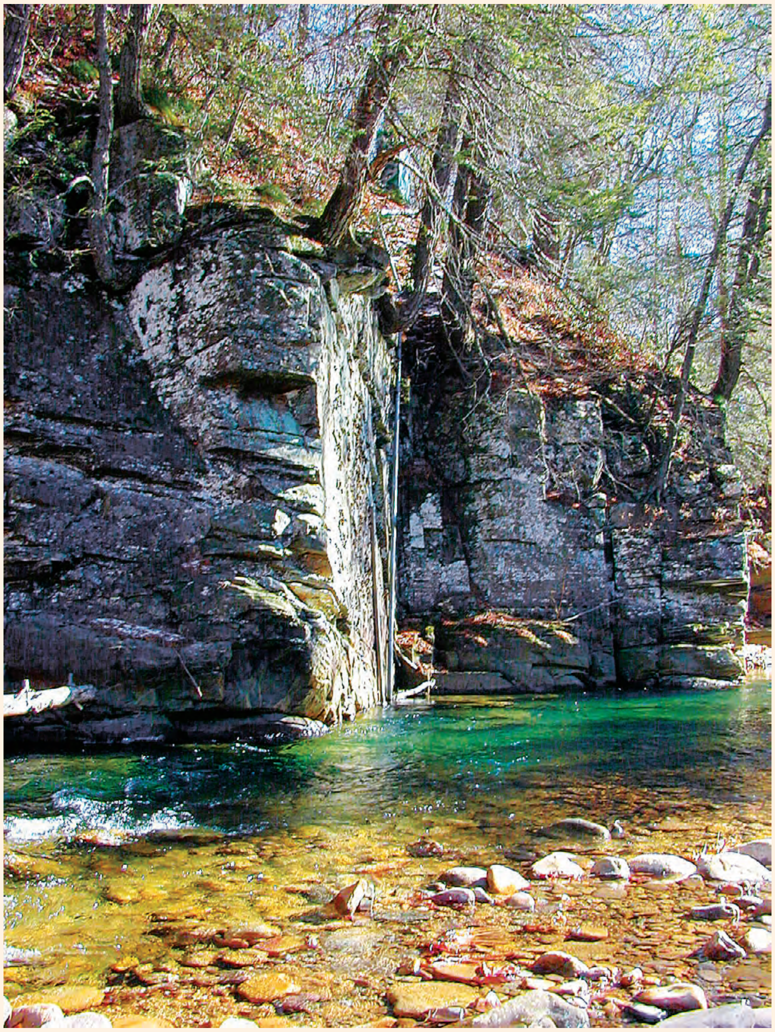
National Water-Quality Assessment Program

Contributions of Phosphorus from Groundwater to Streams in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces, Eastern United States



Scientific Investigations Report 2010–5176

U.S. Department of the Interior
U.S. Geological Survey

Cover. Photo showing area near U.S. Geological Survey surface-water site 01620500 North River near Stokesville, VA. Photo by U.S. Geological Survey.

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By Judith M. Denver, Charles A. Cravotta III, Scott W. Ator, 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 ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, 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 (2001–2012), 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 ground water, 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 and Datum

Multiply	By	To obtain
	Length	
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
	Area	
square meter (m^2)	10.76	square foot (ft^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
	Flow rate	
millimeter per year (mm/yr)	0.03937	inch per year (in/yr)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)

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

°F=(1.8×°C)+32

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29).

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

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

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Contributions of Phosphorus from Groundwater to Streams in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces, Eastern United States

By Judith M. Denver, Charles A. Cravotta III, Scott W. Ator, and Bruce D. Lindsey

Abstract

Phosphorus from natural and human sources is likely to be discharged from groundwater to streams in certain geochemical environments. Water-quality data collected from 1991 through 2007 in paired networks of groundwater and streams in different hydrogeologic and land-use settings of the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces in the eastern United States were compiled and analyzed to evaluate the sources, fate, and transport of phosphorus. The median concentrations of phosphate in groundwater from the crystalline and siliciclastic bedrock settings (0.017 and 0.020 milligrams per liter, respectively) generally were greater than the median for the carbonate setting (less than 0.01 milligrams per liter). In contrast, the median concentrations of dissolved phosphate in stream base flow from the crystalline and siliciclastic bedrock settings (0.010 and 0.014 milligrams per liter, respectively) were less than the median concentration for base-flow samples from the carbonate setting (0.020 milligrams per liter). Concentrations of phosphorus in many of the stream base-flow and groundwater samples exceeded ecological criteria for streams in the region.

Mineral dissolution was identified as the dominant source of phosphorus in the groundwater and stream base flow draining crystalline or siliciclastic bedrock in the study area. Low concentrations of dissolved phosphorus in groundwater from carbonate bedrock result from the precipitation of minerals and (or) from sorption to mineral surfaces along groundwater flow paths. Phosphorus concentrations are commonly elevated in stream base flow in areas underlain by carbonate bedrock, however, presumably derived from in-stream sources or from upland anthropogenic sources and transported along short, shallow groundwater flow paths.

Dissolved phosphate concentrations in groundwater were correlated positively with concentrations of silica and sodium, and negatively with alkalinity and concentrations of calcium, magnesium, chloride, nitrate, sulfate, iron, and aluminum. These associations can result from the dissolution of alkali feldspars containing phosphorus; the precipitation of apatite; the precipitation of calcite, iron hydroxide, and aluminum hydroxide with associated sorption of phosphate ions; and the potential for release of phosphate from iron-hydroxide and other iron minerals under reducing conditions. Anthropogenic sources of phosphate such as fertilizer and manure and processes such as biological uptake, evapotranspiration, and dilution also affect phosphorus concentrations. The phosphate concentrations in surface water were not correlated with the silica concentration, but were positively correlated with concentrations of major cations and anions, including chloride and nitrate, which could indicate anthropogenic sources and effects of evapotranspiration on surface-water quality. Mixing of older, mineralized groundwater with younger, less mineralized, but contaminated groundwater was identified as a critical factor affecting the quality of stream base flow. In-stream processing of nutrients by biological processes also likely increases the phosphorus concentration in surface waters.

Potential geologic contributions of phosphorus to groundwater and streams may be an important watershed-management consideration in certain hydrogeologic and geochemical environments. Geochemical controls effectively limit phosphorus transport through groundwater to streams in areas underlain by carbonate rocks; however, in crystalline and siliciclastic settings, phosphorus from mineral or human sources may be effectively transported by groundwater and contribute a substantial fraction to base-flow stream loads.

Introduction

Phosphorus is the limiting nutrient controlling biological productivity in most freshwater environments. Concentrations of dissolved phosphorus in freshwaters tend to be maintained at low levels (less than 0.1 mg/L, or milligrams per liter) because of the rapid uptake of phosphorus by algae and plants and its tendency to combine with calcium, iron, and aluminum as sparingly soluble “metal-phosphate” minerals and (or) to sorb on surfaces of other common minerals (Hem, 1985; Stumm and Morgan, 1996; Drever, 1997; Filippelli, 2008;

Oelkers and Valsami-Jones, 2008). Consequently, most of the phosphorus transported to and within streams is associated with suspended sediment, particularly during and following storm runoff events (Pionke and others, 1999; Litke, 1999; Bowes and others, 2005). Transport of dissolved phosphorus in groundwater as base flow to streams and lakes generally is presumed to be minor in comparison to overland transport. Nevertheless, even very small amounts of phosphorus transported by groundwater to surface waters may have ecological impacts (Kang and others, 2005).

Effective nutrient management of a watershed requires quantitative information on possible phosphorus sources and transport processes. Natural phosphorus sources include wastes and skeletal remains from fish, water fowl, and other animals; decay of foliage and leaf litter; and weathering of certain minerals in rocks and soils (Litke, 1999; Filippelli, 2008). Although phosphorus occurs naturally in such biological and geological substances, anthropogenic sources, such as fertilizers, animal manure, and sewage, typically dominate in waters draining agricultural and urban areas.

Elevated concentrations of phosphorus in streams, lakes, and reservoirs can promote the rapid growth of algae, resulting in eutrophication (Wetzel, 2001). To minimize nutrient enrichment and eutrophication of freshwaters, the U.S. Environmental Protection Agency (USEPA) (1986) recommended national nutrient water-quality criteria for total phosphorus of 0.025 mg/L in reservoirs, 0.05 mg/L in streams directly discharging to reservoirs, and 0.1 mg/L in streams not directly discharging to reservoirs. In consideration of regional variability in geology, climate, soils, and other natural conditions that may affect phosphorus concentrations, the USEPA expanded the strategy for adapting these criteria on the basis of 14 level III ecoregions (U.S. Environmental Protection Agency, 2000a, 2000b). Proposed criteria for streams in Ecoregion IX, which includes the Piedmont Physiographic Province, and Ecoregion XI, which includes the Blue Ridge and Valley and Ridge Provinces, are lower than those proposed for the Nation in 1986 (fig. 1, table 1).

Groundwater discharge provides a large amount of water to streams, reservoirs, and lakes (particularly in the eastern United States), and, therefore, may contribute dissolved phosphorus to surface waters. Such contributions may be particularly critical during periods of diminished precipitation when groundwater discharge sustains streamflows and lake levels. Overall, concentrations of phosphorus in shallow groundwater in selected parts of the Nation from 1991 through 2001 were generally less than 0.01 mg/L and not significantly different among undeveloped, agricultural, and urban settings (Nolan and Hitt, 2003). Concentrations of dissolved phosphorus in groundwater in selected areas of the eastern Piedmont frequently exceeded regional criteria, however, especially in crystalline and siliciclastic rocks, and were comparable to estimated total phosphorus concentrations in undeveloped headwater streams of the area (Smith and others, 2003). Contributions from natural phosphorus sources to surface waters may be an important consideration in nutrient-management strategies for the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces given the potential for concentrations of dissolved phosphorus in groundwater to exceed 0.01 mg/L in certain areas (Sharpley and others, 1994, 2003; Abrams and Jarrell, 1995). Groundwater in contact with phosphate minerals, such as apatite, has been suggested as a possible natural source of high phosphorus concentrations in some streams of the North Carolina Coastal Plain (Spruill and others, 1998; Fuhrer and others, 1999). The dissolution of feldspar containing traces of phosphorus is another possible source (Manning, 2008). Thus, total phosphorus concentrations in certain streams, lakes, and reservoirs may equal or exceed the recommended Federal nutrient criteria in parts of Ecoregions IX and XI because of the contribution of dissolved minerals in groundwater and geochemical conditions that allow elevated concentrations of phosphorus to persist in groundwater. To address this issue, the U.S. Geological Survey (USGS), as part of the National Water-Quality Assessment (NAWQA) Program, assembled and analyzed data on water chemistry; and the geologic and land-use characteristics of the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces to study sources of phosphorus to groundwater and the potential for phosphorus transport from groundwater to surface water in this region.

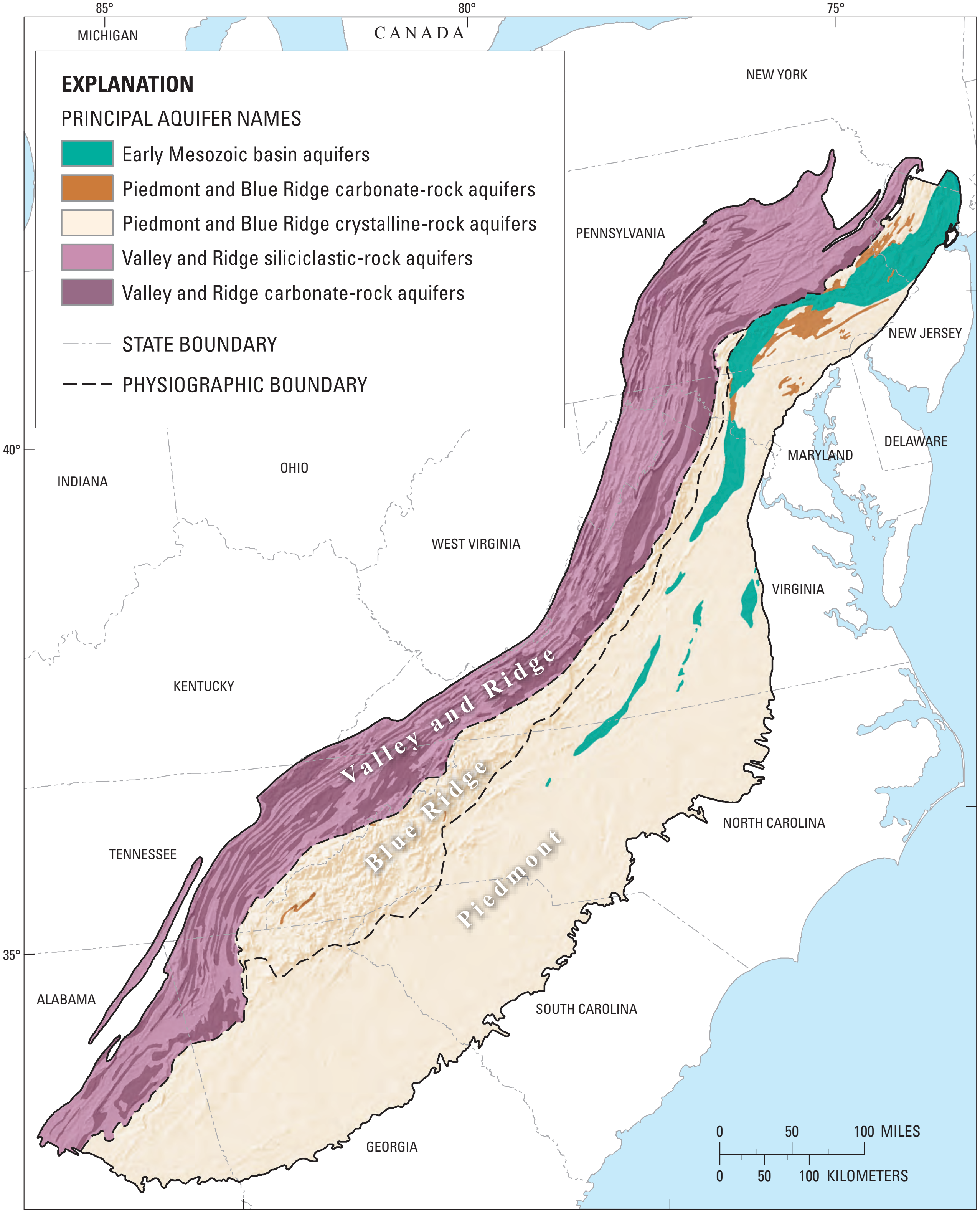
Purpose and Scope

Potential contributions of phosphorus from natural and anthropogenic sources to groundwater and from groundwater to streams in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces in the eastern United States (fig. 1) are described and discussed in this report. Water-quality data collected from 1991 through 2007 from more than 600 wells and more than 350 streams during base-flow conditions in various hydrogeologic and land-use settings from northern Alabama to New Jersey are presented. Graphical and statistical techniques are used to compare phosphorus concentrations

Table 1. Nutrient criteria for concentrations of phosphorus and nitrate in streams and reservoirs in Ecoregions IX and XI as recommended by the U.S. Environmental Protection Agency (2000a, 2000b).

[mg/L, milligrams per liter]

Nutrient	Physiographic Province (Ecoregion)	Stream criterion (mg/L)	Reservoir criterion (mg/L)
Phosphorus	Piedmont (IX)	0.037	0.02
	Blue Ridge/Valley and Ridge (XI)	0.01	0.008
Nitrate	Piedmont (IX)	0.69	0.36
	Blue Ridge/Valley and Ridge (XI)	0.31	0.46



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. The Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces and principal aquifers.

in groundwater and streams among different hydrogeologic and land-use settings and to proposed ecoregion nutrient criteria. Interactions between groundwater and streams in various settings inferred through comparison of major-ion chemistry are described. Geochemical models are used to identify and evaluate potential contributions from various sources of phosphorus in different settings, and geochemical and hydrologic processes affecting phosphorus fate and transport through groundwater to streams. Implications of observations and conclusions for regional nutrient management and proposed criteria are discussed.

Phosphorus Geochemistry

Phosphorus is a minor element in rock, soil, and water, but it is essential for the growth of microorganisms, plants, and animals (Rudnick and Gao, 2003; Krauskopf, 1979; Hem, 1985). In rocks and water near the surface of the Earth, phosphorus occurs primarily as the anion PO_4^{3-}, which is referred to as orthophosphate or phosphate (Hem, 1985). The most abundant phosphate mineral is apatite, a calcium-phosphate compound with varying amounts of fluorine, chlorine, and (or) hydroxide ($Ca_5(PO_4)_3(F,Cl,OH)$), that occurs widely as an accessory in all types of rocks (Dietrich and Skinner, 1979; Oelkers and Valsami-Jones, 2008). In igneous and metamorphic (crystalline) rocks, the main phosphate-bearing mineral is fluorapatite, whereas in sedimentary (siliciclastic and carbonate) rocks, phosphorous is typically associated with detrital fluorapatite and authigenic carbonate-fluorapatite ($Ca_{9.316}Na_{0.36}Mg_{0.144}(PO_4)_{4.8}(CO_3)_{1.2}F_{2.48}$) (Guidry and MacKenzie, 2003; Oelkers and Valsami-Jones, 2008). Monazite, a compound of rare-earth elements and phosphate, is rare, but can be found in high-grade metamorphic and granitic intrusions in parts of the eastern United States (Feiss and others, 1991). About 25 percent of United States monazite production is from the Carolina Slate Belt in the Piedmont Physiographic Province, which extends from southern Virginia to northern Georgia (Feiss and others, 1991).

Although apatite is a common accessory mineral in many types of rocks, the assumption that apatite is the dominant "natural" source of dissolved phosphorus in groundwater may be incorrect. Feldspars are widely distributed and are the dominant mineral (40–50 percent) in igneous, metamorphic, and associated siliciclastic sedimentary rocks that constitute the continental crust of the Earth (Dietrich and Skinner, 1979; Krauskopf, 1979). Due to their abundance and their potential to contain trace amounts of phosphorus through the Berlinite substitution, where phosphorus and aluminum can replace silicon in the mineral lattice ($2Si^{4+} = Al^{3+} + P^{5+}$), feldspars can account for 50 to 90 percent of the estimated crustal P_2O_5 content (Manning, 2008). Feldspars in granite can contain up to 1 percent P_2O_5 in this form, but more commonly they contain 0.2 to 0.3 percent (Kontak and others, 1996). Accordingly, the formula for alkali feldspar containing 0.3 percent P_2O_5 can be written as $(Na,K)Al_{1.011}Si_{2.978}P_{0.011}O_8$.

Whether dissolved phosphorus has originated from natural biological or anthropogenic sources, or the weathering of rocks, its transport may be affected by the presence of certain dissolved elements or its contact with common minerals, plants, and microorganisms. Dissolved calcium, aluminum, and iron can combine with phosphate to form sparingly soluble phosphate minerals such as apatite, variscite ($AlPO_4 \cdot 2H_2O$), or strengite ($FePO_4 \cdot 2H_2O$), for example, which may limit phosphate availability in water (McBride, 1994; Oelkers and Valsami-Jones, 2008). In anoxic environments, the ferrous phosphate mineral vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) also may limit dissolved phosphorus concentrations (Drever, 1997). Furthermore, concentrations of dissolved phosphate may be limited by adsorption to surfaces of other solids such as calcium carbonate, aluminum oxides and silicates, and hydrous iron and manganese oxides (Kuo and Lotse, 1972; Borggaard, 1983; Parfitt, 1989; Borggaard and others, 1990; Geelhoed and others, 1997; Maine and others, 2007; Filippelli, 2008). Adsorption or coprecipitation of phosphate with calcium carbonate could account for the active removal of dissolved phosphate from groundwater in carbonate aquifers, for example (Jarvie and others, 2005), and from sewage effluent in constructed wetlands (Maine and others, 2007).

Adsorption-desorption processes and biological uptake-decay processes tend to occur at faster rates than mineral dissolution-precipitation processes; they also tend to sequester phosphorus as more labile forms (Bennett and others, 2001; Filippelli, 2008). Hydrous ferric oxides, such as goethite (FeOOH) and ferrihydrite ($Fe(OH)_3$), that commonly form in well-drained soils and other oxidizing environments, for example, can be important as sinks or sources of dissolved phosphate in aquatic environments. At typical pH (5–8) of natural water, dissolved phosphate species ($H_2PO_4^-$, HPO_4^{2-}) tend to be strongly adsorbed by hydrous ferric oxides, with sorption increasing as pH decreases (Dzombak and Morel, 1990; Geelhoed and others, 1997). Such phases commonly constitute the main, long-term storage pool for soil phosphorus (Filippelli, 2008). Accordingly, a large fraction of phosphorus transported by runoff may be associated with iron oxide coatings on soil particles (Eghball and others, 1996; Pionke and others, 1999). The sorbed phosphate may be displaced by other ions such as silica and sulfate, however (Obihara and Russell, 1972; Parfitt, 1989; Geelhoed and others, 1997), and, if subjected to reducing conditions, the oxidized iron compounds may dissolve, releasing phosphorus (Borggaard, 1983; Ehrlich, 1990). The reductive dissolution of ferric oxides typically is coupled with the oxidation of organic compounds after supplies of dissolved oxygen, nitrate, and nitrite and manganese oxides have been depleted (Stumm and Morgan, 1996; Drever, 1997; McMahon and Chapelle, 2008). Consequently, dissolved phosphorus, iron, and manganese concentrations may be elevated in anoxic aquatic environments that lack dissolved nitrate and nitrite, and dissolved phosphorus concentrations may be diminished through sorption and coprecipitation reactions in oxidizing aquatic environments with abundant iron and aluminum oxides and (or) calcium carbonates.

Phosphorus cycling in the aquatic environment is complex. Once phosphorus enters the aquatic environment, concentrations are largely controlled by plant uptake and degradation and by geochemical reactions (Drever, 1997). During photosynthesis, plants will grow until the available phosphorus or nitrate is depleted, at which point photosynthesis ceases and respiration and decay begin. Naturally occurring bacteria degrade plant matter, releasing phosphorus and other chemical constituents back to the aquatic system. Under natural conditions, the cycle of biological uptake and decay generally maintains a nutrient balance. Anthropogenic inputs of nutrients and processes such as bacterial denitrification can disrupt the balance, however—bacterial denitrification can lead to the accumulation of excess phosphate and the deposition of inorganic phosphate compounds such as carbonate fluorapatite (Ehrlich, 1990).

Description of Study Area

The Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces (Fenneman and Johnson, 1946) study area includes 368,000 km^2 (square kilometers) in parts of 11 states and the District of Columbia and extends from northern Alabama to New Jersey in the eastern United States (fig. 1). Land characteristics, geology, hydrology, and water quality in the area are described in detail in Hollyday and Hileman (1996), Rutledge and Mesko (1996), Briel (1997), Trapp and Horn (1997), Swain and others (2004), and Lindsey and others (2006), and are summarized below.

Physiography and Geology

The study area is underlain by consolidated sedimentary (siliciclastic or carbonate) and crystalline (igneous or metamorphic) bedrock and includes areas of steep topography and considerable relief. Unconsolidated regolith (weathered rock) overlies the bedrock in most areas, and is typically thinner in uplands than in adjacent valleys. Topographic features (mountains and valleys) are generally aligned from southwest to northeast (Fenneman and Johnson, 1946). Land-surface altitudes range from around 90 m (meters) in Piedmont Lowlands to over 1,800 m in the highest peaks of the Blue Ridge Mountains.

The Valley and Ridge Province (fig. 1) is underlain by folded and faulted, unmetamorphosed sedimentary bedrock. Siliclastic rocks (shale, sandstone, arkose, greywacke, and conglomerate) dominate in uplands, whereas carbonate rocks (limestone and dolomite) dominate in valleys (Swain and others, 1991). Karst terrain with associated caves, sinkholes, and other solution features is common in the carbonate valleys (Hollyday and Hileman, 1996). The rocks of the Valley and Ridge are structurally deformed by folding and thrust faulting, which are important controls on the landforms and the orientation and abundance of fractures (Woodward, 1985).

The Blue Ridge Province (fig. 1) is an area of high relief that is underlain by crystalline and siliciclastic bedrock. Crystalline metamorphic and igneous rocks dominate northward from Virginia, and metamorphic and sedimentary rocks dominate southward from North Carolina (Mesko and others, 1999). Metamorphic rocks are generally more abundant than igneous rocks in the crystalline terrains. Sedimentary rocks are predominantly sandstone, shale, and conglomerate and include minor coal in North Carolina and Virginia. As in the Valley and Ridge, the rocks of the Blue Ridge are faulted, folded, and fractured.

Crystalline metamorphic and igneous rocks underlie 92 percent of the Piedmont Province (fig. 1). The crystalline rocks generally are resistant to erosion and form hilly terrain of moderate relief (Lindsey and others, 2006). Siliciclastic rocks underlie approximately 7 percent of the Piedmont and are present from northern North Carolina to New Jersey. Siliciclastic rocks in the Piedmont are primarily restricted to fault-bound basins in the surrounding crystalline-rock lowlands. The basins contain sequences of Triassic and Jurassic sandstone and siltstone that can exceed a total thickness of 6,000 m (Bain and Brown, 1981). Carbonate rocks, including limestone, dolomite, and marble, also are present in the Piedmont of Maryland and Pennsylvania. Marble also is present in other parts of the Piedmont, but is a minor rock type compared to the igneous and other metamorphic rocks (Overstreet and Bell, 1965).

Climate and Hydrology

Climate in the study area is humid and primarily temperate to subtropical (Swain and others, 1991). Average annual precipitation (from 1951 through 1980) ranged from 1,020 to 1,270 mm/yr (millimeters per year) in most of the Piedmont and Blue Ridge Provinces to over 1,500 mm/yr in the southern part of the Blue Ridge in North and South Carolina, Tennessee, and Georgia (Swain and others, 1991).

Groundwater flow in the study area occurs primarily in fractures, solution cavities, and other secondary openings in the generally impermeable bedrock, and in intergranular and secondary voids in the overlying regolith. Local and regional groundwater-flow systems are defined by topography and associated hydraulic gradients, and the influence of geologic structure and mineral weathering on the formation of secondary voids in the rocks. The regolith serves as a reservoir for storage of recently recharged water and supplies recharge to the fractures in the underlying crystalline and siliciclastic bedrock and contributes to stream base flow (Heath, 1980). In contrast with the crystalline and siliciclastic bedrock, fractures and other secondary openings are commonly enlarged by dissolution of the carbonate bedrock, and groundwater flow can be rapid (Lindsey and others, 2006). Due to the extensive secondary porosity, carbonate aquifers typically provide much greater well yields than crystalline or siliciclastic aquifers.

Groundwater typically flows along relatively short flow paths from recharge areas in uplands to discharge areas in local streams or springs, although the direction of flow is controlled by the orientation of fractures and other secondary openings in the rock. Groundwater is an important component of flow to streams in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces. Previous studies in this region calculated the proportion of total streamflow derived from groundwater, referred to as the "base-flow index," to be greater than 50 percent in most areas (Bachman and others, 1998; Rutledge and Mesko, 1996).

The overall relations among major bedrock type, geohydrology, 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 terrains, slow weathering of silicate minerals tends to produce natural groundwater with low concentrations of dissolved solids, alkalinity, and hardness. In contrast, in the siliciclastic-rock and carbonate-rock terrains, because of faster weathering of carbonates and associated minerals, the water commonly has greater concentrations of dissolved solids, alkalinity, and hardness under natural conditions than water in the adjacent crystalline rocks (Risser and Siwiec, 1996)

Land Use and Anthropogenic Phosphorus Sources

Land cover in the study area is primarily forest, particularly in areas of steep topography and along relatively inaccessible ridge tops (fig. 2). Agricultural and urban land uses are present primarily in the valleys in the Valley and Ridge and in flatter areas of the Piedmont. Many of these areas are underlain by carbonate rocks, and local groundwater is therefore particularly vulnerable to contamination from human activities (Lindsey and others, 2009). Areas of intensive agriculture include the Great Valley in the northern Valley and Ridge and the northern Piedmont. Densely populated urban areas include those around Atlanta, Washington, D.C., Philadelphia, and New York City.

Although phosphorus may be derived from a variety of sources, anthropogenic sources such as inorganic fertilizer, manure, and sewage generally dominate in agricultural and urban areas. In the Potomac River Basin, the wider Chesapeake Bay watershed, and the Albemarle and Pamlico Sound watersheds, most of the phosphorus in surface water is derived from fertilizer and manure; point sources such as sewage effluent are relatively minor contributors (Blomquist and others, 1996; Spruill and others, 1998; Alexander and others, 2008). Additional anthropogenic sources of phosphorus can be important locally, such as industrial discharges to the South Fork Catawba River in South Carolina (Hughes and others, 2000), and combined and sanitary sewer effluent in urban and suburban areas (Frick and others, 1998; Hampson and others, 2000).

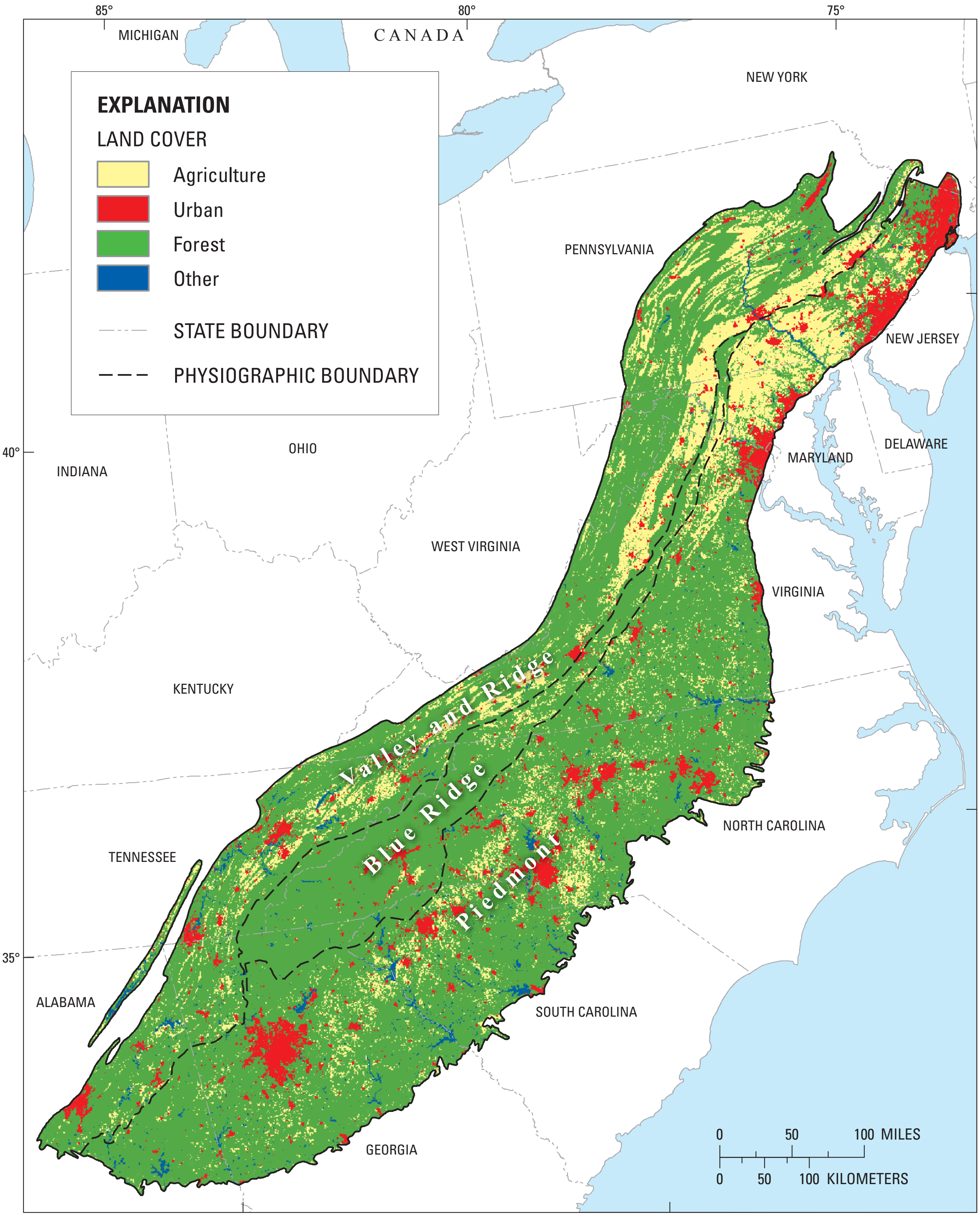
Phosphorus from fertilizer and manure can be removed from soil water by plant uptake, adsorption, and mineral precipitation processes (McBride, 1994; Drever, 1997; Litke, 1999). Thus, phosphorus unused by crops tends to be retained in the upper soil horizons in association with minerals or biomass (Sharpley and others, 2003). Where fertilizer or manure is repeatedly applied to agricultural fields, disposal sites, and urban lawns, however, the phosphorus retention capacity of the soil may be exceeded (Eghball and others, 1996; Beauchemin and others, 1996, 1998). Consequently, runoff and soil water that infiltrates to groundwater may contain elevated concentrations of dissolved phosphate (Sharpley and others, 1994, 2003).

Methods

Groundwater and stream-quality data collected as part of the USGS NAWQA Program (Gilliom and others, 1995) from 1991 through 2007 were compiled to support a regional interpretation of water quality (particularly phosphorus concentrations) in the study area. The NAWQA design is discussed in Gilliom and others (1995) and Lapham and others (1995); protocols for collection of water-quality data are presented in Shelton (1994) and Koterba and others (1995).

Data Compilation

Groundwater data were collected from 609 bedrock wells in 18 networks that were designed to document and explain the occurrence and distribution of selected chemical compounds in groundwater in particular settings (Gilliom and others, 2006) (table 2, fig. 3). A variety of crystalline, siliciclastic, and carbonate bedrock types with associated lithologies were sampled by use of these wells. Stream base-flow water-quality data were collected and compiled from 358 streams in 18 networks in the study area, which are commonly co-located with groundwater networks. Data include analyses from one round of sampling in each network. The base-flow stream-synoptic surveys (table 2) were designed to assess the quality of water in small streams of particular settings during base-flow conditions when groundwater supplies most of the streamflow. Most of these data were collected from the late spring through the late summer. Although the groundwater quality and stream-synoptic survey data were collected over a period of 17 years (from 1991 through 2007), the data were assumed to be comparable for the purpose of evaluating spatial patterns in water quality for this study. Additionally, routine (typically monthly) water-quality data collected over multiyear periods at 40 streams in the study area were compiled for evaluation of seasonal or temporal patterns in stream base flow in selected settings. Selected data from these compilations are presented in this report; all data compiled for this report are



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. Generalized land use and land cover in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces.

Table 2. Description of groundwater and surface-water networks in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces.

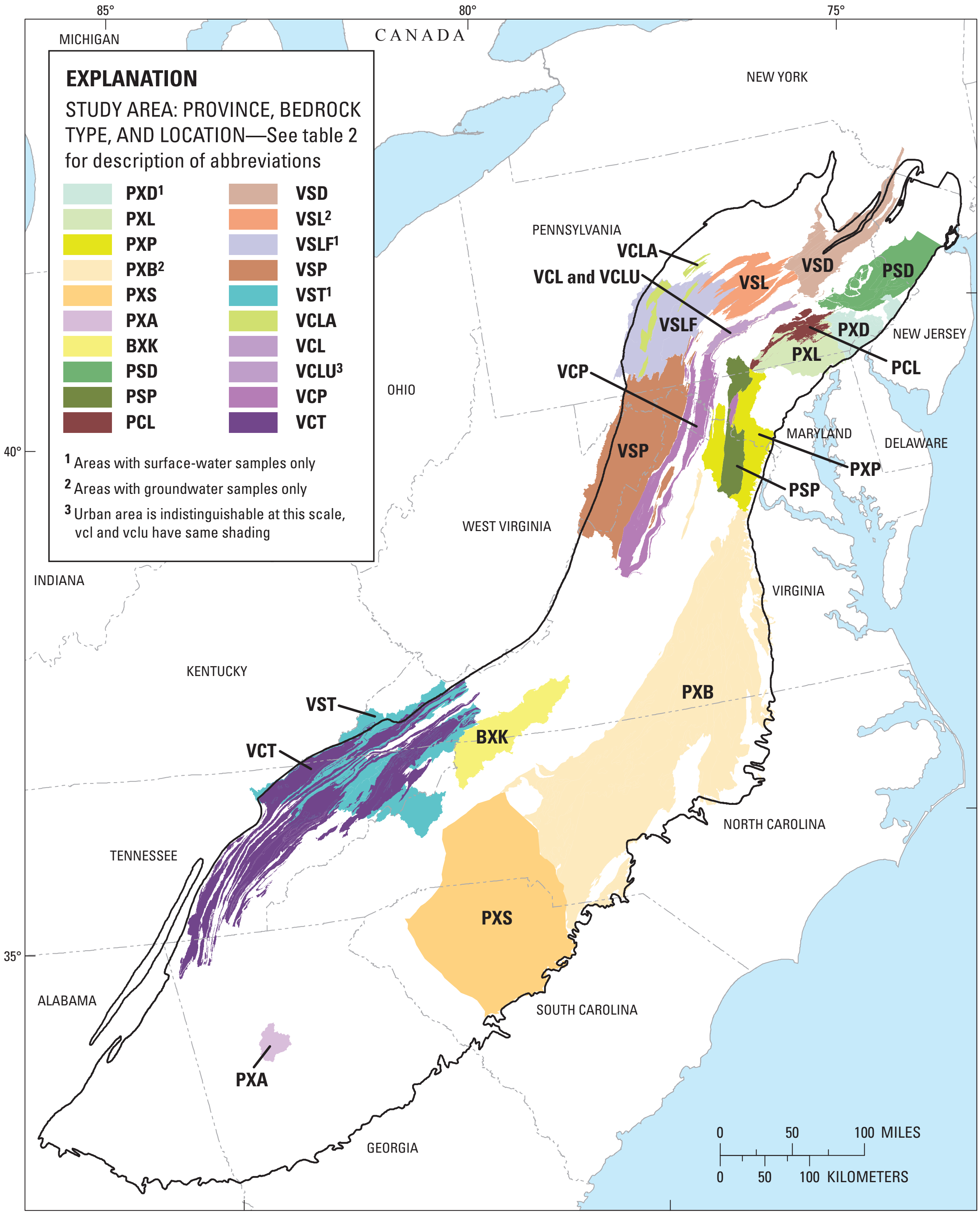
[Network code abbreviations: P=Piedmont, V=Valley and Ridge, B=Blue Ridge, X=crystalline, S=siliciclastic; C=carbonate, third letter in network code indicates location; F=forest; "-" indicates no samples collected; predominant land-use designations: AG = predominantly agricultural (greater than 50 percent agricultural and less than 5 percent urban), URB = predominantly urban (greater than 25 percent urban and less than 25 percent agricultural), UND = predominantly undeveloped (less than 25 percent agricultural and less than 5 percent urban), MIX = mixed land use (any sampling site not meeting the criteria for AG, URB, or UND)]

Network code	River Basin/Location	Predominant Land Use		Principal Aquifer/ Physiographic Province
		Groundwater	Surface water	
		Crystalline Bedrock		
PXD	Delaware/Northern New Jersey	URB	MIX	Piedmont and Blue Ridge crystalline rock
PXL	Lower Susquehanna	AG	AG	Piedmont and Blue Ridge crystalline rock
PXP	Potomac	MIX	MIX	Piedmont and Blue Ridge crystalline rock
PXB	Albemarle-Pamlico	MIX	-	Piedmont and Blue Ridge crystalline rock
PXS	Santee	UND	MIX	Piedmont and Blue Ridge crystalline rock
PXA	Apalachicola-Chattahoochee-Flint	URB	MIX	Piedmont and Blue Ridge crystalline rock
BXK	Kanawha-New	MIX	UND	Piedmont and Blue Ridge crystalline rock
		Siliciclastic Bedrock		
PSD	Delaware	MIX	MIX	Early Mesozoic basin (Piedmont)
PSP	Potomac	AG	AG	Early Mesozoic basin (Piedmont)
VSD	Delaware	MIX	MIX	Valley and Ridge siliciclastic rock
VSL	Lower Susquehanna	AG	-	Valley and Ridge siliciclastic rock
VSLF	Lower Susquehanna	-	UND	Valley and Ridge siliciclastic rock
VSP	Potomac	AG	UND	Valley and Ridge siliciclastic rock
VST	Upper Tennessee	-	UND	Valley and Ridge siliciclastic rock
		Carbonate Bedrock		
PCL	Lower Susquehanna	AG	AG	Piedmont carbonate-rock
VCLA	Lower Susquehanna (Appalachian Section)	AG	AG	Valley and Ridge carbonate-rock
VCL	Lower Susquehanna (Great Valley Section)	AG	AG	Valley and Ridge carbonate-rock
VCLU	Lower Susquehanna (Urban)	URB	MIX	Valley and Ridge carbonate-rock
VCP	Potomac	AG	MIX	Valley and Ridge carbonate-rock
VCT	Upper Tennessee	MIX	MIX	Valley and Ridge carbonate-rock

accessible on the World Wide Web at *http://infotrek.er.usgs.gov/traverse/f?p=NAWQA:HOME:0*.

Most samples were analyzed for selected nutrients (including phosphorus and nitrogen compounds), major ions, various trace elements (including iron, manganese, and aluminum), and dissolved organic carbon (DOC), as well as temperature, specific conductance (SC), pH, and concentrations of dissolved oxygen (DO). Nutrient, major-ion, and DOC 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). The water temperature, SC, pH, and DO concentrations were measured in the field immediately prior to sample collection. Bicarbonate concentrations were calculated on the basis of alkalinity titrations conducted in the field.

Water-quality data were screened to maximize their utility for evaluating regional patterns in phosphorus concentrations and possible water-quality relations between groundwater and streams in the study area. Water-quality data from streams draining watersheds containing known sewage outfalls or other point sources were omitted, as phosphorus loads from such sources often greatly exceed those from natural sources and (or) groundwater discharge. Water-quality samples collected from streams during periods of known or likely overland runoff (such as following precipitation) also were omitted. Total and dissolved concentrations of phosphorus were determined for surface-water samples. Because only dissolved concentrations of phosphorus and other constituents occur in groundwater, however, analyses for dissolved phosphate (also referred to as orthophosphate) were used for



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

Principal Aquifers from U.S. Geological Survey, 2003

Figure 3. The distribution of groundwater and surface-water sampling networks in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces.

all comparisons of phosphorus concentrations between surface water and groundwater.

Ancillary geospatial data were compiled to describe the physical characteristics of the watersheds draining to sampled streams and the potential contributing areas within 500 m of sampled wells. Each surface-water and groundwater sampling site was classified on the basis of the bedrock type (crystalline, siliciclastic, or carbonate) and physiographic setting (table 2). Land-cover data were compiled and used to compute the percentage of four major land uses (wetland, forested, agricultural, and urban) within 500 m of sampled wells and within watersheds of sampled streams. 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).

Graphical and Statistical Analyses

Various graphical and statistical techniques were used to compare water quality in different geologic settings, to estimate natural and anthropogenic sources of phosphate, and to identify possible factors affecting the transport of phosphate from groundwater to streams in the study area. In general, nonparametric, rank-based statistical approaches were used to accommodate non-normally distributed and censored data (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 lower common level before ranks were computed for use in statistical tests. Relations between continuous variables were evaluated with scatter plots and correlation coefficients (Spearman's rho, Kendall's tau); distributions of continuous variables were compared among different groups (such as geologic settings) using boxplots and rank-sum or rank-transform analysis-of-variance (ANOVA) (Helsel and Hirsch, 2002).

Groundwater and stream interactions within and among different geologic settings were evaluated using graphical techniques. Considering bedrock and redox classifications, boxplots and probability graphs were used to compare univariate distributions of the water-quality data (Helsel and Hirsch, 2002). The redox class was determined on the basis of concentrations of DO, nitrate, manganese, iron, and sulfate (McMahon and Chapelle, 2008). Trilinear diagrams (Drever, 1997) were used to illustrate dominant geochemical conditions in streams and groundwater in different settings and infer likely interactions between regional groundwater and stream base flow. The relative contribution of base flow to total streamflow over multiyear periods and during collection of individual samples at continuously monitored streams was evaluated by hydrograph separation with the PART computer program (Rutledge, 1998). The relative importance of groundwater discharge and overland runoff to the transport of selected chemical compounds to continuously monitored streams in different settings was inferred through evaluations of the relation between concentrations and flow condition (stream discharge).

Geochemical Modeling

Geochemical models were developed to explain relations among concentrations of dissolved phosphate and other constituents in groundwater and stream water. Aqueous speciation computations with WATEQ4F (Ball and Nordstrom, 1991) and mass-transfer computations with PHREEQC (Parkhurst and Appelo, 1999) using the WATEQ4F database were used to test the following hypotheses: (1) evaporation of typical rainfall and dissolution of minerals can produce observed concentrations of phosphate and other trace constituents in "natural" (background) groundwater; (2) mineral-solubility processes can explain the range of concentrations of phosphate in groundwater and surface water in different geologic settings; and (3) even if they are undersaturated with phosphate minerals, adsorption of phosphate by hydrous ferric oxide, aluminum oxide, and (or) calcium carbonate minerals could be an important control on dissolved phosphate concentrations.

Inverse modeling with PHREEQC was used to evaluate mass-transfer processes that could feasibly produce the observed concentrations of constituents in the groundwater and surface-water samples (Parkhurst and Appelo, 1999; Nordstrom, 2003). The first set of models simulated reactions between partially evaporated rainfall (concentrated by a factor of 3) and ubiquitous mineral phases that could produce background groundwater quality for each geologic setting (crystalline, siliciclastic, or carbonate bedrock). The background quality was estimated using the medians for samples with measurable DO (greater than 0.5 mg/L), but concentrations of nitrate less than 1.0 mg/L and chloride less than 10 mg/L. Censored concentrations were set at half the detection limit for aqueous speciation and mass-transfer calculations.

A second set of inverse models was developed to evaluate possible anthropogenic sources of phosphate and associated contaminants (NO_3, Cl, Na, and K) in groundwater and streams of the study area. Paired groundwater- and surface-water-quality datasets that indicated primarily natural conditions or human impacts on water quality in specific land-use and geologic settings (networks) were selected for these models. The median water quality for all samples in a specific network was used to estimate the composition of the groundwater (initial solution) and the surface water (final solution). Censored concentrations were set at half the detection limit.

The generalized mineral assemblage for a particular bedrock setting, based on lithogeochemical classifications, and the computed saturation index (SI) values for various minerals were used to constrain the mineral reactants and products in the inverse models (Nordstrom, 2003). If the initial and final solutions were undersaturated (SI less than 0) with respect to the mineral phase, that phase was specified to dissolve (reactant). Likewise, if the initial and final solutions were supersaturated (SI greater than 0) with respect to a mineral, that phase was specified to precipitate (product) or was excluded from the mass-transfer model.

Adsorption and desorption of phosphate on hydrous ferric oxide-coated surfaces were evaluated using a diffuse double-layer modeling approach with PHREEQC (Parkhurst and Appelo, 1999) and surface complexation data from Dzombak and Morel (1990). The hydrous ferric oxide was specified as a 0.09 grams per kilogram solution, with a specific surface area of 600 cubic meters per gram consisting of 5 x 10^{-6} moles of strong binding sites and 2 x 10^{-4} moles of weak binding sites. Aqueous speciation and adsorption distribution for a range of pH values were computed for initial phosphate concentrations of 0.001 mol/kg (moles per kilogram, or 31 mg/L) and 0.1 mol/kg (3,100 mg/L) in a 10-mol/kg sodium chloride background matrix. Plots were created to summarize the percentage of phosphate distributed between the solution and sorbent as a function of pH.

Contributions of Phosphorus from Groundwater to Streams

Phosphorus from natural and human sources may be discharged from groundwater to streams in certain geochemical environments. Thus, some of the phosphorus in streams during base flow, when most water is discharging groundwater, is potentially derived from groundwater. Base flow is an important component of streamflow throughout the study area, comprising more than 50 percent of the total annual streamflow in most settings (fig. 4). The highest base-flow indices (which indicate the percentage of water in a stream that is from groundwater) are in the Valley and Ridge Carbonate setting and the lowest are in the Piedmont Siliciclastic setting. Estimated base-flow indices for streams included in this study are similar to, although somewhat higher than, those from previous studies in this area (Bachman and others, 1998; Rutledge and Mesko, 1996).

Phosphorus in Streams and Groundwater

Concentrations of dissolved phosphate in the study area varied by rock type, but commonly were higher in streams than in groundwater (fig. 5a). Dissolved phosphate concentrations in the 609 groundwater samples ranged from less than 0.01 to 0.54 mg/L, with a median of 0.010 mg/L; dissolved phosphate concentrations during base flow in 358 streams ranged from less than 0.01 to 1.23 mg/L, with a median of 0.016 mg/L. Median concentrations of dissolved phosphate in groundwater from crystalline and siliciclastic rocks (0.017 and 0.020 mg/L, respectively) were greater than median concentrations in groundwater from carbonate rocks (<0.01 mg/L) (fig. 5a). In contrast, the median concentrations of dissolved phosphate in streams draining crystalline and siliciclastic bedrock (0.010 and 0.014 mg/L, respectively) were less than those in streams draining carbonate bedrock (0.020 mg/L) (fig. 5a).

The reported concentrations of dissolved phosphate in streams during base flow were commonly higher than recommended ecoregion nutrient criteria (table 1, fig. 6). This finding is important as these criteria are based on total phosphorus

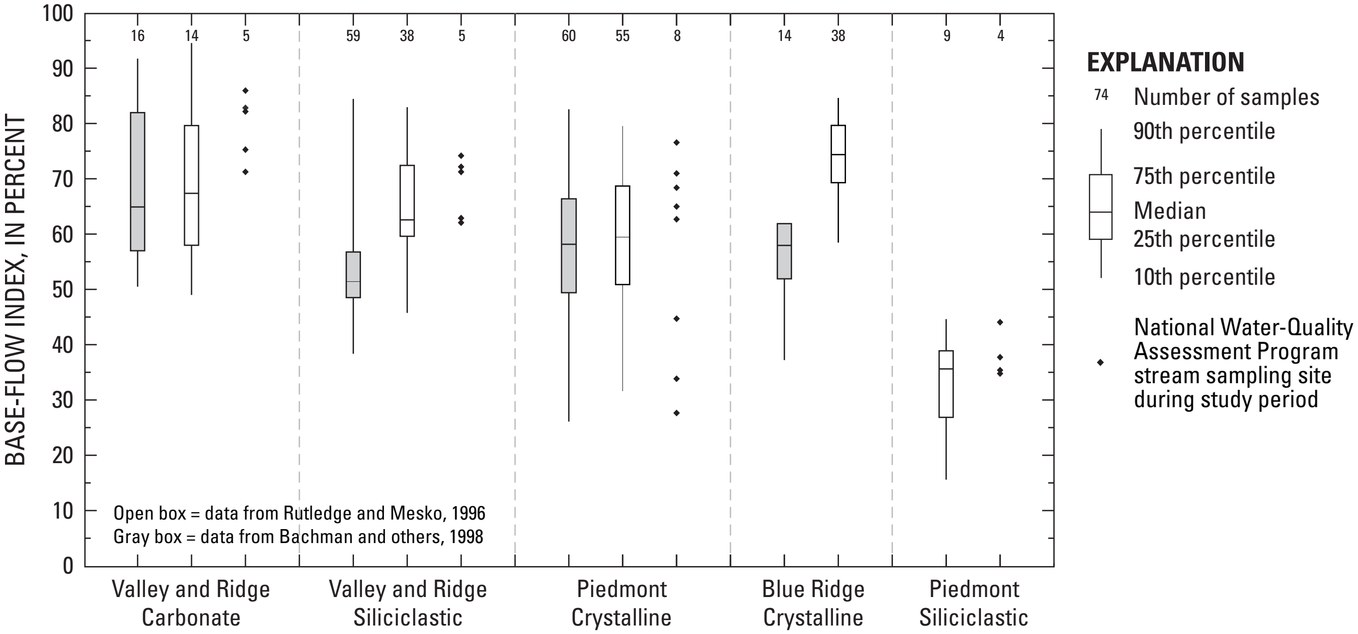


Figure 4. Base-flow indices for different bedrock types in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces.

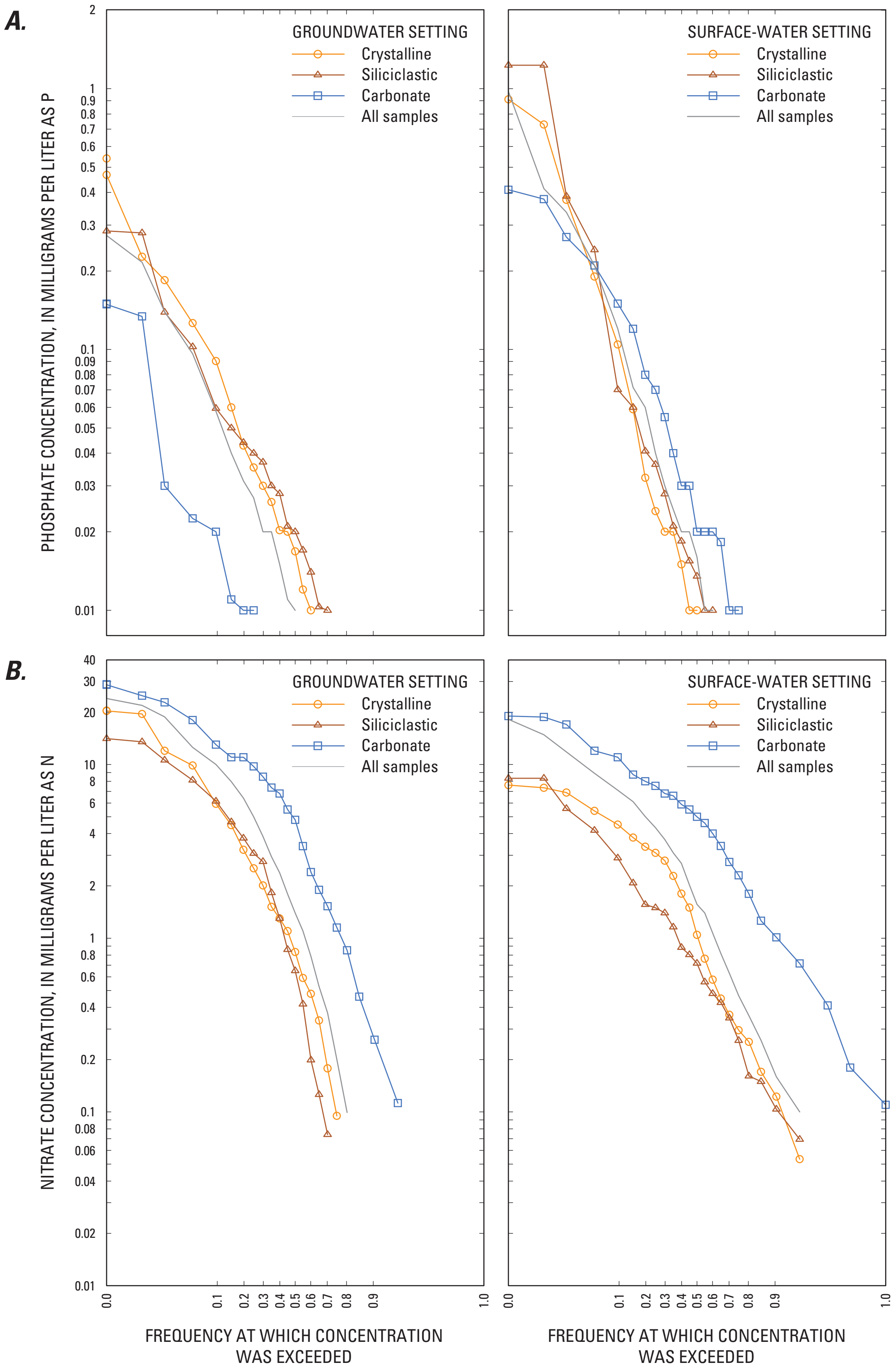


Figure 5. Distribution of dissolved concentrations of (*A*) phosphate and (*B*) nitrate in groundwater (left) and streams (right) for crystalline, siliciclastic, and carbonate bedrock of the Piedmont, Blue Ridge, and Valley and Ridge study area.

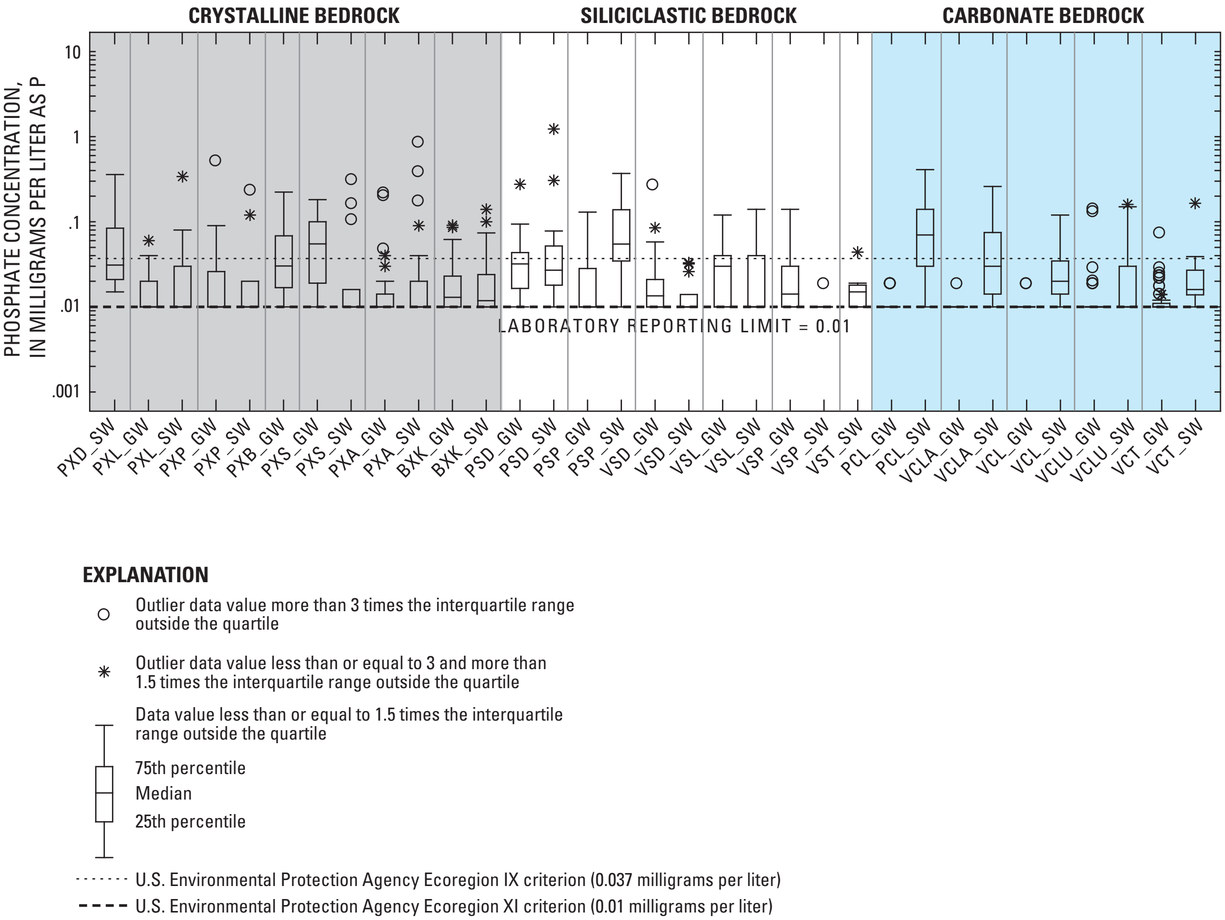


Figure 6. Concentrations of dissolved phosphate in groundwater and surface water by network for different bedrock types of the Piedmont, Blue Ridge, and Valley and Ridge study area.

concentrations, which include concentrations of both dissolved and particulate phosphorus. In the Piedmont, the phosphorus criterion of 0.037 mg/L was exceeded at some of the streams in each network and at more than half of the streams in the PSP and PCL networks (fig. 6; see table 2 for identification and description of networks). Median dissolved phosphate concentrations in four carbonate and two siliciclastic synoptic stream networks exceeded the 0.01-mg/L criterion in the Valley and Ridge (fig. 6). Phosphorus concentrations during base flow may vary seasonally in streams and are often higher during the summer (fig. 7), when most synoptic samples were collected for this study.

Although the recommended ecoregion nutrient criteria apply specifically to streams, concentrations of dissolved phosphate greater than regional criteria in groundwater are noteworthy as a potential source of phosphorus to streams. Dissolved phosphate was consistently present in groundwater from the crystalline and siliciclastic aquifers, but seldom greater than 0.01 mg/L in carbonate aquifers (fig. 6). In the Piedmont, the median phosphate concentration in groundwater exceeded the criterion only in the PXS network (table 2); the lower Blue Ridge and Valley and Ridge criterion was exceeded by the median concentrations of all three Valley and Ridge siliciclastic networks and in the crystalline Blue Ridge network (fig. 6).

Although phosphate concentrations commonly differed between groundwater and surface water in a given bedrock setting or sampling network (figs. 5 and 6), there were similarities in the major-ion characteristics of the groundwater and surface water in each setting (fig. 8). The differences in major-ion composition among the three major bedrock types resulted from variable contributions from predominant minerals, such as carbonates in the carbonate setting and silicates and sulfides in the other settings. Although the similarity in major-ion proportions for the groundwater and surface water of a particular setting indicates common water-rock interactions in that setting, additional processes such as dilution and evaporation (atmospheric exchange) plus contributions from anthropogenic sources affect the concentrations of dissolved ions and associated water-quality characteristics such as specific conductance, pH, and DO. An increase in the proportion of nitrate and chloride is apparent for waters impacted by human activities in all three settings (fig. 8). This increase was observed in surface water more commonly than in groundwater.

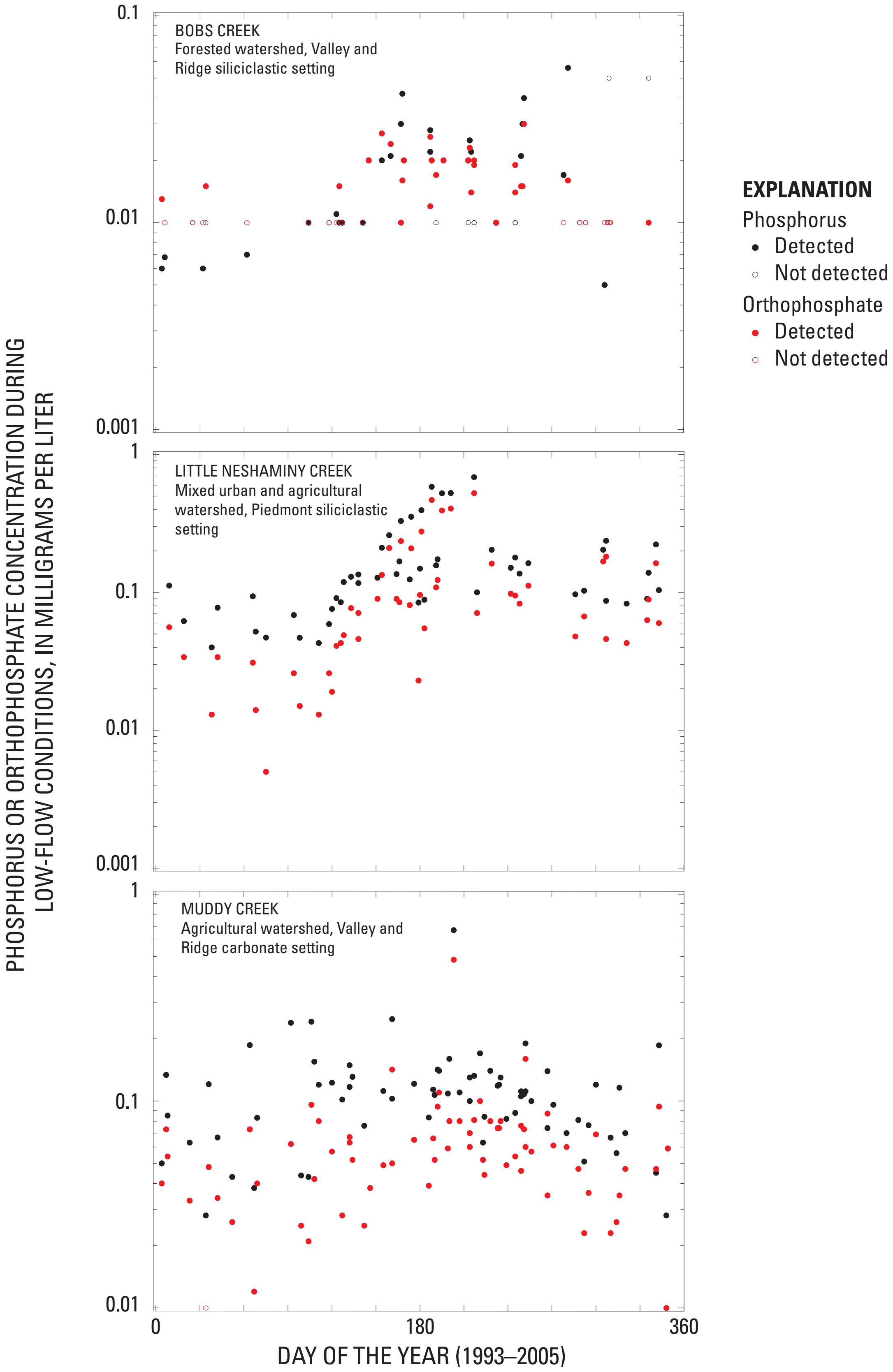


Figure 7. Seasonal trends in base-flow concentrations of phosphorus in three streams draining watersheds of varying hydrogeologic and land-use characteristics.

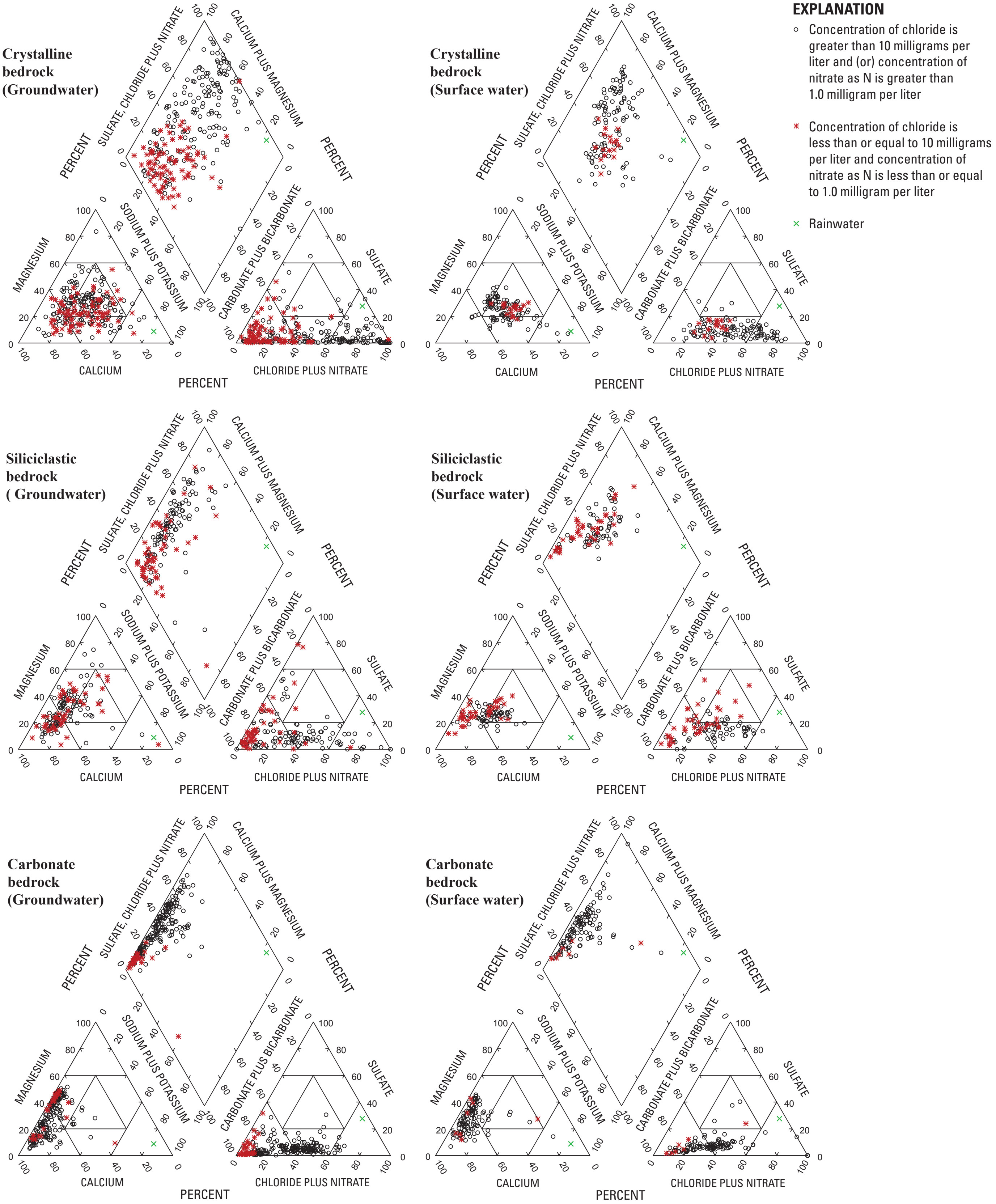


Figure 8. Major-ion composition of groundwater and stream base-flow samples from different bedrock settings of the Piedmont, Blue Ridge, and Valley and Ridge study area.

Sources, Fate, and Transport of Phosphorus

Identification of the source(s) of phosphorus in water samples is complicated by multiple sources and hydrological, geochemical, and biological processes affecting phosphorus fate and transport. Groundwater sampled in a given network may not represent all of the water being discharged to streams, for example. In areas of carbonate bedrock, dissolved phosphate exceeded the detection limit of 0.01 mg/L in 75 percent of the surface-water samples but was detected in only 25 percent of the groundwater samples (fig. 5a). The greater frequency of detection of phosphorus in surface water could result from in-stream biological cycling of nutrients, as well as shallow or near-stream groundwater sources that are not represented by groundwater sampling. Greater phosphorus concentrations in relatively shallow groundwater than in deeper groundwater have been reported in areas of carbonate (Galeone and others, 2006) and siliciclastic (Lindsey and others, 2003) aquifers in the study area. Although shallow groundwater sources could be an important component of the stream base flow in some settings, most of the groundwater data available for this analysis represent deeper sources used for domestic supplies.

DO concentrations in groundwater generally were less than those in associated surface water in each of the three bedrock settings (fig. 9). Generally, concentrations of DO were lower in groundwater from the crystalline and siliciclastic bedrock aquifers than in groundwater from the carbonate aquifer, implying groundwater was not completely isolated from the atmosphere in the carbonate setting or that DO persists because of a lack of available electron donors to support its reduction in the flow system. After groundwater enters the stream environment, atmospheric exchange results in the loss of CO_2 and gain of O_2. The concentrations of these dissolved gases also can be influenced by photosynthesis by aquatic plants. As the concentration of dissolved CO_2 decreases, the pH tends to increase. Consequently, the pH of surface water typically was 0.5 to 1 unit higher than that of the associated groundwater (fig. 9). Such changes in DO and pH could affect phosphate mobility through processes involving dissolution-precipitation, oxidation-reduction, and adsorption-desorption reactions.

Information on the concentrations of various chemical constituents associated with mineral dissolution or a particular land use can help to resolve the sources and causes of variability in phosphorus concentrations in associated samples. Differences in the median specific conductance (an indicator of ionic strength) and dissolved silica (an indicator of groundwater age) between groundwater and surface water from paired networks indicate that other (unsampled) groundwater is contributing to stream base flow. Samples from many stream networks have lower median specific conductance and median concentrations of silica than samples from the paired groundwater network, which could indicate the stream is also receiving a substantial portion of flow from groundwater that is younger and more dilute (fig. 10, table 3). Conversely, specific conductance that is substantially higher in stream base flow than in sampled groundwater could indicate greater amounts of anthropogenic chemicals in shallow (unsampled) groundwater than in deeper (sampled) groundwater sources and (or) loss of surface water to evapotranspiration. For processes such as dilution and evapotranspiration, the specific conductance will decrease or increase, respectively, but the proportions of major ions will remain constant. In contrast, mineral dissolution and precipitation processes can change both the specific conductance and the proportions of constituents involved in such reactions.

The potential for human impacts on water chemistry also may be indicated by the presence of certain chemicals, in addition to phosphorus, that are associated with a particular land use and that are not commonly mobilized by mineral dissolution or desorption processes. Elevated concentrations of chloride and nitrate, in particular, can be indicators of human impacts. Both of these solutes are relatively mobile in groundwater and surface water, although nitrate may be reduced in areas with low DO. Elevated concentrations of chloride are associated with agricultural applications of “potash” (KCl) and manure and with discharges of sewage effluent, although the highest concentrations are associated with the application of road deicing salts such as sodium chloride (NaCl) and, more recently, calcium chloride ($CaCl_2$) in the northern part of this region. Chloride concentrations greater than 10 mg/L are substantially greater than background levels in atmospheric precipitation. Nevertheless, concentrations greater than 10 mg/L are common in many areas (fig. 11a).

Natural levels of nitrate in streams from rainfall and plant and animal sources are generally less than 1 mg/L in this region (Peters and Bonelli, 1982; Puckett, 1994; Holloway and others, 1998). Elevated concentrations of nitrate are most commonly associated with agriculture and turf (lawns, golf courses) in a watershed, and also with discharges from septic systems or sewage-treatment plants. The recommended nutrient criteria for nitrate in the Piedmont (0.69 mg/L) and Blue Ridge and Valley and Ridge (0.31 mg/L) were commonly exceeded in streams and groundwater in this study (table 1, figs. 5b and 11b). Although most groundwater is well-oxygenated (92 percent of 609 samples had DO concentrations greater than 0.5 mg/L), reducing conditions affect nitrate concentrations in groundwater in parts of this region, especially in groundwater in areas with siliciclastic rocks, where DO concentrations are frequently less than 0.5 mg/L (fig. 9a). Under such anoxic conditions, reduction of nitrate to gaseous nitrogen by bacterial denitrification can decrease nitrate concentrations to values that can not be detected (McMahon and Chapelle, 2008).

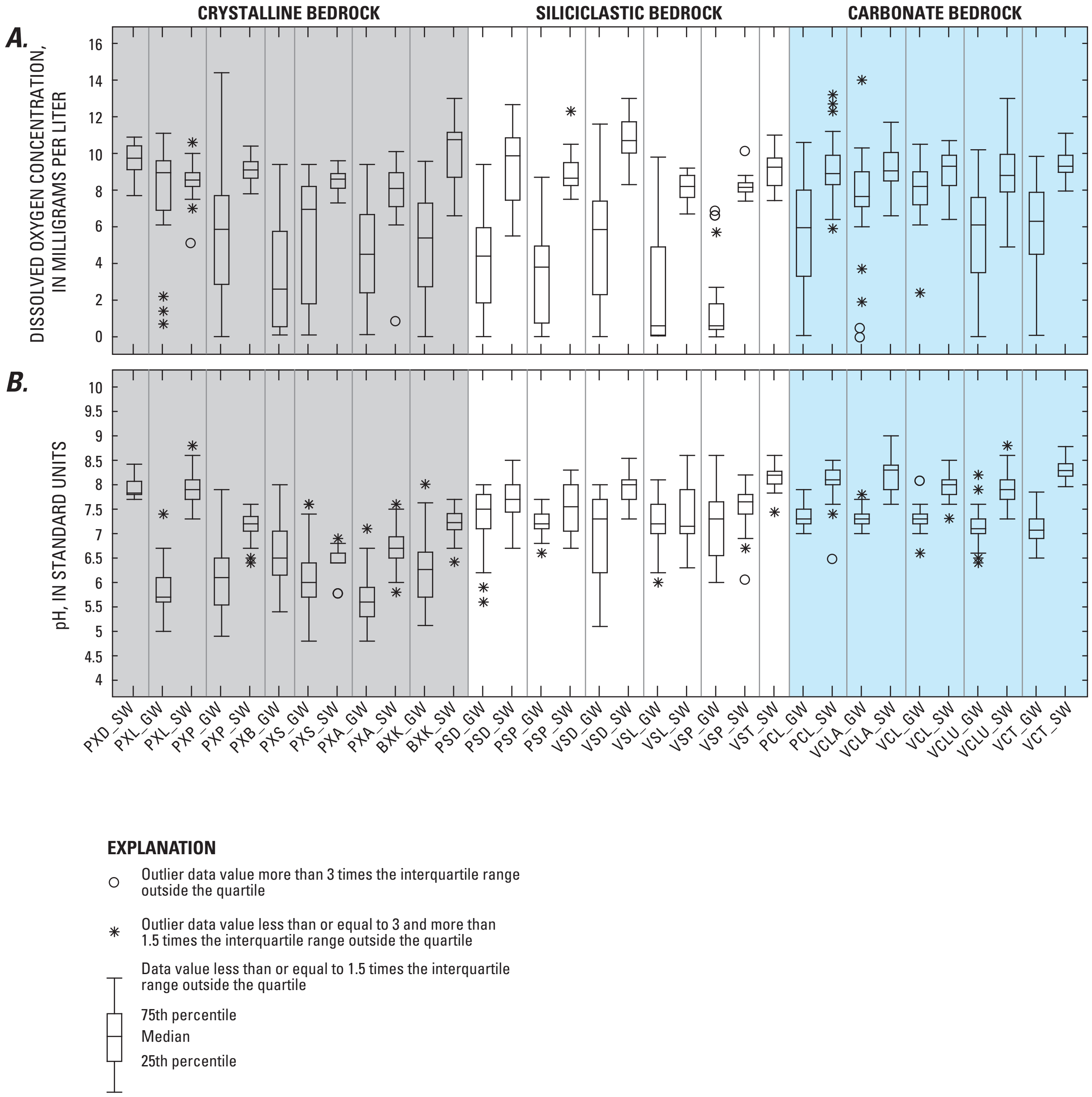


Figure 9. Comparison of (*A*) dissolved oxygen and (*B*) pH of groundwater and surface water by network for different bedrock types of the Piedmont, Blue Ridge, and Valley and Ridge study area.

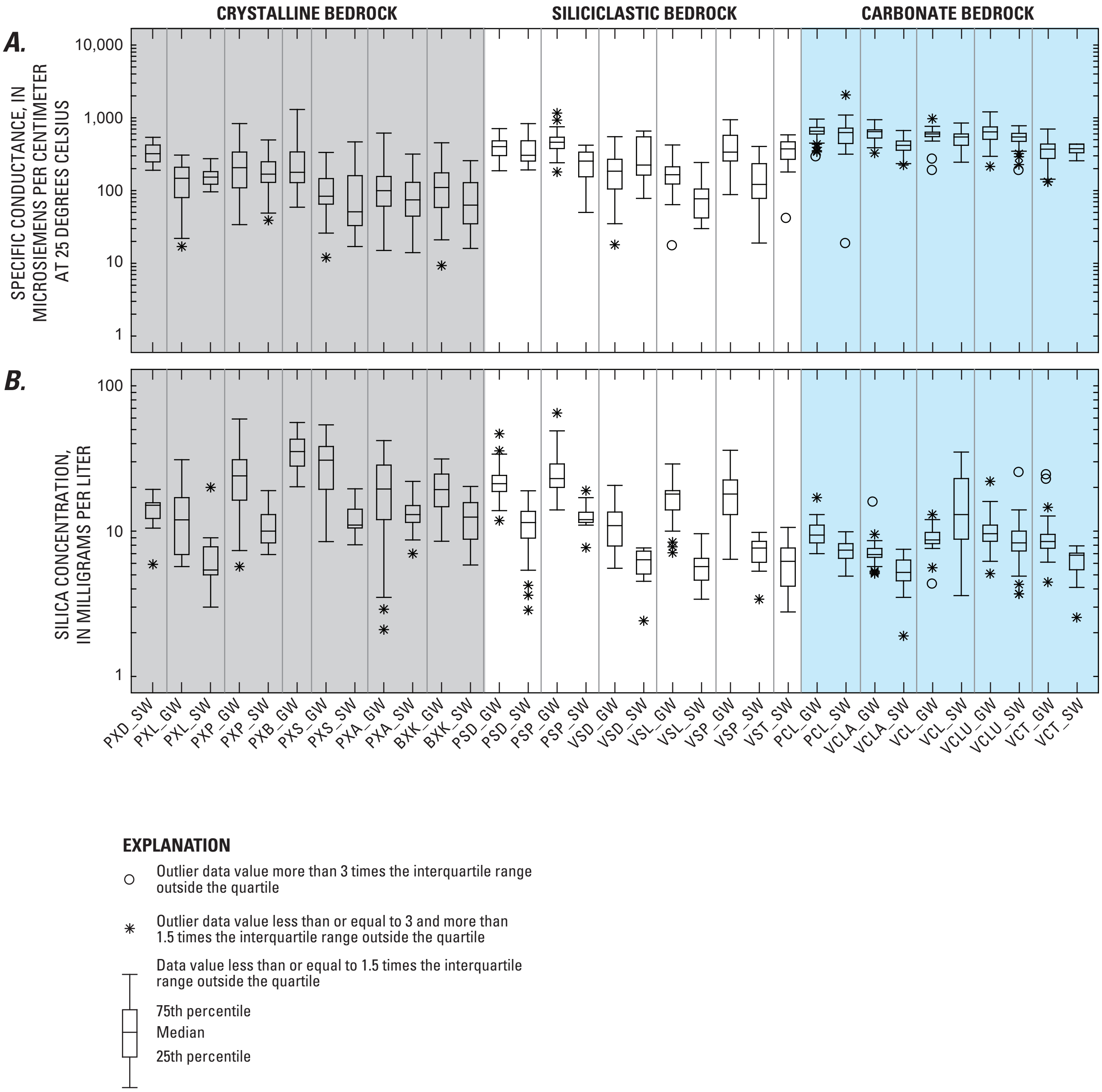


Figure 10. Comparison of (*A*) specific conductance, and (*B*) concentrations of dissolved silica in groundwater and surface water by network for different bedrock types of the Piedmont, Blue Ridge, and Valley and Ridge study area.

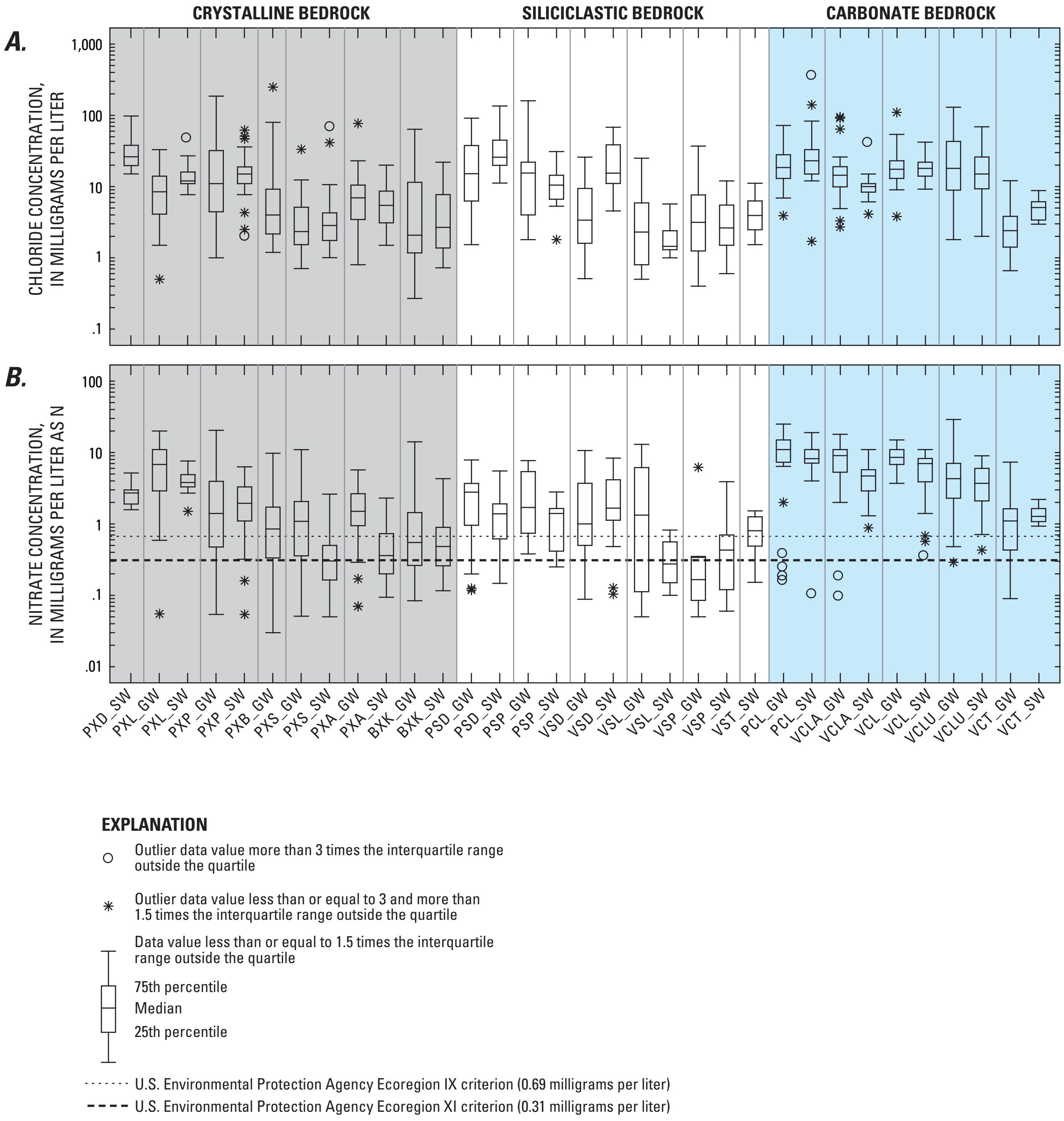


Figure 11. Comparison of (*A*) chloride and (*B*) nitrate in groundwater and surface water by network for different bedrock types of the Piedmont, Blue Ridge, and Valley and Ridge study area.

Table 3. Median concentrations of dissolved phosphate and associated water-quality constituents in groundwater and surface water from selected networks with natural or nearly natural water quality, or with water quality impacted by human activities in the Piedmont, Blue Ridge, and Valley and Ridge study area.

[Location of networks shown in figure 3; networks described in table 2; medians are shown as groundwater / surface water; mg/L, milligrams per liter; mS/cm, microsiemens per centimeter at 25 degrees Celsius; <, less than]

Constituent	Phosphate (PO_4-P, mg/L)	Nitrate (NO_3-N, mg/L)	Chloride (Cl, mg/L)	Silica (SiO_2, mg/L)	Specific conductance (SC, µS/cm)
			Networks with Natural Water Quality		
BXK	0.013 / 0.012	0.42 / 0.49	2.1 / 2.7	19.3 / 12.5	110 / 63
PXS	0.055 / <0.01	0.70 / 0.29	2.3 / 2.9	30.8 / 11.0	198 / 51
VSP	0.02 / <0.01	<0.05 / 0.42	3.2 / 2.7	18 / 7.7	340 / 122
VSL	0.03 / <0.01	0.13 / 0.28	2.3 / 1.5	18 / 5.7	165 / 77
VCT	<0.01 / 0.16	1.04 / 1.27	2.4 / 5.08	8.5 / 6.8	370 / 375
			Networks with Human Impacts on Water Quality		
PXL	<0.01 / <0.01	6.6 / 3.8	8.6 / 12	12 / 5.4	148 / 153
PSD	0.033 / 0.027	2.5 / 1.4	15.5 / 25.8	21.2 / 11.5	401 / 305
PCL	<0.01 / 0.07	11 / 8.2	18.5 / 23	9.4 / 7.4	654 / 626

Phosphorus from Natural Sources

To identify possible natural sources of phosphorus in groundwater, it is necessary to examine waters that are minimally impacted by human activities. Natural or nearly natural background conditions (NO_3-N less than 1 mg/L where the concentration of DO is greater than 0.5 mg/L and (or) that of Cl is less than 10 mg/L) were indicated for 62 of 246 (26.4 percent) groundwater samples from the crystalline bedrock setting, 24 of 154 (15.6 percent) samples from the siliciclastic bedrock setting, and 26 of 209 (12.4 percent) samples from the carbonate bedrock setting. For the natural groundwaters, the concentration of dissolved phosphate ranged from less than 0.01 to 0.285 mg/L, with medians of 0.029, 0.018, and less than 0.01 mg/L for the crystalline, siliciclastic, and carbonate bedrock settings, respectively. For the surface-water samples, natural conditions were indicated for 17 of 136 (12.5 percent) samples from the crystalline bedrock setting, 35 of 98 (35.7 percent) samples from the siliciclastic bedrock setting, and 7 of 124 (5.6 percent) samples from the carbonate bedrock setting. For these natural surface waters, the concentration of dissolved phosphate ranged from less than 0.01 to 0.074 mg/L, with medians of 0.01 mg/L for the carbonate bedrock setting and less than 0.01 mg/L for the crystalline and siliciclastic bedrock settings.

Natural or nearly natural water chemistry was indicated in both groundwater and surface water from two of the paired networks in the crystalline region (BXK and PXS; table 2) and two in the siliciclastic region (VSP and VSL) (table 3, fig 11). In addition, data from one carbonate network, VCT, represents water with concentrations of nitrate and chloride that were only slightly greater than the presumed natural levels. Elevated concentrations of dissolved phosphate in groundwater from these networks would be primarily associated with natural mineral sources, and could potentially be sources of phosphorus to surface water. In three of the networks, feldspar dissolution as a source of phosphorus could be indicated by dissolved phosphate concentrations in groundwater that are positively correlated with concentrations of silica (PXS: tau=0.53, $p<0.0001$; BXK: tau=0.34, $p=0.0118$; VSL: tau=0.31, $p=0.0347$). In the two Valley and Ridge siliciclastic networks, VSP and VSL, reducing conditions (median DO concentration less than 0.5 mg/L) are exhibited in many of the groundwater samples and are associated with elevated concentrations of phosphorus (fig. 9a). In addition, in the VSP network, elevated concentrations of dissolved iron (median 440 micrograms per liter) and negligible concentrations of dissolved nitrate indicate strongly reducing conditions. Concentrations of phosphorus in groundwater from the carbonate network with nearly natural conditions, VCT, were very low, as they were in all of the carbonate networks.

Median concentrations of dissolved phosphate were generally higher in groundwater than in surface water in three of the crystalline and siliciclastic networks with inferred natural water chemistry, and were similar in the groundwater and surface water of the BXK network (table 3, fig. 6). Median concentrations of dissolved phosphate in groundwater exceeded the 0.037-mg/L criterion for total phosphorus in Piedmont streams (Ecoregion IX) in the PXS network and the 0.01-mg/L criterion for Blue Ridge and Valley and Ridge streams (Ecoregion XI) in the BXK, VSP, and VSL networks. The median dissolved phosphate concentrations were less than

0.01 mg/L in the associated Valley and Ridge stream networks. In the VCT network, phosphorus concentrations were greater in surface water than in groundwater; concentrations of nitrate were slightly greater than 1 mg/L, and chloride concentrations were elevated in surface water relative to groundwater, indicating human impacts on groundwater from shallower sources that were not sampled were potentially affecting phosphorus concentrations in surface water.

With the exception of specific conductance in the VCT network, specific conductance and concentrations of silica were lower in surface water than in groundwater from the networks representing predominantly natural conditions (table 3, fig. 10b). Dilution with younger (unsampled) groundwater with a lower concentration of phosphorus or biotic uptake may produce the lower concentration of phosphorus in stream water.

Phosphorus can be added to that contributed from groundwater by the microbial decomposition of terrestrial plant material that enters most streams. Such in-stream production of phosphorus from leaves and associated organic matter is indicated by concentrations of phosphate during base flow that are commonly highest during warmer months with longer days when the growth and decay of algae and other aquatic plants are likely to be fueling in-stream cycling of phosphorus (fig. 7). In addition, the mineralization of phosphorous sequestered in streambank and streambed sediments is generally greater in warmer than colder months (Surridge and others, 2007). This seasonal biological cycling of phosphorus can enrich phosphate in streams relative to the amount delivered by groundwater or overland sources (Manny and Wetzel, 1973; Kaplan and Bott, 1982; Carlton and Wetzel, 1988). As the majority of base-flow synoptic samples for this study were collected during the growing season, in-stream biological cycling of nutrients is a potential factor affecting observed phosphorus concentrations in surface water.

Phosphorus from Human Sources

Elevated dissolved phosphate concentrations in streams are commonly associated with human sources. In most networks, for example, elevated phosphorus is associated with elevated concentrations of nitrate and agricultural land use (tables 2 and 3, fig. 11b). An anthropogenic groundwater source for phosphorus is indicated in PSD by similar concentrations of dissolved phosphate in groundwater and surface water and a positive correlation between dissolved phosphate and nitrate in groundwater and surface water (groundwater: tau = .39, p = <.0001; streams: tau = .43, p = .0029). In PCL, where agricultural land use is dominant and concentrations of both chloride and nitrate are elevated in groundwater and surface water, the median dissolved phosphate concentration was less than the reporting limit in groundwater and higher in surface water, as is commonly seen in other paired networks in a carbonate setting (table 3, figs. 6 and 11). The elevated concentrations in streams could indicate a shallow groundwater source for phosphorus associated with anthropogenic sources, or biological cycling of phosphorus transported in overland runoff or sequestered in near-stream sediments. Concentrations of dissolved phosphate are commonly low in surface water from the crystalline networks even where nitrate concentrations in groundwater and surface water are elevated, as, for example, in the PXL network, where the median dissolved phosphate concentrations were below 0.01 mg/L in both groundwater and surface water (table 3, figs. 6 and 11b).

Fate and Transport of Phosphorus

Examination of overall water chemistry and land use indicates that concentrations of dissolved phosphate sometimes may be attributed to mineral dissolution in groundwater, particularly in siliciclastic and crystalline bedrock settings, and to anthropogenic inputs in surface water, particularly in carbonate bedrock settings. Considering all 609 groundwater samples from the crystalline (N = 246), siliciclastic (N = 154), and carbonate (N = 209) aquifers as a single dataset, Spearman's rank correlation coefficients (rho) generally indicated that the concentration of dissolved phosphate was correlated ($p < 0.001$) positively with temperature and concentrations of silica and sodium, and negatively with alkalinity and concentrations of calcium, magnesium, chloride, nitrate, sulfate, iron, and aluminum (table 4). Additionally, the phosphate concentration in groundwater was positively correlated with the percentages of wetland and forested land uses and negatively correlated with the percentage of agricultural land use in the vicinity of sampled wells. In contrast, the phosphate concentration in the 358 surface-water samples was not correlated with the concentration of silica, but was positively correlated with concentrations of all other major cations and anions, including chloride and nitrate, which could indicate anthropogenic sources and effects of evapotranspiration on stream-water quality; and with concentrations of calcium, magnesium, and bicarbonate, which could indicate dissolution of carbonate minerals (table 4). Phosphate concentration in surface water was positively correlated with the percentage of agricultural and urban land uses, negatively correlated with the percentage of forested land use, and not correlated with the percentage of wetland land use in the watershed.

Geochemical models were developed to evaluate mineral weathering and other hydrochemical processes that could control concentrations of phosphorus in groundwater and surface water. Background, or natural, quality for groundwater was estimated using the medians for samples that contained measurable DO (greater than 0.5 mg/L) and relatively low concentrations of nitrate (less than 1.0 mg/L) and chloride (less than 10 mg/L) and literature values for rainfall composition (Peters and Bonelli, 1982; Hem, 1985) (table 5). Although DO is reduced in some groundwater, it was greater than 0.5 mg/L in 92 percent of the samples and assumed to be present in all initial recharge; for these reasons, it was used in the definition of natural groundwater. The medians for paired groundwater and surface-water-quality data that had been identified as natural or affected by human influences (tables 3 and 5) were

Table 4. Spearman's rank correlation coefficients for dissolved phosphate, major chemical constituents, and land use for 609 groundwater samples and 358 surface-water samples from the Piedmont, Blue Ridge, and Valley and Ridge study area.

[Coefficient values multiplied by 100 and rounded; values shown are significant at $p<0.0001$; "--" indicates correlation was insignificant; *n.a.*, not applicable]

Constituent or Property	Groundwater	Surface Water
Specific Conductance	-32	44
Dissolved Oxygen	--	--
pH	--	23
Dissolved Organic Carbon	-16	--
Alkalinity	-29	31
Calcium	-30	30
Magnesium	-30	38
Sodium	18	43
Potassium	-14	53
Iron	--	--
Manganese	--	--
Aluminum	-24	*n.a.*
Silica	53	--
Chloride	-17	45
Sulfate	-23	41
Fluoride	--	21
Bromide	-15	--
Nitrate	-18	42
Ammonia		27
Land-Use Percentage	**Groundwater**	**Surface Water**
Wetland	21	--
Forested	29	-33
Urban	--	20
Agricultural	-22	32

evaluated to indicate varying effects of natural processes and anthropogenic contaminants on phosphorus fate and transport.

The SI values for major and accessory minerals, computed for individual samples (figs. 12–14) and using the median values for background and human-influenced water quality (table 6), were interpreted to indicate thermodynamically feasible mineral reactants and products in mass-transfer models. Groundwaters and surface waters from the crystalline setting typically were undersaturated with apatite (hydroxyapatite, fluorapatite, carbonate-fluorapatite) and other phosphate minerals (variscite, strengite, vivianite, $MnHPO_4$), whereas the waters from the carbonate and siliciclastic settings frequently were supersaturated with respect to carbonate-fluorapatite, strengite, and (or) $MnHPO_4$ (table 6; figs. 12–14). Additionally, the groundwater and surface-water samples from all settings generally were undersaturated with respect to primary aluminosilicate minerals such as feldspars (anorthite, albite, adularia), amphiboles and pyroxenes (diopside), and micas (chlorite, illite), but were saturated or supersaturated with associated secondary minerals (kaolinite, gibbsite, quartz) (table 6). Thus, negative SI values indicate that dissolution of alkali feldspar, hydroxyapatite, and (or) fluorapatite could provide a source of phosphate, whereas positive SI values indicate that precipitation of various other phosphate minerals (carbonate-fluorapatite, strengite, variscite) could impose an upper limit on phosphate concentrations. Additionally, positive SI values for calcite and (or) oxides of iron, aluminum, and manganese indicate that these minerals could be feasible sorbents of phosphate.

Inverse models were developed with PHREEQC to evaluate mass transfer of possible sources and sinks of phosphate and other solutes in the groundwater and surface water. In addition to specific minerals, oxygen, carbon dioxide, and organic matter ($C_{106}H_{263}O_{110}N_{16}P$) were included as possible reactants for each bedrock setting (table 7). Instead of the general formula CH_2O, the formula for organic matter with a molar C:N:P ratio of 106:16:1 (Redfield, 1934; Drever, 1997) was used to simulate nutrient release by decay of vegetation (reactant) or uptake by photosynthesis (product). Furthermore, phosphorus equivalent to 0.3 percent P_2O_5 (Manning, 2008) was included in the formulas for Na-feldspar ($NaAl_{1.011}Si_{2.978}P_{0.011}O_8$) and K-feldspar ($NaAl_{1.011}Si_{2.978}P_{0.011}O_{8).}$

The first set of inverse models simulated reactions of rainfall (concentrated by a factor of 3 to represent evaporation prior to recharge) with a generalized mineral assemblage that could produce the background water quality for each of the three bedrock types (table 7). To produce background groundwater for the crystalline bedrock setting, the principal reactants were diopside, anorthite, Na-feldspar, K-feldspar, biotite, and chlorite, plus fluorapatite, fluorite, pyrite, and halite; carbonate minerals were excluded. In contrast, for the carbonate bedrock setting, calcite, dolomite, mangano-siderite, and gypsum, plus fluorite and illite, were principal reactants. For the siliciclastic setting, a combination of these mineral reactants with intermediate mass-transfer values was indicated.

One or more minerals were indicated as a possible sink for phosphorus, which could be released in excess of the groundwater concentration by various reactants. For siliciclastic and carbonate groundwaters, carbonate-fluorapatite (FCO3Apatite) was indicated as a possible product, whereas for crystalline groundwater, strengite and variscite were indicated as possible products. Although strengite and variscite commonly were undersaturated (table 6, fig. 14), these phases were used as proxies for adsorption of phosphate by hydrous ferric and aluminum oxides. Other phases that were plausible products in the background groundwater-quality models include ferrihydrite ($Fe(OH)_3(a)$), gibbsite, and quartz (table 7).

The second set of inverse models simulated reactions with groundwater, minerals, and various anthropogenic

Table 5. Compositions of rainwater and background groundwater from crystalline (CRY), siliciclastic (SIL), and carbonate (CAR) aquifers plus paired groundwater and surface water from selected monitoring networks in these settings.

[Units are milligrams per liter unless otherwise indicated; *italics* indicate estimated concentrations for constituent medians that were less than laboratory reporting limits; solution name with suffix "_GW" is median groundwater and "_SW" is median surface water; paired groundwater-to-surface-water models involve monitoring networks identified in tables 2 and 3, row shading indicates network rock type: gray indicates crystalline, blue indicates carbonate, no shading indicates siliciclastic; °C, degrees Celsius]

Solution Identification	Temperature, °C	pH	Oxygen	Alkalinity ($CaCO_3$)	Calcium (Ca)	Magnesium (Mg)	Sodium (Na)	Potassium (K)	Silicon (Si)	Sulfate (SO_4)	Chloride (Cl)	Fluoride (F)	Nitrate (NO_3-N)	Phosphate (PO_4-P)	Iron (Fe)	Manganese (Mn)	Aluminum (Al)
Rainwater to "background" groundwater models																	
RAINWATER	15.0	4.9	10.0	0.1	0.03	0.02	0.3	0.1	0.016	0.6	0.5	0.014	0.05	0.005	0.0001	0.0001	0.0001
CRY_GW	16.1	6.2	6.6	33.5	7.0	2.0	5.7	1.1	11.8	0.8	1.8	*0.05*	0.22	0.029	0.003	0.002	0.002
SIL_GW	12.4	7.4	6.2	57.6	19.5	4.7	4.1	0.6	5.0	5.3	1.7	*0.05*	0.21	0.018	*0.003*	*0.001*	*0.001*
CAR_GW	14.3	7.0	6.9	156.0	34.9	14.1	0.9	0.9	3.8	2.4	1.4	*0.05*	0.36	*0.005*	*0.003*	*0.001*	*0.001*
Paired groundwater to surface-water models																	
BXK_GW	13.0	6.3	5.4	34.3	10.2	1.5	4.3	1.5	9.0	3.4	2.1	*0.05*	0.42	0.013	0.005	0.001	0.003
PXS_GW	19.0	6.0	7.0	31.0	7.0	2.3	6.8	1.5	14.4	0.7	2.3	*0.05*	0.70	0.055	0.005	0.002	0.001
VSP_GW	13.5	7.3	0.6	125.0	29.5	12.5	8.7	0.9	8.4	25.0	3.2	*0.05*	0.05	0.015	0.395	0.115	0.001
VSL_GW	12.3	7.2	0.6	59.4	16.0	5.6	6.3	0.6	8.4	8.0	2.3	0.10	0.13	0.030	0.018	0.046	0.001
PSD_GW	13.4	7.5	4.4	135.0	45.8	13.8	11.6	1.0	9.1	19.9	15.2	*0.05*	2.5	0.032	0.005	0.001	0.001
VCT_GW	14.4	7.1	6.3	172.0	46.4	17.3	1.2	1.3	4.0	3.9	2.4	*0.05*	1.04	*0.005*	0.001	0.001	*0.001*
PCL_GW	13.1	7.3	6.0	210.5	74.5	24.5	5.7	2.0	4.4	37.5	18.5	*0.05*	11.0	0.005	0.003	0.001	*0.001*
BXK_SW	13.5	7.2	10.8	16.1	4.1	1.6	3.7	1.5	5.8	4.9	2.7	*0.05*	0.49	0.012	0.068	0.021	*0.001*
PXS_SW	16.5	6.4	8.6	13.0	3.1	1.6	2.5	2.5	5.1	1.6	2.8	*0.05*	0.29	*0.005*	0.116	0.016	*0.001*
VSP_SW	19.8	7.7	8.2	36.0	14.0	3.5	2.5	1.9	3.6	10.2	2.7	*0.05*	0.43	*0.005*	0.029	0.004	*0.001*
VSLF_SW	22.3	7.2	8.2	23.0	8.3	2.5	1.5	1.0	2.7	6.4	1.5	*0.05*	0.28	0.010	0.062	0.009	*0.001*
PSD_SW	19.8	7.7	9.9	63.4	25.4	9.1	15.5	2.2	5.4	24.0	25.8	*0.05*	1.35	0.027	0.028	0.020	*0.001*
VCT_SW	20.7	8.3	9.3	160.0	54.4	16.7	2.5	2.3	3.2	6.6	5.1	0.14	1.3	0.016	0.003	0.009	*0.001*
PCL_SW	20.0	8.1	8.9	174.0	59.0	14.0	9.6	4.0	3.5	28.0	23.0	0.10	8.2	0.070	0.009	0.022	*0.001*

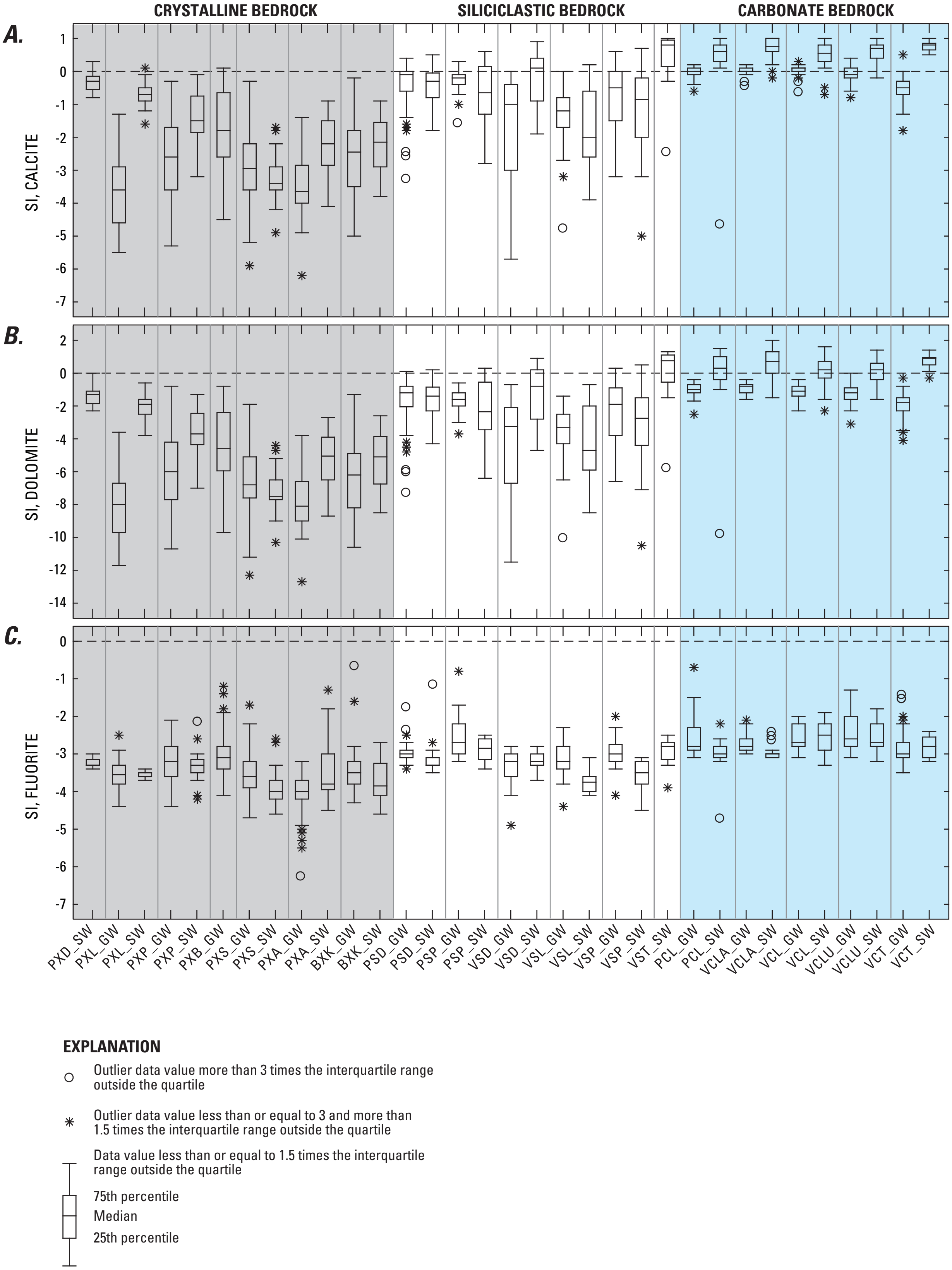


Figure 12. Saturation indices (SI) for calcite, dolomite, and fluorite in groundwater and surface water by network for different bedrock types of the Piedmont, Blue Ridge, and Valley and Ridge study area.

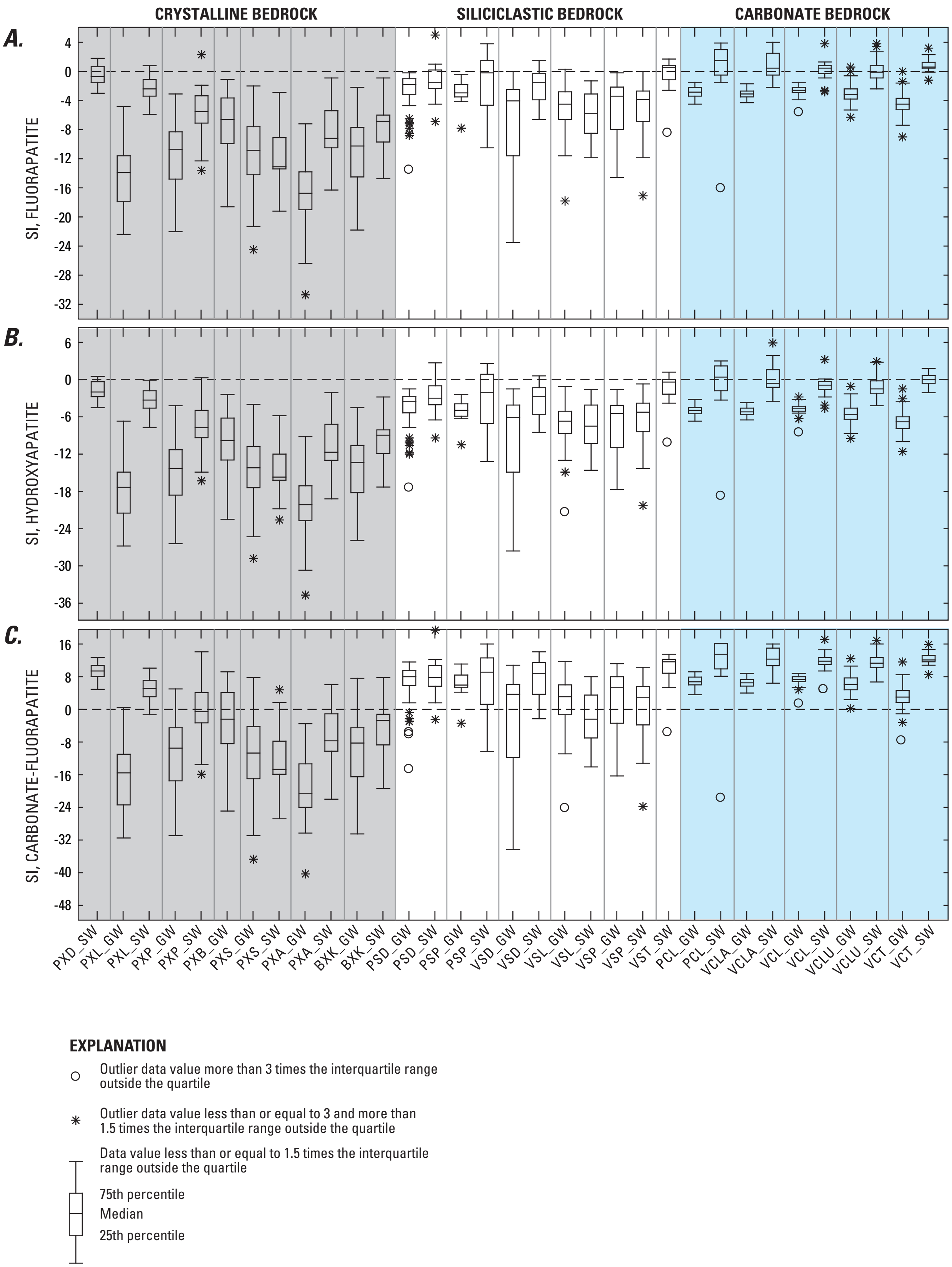


Figure 13. Saturation indices (SI) for apatite in groundwater and surface water by network for different bedrock types of the Piedmont, Blue Ridge, and Valley and Ridge study area.

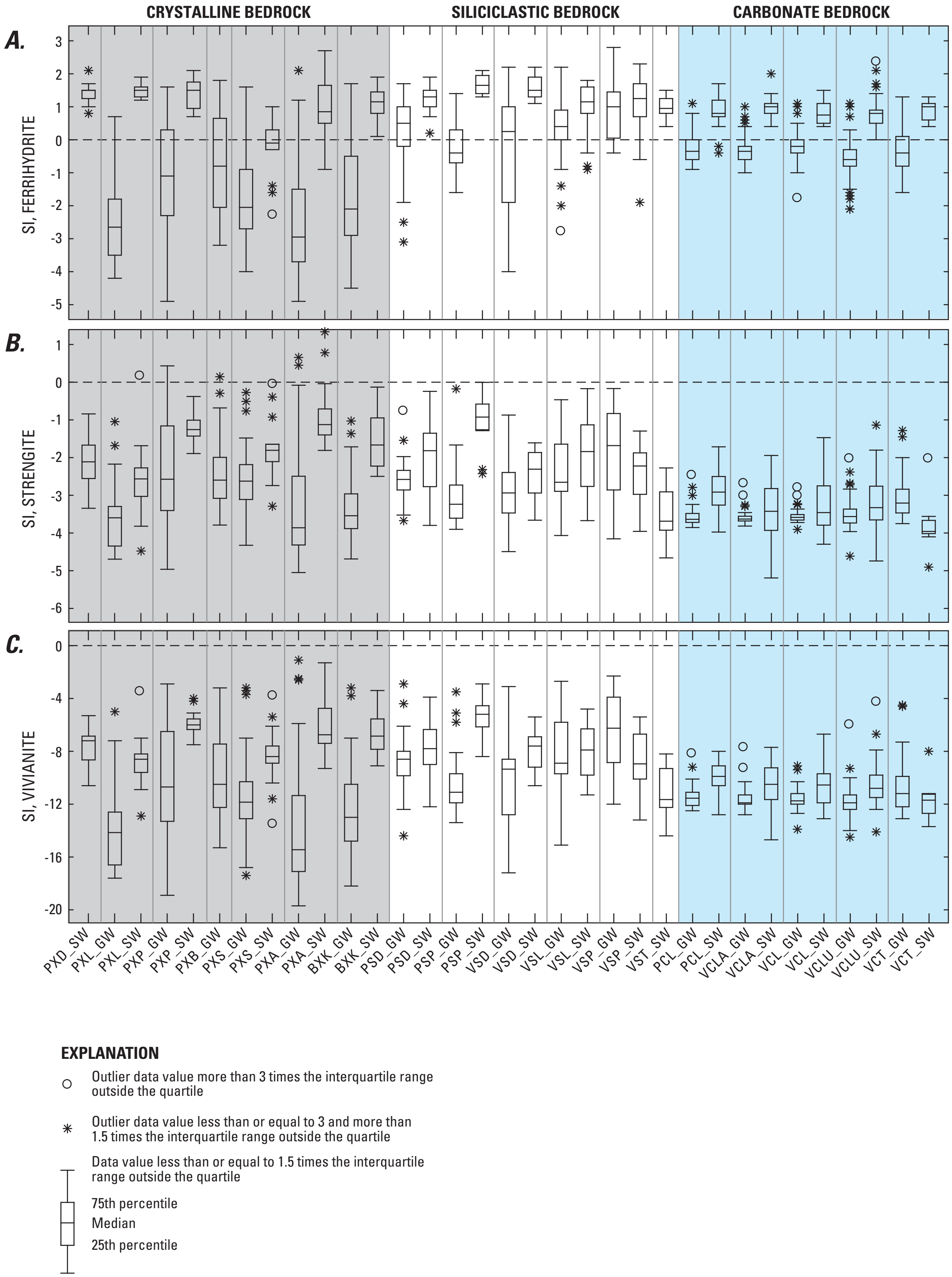


Figure 14. Saturation indices (SI) for ferrihydrite, strengite, and vivianite in groundwater and surface water by network for different bedrock types of the Piedmont, Blue Ridge, and Valley and Ridge study area.

Table 6. Saturation index (SI) values computed with PHREEQC[2] for compositions of solutions used in inverse mass-transfer models.

[Negative value indicates undersaturation, positive value (**red**) indicates saturated; solution name with suffix "_GW" is median groundwater and "_SW" is median surface water; input solution compositions indicated in table 5; formula for phases with "*" in parentheses indicated in table 7; yellow shading indicates phase contains phosphorus; row shading in paired groundwater to surface-water models indicates network rock type: gray indicates crystalline, blue indicates carbonate, no shading indicates siliciclastic]

Solution Identification	Adularia ($KAlSi_3O_8$)	Albite ($NaAlSi_3O_8$)	Anorthite (*)	Calcite (*)	Chlorite14A (*)	Diopside (*)	Dolomite (*)	FCO3Apatite (*)	$Fe(OH)_3$(a)	Fluorapatite (*)	Fluorite (*)	Gibbsite (*)	Gypsum (*)	Halite (*)	Hydroxyapatite ($Ca_5(PO_4)_3OH$)	Illite (*)	Kaolinite ($Al_2Si_2O_5(OH)_4$)	$MnHPO_4$	Pyrolusite (*)	Quartz (*)	Siderite ($FeCO_3$)	Strengite (*)	Variscite (*)	Vivianite ($Fe_3(PO_4)_2$:$8H_2O$)
Rainwater to "background" groundwater models																								
RAIN	-17.6	-19.6	-26.5	-8.1	-63.0	-26.5	-16.1	-52.1	-2.7	-32.4	-7.7	-3.5	-7.6	-11.3	-36.0	-23.4	-11.0	-4.9	**1.0**	-2.4	-15.3	-2.8	-4.7	-44.8
RAIN3X	-11.6	-13.6	-16.9	-6.8	-42.2	-20.2	-13.6	-32.6	-1.1	-21.6	-6.3	-0.5	-6.7	-10.4	-24.6	-13.3	-4.1	-2.9	**3.6**	-2.0	-15.2	-1.9	-2.3	-41.3
CRY_GW	-2.6	-4.4	-7.8	-2.9	-23.8	-11.4	-6.0	-9.7	-0.0	-10.7	-4.3	**0.6**	-4.4	-9.5	-13.4	-1.6	**2.8**	-1.8	**4.6**	**0.4**	-12.2	-0.7	-1.1	-37.5
SIL_GW	-3.0	-4.7	-6.4	-1.0	-12.2	-6.7	-2.5	**5.0**	**1.0**	-3.2	-3.9	**0.3**	-3.2	-9.7	-4.9	-2.2	**1.6**	-1.2	**7.1**	**0.1**	-12.5	-1.6	-3.4	-39.1
CAR_GW	-3.3	-5.8	-6.6	-0.7	-13.2	-7.7	-1.6	**1.2**	**0.5**	-5.5	-3.7	**0.6**	-3.4	-10.4	-7.5	-2.3	**1.8**	-2.4	**6.0**	-0.1	-12.0	-2.1	-3.1	-40.1
Paired groundwater to surface-water models																								
BXK_GW	-2.3	-4.4	-7.2	-2.6	-23.7	-11.4	-5.9	-8.6	**0.5**	-10.4	-4.1	**0.9**	-3.6	-9.6	-13.2	-1.0	**3.3**	-2.3	**4.5**	**0.3**	-12.0	-0.7	-1.3	-37.7
PXS_GW	-3.0	-4.8	-8.7	-3.0	-24.9	-11.5	-6.2	-10.0	-0.1	-10.5	-4.4	**0.1**	-4.5	-9.3	-13.3	-2.6	**1.9**	-1.6	**4.3**	**0.5**	-11.9	-0.2	-1.2	-36.2
VSP_GW	-2.2	-3.7	-5.9	-0.6	-10.3	-6.1	-1.5	**5.3**	**3.0**	-3.3	-3.8	**0.4**	-2.4	-9.1	-5.1	-1.3	**2.1**	**0.3**	**8.1**	**0.3**	-9.7	**0.4**	-3.3	-32.0
VSL_GW	-2.3	-3.8	-6.1	-1.3	-12.8	-7.1	-2.9	**4.6**	**1.7**	-3.5	-3.3	**0.5**	-3.1	-9.4	-5.7	-1.1	**2.4**	**0.3**	**7.6**	**0.3**	-11.3	-0.4	-2.6	-35.1
PSD_GW	-2.0	-3.4	-5.6	-0.2	-8.3	-4.9	-0.8	**10.0**	**1.2**	-0.8	-3.6	**0.2**	-2.4	-8.3	-2.3	-1.2	**1.9**	-1.5	**6.8**	**0.4**	-11.9	-1.4	-3.5	-38.2
VCT_GW	-3.2	-5.7	-6.4	-0.5	-12.3	-7.2	-1.3	**2.6**	**0.3**	-4.8	-3.6	**0.5**	-3.1	-10.1	-6.8	-2.2	**1.7**	-2.4	**6.0**	-0.0	-12.3	-2.5	-3.3	-41.1
PCL_GW	-2.7	-4.8	-6.1	-0.1	-10.0	-6.1	-0.5	**6.1**	**0.9**	-3.3	-3.4	**0.4**	-2.0	-8.5	-5.1	-1.9	**1.6**	-2.4	**6.4**	**0.0**	-11.9	-2.2	-3.9	-40.3
BXK_SW	-2.5	-4.6	-7.0	-2.4	-15.4	-8.3	-4.9	-3.7	**2.2**	-7.5	-4.5	**0.4**	-3.8	-9.5	-9.3	-1.7	**1.9**	-0.3	**7.9**	**0.1**	-11.6	-0.2	-3.1	-35.0
PXS_SW	-3.1	-5.6	-8.2	-3.3	-22.5	-11.5	-6.7	-13.0	**1.8**	-12.2	-4.6	**0.6**	-4.4	-9.7	-14.8	-2.3	**2.2**	-1.0	**6.1**	**0.0**	-11.0	**0.4**	-1.8	-33.6
VSP_SW	-3.5	-5.8	-7.1	-1.0	-10.0	-5.7	-2.3	**2.3**	**1.6**	-4.2	-4.1	-0.3	-3.0	-9.7	-5.3	-3.7	-0.1	-1.4	**7.9**	-0.2	-11.8	-1.9	-4.9	-37.8
VSL_SW	-4.4	-6.6	-7.6	-1.9	-14.6	-8.0	-3.9	-2.3	**1.7**	-6.1	-4.3	**0.1**	-3.4	-10.2	-7.7	-4.2	**0.3**	-0.9	**7.3**	-0.3	-11.2	-0.6	-3.3	-34.8
PSD_SW	-2.9	-4.5	-6.5	-0.5	-7.2	-4.5	-1.1	**8.4**	**1.6**	-1.0	-3.9	-0.4	-2.5	-7.9	-2.1	-3.1	**0.1**	-0.1	**8.7**	**0.0**	-11.6	-1.3	-4.4	-36.7
VCT_SW	-3.7	-6.0	-6.7	**0.8**	-1.8	-2.0	**1.4**	**14.4**	**0.6**	**1.8**	-2.7	-1.0	-2.8	-9.5	**0.9**	-4.7	-1.7	-1.3	**9.0**	-0.2	-12.8	-3.8	-6.5	-42.6
PCL_SW	-3.3	-5.3	-6.6	**0.7**	-3.8	-2.8	**1.0**	**16.6**	**1.1**	**3.1**	-3.0	-0.8	-2.2	-8.2	**2.2**	-4.1	-1.1	-0.0	**9.2**	-0.2	-12.0	-2.3	-5.2	-39.0

[2] Parkhurst and Appelo, 1999

Table 7. Mass-transfer estimates (minimum/maximum) to obtain median background groundwater quality (final solution) by reactions with evaporated rainfall (initial solution) in crystalline, siliciclastic, and carbonate bedrock settings.

[PHREEQC[a] used to compute mass transfer given input-solution compositions in table 5 and saturation indices in table 6; values are in millimoles; positive value indicates phase added to solution; negative value (**red**) indicates phase removed from solution; "." indicates phase excluded from model; yellow shading indicates phase contains phosphorus; CRY, crystalline, SIL, siliciclastic; CAR, carbonate]

Phase name in PHREEQC	Composition used in Mass-Transfer Models	CRY50_GW	SIL50_GW	CAR50_GW
Diopside	$CaMgSi_2O_6$	0 / 0.079	.	.
Anorthite	$CaAl_2Si_2O_8$	0.082 / 0.170	.	.
Na-Feldspar	$NaAl_{1.011}Si_{2.978}P_{0.011}O_8$	0.188 / 0.200	0.139 / 0.139	.
K-Feldspar	$KAl_{1.011}Si_{2.978}P_{0.011}O_8$	0 / 0.022	0 / 0.008	.
Biotite	$KMg_3AlSi_3O_{10}(OH)_2$	0 / 0.022	.	.
Chlorite14A	$Mg_5Al_2Si_3O_{10}(OH)_8$	0 / 0.016	0 / 0.035	.
Illite	$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$	.	0 / 0.014	0.028 / 0.029
Calcite	$CaCO_3$	.	0.265 / 0.453	0.318 / 0.352
Dolomite	$CaMg(CO_3)_2$	.	0 / 0.174	0.573 / 0.573
Mn-Siderite	$Fe_{0.95}Mn_{0.05}CO_3$	.	0 / 0.932	0 / 2.163
Fluorite	CaF_2	.	0.001 / 0.003	0 / 0.005
Gypsum	$CaSO_{4.2}H_2O$	.	.	0.022 / 0.022
Pyrite	FeS_2	0.003 / 0.003	0.026 / 0.026	.
Pyrolusite	MnO_2	.	**-0.047** / 0	**-0.108** / 0
Quartz	SiO_2	**-0.840** / **-0.767**	**-0.484** / **-0.356**	**-0.038** / **-0.033**
Fluorapatite	$Ca_5(PO_4)_3F$	0 / 0.0004	.	.
FCO3Apatite	$Ca_{9.316}Na_{0.36}Mg_{0.144}(PO_4)_{4.8}(CO_3)_{1.2}F_{2.48}$	.	**-0.0021** / 0	**-0.0043** / **-0.0001**
Fe(OH)3(a)	$Fe(OH)_3$	**-0.003** / 0	**-0.911** / **-0.026**	**-2.055** / 0
Gibbsite	$Al(OH)_3$	**-0.584** / **-0.385**	**-0.241** / **-0.149**	**-0.066** / **-0.063**
Strengite	$FePO_{4.2}H_2O$	**-0.003** / 0	.	.
Variscite	$AlPO_{4.2}H_2O$	**-0.004** / 0	.	.
Halite	$NaCl$	0.009 / 0.009	.	.
Sylvite	KCl	.	.	.
NH4H2PO4	$NH_4H_2PO_4$	.	.	.
Urea	NH_2CONH_2	.	.	.
Organic matter	$C_{106}H_{263}O_{110}N_{16}P$	0.001 / 0.001	0 / 0.206	0 / 0.455
CO2(g)	CO_2	1.722 / 1.754	0 / 0.932	0 / 2.060
O2(g)	O_2	.	0 / 0.984	0 / 2.262
N2(g)	N_2	**-0.008** / **-0.006**	**-0.069** / 0	**-0.161** / 0
H2O(g)	H_2O	.	.	.

[a] Parkhurst and Appelo, 1999

compounds plus evaporation or dilution to produce the median base-flow stream-water quality in various geologic settings (table 8). Phases added to represent anthropogenic sources included urea, ammonium phosphate, and sylvite, which are common constituents in commercial fertilizer (Teply and others, 1980). To simulate evaporation and dilution processes in the groundwater-to-surface-water models, moles of water (H_2O) were subtracted (product) or added (reactant) as an additional phase (table 8). As 1 kg of solution contains 55.5 moles of H_2O, the fraction of the initial groundwater solution was decreased or increased accordingly to maintain a constant 1-kg mass of solution. Dilution of groundwater was indicated if the concentrations of chloride, sodium, and other major solutes in the groundwater were greater than those in surface water. Thus, dilution could represent addition of a younger source of groundwater not represented by sampling for this study. Evaporation and (or) dissolution of mineral sources or addition of anthropogenic sources was indicated if the concentrations of chloride, sodium, and other major solutes in the groundwater were less than those in surface water.

Generally, the major-ion composition of the initial groundwater solutions for the groundwater-to-surface-water models was similar to that for background (natural) groundwater in a particular bedrock setting and, to a lesser extent, to that for the associated surface water (table 5). Consequently, the same principal mineral reactants and products but smaller mole transfers were indicated in the groundwater to surface-water models (table 8) than in the rainwater-to-background-groundwater models (table 7).

For the crystalline bedrock setting, inverse models relating paired groundwater and surface-water quality were developed for the BXK and PXS networks, which had been described as representing relatively natural conditions (table 3). The groundwater in these networks contained appreciable dissolved phosphate (medians were 0.013 and 0.055 mg/L, respectively) (table 5). Generally, the median concentrations of phosphate in surface water for both networks were less than or equal to the concentration in the groundwater (table 5), indicating that groundwater could be a principal source of dissolved phosphate in the base flow. In addition, the median concentration of silica and median specific conductance in surface water were less than those in groundwater, indicating that dilution could attenuate solute concentrations in these two settings (table 3). With dilution of the groundwater, the inverse models indicated that minor additions of phosphate by dissolution of fluorapatite and (or) Na-feldspar plus the addition of potassium and chloride by the dissolution of sylvite could produce the surface-water composition (table 8). Excess phosphate was balanced by the precipitation of strengite or the production of organic matter (table 8). As the production of organic matter also removed nitrogen, the final nitrogen mole balance was achieved by the addition of urea. The mole transfers indicated for sylvite and urea (anthropogenic sources) were small, but comparable in magnitude to the transfers for minerals needed to balance major solutes. Therefore, the inverse models indicated that the concentration of phosphate in the groundwater could account for all or nearly all of the dissolved phosphate in the surface water for the PXS network, with minor contributions from minerals (little or no mass transfer); for the BXK network, the concentration of phosphate in groundwater was estimated to supply about half of the dissolved phosphate in the surface water, with the remainder contributed by the dissolution of feldspar and fluorapatite (table 9).

For networks in the siliciclastic setting (VSP, VSL, and PSD) and the carbonate setting (VCT and PCL), the concentrations of major ions, including calcium, magnesium, and silica, and alkalinity in the surface water were less than those in the groundwater (tables 3 and 5). Thus, as for the crystalline setting, dilution was indicated for the inverse models relating paired groundwater and surface-water quality in the siliciclastic and carbonate settings (table 8). For networks in the siliciclastic setting, the concentrations of phosphate in surface water were less than those in the associated groundwater, indicating that groundwater could be a principal source of dissolved phosphate in surface water. For the networks in the carbonate setting, the concentrations of phosphate in surface water were greater than those in groundwater, however, indicating that sources of phosphate in addition to the dissolved concentration in groundwater would be needed to achieve the concentrations in surface water. After dilution, the concentrations of chloride, nitrate, sodium, and (or) potassium in groundwater were less than those in surface water for the siliciclastic and carbonate networks. To maintain the mole balances for these constituents, the inverse models involved contributions from halite, sylvite, ammonium phosphate, and (or) urea, even for the networks that previously had been identified as having natural water quality (VSP, VSL, and VCT) (table 3). Hence, these mass transfers may be accounting for chemicals released into surface water by the decomposition of plant material. The networks with human impacts on water quality (PSD, PCL) (table 3) could be distinguished from the other pairs mainly by greater additions of halite (table 8). In the models for networks in siliciclastic settings, a small amount of phosphate was added by the dissolution of fluorapatite, whereas in the models for networks in carbonate settings, greater amounts of phosphate were added by the dissolution of ammonium phosphate fertilizer. To maintain mole balances, excess phosphate was removed by the precipitation of strengite and carbonate-fluorapatite or by the production of organic matter (table 8). Thus, for the siliciclastic bedrock setting, the models indicate that groundwater supplied 70 to 90 percent of the dissolved phosphate in the surface water (table 9). For the carbonate setting, however, the groundwater potentially supplied only 5 percent of the dissolved phosphate to surface water in the PCL network, which has substantial anthropogenic inputs, and about 30 percent of the dissolved phosphate to surface water in the VCT network, which represented nearly natural groundwater quality (table 9).

Alkali feldspar containing 0.3 percent P_2O_5 ((Na, K) $Al_{1.011}Si_{2.978}P_{0.011}O_8$), was indicated as a possible source of dissolved phosphate in the crystalline and siliciclastic bedrock

Table 8. Mass-transfer estimates (minimum/maximum) that produce median surface-water quality (final solution) by reactions with median groundwater quality (initial solution) in selected networks.

[Location of networks shown in figure 3; networks described in table 2; PHREEQC used to compute mass transfer given solution compositions in table 5, saturation indices in table 6, and phase compositions in table 7; values are in millimoles, except H_2O, which is in moles; positive value indicates phase added to solution; negative value (**red**) indicates phase removed from solution; "." indicates phase excluded from model; yellow shading indicates phase contains phosphorus; column shading indicates network rock type: gray indicates crystalline, blue indicates carbonate, no shading indicates siliciclastic]

	BXK	**PXS**	**VSP**	**VSL**	**PSD**	**VCT**	**PCL**
GW Fraction	0.426 / 0.461	0.365 / 0.366	0.284 / 0.301	0.281 / 0.281	0.600 / 0.614	0.985 / 1	0.672 / 0.69
Diopside	.	.	.	.	.	.	.
Anorthite	.	.	.	.	.	.	.
Na-Feldspar	0.037 / 0.080	.	0 / 0.007	.	.	.	.
K-Feldspar	.	.	0 / 0.006	.	.	.	.
Biotite	0 / 0.013	.	.	.	.	.	.
Chlorite14A	0 / 0.009	0.005 / 0.005	.	.	.	.	.
Illite	**-0.041** / **-0.024**	.	0 / 0.005	.	0 / 0.068	0 / 0.033	.
Calcite	.	.	0 / 0.071	.	.	.	0.212 / 0.327
Dolomite	.	.	.	0.055 / 0.055	.	.	.
Mn-Siderite	.	.	0 / 0.072	.	0.007 / 0.007	0.003 / 0.003	0.008 / 0.008
Fluorite	.	.	.	.	.	0.002 / 0.012	0.002 / 0.002
Gypsum	.	.	.	.	.	0.028 / 0.035	.
Pyrite	0.017 / 0.018	0.008 / 0.008	0.005 / 0.016	0.022 / 0.022	0.052 / 0.063	.	.
Pyrolusite	.	.	**-0.004** / **-0.001**	.	.	.	.
Quartz	**-0.102** / 0	.	.	.	**-0.247** / 0	**-0.128** / 0	.
Fluorapatite	0.001 / 0.001	0.002 / 0.002	0.002 / 0.077	0.001 / 0.001	0.001 / 0.001	.	.
FCO3Apatite	.	.	**-0.030** / 0	.	.	**-0.008** / 0	.
Fe(OH)3(a)	**-0.017** / **-0.016**	**-0.006** / 0	.	**-0.021** / **-0.021**	**-0.069** / **-0.059**	**-0.003** / **-0.003**	**-0.007** / **-0.007**
Gibbsite	.	**-0.010** / **-0.010**	**-0.012** / **-0.006**	.	**-0.156** / 0	**-0.076** / 0	.
Strengite	.	**-0.006** / 0	**-0.085** / **-0.007**	.	.	.	.
Variscite	.	.	.	.	.	.	.
Halite	.	.	.	.	0.398 / 0.404	0.056 / 0.062	0.247 / 0.251
Sylvite	0.035 / 0.036	0.052 / 0.052	0.038 / 0.042	0.021 / 0.021	0 / 0.040	0 / 0.026	0.067 / 0.068
NH4H2PO4	.	.	.	.	.	0 / 0.038	0.002 / 0.003
Urea	0.038 / 0.039	0.002 / 0.272	0.013 / 0.015	0.472 / 0.474	.	0 / 1.927	.
Organic matter	**-0.004** / **-0.003**	**-0.005** / 0	.	**-0.004** / **-0.004**	**-0.002** / **-0.002**	**-0.026** / 0	**-0.001** / 0
CO2(g)	.	**-0.271** / 0	.	.	.	**-0.861** / 0	.
O2(g)	.	0 / 0.224	0.321 / 0.386	0.577 / 0.578	0.133 / 0.196	0 / 0.136	0 / 0.159
N2(g)	.	**-0.228** / 0	.	**-0.432** / **-0.431**	.	**-1.727** / 0	.
H2O(g)	29.93 / 31.86	35.19 / 35.26	38.8 / 39.72	39.89 / 39.99	21.45 / 22.2	0 / 0.86	17.2 / 18.21

Table 9. Estimated fraction of phosphate concentration in median surface water (final solution) that originated from groundwater (initial solution) in selected networks.

[Network locations shown in figure 3; networks described in table 2; PHREEQC[a] used to compute groundwater fraction and mass-transfer estimates in table 7; kg, kilogram; <, less than; >, greater than; mg/L, milligrams per liter; median concentration less than laboratory reporting limit of 0.01 mg/L were estimated at 0.005 mg/L and are shown in *italics*; row shading indicates network rock type: gray indicates crystalline, blue indicates carbonate, no shading indicates siliciclastic]

Network	Fraction of 1 kg initial groundwater solution in 1 kg final surface-water solution (values <1 indicate dilution; values >1 indicate evaporation)		Median phosphate concentration (mg/L)		Estimated phosphate concentration in groundwater after dilution or evaporation to produce the fraction in surface water		Estimated percentage of phosphate in surface water that was derived from groundwater	
	Minimum	Maximum	Surface water	Groundwater	Minimum	Maximum	Minimum	Maximum
BXK	0.426	0.461	0.012	0.013	0.0055	0.0060	46	50
PXS	0.365	0.366	*0.005*	0.055	0.0201	0.0201	100	100
PSD	0.600	0.614	0.027	0.032	0.0192	0.0196	71	73
VSP	0.284	0.301	0.005	0.015	0.0043	0.0045	85	90
VSL	0.281	0.281	0.010	0.030	0.0084	0.0084	84	84
PCL	0.672	0.690	0.070	*0.005*	0.0034	0.0035	<5	5
VCT	0.985	1.000	0.016	*0.005*	0.0049	0.0050	<31	31

[a] Parkhurst and Appelo, 1999.

settings. Congruent dissolution of this phase by pure water would produce a Si/P mass ratio of 299:1. In comparison, the median ratios of dissolved concentrations of silica and phosphate (SiO_2-Si/PO_4-P) for groundwater and surface water in this study were 402 and 234, respectively. Smaller values for the Si/P ratio in surface water than in groundwater may result from the addition of phosphate to surface water from enriched natural sources (apatite, organic matter) or anthropogenic sources (fertilizer, manure, sewage) and (or) the attenuation of silica transport (precipitation of quartz or kaolinite). In addition, both silica and phosphorus may be taken up by plants in surface water, which may change this ratio. Higher values for Si/P in groundwater may result from the attenuation of phosphate transport (adsorption, precipitation, uptake) and (or) from lower concentrations of phosphate in feldspar than are assumed in the models. Although not precisely the stoichiometry considered in the mass-transfer models, the median Si/P ratio of 402 for the groundwater samples is consistent with the dissolution of nutrient-enriched feldspar with 0.22 percent P_2O_5 content ($(Na,Al)_{1.008}Si_{2.984}P_{0.008}O_8$), which is within the reported range of 0.2 to 0.3 percent (Kontak and others, 1996; Manning, 2008). Such nutrient-enriched feldspar may weather more rapidly than other silicate minerals because of selective dissolution of nutrient-bearing minerals by microorganisms and plants (Bennett and others, 2001; Manning, 2008), particularly in areas of groundwater recharge and discharge where plant roots may access groundwater.

Although carbonate-fluorapatite was considered a potential sink for phosphate in groundwater, kinetic barriers to the precipitation of this mineral may be indicated by its supersaturation (fig. 13). The precipitation-dissolution kinetics of apatite and feldspar generally occur at slow rates compared to typical groundwater velocities and compared to adsorption-desorption and biological uptake-decay processes. Consequently, precipitation-dissolution of minerals with favorable kinetics, such as calcite and amorphous iron hydroxide, and their sorption/release of phosphate ions could be the primary mechanisms that control phosphate concentrations in the groundwater systems. Nevertheless, despite the slow kinetics of feldspar dissolution, phosphate concentrations could become elevated in certain crystalline and siliciclastic rock settings where a solution remains undersaturated with calcite and apatite and where conditions are strongly reducing (ferric iron reduction). As the stability of apatite minerals and calcite generally would not be affected by DO whereas the stability of iron minerals would be affected by redox conditions, the relative importance of solubility control by apatite and (or) sorption by calcite or ferric iron minerals likely would not vary with redox conditions.

The inverse models emphasized mineral precipitation as a mechanism for removal of phosphate from solution and did not simulate adsorption processes as possible controls on transport. Nevertheless, sorption and coprecipitation of phosphate with carbonate or iron oxide could be the primary mechanisms for removal of phosphate rather than precipitation of a pure phase such as apatite or strengite (Golterman, 1973; Jarvie and others, 2005; Maine and others, 2007). Several mass-transfer models indicated precipitation of strengite or variscite (tables 7 and 8). Although typically undersaturated (table 6), these ferric iron and aluminum phosphate phases were included in the models as proxies for phosphate adsorption by the oxides of ferric iron and aluminum. Adsorption processes could be particularly important in surface-water environments because of the tendency for pH to increase and mineral precipitation (for example, $CaCO_3$, $Fe(OH)_3$) to take place after groundwater that enters the stream begins to equilibrate with the atmosphere (loss of CO_2 and gain of O_2):

$$Ca^{2+} + 2\ HCO_3^- = CaCO_3 + H_2O + CO_2(g).$$

$$Fe^{2+} + 1/4\ O_2(g) + 2\ 1/2\ H_2O = Fe(OH)_3 + 2\ H^+ .$$

Consequently, the pH and SI values for calcite and $Fe(OH)_3(a)$ of surface water generally were greater than those of groundwater in the same network (table 5, figs. 12 and 14). Such freshly precipitated solids generally consist of fine particles with relatively large surface areas that may be suspended or form coatings on bed material.

Using PHREEQC with adsorption coefficients from Dzombak and Morel (1990), the potential for adsorption of phosphate by $Fe(OH)_3(a)$ was evaluated (fig. 15). With increased pH from 6 to 9, the adsorbed fraction of orthophosphate decreases from more than 90 percent to less than 20 percent. Hence, adsorption and desorption in response to changes in pH within the stream environment could be an important factor affecting phosphorus concentrations. Although silica and sulfate are less strongly sorbed than phosphorus, elevated concentrations of these major ions have been shown to influence phosphorus sorption (Geelhoed and others, 1997; Caraco and others, 1989). Under anoxic conditions, however, reductive dissolution of the ferric hydroxide could occur and result in the release of phosphate to solution.

Summary and Implications

Various natural and anthropogenic sources contribute phosphorus to groundwater and surface water in the Piedmont, Blue Ridge, and Valley and Ridge Physiographic Provinces. As groundwater is an important source of water to streams and provides more than 50 percent of annual flow in most settings, phosphorus dissolved in groundwater is likely to contribute to the nutrient load in streams. To determine settings where this may occur, the U.S. Geological Survey compiled and evaluated water-quality data for a total of 358 stream base-flow samples and 609 groundwater samples that were collected from 1991 through 2007 from paired networks of groundwater and surface-water sites in different hydrogeologic and land-use settings. The dissolved phosphate concentrations for the stream base-flow samples ranged from less than 0.01 to 1.23 milligrams per liter, with a median of 0.016 milligrams per liter; those for the groundwater samples ranged from less than 0.01 to 0.54 milligrams per liter, with a median of 0.010 milligrams per liter. The phosphate concentrations in groundwater from the crystalline and siliciclastic bedrock settings (medians of 0.017 and 0.020 milligrams per liter, respectively) generally were greater than those in groundwater from the carbonate bedrock setting (median of less than 0.01 milligrams per liter). In contrast, the median concentrations of dissolved phosphate in surface water from the crystalline and siliciclastic bedrock settings (0.010 and 0.014 milligrams per liter, respectively) were less than the median in surface-water samples from the carbonate setting (0.020 milligrams per liter).

The reported concentrations of phosphorus in streams during base flow were commonly higher than ecoregion nutrient criteria of 0.037 milligrams per liter for the Piedmont and 0.01 milligrams per liter for the Blue Ridge and Valley and

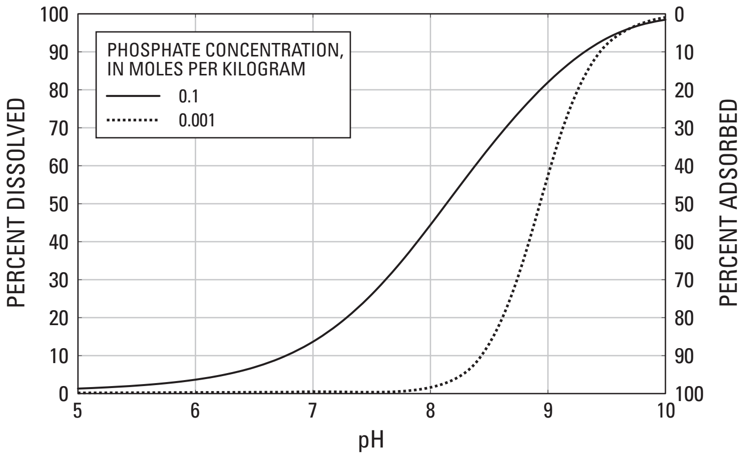


Figure 15. Equilibrium fractions of initial concentrations of phosphate (0.1 and 0.001 moles per kilogram) that may be dissolved or adsorbed on a finite amount of hydrous ferric oxide at 25 degrees Celsius as a function of pH.

Ridge Physiographic Provinces. In the Piedmont, the criterion was exceeded at some sites in each of the eight surface-water networks, with the median concentrations for two networks exceeding the criterion. The Blue Ridge and Valley and Ridge criterion also was exceeded at some sites in each of the nine surface-water networks, with the medians exceeding the criterion in four carbonate and two siliciclastic networks. Although the recommended ecoregion criteria do not apply to groundwater, the 0.037-milligram-per-liter Piedmont criterion was exceeded by the median concentration of dissolved phosphate in one Piedmont crystalline groundwater network, and the 0.01-milligram-per-liter criterion was exceeded by median concentrations in all three siliciclastic networks in the Valley and Ridge and in the crystalline Blue Ridge network. These data indicate that groundwater from the crystalline and siliciclastic settings could be an important source of phosphorus to streams, especially during base-flow conditions.

Identifying chemical indicators of sources of phosphorus in water samples is important in determining whether natural or human sources are impacting water chemistry. Groundwater that had low but measurable concentrations of dissolved nitrate (less than or equal to 1.0 milligram per liter) and chloride (less than or equal to 10 milligrams per liter) was considered to indicate natural phosphate concentrations. For the samples representing “natural” groundwaters, the median concentration of dissolved phosphate was 0.029, 0.018, and less than 0.01 milligram per liter for the crystalline, siliciclastic, and carbonate bedrock settings, respectively. Most of the natural groundwaters were associated with forested areas and wetlands where minerals in soil and rock are the principal sources or sinks of phosphorus and other solutes. Phosphate minerals such as apatite and aluminosilicate minerals such as feldspar could be sources in crystalline and siliciclastic rock settings, for example, whereas apatite could be a source or sink of dissolved phosphate in carbonate rock settings. In the siliciclastic setting, in particular, phosphorus could be desorbed from iron hydroxides where groundwater is under reducing conditions. The potential presence of such minerals generally was inferred by the lithology of the bedrock in the study area and by the computed mineral saturation indices. In other samples, possible anthropogenic sources of phosphorus were indicated by the presence of elevated concentrations of nitrate (greater than 1 milligram per liter) or chloride (greater than 10 milligrams per liter) in the groundwater or surface water. These solutes are not commonly acquired from natural geologic sources, but typically are associated with animal manure, fertilizer, sewage, and road deicing salts used in agricultural and urban areas.

Mixing of deep, mineralized groundwater with shallow, less mineralized, but contaminated groundwater was identified as a critical factor affecting stream base-flow water quality. In particular, samples from many surface-water networks had lower median specific conductance (an indicator of solute concentrations) and median concentrations of silica (an indicator of groundwater age) than samples from the paired groundwater networks, which could indicate the stream is receiving a substantial portion of flow from water that is younger and more dilute than that in the part of the aquifer sampled. In the carbonate setting, the concentrations of phosphate in surface water were much greater than those in groundwater; however, in the crystalline and siliciclastic bedrock settings, the concentrations of phosphate in surface water commonly were less than or equal to those in groundwater. The elevated concentrations of chloride and nitrate and the persistence of phosphate in surface water indicate that near-surface sources and (or) transport pathways could be important, in particular in the carbonate setting, in addition to the groundwater sources of phosphorus, which are more important in the crystalline and siliciclastic settings.

Geochemical models were used to infer potential contributions of phosphate from the dissolution of minerals and to evaluate hydrochemical processes that could affect transport of phosphate from groundwater to surface water in different settings. Initial models demonstrated that dissolved phosphate and associated solutes in natural groundwater can be derived by the interaction of rainwater with the generalized mineral assemblage for each bedrock setting. Considering the positive correlations of phosphate, sodium, and silica in the groundwater, alkali feldspar containing phosphorus as an impurity ($(\mathrm{(Na,K)Al_{1.011}Si_{2.978}P_{0.011}O_8})$) was indicated as a possible source of dissolved phosphate in the crystalline and siliciclastic bedrock settings. The addition of phosphate from other natural sources (apatite, organic matter) or anthropogenic sources (fertilizer, manure, sewage) was also considered in the models.

The generalized geochemical mass-transfer models relating groundwater and stream base-flow surface-water quality in the crystalline and siliciclastic bedrock settings indicate that groundwater, which acquired phosphate by mineral dissolution, could be a major source of phosphate in surface water (estimates range from 46 to 100 percent). Additional sources, such as ammonium phosphate in fertilizers, must be considered in the carbonate bedrock setting, where 5 to 30 percent of the phosphorus in surface water was estimated to be from groundwater (mineral) sources. Because dilution was indicated as a critical process for most of the paired groundwater and surface-water models, the direct contribution of phosphate from groundwater to surface water and the importance of other sources or attenuation processes were difficult to demonstrate. The models assumed that median values for pH and solute concentrations represented steady-state compositions of the two end-member solutions. The compositions of surface water and recharge could vary seasonally, however, depending on the extent of evaporation and inputs from anthropogenic sources such as road deicing salt, fertilizer, manure, and sewage, as well as in-stream processing of nutrients. This recharge may travel along shallow flow paths, eventually mixing with deeper, more mineralized groundwater to produce the stream base flow.

Although the geochemical mass-transfer models could be interpreted to indicate major processes along a flow path (recharge to groundwater to surface water), spatial and temporal variables were not considered. Additional work would be needed to document interactions with specific minerals containing phosphorus, the effects of pH on sorption processes, contributions from shallow and deep water sources, and the temporal variability of hydrological processes (evaporation and dilution) and biological processes (microbial release and plant uptake of phosphorus). Groundwater flow-path studies in selected settings may be helpful in identifying spatial and temporal variability in the compositions of groundwater and base flow and verifying the existence and compositions of relevant solid phases that could affect phosphorus concentrations and transport. Watershed studies in selected settings that utilize continuous streamflow data coupled with periodic water-quality measurements at the outlet of the watershed also may be useful in developing phosphorus and other chemical budgets. For such studies, the chemical inputs and outputs can be computed to infer contributions from mineral and anthropogenic sources, and potential rates of transport. Data obtained from watershed studies may be applicable for the development of nutrient management plans.

Determining potential geologic contributions of phosphate may be an important component of managing phosphorus sources to meet nutrient criteria for surface-water bodies, particularly in crystalline and siliciclastic bedrock settings in the eastern United States, where conditions could be favorable for transport of phosphorus by groundwater. An understanding of geologic sources of phosphate, the relation between total phosphorus load and base-flow phosphorus load in streams, and the fate of phosphorus in groundwater discharge areas would aid in effective resource management. In discharge areas, the deeper groundwater represented by sampling in this study may interact with shallow groundwater and surface water, and geochemical conditions are likely to vary because of evapotranspiration, plant uptake, and microbial processes. An understanding of the potential for the release of phosphorus from natural sources and the processes affecting its transport would be needed for resource managers to determine whether phosphorus loading from groundwater is sufficiently large to warrant additional guidelines for in-stream phosphorus criteria.

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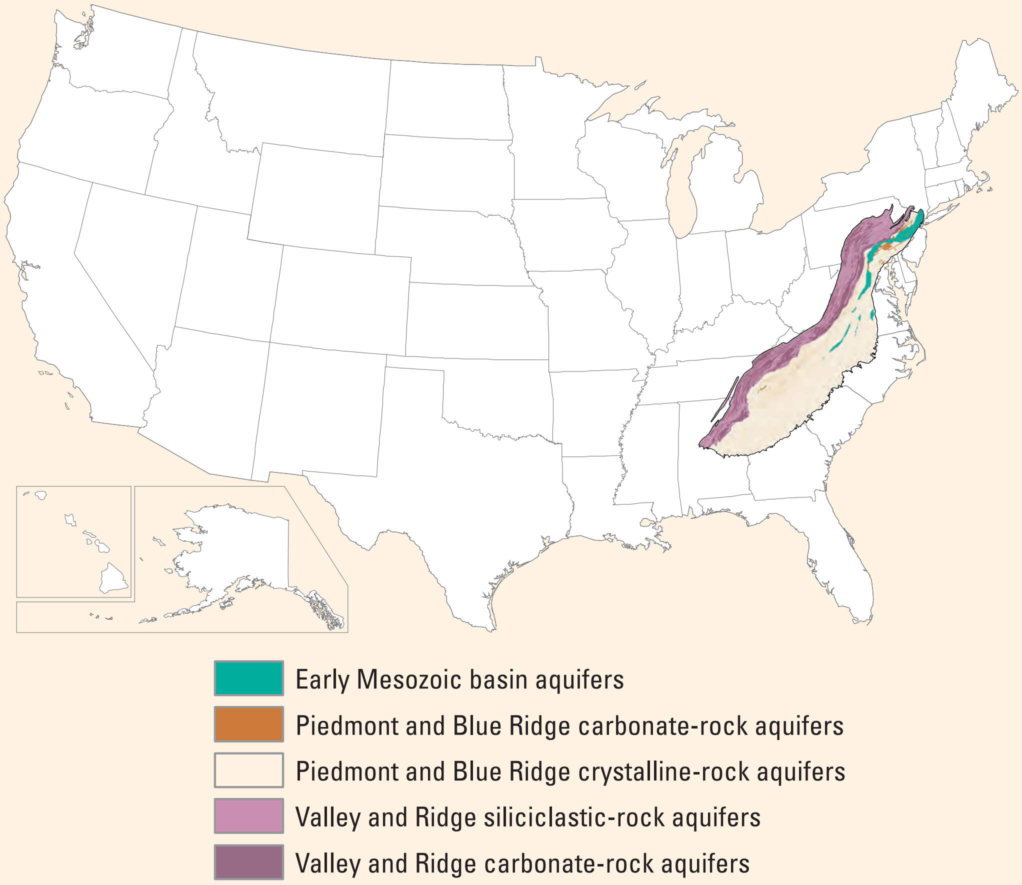

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