RELATION OF NITROGEN AND PHOSPHORUS IN GROUND WATER TO LAND USE IN FOUR SUBUNITS OF THE POTOMAC RIVER BASIN

By Scott W. Ator and Janet M. Denis

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
inch per year (in/yr)	25.4	millimeter per year

Physical and Chemical Water-Quality Units

Temperature: Water and air temperature are given in degrees Fahrenheit (°F), which can be converted to degrees Celsius (°C) by use of the following equation:

$$°C = 5/9 \times (°F-32)$$

Maximum Contaminant Level (MCL): An enforcable, health-based drinking-water regulation established by the U.S. Environmental Protection Agency.

Method Detection Limit (MDL): The minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample given matrix containing analyte.

Micrometer (µm): The millionth part of the meter--the pore diameter of filter membranes is often given in micrometer units.

Milligrams per liter (mg/L): Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as mass (milligrams) of solute per unit volume (liter) of water.

Relation of Nitrogen and Phosphorus in Ground Water to Land Use in Four Subunits of the Potomac River Basin

By Scott W. Ator and Janet M. Denis

ABSTRACT

Ground-water samples collected from 97 wells in four subunits of the Potomac River Basin were analyzed for selected nitrogen and phosphorus species (nitrate, ammonia, organic nitrogen, and orthophosphate) as part of the National Water-Quality Assessment program of the U.S. Geological Survey. As essential nutrients, nitrogen and phosphorus are used in natural and synthetic compounds to enhance plant growth. When unused by plants, these compounds may seep into the ground water. Ground water containing elevated concentrations of nitrogen or phosphorus can cause health problems when consumed, and adverse environmental impacts when discharged to streams. Nitrate was detected in ground water in all four subunits, typically at concentrations indicative of anthropogenic sources. In each subunit, most samples contained detectable ammonia and about half contained detectable orthophosphate. Concentrations of ammonia and orthophosphate were typically lower than would be expected from anthropogenic sources. Of the 97 samples collected, only 1 contained detectable organic nitrogen.

A network of 25 to 30 randomly selected wells was sampled within each of four subunits of the Potomac River Basin that were defined mainly by physiography and lithology. In the Valley and Ridge and Great Valley Carbonate subunits, agricultural areas were targeted exclusively. In the Piedmont and Triassic Lowlands subunits, the entire subunits were sampled, regardless of land use. The maximum concentration of each nutrient in natural ground water was estimated on the basis of statistical distributions of nutrient concentrations. Ground-water nutrient concentrations were compared to field-mapped land-use data within 0.25 mile of each sampled well and to county-level agricultural census data for 1992.

The concentrations of nitrate in ground water are higher in agricultural and urban areas of the Potomac River Basin than in forested areas, possibly because of anthropogenic sources in these areas. Among agricultural land uses, crop production contributes more nitrate to ground water than does livestock grazing, although both are probable nitrate sources. Ammonia concentrations are higher in forested areas, mainly in the Valley and Ridge subunit, than in agricultural or urban areas. This is possibly a result of the incomplete nitrification of ammonia that is formed naturally from organic nitrogen in leaves and other natural debris. Orthophosphate concentrations are typically low in ground water in the four sampled subunits and cannot generally be related to land use.

Bedrock lithology affects ground-water flow in fractured media and is therefore important when considering the movement of dissolved nutrients through the saturated zone. In agricultural areas, ground-water nitrate concentrations are higher in carbonate areas than in areas underlain by other rock types. This may indicate that the relatively large solution cavities that typically develop in carbonate rocks can allow surficial contaminants such as nitrate to be transported more quickly and easily in those aquifers than in other fractured-rock systems; however, it may merely reflect the fact that more nitrogen is applied per unit area to carbonate areas of the Potomac River Basin than to other areas. In areas underlain by noncarbonate rocks, surface topography reflects the general direction of ground-water flow and should therefore be considered when attempting to relate land use to ground-water quality.

INTRODUCTION

Nitrogen and phosphorus are essential nutrients and are used in natural and synthetic compounds to enhance plant growth. When unused by plants, these compounds may seep into the ground water. Ground water containing elevated concentrations of nitrogen or phosphorus can cause health problems when consumed, and adverse environmental impacts when discharged to streams. Dissolved concentrations of selected nitrogen and phosphorus species in ground-water samples from 97 wells in the Potomac River Basin were analyzed to establish the occurrence of nutrients in ground water within the basin and to link that occurrence to land-use practices. This information may be useful to managers trying to understand the relations between certain land-use practices and the propagation of potentially harmful nutrients to ground water, streams, and larger water bodies such as Chesapeake Bay. In 1987, Maryland, Pennsylvania, Virginia, the District of Columbia, and the Federal Government established the goal of reducing nitrogen and phosphorus loads to Chesapeake Bay by 40 percent (based on 1985 levels) by the year 2000 (Zynjuk, 1995).

Purpose and Scope

This report describes the relation of land use to dissolved concentrations of selected nitrogen and phosphorus species (nitrate, ammonia, organic nitrogen, and orthophosphate) in ground water of the Potomac River Basin. Ground-water nutrient concentrations are also contrasted between and among geographic areas within the Potomac River Basin and compared to estimated background levels and established standards for drinking water.

Ground-water-quality data cited in this report were collected as part of water-quality assessments conducted in four subunits in the Valley and Ridge and the Piedmont Physiographic Provinces of the Potomac River Basin from 1993 through 1995. For comparison to water quality, land use was field-mapped within 0.25 mile of each sampled well and compiled from county-level agricultural land-use data.

Importance, Sources, and Effects of Nitrogen and Phosphorus

Nitrogen and phosphorus are essential nutrients to plants and animals. For plants, these nutrients are generally required in relatively large amounts. Commercial fertilizers, synthetic organic compounds, and animal manure containing nitrogen and phosphorus are used to enrich soil for enhancing plant growth. In recent decades, farmers have increased their use of fertilizers (U.S. Department of Commerce 1989, 1995) for cultivating fields with marginal soil fertility. Fertilizers are also commonly used on suburban lawns (Conservation Foundation, 1987), parks, and recreation areas.

Various forms of nitrogen and phosphorus are present in the environment. In ground water, nitrogen most commonly exists as nitrate (NO_3^-), although it can also occur as ammonium (NH_4^+), ammonia (NH_3), nitrite (NO_2^-), nitrogen (N_2), nitrous oxide (N_2O), and organic nitrogen (Freeze and Cherry, 1979). Nitrate is very soluble and is the most stable form of nitrogen under oxidizing conditions. It can move freely with ground-water flow and commonly migrates long distances from its source in certain hydrogeologic environments (Freeze and Cherry, 1979). Under anaerobic conditions, nitrate can be reduced to nitrous oxide, nitrogen gas, or - less commonly - ammonium (Freeze and Cherry, 1979). Ammonium is soluble in water but typically adheres to anionic soil surfaces or is converted to nitrate under aerobic conditions in the soil zone. Organic nitrogen is water-soluble at intermediate oxidation states (Hem, 1985) but is typically converted to ammonium in the soil zone (Freeze and Cherry, 1979). Phosphate is the only form of soluble phosphorus that is significant in natural water (Hem, 1985). Orthophosphate (PO_4^{3-}), in various compounds with hydrogen, is the most stable form of phosphate (Mueller and others, 1995). Because phosphates are only moderately soluble, they are not very mobile in soils and ground water (Mueller and others, 1995).

Although natural sources of nitrogen and phosphorus exist, elevated concentrations of these nutrients in ground water are typically anthropogenic (human-derived). Natural sources include minerals in rocks and soils, animal wastes from unconfined areas, microbial assimilation, and biodegradation (Hem, 1985). The major sources of nitrogen and phosphorus to ground water are anthropogenic and include atmospheric deposition of nitrogen from fossil fuel combustion, animal wastes from confined areas, applied manure and commercial fertilizers, and septic systems. Discharges from wastewater treatment plants and industries are primary point sources to surface water (Puckett, 1994) but are not major sources to ground water.

Excessive nutrients in ground water are a concern to water users because of the potential for harmful effects on human health and the environment. Ground water is a major source of water for human consumption. The U.S. Environmental Protection Agency (USEPA) has established a Maximum Contaminant Level (MCL) for nitrate in drinking water of 10 milligrams per liter (mg/L) as nitrogen. Drinking water containing dissolved nitrate in excess of the MCL can cause methemoglobinemia (blue-baby syndrome), a potentially fatal condition in infants. There are no primary drinking water standards for ammonia, organic nitrogen, or orthophosphate (U.S. Environmental Protection Agency, 1991). Elevated nutrient concentrations in ground water when discharged to streams can cause eutrophication, a condition whereby aquatic plants and algae are over-produced. This algae can consume dissolved oxygen, smother larger plants, block sunlight from the water, and produce toxins that are harmful and possibly fatal to other aquatic life (Allaby, 1989).

The National Water-Quality Assessment Program

This study of the Potomac River Basin was conducted as part of the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) program. Two goals of the NAWQA program are to assess the quality of a representative portion of the Nation's ground-water resource and to link that assessment to an understanding of the natural and human factors that can affect ground-water quality (Gilliom and others, 1995).

The Potomac River Basin

The Potomac River drains 14,670 square miles in parts of four states (Maryland, Pennsylvania, Virginia, and West Virginia) and the District of Columbia (fig. 1). The basin is characterized by a moderate, humid climate. The average-annual temperature ranges from 47 to 58 degrees Fahrenheit and the average-annual precipitation ranges from 32 to 48 inches per year (Blomquist and others, 1996).

The Potomac River Basin includes parts of five physiographic provinces--the Appalachian Plateau, Valley and Ridge, Blue Ridge, Piedmont, and Coastal Plain. The Appalachian Plateau is the westernmost province and is characterized by narrow valleys and steep ridges underlain primarily by siliciclastic rocks. The Valley and Ridge is characterized by resistant ridges underlain primarily by sandstone and narrow valleys underlain primarily by shale and carbonate rock. These sedimentary rocks have been intensely folded and faulted. In the eastern portion of the Valley and Ridge is the Great Valley subprovince, a wide valley with low relief that is underlain by shale and carbonate rock. Some carbonate areas of the Great Valley exhibit well-developed Karst terrain. The Blue Ridge, which runs through the center of the basin, is characterized by high relief and is underlain by metamorphic rocks. The Piedmont is characterized by rolling hills with low to moderate relief and is underlain primarily by metamorphic bedrock. The Triassic Lowlands, a subprovince of the Piedmont, is underlain by Mesozoic-aged siliciclastic rocks and diabase intrusions. The Coastal Plain is characterized by low relief and is underlain by unconsolidated sediments. A detailed discussion of the physiography and geology of the Potomac River Basin is included in Blomquist and others (1996).

The three major land uses in the Potomac River Basin are forested, agricultural, and urban (fig. 2). Forest is predominant in the Appalachian Plateau, Valley and Ridge, Blue Ridge, and Coastal Plain Provinces. Agricultural land--mostly cropland and pasture--is predominant in the Piedmont Province and in the Great Valley

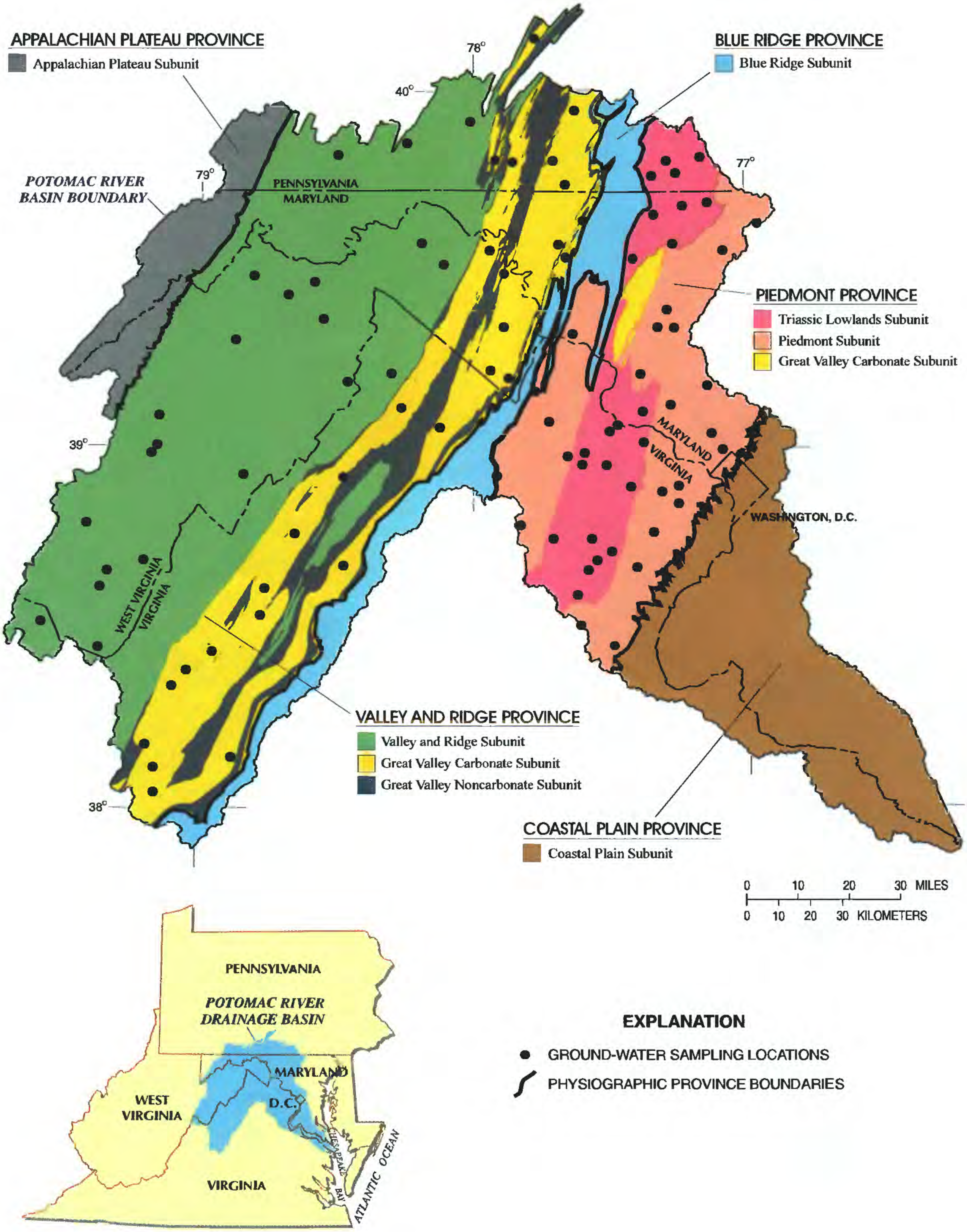


Figure 1. Physiographic provinces, subunits, and ground-water sampling locations within the Potomac River Basin.

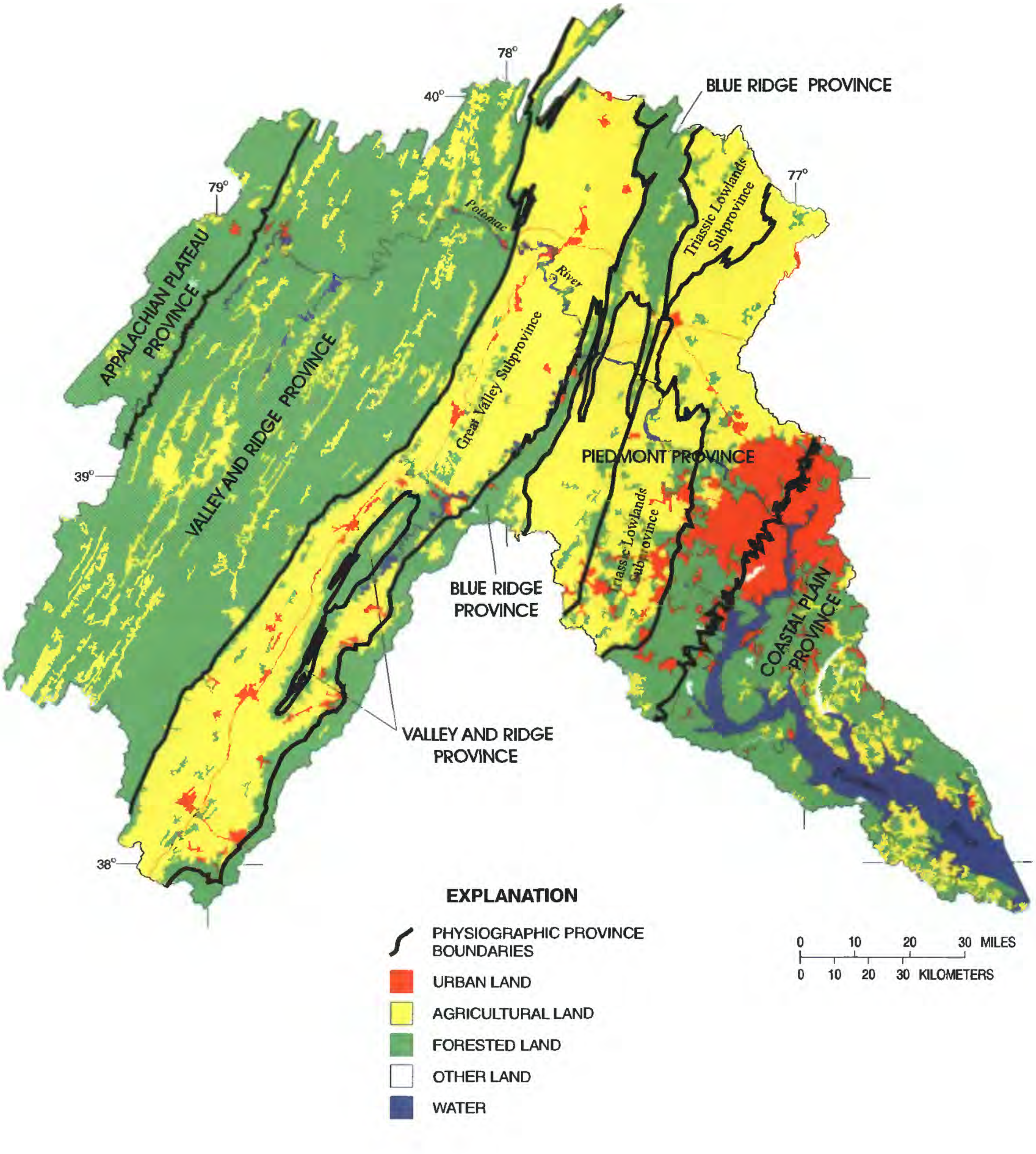


Figure 2. Generalized land use and physiography in the Potomac River Basin.

and Triassic Lowlands subprovinces. The dominant row crop in the basin is corn; barley, oats, wheat, sorghum, and soybeans are produced in lesser amounts. Most urban land in the basin is located in the Washington, D.C., area in the Piedmont and Coastal Plain Provinces.

Nitrogen and phosphorus inputs to the Potomac River Basin are mainly from nonpoint sources and vary greatly among physiographic provinces. As part of a retrospective analysis of nutrients in waters of the Potomac River Basin, Blomquist and others (1996) estimated inputs of nitrogen and phosphorus from various sources to the basin for 1990. They attributed 55 percent of total nitrogen and 93 percent of total phosphorus inputs to the basin for that year to commercial fertilizer and manure. An additional 32 percent of nitrogen inputs were attributed to atmospheric deposition. The Great Valley subprovince received the greatest inputs of both nitrogen and phosphorus per unit area in 1990, followed by the Triassic Lowlands and the remainder of the Piedmont. Most nitrogen in these areas was attributed to commercial fertilizers and manure. The Appalachian Plateau, Blue Ridge, and Coastal Plain Provinces and the remainder of the Valley and Ridge Province received smaller inputs of nitrogen and phosphorus per unit area. The majority of nitrogen input to these areas was attributed to atmospheric deposition (Blomquist and others, 1996).

Acknowledgments

The authors would like to thank the many citizens who allowed their wells to be sampled as part of this project. Without their cooperation, this work would have been impossible. Thanks are also due to volunteers Kalman and Phyllis Illyefalvi for their generous donation of time and effort in land-use verification.

STUDY DESIGN AND METHODS

Highlights of NAWQA approaches and procedures particularly relevant to the assessment of ground-water quality in four subunits of the Potomac River Basin are summarized in this section. A more detailed and comprehensive discussion of the design of the Potomac NAWQA study can be found in Gerhart and Brakebill (1997).

Subunit Approach

For the purpose of water-quality investigations for the NAWQA program, the Potomac River Basin was divided into eight subunits based primarily on physiography and lithology. Most of these subunits correspond to physiographic provinces or subprovinces. Because carbonate areas generally exhibit unique hydrogeologic and water-quality characteristics, the Great Valley was further subdivided on the basis of lithology. The eight subunits are: the Appalachian Plateau, Valley and Ridge, Great Valley Carbonate, Great Valley Noncarbonate, Blue Ridge, Piedmont, Triassic Lowlands, and Coastal Plain (fig. 1). The small area of the Piedmont Province that is underlain by carbonate rocks is included in the Great Valley Carbonate subunit.

Ground-water-quality assessments were conducted independently within each of four subunits of the Potomac River Basin. The Great Valley Carbonate subunit (with the exception of the small outlier east of the Blue Ridge subunit) was sampled in 1993, the Piedmont and Triassic Lowlands subunits were sampled in 1994, and the Valley and Ridge subunit was sampled in 1995. These four subunits were chosen for assessment because they encompass nearly 60 percent of the basin population (Gerhart and Brakebill, 1997). Sampling was conducted in the late spring and summer of each year. Historical records (Durlin and Schaffstall, 1996; Prugh and Powell, 1996; Smigaj and Saffer, 1996; Ward and others, 1996) indicate that ground-water levels in most areas of the four subunits were very similar during that season from 1993 through 1995. For this reason, it is assumed that hydrologic conditions were comparable during that period and that ground-water-quality data may be compared from different years.

Depending on the goals of each subunit assessment, one of two approaches was used to select wells for sampling within each subunit. (1) *Land-use studies* were designed to assess the quality of shallow ground water within a particular land-use setting (agricultural or urban) within a subunit. Wells were selected for sampling only from within that land-use setting (Gilliom and others, 1995). Agricultural land-use studies were conducted in the Valley and Ridge and Great Valley Carbonate subunits. (2) *Subunit surveys* were designed to assess the quality of ground water within an entire subunit. Wells were selected for sampling from the entire subunit, regardless of land use (Gilliom and others, 1995). Subunit surveys were conducted in the Piedmont and Triassic Lowlands subunits.

Well Inventory and Selection

Wells were randomly selected for sampling within the target area of each subunit (either agricultural land within the subunit or the entire subunit) to create a spatially unbiased network within that area. Using a stratified-random-selection computer program (Scott, 1990), 25 to 30 points were selected within the target area of each subunit. An inventory of existing wells was then conducted near each point. One well was selected for sampling near each point based on several criteria, including the construction, age, depth, and accessibility of the well and the ability to bypass any installed treatment systems (Gerhart and Brakebill, 1997). A complete discussion of NAWQA well selection and inventory protocols is included in Lapham and others (1995).

Sampling Procedures

Consistent procedures were followed during the sampling of each well to ensure the quality of the data and comparability of analytical results between different wells and different subunits. Most wells were purged prior to sampling of the equivalent of at least three times the volume of standing water in the well. In cases where three standing-water volumes were not purged from a well prior to sampling, stability of water temperature, pH, specific conductance, and dissolved oxygen levels (which were monitored during all purges) with time was used to judge whether discharging water was coming immediately from the aquifer. Samples were collected prior to any water treatment using a submersible or--in a few cases--a jet pump. Samples collected for nutrient analysis were passed through a 0.45-micrometer filter and--prior to 1995--preserved with mercuric chloride. By 1995, mercuric chloride preservation was proven unnecessary and discontinued (David A. Rickert, U.S. Geological Survey, written commun., 1994). Quality-assurance samples (equipment blanks and/or duplicate samples) were taken at 16 to 27 percent of sites sampled during each year. All equipment and supplies were decontaminated between sites. Samples were chilled and shipped overnight to the USGS National Water-Quality Laboratory in Arvada, Colorado, for analysis. NAWQA ground-water-sampling protocols are discussed in detail in Koterba and others (1995).

Sampling and analytical problems resulted in the loss of several nutrient samples from some subunits. This left nutrient concentration data for 28 wells in the Great Valley Carbonate subunit, 25 wells in the Piedmont subunit, and 22 wells in each of the Valley and Ridge and Triassic Lowlands subunits available for analysis.

Ancillary Data Collection

To augment the interpretation of water-quality data, ancillary information was collected for each sampled well. Well depth and other construction data were measured directly in the field or determined from driller's logs or well completion reports. Where driller's logs and completion reports were unavailable, aquifer lithology was determined from published geologic maps (Berg, 1980; Cardwell and others, 1986; Cleaves and others, 1968; and Milici and others, 1963). Geologic maps typically do not provide sufficient detail for identifying the specific hydrogeologic units contributing water to individual wells but are useful for identifying broadly defined aquifer lithology. Lithology is fairly homogeneous within each subunit.

Land-use data were collected near each well for comparison to ground-water quality. With the aid of high-altitude aerial photography, land use was field-mapped in a circle with a radius of 0.25 mile around each sampled well. Topographic maps were used to delineate the upgradient half and quarter segments of each 0.25-mile circle, based on surface topography. These areas were digitized and land-use percentages were calculated for each circle segment at each well. Examples of field-mapped land use and delineated circle segments for one sampled well in the Valley and Ridge subunit are shown in figure 3.

Although the contributing area of each sampled well is unlikely to correspond exactly to the 0.25-mile circle around the well, the land use within this distance probably affects ground-water quality at the well. Localized ground-water-flow systems typically develop in humid areas with local relief (Fetter, 1994; Freeze and Cherry, 1979) and closely spaced streams. LeGrand (1967) describes local ground-water-flow systems in the Piedmont Physiographic Province of the Southeastern United States. Although topography differs in the Valley and Ridge subunit, stream density (stream miles per unit area) calculated from digital line graphs (U.S. Geological Survey, 1989) in the Valley and Ridge is similar to that in the Piedmont and Triassic Lowlands subunits. In carbonate areas such as the Great Valley, the interconnecting networks of fractures and solution cavities that typically develop make it very difficult to delineate ground-water-flow systems. However, because land use in the Great Valley Carbonate subunit is predominantly and uniformly agricultural (fig. 2), the land use where any well in that subunit is recharged is likely to be agricultural.

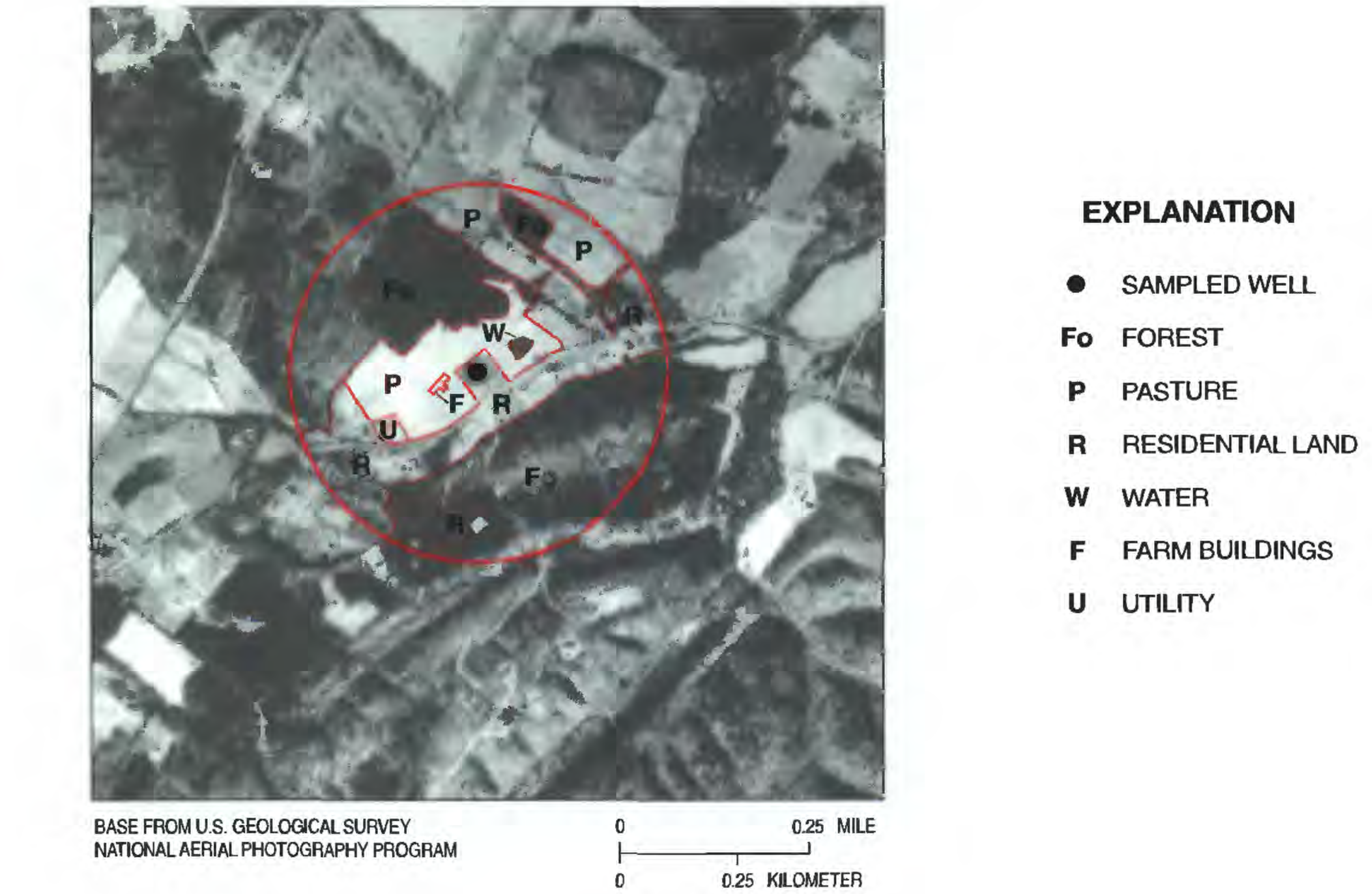
Data Analysis

All concentrations reported from the laboratory and cited in this report are expressed as equivalent masses of elemental nitrogen or phosphorus, as appropriate. *Nitrate*, as reported here, was calculated from laboratory-reported concentrations of *dissolved nitrite plus nitrate* and *dissolved nitrite*. In cases where no nitrite was detected, all *dissolved nitrite plus nitrate* is assumed to be nitrate. Similarly, *organic nitrogen* concentrations were calculated from laboratory-reported concentrations of *dissolved ammonia plus organic nitrogen* and *dissolved ammonia.* Reported concentrations of dissolved ammonia refer to total dissolved ammonia (aqueous NH_3) and ammonium (ionic NH_4^+), although pH conditions indicate that any ammonia nitrogen in ground-water samples in this study would be in the form of ammonium (Hem, 1985).

Analytical results of 12 duplicate samples and 9 equipment blanks were examined to provide an estimate of the reliability and precision of reported nutrient concentrations. Duplicate samples were used to estimate the standard deviation in measurements of each nutrient species (Taylor, 1987) and blank analyses were used to evaluate the reliability of concentrations reported to be near, at, or below analytical detection limits. Estimated standard deviations are 0 mg/L for nitrite, 0.074 mg/L for nitrite plus nitrate, 0.0041 mg/L for ammonia, 0.0041 mg/L for orthophosphate, and 0 mg/L for ammonia plus organic nitrogen. There is some uncertainty in the detection of small concentrations of orthophosphate. Results of analyses of 4 of 12 duplicates disagreed on the detection of this constituent, although only 1 of 9 blank samples contained detectable orthophosphate. Some uncertainty is also present in the measurement of small concentrations of ammonia; 4 of 9 blanks contained detectable ammonia. None of the other nutrients was detected in more than one blank sample.

The data were analyzed using non-parametric statistical tests that allow for unequal sample sizes among groups (Helsel and Hirsch, 1992). Unless otherwise indicated, test statistics and p-values cited are large-sample or rank-transform approximations and null-hypotheses were accepted or rejected at the 95-percent confidence level (alpha=0.05). For hypothesis tests, censored data (concentrations reported as less than the analytical method detection limit) were set to one-half of the detection limit to separate them from concentrations detected at the detection limit.

To identify nutrient concentrations indicative of anthropogenic sources, a qualitative graphical technique was used to estimate the probable maximum natural or "background" level of each nutrient in ground water. The steep inflection point on a probability plot of nutrient concentrations, which marks the boundary between two statistical populations, was inter-



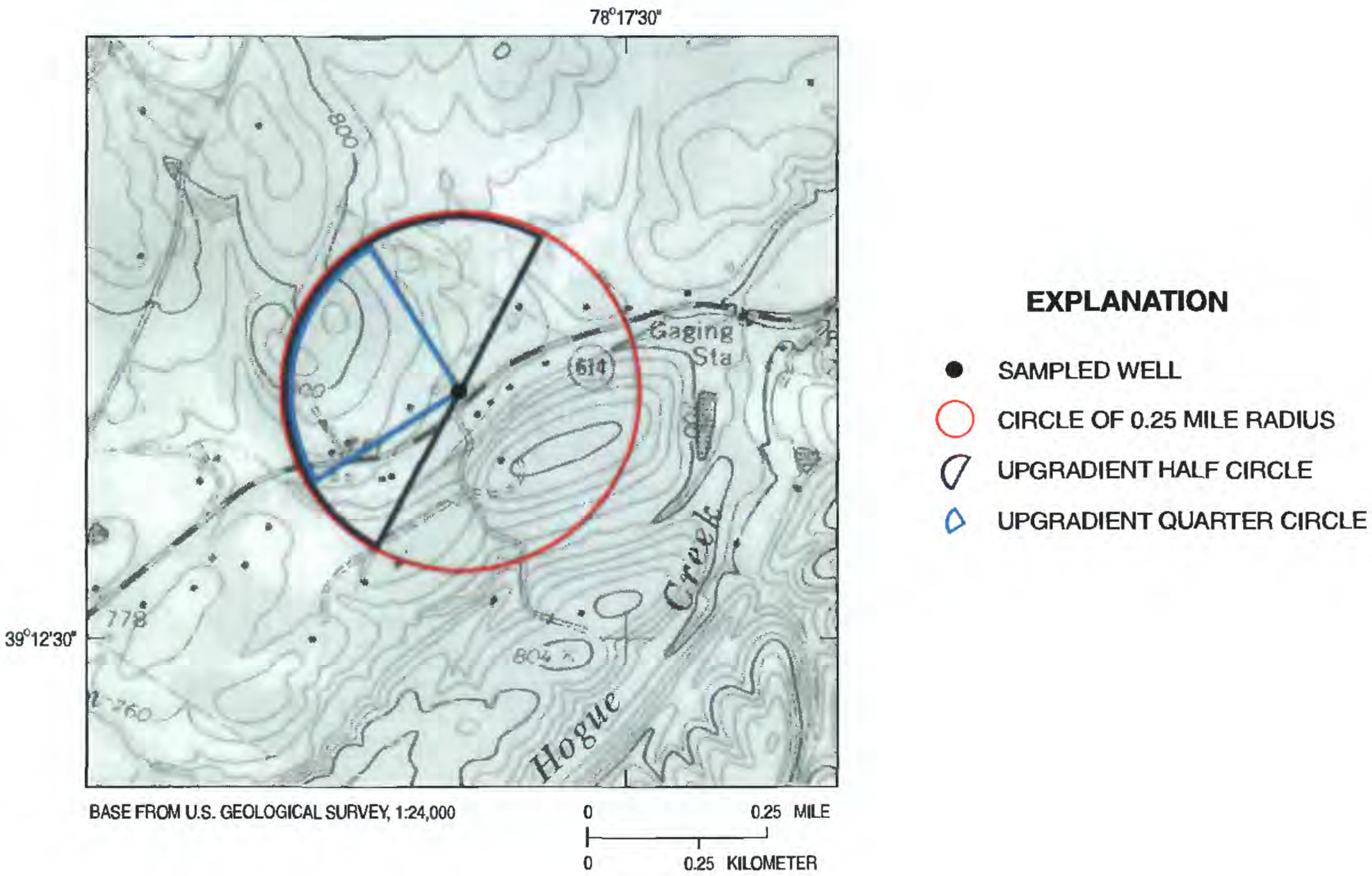


Figure 3. Land use and topography within 0.25 mile of one sampled well in the Valley and Ridge subunit.

preted as the threshold value between natural ground water and ground water that probably is affected by human activities. In cases where probability plots contained multiple steep inflection points, the threshold was interpreted as the inflection point at the lowest concentration. In using this technique, it is assumed that the data set contains both natural and human-affected samples and that the statistical population of lowest concentrations is that of natural ground water. This graphical technique can identify water samples that are likely affected by anthropogenic nutrient sources; however, it cannot be used alone to identify natural samples conclusively. Nutrients at concentrations below the estimated threshold level may be natural or human affected. Based on the data collected for this study, estimated maximum background nutrient levels are 0.4 mg/L for nitrate, 0.1 mg/L for ammonia, and 0.07 mg/L for orthophosphate. The data do not support the estimation of a threshold concentration for organic nitrogen. For nitrate, this level is comparable to the level of 0.4 mg/L cited by Hamilton and others (1993) for shallower wells in an unconsolidated surficial aquifer and to that of 0.2 to 3.0 mg/L cited by Madison and Brunett (1984).

Simple comparisons of nutrient concentrations among the four subunits cannot be made because two different sampling approaches--the land-use study and the subunit survey--were employed. For this reason, two different analytical approaches were employed in comparing ground-water nutrient concentrations among the subunits. Assessments of the Valley and Ridge and the Great Valley Carbonate subunits were conducted as agricultural land-use studies. The results of those surveys were therefore used to compare the nutrient concentrations in ground water in agricultural areas of those two subunits. The Piedmont and Triassic Lowlands subunits were studied using the subunit-survey approach. Therefore, the results of those studies were used to compare the ground-water quality of those entire subunits. Land use in the Great Valley Carbonate subunit is so predominantly agricultural that wells chosen to represent the agricultural area of that subunit are also representative of the entire subunit. Average land-use percentages within 0.25 mile of each well chosen for this study are comparable to land-use percentages for the entire subunit (table 1). The Great Valley Carbonate subunit was included in both comparisons for that reason.

Although an attempt was made to sample wells within a previously selected range of depths for each subunit assessment, all subunit networks contain wells of widely varying depths (table 2). The distribution of well depths is not significantly different in the Valley and Ridge and Great Valley Carbonate subunits ($p=0.2529$) or in the Great Valley Carbonate, Piedmont, and Triassic Lowlands subunits ($p=0.8045$); therefore the depth variable should not affect comparisons of nutrient concentrations among subunits. Casing lengths are not available for most sampled wells. Therefore, determining the range of depths over which each well is actually receiving water is not possible.

Ground-water levels (table 2) were measured in most wells prior to purging. Statistical tests indicate that the depth to water is significantly greater in the Great Valley Carbonate subunit than in the Valley and Ridge ($p=0.0317$). Water levels in the Great Valley Carbonate subunit are not significantly different from those in the Piedmont but are significantly deeper than those in the Triassic Lowlands ($p=0.0198$). Ground-water levels in the Piedmont and Triassic Lowlands subunits are not significantly different. Because nutrient sources are typically surficial, these water-level differences could result in differences in the movement of nutrients below the surface and could therefore affect the validity of comparisons of ground-water nutrient concentrations among the subunits.

NITROGEN AND PHOSPHORUS SPECIES IN GROUND WATER

Concentrations of dissolved nitrate, ammonia, organic nitrogen, and orthophosphate in ground water in each subunit are presented and compared to estimated maximum background concentrations. Statistical comparisons of the distributions of nitrate, ammonia, and orthophosphate among subunits are also presented.

Table 1. Percentages of urban, agricultural, and forested land within four subunits of the Potomac River Basin

[Digital land-use data obtained from the Geographic Information Retrieval and Analysis System (GIRAS) of the U.S. Geological Survey (1979a, b, c, d; 1980a, b, c, d) updated with 1990 Census of population and housing data from the Bureau of the Census (1991)]

	Subunit							
	Valley and Ridge		Great Valley Carbonate		Piedmont		Triassic Lowlands	
Land use	GIRAS[1]	0.25 mile[2]	GIRAS	0.25 mile	GIRAS	0.25 mile	GIRAS	0.25 mile
Urban	1	11	11	11	27	37	14	20
Agricultural	18	50	74	77	48	33	64	45
Forested	80	35	15	9	24	26	21	20

[1] Percentage of land use in entire subunit, from GIRAS.

[2] Average percentage of field-mapped land use within 0.25 mile of sampled wells in that subunit.

Table 2. Statistical summary of well depths and water levels for sampled wells within four subunits of the Potomac River Basin

[**VR**, Valley and Ridge subunit; **GV**, Great Valley Carbonate subunit; **PD**, Piedmont subunit; **TR**, Triassic Lowlands subunit, IQR, Interquartile range]

		Subunit			
Variable	**Statistic**	**VR**	**GV**	**PD**	**TR**
Depth of well (feet)	Number	22	28	25	20
	Maximum	350	290	365	326
	Median	121	145	134	147
	Minimum	56	65	71	75
	IQR	129	58	55	142
Depth to water (feet)	Number	12	28	23	16
	Maximum	117.08	89.03	74.45	81.79
	Median	31.30	42.76	34.17	27.08
	Minimum	17.67	21.09	10.54	7.04
	IQR	21.26	19.30	26.33	23.57

Nitrate is the dominant dissolved nitrogen species in ground water in most sampled subunits. In the Great Valley Carbonate, Piedmont, and Triassic Lowlands subunits, a majority of samples contained nitrate at concentrations greater than the estimated maximum background concentration. Ammonia was detected in most samples from all four subunits and is the dominant dissolved nitrogen species in ground water of the Valley and Ridge subunit. Of 97 samples collected for this study, only one contained detectable organic nitrogen. Orthophosphate was detected in about half of the samples collected in each subunit but rarely at concentrations that would indicate anthropogenic sources.

Nitrate

Dissolved nitrate is present at detectable levels in ground water from each of the four subunits (fig. 4). Concentrations of nitrate in samples collected for this study ranged from less than 0.05 mg/L (undetected) to 29 mg/L with an overall median of 1.4 mg/L.

In the Valley and Ridge subunit, only 6 of 22 samples (27 percent) contained detectable nitrate (fig. 4). Of these, only one contained nitrate at a concentration greater than 0.4 mg/L, the estimated maximum background concentration. This sample, with a nitrate concentration of 6.2 mg/L, was the only one in the Valley and Ridge collected from a well completed in a carbonate aquifer.

Of 28 samples collected in the Great Valley Carbonate subunit, all contained detectable nitrate and 27 (96 percent) contained nitrate at concentrations greater than 0.4 mg/L. The maximum nitrate concentration among Great Valley Carbonate samples was 29 mg/L and the median was 4.6 mg/L. Samples from seven sites (25 percent) contained nitrate at concentrations greater than the MCL of 10 mg/L. No samples collected in other subunits contained nitrate at concentrations greater than the MCL.

In the Piedmont, 19 of 25 samples (76 percent) contained detectable nitrate and 16 samples (64 percent) contained nitrate at concentrations greater than 0.4 mg/L. The maximum nitrate concentration detected in the Piedmont was 8.5 mg/L and the median was 1.4 mg/L.

Of 22 samples collected in the Triassic Lowlands, 18 (82 percent) contained detectable nitrate and 17 (77 percent) contained nitrate at concentrations greater than 0.4 mg/L. The maximum nitrate concentration was 7.7 mg/L and the median was 1.1 mg/L.

Ground-water nitrate concentrations are significantly higher in agricultural areas of the Great Valley Carbonate subunit than in agricultural areas of the Valley and Ridge subunit (fig. 4). Nitrate concentrations in ground water in the Great Valley Carbonate subunit are also significantly higher than in the Piedmont or Triassic Lowlands subunits. These results reflect the fact that, according to estimates for 1990, more pounds of nitrogen per unit area from various sources are applied to the Great Valley Carbonate subunit than to the Valley and Ridge, Piedmont, or Triassic Lowlands subunit (Blomquist and others, 1996). These results also may indicate that even though ground-water levels are lower in the Great Valley Carbonate subunit, the relatively large solution cavities that can develop in carbonate rocks allow nitrate from surficial sources to be transported relatively quickly and easily throughout the aquifers of this subunit. Nitrate concentrations in the Piedmont and Triassic Lowlands subunits are not significantly different.

Ammonia

Dissolved ammonia is present at detectable levels (not less than 0.015 mg/L for Valley and Ridge samples, 0.01 mg/L for all others) in ground water in each subunit (fig. 4); however, concentrations are typically less than 0.1 mg/L, the estimated maximum background concentration. Of 22 samples collected in the Valley and Ridge subunit, all contained detectable ammonia and 9 (41 percent) contained ammonia at concentrations greater than 0.1 mg/L. In the Great Valley Carbonate, Piedmont, and Triassic Lowlands subunits, most samples contained ammonia at concentrations less than 0.1 mg/L. Of 28 Great Valley Carbonate samples, 27 (96 percent) contained detectable ammonia, but only 1 sample contained ammonia at a concentration greater than

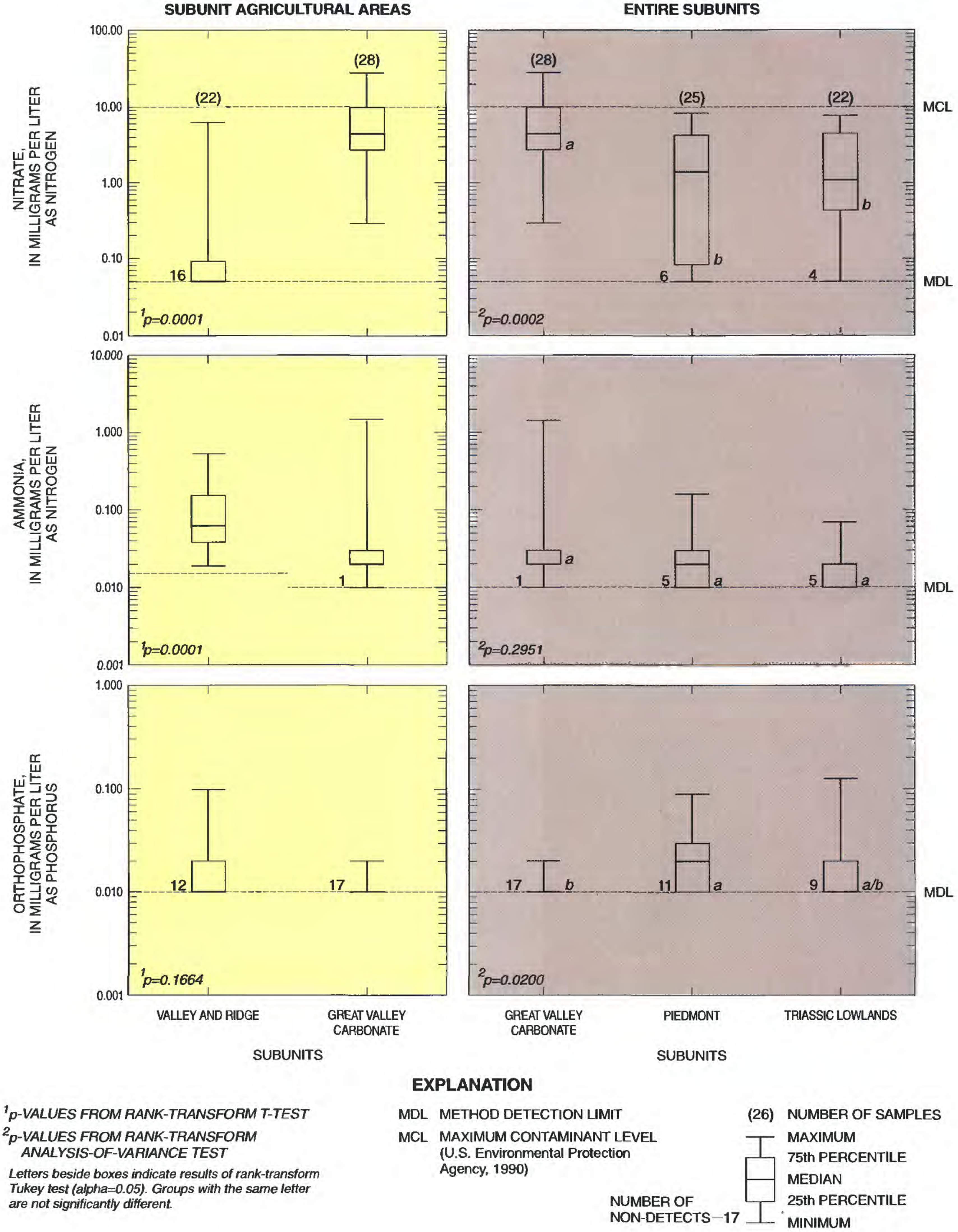


Figure 4. Distributions of nitrate, ammonia, and orthophosphate in ground water within four sampled subunits of the Potomac River Basin and comparisons of distributions among subunits. (Comparisons were done separately for subunits assessed with land-use study and subunit survey approaches.)

0.1 mg/L. In the Piedmont, 20 of 25 samples (80 percent) contained detectable ammonia; only one concentration was greater than 0.1 mg/L. Seventeen of 22 samples (77 percent) from the Triassic Lowlands contained detectable ammonia; none contained more than 0.1 mg/L.

Ammonia concentrations are significantly higher in ground water in agricultural areas of the Valley and Ridge subunit than in the Great Valley Carbonate subunit (fig. 4). Considering that ammonia sources are typically surficial, this could be due to the higher ground-water levels in the Valley and Ridge subunit relative to the Great Valley Carbonate. Nitrate results, however, indicate that ground water in the Great Valley Carbonate subunit is well connected to the surface despite the fact that water levels are lower. The higher ammonia concentrations in the Valley and Ridge subunit are probably reflective of reducing conditions. Dissolved oxygen concentrations are significantly lower in ground water in the Valley and Ridge than in the Great Valley Carbonate ($p=0.0001$).

Ground-water ammonia concentrations are not significantly different in the Great Valley Carbonate, Piedmont, and Triassic Lowlands subunits. The median ammonia concentration was 0.02 mg/L in each of these three subunits.

Organic Nitrogen

Organic nitrogen is not typically present at detectable levels (not less than 0.2 mg/L) in ground water in the areas of the Potomac River Basin sampled for this study. Of 97 samples collected in the four subunits, only one contained detectable organic nitrogen (0.3 mg/L). This sample, from a site in the Great Valley Carbonate, also contained the highest nitrate and ammonia concentrations (29 mg/L and 1.5 mg/L, respectively) of all those collected. The presence of organic nitrogen along with elevated levels of nitrate and ammonia may indicate that ground water at this site is affected by a local point source of contamination. Field investigations confirmed the location of a manure-storage structure within 100 feet of this well.

Orthophosphate

Orthophosphate is present in ground water in all four subunits (fig. 4); although concentrations are typically lower than 0.07 mg/L, the estimated maximum background concentration. In the Valley and Ridge, 10 of 22 samples (45 percent) contained detectable orthophosphate; only one concentration was greater than 0.07 mg/L. Of 28 samples collected in the Great Valley Carbonate subunit, 11 (39 percent) contained detectable orthophosphate; although the maximum concentration was only 0.02 mg/L. Orthophosphate was detected in 14 of 25 samples (56 percent) from the Piedmont and 13 of 22 samples (59 percent) from the Triassic Lowlands. One sample from the Piedmont and two samples from the Triassic Lowlands contained orthophosphate at concentrations greater than 0.07 mg/L.

Concentrations of orthophosphate in ground water are not significantly different in agricultural areas of the Valley and Ridge and Great Valley Carbonate subunits (fig. 4). The majority of samples in both subunits contained undetectable (less than 0.01 mg/L) orthophosphate. Tukey test results indicate that orthophosphate concentrations are not significantly different in ground water from the Piedmont and Triassic Lowlands subunits and from the Triassic Lowlands and Great Valley Carbonate subunits. The Piedmont is the only subunit where the median detected orthophosphate concentration (0.02 mg/L) was greater than the detection limit.

RELATION OF NITROGEN AND PHOSPHORUS IN GROUND WATER TO LAND USE

For the purpose of detecting relations of land use to ground-water quality, concentrations of nitrate, ammonia, and orthophosphate in ground water of each subunit were compared to field-mapped land use within 0.25 mile of each sampled well and to 1992 agricultural census data (U.S. Department of Commerce, 1995).

Land Surrounding Sampled Wells

Most of the land surrounding sampled wells in each subunit is either forested, agricultural, or urban. These three land uses encompass greater than 80 percent of the land within 0.25 mile of 91 percent of the wells (88 of 97) where nutrient data were collected. Six of the nine wells that are surrounded by less than 80 percent forested, agricultural, and urban land are in the Triassic Lowlands subunit surrounded by high percentages of fallow or otherwise cleared but unused land. Most agricultural land around sampled wells is either cropland or pasture. Cropland and pasture account for greater than 90 percent of agricultural land near (within 0.25 mile of) 79 of 85 sites near any agricultural land. Four of the six exceptions are wells in the Great Valley Carbonate subunit that are near orchards. Most urban land within 0.25 mile of sampled sites is residential. Residential land accounts for greater than 80 percent of urban land at 74 of 91 sites near any urban land. This is likely a result of the fact that most sampled wells are privately owned domestic wells that serve single-family homes.

In the Valley and Ridge, Piedmont, and Triassic Lowlands subunits, surface topography reflects the general direction of ground-water flow and should be considered when attempting to characterize the effects of land use on ground-water quality. Within a 0.25-mile radius of wells in these subunits, land use within the upgradient quarter-circle segment (fig. 3) correlates more closely with ground-water quality than does land use within the upgradient half-circle segment or the entire 0.25-mile circle. Statistical relations of nutrient concentrations with mapped land-use percentages (where they are significant) are typically stronger (higher correlation coefficients) and more significant (lower p-values) for land use in the upgradient quarter circle than for the half or whole circles. An example of this relation is shown in table 3.

In the Great Valley Carbonate subunit, surface topography is not as reliable an indicator of the general direction of ground-water flow as it is in the Valley and Ridge, Piedmont, or Triassic Lowlands subunits. Statistical relations between nutrient concentrations and land-use percentages within 0.25 mile of wells are typically comparable in strength and significance for all three circle segments. This is possibly due to the irregular network of fractures and solution cavities that is typical of carbonate areas and can allow delivery of a mixture of water to a well from a variety of recharge zones.

Nutrient concentrations in ground water of the Potomac River Basin are related to land use within 0.25 mile of the sampled well. In each of the four subunits, ground-water nutrient concentrations (nitrate, ammonia, and orthophosphate) were statistically correlated with percentages of five different land uses (urban, forested, total agricultural, cropland, and pasture) within the upgradient quarter-circle within 0.25 mile of each well (table 4). Dissolved nitrate concentrations are correlated to agricultural or urban land in most subunits. Ammonia concentrations are typically related to land use only in the Valley and Ridge subunit, where detected ammonia concentrations are consistently highest. Orthophosphate concentrations are typically not related to land use. Orthophosphate is positively correlated (alpha=0.10) with urban land in the Valley and Ridge subunit and with forested land in the Piedmont subunit; however, orthophosphate concentrations are very low in all subunits. Only 4 of the 97 wells sampled for this study contained orthophosphate at concentrations greater than 0.07 mg/L, the estimated maximum background concentration.

Nitrate concentrations are higher in ground water in urban areas than in non-urban areas. In the Piedmont, there is a positive correlation between nitrate concentration and the percentage of urban land upgradient from the well (table 4). Although this effect is probably not unique to the Piedmont subunit, the correlation is not statistically significant in any other subunit, possibly because no other subunit contains much urban land. Sources of nitrate to ground water in urban areas include atmospheric deposition, septic tanks, and fertilizers applied to lawns, parks, golf courses, and other recreational areas.

Table 3. Correlations between nitrate concentrations in ground water and percentages of total agricultural land within 0.25 mile of sampled wells in the Triassic Lowlands subunit, Potomac River Basin

Circle segment	Correlation coefficient (Spearman's rho)	p-value
Upgradient quarter	0.492	0.0200
Upgradient half	.394	.0699
Whole	.356	.1039

Table 4. Statistically significant correlation coefficients (Spearman's rho) between nitrate, ammonia, and orthophosphate in ground water and percentages of five land uses within upgradient quarter segments of 0.25-mile radius circles delineated around sampled wells in each subunit, Potomac River Basin

[**VR**, Valley and Ridge subunit; **GV**, Great Valley Carbonate subunit; **PD**, Piedmont subunit; **TR**, Triassic Lowlands subunit]

Nutrient variable	Subunit	Principle upgradient land use				
		Urban	Forested	Agricultural (total)	Cropland	Pasture
Nitrate	**VR**		-0.569	0.417		
	GV				0.667	-0.592
	PD	0.412				
	TR			0.492	0.477	
Ammonia	**VR**	-0.360	0.475	-0.469		
	GV					
	PD					
	TR					-0.590
Orthophosphate	**VR**	0.419				
	GV					
	PD		0.393			
	TR					

-0.569	Correlation significant at 95-percent confidence level
0.417	Correlation significant at 90-percent confidence level
	No significant correlation

Nitrate concentrations are higher in ground water in agricultural areas--particularly croplands--than in areas with little or no agriculture. In most subunits, there is a significant positive correlation between nitrate concentration and the percentage of cropland and/or total agricultural land upgradient of the well (table 4). In the Great Valley Carbonate subunit, nitrate concentration is significantly correlated with cropland but not with total agricultural land. This is probably because data from few non-agricultural wells in this subunit are available for comparison. In the Valley and Ridge subunit, nitrate is positively correlated with total agricultural land; however, nitrate concentrations are extremely low throughout that subunit. In the Piedmont subunit, no statistically significant relations between ground-water nitrate and agricultural land uses could be identified, possibly because there are few agricultural sites in that subunit for comparison. Sources of nitrate to ground water in agricultural areas include commercial fertilizers and animal wastes from confined feeding operations. The negative correlation between nitrate and pasture land in the Great Valley Carbonate subunit indicates that pasture is a smaller source of ground-water nitrate (per unit area) than is cropland. Nitrogen is typically applied in greater quantities to crops in the form of commercial fertilizer and manure than to pastures in the form of manure.

Nitrate concentrations in ground water are lower in forested areas than in other areas. In the Valley and Ridge subunit, nitrate is negatively correlated with forested land (table 4), although nitrate concentrations are low throughout this subunit. Forested areas probably contain fewer anthropogenic nitrate sources than do other areas. This correlation is not significant in the Great Valley Carbonate, Piedmont, or Triassic Lowlands subunit, where there is relatively little forested land.

Ground-water ammonia concentrations are higher in forested areas than in urban or agricultural areas. In the Valley and Ridge subunit, ammonia concentrations are positively correlated with percentages of forest upgradient of sampled wells and negatively correlated with percentages of urban and agricultural land (table 4). These correlations are not statistically significant in the other subunits where there are very few sites with a predominance of upgradient forest. Correll and others (1994) found that surface-water ammonia concentrations in some small tributaries to the Chesapeake Bay increase with increasing percentage of forest in the watershed. In the Triassic Lowlands subunit, ammonia is negatively correlated with pasture, although ammonia concentrations are low throughout this subunit.

The higher ammonia concentrations in forested areas could be a result of the incomplete nitrification of ammonia in a reducing environment. Ammonia can be formed naturally in the soil zone from the conversion of nitrogen in organic materials (Freeze and Cherry, 1979). In forested areas, the large amounts of leaves and other natural debris on the ground would constitute a readily available source of organic nitrogen. In oxidizing environments, this ammonia is normally converted by soil bacteria to nitrate through nitrification (Manahan, 1994). Ground water in forested areas is in a more reduced state than in other areas. In the Valley and Ridge, the only subunit that contains large forested areas, dissolved oxygen is negatively correlated (rho= -0.620, p=0.0036) with the percentage of forest upgradient from the well. Because of the reduced state of ground water in forested areas, ammonia formed from conversion of organic nitrogen may not be fully oxidized to nitrate. Dissolved ammonia is negatively correlated with dissolved nitrate (rho= -0.500, p=0.0178) in the Valley and Ridge. Nitrate that does form in the soil zone or is input from other sources could be reduced to form ammonia in the ground water, although most would form nitrous oxide or nitrogen gas instead (Freeze and Cherry, 1979).

Nitrogen and Phosphorus Differences Among Land Uses

Although ground-water nutrient concentrations have been shown to be related to land use, the data collected for this study are insufficient for identifying statistically significant differences in nutrient concentrations among discrete land-use groups. Wells in the Piedmont and Triassic Lowlands subunits were classified as "urban," "agricultural," or "forested" if they contain a predominance of that land use within the quarter-circle segment upgradient from the wells. Wells with no predominant land-use upgradient were classified as "mixed," and agricultural sites were further subdivided on the basis of whether they are predominantly cropland or pasture. The Valley and Ridge and Great Valley Carbonate subunits were excluded from these analyses because only agricultural sites were targeted in those subunits. Exact Kruskal-Wallis tests (Ott, 1993) found no significant differences (alpha=0.05) in the concentrations of nitrate, ammonia, or orthophosphate among different land-use groups (with at least three samples) in either the Piedmont or Triassic Lowlands subunit (fig. 5). Correlations (table 4) indicate that ammonia and orthophosphate concentrations in the Piedmont and Triassic Lowlands subunits are not typically related to land use. The concentrations of these constituents are uniformly low in these subunits. Nitrate concentrations, however, are related to urban land in the Piedmont and to agricultural land in the Triassic Lowlands. These relations are probably undetected by the Kruskal-Wallis test because there are few sites within each land use in each subunit.

When Piedmont and Triassic Lowlands sites are analyzed together, nitrate concentrations are shown to be significantly higher in cropland areas than in forested areas, although any statistically significant differences in ammonia and orthophosphate concentrations remain undetectable. To increase statistical power by raising the number of sites in each land-use group, sites from both subunits were considered together when land-use groups were compared (fig. 5). An analysis-of-variance test (p=0.0088) indicated that at least one group of nitrate concentrations is significantly different from the others and a Tukey test showed that nitrate concentrations in cropland areas are higher than in forests. No other land-use groups were shown to be significantly different from one another. More samples within each land-use group would be required to clearly identify other differences that may exist.

Nitrogen and Phosphorus Within Agricultural Lands

Ground-water nitrate concentrations are higher in agricultural areas used for row crops than in areas used for other agricultural purposes such as pastures or orchards. Concentrations of ammonia and orthophosphate in ground water are not related to differences in agricultural land use. Nitrate concentrations are higher and orthophosphate concentrations are lower in ground water from agricultural areas underlain by carbonate bedrock than in those areas underlain by siliciclastic or metamorphic rocks. Ammonia concentrations in agricultural areas are not related to bedrock type.

A two-way analysis-of-variance test was used to determine whether ground-water nutrient concentrations at agricultural sites (those sites with a majority of agricultural land within 0.25 mile upgradient) are significantly different between areas devoted to different types of agricultural land use, different bedrock lithologies, and the combination of these two variables. Using county-level agricultural census data from 1992 (U.S. Department of Commerce, 1995), the percentage of agricultural land used for certain crops (corn, sorghum, wheat, barley, oats, or soybeans) was calculated for each of the 30 counties contained wholly or partially within the four sampled subunits. The steepest point on the probability plot of county crop percentages was used to split these counties into two groups. Seven counties in the northeastern part of the study area are the only ones with greater than 20 percent of their agricultural land devoted to these row crops (fig. 6). Because data from all four subunits and a variety of aquifer lithologies were used in these analyses and because ground-water flow through carbonate rocks is typically different than flow through other fractured-rock systems, the data also were tested to determine whether nutrient concentrations at agricultural sites are significantly different in areas underlain by carbonate rocks than in areas underlain by other rock types.

Ground-water nitrate concentrations at agricultural sites are significantly higher in the seven

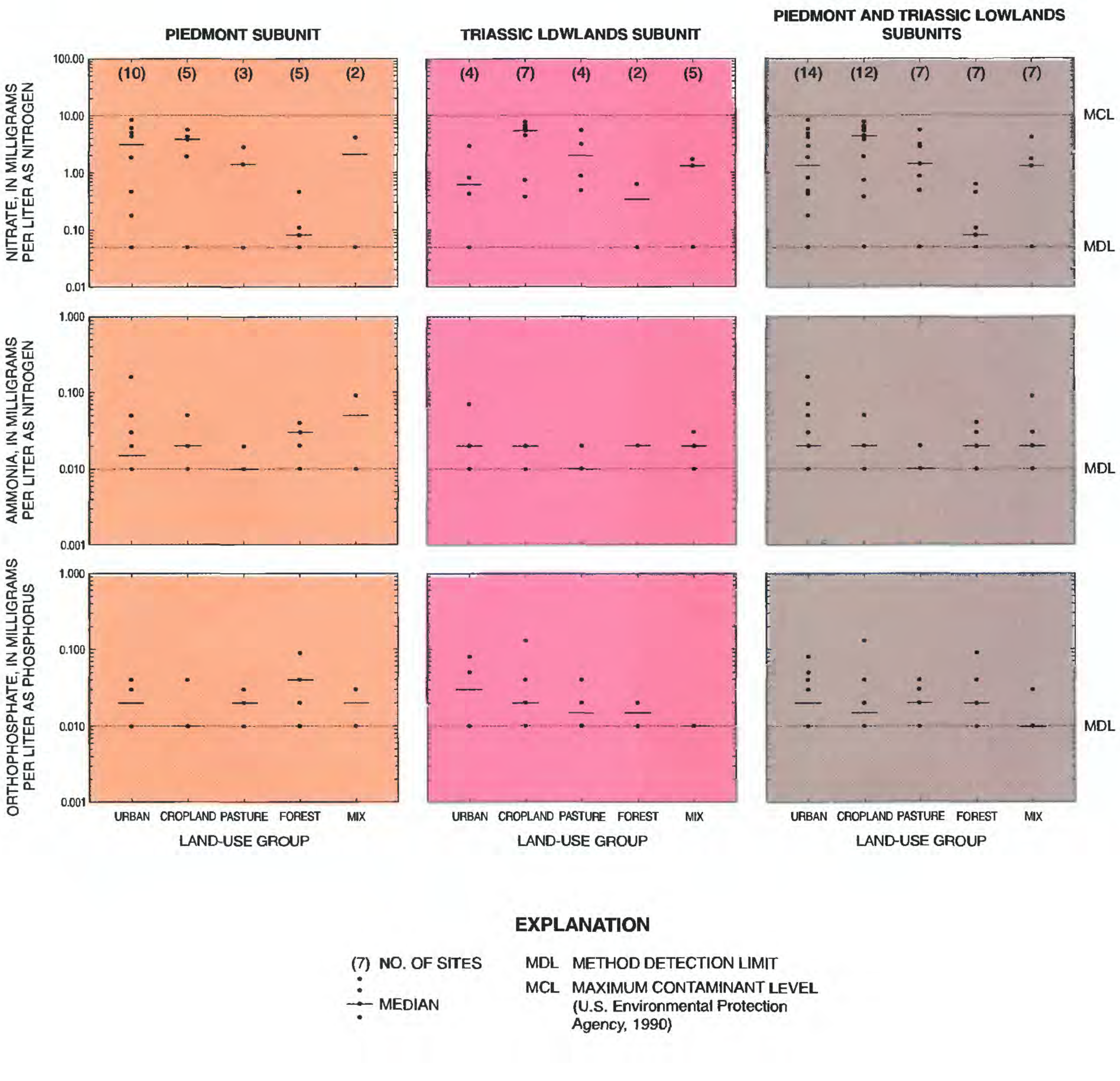


Figure 5. Concentrations of nitrate, ammonia, and orthophosphate in ground water within five land-use groups among and within the Piedmont and Triassic Lowlands subunits, Potomac River Basin.

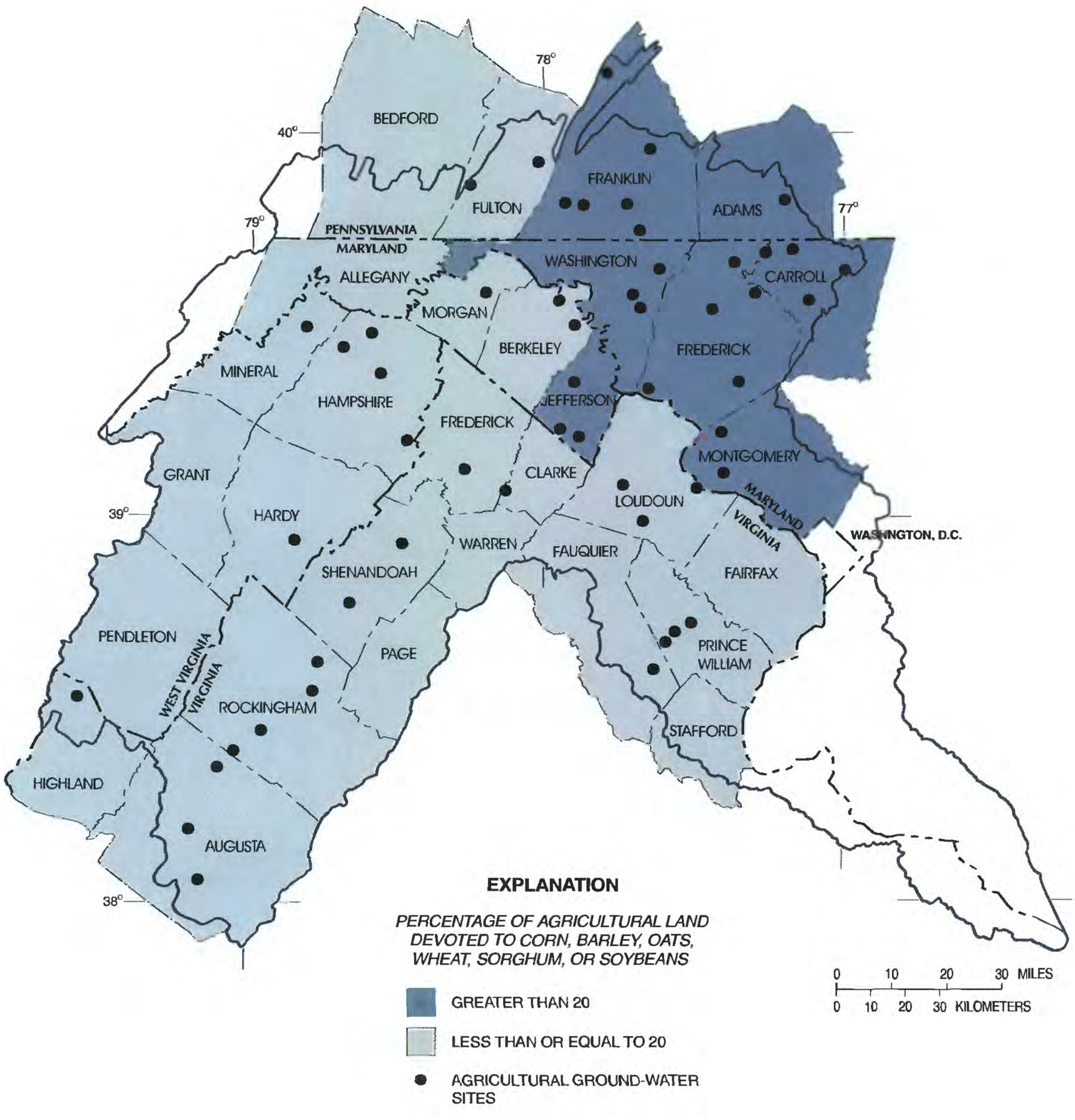


Figure 6. Percentage of agricultural land devoted to corn, barley, oats, wheat, sorghum, or soybeans in the 30 counties contained wholly or partially within the sampled areas of the Potomac River Basin (U.S. Department of Commerce, 1995).

most-heavily cropped counties than in the other counties and in areas underlain by carbonate rocks than in those underlain by siliciclastic or metamorphic rocks (fig. 7). Simple correlations demonstrated that nitrate concentrations in ground water in most subunits are related to agricultural land uses (table 4). The relatively large solution cavities that commonly develop in carbonate rocks could allow any nitrate from surficial sources to be easily and quickly transported throughout these aquifer systems. Also, more nitrogen is applied per unit area to the Great Valley Carbonate subunit (which contains most carbonate aquifers in the study area) than to any other subunit.

Analyses of data collected for this study indicate that ammonia and orthophosphate concentrations are not related to different types of agricultural land use. Ammonia concentrations are also not related to bedrock lithology, although orthophosphate concentrations are significantly lower in carbonate aquifers than in aquifers of other lithologies. This may be because the ground water in carbonate systems is typically so supersaturated with respect to carbonate minerals that any phosphate minerals (such as apatite) that may be present are not dissolved.

No significant interaction effect was detected between the agricultural land-use and lithology variables for nitrate ($p=0.5371$), ammonia ($p=0.0717$), or orthophosphate ($p=0.8385$). This indicates that detected relations between nutrient concentrations and each of the two variables are equally valid for all levels of the other variable.

SUMMARY AND CONCLUSIONS

Dissolved nutrients are present in ground water throughout the Valley and Ridge, Great Valley Carbonate, Piedmont, and Triassic Lowlands subunits of the Potomac River Basin. Nitrate concentrations are typically higher than would be expected from anthropogenic sources. Only in the Valley and Ridge subunit did less than 60 percent of samples contain nitrate at concentrations greater than the estimated maximum background concentration. In each subunit, most samples contained detectable ammonia and about half contained detectable orthophosphate. Concentrations of these nutrients were typically lower than would be expected from anthropogenic sources. Dissolved organic nitrogen is rarely present at detectable levels in ground water in the sampled areas.

Anthropogenic sources of nitrate to ground water include agricultural and urban land uses. Among agricultural land uses, crop production contributes more nitrate to ground water than does livestock grazing, although both are probable nitrate sources. Forests have fewer anthropogenic nitrate sources than do urban or agricultural areas. Nitrate that is deposited in a forest is likely reduced to nitrous oxide, nitrogen gas, or ammonia. In the Valley and Ridge, the only subunit with large forested areas, only 27 percent of ground-water samples contained detectable nitrate even though agricultural areas were specifically targeted in the sampling design.

Elevated concentrations of ammonia in ground water are attributed primarily to natural sources in forested areas and are not typically found in agricultural or urban areas. Although ammonia was detected in most samples from each subunit, most elevated levels were found in samples from forested areas of the Valley and Ridge. Ammonia is positively correlated with forest and negatively correlated with agricultural and urban land in that subunit. The relatively high ground-water ammonia levels in forested areas are possibly a result of the incomplete oxidation of naturally formed ammonia in a reducing environment -- one with little or no dissolved oxygen. Organic nitrogen in leaves and other natural debris would be a more readily available source of naturally formed ammonia in forested areas than in cleared areas. Also, ammonia from any source would likely be converted to nitrate in non-forested areas with more oxygen-rich ground water.

Bedrock lithology affects ground-water flow in fractured media and is therefore important when considering the movement of dissolved nutrients through the saturated zone. Ground-

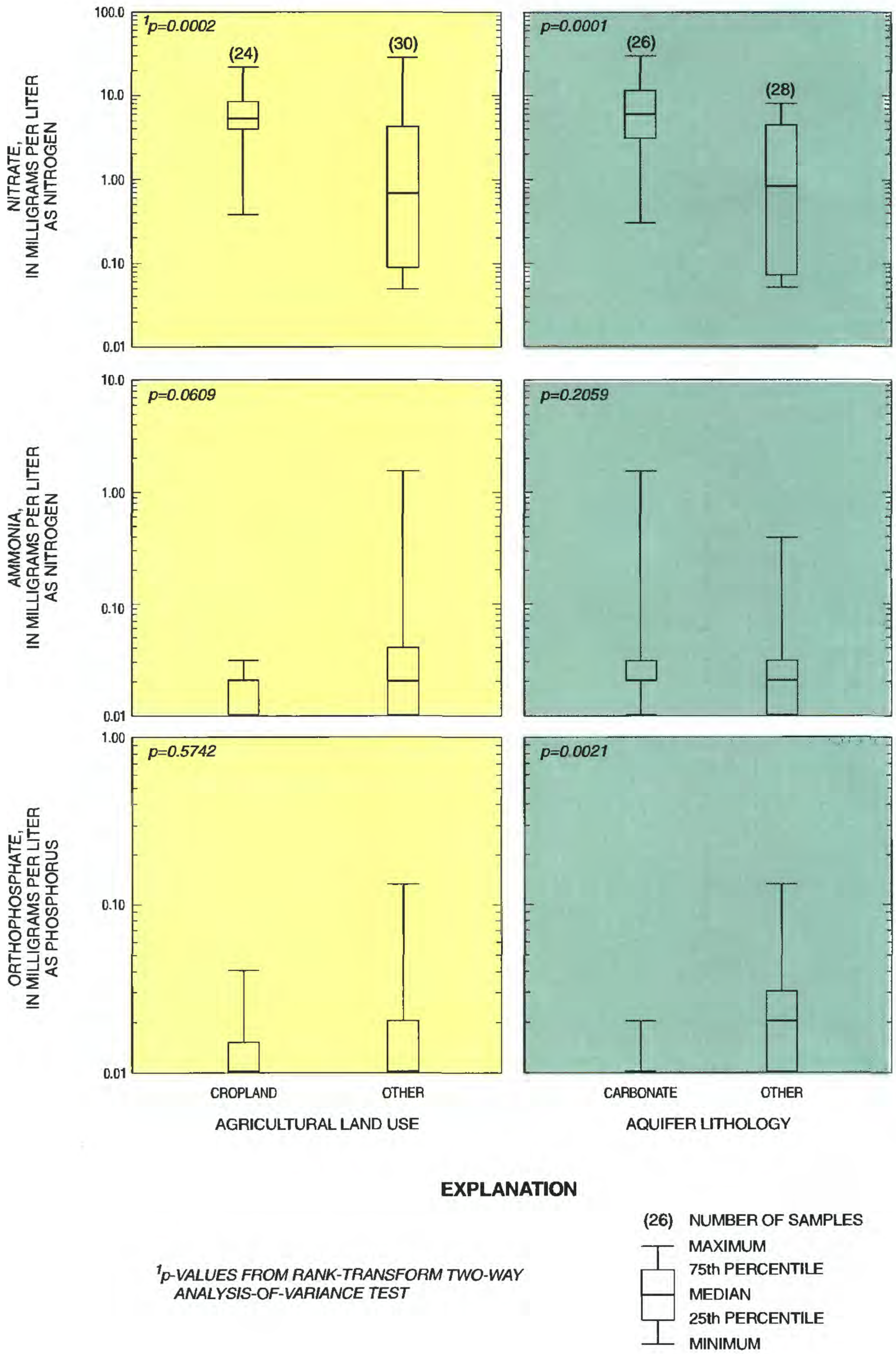


Figure 7. Distribution of nitrate, ammonia, and orthophosphate in ground water at agricultural sites within the Potomac River Basin. (Data are grouped separately by type of agricultural land use and aquifer lithology.)

water nitrate concentrations are higher in agricultural areas underlain by carbonate rocks than in those underlain by rocks of other types. This may indicate that the relatively large solution cavities that typically develop in carbonate rocks can allow surficial contaminants to be transported more quickly and easily in those aquifers than in other fractured-rock systems, although it may merely reflect the fact that more nitrogen per unit area is applied to carbonate areas of the Potomac River Basin than to other areas. In areas underlain by noncarbonate rocks, surface topography reflects the general direction of ground-water flow and should be considered when analyzing effects of land use on ground-water quality.

A more thorough understanding of the effects of land use on ground-water quality within the Potomac River Basin would benefit from further study. Periodic sampling would show how ground-water nutrient concentrations in different land-use settings evolve seasonally and over time. Additional sampling of ground water within different land uses in the Piedmont and Triassic Lowlands subunits may provide the data and statistical power necessary to detect more significant differences in the ground-water quality among various land uses in those areas. Similarly, sampling of more non-agricultural sites in carbonate areas is necessary to clarify the effects of land-use on ground-water quality in those unique hydrogeologic environments. More statistically significant correlations between land use percentages and nutrient concentrations may become apparent if a rigorous approach is used to define the contributing areas to sampled wells.

REFERENCES

Allaby, Michael, 1989, Dictionary of the environment (3d ed.): New York, New York University Press, 423 p.

Berg, T.M., chief comp., 1980, Geologic map of Pennsylvania: Pennsylvania Topographic and Geological Survey, 4th Series, 1 map on 2 sheets, scale 1:250,000, plus 1 sheet of cross sections.

Blomquist, J.D., Fisher, G.T., Denis, J.M., Brakebill, J.W., and Werkheiser, W.H., 1996, Water-quality assessment of the Potomac River Basin--Basin description and analysis of available nutrient data, 1970-1990: U.S. Geological Survey Water-Resources Investigations Report 95-4221, 88 p.

Bureau of the Census, 1991, Census of population and housing, 1990: Public Law 94-171 data (United States) [machine-readable data files]: Washington, D.C., The Bureau [producer and distributor].

Cardwell, D.H., Erwin, R.B., and Woodward, H.P., comps., 1968 (slightly revised 1986), Geologic map of West Virginia: West Virginia Geological and Economic Survey, 2 sheets, scale 1:250,000.

Cleaves, E.T., Edwards, Jonathan, Jr., and Glaser, J.D., comps., 1968, Geologic map of Maryland: Maryland Geological Survey, 1 sheet, scale 1:250,000.

Conservation Foundation, 1987, State of the environment -- A view toward the nineties: Washington D.C., The Conservation Foundation, 614 p.

Correll, D.L., Jordan, T.E., and Weller, D.E., 1994, The Chesapeake Bay watershed-- Effects of land use and geology on dissolved nitrogen concentrations: Chesapeake Research Consortium Publication No. 149, 9 p.

Durlin, R.R. and Schaffstall, W.P., 1996, Water resources data - Pennsylvania - Water Year 1994 - Volume 2 - Susquehanna and Potomac River Basins: U.S. Geological Survey Water Data Report PA-94-2, 436 p.

Fetter, C.W., 1994, Applied hydrogeology (3d ed.): New York, Macmillan College Publishing Company, Inc., 691 p.

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

Gerhart, J.M., and Brakebill, J.W., 1997, Design of a sampling strategy for a water-quality assessment of the Potomac River Basin: U.S. Geological Survey Water-Resources Investigations Report 96-4034, 31 p.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the national water-quality assessment program -- Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.

Hamilton, P.A., Denver, J.M., Phillips, P.J., and Shedlock, R.J., 1993, Water-quality assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia - Effects of agricultural activities on, and distribution of, nitrate and other inorganic constituents in the surficial aquifer: U.S. Geological Survey Open-File Report 93-40, 87 p.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: New York, Elsevier Science Publishing Company, Inc., 522 p.

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

Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the national water-quality assessment program -- Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.

Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the national water-quality assessment program -- Selection, installation, and documentation of wells, and collection of related data: U.S. Geological Survey Open-File Report 95-398, 69 p.

LeGrand, H.E., 1967, Ground Water of the Piedmont and Blue Ridge Provinces in the southeastern states: U.S. Geological Survey Circular 538, 11 p.

Madison, R.J., and Brunett, J.O., 1984, Overview of the occurrence of nitrate in ground water of the United States in national water summary 1984 -- hydrologic events, selected water-quality trends, and ground-water resources: U.S. Geological Survey Water-Supply Paper 2275, p. 93-105.

Manahan, S.E., 1994, Environmental chemistry (6th ed.): Boca Raton, Fla., Lewis Publishers, 811 p.

Milici, R.C., Spiker, C.T., Jr., and Wilson, J.M., comps., 1963, Geologic map of Virginia: Charlottesville, Virginia Division of Mineral Resources, 1 sheet, scale 1:500,000.

Mueller, D.K., Hamilton, P.A., Helsel, D.R., Hitt, K.J., and Ruddy, B.C., 1995, Nutrients in ground water and surface water of the United States -- An analysis of data through 1992: U.S. Geological Survey Water-Resources Investigations Report 95-4031, 74 p.

Ott, R.L., 1993, An introduction to statistical methods and data analysis (4th ed.): Belmont, Calif., Marion Merrell Dow, Inc., 1183 p.

Prugh, B.J., Jr., and Powell, E.D., 1996, Water resources data - Virginia - Water Year 1995 - Volume 2 - Ground-water-level and ground-water-quality records: U.S. Geological Survey Water Data Report VA-95-2, 472 p.

Puckett, L.J., 1994, Nonpoint and point sources of nitrogen in major watersheds of the United States: U.S. Geological Survey Water-Resources Investigations Report 94-4001, 6 p.

Scott, J.C., 1990, Computerized stratified random site-selection approaches for design of a ground-water-quality sampling network: U.S. Geological Survey Water-Resources Investigations Report 90-4101, 109 p.

Smigaj, M.J., and Saffer, R.W., 1996, Water resources data - Maryland and Delaware - Water Year 1995 - Volume 2 - Ground-water data: U.S. Geological Survey Water Data Report MD-DE-95-2, 588 p.

Taylor, J.K., 1987, Quality assurance of chemical measurements: Chelsea, Mich., Lewis Publishers, Inc., 328 p.

U.S. Department of Commerce, 1989, 1972 Census of agriculture, final county file: Bureau of the Census, Washington, D.C.

_____1995, 1992 Census of Agriculture--Geographic series 1B: Bureau of the Census, Washington, D.C.

U.S. Environmental Protection Agency, 1990, Fact sheet--National pesticide survey-nitrate: Washington D.C., U.S. Government Printing Office, 4 p.

_____ 1991, Fact Sheet: National primary drinking water standards: Washington, D.C., U.S. Government Printing Office, 8 p.

U.S. Geological Survey, 1979a, Land use and land cover, 1970-72, Pittsburgh, Pennsylvania: U.S. Geological Survey Land Use Series, Map L-34, 1 sheet, scale 1:250,000.

_____ 1979b, Land use and land cover, 1972, Harrisburg, Pennsylvania: U.S. Geological Survey Land Use Series, Map L-32, 1 sheet, scale 1:250,000.

_____ 1979c, Land use and land cover, 1973-77, Charlottesville, Virginia, West Virginia: U.S. Geological Survey Land Use Series, Open-File Report 79-403-1, 1 sheet, scale 1:250,000.

_____ 1979d, Land use and land cover, 1974-77, Roanoke, Virginia: U.S. Geological Survey Land Use Series, Open-File Report 79-407-01, 1 sheet, scale 1:250,000.

_____ 1980a, Land use and land cover, 1972, Washington, D.C., Maryland, Virginia: U.S. Geological Survey Land Use Series, Map L-201, 1 sheet, scale 1:250,000.

_____ 1980b, Land use and land cover, 1973, Cumberland, Maryland, West Virginia, Pennsylvania, Virginia: U.S. Geological Survey Land Use Series, Map L-111, 1 sheet, scale 1:250,000.

_____ 1980c, Land use and land cover, 1973, Richmond, Virginia, Maryland: U.S. Geological Survey Land Use Series, Map L-140, 1 sheet, scale 1:250,000.

_____ 1980d, Land use and land cover, 1974-76, Baltimore, Maryland, Pennsylvania, Virginia, West Virginia: U.S. Geological Survey Land Use Series, Map L-113, 1 sheet, scale 1:250,000.

_____ 1989, Digital line graphs from 1:100,000-scale maps - Data Users Guide 2: U.S. Geological Survey, National Mapping Division, 88p.

Ward, S.M., Taylor, B.C., and Crosby, G.R., 1996, Water resources data - West Virginia - Water Year 1995: U.S. Geological Survey Water Data Report WV-95-1, 330 p.

Zynjuk, L.D., 1995, Chesapeake Bay-- Measuring pollution reduction: U.S. Geological Survey Fact Sheet FS-055-95, 2 p.