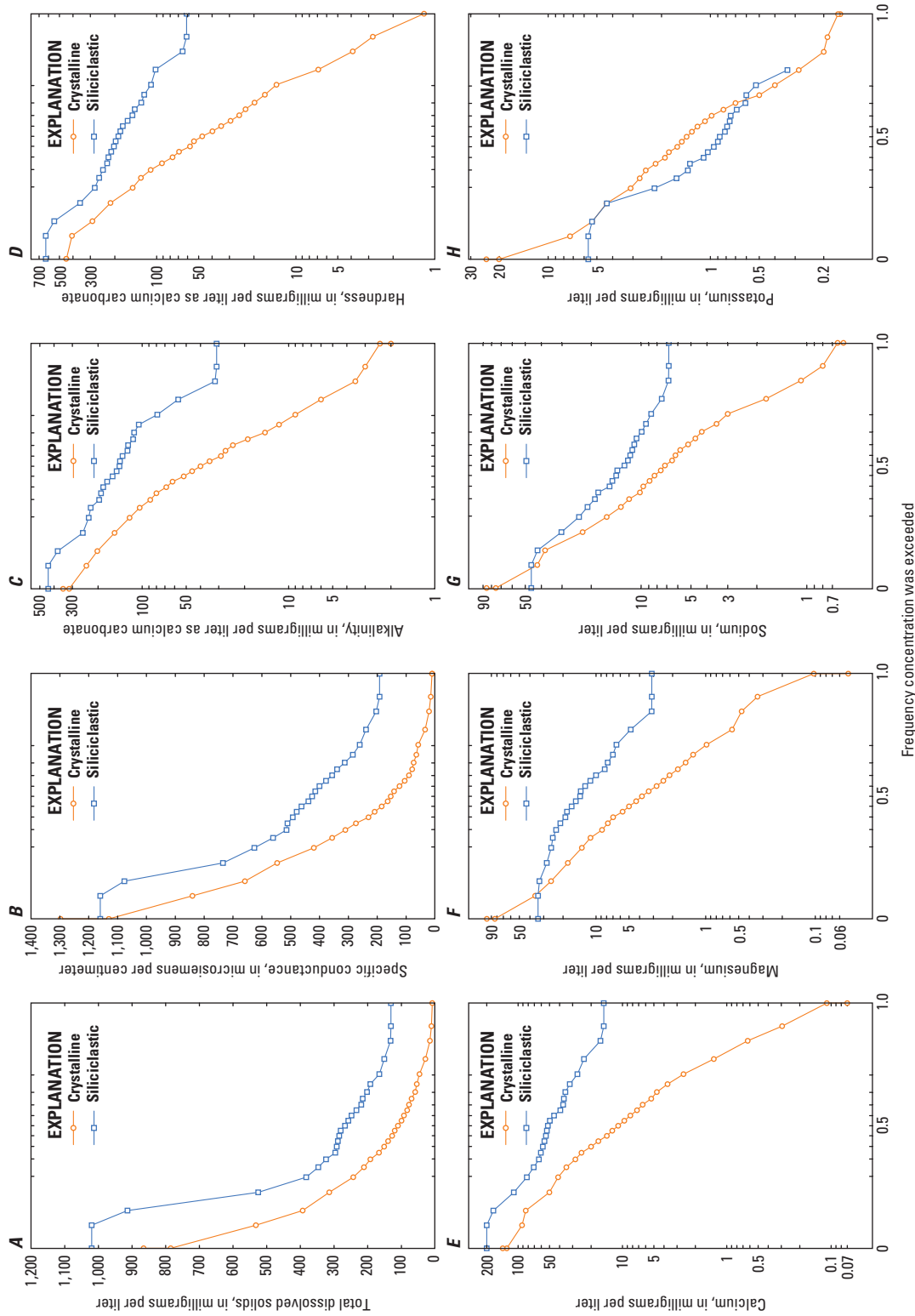


Figure 10. Probability plots of groundwater-quality data for siliciclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. A, total dissolved solids; B, specific conductance; C, alkalinity; D, hardness; E, calcium; F, magnesium; G, sodium; and H, potassium.

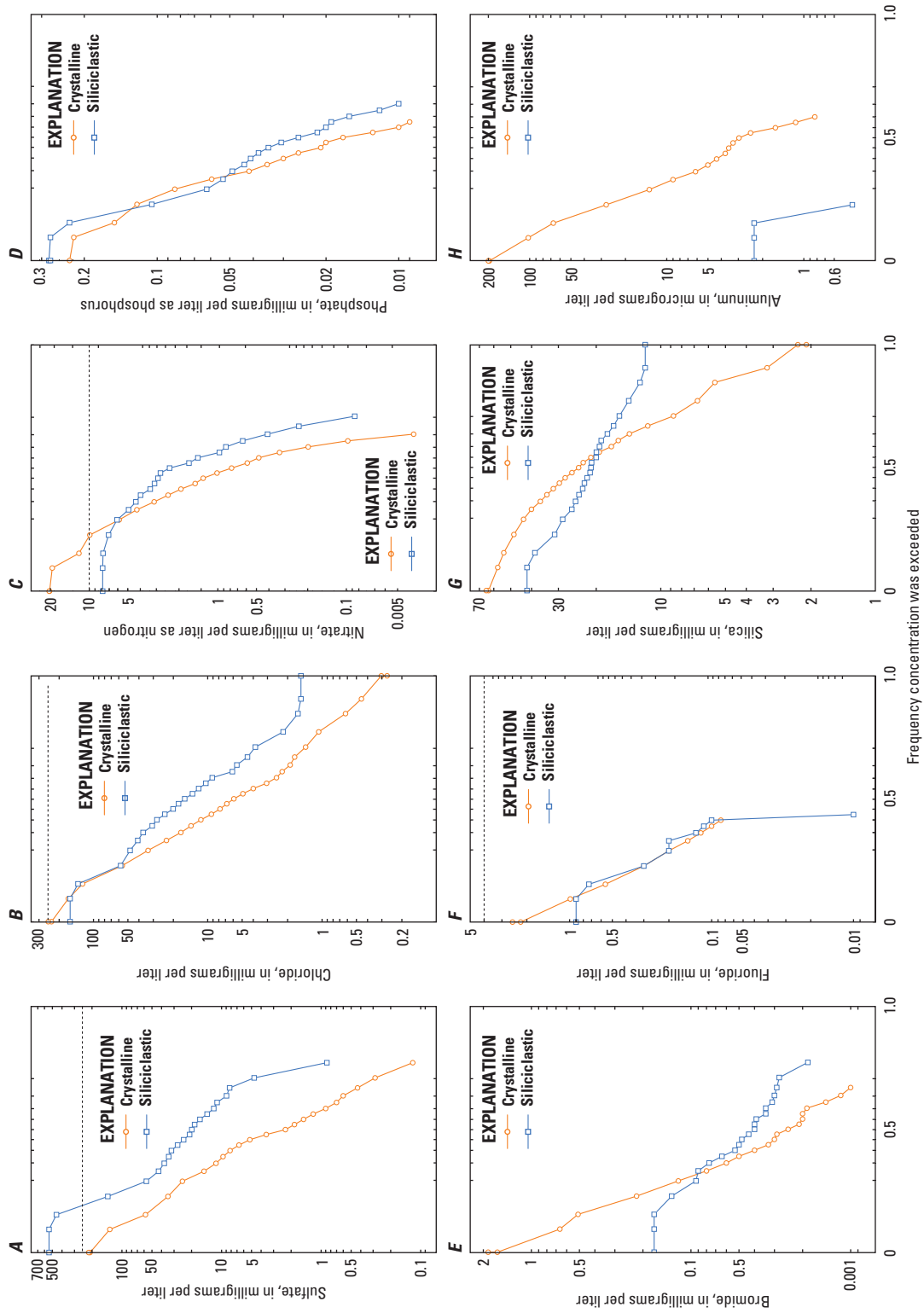


Figure 11. Probability plots of groundwater-quality data for siliclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. A, sulfate; B, chloride; C, nitrate; D, phosphate; E, bromide; F, fluoride; G, silica; and H, aluminum.

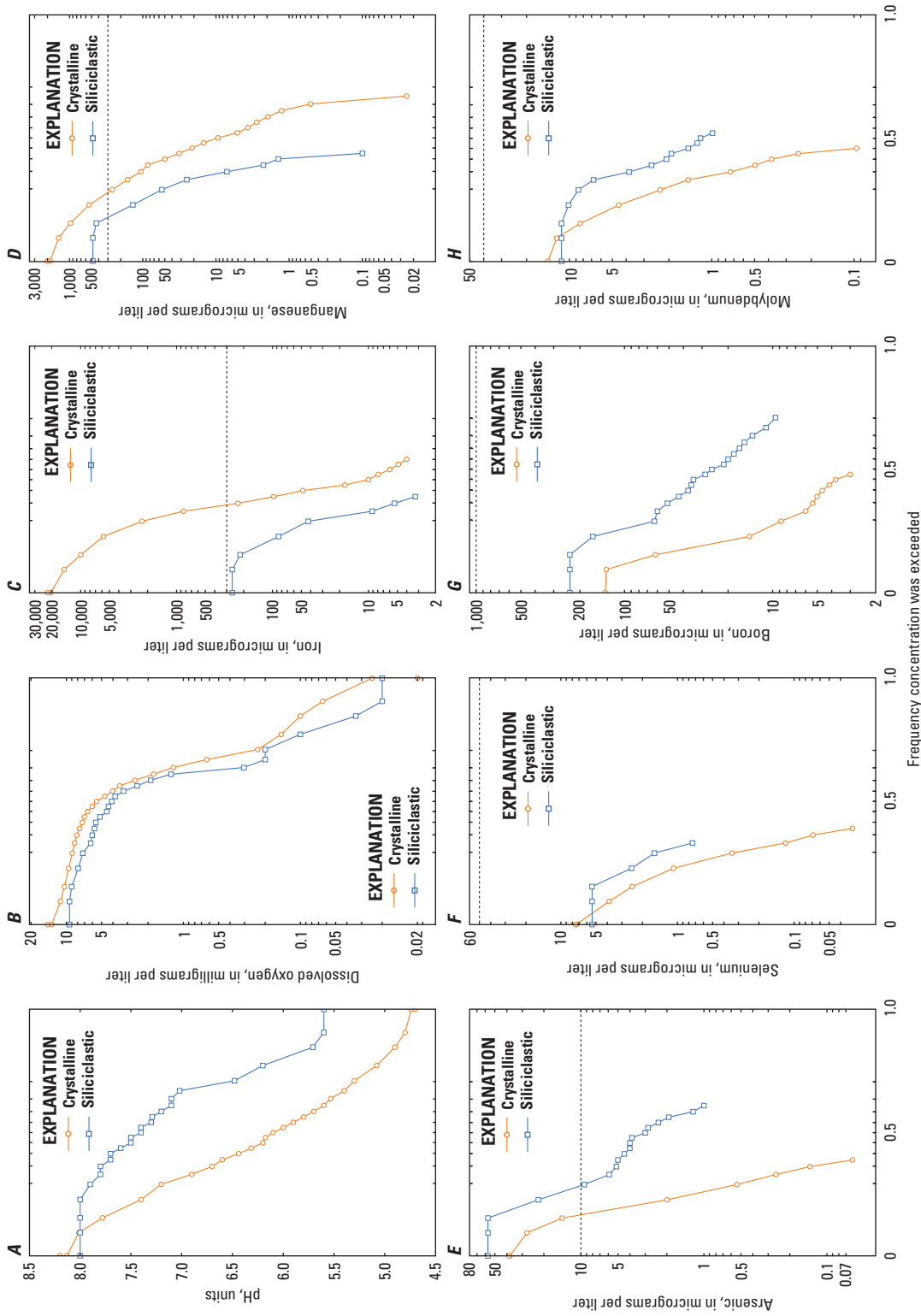


Figure 12. Probability plots of groundwater-quality data for siliciclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. A, pH; B, dissolved oxygen; C, iron; D, manganese; E, arsenic; F, selenium; G, boron; and H, molybdenum.

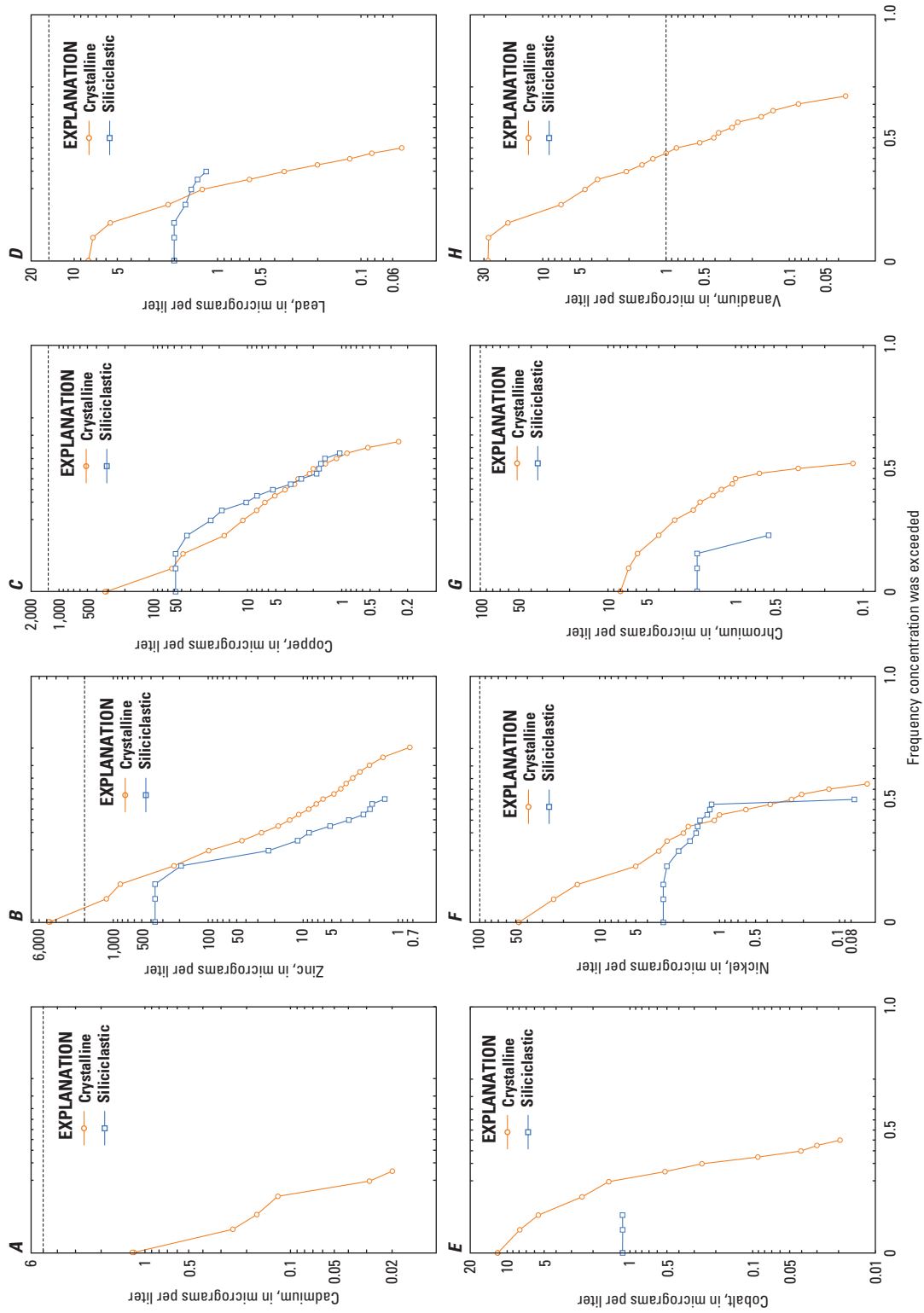


Figure 13. Probability plots of groundwater-quality data for siliclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. A, cadmium; B, zinc; C, copper; D, lead; E, cobalt; F, nickel; G, chromium; and H, vanadium.

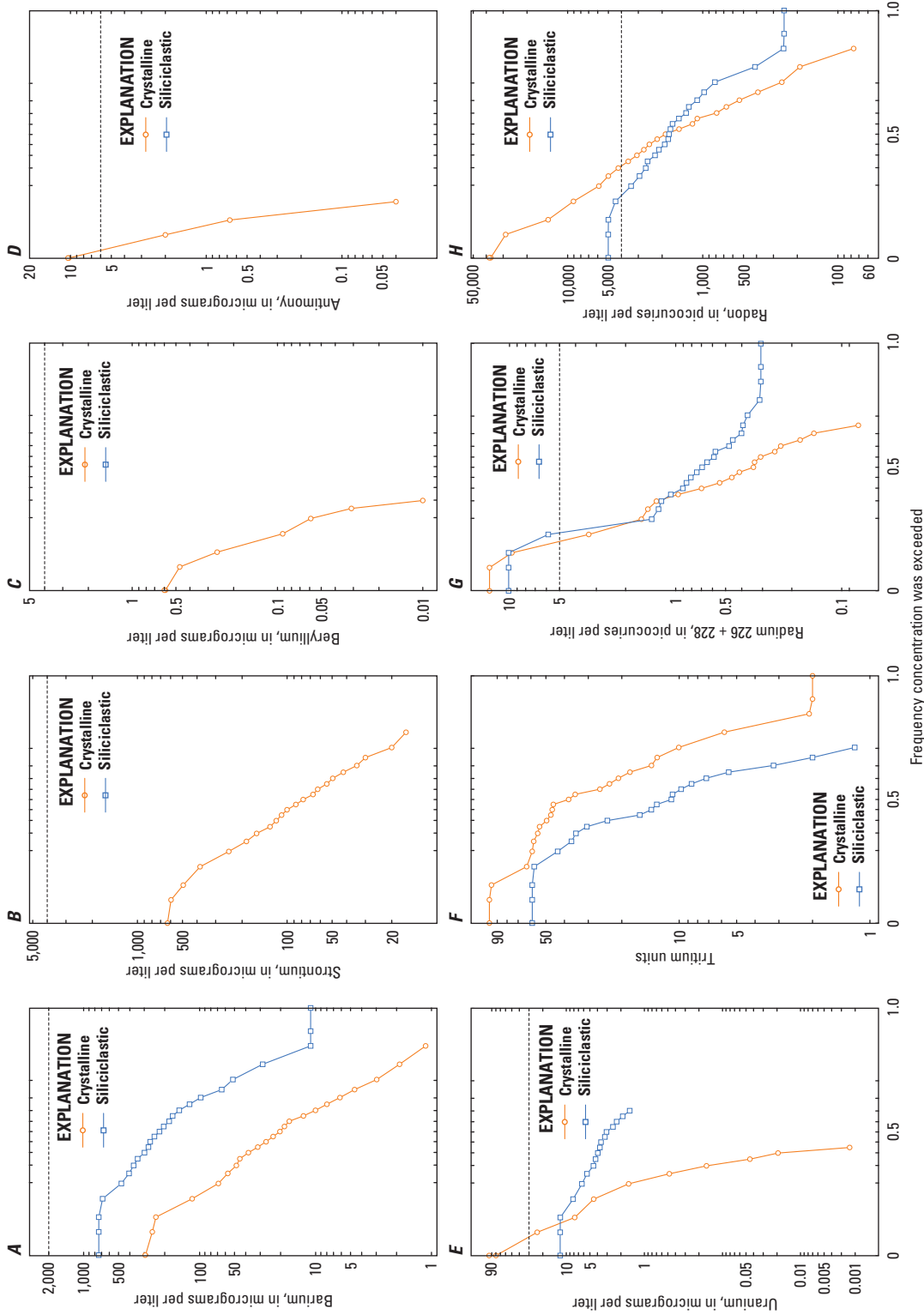


Figure 14. Probability plots of groundwater-quality data for siliciclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. A, barium; B, strontium; C, beryllium; D, antimony; E, uranium; F, tritium; G, radium; and H, radon.

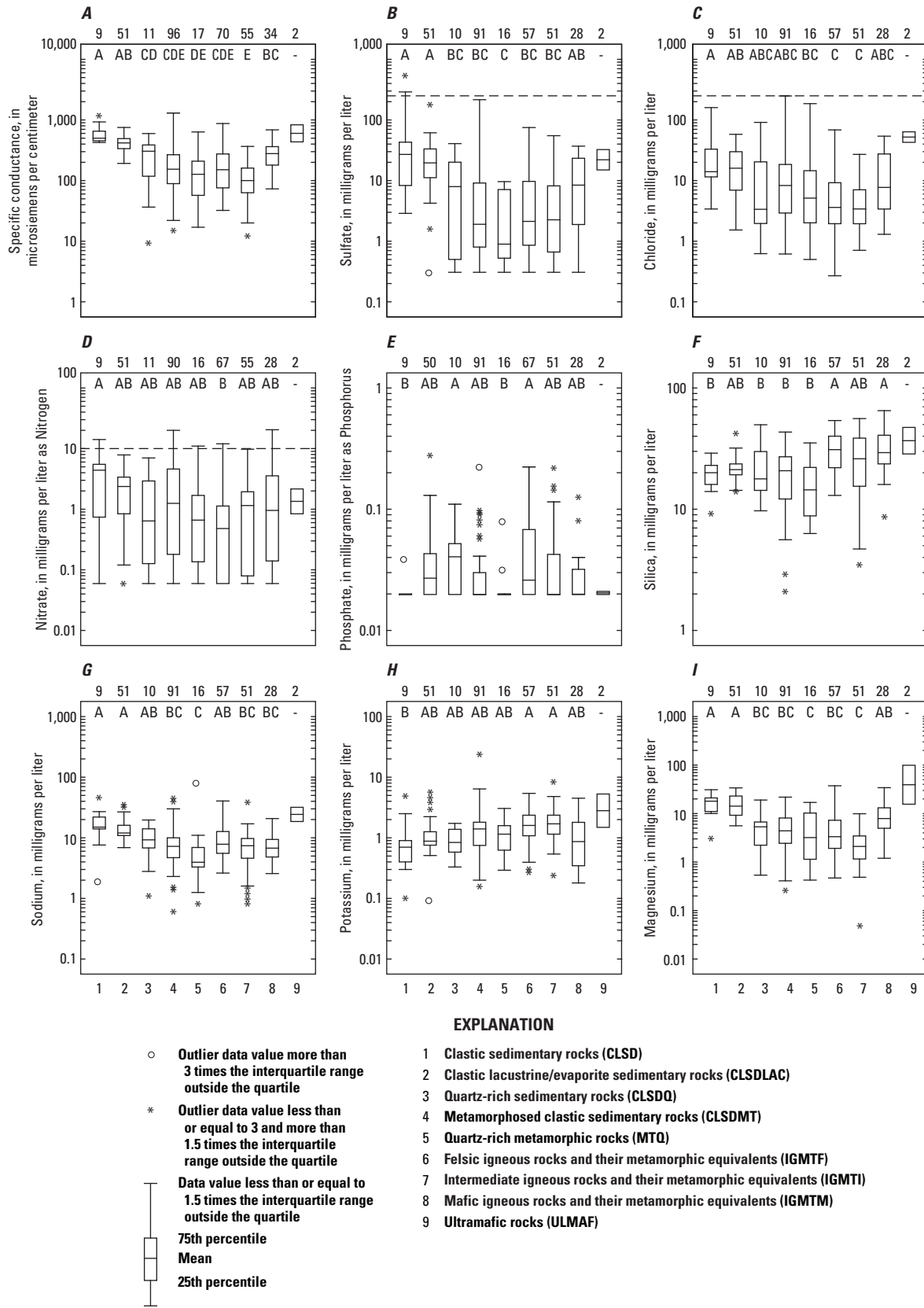


Figure 15. Groundwater-quality data by lithologic groups of siliclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. *A*, specific conductance; *B*, sulfate; *C*, chloride; *D*, nitrate; *E*, phosphate; *F*, silica; *G*, sodium; *H*, potassium; and *I*, magnesium.

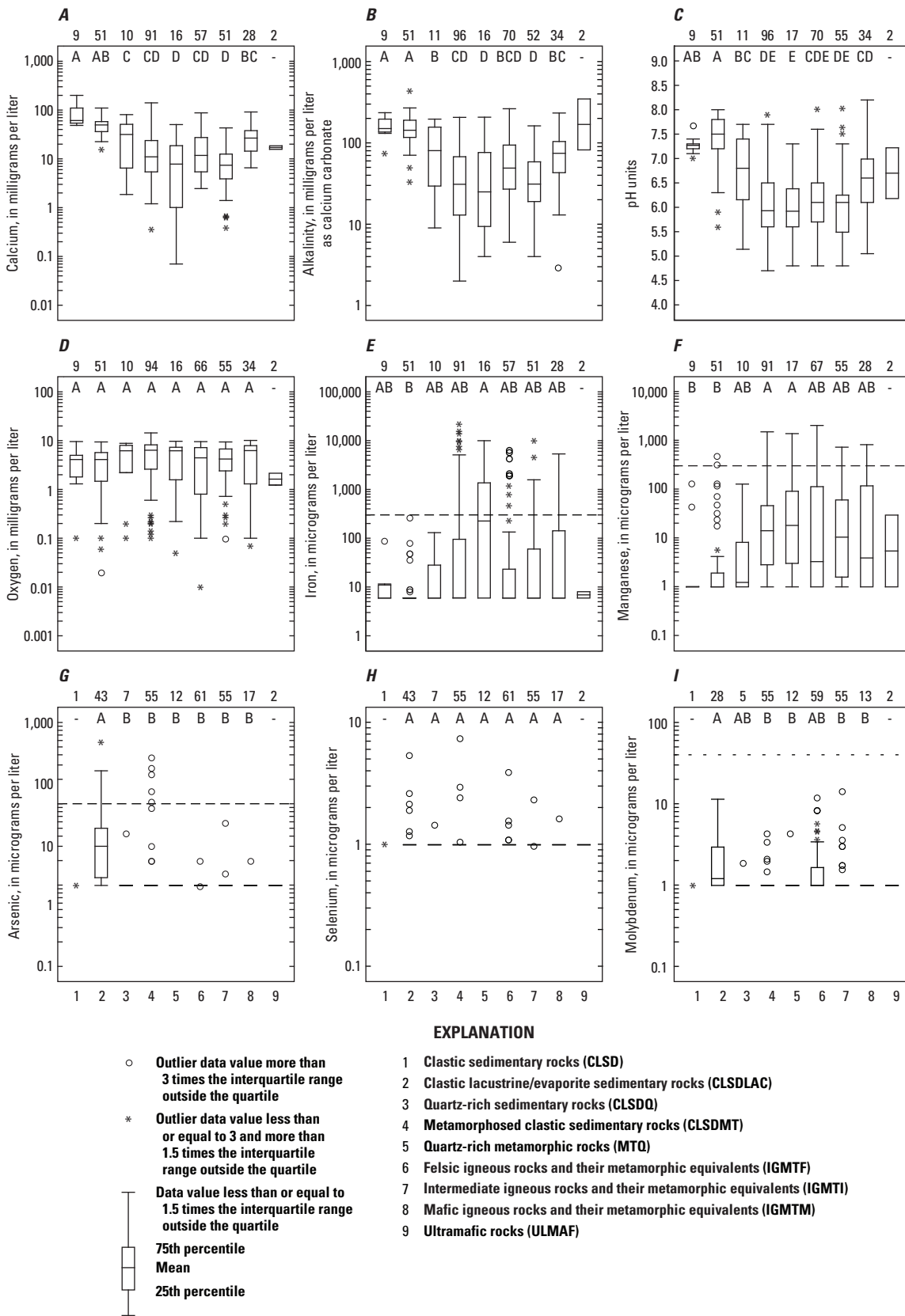


Figure 16. Groundwater-quality data by lithologic group of siliclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. *A*, calcium; *B*, alkalinity; *C*, pH; *D*, dissolved oxygen; *E*, iron; *F*, manganese; *G*, arsenic; *H*, selenium; and *I*, molybdenum.

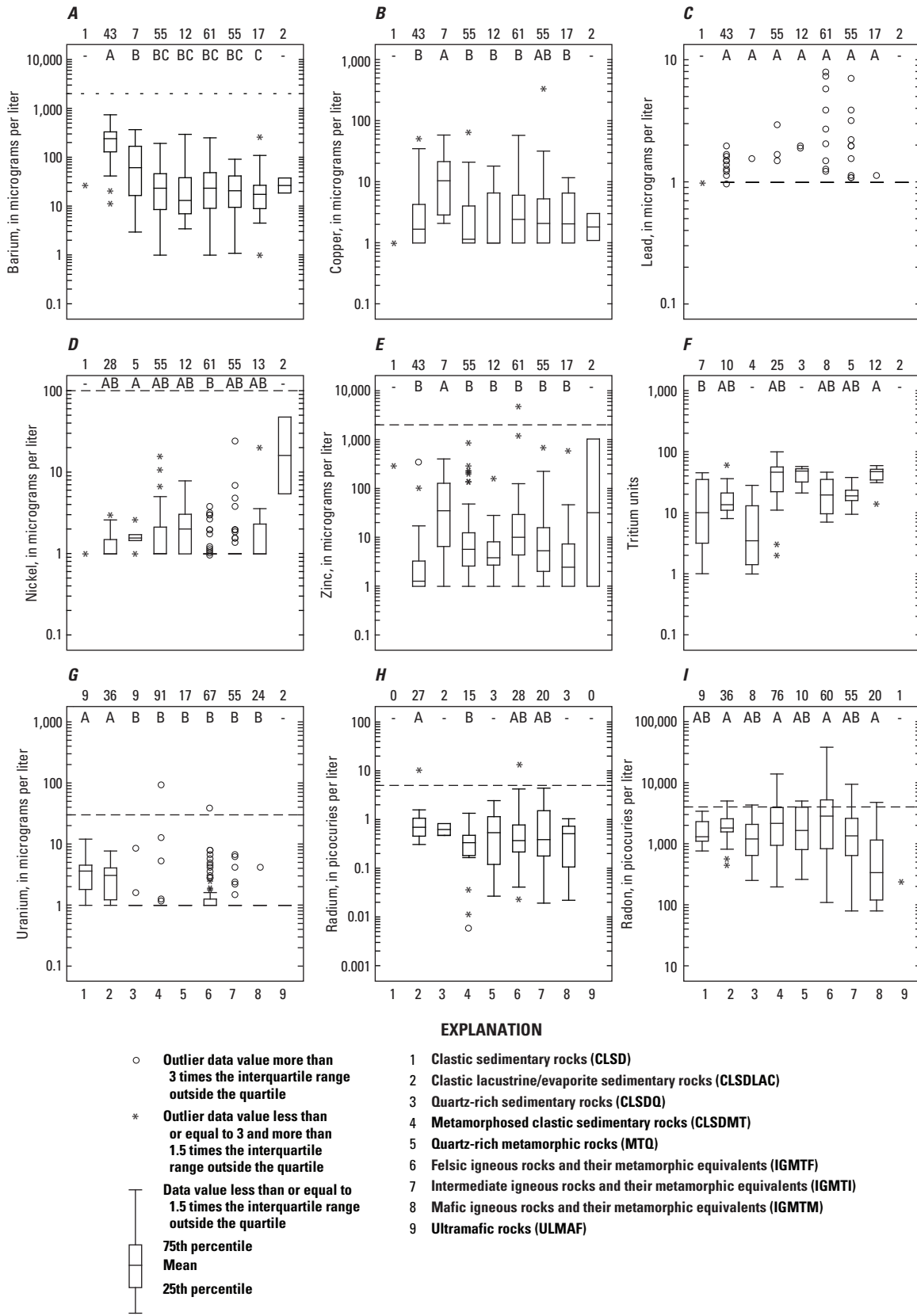


Figure 17. Groundwater-quality data by lithologic group of siliclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. A, barium; B, copper; C, lead; D, nickel; E, zinc; F, tritium; G, uranium; H, radium 226+228; and I, radon-222.

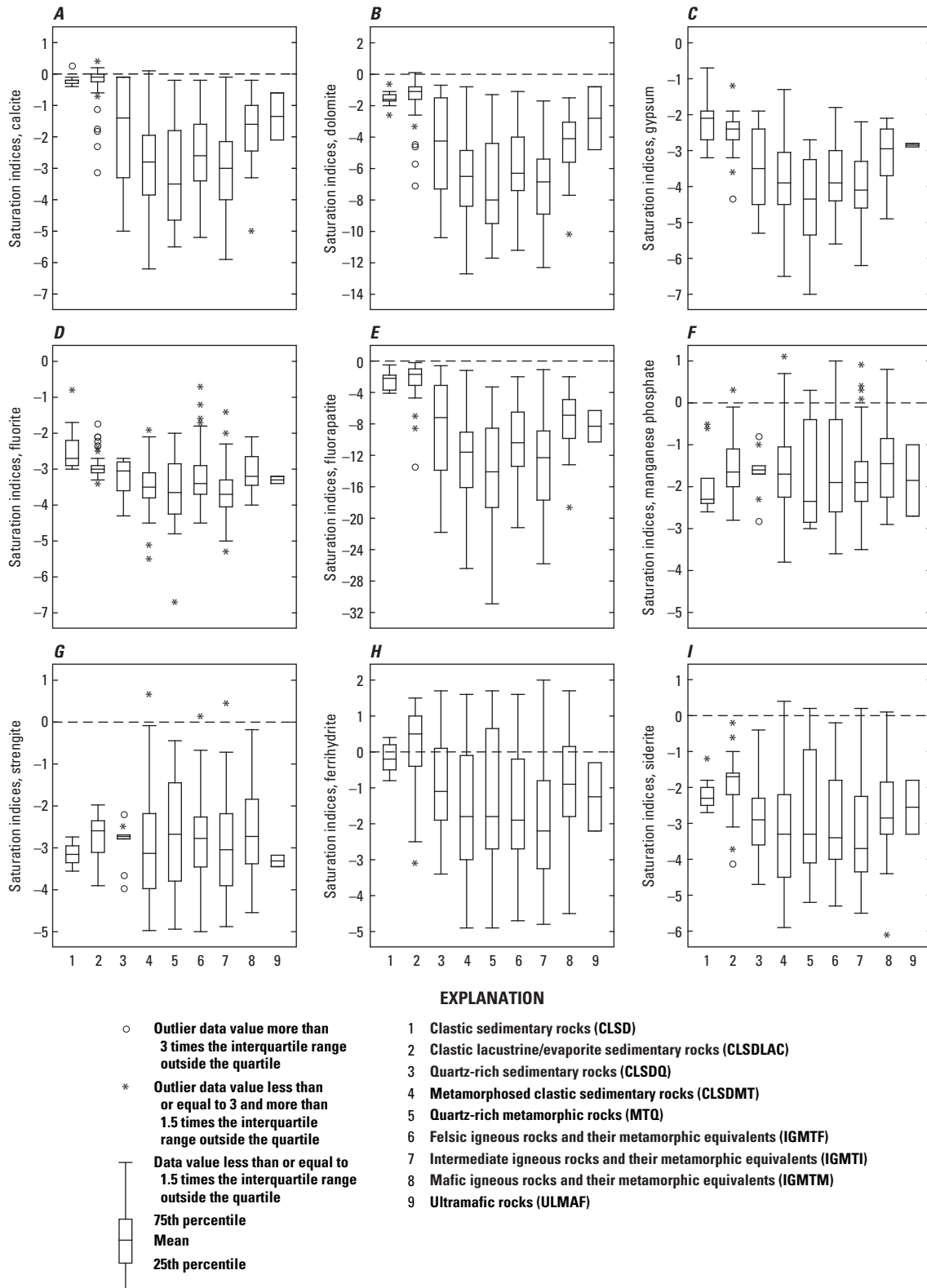


Figure 18. Saturation indices (SI) for selected minerals in groundwater by lithologic group of siliciclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces. *A*, calcite; *B*, dolomite; *C*, gypsum; *D*, fluorite; *E*, fluorapatite; *F*, manganese phosphate; *G*, strengite; *H*, ferrihydrite; and *I*, siderite.

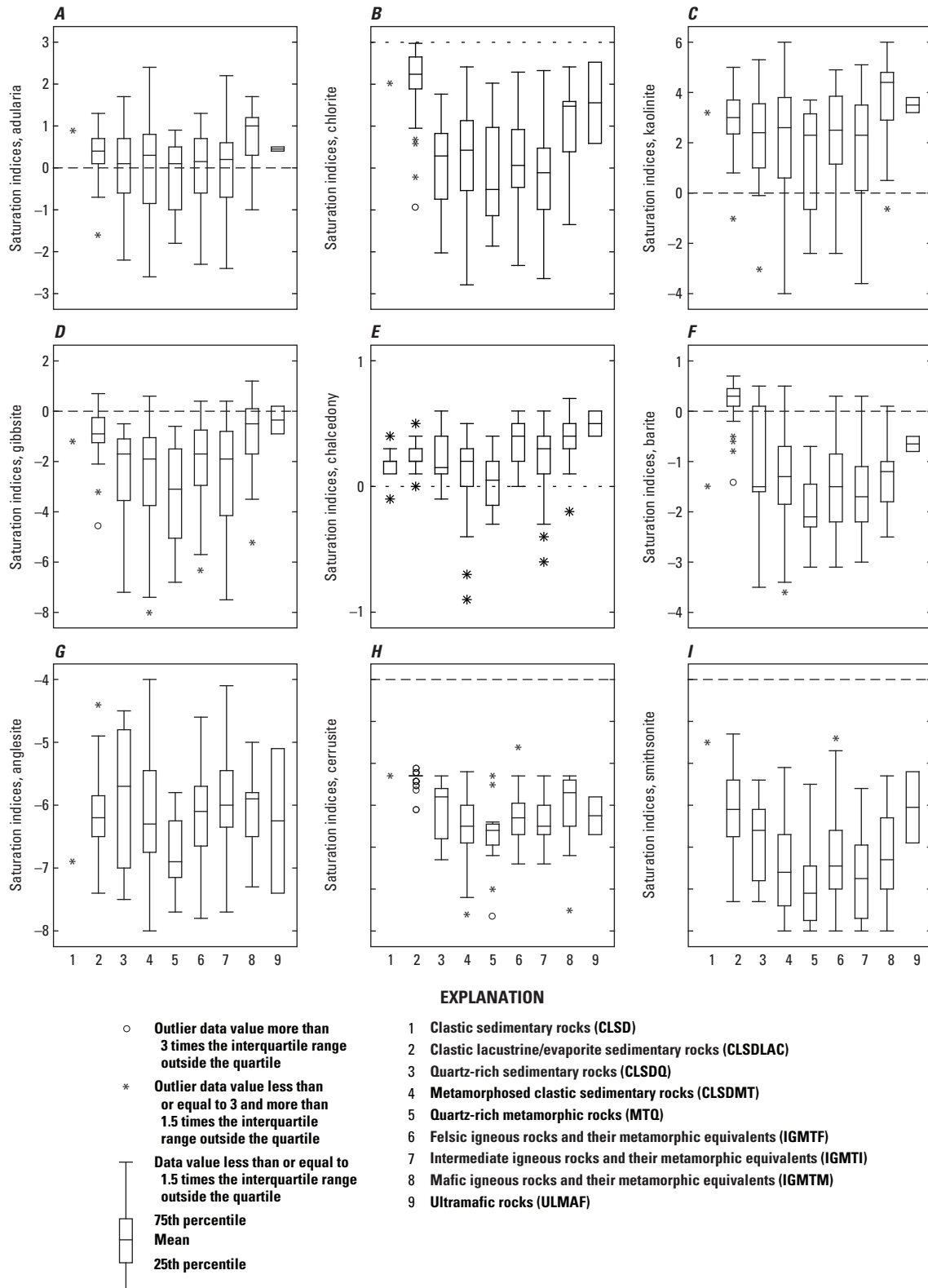


Figure 19. Saturation indices (SI) for selected minerals in groundwater by lithologic group of siliclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces. A, andularia; B, chlorite; C, kaolinite; D, gibbsite; E, chalcedony; F, barite; G, anglesite; H, cerrusite; and I, smithsonite.

A. All samples: 9 lithologic subgroups (n=337)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	2.7 (9)	8.6 (29)	3.3 (11)
Mixed	3.9 (13)	9.8 (33)	4.7 (16)	0.3 (1)
Oxic	9.2 (31)	33.2 (112)	15.1 (51)	9.2 (31)

B. CLSD: Clastic sedimentary (n=9)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	x	11.1 (1)	x
Mixed	x	x	x	x
Oxic	x	x	77.8 (7)	11.1 (1)

C. CLSDQ: Quartz-rich sedimentary (n=10)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	x	x	10.0 (1)
Mixed	10.0 (1)	10.0 (1)	10.0 (1)	x
Oxic	x	20.0 (2)	20.0 (2)	20.0 (2)

D. CLSDLAC: Clastic lacustrine (n=51)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	x	7.8 (4)	13.7 (7)
Mixed	x	x	2.01 (1)	x
Oxic	x	7.8 (4)	27.5 (14)	41.2 (21)

E. CLSDMT: Metamorphosed clastic sedimentary (n=94)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	5.3 (5)	4.3 (4)	x
Mixed	2.1 (2)	16.0 (15)	4.3 (4)	x
Oxic	14.9 (14)	35.1 (33)	13.8 (13)	4.3 (4)

F. MTO: Quartz-rich metamorphic (n=16)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	x	12.5 (2)	x
Mixed	18.8 (3)	18.8 (3)	x	x
Oxic	6.3 (1)	37.5 (6)	6.3 (1)	x

G. IGMTF: Felsic igneous or metamorphic (n=66)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	4.5 (3)	10.6 (7)	4.5 (3)
Mixed	3.0 (2)	13.6 (9)	6.1 (4)	x
Oxic	9.1 (6)	43.9 (29)	4.5 (3)	x

H. IGMTI: Intermediate igneous or metamorphic (n=55)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	1.8 (1)	7.3 (4)	x
Mixed	7.3 (4)	7.3 (4)	9.1 (5)	1.8 (1)
Oxic	18.2 (10)	43.6 (24)	x	3.6 (2)

I. IGMTM: Mafic igneous or metamorphic (n=34)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	x	17.6 (6)	x
Mixed	2.9 (1)	2.9 (1)	2.9 (1)	x
Oxic	x	38.2 (13)	29.4 (10)	2.9 (1)

J. ULMAF: Ultramafic (n=2)

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	x	x	x
Mixed	x	x	x	x
Oxic	x	50.0 (1)	50.0 (1)	x

EXPLANATION

- No data
- Less than 10 percent of samples in dataset or subset
- 10 to 20 percent of samples in dataset or subset
- 20 to 50 percent of samples in dataset or subset
- Greater than 50 percent of samples in dataset or subset

Figure 20. Redox/pH matrix summarizing groundwater-quality samples by lithologic group of siliciclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008. *A*, all nine lithologic groups; *B*, clastic sedimentary; *C*, clastic lacustrine/evaporite; *D*, quartz-rich sedimentary; *E*, metamorphosed clastic sedimentary; *F*, quartz-rich metamorphic; *G*, felsic igneous or metamorphic; *H*, intermediate igneous or metamorphic; *I*, mafic igneous or metamorphic; and *J*, ultramafic.

when ingested (Mays and others, 1985; U.S. Environmental Protection Agency, 1999). The risk is presumed to be linearly proportional to exposure (amount and duration; U.S. Environmental Protection Agency, 1999) and was used to determine conservative standards (MCLs) designed to limit exposure. Because the standards for radionuclides are slightly different and somewhat more complex than those for other trace elements, they are listed here in detail. The MCLs promulgated for radionuclides in 2000 are as follows: gross alpha-particle activity (including radium-226 but excluding uranium and

radon), 15 pCi/L; gross beta-particle activity, 4 millirems per year (isotope-specific dose to be evaluated when a sample exceeds 50 pCi/L); uranium, 30 µg/L; and for radium [the sum of radium-226 and radium-228 (generally termed combined radium, and conveniently abbreviated as “Ra TOT”) in selected tables and figures in this report, including table 4], 5 pCi/L (table 4). Gross alpha-particle activity had also been suggested for use as a compliance-monitoring “screen” for combined radium (Hess and others, 1985). In addition, radon has had a proposed (health-based) MCL of 300 pCi/L and a

A. Nitrate: HHB = 10 49.7% (159/320) > 0.1 HHB

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	22.2 (9)	10.3 (29)	0 (11)
Mixed	58.3 (12)	42.4 (33)	18.8 (16)	0 (1)
Oxic	66.7 (30)	60.0 (100)	61.2 (49)	66.7 (30)

B. Manganese: HHB = 300 32.1% (106/330) > 0.1 HHB

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	77.8 (9)	71.4 (28)	36.4 (11)
Mixed	100 (13)	93.9 (33)	100 (16)	100 (1)
Oxic	6.7 (30)	7.0 (100)	4.0 (50)	3.3 (30)

C. Sulfate: HHB = 250 14.9% (46/309) > 0.1 HHB

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	22.9	24.0 (25)	72.7 (11)
Mixed	15.4 (13)	6.3 (32)	13.3 (15)	0 (1)
Oxic	0 (28)	8.3 (96)	20.4 (49)	20.0 (30)

D. Iron: HHB = 300 26.5% (82/309) > 0.1 HHB

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	66.7 (9)	68.0 (25)	36.4 (11)
Mixed	53.8 (13)	78.1 (32)	80.0 (15)	100 (1)
Oxic	0 (28)	7.3 (96)	4.1 (49)	3.3 (30)

E. Phosphate: HCRL = 0.02 49.8% (159/319) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	44.9 (9)	42.9 (28)	27.3 (11)
Mixed	33.3 (12)	15.2 (33)	37.5 (16)	100 (1)
Oxic	30.0 (30)	63.0 (100)	67.3 (49)	63.3 (30)

F. Lead: HCRL = 1 14.2% (36/253) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	0 (9)	15.0 (20)	20.0 (10)
Mixed	10.0 (10)	0 (28)	7.1 (14)	0 (1)
Oxic	50.0 (22)	14.7 (75)	10.0 (30)	11.1 (27)

G. Arsenic: HCRL = 2 17.1% (42/246) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	11.1 (9)	25.0 (20)	80.0 (10)
Mixed	0 (10)	0 (28)	7.1 (14)	0 (1)
Oxic	0 (22)	1.3 (75)	20.0 (30)	74.1 (27)

H. Zinc: HCRL = 20 5.5% (14/253) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	44.4 (9)	35.0 (20)	0 (10)
Mixed	40.0 (10)	7.1 (28)	21.4 (14)	0 (1)
Oxic	27.3 (22)	24.0 (75)	23.3 (30)	3.7 (27)

I. Selenium: HCRL = 1 7.7% (19/246) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	11.1 (9)	10.0 (20)	10.0 (10)
Mixed	20.0 (10)	0 (28)	0 (14)	0 (1)
Oxic	0 (22)	5.3 (75)	16.7 (30)	14.8 (27)

J. Chromium: HCRL = 1 34.6% (84/243) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	33.9 (9)	15.0 (20)	20.0 (10)
Mixed	70.0 (10)	25.0 (28)	7.1 (14)	0 (1)
Oxic	54.5 (22)	55.4 (74)	17.2 (29)	11.5 (26)

K. Molybdenum: HCRL = 1 21.4% (48/224) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	11.1 (9)	26.3 (19)	100 (6)
Mixed	0 (10)	3.6 (28)	50.0 (14)	0 (1)
Oxic	0 (21)	10.8 (74)	36.0 (25)	64.7 (17)

L. Nickel: HCRL = 1 37.3% (84/225) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	66.7 (9)	26.3 (19)	50.0 (6)
Mixed	70.0 (10)	78.6 (28)	28.6 (14)	0 (1)
Oxic	40.9 (22)	29.7 (74)	24.0 (25)	0 (17)

M. Barium: HHB = 2,000 12.6% (31/246) > 0.1 HHB

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	0 (9)	15.0 (20)	10.0 (10)
Mixed	20.0 (10)	0 (28)	7.1 (14)	0 (1)
Oxic	0 (22)	5.3 (75)	26.7 (30)	44.4 (27)

N. Cobalt: HCRL = 1 11.1% (25/225) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	33.3 (9)	5.3 (19)	0 (6)
Mixed	30.0 (10)	46.4 (28)	14.3 (14)	0 (1)
Oxic	9.1 (22)	1.4 (74)	0 (25)	0 (17)

O. Uranium: HCRL = 1 21.3% (64/301) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	22.2 (9)	42.9 (28)	71.4 (7)
Mixed	7.7 (13)	3.3 (33)	25.0 (16)	0 (1)
Oxic	3.3 (30)	5.1 (99)	40.0 (45)	75.0 (20)

P. Copper: HCRL = 1 64.2% (158/246) > HCRL

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	55.6 (9)	25.0 (20)	10.0 (10)
Mixed	70.0 (10)	46.4 (28)	21.4 (14)	0 (1)
Oxic	95.5 (22)	85.3 (75)	70.0 (30)	66.7 (27)

Q. Radon 222: HHB = 4,000 18.4% (49/267) > HHB

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	14.3 (7)	7.4 (27)	0 (7)
Mixed	30.0 (10)	21.1 (19)	16.7 (12)	0 (1)
Oxic	25.0 (28)	28.0 (93)	4.5 (44)	10.5 (19)

R. Radium TOT: HHB = 5 23.4% (22/94) > 0.2 HHB

Redox / pH	4.5 to <5.5	5.5 to <6.5	6.5 to <7.5	7.5 to <8.5
Anoxic	x	66.7 (3)	42.9 (14)	66.7 (3)
Mixed	x	40.0 (5)	37.5 (8)	0 (1)
Oxic	0 (3)	15.4 (26)	12.5 (16)	6.7 (15)

EXPLANATION

- x No data
- All results below highest common reporting limit (HCRL) or human health benchmark (HHB)
- 10 percent of samples exceed HCRL or HHB
- 10 to 20 percent of samples exceed HCRL or HHB
- Greater than 20 to 50 percent of samples exceed HCRL or HHB
- Greater than 50 percent of samples exceed HCRL or HHB

Figure 21. Redox-pH matrix summarizing groundwater-quality samples greater than or equal to the highest common reporting level (HCRL) or human health benchmark (HHB). A, nNitrate; B, manganese; C, sulfate; D, iron; E, phosphate; F, lead; G, arsenic; H, zinc; I, selenium; J, chromium; K, molybdenum; L, nickel; M, barium; N, cobalt; O, uranium; P, copper; Q, radon-222; and R, radium-226+228 (TOT).

proposed AMCL of 4,000 pCi/L that may be used if airborne remediation or risk reduction approaches are implemented (U.S. Environmental Protection Agency, 1991); while proposed, the radon standards have yet to be adopted and fully implemented.

Five trace-element constituents (arsenic, antimony, iron, manganese, zinc) were detected in one or more water samples at concentrations greater than established human health-based benchmarks, and 10 additional constituents (barium, beryllium, cadmium, copper, lead, selenium, boron, molybdenum, nickel, and strontium) were detected at concentrations greater than a threshold of one-tenth the established health-based levels (table 4; figs. 12–17). Arsenic was detected at concentrations greater than the MCL of 10 $\mu\text{g/L}$ in 9 of 253 samples, and antimony was detected at concentrations greater than the MCL of 6 $\mu\text{g/L}$ in 1 of 232 samples. Manganese was detected at concentrations greater than the HBSL of 300 $\mu\text{g/L}$ in 24 of 330 samples, and zinc was detected at concentrations greater than the HBSL of 2,000 $\mu\text{g/L}$ in 1 of 253 samples. Iron was detected at concentrations greater than the SMCL of 300 $\mu\text{g/L}$ in 46 of 315 samples.

The trace elements most frequently detected at concentrations greater than one-tenth of the MCL or HBSL were arsenic (47 of 253 samples > 1 $\mu\text{g/L}$), manganese (106 of 330 samples > 30 $\mu\text{g/L}$), zinc (14 of 253 samples > 200 $\mu\text{g/L}$), barium (31 of 253 samples > 200 $\mu\text{g/L}$), molybdenum (16 of 230 samples > 4 $\mu\text{g/L}$), and lead (23 of 253 samples > 1.5 $\mu\text{g/L}$). Additionally, iron (84 of 315 samples > 30 $\mu\text{g/L}$) commonly was present at concentrations greater than one-tenth of the SMCL. Considering concentrations greater than one-tenth of the relevant threshold, the crystalline lithologies of the PBR had a larger percentage of samples (by a factor of two) containing iron, manganese, or fluoride, whereas the siliciclastic lithologies of the Early Mesozoic basins had a larger percentage of water samples containing arsenic, barium, selenium, boron, molybdenum, uranium, chloride, or sulfate (table 4).

Of the radionuclides analyzed, radon-222 frequently was detected at concentrations greater than the proposed MCL of 300 pCi/L (248 of 275 samples) or the proposed AMCL of 4,000 pCi/L (51 of 275 samples) (table 4). Although rarely present at concentrations exceeding their respective MCLs, uranium (43 of 310 samples > 3 $\mu\text{g/L}$) and radium [Ra-226 plus Ra-228, abbreviated as (RaTOT)] (47 of 98 samples > 1.0 pCi/L) frequently were detected at concentrations greater than one-tenth and one-fifth of their MCLs. Although the siliciclastic lithologies had a greater frequency of elevated uranium concentrations, radon and radium were commonly detected in groundwater from siliciclastic and crystalline lithologies. Only 2.0 percent of 98 samples had combined radium [Ra-226 plus Ra-228, abbreviated as (RaTOT)] concentrations greater than the MCL of 5.0 pCi/L, and these detections were evenly split among siliciclastic and crystalline lithologies; 0.6 percent of 310 samples had uranium concentrations greater than the MCL of 30 $\mu\text{g/L}$, all from crystalline lithologies. Only 6 percent of 50 samples had

radon-222 concentrations greater than the proposed AMCL of 4,000 pCi/L among the siliciclastic lithologies, but 21 percent of 225 samples had concentrations greater than the proposed AMCL from crystalline lithologies, most commonly from granites.

Considering nutrients and major ions that may be derived from natural and human-related sources, few samples had concentrations of nitrate (12 of 329 samples) greater than the MCL of 10 mg/L as nitrogen (N) or sulfate (2 of 315 samples) greater than the SMCL of 250 mg/L, and none had concentrations of chloride greater than the SMCL of 250 mg/L (table 4). Nevertheless, many samples had concentrations of nitrate (161 of 329 samples), sulfate (47 of 315 samples), or chloride (56 of 315 samples) greater than one-tenth of the respective MCL or SMCL thresholds. Few samples exceeded this lower threshold for fluoride (10 of 315 samples) or nitrite (2 of 331 samples) (table 4). Generally, mineral weathering can be an important source of sulfate; however, elevated concentrations of nitrate and nitrite may be attributed to anthropogenic contamination. Likewise, although mineral weathering can be a source of background concentrations of chloride and fluoride, anthropogenic sources also can produce anomalous concentrations of these constituents.

The concentration of dissolved nitrate in groundwater for the study ranged from less than 0.1 to 20.5 mg/L as N, with a median of 0.96 mg/L as N (fig. 11C). The siliciclastic and crystalline lithologies had median concentrations of nitrate of 2.37 and 0.78 mg/L as N, respectively. Natural levels of nitrate in groundwater from rainfall and plant and animal sources generally are less than 1 mg/L as N in the eastern United States (Peters and Bonelli, 1982; Puckett, 1994; Holloway and others, 1998). Concentrations of nitrate that are greater than background concentrations are most commonly associated with agricultural and turf (lawns, golf courses) fertilizers and also with discharges from septic systems or sewage treatment plants (Denver and others, 2010).

The concentration of chloride in groundwater for the study ranged from 0.27 to about 250 mg/L with a median of 7.0 mg/L (fig. 11B). Groundwater from the siliciclastic-rock aquifers and crystalline-rock aquifers had median concentrations of chloride of 15.9 and 5.9 mg/L, respectively, which are significantly greater than background levels in atmospheric precipitation (Peters and Bonelli, 1982). Concentrations of chloride that are greater than background concentrations may be associated with agricultural applications of “potash” or potassium chloride (KCl) and manure and discharges of sewage effluent, although highest concentrations are associated with the application of road deicing salts such as sodium chloride (NaCl) and calcium chloride (CaCl_2) in urban areas of the northern part of the region (Denver and others, 2010). Although chloride transport is conservative, nitrate and other forms of nitrogen may be attenuated by denitrification (dissimilatory reduction) or biological uptake (assimilation). Hence, the relative abundances of nitrate and chloride may be useful with other chemical indicators to identify geochemical

conditions within the aquifer where naturally occurring contaminants may or may not be attenuated or mobilized.

The saturation index for selected minerals was evaluated to indicate the general corrosivity of the groundwater and the potential for specific major and trace minerals to dissolve or precipitate, thus increasing or decreasing concentrations of solutes in the groundwater. Most groundwaters from all lithologies were undersaturated (SI less than 0) with respect to common sulfides (pyrite, FeS_2), sulfates (gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), carbonates [calcite, CaCO_3 ; dolomite $\text{CaMg}(\text{CO}_3)_2$], and aluminosilicates [andalusia, KAlSiO_3 ; albite, NaAlSiO_3 ; anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$; chlorite, $\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$] (figs. 18 and 19), indicating that weathering of major rock-forming minerals and trace minerals is a likely source of major and trace constituents in the groundwater. However, some groundwater samples, particularly those from the clastic sedimentary and clastic lacustrine/evaporite sedimentary lithologies of the Early Mesozoic basin aquifers, approached saturation or were saturated (SI approximately equal to 0) with respect to calcite and dolomite (figs. 18 and 19), indicating that their dissolution and precipitation could maintain or limit constituent concentrations. Likewise, most groundwater samples were supersaturated or saturated (SI greater than or equal to 0) with respect to kaolinite [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$], gibbsite [$\text{Al}(\text{OH})_3$], and ferrihydrite [amorphous $\text{Fe}(\text{OH})_3$], indicating that the precipitation of these secondary phases feasibly could limit concentrations of silica, aluminum, and iron. Although concentrations of manganese and barium frequently were at saturation levels with respect to certain solid phases (manganese phosphate, MnHPO_4 ; barite, BaSO_4), most other trace elements, including arsenic, selenium, uranium, lead, zinc, copper, cadmium, and strontium, were undersaturated with respect to pure mineral phases, suggesting that mineral precipitation would not be likely to limit concentrations of these contaminants. However, some trace elements, particularly divalent cations, may substitute for major ions such as calcium and magnesium in minerals that are supersaturated, and thus be reduced in concentration in the aqueous phase compared to the solubility of the pure trace mineral phase.

The overall relations among bedrock lithology and water quality in the study area are consistent with different water-quality characteristics for major rock types described by Drever (1997). Specifically, in crystalline-rock aquifers, slow weathering of silicate minerals tends to produce natural groundwater with low concentrations of dissolved solids, alkalinity, and hardness (figs. 10–17). Consequently, most major carbonate, sulfate, and hydroxide minerals are undersaturated in these settings (figs. 18 and 19). In contrast, groundwater in the siliciclastic-rock aquifers commonly has greater concentrations of dissolved solids, alkalinity, and hardness than groundwater in adjacent crystalline-rock aquifers. The siliciclastic lithologies of the Early Mesozoic basins typically are cemented by carbonate minerals and in some places are cemented by sulfate minerals (Van Houten, 1965), and these minerals tend to dissolve rapidly (Van Houten, 1965; Langmuir, 1971). Concentrations of trace elements may increase

with concentrations of dissolved solids because of the release of trace constituents dissolved from major minerals and because of the displacement of trace ions from surface sorption sites by major ions. In some instances, natural constituent concentrations may exceed thresholds established to protect human health.

Correlations Among Major and Trace Constituents and Environmental Factors

Principal component analysis (PCA) provides insight on hydrochemical processes affecting groundwater chemistry in the study area by indicating intercorrelations among chemical constituents and environmental variables, such as land use and well depth. Five principal components (PCs) explain nearly 76 percent of the variance in the regional groundwater dataset and consist of 18 routinely detected constituent loadings (table 5). Associations of additional chemical and physical variables excluded from the model are indicated by the Spearman-rank coefficient of correlation of these variables with the principal component scores (table 5; appendix 1, table 1-7).

PC1 has positive loadings by alkalinity, pH, calcium, magnesium, sodium, sulfate, and specific conductance and negative loading by dissolved oxygen (table 5). These loadings are related to increasing dissolved solids associated with the weathering of carbonate-bearing and sulfur-bearing minerals. Scores on PC1 generally were greater for siliciclastic lithologies than for crystalline lithologies and were positively correlated with agriculture, latitude, well depth, and water-quality constituents excluded from the PCA model, including hardness, total dissolved solids, strontium, uranium, boron, arsenic, molybdenum, fluoride, and barium; scores were negatively correlated with aluminum, chromium, tritium, and copper (table 5). Positive correlations with hardness and trace constituents, such as strontium and barium, are consistent with the weathering of alkaline-earth carbonate and sulfate minerals that are present as cements, fracture filling, and clasts in siliciclastic rocks. As explained previously (fig. 7) and in more detail below, several of the positively correlated trace constituents, specifically arsenic, molybdenum, and uranium, tend to be mobile as anions under high-pH conditions (Hodge and others, 1998), whereas negatively correlated trace constituents, specifically aluminum, chromium, and copper, tend to be mobile as cations under low-pH conditions. The positive associations of PC1 with well depth and negative associations with tritium and dissolved oxygen are consistent with increased mineralization and age of groundwater along flow paths. Likewise, positive correlations with latitude could relate to less extensively weathered bedrock in northern areas compared to more deeply weathered (leached) saprolitic and lateritic horizons in the southern parts of the study area.

PC2 has positive loadings by chloride, bromide, sodium, magnesium, nitrate, dissolved organic carbon, and specific conductance (table 5). Although the constituents could

Table 5. Principal components analysis model of major factors controlling the chemistry of groundwater from siliciclastic-rock and crystalline-rock aquifers of the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008.

[Varimax rotation factor pattern for rank-transformed data (SAS, 1988); minimum eigenvalue >1; >, greater than; loading and correlation coefficient values multiplied by 100 and rounded; *, indicates significant loadings ($p < 0.001$). PC, principal component]

	PC1	PC2	PC3	PC4	PC5	
	Alkalinity- pH	Chloride- nitrate	Redox	Temp- erature- silica	Radon- potassium	Communi- calities
Constituent loadings						
Alkalinity	91 *	18	-3	19	-18	0.93
pH	89 *	-12	-4	6	-16	0.85
Calcium	88 *	37	-5	1	-6	0.92
Specific conductance	81 *	55 *	1	-3	-5	0.96
Magnesium	69 *	53 *	-5	-11	-6	0.78
Sulfate	67 *	35	22	-17	3	0.66
Dissolved oxygen	-64 *	-2	-46 *	-32	2	0.74
Chloride	30	86 *	-2	-15	13	0.86
Bromide	26	71 *	6	29	-7	0.67
Nitrate	-21	63 *	-43 *	-34	19	0.78
Sodium	55 *	59 *	-4	32	9	0.76
Dissolved organic carbon	20	58 *	10	0	-36	0.51
Manganese (>1)	-1	11	90 *	-1	-2	0.79
Iron (>6)	1	-11	82 *	-1	-12	0.67
Temperature	-18	15	8	86 *	-11	0.81
Silica	26	-13		77 *	11	0.69
Radon-222	-18	0	-19	-9	81 *	0.72
Potassium	-1	1	46 *	25	48 *	0.54
Eigenvalue:	6.61	2.76	1.66	1.57	1.05	13.64
Cumulative percent variance explained:	36.67	51.68	61.28	70.04	75.85	
Spearman Correlations (only values significant at $p < 0.05$ are reported):						
Latitude	37	--	--	-63	--	
Agricultural land-use percentage	27	--	--	-43	--	
Urban land-use percentage	--	22	--	--	--	
Forested land-use percentage	--	-43	--	35	--	
Wetland land-use percentage	--	--	--	--	--	
Well depth	25	-23	--	--	--	
Hardness	85	46	--	--	--	
Total dissolved solids	81	53	--	--	--	
Strontium	58	46	--	--	--	
Uranium	57	--	--	--	--	
Boron (>8)	56	43	--	-72	--	

Table 5. Principal components analysis model of major factors controlling the chemistry of groundwater from siliciclastic-rock and crystalline-rock aquifers of the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008.—Continued

[Varimax rotation factor pattern for rank-transformed data (SAS, 1988); minimum eigenvalue >1; >, greater than; loading and correlation coefficient values multiplied by 100 and rounded; *, indicates significant loadings (p <0.001). PC, principal component]

	PC1	PC2	PC3	PC4	PC5	Communalities
	Alkalinity-pH	Chloride-nitrate	Redox	Temperature-silica	Radon-potassium	
Spearman Correlations (only values significant at p <0.05 are reported):—Continued						
Arsenic (>1)	50	26	--	--	--	
Molybdenum	47	--	--	--	--	
Fluoride	38	--	--	--	--	
Barium	28	53	--	-27	--	
Chromium	-35	--	--	--	--	
Copper	-47	--	-28	--	--	
Tritium	-58	--	--	-45	--	
Aluminum (>1.6)	-62	--	--	--	--	
Nickel	--	45	33	--	--	
Radium-226	--	--	54	--	--	
Radium-226 plus radium-228	--	--	41	--	--	
Cobalt	--	--	26	--	--	
Ammonia	--	--	26	--	--	
Phosphate	--	--	-37	39	--	
Vanadium	--	--	-76	--	--	
Lithium	--	--	--	--	47	
Silver	--	--	--	--	--	
Beryllium	--	--	--	--	--	
Cadmium	--	--	--	--	--	
Lead	--	--	--	--	--	
Radium-228	--	--	--	--	--	
Antimony	--	--	--	--	--	
Selenium	--	--	--	--	--	
Thalium	--	--	--	--	--	
Zinc (>1)	--	--	--	--	--	

originate from natural sources, their corresponding positive associations are interpreted to indicate anthropogenic sources of contamination, such as road-deicing salt, fertilizer, and sewage. Scores on PC2 were negatively correlated with well depth and forest area and positively correlated with urban area, hardness, total dissolved solids (TDS), barium, strontium, nickel, boron, and arsenic. Although PC2 scores ranged more widely for crystalline lithologies compared to siliciclastic lithologies, the median score for siliciclastic lithologies was larger

than that for crystalline lithologies. The land use overlying the siliciclastic lithologies tends more frequently to be urban and less frequently to be forested than that for the more steep terrains associated with the crystalline-rock lithologies (figs. 2 and 4).

PC3 has positive loadings by manganese, iron, and potassium and negative loadings by dissolved oxygen and nitrate (table 5). High scores on PC3 are interpreted to indicate isolation from the atmosphere and the development of reducing

conditions. Scores on PC3 generally were larger for crystalline lithologies than siliciclastic lithologies and were not correlated with land use. Scores on PC3 were positively correlated with radium-226, combined radium (Ra-226+Ra-228), cobalt, nickel, and ammonia and negatively correlated with vanadium, phosphate, and copper. Nitrate is stable under oxidizing conditions where iron and manganese concentrations may be limited by precipitation of iron and manganese oxides; ammonia is stable under reducing conditions. The positive associations of potassium and radium on PC3 and potassium and radon on PC5 (described below) are consistent with felsic, granitic, or arkosic rocks as a source of radioactive elements in groundwater. As explained previously (figs. 8 and 9) and in more detail below, radon is a highly mobile noble gas, whereas radium, cobalt, and other cations can be adsorbed by iron and manganese oxides. Subsequent dissolution of the iron and manganese oxides under reducing conditions will mobilize the sorbed constituents, such as radium and cobalt. The negative correlations of vanadium, phosphate, and copper with PC3 could indicate greater mobility of these constituents under oxidizing conditions, where the concentrations of iron and manganese are low.

PC4 has positive loadings by temperature and silica (table 5). Scores on PC4 were positively correlated with forest and phosphate and negatively correlated with latitude, agriculture, boron, tritium, and barium. Denver and others (2010) explained that co-occurrence of phosphate and silica in groundwater from forested areas could result from the weathering of common silicate minerals containing phosphorus as a trace constituent. Generally, the mean annual temperature of groundwater decreases with latitude, and tritium concentration decreases with groundwater age. Thus, these associations on PC4 may indicate that increased temperature or longer residence time in the aquifer promotes greater rates and extent of weathering of silicate minerals. The range of and median PC4 scores for crystalline lithologies, which predominate in southern latitudes, were larger than those for siliciclastic lithologies (appendix 2).

PC5 has positive loadings by radon and potassium and positive correlations with lithium (table 5). Although the range of PC5 scores for crystalline lithologies is greater than that for siliciclastic lithologies, the median scores for the two lithologies are comparable. As explained in more detail below, these associations and distributions are consistent with the emanation of radon from felsic, granitic, or arkosic rocks that tend to be rich in uranium, potassium, and lithium (Speer and others, 1981; Michel, 1984). Radon, potassium, and lithium tend to be mobile in a wide range of groundwater environments compared to other constituents that tend to be affected by variations in pH and (or) redox conditions.

Geochemical Conditions Associated with Elevated Concentrations of Naturally Occurring Constituents

The associations of certain trace elements and radionuclides in groundwater may be explained by similar rock sources and (or) geochemical processes. These constituents are discussed separately below, however, because of differences in monitoring frequency, reporting protocols, and human-health thresholds.

Trace Elements

Arsenic, manganese, and zinc were identified as trace elements of concern in groundwater of the study area on the basis of their relatively high frequencies of exceedance of human health benchmarks for drinking water (table 4). Additionally, lead, barium, antimony, and molybdenum were noteworthy because of relatively high frequencies of detection of these constituents at concentrations greater than one-tenth of their respective health-based thresholds. Specific settings and geochemical conditions associated with anomalous concentrations of these constituents are described in more detail below.

Arsenic

Although arsenic concentrations were less than 1 $\mu\text{g/L}$ in nearly 80 percent of the 253 groundwater samples analyzed in the study, 8.5 percent of sampled wells in the Early Mesozoic basin aquifers and 2.4 percent of the sampled wells in the Piedmont and Blue Ridge aquifers had arsenic concentrations greater than the USEPA MCL of 10 $\mu\text{g/L}$ (table 4). Arsenic concentrations greater than 1 $\mu\text{g/L}$ were detected in samples from wells from all lithologies in these aquifers, but all concentrations greater than the MCL were present in groundwater from clastic lacustrine sedimentary rocks of the Early Mesozoic basin aquifers and from metamorphosed clastic sedimentary rocks of the PBR aquifers (fig. 16G). Maximum arsenic concentrations in water samples from these aquifers were 57 and 38 $\mu\text{g/L}$, respectively (tables 1-3 and 1-4). Both lithologic groups are composed of fine-grained sedimentary rocks, such as mudstone, shale, siltstone, and their metamorphic equivalents.

Although redox conditions typically control the mobility of arsenic in groundwater (Smedley and Kinniburgh, 2002; Welch and Stollenwerk, 2003; Serfes and others, 2010), the dominant factor controlling arsenic mobility in the study area appears to be pH, with elevated arsenic concentrations associated with alkaline pH conditions (fig. 21G). Arsenate and arsenite, which are the predominant forms of arsenic in groundwater, tend to adsorb to iron-oxide surfaces at acidic to neutral pH, but not at alkaline pH conditions (fig. 8). Thus, arsenic concentrations greater than 1 $\mu\text{g/L}$ were associated with a range of oxic to anoxic redox conditions, primarily where pH values were greater than 7.5 (fig. 21G). Of the nine samples for which arsenic concentrations were greater than

10 µg/L, six were classified as oxic and three as anoxic, and seven had a pH of 7.2 or greater (maximum pH, 8.0). The clastic lacustrine/evaporite sedimentary and metamorphosed clastic sedimentary lithologic groups and associated lithochemical subgroups that had the highest mean ranks of arsenic on the basis of Tukey tests also had the highest mean ranks of pH [fig. 16C and G; table 6 (table 6 available online at <http://pubs.usgs.gov/sir/2013/5072/>)]. One other factor that supports the concept that the arsenic mobility is controlled by sorption processes is the consistent correlation of arsenic concentrations with other oxyanions, including boron, uranium, antimony, and molybdenum (appendix 1, table 1-7). The mobility of these oxyanions also is primarily controlled by adsorption at acidic to neutral pH and desorption at alkaline pH conditions (figs. 8 and 21).

The spatial distribution pattern for elevated arsenic concentrations indicates locations with elevated levels of arsenic in the rock and geochemical conditions favoring transport of arsenic. Although 72 percent of the 47 samples from the Early Mesozoic basin aquifers had arsenic concentrations greater than 1 µg/L, only 6.3 percent of the 206 samples from the PBR crystalline-rock aquifers had arsenic concentrations greater than 1 µg/L (table 4). However, 46 percent of the samples from two crystalline-rock lithologies, metasedimentary rocks and meta-argillite, had concentrations greater than 10 µg/L. The results for the samples from the Early Mesozoic basin aquifers with respect to arsenic obtained in this study are consistent with results of previous studies for these aquifers (Serfes, 1994, 2004; Lindsey and others, 2006; Senior and Sloto, 2006; Harden and others, 2009; Serfes and others, 2010). Although the overall exposure of the population in the study area to arsenic is low, arsenic concentrations are likely to be elevated in some areas that are densely populated in Pennsylvania and New Jersey (figs. 2 and 22). Even in these areas of possible elevated arsenic concentrations in groundwater, the frequency for exceeding the MCL was less than 15 percent.

Manganese

Manganese concentrations were greater than or equal to 4 µg/L in 75 percent of the 330 groundwater samples analyzed in the study; 7.3 percent and 32.1 percent of the samples had concentrations greater than the HBSL of 300 µg/L and one-tenth of the HBSL, respectively (table 4). Manganese concentrations generally were elevated in groundwater from the PBR crystalline-rock aquifers (figs. 12D and 16F) where the bedrock and overlying geologic materials contain manganese-bearing minerals and geochemical conditions in the aquifer facilitate manganese transport. Only the clastic sedimentary rocks and quartz-rich sedimentary rocks of the Early Mesozoic basin aquifers had concentrations of manganese less than 300 µg/L in all samples (fig. 16F). On the basis of Tukey tests, the mean rank manganese concentrations for the metamorphosed clastic sedimentary and quartz-rich metamorphic lithologic groups of the PBR crystalline-rock aquifers were greater than those for the clastic sedimentary and clastic lacustrine/evaporite sedimentary lithologic groups of the

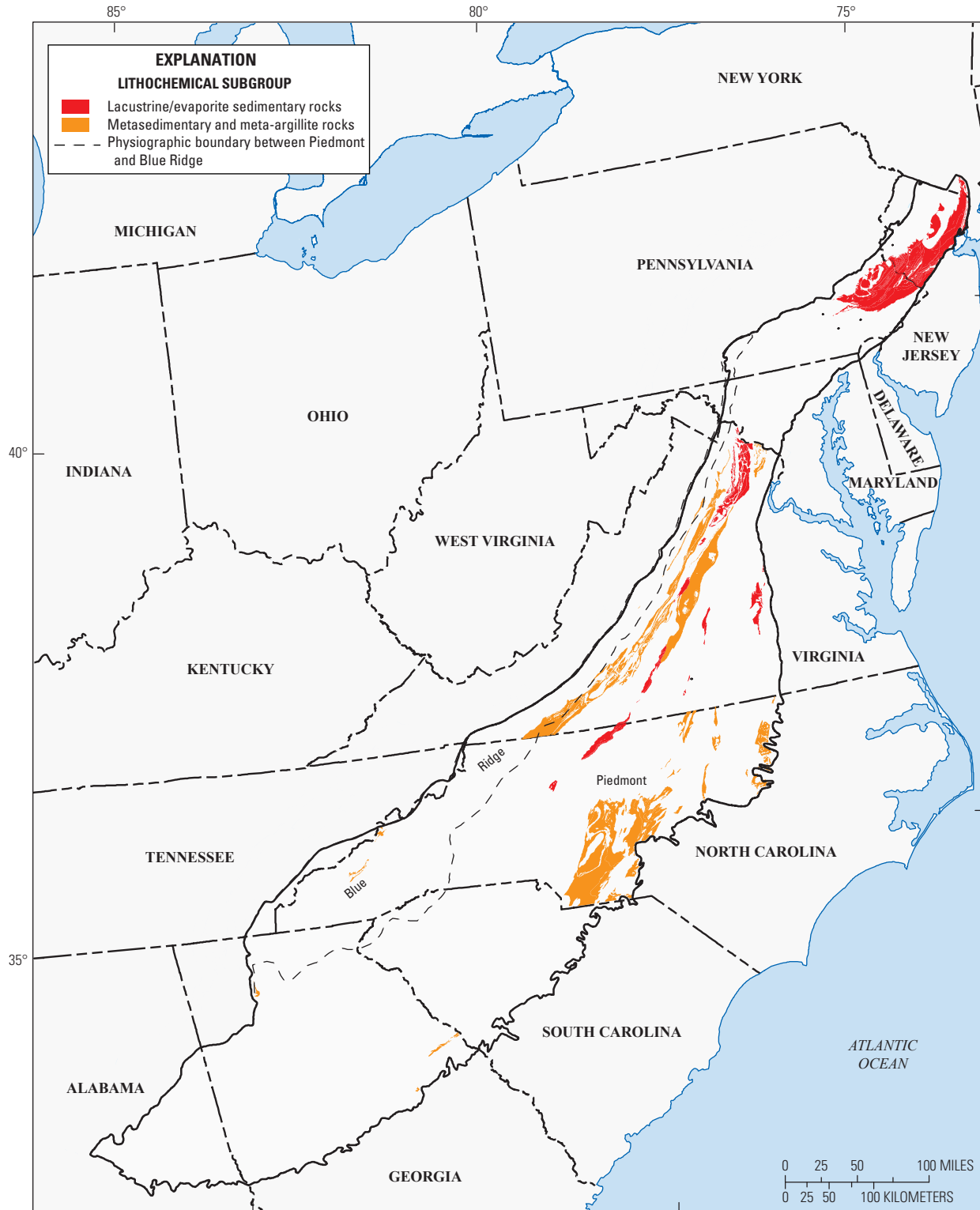
Early Mesozoic basin aquifers (fig. 16F). The lithochemical subgroup 43 of the mafic igneous and metamorphic lithologic group had the greatest median concentration of manganese (54 µg/L) of all lithochemical subgroups (table 6). Lithochemical subgroup 43 consists of massive mafic rocks including diorite, gabbro, monzodiorite, diabase, and basalt (table 3 and appendix 1, table 1-1).

The concentration of manganese in groundwater was positively correlated with iron, cobalt, nickel, aluminum (censored at 10 µg/L), and ammonia and negatively correlated with dissolved oxygen, nitrate, phosphate, and vanadium (appendix 1, table 1-7). The relations between dissolved oxygen, manganese, iron, nitrate, and ammonia are consistent with elevated mobility of the reduced forms of manganese (Mn^{+2}) and iron (Fe^{+2}) under reducing conditions (fig. 21B). The positive correlations between manganese, iron, nickel, and cobalt could be attributed to the reductive dissolution of Mn(III-IV) and Fe(III) oxides and the consequent release of sorbed cations (Loganathan and Burau, 1973; Kooner, 1993), whereas the negative correlations between manganese, phosphate, and vanadium could be attributed to the precipitation of Mn(II)-phosphate and associated vanadate compounds under reducing conditions as indicated by the saturation indices for $MnHPO_4$ and $Mn_3(PO_4)_2$ (appendix 1, table 1-7). Hence, the frequencies of elevated concentrations of manganese, iron, cobalt, and nickel generally are the opposite of those of nitrate, phosphate, and vanadium as functions of pH and redox conditions (fig. 21B).

Although reductive dissolution of Mn(III-IV) oxides could be a primary source of dissolved manganese and associated trace elements in many groundwater samples, it is noteworthy that the highest concentrations of dissolved manganese are associated with low to intermediate values of pH and high concentrations of aluminum (fig. 21 and appendix 1, table 1-7). Low pH can promote the dissolution of various potential sources of manganese, including manganese oxides, common aluminosilicate minerals, such as chlorite, and carbonate minerals, such as calcite and siderite. The carbonate and aluminosilicate minerals, in which Mn^{+2} and Fe^{+2} commonly substitute for magnesium (Mg^{+2}), would tend to be stable under reducing conditions, but not under acidic conditions. Because of incongruent dissolution, the weathering of chlorite and other aluminosilicates may preferentially leach magnesium, iron, manganese, and, to a lesser extent, aluminum, relative to silica (Drever, 1997).

Zinc

Zinc concentrations were greater than or equal to 20 µg/L in 21 percent of the 253 groundwater samples analyzed in the study; 0.4 percent and 5.5 percent of the samples had concentrations greater than the HBSL of 2,000 µg/L and one-tenth of the HBSL, respectively (table 4). Although the highest zinc concentrations were recorded for groundwater samples from the PBR crystalline-rock aquifers (figs. 13B and 17E), the quartz-rich sedimentary lithologic group of the Early Mesozoic basin siliciclastic-rock aquifers had a higher mean rank



Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 Lithologic group data from Dicken and others, 2005a and
 2005b and Nicholson and others, 2005 and 2006

Figure 22. Areal occurrence of lithochemical subgroups having elevated arsenic concentrations (based on the Tukey mean rank test, table 6) in groundwater within the Piedmont and Blue Ridge Physiographic Provinces.

zinc concentration than all other lithologic groups (fig. 17E). In some parts of the study area, this lithologic unit is a local host of zinc ore minerals (Smith, 1977) and, regionally, may have elevated background concentrations of zinc.

Various natural and anthropogenic materials can be important sources of dissolved zinc in groundwater. Zinc may be present as a trace mineral, such as sphalerite (ZnS) or smithsonite (ZnCO₃), or as a trace substitution for calcium, magnesium, or other divalent cations in common carbonate and silicate minerals in aquifers of the study area (Smith, 1977; Hanshaw and Back, 1979). Furthermore, dissolved zinc concentrations and transport can be affected by sorption reactions with carbonate minerals and iron and aluminum oxides (Zachara and others, 1991; Kooner, 1993; Coston and others, 1995). As described previously, dissolved cations, such as Zn²⁺, tend to be poorly adsorbed and are relatively mobile at acidic pH, whereas at alkaline pH, the cation concentrations tend to be attenuated by adsorption on HFO and other oxide surfaces (fig. 8). Additionally, zinc can be derived from the corrosion of galvanized casing and pipes used for well construction and water distribution.

The concentration of zinc in groundwater was positively correlated with concentrations of copper, lead, and aluminum and with percentage of forested land use and negatively correlated with pH, concentrations of calcium, magnesium, alkalinity (as calcium carbonate), sulfate, arsenic, and total dissolved solids, percentage of urban land use, and saturation index of calcite and many other minerals (appendix 1, table 1-7). These correlations are consistent with elevated mobility of zinc under acidic, corrosive conditions associated with low pH and low ionic strength. Samples with oxic to anoxic redox conditions and pH less than 7.5 had a higher frequency of elevated zinc concentrations (greater than 10 mg/L) than samples with alkaline pH (fig. 21H). Likewise, concentrations of chromium, copper, lead, cobalt, and nickel were more frequently detected in groundwater samples with low to moderate pH than in groundwater samples with alkaline pH conditions (fig. 21). Low-pH conditions may mobilize zinc and other metals from natural mineral sources or plumbing and inhibit its adsorption by Fe(III), Mn(III-IV), and aluminum-oxides in the aquifer.

Zinc, iron, copper, lead, chromium, nickel, and other metals are commonly used materials for the construction of wells and associated plumbing systems. Different casing types may be used for different hydrogeological conditions. For example, steel and galvanized casing typically are used for small bore, deep wells in fractured bedrock, whereas concrete and plastic casing typically are used for larger bore, shallow wells in regolith or unconsolidated materials or where the water may be corrosive.

To evaluate the ability of plumbing materials to contribute dissolved metals to groundwater samples, boxplots were generated on the basis of the well-casing type (steel, galvanized, concrete, plastic, other) identified with each groundwater sample, and Tukey tests were conducted to evaluate differences among the mean rank concentration values for these sample groups (fig. 23). Although concentrations of

iron and dissolved oxygen were similar for the five different casing types, indicating comparable redox conditions among the groups, the maximum and mean rank zinc concentrations were greatest for samples from wells constructed using galvanized casing, and the mean rank copper concentration was greater for samples from wells constructed using concrete casing (fig. 23). Increased concentrations of zinc may be related to higher pH in deeper bedrock wells with steel or galvanized steel casing, whereas the more acidic pH in shallow wells (generally regolith material) may increase copper concentrations (table 5). Furthermore, the pH was higher for the samples associated with galvanized casing than for the samples associated with concrete casing. These water-quality differences suggest that the aquifer characteristics affect the type of well construction and (or) that the casing type affects the water chemistry.

To evaluate the apparent effect of galvanized casing on zinc concentrations, the 24 samples identified with galvanized casing were eliminated from the dataset before recreating the boxplots and the Tukey tests for the nine major lithologic groups. Although fewer samples were associated with each of the lithologic groups, the boxplots and Tukey test results did not differ from the original results. Despite eliminating samples associated with galvanized well casing, the quartz-rich sedimentary lithologic group of the Early Mesozoic basin siliciclastic-rock aquifers had a higher mean rank zinc concentration than all other lithologic groups (fig. 17E). The concentration of zinc in groundwater from the ultramafic lithologic group also was elevated, but this group only had a sample size of two, so the data could not be rigorously evaluated.

Alkalinity, Hardness, and Dissolved Solids

Calcite clasts, fracture filling, and cements in some sedimentary-rock aquifers can dissolve easily and lead to high levels of alkalinity, hardness, and TDS. High alkalinity in such aquifers helps to maintain stable, near neutral pH (6 to 8). Thus, corrosivity, pH, hardness, and TDS generally are related by the calcite saturation index, which is equal to the Langelier index of corrosivity (Drever, 1997). In general, the samples from the clastic sedimentary and clastic lacustrine/evaporite sedimentary lithologic units had the highest overall saturation indices for calcite, dolomite, and other carbonate minerals (fig. 18).

Only a few wells sampled from the Early Mesozoic basin siliciclastic-rock aquifers had groundwater that was classified as hard (calcium carbonate equivalent 150 to 300 mg/L) or very hard (calcium carbonate equivalent greater than 300 mg/L) (fig. 10D). Samples of water from the PBR crystalline-rock aquifers frequently were characterized as soft and had pH values less than the recommended pH of 6.5 (fig. 12A). Moderate hardness with neutral pH is considered desirable because soft water with low pH can corrode plumbing and facilitate the dissolution of various aquifer minerals, whereas hard water with high pH can lead to scaling and clogged plumbing (encrustation) (Hem, 1985).

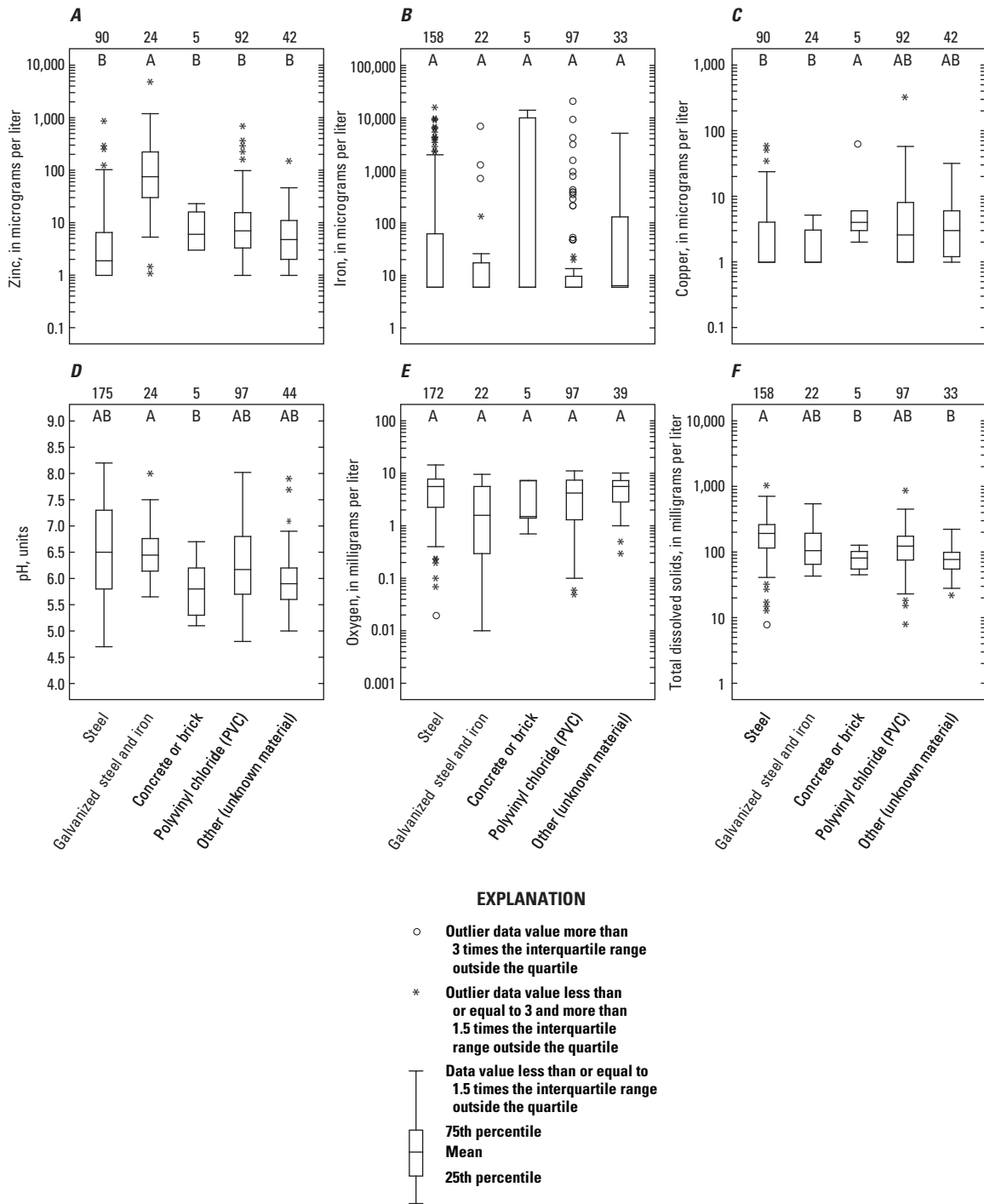


Figure 23. Concentrations of selected metals and associated constituents in groundwater by casing type for wells in siliciclastic- and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces.

Antimony, Lead, Barium, and Molybdenum

Antimony was detected in only 11 of 202 samples from crystalline-rock aquifers; none of the 30 samples from siliciclastic-rock aquifers had detectable concentrations of antimony (table 4, fig. 14D). One sample from the metamorphosed clastic sedimentary lithologic group of the crystalline-rock aquifers had a concentration of antimony of 10.4 $\mu\text{g/L}$, which exceeded the MCL of 6 $\mu\text{g/L}$; four samples had concentrations greater than one-tenth of the MCL (table 4).

None of the samples evaluated for this study had concentrations of lead, barium, or molybdenum greater than their respective MCLs (table 4). However, 23 of 253 samples analyzed for lead had concentrations greater than one-tenth of the 15- $\mu\text{g/L}$ MCL (9.0 percent of samples had concentrations greater than 1.5 $\mu\text{g/L}$); 31 of 253 samples analyzed for barium had concentrations greater than one-tenth of the 2,000- $\mu\text{g/L}$ MCL (12.3 percent of samples had concentrations greater than 200 $\mu\text{g/L}$); and 16 of 230 samples analyzed for molybdenum had concentrations greater than one-tenth of the 40- $\mu\text{g/L}$ HBSL (7.0 percent of samples had concentrations greater than 4 $\mu\text{g/L}$). A greater frequency of elevated barium concentrations was observed for groundwater samples from siliciclastic-rock aquifers compared to those from crystalline-rock aquifers (table 4, figs. 14A and 17A), whereas lead concentrations were more frequently elevated in samples from the crystalline-rock aquifers (table 4, figs. 13D and 17C).

Lead and barium generally occur as divalent cations in carbonate, sulfate, and sulfide minerals and associated groundwater. These trace cations commonly substitute for calcium or magnesium in major carbonate and sulfate minerals in aquifers (Back and others, 1979). The sulfate minerals anglesite (PbSO_4) and barite (BaSO_4) and the carbonate minerals cerrusite (PbCO_3) and witherite (BaCO_3) can be stable in surficial environments where concentrations of sulfate or alkalinity (dissolved carbonate) are elevated (Cravotta, 2008b). For example, barite saturation index values greater than 0 for many samples from the clastic lacustrine/evaporite sedimentary lithologic group and for one or more samples from several other lithologic groups indicate potential for barite precipitation to limit the concentration of barium. Generally, samples that were saturated with barite had elevated concentrations of sulfate and barium (figs. 15 and 17), which were positively correlated for the dataset as a whole (appendix 1, table 1-7). However, negative values of saturation indices for witherite for all samples and for barite for a majority of samples indicate that these minerals feasibly could dissolve, under most of the geochemical conditions under which these samples were collected, if present in the aquifer (fig. 19). Likewise, all the groundwater samples analyzed in this study were undersaturated with respect to anglesite, cerrusite, and other lead minerals, indicating that such minerals could feasibly dissolve (fig. 19).

Iron oxides can adsorb lead at relatively low pH values, with increasing potential for adsorption as pH increases; however, iron oxides are not strong adsorbents of barium at pH values less than 8 (fig. 8). Consequently, groundwater

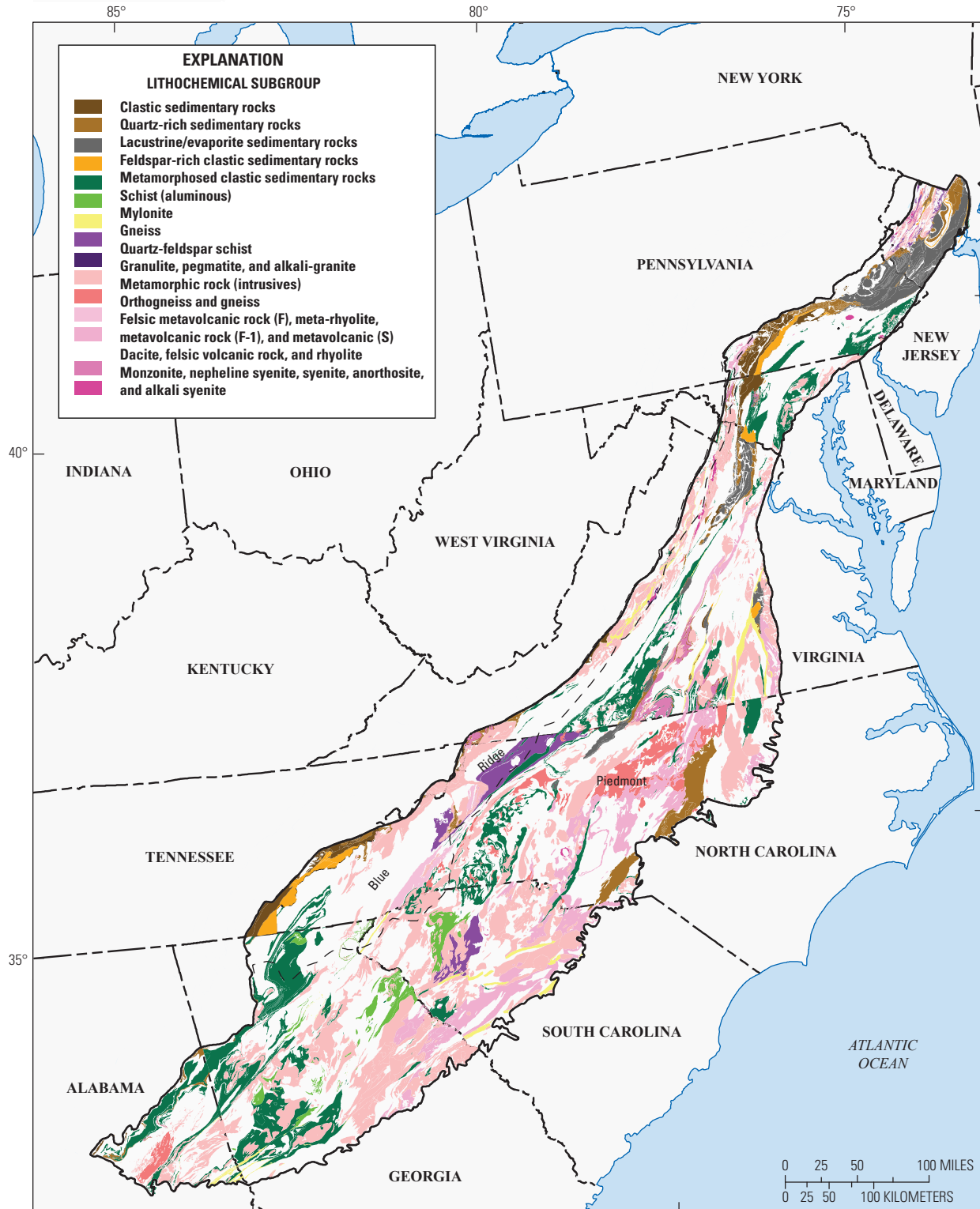
samples with low pH (4.5 to 5.5) had the greatest frequency of lead concentrations greater than the 1- $\mu\text{g/L}$ HCRL (fig. 21F), whereas groundwater with neutral to alkaline pH had the highest frequency of barium concentrations greater than one-tenth of the 2,000- $\mu\text{g/L}$ MCL (fig. 21M). In contrast with lead and barium, molybdenum tends to occur in groundwater as the oxyanion molybdate, with characteristics similar to chromate and tungstate ions (Cotton and others, 1999). As for other oxyanions with decreased adsorption at neutral to alkaline pH (fig. 8), groundwater with pH greater than or equal to 6.5 had the greatest frequency of molybdenum concentrations greater than the 1- $\mu\text{g/L}$ HCRL (fig. 21K).

Radionuclides

The presence of uranium and radium in water requires a uranium source (parent of radium) in the host rock (fig. 9) and geochemical conditions in the aquifer that are conducive to transport of these elements. Radon, however, is highly soluble and is related primarily to the abundance of uranium in the rock. The variation in uranium content in rocks is generally understood, and this provides key background information on the potential sources of uranium, and thus radium and radon, its progeny. Overall, a comparison of the aquifers in the study area suggests that the elevated concentrations of the various radionuclides are distributed in ways that are consistent with their lithological sources and their chemical and radiological properties. Thorium is the source of two isotopes of radium, but it is insoluble in common water geochemical types found in the natural environment, except in those representing the most extreme geochemical environments (strongly acidic or strongly alkaline; Langmuir and Herman, 1980) that are not found in the aquifers in the study area.

For some radionuclide contaminants, knowledge of specific lithology (for example, felsic compared to mafic rocks or lacustrine compared to quartzose siliciclastic rocks) is needed to explain differences in occurrence that gross lithology (siliciclastic compared to crystalline) cannot. The lithochemical framework developed for the PBR crystalline-rock aquifers and the Early Mesozoic basin aquifers discussed in earlier sections of this report was used to identify specific lithologic groups with greater potential for radiochemical contaminants. Uranium is present in trace amounts in all rock types but can become enriched relative to background concentrations in certain rock types because of its high solubility in certain water types and because of the wide variety of chemical reactions in which it can participate (Langmuir, 1978; Turner-Peterson, 1980; Hodge and others, 1998).

Water from areas underlain by more felsic crystalline bedrock (fig. 24) is assumed to be more likely to contain elevated concentrations of these naturally occurring radionuclides; however, differential weathering of specific minerals and rock types (Speer and others, 1981; Michel, 1984) may control the geochemical environment and thereby the concentrations of radionuclides and associated constituents in



Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 Lithologic group data from Dicken and others, 2005a and
 2005b and Nicholson and others, 2005 and 2006

Figure 24. Areal occurrence of felsic lithologic groups within the Piedmont and Blue Ridge Physiographic Provinces.

groundwater. Transport characteristics of uranium, radium, and radon differ; thus, areas underlain by rocks with the highest uranium content, which are the felsic rocks in the PBR crystalline-rock aquifers, do not always have the highest concentrations of all three of these radionuclides.

Uranium

Less than 1 percent of the samples from the aquifers exceeded the 30- $\mu\text{g/L}$ MCL for uranium (table 4). Although the highest single measurement of uranium of 97 $\mu\text{g/L}$ was in a sample taken from paragneiss from the metamorphosed clastic sedimentary lithologic group in the PBR crystalline-rock aquifers, samples from the Early Mesozoic basin aquifers had statistically higher concentrations of uranium than the samples from the PBR crystalline-rock aquifers (table 6; fig. 17). Previous studies indicate that these two areas have a combination of sources of uranium in or near the aquifer, with conditions conducive to mobilization and transport of uranium (Turner-Petersen, 1980; Szabo and Zapezca, 1991).

Clastic sedimentary and lacustrine clastic sedimentary lithologic groups within the Early Mesozoic basin aquifers had elevated median concentrations of uranium (greater than 1 $\mu\text{g/L}$) (fig. 17). The highest median uranium concentration values of 3.6 and 3.1 $\mu\text{g/L}$ were for the clastic sedimentary (CLSD group, subgroup 21) and clastic lacustrine (CLSDLAC group, subgroup 22e) lithologic groups, respectively, of the Early Mesozoic basin (tables 3, 6, and 1-1). Of 50 water samples from Early Mesozoic basin sedimentary-rock aquifers analyzed for uranium, the concentrations were greater than 4 $\mu\text{g/L}$ in about 26 percent (13 samples) and were greater than 3 $\mu\text{g/L}$ in 46 percent of the samples (appendix 1, tables 1-3 and 1-4). For these rock types, only 22 percent of the samples contained uranium concentrations that were less than 1 $\mu\text{g/L}$; however, only 2 percent of the samples had uranium concentrations that exceeded 10 $\mu\text{g/L}$, and the maximum uranium concentration was 12 $\mu\text{g/L}$.

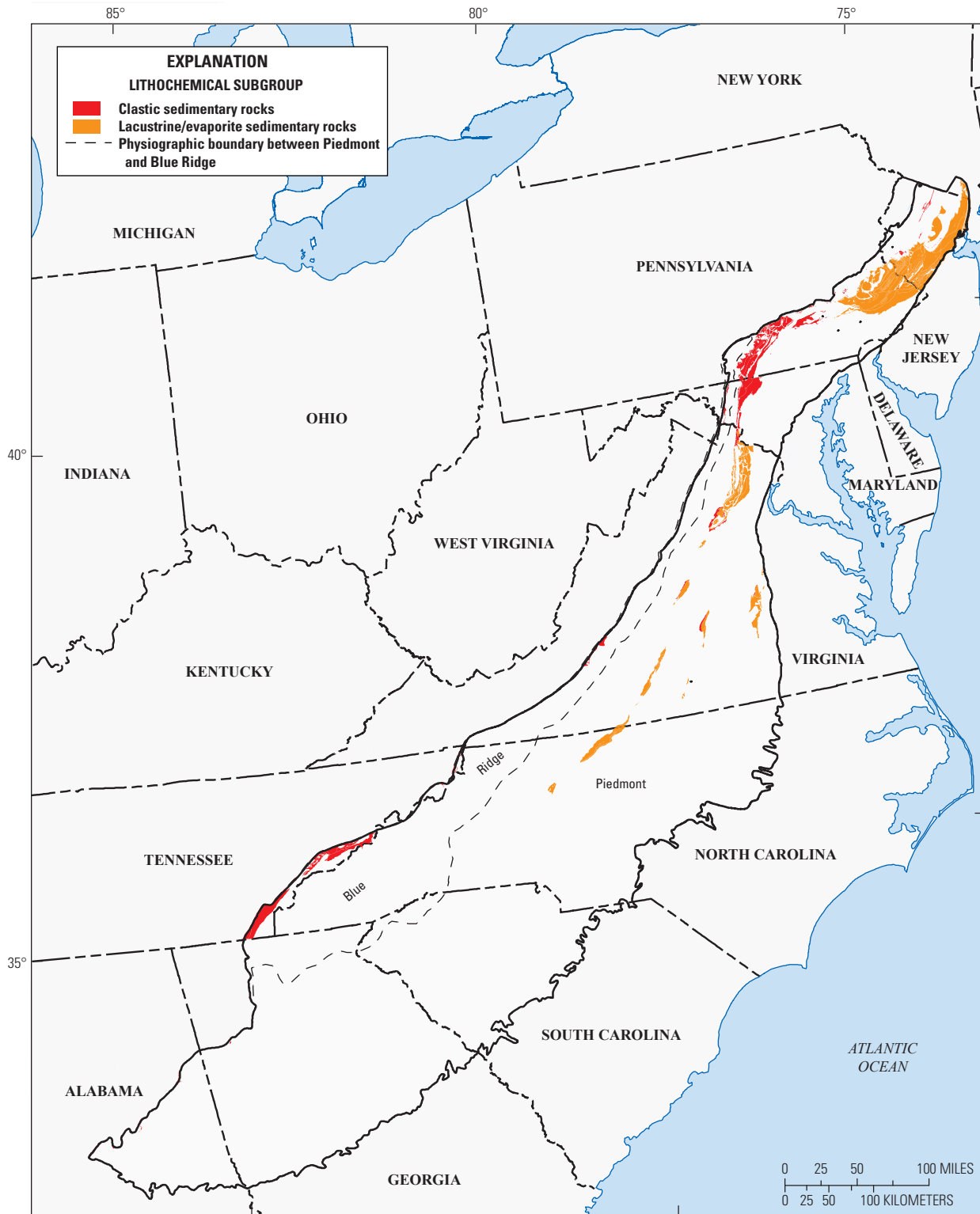
The uranium concentration distribution was more bimodal for the water samples from most crystalline-rock aquifers, especially the granites, metasediments, biotite gneisses, and paragneisses, which have sedimentary origin and had the highest individual uranium concentrations (tables 3 and 1-1). A few water samples (1.1 percent) from these crystalline-rock aquifers contained uranium concentrations in excess of 10 $\mu\text{g/L}$, and a few samples (0.8 percent) contained uranium concentrations in excess of the 30- $\mu\text{g/L}$ MCL; however, the majority of samples (89 percent) contained concentrations less than 1 $\mu\text{g/L}$ (appendix 1, table 1-4). Of water samples from the crystalline-rock aquifers, only about 6 percent contained uranium concentrations greater than 4 $\mu\text{g/L}$, and about half of those samples (7), were from granite and granite gneiss. The two highest uranium concentrations, 97 and 39 $\mu\text{g/L}$, were detected from paragneiss (sedimentary origin, now metamorphosed) and granite, respectively.

The geographic distribution of these clastic sedimentary (CLSD group, subgroup 21, appendix 1, tables 1-3 and 1-1)

and clastic lacustrine sedimentary (CLSDLAC group, subgroup 22e) lithochemical subgroups is shown in figure 25. Common lithologies for these siliciclastic groups are argillite, arkose, conglomerate, fine-grained mixed clastic, mudstone, sandstone, shale, siltstone, and greywacke. Common lithologies for the crystalline groups are granite, biotite gneiss, gneiss, and other metasediments. (Note that some clastic sedimentary rocks are mapped in the Blue Ridge Physiographic Province; fig. 25). The clastic sedimentary and lacustrine clastic sedimentary lithologic subgroups of the Early Mesozoic basin aquifers and the PBR crystalline-rock aquifers have a source of uranium and geochemical characteristics conducive to transport of uranium.

Uranium in the PBR crystalline-rock aquifers and Early Mesozoic basin aquifers occurs most commonly in groundwater that has higher values of pH under oxic geochemical conditions. Of the 29 water samples with the highest uranium concentrations (>4 $\mu\text{g/L}$), 16 (55 percent) had pH values greater than or equal to 7.3. In the grouping of samples in which the concentrations of uranium exceeded 1 $\mu\text{g/L}$, 73.4 percent (47 of 64 samples) had pH values that were neutral to alkaline (greater than or equal to 7.0), and 32.8 percent (21 of 64 samples) had a pH greater than or equal to 7.5. Conversely, in samples where uranium concentrations were low (less than 1 $\mu\text{g/L}$), the samples were overwhelmingly acidic, with pH less than 7.0 in 211 (86.8 percent) of 243 samples with pH measurement. For samples with pH less than 7.0, the samples with near-neutral pH (6.5–7.0) had the greatest frequencies for exceeding 1 $\mu\text{g/L}$ highest common reporting level (fig 21.O). The strong correlation between uranium concentrations and pH in groundwater is not surprising because of the important role pH and alkalinity (carbonate complexation) play in the geochemical mobilization of uranium. Uranium concentrations were positively correlated with pH, specific conductance, and concentrations of alkalinity, calcium, sodium, sulfate and several trace elements. The trace elements having the strongest positive correlations with pH and alkalinity were arsenic, boron, and molybdenum, all of which form oxyanions (Hodge and others, 1998) that tend to be mobile in alkaline environments (tables 5 and 1-7).

Higher concentrations of arsenic and uranium tend to occur in water with elevated pH conditions; this association is indicative of increased weathering processes (PC1, table 5). The high concentrations are consistent with the hypothesized increase in the mobility of the oxyanions under high-pH conditions, as the calculated adsorption/desorption model profiles for uranium and arsenic indicate (fig. 8). Laboratory experiments have repeatedly shown that while uranium sorbs strongly to iron-hydroxides and clays, uranium is readily desorbed from iron hydroxides and clays with increasing pH, especially in the presence of carbonate alkalinity (Hsi and Langmuir, 1985; Echevarria and others, 2001; Logue and others, 2004). Uranium concentrations are negatively correlated with concentrations of DO and iron (appendix 1, table 1-7), which is a constituent whose occurrence is strongly affected by redox conditions. These correlations are consistent with



Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 Lithologic group data from Dicken and others, 2005a and
 2005b and Nicholson and others, 2005 and 2006

Figure 25. Areal occurrence of lithochemical subgroups having elevated uranium concentrations in groundwater (based on Tukey mean rank tests, table 6) within the Piedmont and Blue Ridge Physiographic Provinces.

the thermodynamic property of uranium—the more oxidized species form oxyanions that are much more soluble than the reduced species (Langmuir, 1978), especially with more alkaline pH. Uranium concentrations also are negatively correlated with concentrations of aluminum. Aluminum is not a redox-sensitive constituent, but its solubility increases with decreasing pH (more acidic conditions); uranium solubility is optimal in the opposite conditions (with increasing pH or more alkaline conditions).

The general lack of correlation between radon and uranium concentrations among the water samples, previously noted for sediments of the Early Mesozoic basins by Szabo and Zapezca (1991), indicates that geochemical environment more strongly controls the dissolution of uranium than that of radon. A favorable geochemical environment (high pH and alkalinity) is critical for mobilizing uranium, whereas radon is readily soluble in any type of water (either acidic or alkaline). Previous sampling and analysis of the Early Mesozoic basin sediments have similarly shown that uranium concentrations tend to be highest (uranium is most mobile) in oxidizing alkaline water (Szabo and Zapezca, 1991). Previous sampling efforts for granites and gneisses of the Blue Ridge also indicate the lack of correlation between radon and uranium concentrations but indicate that high pH and alkalinity tend to be the favorable geochemical conditions for uranium occurrence (Vinson and others, 2009).

Radon

Concentrations of radon-222 exceeded the proposed AMCL of 4,000 pCi/L in 19 percent of the samples from the PBR crystalline-rock aquifers and from the Early Mesozoic basin siliciclastic-rock aquifers (table 4). Concentrations exceeded 3,250 pCi/L in 25 percent of samples, and 30 percent of the samples had a concentration greater than 3,000 pCi/L. Overall, 90 percent of the samples had radon concentrations greater than the proposed MCL of 300 pCi/L. The overall median for the entire sample set is 1,800 pCi/L, thereby exceeding the proposed MCL by a factor of 6. Median concentrations are substantially greater than the proposed MCL of 300 pCi/L, except for the those samples from the combined set of mafic igneous and metamorphic rocks and ultramafic-rock lithologic groups (IGMTM median 355 pCi/L and ULMAF median, 240 pCi/L; tables 3 and 1-1; fig. 17). Median radon concentrations for all of the lithologic groups of aquifers start at about 1,200 pCi/L for the quartz-rich sedimentary and metamorphosed clastic sedimentary lithologic groups and increase substantially for other lithologic groups. The maximum radon concentration was 38,000 pCi/L in a sample from felsic biotite gneiss. Six of the seven wells with the next highest radon concentrations, all greater than 10,000 pCi/L, were from granite.

Within the PBR crystalline-rock aquifers, the highest median concentrations of radon were detected in samples from wells completed in the felsic igneous and the metamorphosed clastic sedimentary lithologic groups (fig. 26). Although radon

had similar mean rank and median concentrations for many lithologic groups in the PBR crystalline-rock aquifer (table 6), each of the lithologic groups had large ranges in concentrations. The mafic/ultramafic lithologies had notably lower concentrations of radon, had the lowest mean rank, and had the lowest median concentration of 240 pCi/L (fig. 17). Half of all samples with radon concentrations less than 200 pCi/L were from the mafic igneous and metamorphic and ultramafic lithologic groups, which is consistent with findings from previous studies in areas of the PBR (Senior, 1998; Sloto, 2000). The median concentrations of 3,530 pCi/L for granite (felsic igneous and metamorphic lithology) and 3,600 pCi/L for schist (metamorphosed clastic sedimentary lithology) were the highest among all of the rock-aquifer types, and these two groups had the statistically highest radon concentrations (table 6; fig. 27). Within the felsic igneous and metamorphic crystalline-rock lithologic group (IGMTF group, tables 3 and A1), samples from areas underlain by a specific rock type (granite, subgroup 61, appendix 1, table 1-1) had concentrations of radon exceeding 4,000 pCi/L in 47 percent of the samples, a frequency that was twice as great as that from any of the other rock types. About 24 percent of samples from the gneiss and schist metasediments had concentrations of radon exceeding 4,000 pCi/L.

The Early Mesozoic basin siliciclastic lithologic groups had radon concentrations that generally are comparable to those of the PBR crystalline-rock aquifer lithologic groups (table 6; fig. 17). The Early Mesozoic basin lacustrine siliciclastic lithologic group within the Piedmont also had a median value that was about 1,800 pCi/L, and a small percentage of samples (about 8 percent) had a concentration greater than 4,000 pCi/L (table 6; fig. 17), with a maximum of 5,000 pCi/L. Concentrations of radon exceeded 8,000 pCi/L in 21 percent of samples from granitic aquifers (IGMTF lithologic group, lithochemical subgroup 61) and in 6 percent of samples from schistose aquifers (CLSDMT group, lithochemical subgroup 32u). The remaining Early Mesozoic basin siliciclastic lithologic groups within the Piedmont also had median concentrations of radon greater than 1,000 pCi/L, but less than 3,000 pCi/L (table 6).

Radon is highly soluble and generally is not affected by chemical reactions because it is a noble gas. Radon gas was ubiquitous, and concentrations exceeded the proposed MCL of 300 pCi/L in samples collected under all geochemical conditions encountered during this study, including pH ranging from 4.5 to 8.5 and oxic and anoxic conditions. The higher proposed AMCL of 4,000 pCi/L was also exceeded in samples collected from all types of geochemical conditions (fig. 21Q). Radon concentrations generally were higher in water that was classified as oxic as opposed to waters that were classified as anoxic. Acidic to neutral groundwater with oxic or mixed redox characteristics had the greatest frequency of samples with concentrations exceeding the 4,000-pCi/L AMCL for radon (fig. 21Q). Radon concentrations were highest where water was most corrosive and substantial rock (mineral) weathering was likely occurring. These geochemical

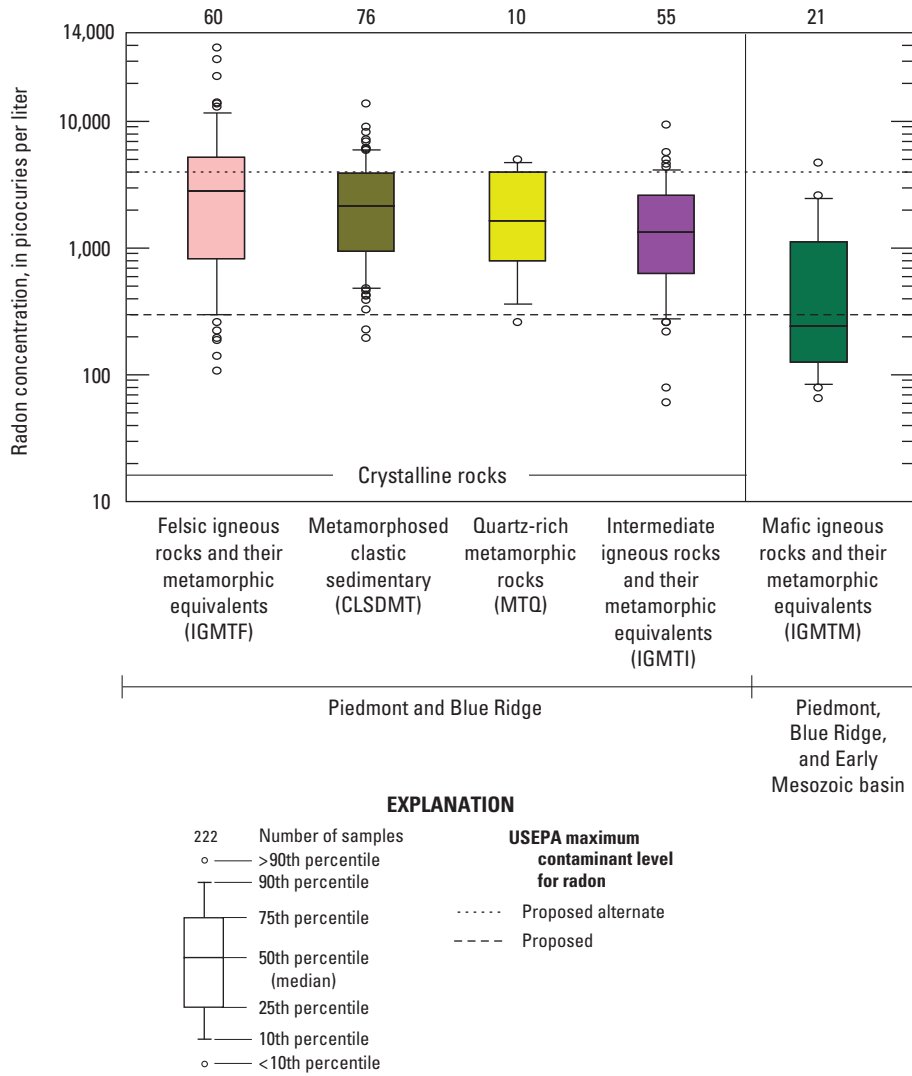


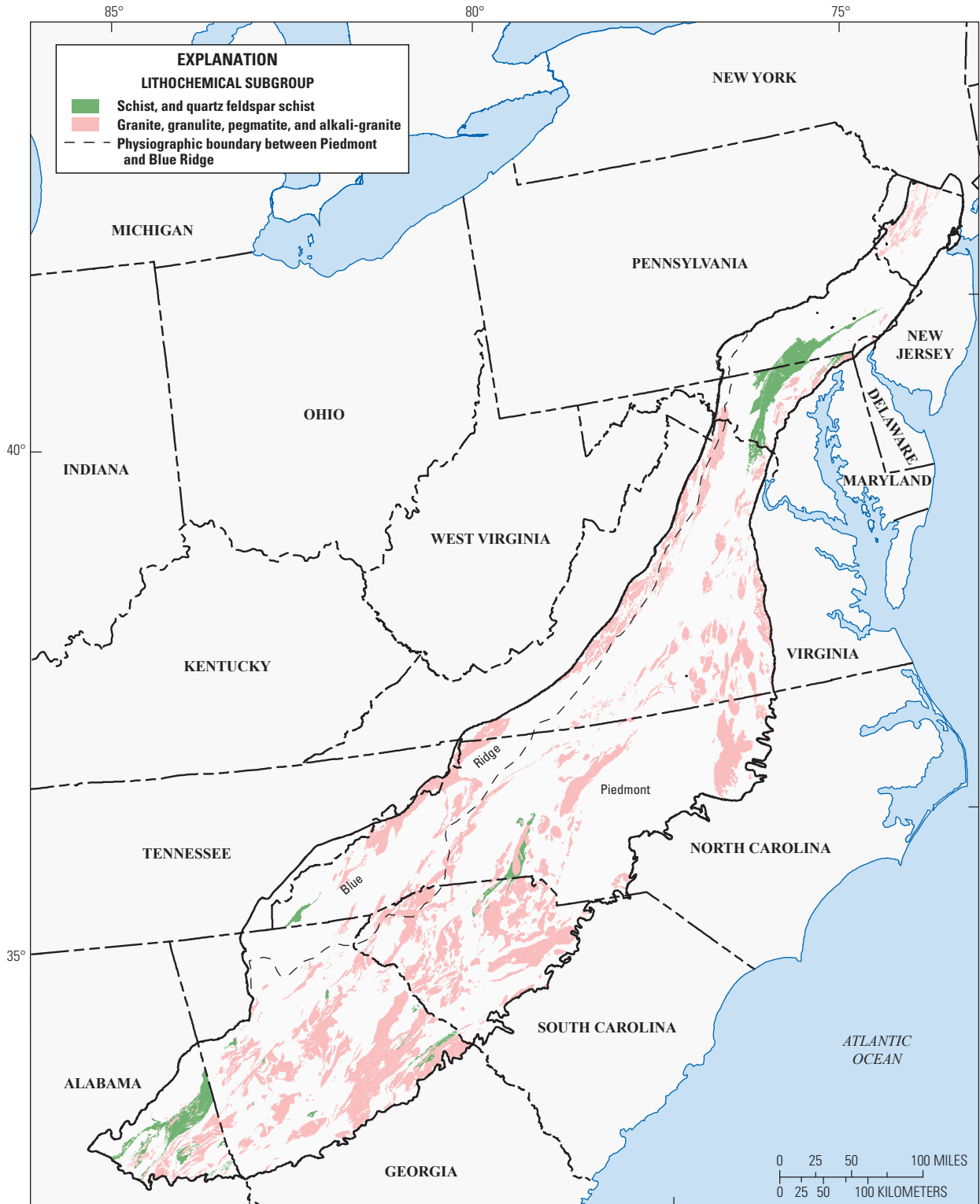
Figure 26. Radon concentrations in groundwater samples related to composition of lithologic group.

conditions are consistent with those noted for granites, which tend to yield the highest radon concentrations. The positive corresponding loading of radon and potassium together in PCA (PC5 in table 5 and 1-7) is also consistent with the highest occurrence of radon in felsic rocks, especially granites, which generally contain potassium feldspar and potassium-bearing mica minerals, such as muscovite, biotite, or phlogopite.

Because radon is highly soluble in waters of all geochemical types encountered in the region, the occurrence of radon is related primarily to the abundance of uranium in the rock. Gamma-ray spectral emission maps constructed from measurements during aerial overflights of the United States in the late 1970s as part of the USGS National Uranium Resource Evaluation (NURE) Program (Duval and Riggle, 1999) reveal a broad range of radionuclide contents. These data include the equivalent uranium-238 content interpolated on the basis of

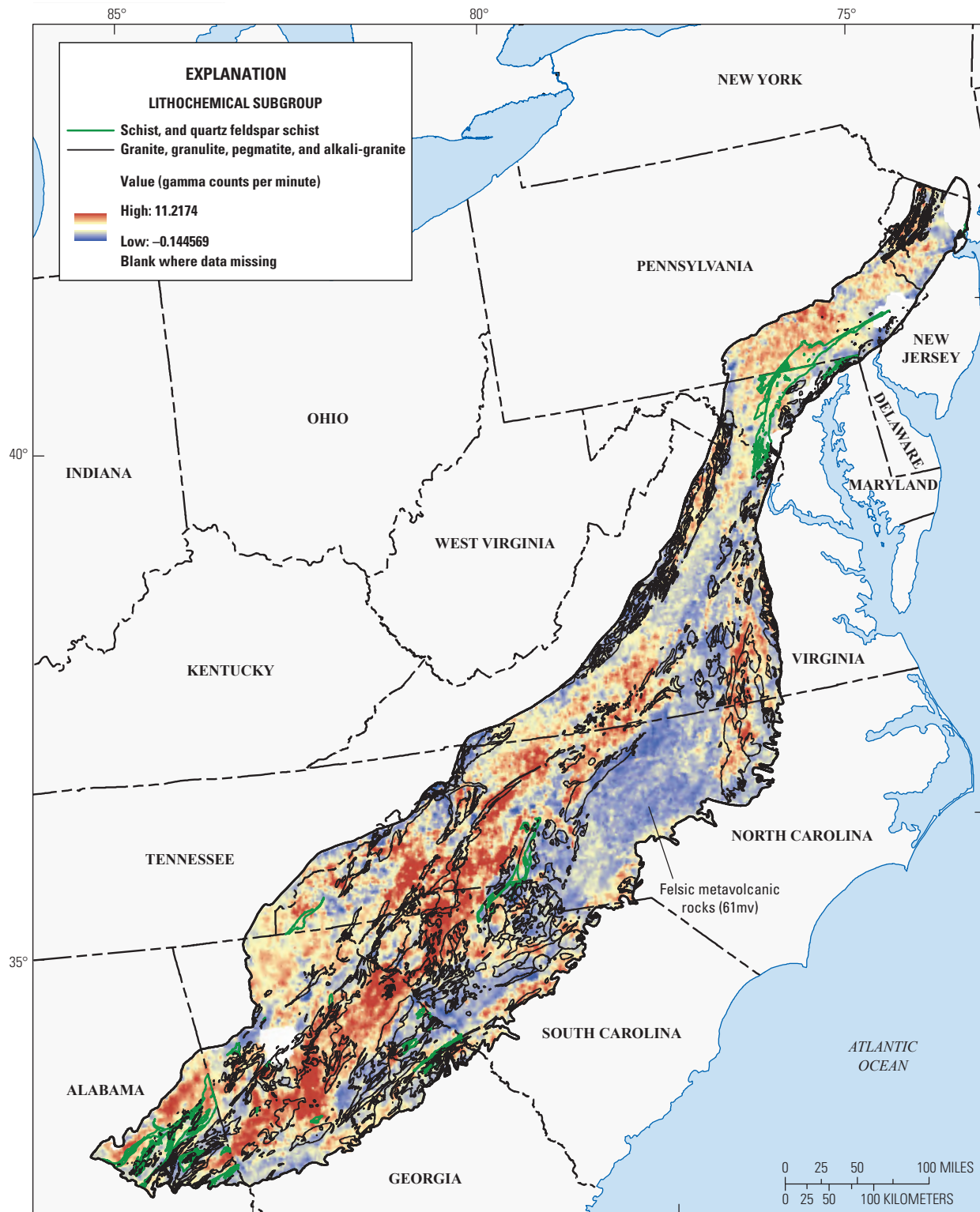
gamma emissions in the upper 25 centimeters of soil, surface sediments, or rock, which can indicate the general presence of radionuclide-enriched rock as shown in figure 28. Results from the Tukey mean rank test suggest that only the granitic rocks (61) and undifferentiated schist (32u) lithochemical subgroups had statistically higher concentrations of radon in groundwater compared to other lithochemical subgroups; however, other areas shown in warm colors in figure 28, such as the eastern Piedmont of North Carolina, suggest that other felsic rocks, including metavolcanics (lithochemical subgroup 61mv), may also be important sources of radon.

Uranium is present in trace amounts in all the rock types from the region but is strongly enriched relative to background concentrations in some of the bedrock types. Overall, a comparison of the aquifers in the study area suggests that elevated concentrations of uranium in bedrock most commonly were noted in the PBR crystalline-rock aquifers, especially granite



Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 Lithologic group data from Dicken and others, 2005a and
 2005b and Nicholson and others, 2005 and 2006

Figure 27. Areal occurrence of lithochemical subgroups having elevated radon-222 concentrations in groundwater (based on the Tukey mean rank test, table 6) within the Piedmont and Blue Ridge Physiographic Provinces.



Base from U.S. Bureau of the Census, 1990, 1:500,000 to 1:5,000,000 and Statistics Canada digital data, 2006
 Albers Equal-Area Conic projection: Standard Parallels 29°30' N and 45°30' N,
 Central Meridian 96°00' W, Latitude of Origin 23°00' N
 Lithologic group data from Dicken and others, 2005a and 2005b and Nicholson and others, 2005 and 2006;
 Uranium gamma counts from National Uranium Resource Evaluation (NURE) database

Figure 28. An overlay of areal occurrence of lithochemical subgroups having elevated radon-222 concentrations and U.S. Geological Survey National Uranium Resource Evaluation Program uranium measurements in groundwater within the Piedmont and Blue Ridge Physiographic Provinces.

and gneiss (metasediment), but high values are also present in most of the region underlain by the Early Mesozoic basin sediments, especially the lacustrine siliciclastic sediments. The variation in uranium content in the rock types of the region provides the key background upon which the concentrations of radon can be overlain and interpreted. The intersecting distribution of elevated uranium concentrations in bedrock and elevated radon concentrations in groundwater demonstrates that bedrock uranium distribution is the source, and thus is the most useful potential explanatory factor for radon concentrations (fig. 28). There is a large difference in the concentration of uranium in the granites relative to concentrations in the mafic rock or in some of the quartz-rich sediment. Thus, the large differences in concentrations of radon-222 that are observed regionally among these rock types is to be expected, based on the variable bedrock uranium contents.

Theoretically, the concentration of radon-222 in groundwater is directly proportional to the concentration of uranium in the rock-aquifer matrix (Wanty and others, 1992). The distribution of radon in water on the basis of the collected concentration data from the sampled well sites from the Piedmont Early Mesozoic basin and PBR crystalline-rock aquifers is consistent with the distribution of uranium in the bedrock, with the most extreme radon values corresponding to the most uraniumiferous lithologic types. The differences in possible concentrations of uranium among the various rock types may be relatively large, as much as a full order of magnitude or more for granites relative to mafic rocks; hence, the lithologic control on radon-222 concentrations is predominant in the PBR crystalline-rock aquifer. Concentrations of radon-222 in groundwater and concentrations of uranium in the rock-aquifer matrix were crudely correlated also for felsic crystalline rock and for the thin glacial sand and gravel aquifer systems in the northeastern United States (Ayotte and others, 2007). Many other factors can affect the radon-222 concentrations to some degree, however, including porosity and the efficiency of radon-222 emanation (Wanty and others, 1992). In the crystalline-rock aquifer types, the common occurrence of the uranium-bearing minerals along grain margins is well documented (Speer and others, 1981; Michel, 1984; Davis and others, 1987), again emphasizing the importance of granites and similar crystalline-rock types for yielding the highest radon concentrations. The variability in emanation can be affected by geochemistry and other associated factors because the geochemistry may directly affect the fate of the radium-226 parent of the radon; for example, sorption of radium to grain surfaces may be enhanced or minimized. Thus, variability in emanation may have a small effect on the overall radon-222 concentrations in the PBR crystalline-rock aquifer. The emanation effect is likely too small to be notable on the regional scale in comparison to the large variability of bedrock uranium concentrations, but may be one minor factor that further explains some of the local-area variation noted within a single rock type. Further evaluation of such local-area variation is outside of the scope of this study.

Radium

Only 2 percent of the samples analyzed for radium had concentrations that exceeded the 5-pCi/L MCL for combined radium-226 and radium-228. Three percent of samples from the Early Mesozoic basin aquifers had concentrations that exceeded the MCL (table 4). [Radium data were not analyzed from some of the lithologic groups, and the number of samples per group was often small (fig. 17H).] Of the aquifers that had radium data, the siliciclastic-rock lacustrine aquifers had the highest median concentrations of radium. The only lithologic groups within the Piedmont that contained samples with concentrations greater than the 5-pCi/L MCL for combined radium-226 and -228 were the felsic igneous and metamorphic lithologic group (IGMTF, tables 3, 4, and 1-1) in the PBR crystalline-rock aquifers (sample from granite with a concentration of 13.19 pCi/L) and the clastic lacustrine/evaporate sedimentary groups of the Early Mesozoic basin aquifers (sample from lacustrine siltstone with a concentration of 10.12 pCi/L; tables 1-3 and 1-4). In two additional samples, the combined radium concentration exceeded 4 pCi/L; one of those samples was from biotite gneiss (IGMTI group, subgroup 34bg), and the other was from granite gneiss, which is derived from granite (IGMTF group, subgroup 61). The mean rank of concentrations was not significantly different among many of the lithologic groups because of the small range in concentrations for each lithochemical subgroup, the large number of samples for which the concentrations of the radium isotopes were low or not detected, and the limited number of samples available for each group (appendix 1, table 1-6 and fig. 17H). Additional issues with regard to the detection of the radium isotopes are briefly discussed in appendix 3.

A few samples collected in areas underlain by uranium-rich sandstone or siltstone in the Early Mesozoic basin aquifers had concentrations of radium-226 that were substantially higher than the associated concentrations of radium-228. In general, the concentration ratios of radium-226 to radium-228 were highly variable among the siliclastic lithologic groups; however, the concentrations of these two radionuclides were nearly equal (about 1:1 ratio) in most samples from the felsic igneous and metamorphic crystalline-rock lithologic group (fig. 29).

Concentrations of radium isotopes exceeded the 5-pCi/L MCL and the 1-pCi/L common detection threshold more frequently in samples with anoxic or mixed geochemical conditions than did concentrations in samples with oxidizing geochemical conditions, usually with neutral to alkaline pH (fig. 21R). The effect of enhanced solubility of radium in the anoxic-type waters is the most important factor explaining the occurrence of the occasionally elevated concentrations of radium in the PBR bedrock aquifers, in terms of statistical significance (as illustrated by the correlation with dissolved oxygen; PC3; appendix 1, table 1-7 and table 5) and in terms of occurrence of the highest concentration values. For the two samples that had a combined radium concentration that exceeded the MCL of 5 pCi/L, the DO concentration was less than 0.5 mg/L and

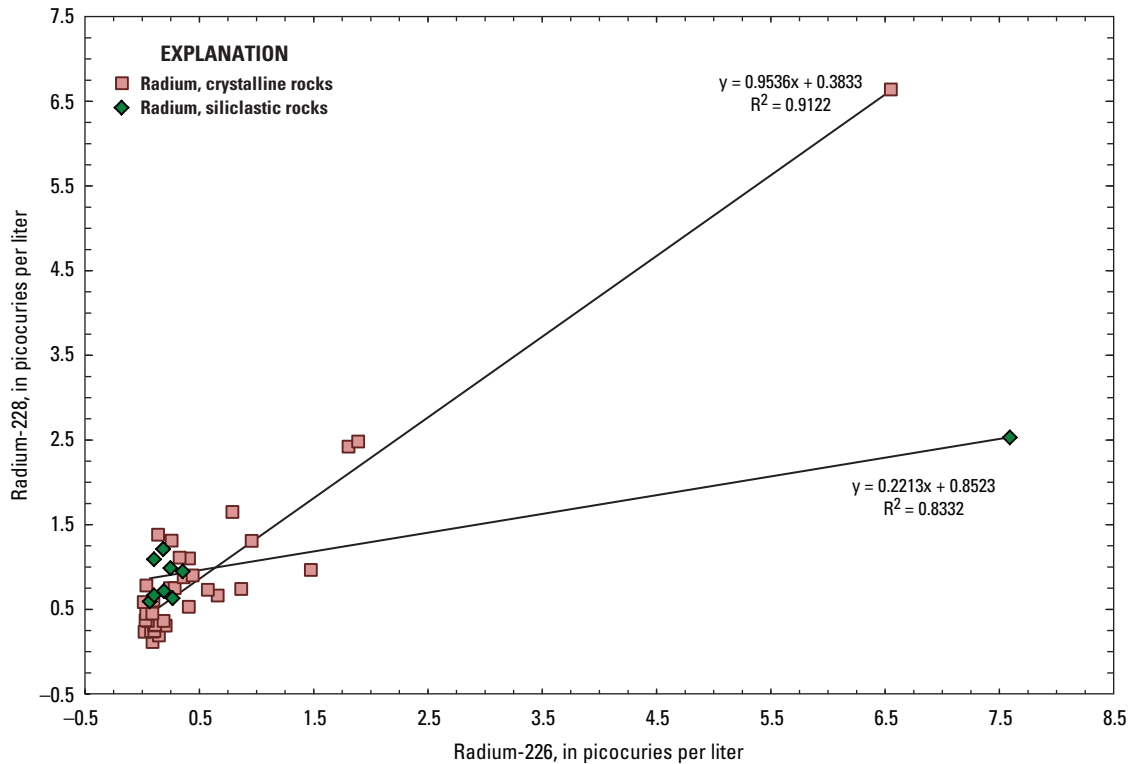


Figure 29. Relations between concentrations of radium-228 and radium-226 in samples from bedrock aquifers of the Piedmont and Blue Ridge Physiographic Provinces.

the concentration of manganese (an element far more soluble in anoxic than in oxic waters) was greater than 0.05 mg/L in both. Of the seven samples in which the combined radium concentration exceeded the level of 2 pCi/L, five samples had DO concentrations less than 0.5 mg/L, and six samples had concentrations of manganese greater than 0.05 mg/L. The frequency of occurrence for concentrations of combined radium to be greater than or equal to 1 pCi/L was evaluated among samples of water from three Ra-bearing rock aquifer groups [felsic igneous and metamorphic lithologic group in the PBR crystalline-rock aquifers, including granite; the lacustrine clastic sedimentary groups of the Early Mesozoic basins aquifers; and biotite gneiss (IGMTI group, subgroup 34bg, tables 3 and 1-1)]. Combined radium was greatest when DO was less than or equal to 1 mg/L (anoxic). Four of the five highest concentrations of radium-226 occurred when DO concentrations were less than 0.5 mg/L.

Concentrations of combined radium are negatively correlated with DO concentration (appendix 1, table 1-7). Concentrations of combined radium with respect to DO are shown in figure 30; the relation is nearly hyperbolic, indicating that radium concentrations are high when DO is absent and lower or absent when DO is abundant. Combined radium-228 and radium-226 (total radium) concentrations also have positive

correlations with iron and manganese concentrations (appendix 1, table 1-7, abbreviated as RaTOT). The indirect correlations of concentrations of radium with concentrations of DO coupled with the direct correlations with the concentrations of iron and manganese are indicative of the ongoing geochemical processes that allow for the most common mobility of radium: lack of adsorption to iron- and manganese-hydroxides and oxyhydroxides in anoxic environments. Laboratory studies have shown that radium is readily adsorbed by clay minerals (Ames and others, 1983a), but has an even stronger pattern of preferential adsorption to amorphous iron- and manganese-oxyhydroxides (Moore and Reid, 1973; Ames and others, 1983b; Benes and others, 1984). A consequence of this strong adsorption pattern for radium is that natural iron-oxyhydroxide samples have shown that they contain much more radium than the surrounding rock matrix (Korner and Rose, 1977). Reductive dissolution of the iron oxyhydroxides in anoxic conditions releases radium to the water as demonstrated by dissolving such oxyhydroxides from sediments and observing the sharp increase in the amount of radium in solution (Landa and others, 1991). The adsorption properties of radium with respect to iron oxyhydroxides (hydrated ferric oxide) under variable pH conditions are illustrated in figure 8. In neutral and alkaline waters, nearly complete adsorption of radium to

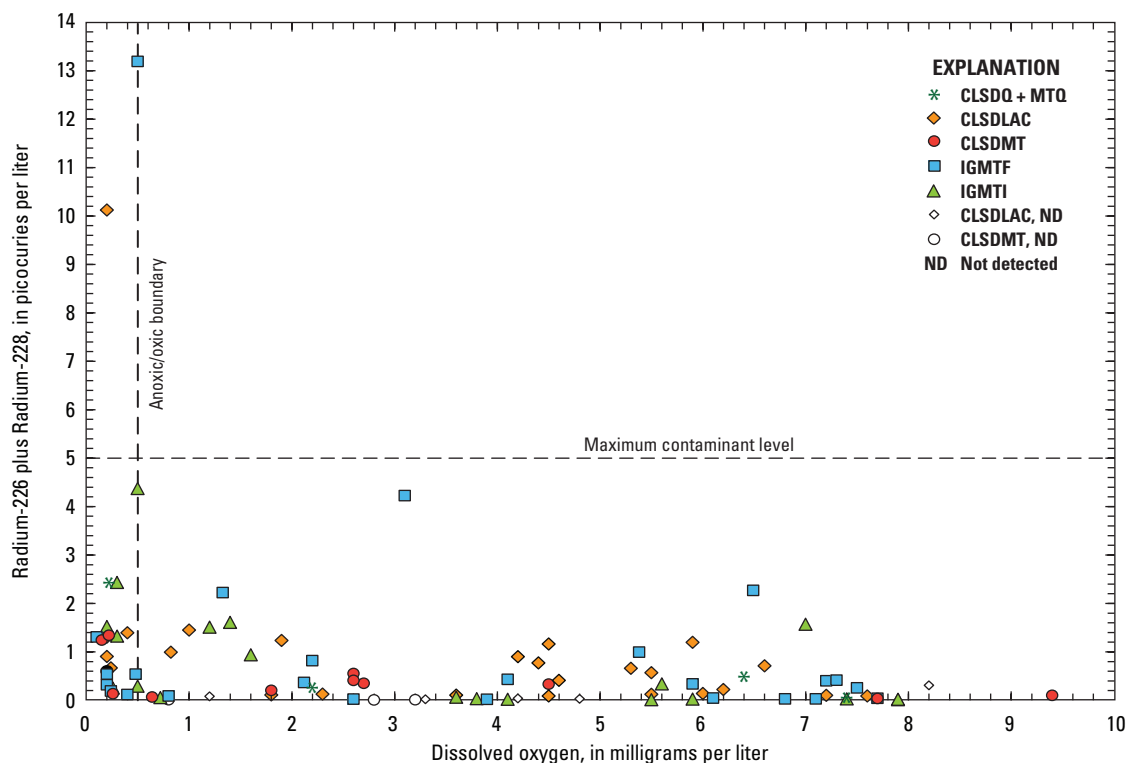


Figure 30. Relations of concentrations of radium-226 plus radium-228 and dissolved oxygen for samples from siliclastic-rock and crystalline-rock aquifers of the Piedmont and Blue Ridge Physiographic Provinces, 1994–2008.

iron oxyhydroxides is indicated. In anoxic conditions with reductive dissolution of iron oxyhydroxides, the aquifer loses a considerable sink for radium from the solid phase, thus allowing for a greater amount of radium to be in solution.

The nearly hyperbolic trend among the concentrations of radium and dissolved oxygen observed in the Appalachian PBR crystalline-rock aquifers is consistent with similar trends observed in other principal aquifers of the United States (Szabo and others, 2012a, fig. 3). The somewhat greater frequency of occurrence of radium in anoxic conditions is the most important factor controlling radium in aquifers used for drinking water supply in the United States (Szabo and others, 2012b). The occurrence pattern, whether in the Appalachian PBR crystalline-rock aquifers or in the larger setting of the continental United States, reflects the critical role that sorption processes, specifically to iron (and manganese) oxyhydroxides, play in controlling the concentration of radium in dilute groundwaters.

Data from this study show that among the Appalachian PBR siliclastic-rock and crystalline-rock aquifers, oxic groundwater is more common than anoxic groundwater, causing a greater frequency of elevated uranium concentrations relative to radium-226. These findings are consistent with results from previous studies (Szabo and Zapecza, 1991; Vinson and others, 2009). Dissolved oxygen was usually present

in detectable amounts for most, though not all, samples that contained uranium; however, dissolved oxygen was usually not present, or was present in very low amounts, for most samples that contained radium. Concentrations of uranium correlated directly and strongly with pH, indicating a lithochemical relation in occurrence patterns to rock types with the presence of bicarbonate-rich, near-neutral to alkaline waters (table 5, PC1).

For samples with oxic characteristics, radium concentrations tended to be low, but exceeded the 1-pCi/L threshold most frequently for low-pH conditions. Low concentrations of radium generally are consistent with the high potential for adsorption of the divalent radium cation by iron oxides under neutral to alkaline conditions, but not under acidic conditions in which radium tends to desorb (fig. 21R). Groundwater in the study area is not usually acidic, but in the adjoining Coastal Plain (fig. 6), pH is commonly less than 5.0, and combined radium concentrations exceed the MCL in about 20 to 30 percent of sampled wells (Szabo and others, 2005, 2012b). Data from other studies indicate that elevated radium-226 and radium-228 concentrations more frequently occur in groundwater in acidic formations in the PBR crystalline-rock aquifers (such as the Chickies Quartzite, Senior and Vogel, 1992). Because of the limited radium data collected for the current study, results of the assessment should not be considered

strictly representative of the probability of elevated radium in the PBR crystalline-rock aquifers in all lithochemical subgroups, which have great diversity in lithochemical composition and geochemical environments.

Gross Alpha-Particle Activity

Approximately 8 percent of the samples analyzed for gross alpha-particle activity from the entire dataset exceeded the MCL of 15 pCi/L. For the measured gross alpha-particle activity to exceed the USEPA drinking water MCL, the activity, excluding that from uranium (all isotopes of uranium emit alpha particles), must exceed 15 pCi/L. Only 2 percent of the samples exceed the gross alpha-particle activity MCL if presumed uranium activity is excluded from the measured gross alpha-particle activity. Perhaps equally important is the concept that gross alpha-particle activity might be of use as a compliance-monitoring “screen” for combined radium (Hess and others, 1985) or as an indicator for the presence of high concentrations of uranium, radium, or both. The measured gross alpha-particle activity is further examined in light of this concept.

Most samples with the highest values of gross alpha-particle activity greater than 15 pCi/L (table 7), contained elevated concentrations of alpha-particle-emitting radium-226 or uranium, and on some occasions, both. The MCL for combined radium or uranium was exceeded in some, but not all, samples with gross alpha-particle activity greater than 15 pCi/L. The maximum uranium concentration among the samples was 97.4 µg/L, and this sample (from paragneiss rock type, appendix 1, tables 1-1 and 1-3; CLSDMT group, subgroup 35gn) had the highest gross alpha-particle activity of 78.3 pCi/L. Similarly, the sample with the second highest uranium concentration (39.3 µg/L) from granite (IGMTF subgroup 61; appendix 1, tables 1-1 and 1-3) had the second highest gross alpha-particle activity (33.1 pCi/L). The two samples with the highest radium-226 concentrations [7.6 and 6.6 pCi/L, respectively, from the siliciclastic lacustrine/evaporite sedimentary rock group (CLSDLAC tables 3 and appendix 1, table 1-1) and the felsic igneous lithologic group (granite rock type; appendix tables 1-1 and 1-3, IGMTF group, subgroup 61)] had gross alpha-particle activity of about 30 pCi/L. Samples with moderate gross alpha-particle activities (5 to 14.99 pCi/L) occasionally contained moderate concentrations of radium-226 (0.95–1.9 pCi/L) or uranium (4–13 µg/L), but the MCL itself was not exceeded for either of these radioactive constituents. Of five samples with radium-226 concentrations greater than 1 pCi/L, all had measured gross alpha-particle activity greater than 5 pCi/L (tables 7 and 1-4). Most of these samples with moderate gross alpha-particle activities were from the siliciclastic-rock clastic lacustrine/evaporite sedimentary lithologic group (CLSDLAC tables 3 and 1-1) within the Early Mesozoic basin aquifers and from the granite (IGMTF group, subgroup 61) and biotite gneiss (intermediate igneous and metamorphic rocks, tables 3 and 1-1 IGMTI group, subgroup 34bg) PBR crystalline-rock

aquifers. The samples from these lithologic groups also had the highest frequency of occurrence of gross alpha-particle activity, radium-226, and uranium, with concentrations above their respective MCLs, and had among the highest median concentrations for uranium or radium or both. Low gross alpha-particle activities (less than 5 pCi/L) corresponded with low concentrations of radium-226 (all samples less than 1 pCi/L) and mostly low concentrations of uranium; less than 10 percent of the samples had concentrations of uranium that were greater than 4 µg/L. However, one sample with 13 µg/L of uranium had less than 5 pCi/L of measured gross alpha-particle activity; such a low gross alpha-particle activity in a sample with that amount of uranium is unusual and implies an atypical uranium isotopic ratio (Osmond and Cowart, 1976) or low analyte recovery.

Table 7. Number of samples with specified ranges of uranium and radium-226 concentrations for 99 water samples for which gross alpha-particle activity was determined.

[pCi/L, picocuries per liter; µg/L, micrograms per liter; MCL, maximum contaminant level; <, less than; >, greater than; --, not detected]

Uranium concentration (µg/L)	Gross alpha activities, in pCi/L		
	<5	5–14.99	>15 (MCL)
>30 (MCL)	--	--	2
10–29.99	1	--	--
4.0–9.99	6	7	3
1.0–3.99	18	6	--
<1	52	2	2
Totals	77	15	7

Radium-226 concentration (pCi/L)	Gross alpha activities, in pCi/L		
	<5	5–14.99	>15 (MCL)
>5 (MCL)	--	--	2
1.0–4.99	--	3	--
0.5–0.99	4	3	--
0.3–0.49	6	2	--
<0.3	67	7	5
Totals	77	15	7

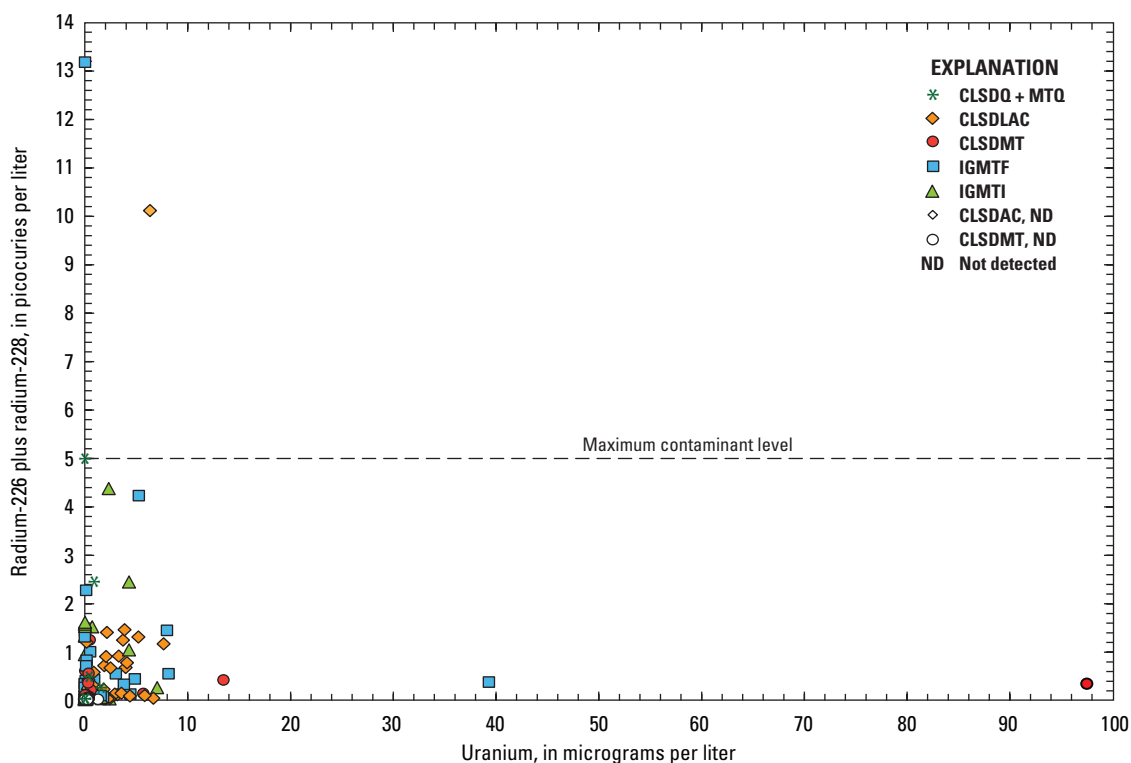


Figure 31. Relations of concentrations of radium-226 plus radium-228 and uranium for samples from bedrock aquifers of the Piedmont and Blue Ridge Physiographic Provinces.

Conventional measurements of the general amount of radioactivity in the water, such as measurements of gross alpha-particle activity, did not prove to be reliable for identifying specifically where concentrations might exceed the combined radium MCL or the uranium MCL. Elevated gross alpha-particle activity indicates the presence of at least one or the other of these alpha-particle-emitting radioactive constituents in relatively high concentrations, but the identity of which of these nuclides is predominant and contributes the most to the radioactivity of the water sample cannot be established on the basis of the gross alpha-particle activity measurement alone. Sample geochemistry (oxic or anoxic) could be helpful in estimating the likelihood of which radionuclide is predominant (fig. 21). The geochemistry of radium and uranium differ, and either one or the other tends to predominate in most, but not all, cases. The adsorption properties of the two elements tend to differ, with uranium most likely to desorb at high pH and radium most likely to desorb at low pH (fig. 8) or in the presence of anoxic water (fig. 21R). The samples with the highest concentrations of radium typically had among the lowest concentrations of uranium, and the converse was also true, regardless of the lithologic group (fig. 31).

Potential for Detrimental Effects from Trace Elements, Radionuclides, and Associated Contaminants

The trace elements arsenic, manganese, and zinc and the radionuclides uranium, radon, and radium are among the most frequently occurring elements that exceed drinking water standards in the United States. The frequencies of occurrence of uranium and arsenic are 1.7 and 6.8 percent, respectively, in samples from domestic wells nationally (DeSimone, 2009). For uranium, combined radium, and arsenic, the frequencies of occurrence in excess of the respective MCLs are 0.65, 2.0, and 3.56 percent, respectively, in the samples from the wells throughout the PBR crystalline-rock aquifers and Early Mesozoic basin aquifers. All of the samples collected from the PBR crystalline-rock and Piedmont Early Mesozoic basin siliciclastic-rock aquifers that were analyzed in this study are generally consistent with the broader national occurrence frequency as reported by DeSimone (2009). Although the frequencies of occurrence for uranium, radium, and arsenic for this region were similar to the national frequencies in general,

the frequency of occurrence for radon concentrations greater than the AMCL was substantially higher for the PBR crystalline-rock aquifers and Early Mesozoic basin aquifers than that for the Nation as a whole. The proposed AMCL was exceeded more often in the PBR crystalline-rock aquifers than in the Early Mesozoic basin aquifers, and granite is the specific rock type in the felsic igneous and metamorphic lithologic groups in which the highest percentage (47 percent) of the samples exceed 4,000 pCi/L. This relation of radon occurrence with lithology represents a readily mapable lithologic target that could be useful in prioritizing monitoring activity for radon.

Summary and Conclusions

The following key findings are from the analyses of 346 groundwater samples collected from wells examined as part of 14 U.S. Geological Survey National Water Quality Assessment (NAWQA) Program studies conducted from 1994 to 2008. These key findings are related to lithologic groups and lithochemical subgroups delineated as part of this study:

- Certain naturally occurring trace elements (arsenic, manganese, zinc) and radionuclides (uranium, radon, radium) in groundwater from wells used as domestic water supplies exceeded public drinking water standards, and 10 additional constituents (barium, beryllium, cadmium, copper, lead, selenium, boron, molybdenum, nickel, and strontium) were detected at concentrations greater than a threshold of one-tenth of the established health-based levels.
- Naturally occurring contaminants, such as arsenic, radon, uranium, and radium, had geographic occurrence patterns that generally were associated with certain mappable lithologic groups (categorized based on primary rock type and mineral assemblages). Although there was some spatial overlap, some lithologic groups associated with the presence of radionuclides were different from others affected by arsenic or other trace elements.
- Arsenic concentrations typically were less than 1 µg/L in groundwater of the study area. Concentrations of arsenic exceeding the 10-µg/L drinking water maximum contaminant level were detected in 8.5 percent of the sampled wells in the Piedmont Early Mesozoic basin siliclastic-rock aquifers and in 2.4 percent of sampled wells in the Piedmont and Blue Ridge crystalline-rock aquifers. The elevated arsenic concentrations were predominantly in groundwater samples from clastic lacustrine sedimentary rocks and metamorphosed clastic sedimentary rocks (meta-mudstone and meta-argillite) and frequently were associated with alkaline pH (measured values of 7.2 to 8.0), under oxic to anoxic geochemical conditions. Although arsenic can be attenuated by adsorption on iron oxides at acidic pH (less than 6.5), alkaline pH can facilitate the desorption and mobilization of arsenic from iron-oxide surfaces.
- Manganese concentrations typically were less than 10 µg/L in groundwater of the study area. Concentrations of manganese exceeding the Health-Based Screening Level of 300 µg/L were detected in 7.3 percent of the wells sampled. Elevated concentrations of manganese were associated with groundwaters from crystalline-rock aquifers that contained less than 0.5 mg/L of dissolved oxygen and more than 100 µg/L of dissolved iron. Many anoxic samples with elevated concentrations of manganese also had acidic pH. Anoxic conditions and (or) low pH can promote the dissolution of manganese oxides and common aluminosilicate minerals, such as chlorite, that contain manganese.
- A small number of the samples from crystalline-rock aquifers contained high uranium concentrations; only 2 of 256 samples (0.8 percent) had concentrations exceeding the 30-µg/L Maximum Contaminant Level (MCL), but the majority (89 percent) contained concentrations less than 1 µg/L. The highest concentration of uranium was 97 µg/L and was detected in a groundwater sample from the Piedmont and Blue Ridge crystalline-rock aquifers (paragneiss from the metamorphosed clastic sedimentary lithologic group). Clastic sedimentary and lacustrine clastic sedimentary lithologic groups within the Piedmont Early Mesozoic basin siliclastic-rock aquifers had elevated median concentrations of uranium (greater than the detection limit of 1 µg/L). The median uranium concentration was 3.6 µg/L for the siliclastic lacustrine siltstones of the Early Mesozoic basin.
- Radon exceeded proposed drinking water standards with a greater frequency than all other naturally occurring constituents, particularly in groundwater from the crystalline-rock aquifers. Concentrations in 19 percent of the samples from these aquifers exceeded the Alternative Maximum Contaminant Level (AMCL) of 4,000 pCi/L for radon, and 90 percent of the samples had radon concentrations greater than the proposed MCL of 300 pCi/L. At least one sample in all of the aquifer lithologic groups except for the mafic and ultramafic rocks (which are known to have low uranium concentrations in the rock matrix) had elevated concentrations of radon. Granites from the felsic igneous lithologic group in the Piedmont and Blue Ridge crystalline-rock aquifers had the greatest frequency of radon occurrence greater than the AMCL at about 46.5 percent.
- Uranium and radium rarely exceeded their respective MCLs (about 1 and 2 percent, respectively). Nevertheless, elevated concentrations of uranium, radium, and radon followed predictable geologic distribution pat-

terns. The geologic patterns of occurrence were somewhat different for each of these radionuclides despite the fact that radium-226 is a progeny of uranium, which emphasizes the importance of aquifer geochemistry for occurrence patterns.

- Radium was typically highest in anoxic waters that contained less than 0.5 mg/L of dissolved oxygen and more than 50 µg/L of manganese and on occasion more than 100 µg/L of iron, but the number of samples that exceeded the MCL of 5 pCi/L was small, only 2 of 98 samples. Both exceedences, along with most of the highest concentrations, were from anoxic waters. The occurrence of radium was most notable among the clastic sedimentary and clastic lacustrine (lakebed silt and feldspathic sand) sediments of the Piedmont Early Mesozoic basin siliclastic-rock aquifers and in the granites of the crystalline-rock aquifers in the Piedmont and Blue Ridge, especially in anoxic conditions in each of these aquifers. The number of elevated occurrences of radium in the granite and gneiss crystalline-rock aquifers (felsic igneous and metamorphic equivalents lithologic group) was small because these rocks commonly tended to have oxic waters.
- Uranium and arsenic generally were elevated in specific aquifers with alkaline pH conditions, especially those with clastic sedimentary and clastic lacustrine (lakebed silt and feldspathic sand) sediments. Concentrations of uranium were elevated in a few samples from the granite and gneiss crystalline-rock aquifers, but in about 89 percent of the samples from the crystalline rocks, the concentration of uranium was less than or equal to 1 µg/L.
- The geographic distributions of samples with elevated concentrations of uranium and of samples with elevated concentrations of radium differed except for a small number of samples. The radium-226 radionuclide was more frequently detected at elevated concentrations in waters from the siliclastic rocks of the Early Mesozoic basin than was the radium-228 radionuclide; however, in waters from the granites and gneisses, the concentrations of the two radium isotopes were nearly equal in almost all cases.
- In addition to their presence in aquifer bedrock and associated geologic materials, the occurrence of most trace elements and radiochemicals was related to the pH and redox characteristics of the groundwater. Anoxic conditions and elevated concentrations of iron and manganese were correlated with concentrations of radium isotopes in nearly all of the lithochemical subgroups of the study. Alkaline pH was correlated with concentrations of uranium and arsenic, and acidic pH was correlated with elevated concentrations of zinc.

The identification of geologic and geochemical factors affecting trace-element and radionuclide occurrence can be

useful to owners of domestic wells because these water systems generally are not monitored regularly for trace elements or radionuclides. Millions of people in the Piedmont and Blue Ridge region consume water from private domestic wells that are not regulated or monitored and could pose a source of exposure to contaminants such as arsenic or radon. Domestic well owners rarely test for these constituents, but should be aware of their potential occurrence in groundwater and the health risks of exposure to concentrations that exceed drinking water standards. A better understanding of these issues and the geochemical environments that are associated with high levels of contaminants allows water managers to focus on the most important problems in specific geographic areas. The trace-element and radionuclide data compiled in this and other large-scale regional studies or measured locally for public-supply wells could be informative to private-well owners and municipal authorities in identifying where potential risks of naturally contaminated groundwater may be highest and provide information for prioritization of testing private wells in these areas. For example, the general knowledge that water from crystalline-rock aquifers tends to have higher levels of radon than water from other aquifer types can be further focused to a specific geographic area because water from rocks in felsic (specifically those of igneous origin and granitic rock types) or metamorphic sedimentary lithologic groups (specifically schist rock types) has the highest radon levels within the crystalline-rock aquifers. Results of this study also may provide information that would be useful in designing future studies, such as prioritizing the radium-226 isotope for analysis where water is withdrawn from uranium-rich sandstone or siltstone in the Early Mesozoic basins, in order to increase the timeliness of results and perhaps minimize analytical costs for local monitoring programs.

Additional testing of domestic wells and continued public education are important, particularly considering the large areas of potential occurrence of naturally occurring inorganic chemicals and radionuclides. Some of the lithologic groups and subgroups identified for comparison with the water-quality data compiled for this study lacked the corresponding water-quality data. Sampling of these aquifer units, particularly for those lithologies with source minerals associated with radionuclide occurrence could fill these data gaps. Of the potential greatest concern are the granite and biotite gneiss and other intermediate igneous and metamorphic rocks of the Piedmont and Blue Ridge crystalline-rock aquifers and the lacustrine sedimentary and feldspar-rich (arkosic) sedimentary lithologic groups within the Piedmont Early Mesozoic basin siliclastic aquifers, as well as similar metasediments found among the Piedmont and Blue Ridge crystalline-rock aquifers. In addition to the direct measure of contaminants, additional measurements to indicate redox characteristics and pH would be useful to document the geochemical environments of contaminant occurrence.

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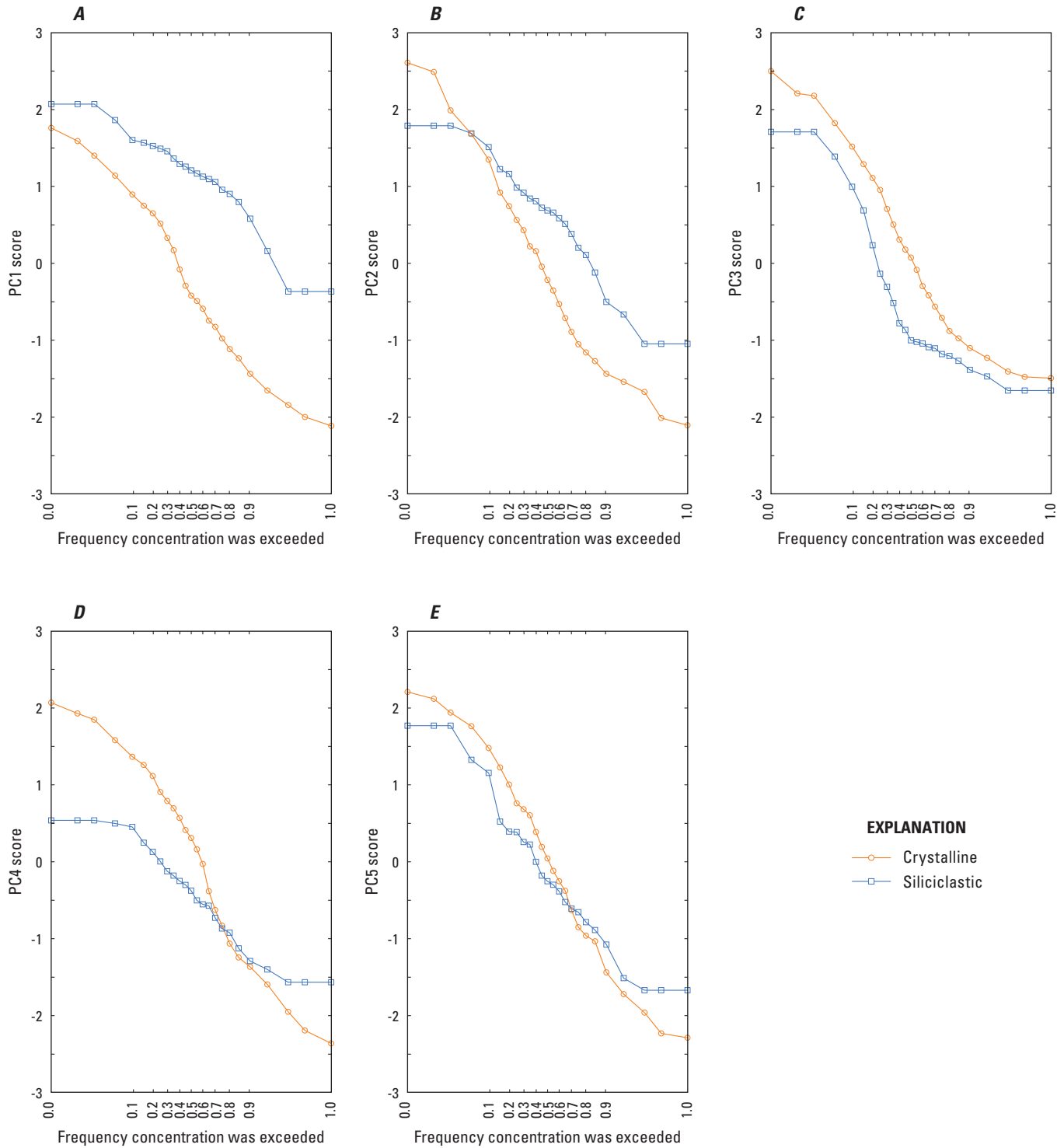
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Appendixes 1, 2, and 3

Appendix 1. Tables. (Excel spreadsheets available online at <http://pubs.usgs.gov/sir/2013/5072/>)

Appendix 2. Probability plots of principal components analysis (PCA) scores for groundwater of siliclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces: *A*, PC1 “Alkalinity-pH”; *B*, PC2 “Chloride-Nitrate”; *C*, PC3 “Redox”; *D*, PC4 “Temperature-Silica”; and *E*, “Radon-Potassium”.

Appendix 3. Analytical Issues Relating to Defining Radium Occurrence.



Appendix 2. Probability plots of principal component analysis (PCA) scores for groundwater of siliclastic-rock and crystalline-rock aquifers in the Piedmont and Blue Ridge Physiographic Provinces: A, PC1 “Alkalinity-pH”; B, PC2 “Chloride-Nitrate”; C, PC3 “Redox”; D, PC4 “Temperature-Silica”; and E, PC5 “Radon-Potassium”. The PCA model is described in table 5 and appendix table 1-7.

Appendix 3. Analytical Issues Relating to Defining Radium Occurrence

Interpreting radiological results requires understanding the concepts of detectability and quantification unique to radiochemistry measurements. For measurements of radionuclides in this study, these concepts primarily are important for measurements of radium concentrations. Uranium concentrations were determined by measuring the mass of the uranium-238 isotope present; therefore, issues unique to radiochemistry measurements were not considered. Concentrations of radon-222 were so high that issues regarding detectability and quantification were again not of consideration. Concentrations of radium (Ra) isotopes, however, while showing considerable ranges, were for many samples at or below detection, or if detected, were low enough that guidelines for quantification could not be met. Furthermore, analytical techniques for radium isotopes underwent considerable changes during the period of study as did reporting requirements. A measured (uncensored) concentration value was reported for nearly all the samples (tables 4 and 1-4), although issues relating to analysis, detection, quantification, and reporting of the measured radium isotope concentrations affect understanding of the radium occurrence. Additional information provided with many of the analyses can be useful in determining the statistical likelihood of detection and quantification.

Random radioactive decay, variable radioactive background noise, and other measurement uncertainties cause measurement signal to vary. For a background blank or an environmental sample, a nonzero signal may be produced even when no radionuclide is present. For this reason, the laboratory analyzes an instrument background or blank sample and subtracts the response signal from the gross signal of the measured environmental sample to obtain the net signal. The critical level (L_c) is the smallest measured concentration that is statistically different from the instrument background (blank). It is the threshold of detection for whether the radionuclide is actually present. The statistical computation is set to minimize the statistical likelihood of a false detection. Because of the random variability in the background signal, the issue of detection of radioactivity in an individual sample result is not in all cases best represented by the general reporting level, therefore, but rather by comparison with the L_c . The sample-specific minimum detectable concentration (ssMDC) is a slightly higher (concentration) value than the L_c that is adequate to distinguish the sample result from that of the blank with statistical confidence. For each sample, the sample-specific parameters such as yield, detector efficiency, and sample aliquot size are used in the formula to determine the SSMDC. In the truly simplest case, the SSMDC is about twice the L_c (Currie, 1968). Reported negative values are possible when the result of a sample is less than that of the blank representing background; these values represent non-detection in the case of a single measurement. The precision estimate of the radiological result is the square root of the sum of

variances of the factors that affect measurement precision. For radionuclides, a large component of the measurement precision is defined by the random decay rate of the radionuclide at any instant in time. Though the average rate of decay conforms to that associated with the half life (the time in which half of the radionuclides would decay), at any instant in time, the rate may randomly be greater or lesser than this average rate, resulting in imprecision in the measurement. A sample result implies true detection if the result is greater than the L_c , but confidence that the value of the result is statistically significantly different from the background is achieved if the value is also greater than the SSMDC, and the sample may still have poor precision. For radionuclide samples analyzed for this study before mid-2003, sample-specific critical levels (ssL_c) were not reported (McCurdy and others, 2008). Comparisons of detectability are reliant on the assumption that the reported SSMDCs were indeed twice the values of the ssL_c s (Currie, 1968). Importantly, the sensitivities of the analyses were such that concentrations great enough to be considered of concern to human health could readily be detected and quantified.

The concentrations of Ra-226 were greater than the individual SSMDCs (when reported, see table 1-4) or L_c s (stored in USGS databases but not reported in table 1-4) in 85 samples, and the reported raw values were greater than zero in all but one sample. The concentrations of Ra-226 were less than the individual SSMDCs in eight samples from the siliclastic lacustrine siltstones of the Early Mesozoic basin sediments, a frequency greater than in the other rock types, even though the highest Ra-226 concentration was also detected in this rock type. The concentrations of Ra-226 in samples collected from the Early Mesozoic basin aquifer were determined by using alpha spectrometry, whereas the radon-emanation method was used for analysis of Ra-226 from samples collected from the remaining aquifers. Alpha spectrometry had a higher detector background than did the radon-emanation method, resulting in the higher SSMDCs (or L_c s). This difference in methodology likely explains why so many sample results were reported as less than the SSMDC for samples collected from the Early Mesozoic basin aquifer, but not from samples collected from the remaining aquifers. Of the remaining rock types, the concentrations of Ra-226 were less than the individual SSMDCs or ssL_c s in only one or two samples, except for the metasediments (CLSDMT, table 3) for which three samples had concentrations less than the L_c . Concentrations of Ra-226 in 53 samples were greater than 0.1 picocurie per liter (pCi/L), but of those, only 1 had a concentration (0.126 pCi/L) that was less than the corresponding SSMDC (0.145 pCi/L) (table 1-4). The high frequency of detection in samples relative to that of Ra-228 is partly attributable to the great sensitivity of the radon emanation technique used for detecting Ra-226.

The concentrations of Ra-228 were greater than the individual SSMDCs (when reported, see table 1-4) or L_c s (stored in USGS databases but not reported in table 1-4) in 48 samples, and reported raw values were greater than zero in all but 9 samples (table 4). The SSMDCs for the beta-particle

emitting Ra-228 (maximum and 75th-percentile values, 0.906 and 0.569 pCi/L, respectively) were higher than those for either of the other Ra isotopes, which are alpha-particle emitters (table 1-4) and have lower background values. A maximum measured Ra-228 concentration of 0.71 pCi/L in one sample, however, was still less than the respective SSMDc, illustrating the difficulty in interpreting the distribution of Ra-228 concentrations that are less than about 0.7 to 0.9 pCi/L (representing the maximum SSMDc). The concentrations of Ra-228 were greater than 0.9 and 1 pCi/L in 17 and 14 samples, respectively, and were generally found at these concentrations in both siliciclastic and crystalline rock aquifers. An additional 22 samples with concentrations ranging from 0.19 to 0.71 pCi/L were considered as detectable in quantifiable amounts because the concentration was greater than the associated SSMDc or L_c . The minimum Ra-228 concentration that was greater than the associated SSMDc was 0.593 pCi/L (table 1-4) and that was greater than the associated L_c that was 0.19 pCi/L.

Ra-224 concentrations were measured in samples only from the sedimentary rock aquifers of the Early Mesozoic basin and were not present at concentrations greater than 1 pCi/L in any of the samples analyzed for this isotope. The median concentration value of 0.10 pCi/L is uncertain (an estimate at best) because it is less than the value of the median of the associated SSMDcs (0.24 pCi/L). The concentrations of Ra-224 for the samples collected from this aquifer were determined by alpha spectrometry, and this technique has high enough SSMDcs to make detection in many samples questionable. The concentrations of Ra-224 were greater than or equal to the individual SSMDcs in 5 samples, and the reported raw values were greater than zero in all but 3 samples (table 4). A maximum measured Ra-224 concentration of 0.47 pCi/L in one sample, however, was still less than the respective SSMDc, illustrating that alpha spectrometry may have performance issues up to a value of about 0.5 pCi/L.

Concentrations of Ra-226 plus Ra-228 (termed combined Ra, the quantity that is specifically considered in drinking water regulations) were quantifiable at about the 1 pCi/L level and could be compared to the 5 pCi/L standard. The concentrations of both these Ra radionuclides were greater than the respective SSMDc or ssL_c for 44 percent of the samples, with

concentrations of combined radium (Ra-226 plus Ra-228) for these samples about equal to or greater than 1.0 pCi/L (fig. 14). At least one of these two Ra radionuclides was detected with respect to the SSMDc or the ssL_c for 88 percent of the samples; the SSMDc in all cases when it was reported was less than 1 pCi/L (table 1-4). All samples had at least one of these two Ra radionuclides reported with a value greater than zero (table 4).

For purposes of statistical calculation, and for plots illustrating population distribution characterization, such as probability plots or boxplots (figs. 14, 17, and 21; tables 1-4 and 1-5), the distribution of the raw reported laboratory results were displayed to provide the sense of the distribution of the raw (uncensored) measured values. Values less than zero were censored for descriptive purposes in table 4. This approach eliminated the need for statistical approaches to estimate low concentration values (such as those described by Helsel and Hirsch, 2002). For scatter diagrams (figs. 29, 30, and 31), when only one Ra radionuclide concentration, Ra-226 or Ra-228, was detectable or quantifiable with the prescribed level of statistical certainty, the concentration of that one isotope was used as the concentration to represent the value of combined Ra. When neither Ra radionuclide concentration, Ra-226 or Ra-228, was detectable or quantifiable with the prescribed level of statistical certainty, the lower of the two reported concentrations was used to represent the value of the combined Ra concentration. As detailed above, all samples had at least one of these two Ra radionuclides reported with a value greater than zero (table 4). For purposes of graphical representation in the latter case, when neither Ra radionuclide concentration, Ra-226 or Ra-228, was detectable, the value of either the combined Ra concentration or the individual Ra radionuclide was represented as an open rather than as a closed symbol. For purposes of the simplest description of the distribution, the use of 1 pCi/L as an approximate cutpoint separating concentrations detected with greatest statistical certainty from those concentrations detected with slightly lesser statistical certainty or those not detected at all is reasonably justified by the distribution of the $ssMDC$ s or $L_{c,s}$. In terms of the human health benchmark (HHB) of 5 pCi/L, this value represents the 20th percentile, and can be described as 0.2 HHB (fig. 21R; table 4).

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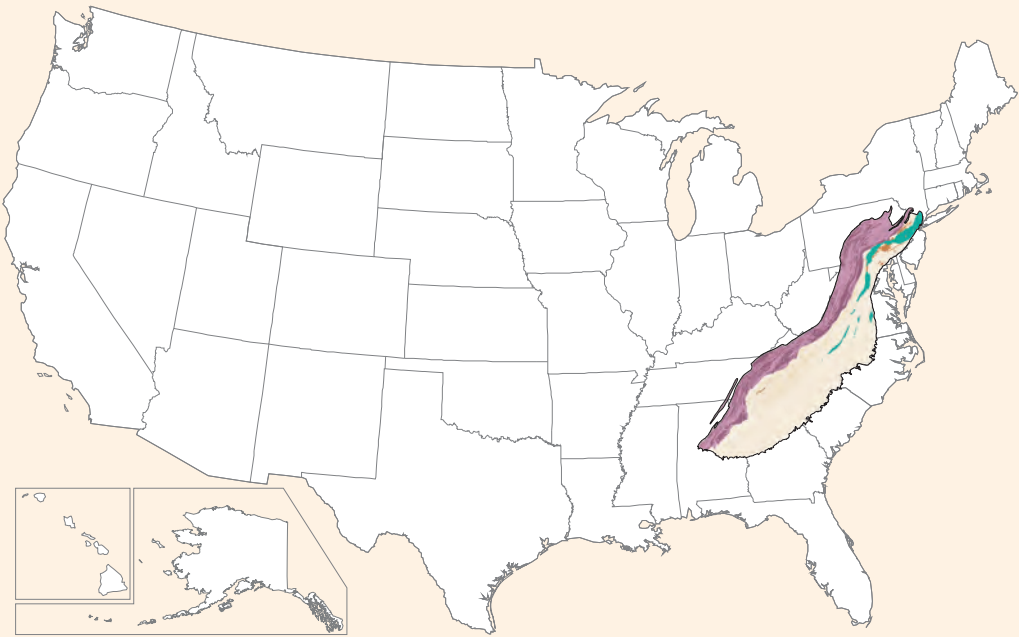
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