science for a changing world

NITRATE IN GROUND WATER AND STREAM BASE FLOW IN THE LOWER SUSQUEHANNA RIVER BASIN, PENNSYLVANIA AND MARYLAND

by Bruce D. Lindsey, Connie A. Loper, and Robert A. Hainly

Water-Resources Investigations Report 97-4146

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

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Lemoyne, Pennsylvania
1997

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Mark Schaefer, Acting Director

For additional information write to:

District Chief
U.S. Geological Survey
840 Market Street
Lemoyne, Pennsylvania 17043-1586

Copies of this report may be purchased from:

U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, Colorado 80225

Information regarding the National Water-Quality Assessment (NAWQA) Program is available on the Internet via the World Wide Web. You may connect to the NAWQA Home Page using the Universal Resource Locator (URL) at:

http://wwwrvares.er.usgs.gov/nawqa/nawqa_home.html

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

Robert M. Hirsch
Chief Hydrologist

CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS—CONTINUED

TABLES

CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

	Multiply	by	To obtain
Length			
	foot (ft)	0.3048	meter
Area			
	square mile (mi^2)	2.590	square kilometer
Flow			
	cubic foot per second (ft^3/s)	0.02832	cubic meter per second
	million gallons per day (Mgal/day)	0.003785	million cubic meters per day
Mass			
	pound (lb)	0.4545	kilogram
	pounds per acre (lb/acre)	1.123	kilograms per hectare
	ton (short, 2,000 pounds)	0.9072	megagram (metric ton)
Temperature			
	degree Fahrenheit (°F)	°C=5/9 (°F-32)	degree Celsius
Specific capacity			
	gallon per minute per foot [(gal/min)/ft]	0.2070	liter per second per meter

Other abbreviations

L	liter
µm	micrometer
mg/L	milligram per liter
mL	milliliter
mm	millimeter

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, called Sea Level of 1929.

Nitrate in Ground Water and Stream Base Flow in the Lower Susquehanna River Basin, Pennsylvania and Maryland

by Bruce D. Lindsey, Connie A. Loper, and Robert A. Hainly

ABSTRACT

High concentrations of nitrate in both ground and surface water have been identified as a significant water-quality issue in the Lower Susquehanna River Basin. This report uses data collected by the National Water Quality Assessment (NAWQA) Program in the basin and compares nitrate concentrations found in ground water and surface water on both a spatial and temporal basis and relates nitrate concentrations to land use.

Nitrate concentrations in the Lower Susquehanna River Basin in Pennsylvania and Maryland were higher in ground water than in surface water in agricultural areas underlain by carbonate bedrock and agricultural areas underlain by crystalline bedrock. Nitrate concentrations were higher in surface water than in ground water in urban areas underlain by carbonate bedrock. Nitrate concentrations also were higher in surface water than ground water in both agricultural and forested areas underlain by sandstone and shale.

Nitrate concentrations in ground water vary in areas with different land use and bedrock type. Ground-water nitrate concentrations were highest in agricultural areas underlain by carbonate bedrock, where 45 percent of the samples exceeded the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) of 10 mg/L (milligrams per liter as N). Waters from 36 percent of the wells in agricultural areas underlain by crystalline bedrock also had nitrate concentrations greater than 10 mg/L. Nitrate concentrations in water from wells in urban areas underlain by carbonate bedrock and in forested and agricultural areas underlain by sandstone and shale seldom exceeded the MCL.

Nitrate concentrations were generally higher in surface water in areas underlain by carbonate bedrock than in areas underlain by noncarbonate bedrock; however, when an agricultural area underlain by carbonate bedrock and an agricultural area underlain by sandstone and shale with similar manure application rates were compared, nitrate concentrations in surface water were not significantly different. A comparison of three agricultural areas underlain by carbonate bedrock shows that the manure application rate is strongly correlated with nitrate concentration.

Nitrate concentrations in stream base flow at seven sites where samples were collected throughout the year were commonly higher in the winter months than in the summer months. A statistically significant correlation between streamflow and nitrate concentration existed for six of the seven sites, indicating that seasonal variability in precipitation may be the cause of some of the seasonal variation in concentration. Other possible explanations for this variation include the seasonal cycle in plant uptake of nitrogen and seasonal fluctuations in uptake of nitrate by algae in streams. Because no information was available about the traveltime for ground water, interpretation of this temporal variation was not conclusive.

Estimates of base-flow loads and yields of nitrate showed that agricultural areas underlain by carbonate bedrock provide the highest yield of nitrate when compared with the other areas studied. Agricultural areas underlain by sandstone and shale and crystalline bedrock also provide large amounts of nitrate to the river. The large amount of nitrate in the water from these areas cause a significant increase in nitrate loads transported by the Susquehanna River to the Chesapeake Bay. Urban areas underlain by carbonate bedrock had a high yield of nitrate but comprise such a small part of the basin that the nitrate load from these areas was small. In contrast, forested areas underlain by sandstone and shale bedrock had low base-flow nitrate yields, but these areas comprise a large percentage of the basin, making the overall nitrate load from these areas high.

INTRODUCTION

The U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program was designed to provide water-quality information for policy makers and managers to address water-quality issues at the national, state, and local levels. The program will be implemented over a 6-year period in 59 separate study units. Study units are river basins or aquifer systems that range from about 1,200 to 50,000 mi^2 and include about 60 to 70 percent of the Nation's water use (Gilliom and others, 1995).

The USGS began to implement the full-scale NAWQA program in 20 study units in 1991. The Lower Susquehanna River Basin was selected to be 1 of the first 20 study units. The investigation of water quality began with planning and analysis of available data during 1991-92, followed by intensive water-quality sampling and interpretation of data during 1993-95. The investigation is now in a low intensity water-quality sampling period, after which a new cycle of intensive data collection is scheduled to begin. One of the primary topics for the Lower Susquehanna River Basin study unit was to determine the occurrence and distribution of nitrate in ground and surface water and to explain, to the extent possible, the natural and human factors that affect nitrate concentration.

Excessive nitrate in ground water and surface water can affect both human health and aquatic organisms. The U.S. Environmental Protection Agency (USEPA) has established 10 mg/L as the Maximum Contaminant Level (MCL) for nitrate in drinking water for public drinking-water supplies (U.S. Environmental Protection Agency, 1996); therefore, water from a stream or well that commonly has nitrate concentrations exceeding 10 mg/L is not a suitable source for drinking-water supply without treatment. Concentrations of nitrate greater than 0.3 mg/L can stimulate excessive growth of algae (McKee and Wolf, 1963). This excessive algal growth has negative effects on living resources within the Susquehanna River.

High concentrations of nitrate are a significant water-quality issue in the Lower Susquehanna River Basin. Although the Lower Susquehanna River Basin only makes up about one third of the entire Susquehanna River Basin, base-flow nitrate concentrations increase from 0.6 mg/L at Sunbury, Pa., at the confluence of the West Branch and main stem of the Susquehanna River, to 1.2 mg/L at Conowingo Dam, Md. (Langland and others, 1995), just upstream of where the Susquehanna River empties into the Chesapeake Bay. About 60 percent of the nitrate load in the Susquehanna River originates in the Lower Susquehanna River Basin (Langland and others, 1995). The Chesapeake Bay, which receives 50 percent of its freshwater from the Susquehanna River (Langland and others, 1995), is also affected by high nitrate concentrations, and much of the nitrate comes from the Lower Susquehanna River Basin. Excessive amounts of nitrogen delivered to the Chesapeake Bay from tributaries to the Susquehanna River have been identified as one of the most important issues confronting the Chesapeake Bay restoration effort (Malone and others, 1993).

Ground water is an important resource for drinking-water supply in the Lower Susquehanna River Basin. Approximately 38 percent of the 800,000 households in the basin rely on water from private wells (U.S. Bureau of the Census, 1992). Rural water users are almost entirely dependent on ground water for domestic supply. Municipal water suppliers serve approximately 59 percent of the residents in the basin, and about 20 percent of the municipal systems use ground water as their source of supply.

A review of previous investigations of nitrate concentration in the Lower Susquehanna River Basin was conducted as an initial step in the study (Hainly and Loper, 1997). This review of the USGS National Water Information System (NWIS) and the U.S. Environmental Protection Agency (USEPA) Storage and Retrieval (STORET) databases showed that a large number of nutrient samples had been collected. These databases contained results of analyses for about 26,000 nutrient samples from 502 stream sites, 60 springs, and 1,157 wells. An additional ground-water database of samples from 4,300 wells was assembled from the Pennsylvania Department of Environmental Protection records.

Although many data were available, the usefulness of the data was limited by (1) inconsistent analytical methodology, (2) vague descriptions of the source of the samples, and (3) differing study objectives resulting in uneven distribution of the data. Except for some field-scale studies, ground-water and surface-water sampling programs were not integrated. Many samples were collected to address a known or suspected water-quality problem, which created a sampling bias. Even with these limitations, however, the data were useful to guide the design of this study. For example, many surface-water samples had been collected in large tributaries, so this study focused on smaller basins with a single predominant land use. Also, the well-sampling program in this study was designed to emphasize spatial distribution and careful documentation of the land use and well characteristics.

Purpose and Scope

This report compares the concentrations of nitrate in ground-water and surface-water samples collected throughout the Lower Susquehanna River Basin and explains the spatial and temporal variation in nitrate concentrations. Estimates of base-flow loads and yields also are calculated. The results are based on samples collected by the NAWQA Program in 1993-95 from 161 wells and 156 surface-water sampling sites in 19 counties in Pennsylvania and 3 counties in Maryland. The surface-water sampling was conducted within selected basins ranging in size from 0.06 to 177 mi^2; ground-water samples and surface-water samples were collected during the same period. Several sampling schemes were used to represent water-quality conditions, and these multiple lines of evidence were used to determine the factors affecting nitrate concentration.

Description of Study Area

The Lower Susquehanna River Basin study unit, hereafter referred to as "the study unit," consists of 9,200 mi^2 of the Susquehanna River Basin from the confluence of the West Branch and the main stem of the Susquehanna River near Sunbury, Pa., downstream to the Chesapeake Bay at Havre de Grace, Md. The study unit also includes 150 mi^2 of basins in Chester County, Pa., and Cecil County, Md., that drain directly to the Chesapeake Bay (fig. 1).

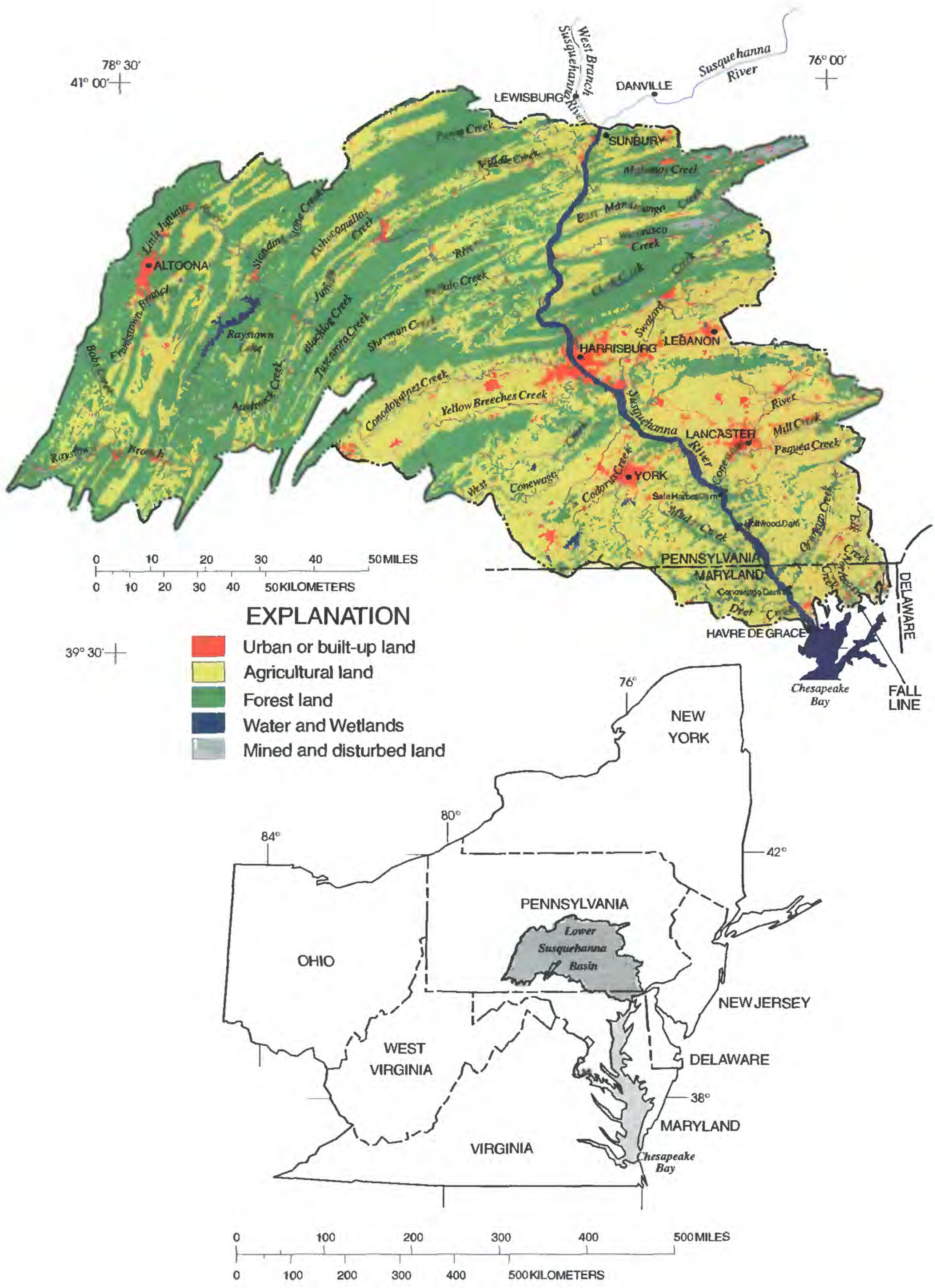


Figure 1. Major physical features and generalized land use in the Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

The study unit contains parts of five physiographic provinces. The Piedmont Physiographic Province and Ridge and Valley Physiographic Province make up about 97 percent of the study unit. The New England Physiographic Province, the Blue Ridge Physiographic Province, and the Appalachian Plateaus Physiographic Province make up the remaining 3 percent. In the Ridge and Valley, major bedrock types include limestone and dolomite (carbonate rocks), sandstone, siltstone, and shale. The Piedmont also has the same major bedrock types as the Ridge and Valley plus areas of crystalline rock.

Land use in the study unit is diverse. Overall land use is 47 percent agricultural, 47 percent forested, 4 percent urban, and 2 percent water bodies or barren land (fig. 1) (Mitchell and others, 1977). The U.S. Bureau of the Census (1992) estimated populations for metropolitan statistical areas (the greater metropolitan area) in the study unit including Harrisburg-Lebanon-Carlisle (588,000), Lancaster (423,000), York (418,000), and Altoona (131,000).

Soils in the study unit are classified on the basis of the parent bedrock material from which they formed (U.S. Department of Agriculture, 1972). Most of these soils are derived from carbonate bedrock, crystalline bedrock, sandstone, or shale, and their locations can be deduced from the locations of the bedrock types. The infiltration capacity of the soils is based on the parent material, slope, soil thickness, land use, and land cover (Susquehanna River Basin Study Coordinating Committee, 1970) and is an important factor in the movement of nitrate. Infiltration rate classifications for soils in the study area include excellent (soils derived from carbonate bedrock), good (soils derived from crystalline bedrock and sandstone), and poor (soils derived from shale).

Acknowledgments

The authors acknowledge the cooperation of the well owners for permitting access to sample their wells and landowners for allowing equipment to be installed to monitor and gage surface-water flow and quality. The authors thank John Yocum, with the Southeast Research Station of Pennsylvania State University in Landisville, Pa., and Terry Troutman, with the Agricultural Research Service's office in Klingerstown, Pa., for their help in providing information on agricultural activities. The authors wish to thank Margaret Maizel and George Muehlbach of the National Center for Resource Innovations, Chesapeake, Inc., for their assistance in obtaining data on manure application rates. The authors also thank the following USGS colleagues: Kevin Breen for his assistance throughout the report-writing process, James Bubb and Steven Siwiec for graphics support, and Kent Crawford, Dennis Risser, and Kim Wetzel as members of the report team.

STUDY DESIGN, ENVIRONMENTAL SUBUNITS, AND SAMPLING SITES

This project was designed to study both natural and human factors affecting water quality; however, to assess these factors in a study area with diverse geology and land use, it was necessary to subdivide the study area. The techniques used to design the study of this diverse area are presented, followed by descriptions of the areas selected for study and information about the sites where samples were collected.

Study Design

The study area was subdivided with a Geographical Information System (GIS) using spatial data sets of physiography (Berg and others, 1980), bedrock type (Berg and others, 1980), and land use (Mitchell and others, 1977). In this report, areas defined by physiography, geology, and land use will be referred to as subunits. Although subdividing the study unit in this manner is helpful in analyzing water-quality issues, this approach results in more subunits than could be studied. The study-unit staff, in cooperation with a liaison committee consisting of Federal, State, and local agencies, prioritized the water-quality issues within the study unit to assist in selecting the subunits that would be studied first. Highest priorities were placed on agricultural areas, areas underlain by carbonate bedrock, urban areas, and undisturbed forested areas. The size and population of the subunit and the water use within that area also were considered. The prioritization resulted in the selection of the seven subunits for study.

Subunits that were studied include (1) agricultural areas underlain by crystalline bedrock in the Piedmont Physiographic Province, (2) agricultural areas underlain by carbonate bedrock in the Piedmont Physiographic Province, (3) agricultural areas underlain by carbonate bedrock in the Great Valley Section of the Ridge and Valley Physiographic Province, (4) urban areas underlain by carbonate bedrock in the Great Valley Section of the Ridge and Valley Physiographic Province, (5) agricultural areas underlain by carbonate bedrock in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province, (6) agricultural areas underlain by sandstone and shale in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province, and (7) forested areas underlain by sandstone and shale in the Appalachian Mountain Section of the Ridge and Valley Physiographic Province. These subunits are shown in figure 2 and are described in table 1.

To help determine the relations between ground-water quality and surface-water quality, the study design integrated sampling of ground-water and surface-water resources in each of the subunits. Ground-water studies were conducted to represent the spatial distribution of nitrate concentrations in ground water at a point in time. Surface-water studies were conducted in these same areas to represent spatial distribution of nitrate concentrations in stream base flow at a point in time. In addition, samples were collected at fixed intervals at surface-water sampling sites in each of the seven subunits to characterize the temporal variation of nitrate concentrations.

The ground-water synoptic studies consisted of the collection of a single sample at seven wells in the forested subunit and at 20-30 wells in each of the remaining six subunits during the 3 years of sampling. Descriptions of wells and criteria used in well selection are given in Siwiec and others (1997). A computerized random-selection program was used to select potential sampling locations within each subunit (Scott, 1990). Field personnel then selected wells near the randomly selected locations (fig. 3, fig. 6, fig. 8). The wells were generally less than 200 ft deep and less than 20 years old. Drillers logs were used as the primary source of information on well characteristics; median casing

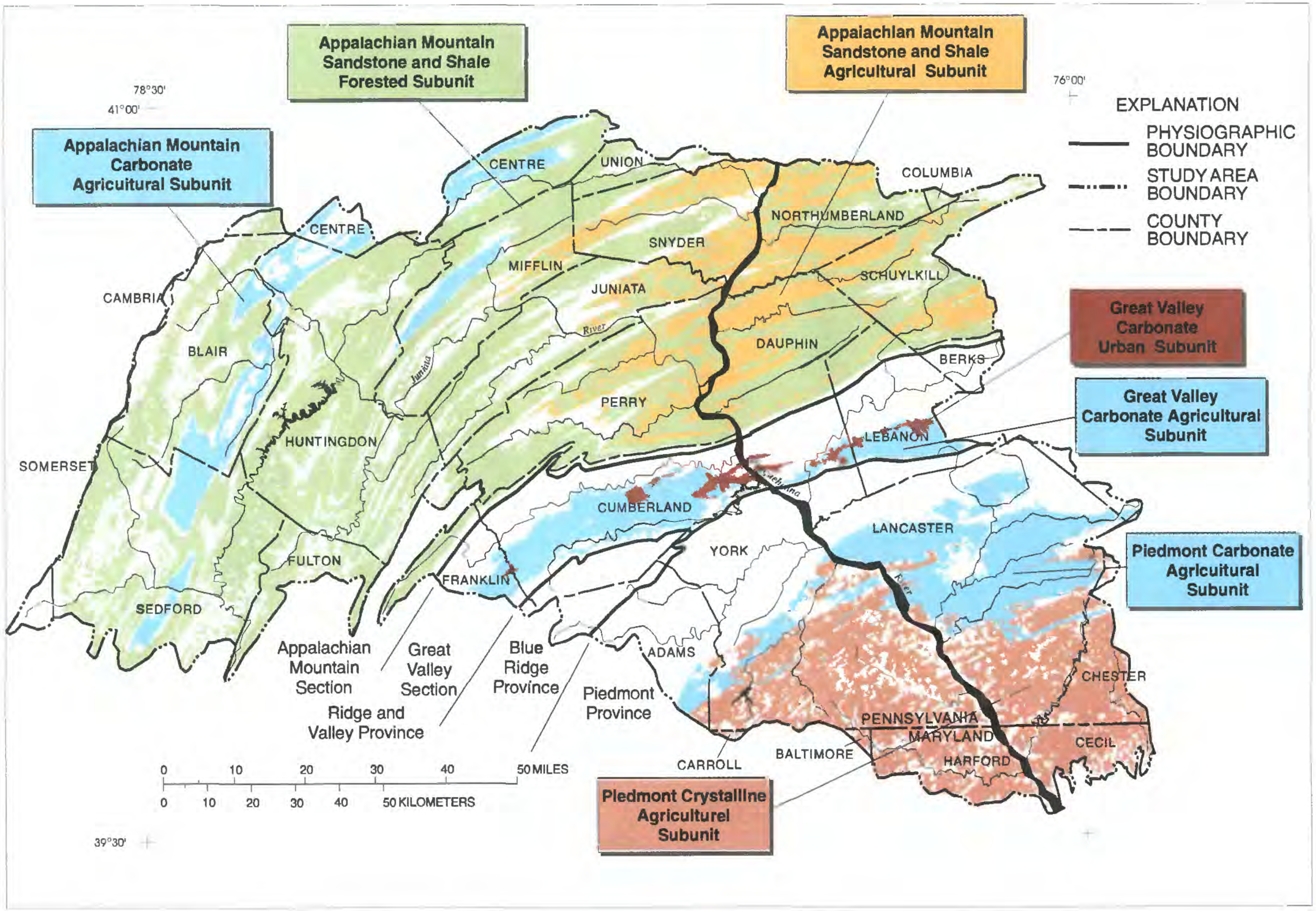


Figure 2. Environmental subunits studied within the Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

Table 1. *Description of environmental subunits studied in 1993-95 as part of the Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

Environmental subunit	Physiographic province (section)	Bedrock type	Dominant land use	Topo-graphic setting	Percentage of study unit
Piedmont crystalline agricultural	Piedmont	igneous and metamorphic	agriculture	hilltop and hillside	9.8
Piedmont carbonate agricultural	Piedmont	limestone and dolomite	agriculture	valley	4.7
Great Valley carbonate agricultural	Ridge & Valley (Great Valley)	limestone and dolomite	agriculture	valley	3.0
Great Valley carbonate urban	Ridge & Valley (Great Valley)	limestone and dolomite	urban	valley	.6
Appalachian Mountain carbonate agricultural	Ridge & Valley (Appalachian Mountain)	limestone and dolomite	agriculture	valley	4.6
Appalachian Mountain sandstone and shale agricultural	Ridge & Valley (Appalachian Mountain)	sandstone, siltstone, and shale	agriculture	valley and hillside	6.3
Appalachian Mountain sandstone and shale forested	Ridge & Valley (Appalachian Mountain)	sandstone, siltstone, and shale	forest	valley and hillside	34.2

lengths of wells within subunits ranged from 33 to 83 ft, and median specific capacities of the wells ranged from 0.56 to 11.35 (gal/min)/ft. Only 7 of the 161 wells were for non-household use; 6 were monitoring wells, and 1 was a public-supply well (table 2).

The surface-water sampling plan was made up of three components. The first component of the plan was to conduct fixed-interval sampling at long-term monitoring sites (fig. 3, fig. 6, fig. 8). Long-term monitoring sites were selected to represent each of the seven studied subunits, and the basins chosen contained from 59 to 85 percent of the targeted land use (table 3). Drainage areas of the selected basins ranged from 7.72 to 71.9 mi^2. The sampling frequency at the long-term sites ranged from weekly to monthly. The second component was to collect a single sample at 10-17 stream sites under base-flow conditions in each of the seven subunits to determine the spatial variability of nitrate concentrations in each subunit and determine if the water quality at the selected long-term site was representative of the rest of the subunit (fig. 3, fig. 6, fig. 8). This component is called the surface-water subunit synoptic study. These sites also were selected to represent the land use and bedrock characteristics of each of the seven subunits. Basin sizes from streams sampled within respective subunits ranged from 1.0 to 177 mi^2 (table 4). The third component of the plan was to collect a single sample at each of 5-19 stream sites within the long-term monitoring site basins under base-flow conditions to describe the spatial variability in water quality due to point and nonpoint nutrient influxes (table 5). This was called the focused synoptic sampling. The site selection for this study focused on sampling the major tributaries upstream of the long-term site, including some known point sources. Details of site selection strategy can be found in Siwiec and others (1997).

Table 2. *Description of aquifer characteristics and well characteristics by environmental subunit, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

[Specific capacity is change in water level in a well at a given flow rate during a pumping test and is measured in gallons per minute per foot, (gal/min)/ft, of drawdown.]

Environmental subunit	Counties	Dates of collection	No. of wells	Depth of wells, in feet		Casing length, in feet, median	Use of water from well	Specific capacity, in (gal/min)/ft, median
				Median	Maximum			
Piedmont crystalline agricultural	Lancaster, York, Chester, Cecil (Md.), Harford (Md.)	6/28 - 7/21/94	22	140	200	52	household	0.75
Piedmont carbonate agricultural	Adams, York, Lancaster	7/08 - 7/28/93	30	160	200	42	household	.67
Great Valley carbonate agricultural	Cumberland, Dauphin, Lebanon, Franklin	6/26 - 8/09/95	30	161	290	83	household	10.62
Great Valley carbonate urban	Cumberland, Dauphin, Lebanon	7/05 - 8/17/95	20	116	225	33	monitoring (6), household (13), public (1)	2.18
Appalachian Mountain carbonate agricultural	Centre, Blair, Huntingdon, Bedford, Mifflin	7/25 - 8/16/94	30	172	243	62	household	11.35
Appalachian Mountain sandstone and shale agricultural	Dauphin, Schuylkill, Northumberland, Juniata, Perry, Snyder	7/26 - 8/11/93	22	153	205	41	household	.56
Appalachian Mountain sandstone and shale forested	Lebanon, Perry, Dauphin	7/28 - 8/11/93	7	160	200	42	household	.61

Table 3. *Description of basin characteristics for long-term monitoring studies, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

Environmental subunit	U.S. Geological Survey station number	Name and location	Latitude/ longitude	County	Dates of collection	Total number of base-flow samples	Drainage area (square miles)	Percent of targeted land use, as per first column	Next higher order stream
Piedmont crystalline agricultural	01577300	Muddy Creek at Muddy Creek Forks, Pa.	39°48′27″/ 76°28′34″	York	4/93 - 8/95	16	71.9	75	Susquehanna River
Piedmont carbonate agricultural	01576540	Mill Creek near Lyndon, Pa.	40°00′36″/ 76°16′39″	Lancaster	3/93 - 8/95	34	54.3	76	Conestoga River
Great Valley carbonate agricultural	01573095	Bachman Run at Annville, Pa.	40°18′59″/ 76°30′58″	Lebanon	3/93 - 8/95	48	7.72	83	Quittapahilla Creek
Great Valley carbonate urban	01571490	Cedar Run at Eberlys Mill, Pa.	40°13′30″/ 76°54′24″	Cumberland	3/93 - 8/95	54	12.6	79	Yellow Breeches Creek
Appalachian Mountain carbonate agricultural	01564997	Kishacoquillas Creek at Lumber City, Pa.	40°39′42″/ 77°36′01″	Mifflin	3/93 - 7/95	16	57.4	59	Juniata River
Appalachian Mountain sandstone and shale agricultural	01555400	East Mahantango Creek at Klingers-town, Pa.	40°39′48″/ 76°41′30″	Schuylkill	3/93 - 9/94	26	44.7	69	Susquehanna River
Appalachian Mountain sandstone and shale forested	01559795	Bobs Creek near Pavia, Pa.	40°16′21″/ 78°35′55″	Bedford	4/93 - 8/95	15	16.6	85	Dunning Creek

Table 4. *Description of basin characteristics for subunit synoptic studies, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

Environmental subunit	Counties	Dates of collection	Total no. of sites	Range of drainage area (square miles)
Piedmont crystalline agricultural	Lancaster, York, Chester, Cecil (Md.), Baltimore (Md.), Harford (Md.)	7/12 - 7/14/94	17	3.40 - 177
Piedmont carbonate agricultural	Adams, York, Lancaster	8/29 - 8/31/94	16	1.00 - 122
Great Valley carbonate agricultural	Cumberland, Lebanon	8/23- 8/25/94	10	2.30 - 23.8
Great Valley carbonate urban	Cumberland, Lebanon, Dauphin, York	7/26 - 7/27/94	11	3.20 - 47.7
Appalachian Mountain carbonate agricultural	Centre, Blair, Huntington, Bedford, Mifflin	8/01 - 8/03/94	16	2.60 - 109
Appalachian Mountain sandstone and shale agricultural	Dauphin, Schuylkill, Northumberland	6/14 - 6/21/93	14	3.00 - 162
Appalachian Mountain sandstone and shale forested	Dauphin, Perry, Juniata, Huntingdon, Union, Blair, Bedford, Fulton, Mifflin	7/31 - 8/02/95	16	1.42 - 82.2

Table 5. *Description of basin characteristics for focused synoptic studies, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

Environmental subunit	Basin	County	Dates of collection	Total no. of sites	Range of drainage area (square miles)
Piedmont crystalline agricultural	Muddy Creek	York	8/07 - 8/08/95	[1]15	1.00 - 71.9
Piedmont carbonate agricultural	Mill Creek	Lancaster	8/14 - 8/16/95	[2]19	.81 - 54.2
Great Valley carbonate agricultural	Bachman Run	Lebanon	6/26/95	[3]9	.06 - 7.30
Great Valley carbonate urban	Cedar Run	Cumberland	7/05/95	[4]8	1.78 - 12.6
Appalachian Mountain carbonate agricultural	Kishacoquillas Creek	Mifflin	7/17 - 7/18/95	[4]11	1.50 - 57.4
Appalachian Mountain sandstone and shale agricultural	East Mahantango Creek	Northumberland, Schuylkill	6/14 - 6/15/93	[4]5	3.00 - 44.7

[1] Number of sites includes long-term monitoring site and one site that represents a basin that is predominantly forested.

[2] Number of sites includes long-term monitoring site, one site that represents a basin that is predominantly forested and underlain by crystalline bedrock, and five end-of-pipe point discharges.

[3] Number of sites includes long-term monitoring site and three sites that represent basins that are predominantly forested.

[4] Number of sites includes long-term monitoring site.

Subunits and Sampling Sites

Although the subunits were defined on the basis of physiography, bedrock type, and land use, many interrelated factors that affect water quality also are represented. Some interrelated factors are directly related to the primary characteristics; for example, soil type and topography are related to the bedrock type. Human influences differed among subunits, such as the relation of specific land-use practices to recharge and discharge areas. Other features of the subunits include the agricultural characteristics such as fertilizer application rates, crop yields, crop rotations, and animal density. For each of the seven subunits, some of these unique features are described, and specific details about the sampling sites are given.

Subunits and Sampling Sites in the Piedmont Physiographic Province

Two subunits were studied in the Piedmont Physiographic Province (fig. 3)—the Piedmont crystalline agricultural subunit and the Piedmont carbonate agricultural subunit. The crystalline subunit contains both lowland and upland sections, and the carbonate subunit contains mostly lowlands.

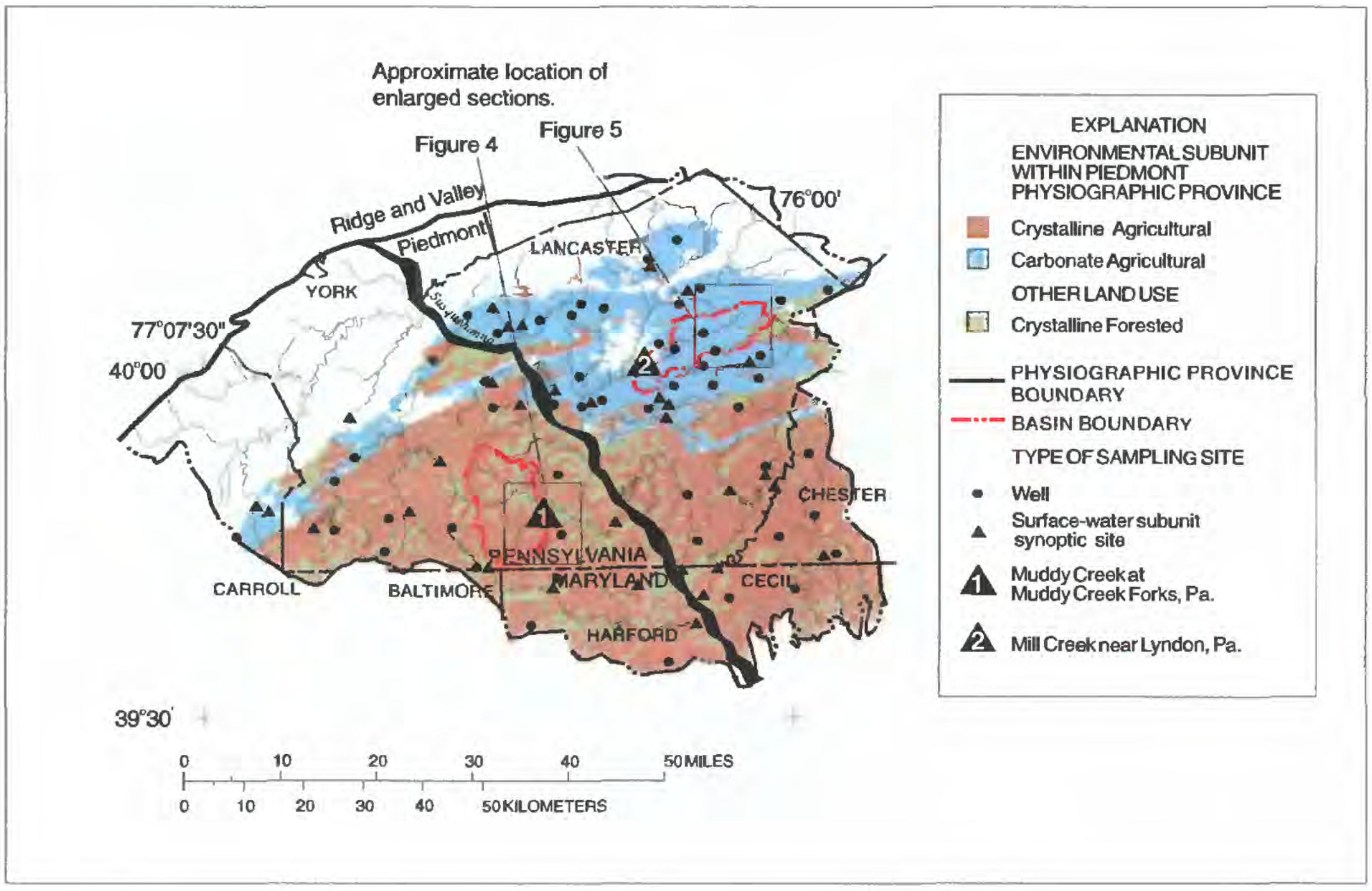


Figure 3. Subunits and sampling locations within the Piedmont Physiographic Province, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

The Piedmont crystalline agricultural subunit is characterized by low rolling hills; altitude ranges from 500 to 800 ft. Crystalline rock includes igneous and metamorphic rocks such as schist, gneiss, gabbro, phyllite, metavolcanic rocks, and quartzite. The crystalline bedrock is covered by a mantle of soil and heavily weathered bedrock. These unconsolidated materials are called regolith and form an important part of the ground-water flow system. Flow through the consolidated bedrock is primarily in small fractures. Ground water in areas underlain by crystalline bedrock exists primarily in the bedrock fractures and pores in the saturated part of the regolith above the crystalline bedrock. The ground-water flow systems are generally separate, local systems defined by the perennial stream basins, and flow generally does not cross topographic divides (McFarland, 1994). In the Piedmont crystalline agricultural subunit, agricultural crops are grown on the hilltops, on some slopes, and on well drained lowlands; pasture and forested areas are common on the slopes and on areas near the streams (fig. 4). The ground water that originates in the agricultural areas commonly passes beneath areas of forested land use before discharging to the streams. Although the predominant land use in the basin is agriculture, 37.2 percent of the stream miles in this area have riparian forest buffers (forested areas that run parallel to the stream) on both sides of the stream extending to 300 ft or more (Day and others, 1996). The infiltration capacity of the soil in this subunit is good.

In the Piedmont crystalline agricultural subunit, samples were collected for the long-term surface-water monitoring study and also for ground-water and surface-water synoptic studies. The long-term surface-water monitoring site in York County (Muddy Creek at Muddy Creek Forks, Pa.) (fig. 3) was sampled monthly from April 1993 to August 1994. During the surface-water subunit synoptic studies, 17 sites (fig. 3) were sampled in a 3-day period in July 1994. Also in 1994, 22 wells (fig. 3) were sampled from June 28 to July 21. During August 1995, 15 surface-water sites were sampled during the Muddy Creek focused synoptic study. One of the sites sampled in the Muddy Creek Basin is predominantly forested. Some additional ground-water samples were collected in forested and mixed land-use areas; however, because only one surface-water site was classified as forested and none were classified as mixed land-use areas, no comparisons of ground water and surface water were made for forested or mixed areas underlain by crystalline bedrock in the Piedmont.

The Piedmont carbonate agricultural subunit is characterized by altitude ranging from 200 to 600 ft (fig. 5). Agricultural activity is the predominant land use, and cropland or pasture commonly extends all the way to the stream banks in this subunit. In contrast to the Piedmont crystalline agricultural subunit, riparian forest buffers extend to 300 ft on both sides of the stream for only 7.3 percent of the stream miles in this subunit (Day and others, 1996). Carbonate bedrock is limestone and dolomite. Ground water in the carbonate-rock aquifers exists in fractures in the bedrock and in the regolith overlying the bedrock. Also, the carbonate bedrock has large fractures due to weathering, and it contains karst features such as sinkholes and caverns that have a significant effect on ground-water flow. Because of the size of the solution channels in the weathered bedrock, ground water and contaminants can move rapidly through the system. The infiltration capacity of the soils is excellent. These factors make internal drainage a common occurrence. In some areas, much of the precipitation infiltrates through the soil into sinkholes or large fractures in the bedrock instead of running off into the streams. The water then travels through large fractures and caverns, discharging to the surface at springs.

Samples were collected in the Piedmont carbonate agricultural subunit at the long-term surface-water monitoring site and at the ground-water and surface-water synoptic sites. The long-term surface-water monitoring site (Mill Creek near Lyndon, Pa.) (fig. 3) was

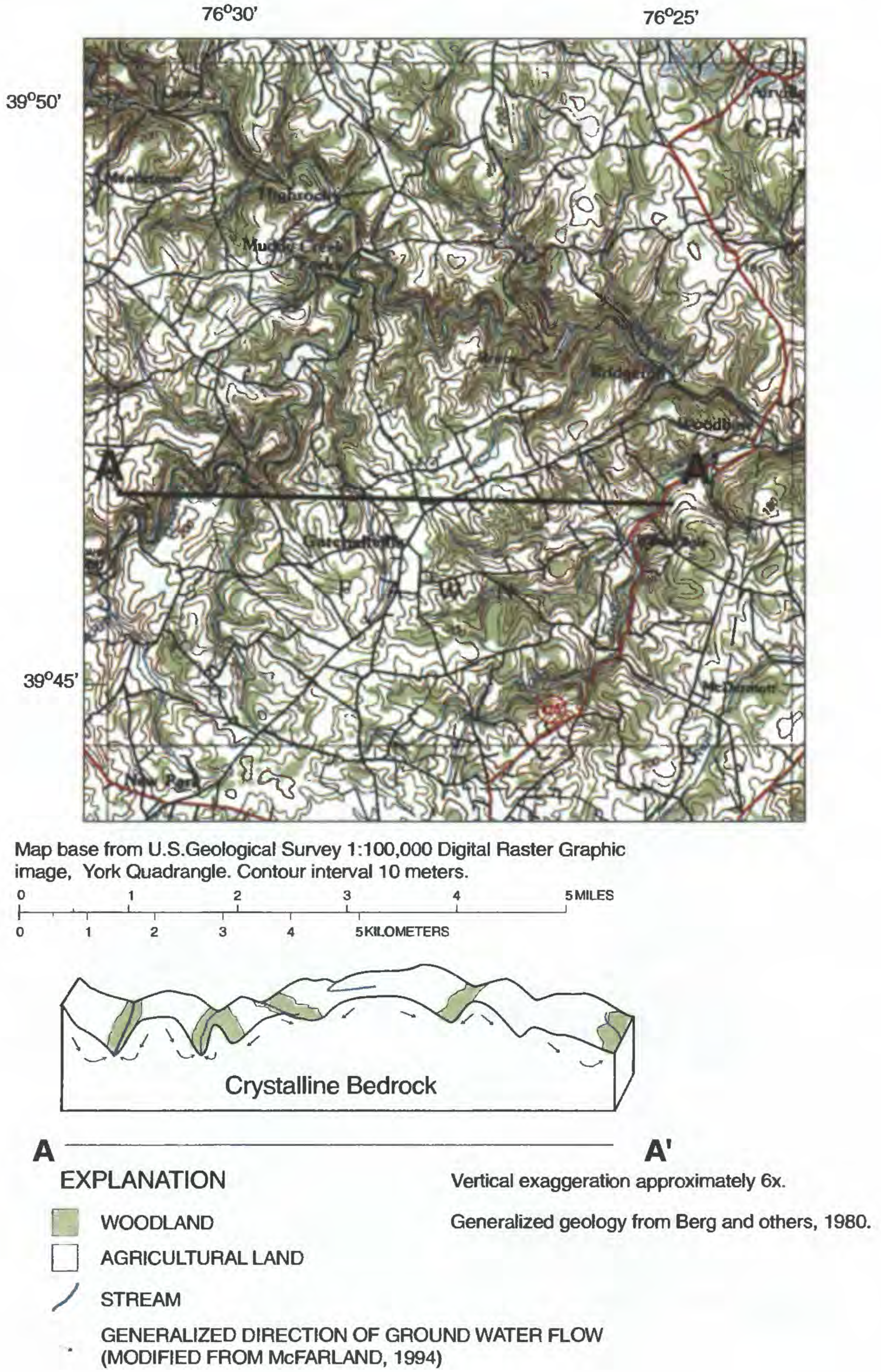


Figure 4. Selected topographic map area and cross-section A - A'; Piedmont crystalline agricultural subunit, Lower Susquehanna River Basin study unit.

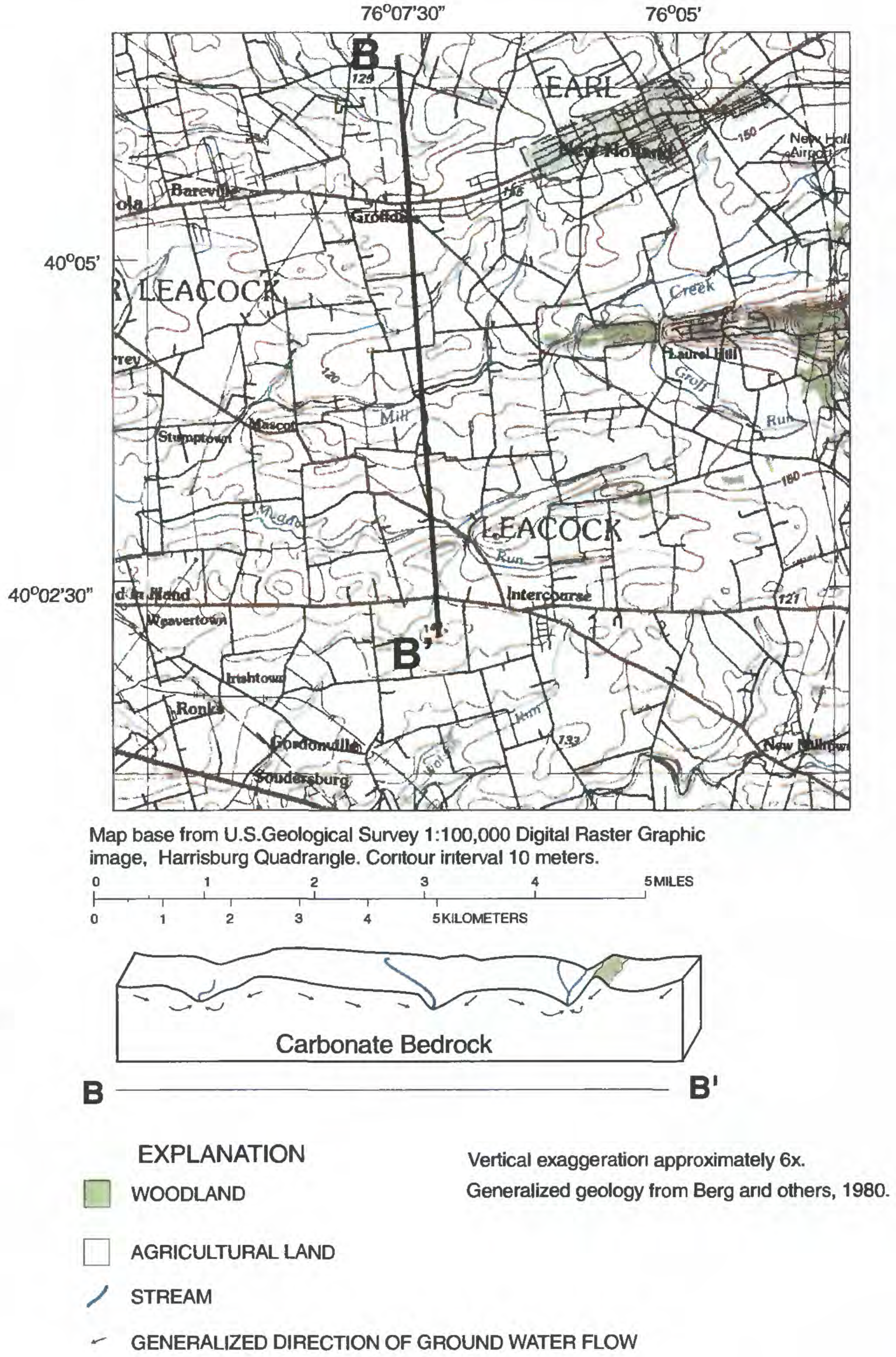


Figure 5. Selected topographic map area and cross-section B - B'; Piedmont carbonate agricultural subunit, Lower Susquehanna River Basin study unit.

sampled weekly during the first year and semimonthly during the second year with the exception of the winter months (December through March), when sampling was done monthly. Sixteen sites (fig. 3) were sampled during a 3-day surface-water subunit synoptic study in August 1994. Ground-water samples were collected from 30 wells (fig. 3) in July 1993. In August 1995, 19 surface-water sites were sampled during the Mill Creek focused synoptic study. Five of the focused synoptic sites represented end-of-pipe discharges from point sources and were not included in statistical summaries. One of the sites sampled in the Mill Creek Basin represents forested land use.

Subunits and Sampling Sites in the Ridge and Valley Physiographic Province

Five subunits were studied in the Ridge and Valley Physiographic Province: two in the Great Valley Section and three in the Appalachian Mountain Section. All five subunits are characterized by long narrow ridges and valleys with relief commonly exceeding 1,000 ft. These linear valleys have formed along the easily erodible rock formations and generally define the stream basins, except for several water gaps. The two subunits studied in the Great Valley Section consisted of a carbonate agricultural subunit and a carbonate urban subunit, and the three subunits studied in the Appalachian Mountain Section consisted of a carbonate agricultural, a sandstone and shale agricultural, and sandstone and shale forested subunit.

The Great Valley Section of the Ridge and Valley Physiographic Province is a broad valley with altitude within the valley ranging from approximately 400 to 900 ft. The southern part of the valley is underlain by carbonate bedrock, and the northern part of the valley is underlain by shale. The two subunits studied in the Great Valley Physiographic Section are the Great Valley carbonate agricultural subunit and the Great Valley carbonate urban subunit (fig. 6).

The Great Valley carbonate agricultural subunit is predominantly flat. The Great Valley also has karst features such as sinkholes, caverns, internal drainage, and large springs. The valley is bounded by forested ridges (fig. 7), Blue Mountain to the north, and South Mountain and other ridges to the south. The streams that drain the Great Valley are affected by both agricultural and forested land. Streams in the center of the valley may flow through predominantly agricultural land, whereas streams that originate on the ridges and flow into the valley drain both forested and agricultural land. Similarly, ground water that infiltrates in the center of the valley may be predominantly influenced by agricultural land use, and ground water closer to the ridge may be influenced by agricultural or forested land. The soils in this subunit have excellent infiltration capacity.

In the Great Valley carbonate agricultural subunit, samples were collected at the long-term monitoring site and at the ground-water and surface-water synoptic sites. The long-term surface-water monitoring site (Bachman Run near Annville, Pa.) (fig. 6) was sampled monthly from March 1993 to August 1994. The Bachman Run site was then chosen for extended sampling to further evaluate nitrate concentrations in an agricultural area of the Great Valley. Semimonthly fixed-interval sampling began in November 1994 and continued until August 1995, with the exception of the winter months, when monthly samples were collected. In addition to fixed-interval samples, an automatic sampler was installed at the Bachman Run site to collect samples through the rising and falling stages of selected spring and summer runoff events. Samples for the surface-water subunit synoptic study were collected at 10 sites (fig. 6) in August 1994. In 1995, ground-water samples were collected from 30 wells (fig. 6) from June 26 to August 9. Also in 1995, nine surface-water samples were collected for the focused synoptic study on June 26. Three of the sites sampled within the Bachman Run Basin represent areas of forested land use.

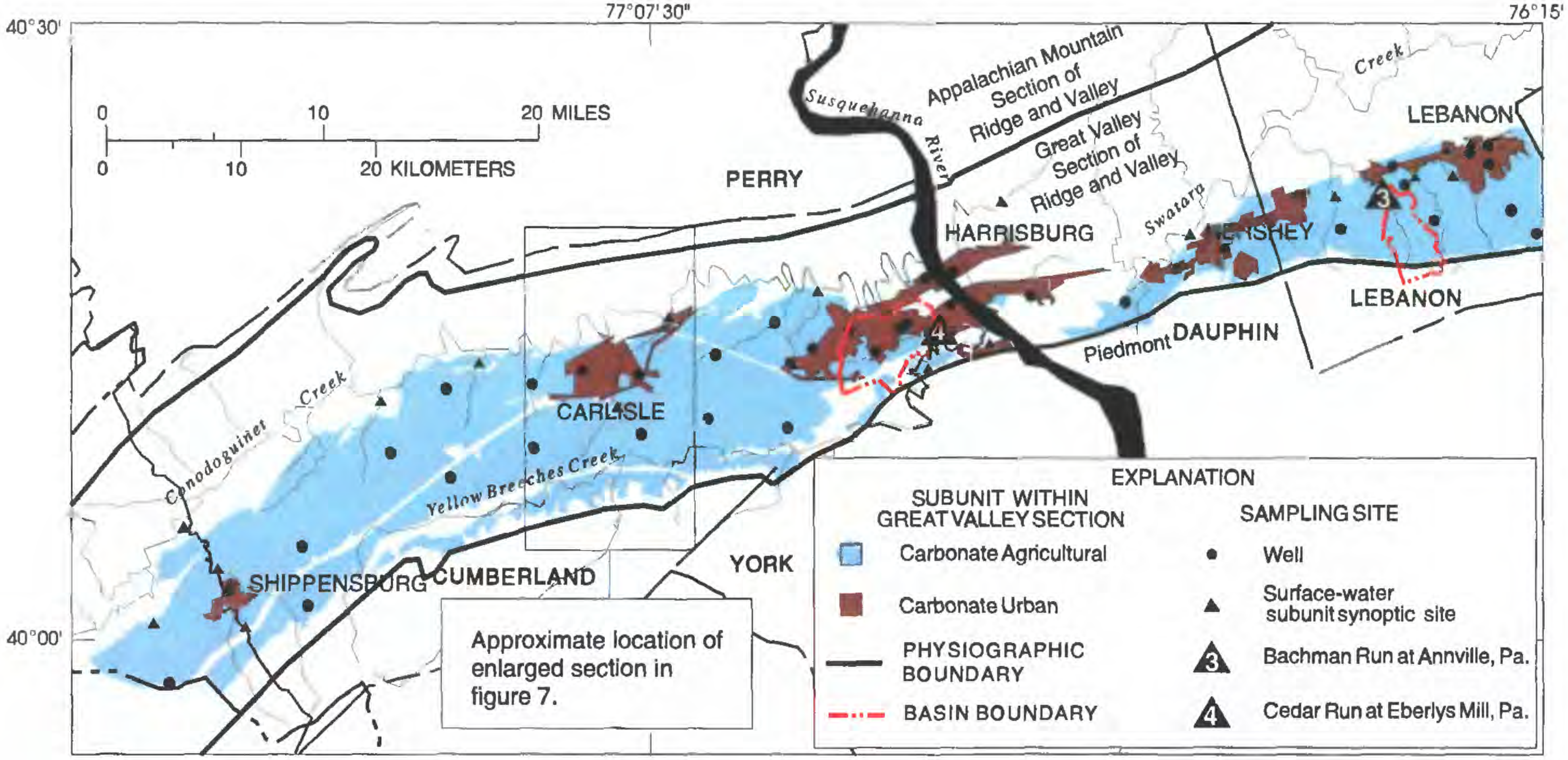


Figure 6. Subunits and sampling locations within the Great Valley Section, Ridge and Valley Physiographic Province, Lower Susquehanna River Basin study unit.

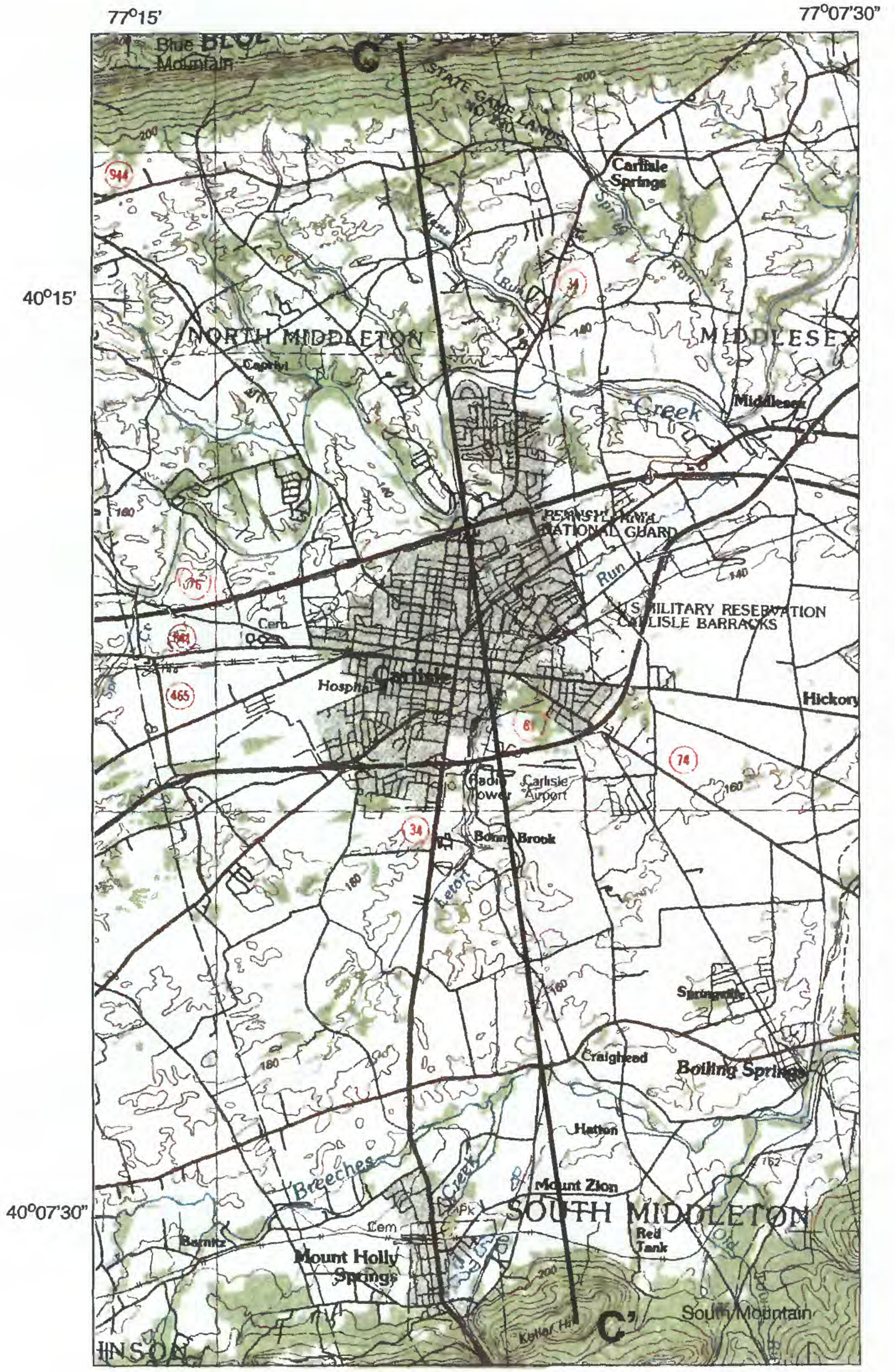


Figure 7. Selected topographic map area and cross section C - C′; Great Valley carbonate agricultural and urban subunits, Lower Susquehanna River Basin study unit.

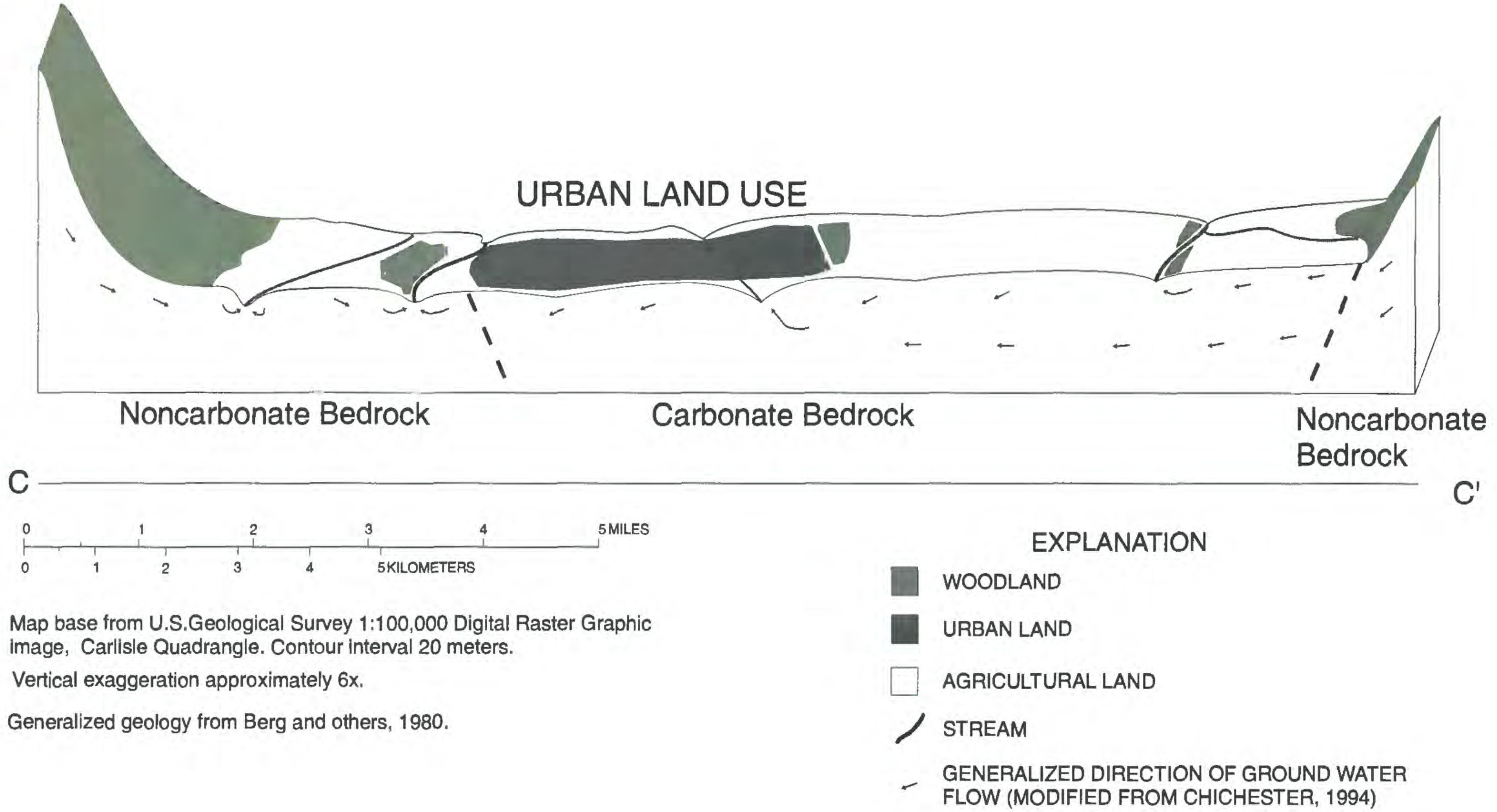


Figure 7. Selected topographic map area and cross section C - C′; Great Valley carbonate agricultural and urban subunits, Lower Susquehanna River Basin study unit—Continued.

The Great Valley carbonate urban subunit is in the center of the Great Valley, surrounded by the Great Valley carbonate agricultural subunit (fig. 6). The valley is a natural transportation corridor with substantial urban development, particularly in the flat areas of the valley underlain by carbonate bedrock. The towns of Shippensburg, Carlisle, Harrisburg, Hershey, and Lebanon and some residential areas around these municipalities are within in the study area. Water in streams and ground-water flow systems in urban areas of the valley are likely to be influenced by the surrounding agricultural land (fig. 6). The soil infiltration capacity is excellent in most of this area, except where the soil is covered with paved roads, parking lots, and buildings, which reduce infiltration and increase runoff. Because of the flat topography in the valley and the lack of surface-water drainage, runoff is commonly directed into stormwater retention ponds or stone-lined drains that allow the runoff to percolate into the ground. In some cases, stormwater runoff is directed into drainage wells for disposal. The combination of large areas of impervious material, the disposal methods for runoff, and the natural karst features in this area alter the response of the surface-water and ground-water systems to precipitation events.

Sampling sites in the Great Valley urban subunit included the long-term monitoring site and the ground-water and surface-water synoptic sites. The long-term monitoring site (Cedar Run at Eberlys Mill, Pa.) (fig. 6) was sampled weekly during the first year and semimonthly during the second year with the exception of the winter months (December through March), when samples were collected monthly. To further evaluate nitrate concentration in an urban area of the Great Valley, the Cedar Run site was then chosen for monthly to semimonthly sampling that began in November 1994 and continued until August 1995. During this time, an automatic sampler was also used to collect samples through the rising and falling stages of spring and summer runoff events. In 1994, 11 surface-water subunit synoptic sites (fig. 6) were sampled from July 26 to July 27, and 20 ground-water samples were collected from wells (fig. 6) in the period between July 5 and August 17. Eight samples were collected on July 5, 1995, during the Cedar Run focused synoptic study.

The Appalachian Mountain Section of the Ridge and Valley Physiographic Province is characterized by a series of forested ridges and agricultural valleys; altitudes range from approximately 300 to 2,000 ft. The three subunits studied are the Appalachian Mountain carbonate agricultural subunit, the Appalachian Mountain sandstone and shale agricultural subunit, and the Appalachian Mountain sandstone and shale forested subunit (fig. 8).

The Appalachian Mountain carbonate agricultural subunit is predominantly flat. The valleys underlain by carbonate bedrock are commonly wider than the valleys underlain by sandstone and shale and have karst features such as sinkholes, caverns, internal drainage, and large springs. These valleys are bounded by forested ridges (fig. 9). Many streams that drain these valleys are affected by agricultural and forested land use. Surface and ground water is influenced by agricultural land use or a mixture of agricultural and forested land use, depending on the source area of the water. The soils in this subunit have excellent infiltration capacities.

In the Appalachian Mountain carbonate agricultural subunit, samples were collected at the long-term surface-water monitoring site (Kishacoquillas Creek near Lumber City, Pa.) (fig. 8) and at synoptic sites. The long-term site was sampled monthly from March 1993 to August 1994. During the surface-water subunit synoptic studies, 16 sites (fig. 8) were sampled from August 1 to August 3, 1994. Also in 1994, 30 ground-water samples were

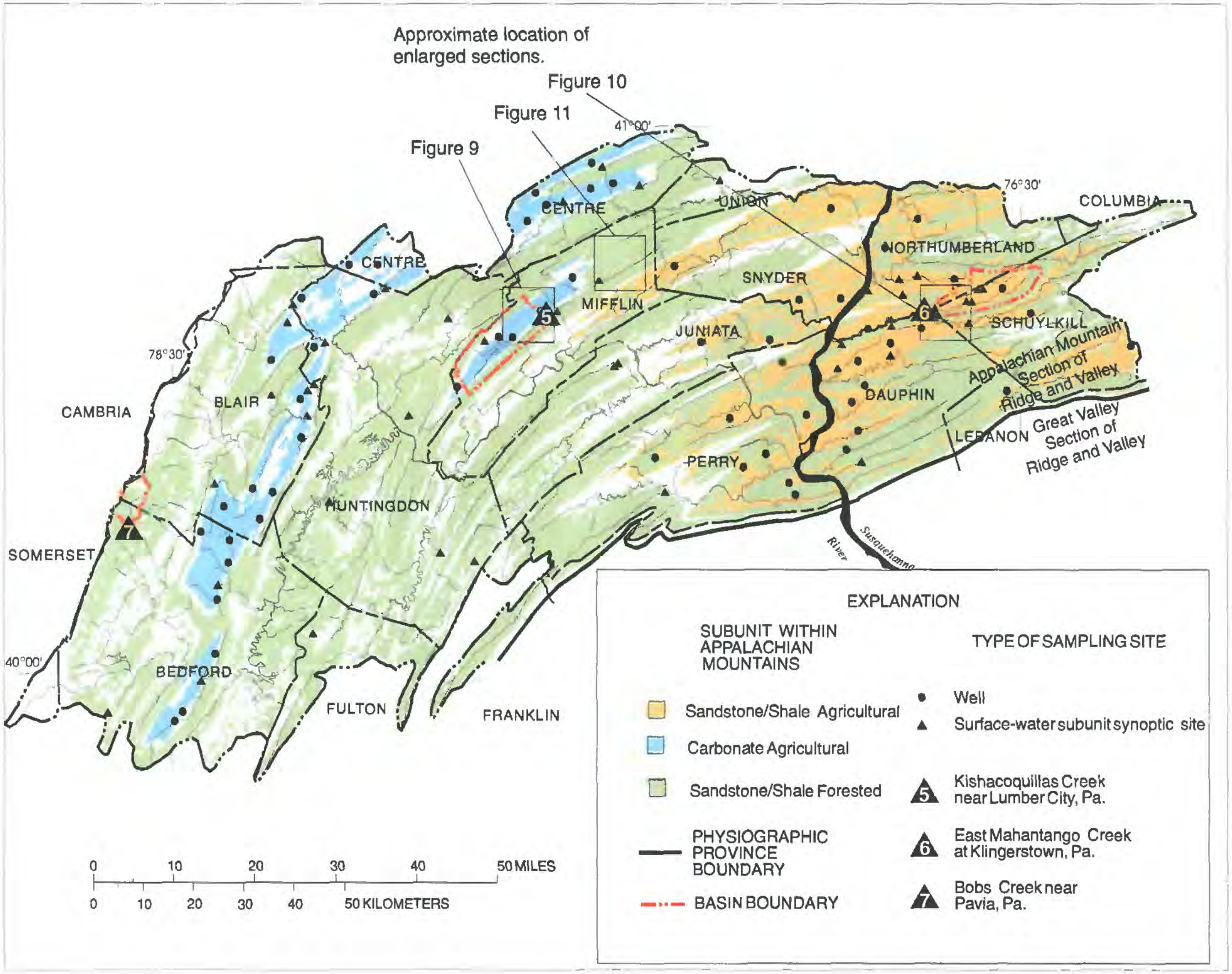
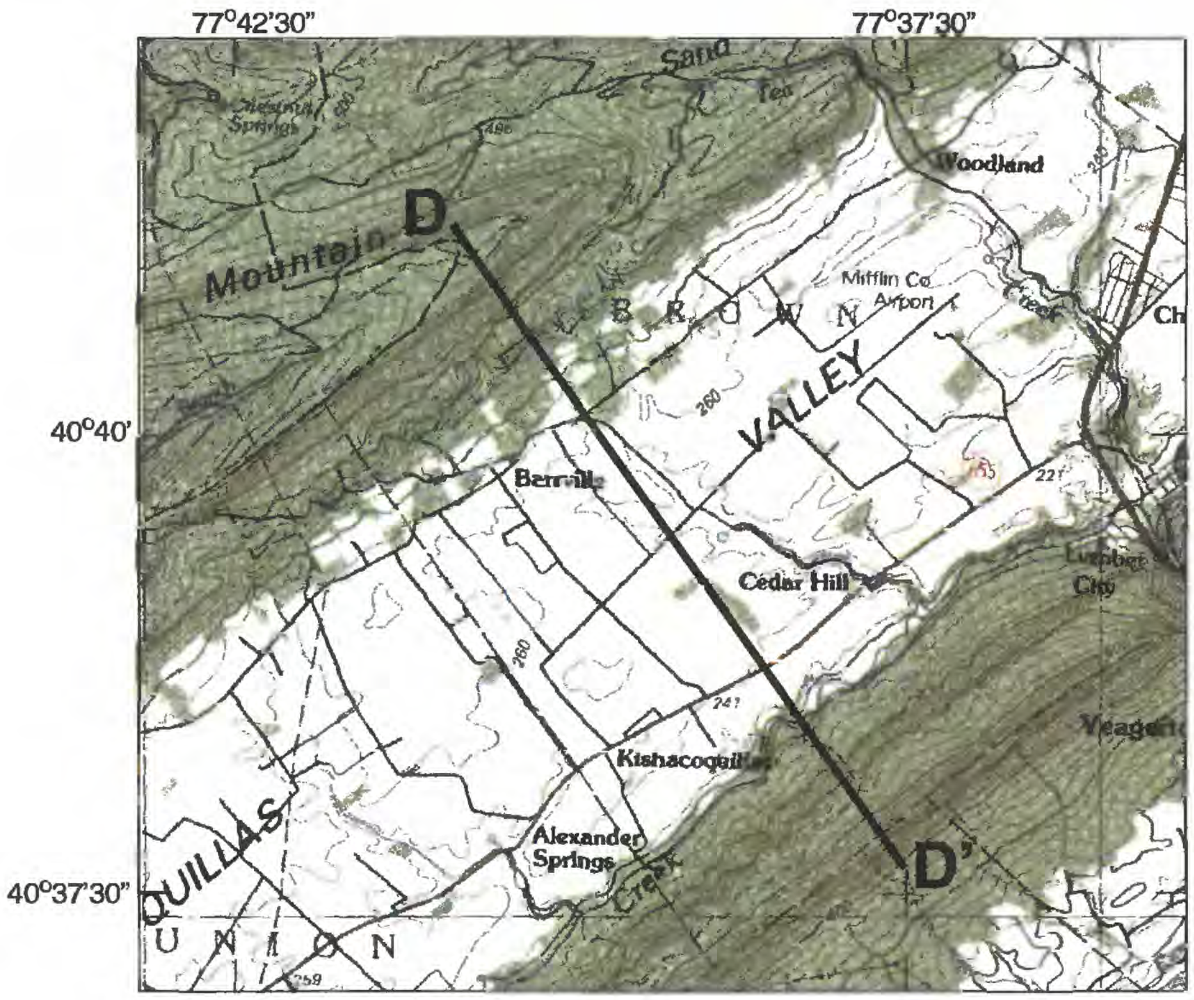
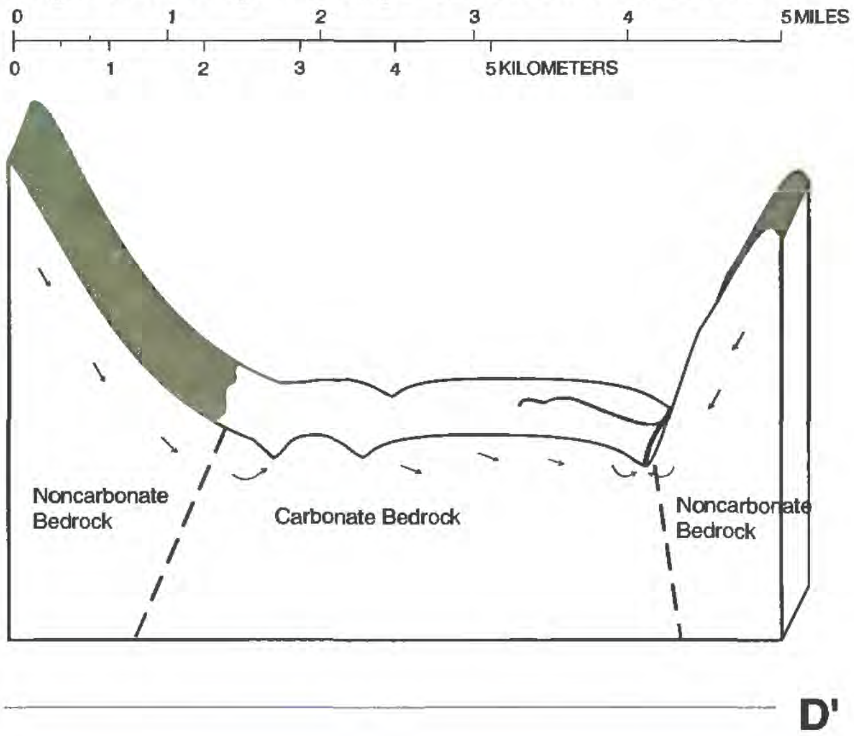


Figure 8. Subunits and sampling locations within the Appalachian Mountain Section, Ridge and Valley Physiographic Province, Lower Susquehanna River Basin study unit.



Map base from U.S.Geological Survey 1:100,000 Digital Raster Graphic image, State College Quadrangle. Contour interval 20 meters.



EXPLANATION

WOODLAND

AGRICULTURAL LAND

STREAM

GENERALIZED DIRECTION OF GROUND WATER FLOW

Vertical exaggeration approximately 6x.

Generalized geology from Berg and others, 1980.

Figure 9. Selected topographic map area and cross-section D - D′; Appalachian Mountain carbonate agricultural subunit, Lower Susquehanna River Basin study unit.

collected from wells (fig. 8) between July 25 and August 16. The Kishacoquillas Creek focused synoptic study was conducted in July 1995; 11 surface-water sites were sampled in 2 days.

The Appalachian Mountain sandstone and shale agricultural subunit is generally confined to the valleys (fig. 10), which are narrower and steeper than the carbonate valleys. Bedrock in this area includes sandstone, siltstone, conglomerate, and shale. Ground water in these bedrock types exists in fractures and regolith that covers the bedrock. The forested ridges are recharge areas for the valley, and they are the headwater areas for streams draining the valley. Therefore, both ground- and surface-water samples collected in streams and wells in this subunit are more likely to be affected by agricultural and forest land use than samples collected in the wider carbonate valleys (fig. 10). The soils have infiltration capacities in the good to poor range. The Appalachian Mountain sandstone and shale agricultural subunit was limited geographically to the eastern area of the basin in the Susquehanna Valley where much of the agricultural activity is concentrated.

Samples were collected in the Appalachian Mountain sandstone and shale agricultural subunit at the long-term monitoring site (East Mahantango Creek at Klingerstown, Pa.) and at the synoptic sites. The long-term surface-water monitoring site (fig. 8) was sampled from March 1993 to September 1994. Samples were collected weekly during the first year and monthly to semimonthly during the second year. As a part of a regional study of surface water in the Lower Susquehanna River Basin, 18 sites (fig. 8) were sampled in the Appalachian Mountain sandstone and shale agricultural subunit in June 1993. The 13 sites that were in the subunit but not within the East Mahantango Creek Basin and the sample collected at the long-term monitoring site comprise the surface-water subunit synoptic study. Four of the sites were within the East Mahantango Creek Basin and comprise the focused synoptic study along with the sample collected at the long-term monitoring site. In 1993, ground-water samples were collected from 22 wells (fig. 8) in the Appalachian Mountain sandstone and shale agricultural subunit as part of a more extensive ground-water survey that encompassed the Appalachian Mountain sandstone and shale region.

The Appalachian Mountain sandstone and shale forested subunit is predominantly on ridges; however, in remote areas of the study unit, both ridges and valleys are forested (fig. 11). The bedrock underlying this subunit is similar to the bedrock in the sandstone and shale agricultural subunit, although the ridges commonly consist of the more resistant sandstone. Flow through the consolidated material is primarily in small bedrock fractures. The ridges are the recharge areas; therefore, surface and ground water in the forested areas are not influenced by other land uses. The soils in this subunit have infiltration capacities that range from good to poor.

In the Appalachian Mountain sandstone and shale forested subunit, samples were collected at the long-term surface-water monitoring site (Bobs Creek near Pavia, Pa.) and the ground-water and surface-water synoptic sites. The long-term surface-water monitoring site (fig. 8) was sampled monthly from April 1993 to August 1994. For the surface-water subunit synoptic study, 16 sites (fig. 8) were sampled between July 31 and August 2, 1995. In 1993, seven wells were sampled in the forested subunit (fig. 8) as part of a larger ground-water study in the Appalachian Mountain sandstone and shale region. Although surface-water samples were collected throughout the subunit, ground-water samples were collected only in the eastern area of the subunit. No focused surface-water synoptic study was conducted for this subunit.

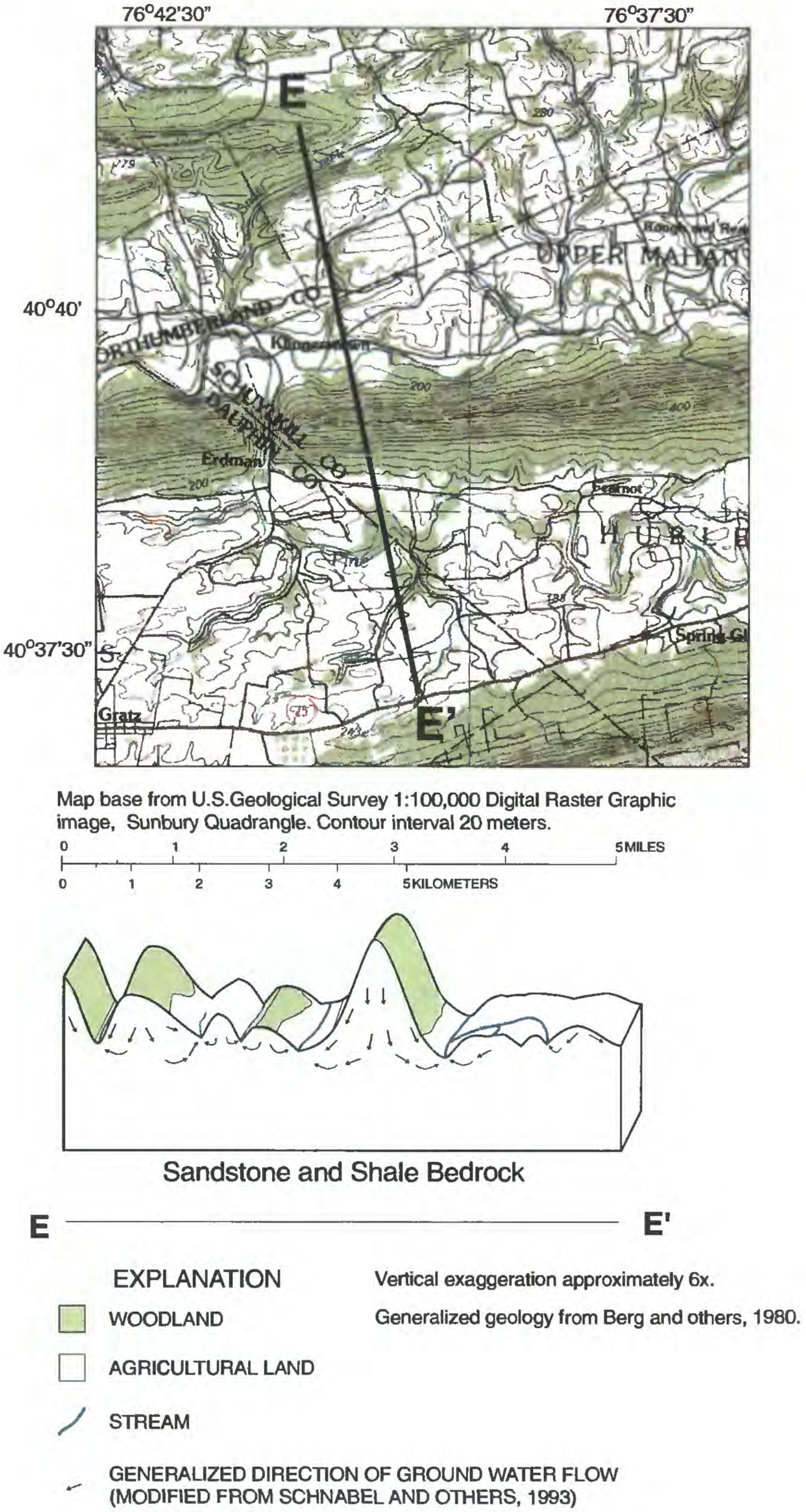
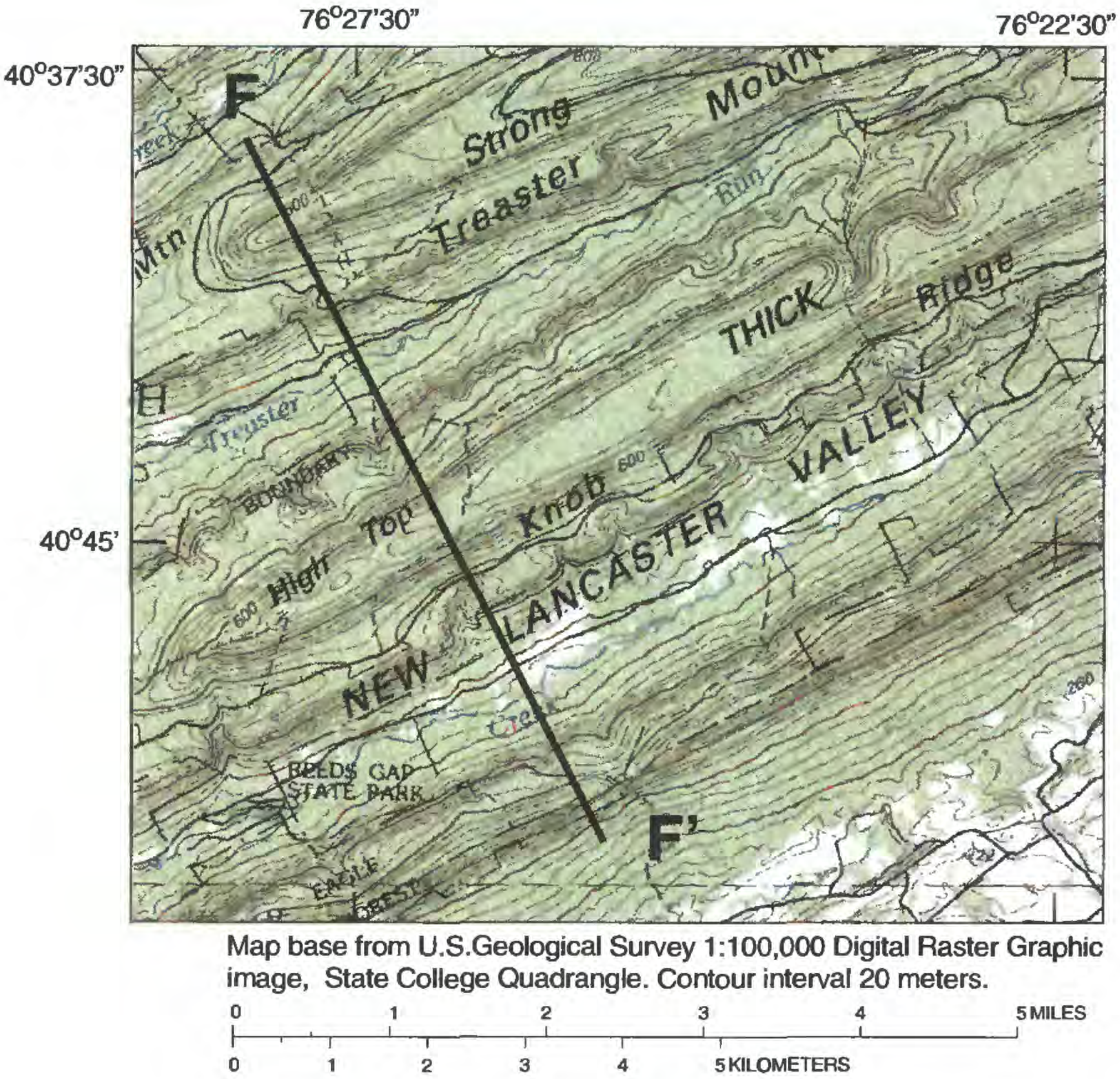
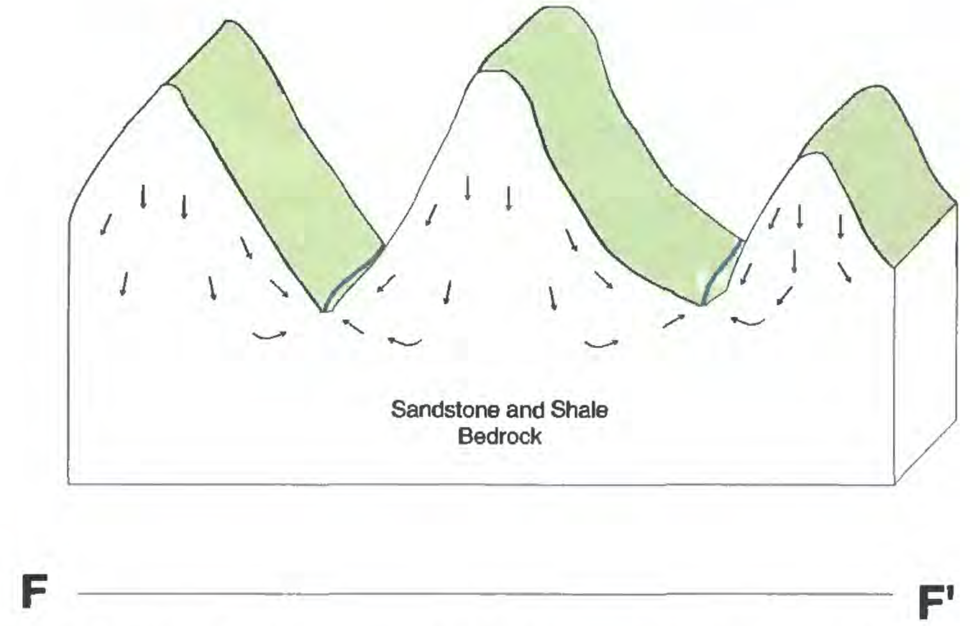


Figure 10. Selected topographic map area and cross-section E - E′; Appalachian Mountain sandstone and shale agricultural subunit, Lower Susquehanna River Basin study unit.





EXPLANATION

WOODLAND

AGRICULTURAL LAND

STREAM

GENERALIZED DIRECTION OF GROUND WATER FLOW (MODIFIED FROM SCHNABEL AND OTHERS, 1993)

Vertical exaggeration approximately 6x.

Generalized geology from Berg and others, 1980.

Figure 11. Selected topographic map area and cross-section F - F'; Appalachian Mountain sandstone and shale forested subunit, Lower Susquehanna River Basin study unit.

NITROGEN CYCLING AND NITROGEN SOURCES

The nitrogen cycle and the sources of nitrogen in the study unit play an important role in the analysis of the data collected. The interpretation of data collected on the temporal and spatial variation in nitrate concentration is related to the nitrogen cycle and nitrogen sources. Background information on the nitrogen cycle and nitrogen sources provides a perspective on how these factors relate to water quality in this study area.

Nitrogen Cycling

The temporal variation of nitrogen concentrations in soil and water is related to the nitrogen cycle in plants and to human efforts to enhance plant growth. Because plant growth is related to temperature and climate, a cyclical pattern of change in nitrate concentration would be expected in this study area. The length of the growing season varies from 160 days in the northern areas to 200 days in the south (Susquehanna River Basin Study Coordinating Committee, 1970). Mean monthly temperatures at Altoona range from 26°F in January to 71°F in July, and mean monthly temperatures at Lancaster range from 28°F in January to 74°F in July (U.S. Department of Commerce, 1995).

For the purposes of this report, the growing season (not the frost-free season) is defined to be the period from April 1 through September 30. The growing season is the time when the most active plant growth occurs, resulting in utilization of available nitrogen in the soil. For agricultural sections of Pennsylvania and Maryland, it is also the time when the most field activity occurs—spring plowing with manure application, fertilizer application during planting, and midsummer fertilizer applications to selected crops. These months were chosen to represent the growing season on the basis of the dates when 50 percent of spring plowing, corn planting, and fall plowing were completed (U.S. Department of Agriculture, 1994, 1995a, 1995b, 1995c, 1995d, 1995e, 1995f, 1995g).

Complex processes affect the gains and losses of nitrogen in agricultural soils during the growing season. Nitrogen plays an important role in the growth of all plants and along with other nutrients must be in adequate supply for plants to thrive. Nitrogen-poor soils result in crops that are stunted and yellow in color. When soil is cultivated in the spring, nitrogen concentrations generally decline. Natural processes such as precipitation, biological nitrogen fixation, and decomposition of organic matter add some nitrogen to soil. Nitrogen fertilizers are used on agricultural cropland and other areas to supplement the naturally occurring nitrogen. Nitrogen losses during the growing season take place through plant uptake and crop removal, erosion, leaching, denitrification, and volatilization (Legg and Meisinger, 1982). Crops harvested and removed from the field represent a real loss of nitrogen; however, crop residues left on the field do not. Erosion and leaching physically remove nitrogen from the field by transporting the nitrogen to the surface-water or ground-water systems. Denitrification is a biological process that commonly occurs in oxygen depleted water or soil and transforms the nitrogen to N_2 gas, which returns to the atmosphere. When temperatures rise above 32°F, nitrogen is removed exponentially with increasing temperature through biological denitrification (Firestone, 1982, p. 315). Volatilization occurs when nitrogen, usually in the form of ammonia, evaporates into the air (Legg and Meisinger, 1982). It is common for the ammonia to return to the ground surface with precipitation, commonly near where the volatilization occurred (Langland and Fishel, 1996).

In urban areas, gains and losses in nitrogen concentrations also occur during the growing season. In recent years, fertilizer use has increased to produce the thick lawns surrounding many homes. Homeowners or commercial lawn care companies usually apply fertilizer in the spring; follow-up applications may be done once or twice throughout the summer. These fertilizers supplement the nitrogen naturally added through precipitation and decomposition of leaves and grass. Growing season nitrogen losses in urban areas result from the same activities and processes that affect losses in agricultural settings.

In forested areas, nitrogen losses generally exceed nitrogen gains throughout the growing season. Gains are limited to nitrogen added through precipitation, decomposition of soil organic matter on the forest floor, and nitrogen fixation. Losses of nitrogen, through plant uptake and volatilization, rapidly exceed the gains to the system, and the result is a decline in nitrogen concentrations in soil. These processes make less nitrate available to leach to the ground-water table and, therefore, can cause a decrease in nitrate concentration in stream base flow.

The nongrowing season is marked by decreased nitrate production and decreased nitrate consumption. Cooler temperatures in the nongrowing season (October 1 - March 31) result in a dormant period for deciduous plants, shrubs, and trees. Many agricultural crops are harvested before hard frosts and freezing temperatures occur, resulting in a reduction in the amount of nitrogen needed to sustain the vegetation of the area. Low soil temperatures in the nongrowing season retard the decomposition rates of soil organic matter and biological nitrogen fixation, processes that add nitrogen to the soil during the growing season. The combination of many seasonal processes can, therefore, affect nitrate concentrations in ground water and surface water.

Nitrogen Sources

Land use is commonly used as a surrogate for sources of nitrogen. For example, fertilizer is applied to agricultural land but not to forested land. The primary agricultural land uses within the study unit were row-crop and pasture. Although many farms had a variety of crops in rotation and some land in pasture, some farms had all of the cropland planted in corn with a large number of animals confined in buildings. Manure produced by a concentrated animal operation commonly contains more nutrients than the crops grown on the farm can utilize. Therefore, the broad classification of agricultural land use can encompass a wide range of manure and fertilizer application rates.

To account for the spatial variation of the amount and type of nitrogen sources, information was compiled to show the major inputs of nitrogen within each subunit (table 6). This variability in nitrogen inputs must be considered when comparing nitrate concentrations in water samples. The predominant nonpoint source of nitrogen in agricultural subunits is animal manure. Although manure application rates vary greatly, manure application within agricultural areas commonly comprises about 70 percent of the total nonpoint sources (table 6). Commercial fertilizer and atmospheric deposition also contribute nitrogen, but the amount from these sources is much less than the amount from animal manure. Nitrogen from septic systems may affect an individual well or stream sample; on a larger scale, however, the contribution of nitrogen from septic systems is negligible (table 6). Nitrogen fixation from legumes and nitrogen decomposition from crop residues was not quantified. Therefore, the variability in manure application rates was emphasized during data analysis.

Manure application is highest in the Piedmont carbonate agricultural subunit. The other four agricultural subunits have nitrogen inputs that are similar, although less than half of the input rate of the Piedmont carbonate agricultural subunit. Nonpoint nitrogen inputs are quite low for the Great Valley carbonate urban subunit and the Appalachian Mountain sandstone and shale forested subunits. The primary nonpoint nitrogen source in these areas is atmospheric deposition.

Table 6. *Estimates of input rate for nonpoint sources of nitrogen within subunits, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

[lb N/acre/year, pounds of nitrogen per acre per year; --, no data available; n/a, not applicable (none or negligible amount)]

Environmental subunit	Nonpoint nitrogen input rates (lb N/acre/year)				
	Animal manure application[1]	Fertilizer nitrogen application[2]	Nitrogen from septic systems[3]	Atmospheric deposition of nitrogen[4]	Totals
Piedmont crystalline agricultural	72	17	4	11.1	103
Piedmont carbonate agricultural	172	21	3	11.1	207
Great Valley carbonate agricultural	73	10	3	15.7	101
Great Valley carbonate urban	--	10	--	15.7	26
Appalachian Mountain carbonate agricultural	69	4.9	1	24.8	100
Appalachian Mountain sandstone and shale agricultural	65	11	3	24.8	103
Appalachian Mountain sandstone and shale forested	n/a	n/a	3	24.8	27

[1] Manure application rates based on animal density (Maizel and others, 1995).

[2] Based on county fertilizer sales (Battaglin and Goolsby, 1995). Uniform application of fertilizer throughout a county was assumed; however, the actual application rates for urban areas are unknown.

[3] Based on 0.04 lb N per person per day (Rupert, 1996, p. 7), 3.5 persons per septic system, and county totals for numbers of septic systems from the U.S Bureau of Census (1992). The urban area in this study is predominantly served by public sewage disposal.

[4] Based on calculations of total atmospheric deposition of nitrogen (Hainly and Loper, 1997).

The relation between total nitrogen input and removal of nitrogen by agricultural crops plays a significant role in determining if excess nitrogen is available to enter the hydrologic system. Agricultural crops grown in the study unit can utilize much of the nitrogen applied to the land surface. The potential nitrogen uptake for corn silage is estimated to be 175 lb/acre in areas underlain by carbonate bedrock, 150 to 175 lb/acre in areas underlain by crystalline bedrock, and 150 lb/acre in areas underlain by sandstone and shale (Serotkin, ed., 1994). However, corn is not the only crop grown in these areas; the nitrogen removed by crops such as soybeans, wheat, and corn harvested for grain is less than the amounts removed by corn silage. Although the nitrogen uptake by crops such as corn exceeds the average nitrogen input, it is assumed that applications of fertilizer and manure are distributed to provide the nitrogen that each crop needs (more is applied to corn and less is applied to wheat). Without precise information on crop acreage and yields, it is not feasible to determine if the amount of nitrogen applied within a subunit exceeds the amount of nitrogen taken up by crops in that subunit. One exception is the Piedmont carbonate agricultural subunit, where the estimate of total nonpoint nitrogen input (table 6) exceeds the estimates of the potential nitrogen removal by any of the major crops grown in that subunit.

The major nitrogen sources within the basins selected for the subunit synoptic studies and the basins selected for long-term monitoring are summarized in table 7. The table lists the number of point sources within the basins (Risser and Siwiec, 1996) and the manure application rates within the basins (Maizel and others, 1995). Actual nitrogen values from the point sources are not given because of the lack of data or lack of reliable data. Although the volume and effluent nitrogen concentrations differ by large amounts among sources, this information is included to show the relative number of major (> 1 Mgal/day) and minor (<1 Mgal/day) point sources discharging to these basins.

Table 7. *Summary of major nonpoint sources and point sources of nitrogen in subunit synoptic basins and long-term monitoring basins for environmental subunits in the Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

[lb N/acre/year, pounds of nitrogen per acre per year; n/a, not applicable (none or negligible amount)]

Environmental subunit	Nitrogen sources					
	Subunit synoptic basins			Long-term monitoring basins		
	Median manure application rate, in lb N/acre/yr	Number of major point-source discharges[1]	Number of minor point-source discharges[2]	Median manure application rate in lb N/acre/yr	Number of major point-source discharges	Number of minor point-source discharges
Piedmont crystalline agricultural	44	0	15	45	0	0
Piedmont carbonate agricultural	159	3	35	167	1	4
Great Valley carbonate agricultural	86	1	6	124	0	1
Great Valley carbonate urban	[3]49	2	10	30	0	0
Appalachian Mountain carbonate agricultural	69	1	8	92	0	3
Appalachian Mountain sandstone and shale agricultural	64	0	13	64	0	0
Appalachian Mountain sandstone and shale forested	n/a	0	8	n/a	0	0

[1] Major point sources with a discharge of greater than one million gallons per day (Risser and Siwiec, 1996).

[2] Minor point sources with a discharge of less than one million gallons per day (Risser and Siwiec, 1996).

[3] Although there is no agricultural land in the urban subunit by definition, some of the urban surface-water basins extend into agricultural land. Manure application rates are for the entire basin.

STUDY METHODS

The data-collection program was developed to involve both baseline stream water quality (long-term monitoring program) and more focused spatial study areas (synoptic studies). The NAWQA program provided protocols that insured consistency in field and laboratory techniques so that the data from samples collected within a particular study unit can be synthesized to characterize the condition of water quality nationwide. The data were analyzed following procedures developed by the USGS.

Sample Collection

Water samples collected from the Lower Susquehanna River Basin during 1993-95 included 161 ground-water subunit synoptic samples, 209 long-term monitoring base-flow samples, 110 long-term monitoring storm-affected samples, 100 surface-water subunit synoptic samples, and 67 surface-water focused synoptic samples. A detailed description of the site-selection strategy, the design and implementation of water-quality studies, the site and basin characteristics, and the sample-collection and processing methodology used in the Lower Susquehanna River Basin study unit can be found in Siwiec and others (1997). Ground-water and surface-water collection methods followed national protocols found in Koterba and others (1995) and Shelton (1994), respectively. Basic sample-collection methods are described below.

The well-sampling equipment was cleaned in accordance with the protocols prior to sample collection. To collect a sample from a well, a Teflon hose was connected to a raw water spigot outside the house or at the pressure tank. Water samples for nutrient analyses were filtered through a 0.45-µm cellulose nitrate filter and collected in 125-mL, polyethylene bottles. Water samples used in nitrate determinations collected in 1993 and 1994 were preserved with 0.5 mL of mercuric chloride. This preservation method was discontinued in 1995 after studies showed that chilling provided adequate preservation of samples (Patton and Truitt, 1995).

The surface-water sampling equipment was cleaned in accordance with the protocols prior to sample collection. All wadeable surface-water-quality samples were collected with a DH-81 hand-held sampler with Teflon or glass bottles using the Equal-Width-Increment (EWI) and depth-integrated methods. A bridge rig and cable-suspended D-77 sampler with a 3-L Teflon bottle were used for high streamflows and large rivers. When stream depth was shallow or stream size was small, the samples were dipped from the centroid of flow. The water-quality sample was split using a decaport Teflon splitter, and the aliquot used for the analysis of dissolved nutrients was filtered through a 0.45-µm, 142-mm cellulose nitrate filter on an aluminum plate filter. Preservation of surface-water nitrate samples was identical to the preservation of ground-water samples described earlier.

Laboratory Analysis

Nutrient samples were sent within 2 days of sample collection to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., in brown 125-mL polyethylene bottles chilled to 4°C. The NWQL analyzes for nitrite plus nitrate ($NO_2 + NO_3$ as N) and nitrite (NO_2 as N). Analytical methods for nutrient determinations used at the NWQL can be found in Fishman and Friedman (1989). If nitrite is detected, nitrate can be calculated by subtracting the value of nitrite from the value of nitrite plus nitrate; however, if nitrite is not detected, nitrate concentration cannot be calculated directly. Over half the samples analyzed had no nitrite detected at the 0.01 mg/L detection level, and the rest had very low concentrations of nitrite (0.01 to 0.82 mg/L). Therefore the values for nitrite plus nitrate are essentially equivalent to nitrate and provide the basis for all data analysis in this report. The laboratory also analyzed the samples for other forms of nitrogen, however, 95 percent of the ammonia (nitrogen ammonia dissolved as N) concentrations were less than 0.12 mg/L and 95 percent of the ammonia plus organic nitrogen (nitrogen, ammonia plus organic dissolved as N) concentrations were less than 0.7 mg/L. This shows that nitrate is the dominant form of nitrogen in the samples analyzed. Water-quality samples collected for the Appalachian Mountain sandstone and shale agricultural subunit synoptic were analyzed by the U.S. Department of Agriculture-Agriculture Research Service (USDA-ARS) laboratory at University Park, Pa., as part of a cooperative study between the USGS and the USDA. These samples were analyzed for nitrate (NO_3 as N).

Quality Assurance

Quality-assurance samples were collected to assess the accuracy and reproducibility of the field data. Blank samples were collected in the field at approximately 10 percent of the sites. This was conducted to ensure that the equipment and field conditions were not a contamination source. After normal cleaning procedures were conducted, inorganic blank water obtained from the USGS Water-Quality Services Unit in Ocala, Fla., was pumped through the equipment and processed in the same manner as other samples. Of the 37 blank samples collected, 32 did not have detectable concentrations of nitrate plus nitrite (less than 0.05 mg/L). Of the five samples that did have detectable concentrations, four were less than 0.1 mg/L. The highest concentration detected in a blank sample was 0.21 mg/L. The environmental samples associated with these five blank samples had concentrations of nitrate that ranged from 30 to 120 times higher than the concentration in the blank samples. Approximately 95 percent of the environmental samples had concentrations of nitrate plus nitrite higher than the highest concentration detected in any blank sample. The trace detections of nitrate in the five blank samples, therefore, do not affect the interpretation of the environmental data collected.

To assess the effects of field and laboratory techniques on reproducibility of the data collected, replicates also were collected at approximately 10 percent of the sites. The ground-water replicates were collected sequentially and submitted for analysis. Of the 17 ground-water replicates collected, the mean difference between the environmental samples and the replicate was 0.009 mg/L over a range of concentrations from 0.05 to 12 mg/L. Surface-water replicates also were collected sequentially, and the mean difference between the sample and replicate for the 20 samples was 0.04 mg/L over a range of 0.57 to 12 mg/L. The Wilcoxon signed-rank test (Wilcoxon, 1945) was used to determine if the differences between the environmental samples and the replicates were statistically significant. No statistically significant differences were found. This indicates a high degree of reproducibility for the nitrate data from samples analyzed by the NWQL.

Several replicate samples also were collected and sent to both the USDA-ARS laboratory and the NWQL. These replicates were collected to assess the accuracy of the ARS laboratory that was used to analyze the 18 samples collected in the Appalachian Mountain sandstone and shale agricultural subunit synoptic study. The samples were part of a larger cooperative study of nutrients and herbicides in the Susquehanna River Basin. During the study, 13 replicate samples were collected to allow comparison of analytical results from the ARS laboratory and the USGS laboratory. These replicates showed a mean difference between the two laboratories of 0.19 mg/L over a range of 0.62 to 8.8 mg/L. Wilcoxon signed-rank test shows no statistically significant differences between the two laboratories (probability = 0.11).

The USGS Quality Assurance Branch conducts a quality-control process for NWQL and other USGS laboratories. This project, called the blind sample program, consists of submitting samples of known concentrations to the laboratory and analyzing the results.

During the sample-collection period of 1993 to 1995, 667 samples were sent to the NWQL through the blind sample program for analysis for nitrite plus nitrate. Of the samples sent to the laboratory, only 4 percent were more than 2 standard deviations from the expected value and 1 percent of the samples were more than 6 standard deviations from the expected value. This independent testing shows that the data from the NWQL have good precision and accuracy.

Data Analysis

Details of data-analysis methodology specific to the Lower Susquehanna River Basin study unit used in the interpretation of data will be presented. This methodology includes hydrograph-separation techniques and statistical methods.

Hydrograph-Separation Techniques

Because this report deals with base-flow concentrations of nitrate in surface and ground water, stormflow samples were not included in the interpretation. For this report, base flow is defined as a period or condition when surface runoff from storms was not a significant component of streamflow, and streamflow was comprised chiefly of ground-water discharge. Stormflow is defined as a period or condition when direct surface runoff and interflow (shallow subsurface runoff) were the predominant contributors of streamflow. A method designed to ensure reproducibility of results was used to evaluate the flow conditions for all stream samples.

One of the first steps was to determine how to classify samples collected for the synoptic studies, where no continuous streamflow record was available. All surface-water synoptic studies were conducted when hydrologic conditions showed that the streams to be sampled were at base flow. This was determined by evaluation of hydrographs from streams located near the sampled basins (Durlin and Schaffstall, 1994, 1996, 1997) and a review of meteorologic conditions in the days preceding the study. Therefore, surface-water synoptic water-quality samples were all designed as base-flow samples. Water-level data from the USGS ground-water monitoring network (Durlin and Schaffstall, 1994, 1996, 1997) were used to verify that ground-water sample collection occurred during periods when recharge was at a seasonal low.

For the long-term monitoring sites where a continuous streamflow record was available, additional data were available to classify individual samples as representing either base flow or stormflow. The steps used included 1) determining the time interval after a storm peak when a sample may be affected by stormflow, 2) determining how much the flow volume had to increase to be considered a storm, and 3) determining how to classify samples collected when field observations did not match the classifications from steps one and two. The methodology used to classify individual samples is as follows:

1) For the samples collected at the long-term monitoring stations, a commonly accepted formula used in hydrograph separation ($N=A^{0.2}$, where N = time in days and A = drainage area in square miles)(Viessman and others, 1977, p. 111) was used to determine the interval from the peak of the storm through the falling limb of the hydrograph when ground-water discharge may not have been the predominant contributor of flow. Visual inspection of the hydrographs for six of the seven long-term monitoring sites showed that the streams had returned to base flow within the calculated number of days. East Mahantango Creek hydrographs did not appear to have returned to base flow using the calculated "N" value. Because $N=A^{0.2}$ did not accurately describe this basin, the period of storm influence was calculated using $N=(A^{0.2}+1)$, which matches observations from the hydrograph. Samples that were collected outside the time interval calculated for each site were considered base-flow samples. Some samples were

collected before stage equipment was installed or during periods of stage equipment malfunction. In these cases, hydrographs from nearby sites (Durlin and Schaffstall, 1994, 1996, 1997) were reviewed and precipitation records were examined to determine whether the sample was collected during base flow. This affects five or fewer samples at each site.

2) For days when elevated streamflow was determined to be from rainfall, snowmelt, or both, the fixed interval method of the HYSEP hydrograph-separation program (Sloto and Crouse, 1996) was used to separate base flow from the total flow. To negate the elimination of samples collected shortly after relatively minor storms, a day of elevated streamflow was considered a storm-affected day only when the total streamflow for the day was 30 percent greater than the expected base flow for the day. Therefore, only those samples that were collected within the calculated 'N' time from the peak of a storm and met or exceeded the 1.3 ratio of total flow to the expected base flow were considered storm samples and were thus excluded from the base-flow sample set. The ratio of 1.3 was selected as an average estimate of storm magnitudes that would not significantly affect water quality.

3) A few samples collected at the long-term monitoring sites at a time when the stage was rapidly rising or rapidly descending were considered storm samples even though the storm produced less than a 30 percent increase over the expected base flow. These samples were considered storm-influenced because observed conditions indicated that they were collected at a time when overland runoff was obviously affecting the flow.

Statistical Analysis

All nitrate-concentration data were first tested for normality using the Wilk-Shapiro test (Wilk and Chen, 1968) before choosing the statistical test for subsequent analysis. Normality refers to the symmetry of the distribution of the data around the mean or median. Many data sets were not normally distributed; therefore, nonparametric tests were chosen. Nonparametric statistical tests make comparisons by ranking the data and are more effective for analyzing data that do not fit a normal distribution curve.

The Tukey test (Tukey, 1977) was used to analyze the data sets for statistical differences among the groups. This test was conducted to compare groups such as bedrock type and land use. The statistical test that was used to determine the relation between two continuous variables was the Spearman's rank correlation (Helsel and Hirsch, 1992). The Spearman's correlation is a nonparametric test that was used to determine if nitrate concentration is associated with another continuous variable such as manure application rate or streamflow. The test will show the mathematical relation between the two variables and does not imply cause and effect.

NITRATE IN GROUND WATER AND STREAM BASE FLOW

One of the goals of the NAWQA program was to determine the occurrence and distribution of nitrate concentrations in ground and surface water and to explain, to the extent possible, the natural and human factors that affect water-quality conditions. To accomplish this goal, the nitrate data were analyzed to describe and explain 1) the relations between concentrations in ground water and surface water, 2) the spatial variations in concentrations, 3) the temporal variations in concentrations, and 4) base-flow load and yield estimates. Factors that could affect nitrate concentrations were examined to help explain the spatial and temporal variations. The data that provide the basis for these interpretations are published in Durlin and Schaffstall (1994, 1996, 1997).

Comparison of Nitrate Concentrations in Ground Water and Stream Base Flow

Determining the relations between ground-water quality and surface-water quality is an important step in understanding nitrate movement in the hydrologic cycle. The data analyzed for this report consist of surface-water samples collected under conditions where runoff from storms was not influencing streamflow, and streamflow was comprised chiefly of discharge from ground water. Ground-water samples were collected during the summer months when water levels were near the seasonal low. During this time, water from a well and base flow in streams are both coming from ground-water storage. Therefore, comparisons can be made within a given subunit between the water in the ground, represented by the well samples, and the water being discharged to the streams, represented by the surface-water synoptic samples. This comparison of well samples and base-flow stream samples has been made for each of the subunits. For each subunit, a brief explanation of the observed conditions is given.

All of the carbonate agricultural subunits had higher median nitrate concentrations in ground-water samples than in the surface-water synoptic samples (fig. 12). This was also true for the Piedmont crystalline agricultural subunit. In these areas, the nitrate in the ground-water reservoir, represented by the well samples, apparently underwent a chemical transformation or was diluted prior to entering the stream, resulting in lower concentrations of nitrate in the streamflow. Possible reasons for this include 1) near-stream or in-stream processes that would reduce nitrate concentrations, and 2) recharge areas for the wells sampled may be more heavily influenced by the nearby agricultural land use than the surface-water basins that invariably include at least some nonagricultural land-use areas.

A near-stream process that may lower the stream concentrations of nitrate is denitrification. Studies have shown that large decreases in nitrate concentration as ground water is discharged to a stream can be attributed to denitrification occurring in the carbon rich, anaerobic sediments near the stream (Haycock and Burt, 1993). Algae growth in surface water may lower the in-stream concentrations of nitrate relative to the concentrations detected in the wells. As ground water nears the streams, vegetation growing near the streams may utilize the nutrients in the ground water before it is discharged to the surface. Uptake of nitrate or conversion of nitrate to another nitrogen form by riparian vegetation is a potential reason for the nearly 4 mg/L difference in median nitrate concentration between the well samples and surface-water samples in the Piedmont crystalline subunit (fig. 12), where the streams are commonly bordered by forested land (fig. 4). Algae growth and plant uptake represent nitrogen storage in the system and, although no long-term nitrogen loss is occurring, these factors could account for the difference between the concentration of nitrate in ground water and stream base flow.

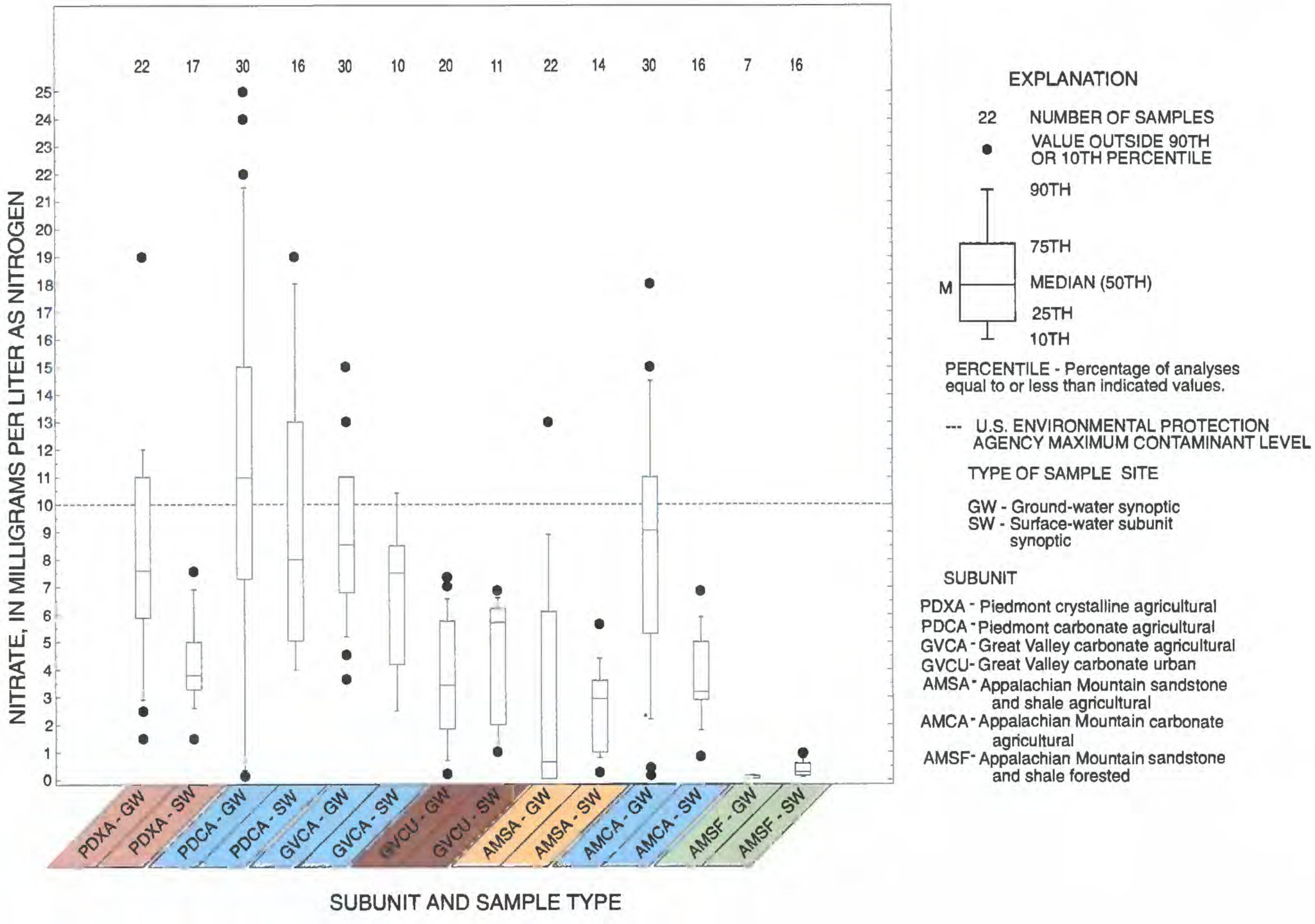


Figure 12. Distributions of nitrate concentrations in subunit surface-water synoptic studies and well synoptic studies among the seven subunits, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

In the carbonate urban subunit, the median nitrate concentration in surface water exceeds the median concentration in ground water (fig. 12). The higher surface-water concentrations could be because some of the urban surface-water basins extended into agricultural land. The urban areas of the Great Valley are surrounded by agricultural land (figs. 6 and 7), making it difficult to locate an urban basin without some agricultural land in its headwaters. This agricultural land in the urban basins contributed a median of 49 lb/acre/year of nitrogen from animal manure to the urban surface-water basins (table 7). The agricultural land use in these basins may actually be the factor that controls nitrate concentration. As with the other areas, the ground-water samples may have been affected more by the immediate land use near the well than the surface-water samples that reflect mixed land uses. Also, concentrations in the urban surface-water samples have been affected by the 2 major point-source discharges and 10 minor point-source discharges within the basins sampled (table 7).

Two sandstone and shale subunits also were characterized by higher median concentrations of nitrate in the surface water than in the ground water (fig. 12). Research by the USDA-ARS (Schnabel and others, 1993) on the relations between ground water and surface water in this area has shown that an aquifer in this subunit has two distinct layers (fig. 10). The shallow layer, composed of more highly fractured bedrock than the deeper layer, is characterized by relatively high transmissivity and relatively high nitrate concentrations. The deeper layer has lower transmissivity and lower nitrate concentrations, because the deeper layer contains water recharged over a variety of land-use types toward the headwaters of the aquifer, including large areas of forested land. Schnabel's work shows that base-flow concentrations of nitrate are influenced by the water with high nitrate concentrations that is being discharged from the shallow layer.

The data collected in the Appalachian Mountain sandstone and shale subunits conform with the concept of a two-layer aquifer presented by the USDA-ARS. The well samples were collected from the deeper layer of the aquifer that the USDA-ARS research showed to have lower nitrate concentrations than the upper layer. Although the land use near the wells was agricultural, the water in a well more than 100 ft deep could contain a mixture of water from the deep layer recharged on the forested ridge and water from the shallow layer recharged on surrounding agricultural land. A stream receiving base flow from the shallow layer of the aquifer would likely have higher nitrate concentrations than water in wells completed in the deeper layer of the aquifer.

Factors Affecting Spatial Distribution of Nitrate Concentrations

The spatial distribution of nitrate concentrations in ground water and surface water is affected by many factors. The subunits, defined by physiography, bedrock type, and land use, represent many interrelated characteristics that affect water quality, including nitrogen sources (table 6), topography, length of ground-water flowpath, infiltration rates, recharge area boundaries, soil type, and crop yields. These factors are detailed in the description of the subunits and are used to help explain the spatial distribution of nitrate concentration.

Bedrock Type

One factor that affects the spatial distribution of nitrate is bedrock type. Areas underlain by carbonate bedrock commonly have high nitrate concentrations in the ground water (Fishel and Lietman, 1986). Intense agricultural activity on fertile soils derived from carbonate bedrock contributes to the higher nitrate concentrations because a greater percentage of the land is used to grow corn, which requires heavy nitrogen fertilizer application, and only a small percentage of the land is idle. Other factors such as drainage of runoff into sinkholes and excellent infiltration capacities of soil are also possible explanations for this observation. Comparisons of nitrate concentrations in carbonate and noncarbonate subunits with similar land use and physiography were made to evaluate the effect of bedrock type on the spatial distribution of nitrate concentrations.

In the Ridge and Valley Physiographic Province, Appalachian Mountain Section, nitrate concentrations in ground water are significantly higher in the carbonate agricultural subunit than in the sandstone and shale agricultural subunit (fig. 13, table 8). This finding is due to several factors. The carbonate bedrock valleys (fig. 9) are wider and flatter than the sandstone and shale valleys (fig. 10) and also have more highly productive soils and more highly weathered bedrock. These soils have a high infiltration rate and a large water-holding capacity that allows rapid infiltration of water with high nitrate concentration into the ground water. The highly weathered bedrock, including karst features such as sinkholes, losing streams, caverns, and conduit-dominated ground-water flow, results in short flowpath times, the exchange of air in the unsaturated zone, and ground water with concentrations of dissolved oxygen that indicate aerated conditions in the aquifer. The oxygenated water makes conditions less favorable for denitrification.

The narrower, steeper sandstone and shale valleys have soils with lower infiltration capacity and generally less leaching of nitrate into the ground water. Because of the topography in the sandstone and shale valleys, the ground-water recharge areas commonly include both forested and agricultural land, even if the well is located in an agricultural setting (fig. 10). The sandstone and shale aquifers commonly have smaller fractures and more tortuous flow paths than carbonate bedrock aquifers. Commonly the ground water in sandstone and shale aquifers becomes anaerobic, which allows denitrification to occur. Of the 29 wells sampled in sandstone and shale bedrock, 11 had dissolved-oxygen concentrations that were less than or equal to 0.2 mg/L. These wells also had correspondingly low nitrate concentrations, and in seven of these wells, the nitrate concentration was below the detection limit of 0.05 mg/L. The relation between nitrate and dissolved oxygen is generally linear for both the Appalachian Mountain carbonate agricultural and Appalachian Mountain sandstone and shale agricultural subunit (fig. 14); however, the sandstone and shale subunit has many more wells with low levels of dissolved oxygen and low levels of nitrate. These data support the hypothesis that denitrification is a factor affecting ground-water nitrate concentrations in the sandstone and shale aquifers.

The Appalachian Mountain carbonate agricultural subunit has a higher base-flow median nitrate concentration and a larger range of concentrations than the Appalachian Mountain sandstone and shale subunit, but this difference is not statistically significant (fig. 12, table 8). This is in contrast to the concentrations of nitrate found in the well samples, where the carbonate subunit had a statistically significant higher median concentration of nitrate than the sandstone and shale subunit. Because the surface-water samples were collected under base-flow conditions, these samples represent discharge from ground water and could be expected to be similar to the results of the well sampling. The nitrogen inputs from nonpoint sources in the surface-water basins are similar in the two areas (table 7), which indicates that the amount of nitrogen applied is more important than lithology in the mass balance of nitrate in a surface-water basin. The statistically significant differences in nitrate concentrations between the well samples in these two areas illustrate that the processes that move nitrate through the system are quite different. Data that would be necessary to describe the differences in these processes adequately were not collected; however, some possible explanations for the observations are given in the previous section that describes the two-layer aquifer concept in the Appalachian Mountain sandstone and shale subunit.

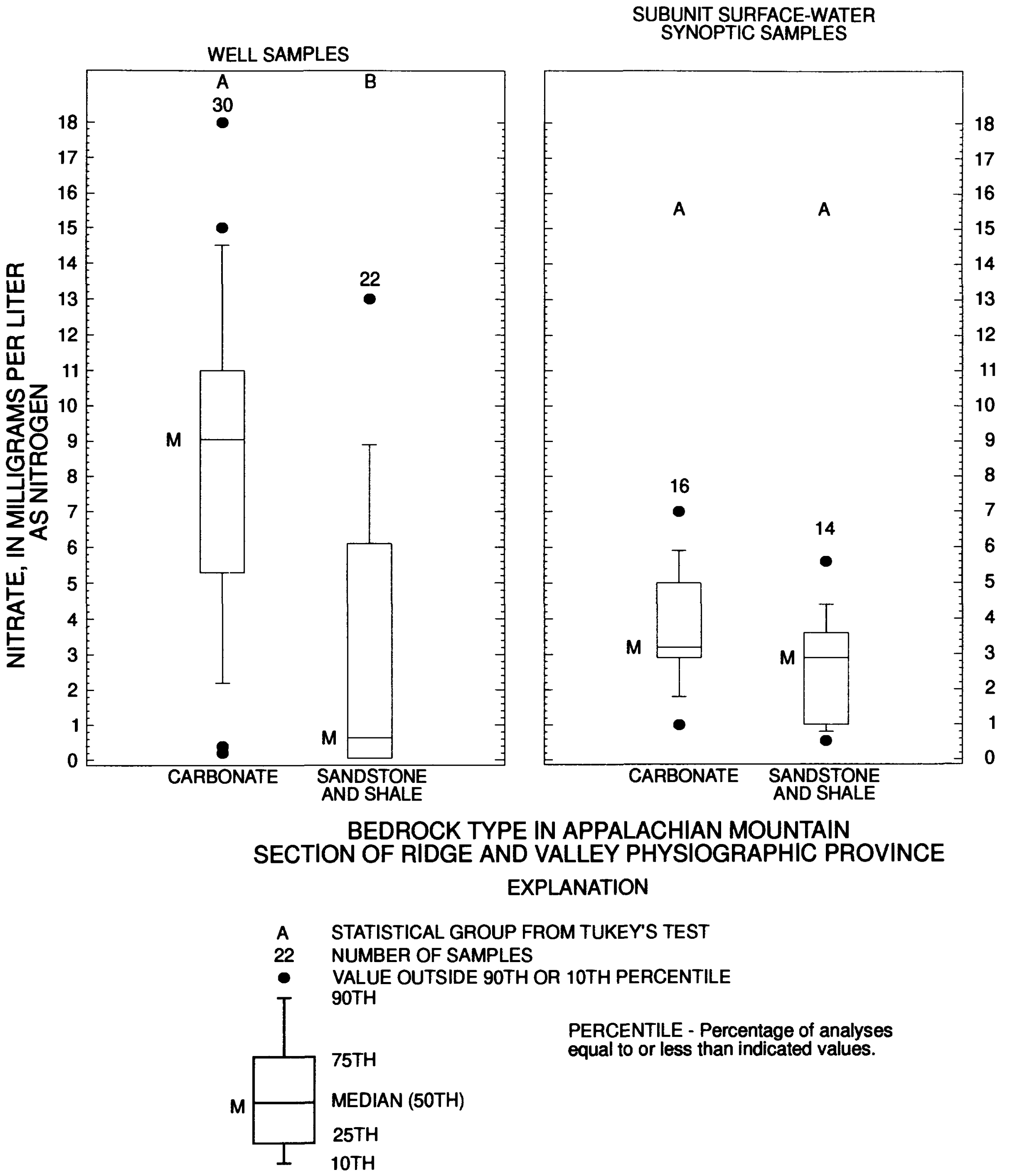
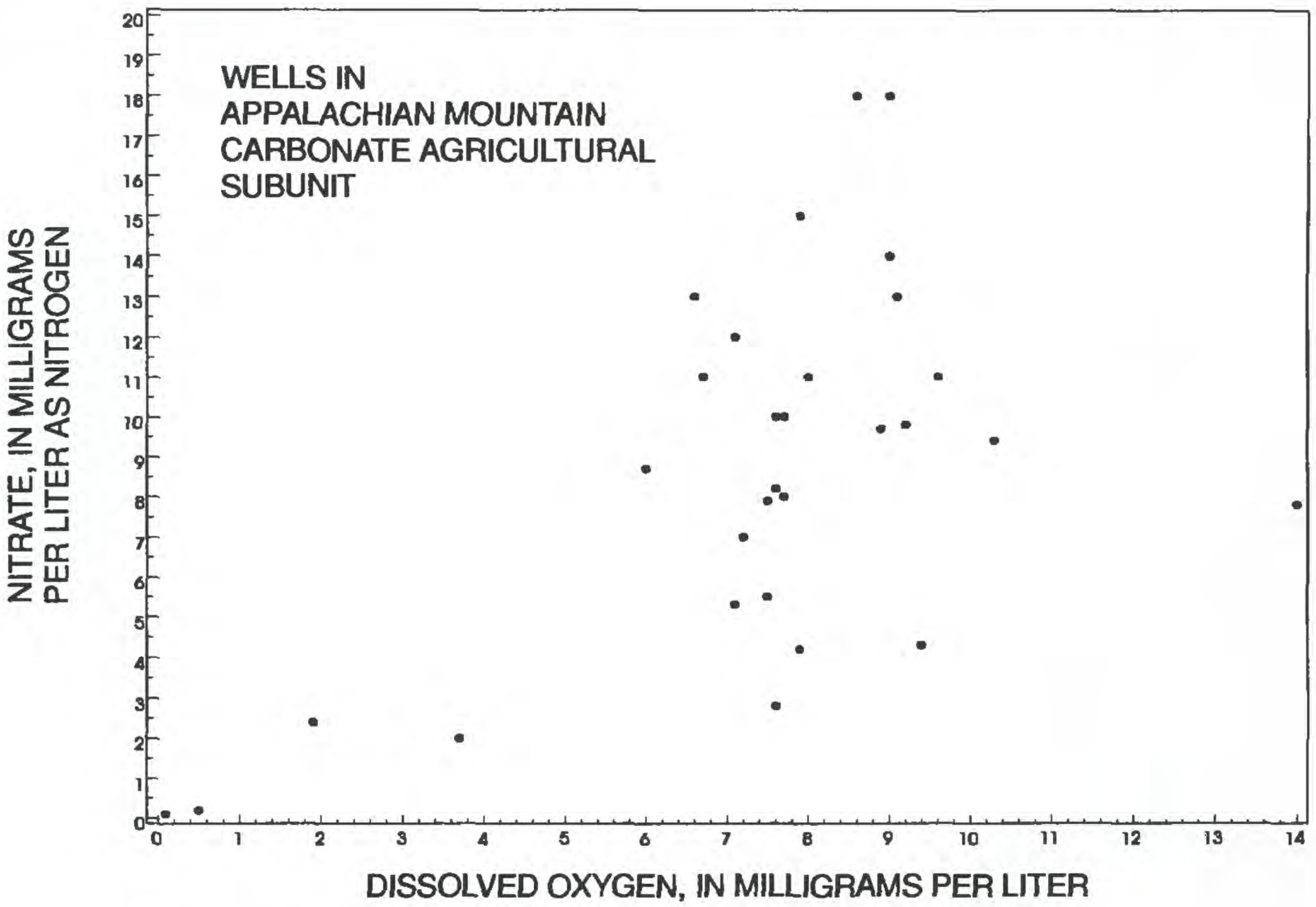


Figure 13. Distribution of nitrate concentrations in subunit surface-water synoptic studies and ground-water synoptic studies in agricultural areas of the Appalachian Mountain Physiographic Section underlain by carbonate rock and sandstone and shale, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.



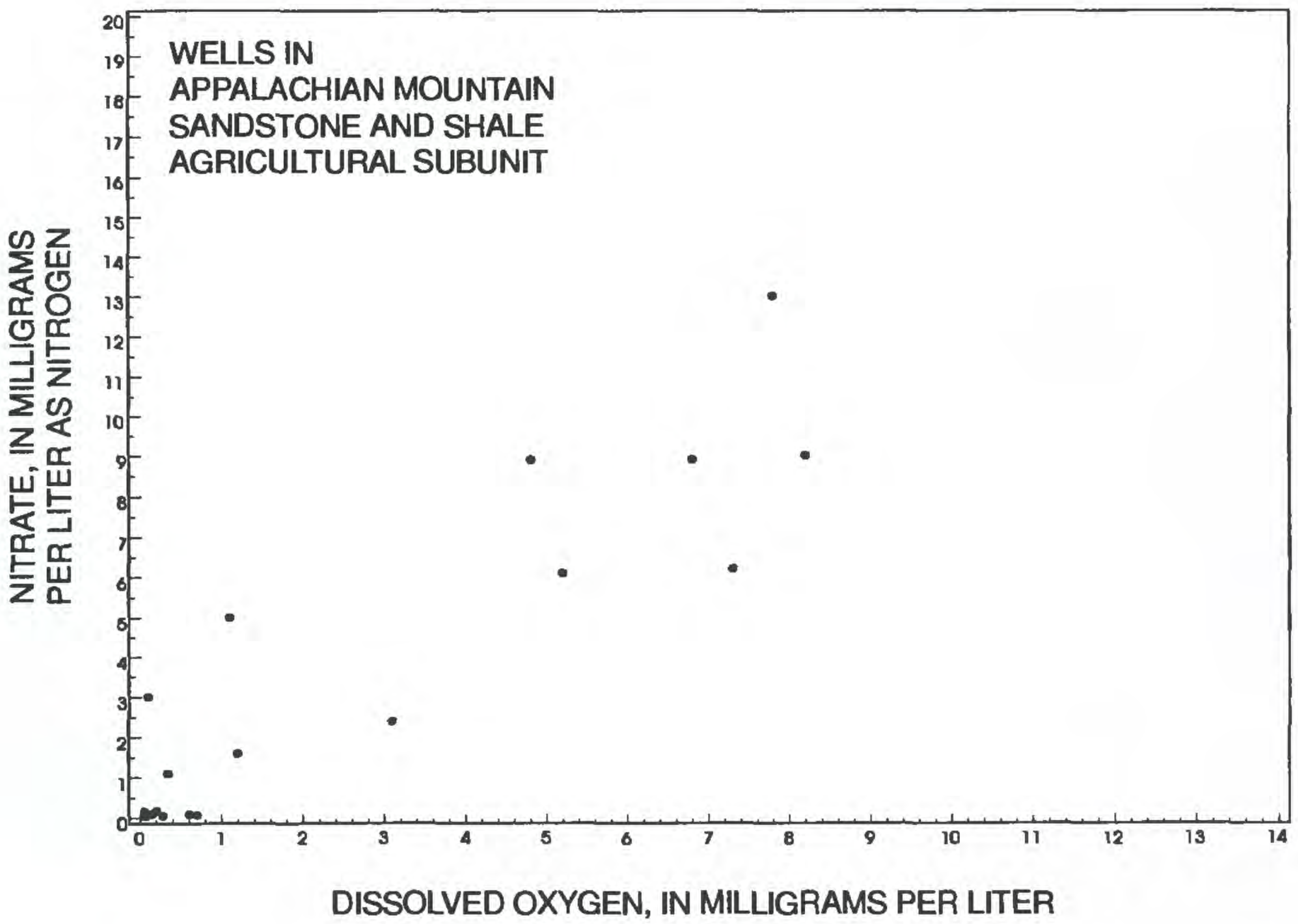


Figure 14. Relation of nitrate concentrations to dissolved oxygen concentrations in wells in agricultural areas of the Appalachian Mountain Physiographic Section underlain by carbonate rock and sandstone and shale, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

Table 8. *Statistical summary of nitrate concentrations by type of study and subunits*

[The symbol "<" is an abbreviation for "less than." A double-dash indicates that the field is not applicable to entry.]

Environmental subunit	Study name	Number of samples	Nitrate concentration, in milligrams per liter as nitrogen							
			Minimum value	Value at indicated percentile					Maxi-mum value	Value at long-term monitoring site during synoptic studies
				10	25	50 (median)	75	90		
Piedmont crystalline agricultural	Well synoptic	22	1.3	2.9	5.9	7.6	11	12	19	3.8
	Long-term monitoring site	16	3.8	4.1	4.3	5.0	5.2	6.0	6.2	--
	Subunit synoptic[1]	16	1.5	2.6	3.2	3.8	5.7	6.9	7.6	3.8
	Focused synoptic[1]	14	2.9	3.0	3.1	4.1	4.9	5.4	5.5	4.1
Piedmont carbonate agricultural	Well synoptic	30	.17	.34	7.3	11	15	22	25	8.0
	Long-term monitoring site	34	7.2	8.0	9.2	10	11	12	13	--
	Subunit synoptic[1]	15	4.0	4.0	5.0	7.9	14	18	19	9.9
	Focused synoptic[1,2]	13	.11	4.6	7.6	8.7	11	11	13	7.6
Great Valley carbonate agricultural	Well synoptic	30	3.7	5.2	6.8	8.6	11	11	15	11
	Long-term monitoring site	48	9.5	9.9	11	11	12	13	16	--
	Subunit synoptic[1]	9	1.4	1.4	4.2	7.0	8.0	11	11	9.8
	Focused synoptic[1]	8	.39	.39	.62	7.2	8.2	11	11	11
Great Valley carbonate urban	Well synoptic	20	<.05	.70	1.8	3.4	5.8	6.6	7.2	3.9
	Long-term monitoring site	54	3.5	3.8	3.9	4.2	4.4	4.6	4.8	--
	Subunit synoptic[1]	10	1.0	1.1	2.0	5.8	6.2	6.7	6.8	4.1
	Focused synoptic[1]	7	.97	.97	1.0	2.4	7.0	9.1	9.1	3.8

Table 8. *Statistical summary of nitrate concentrations by type of study and subunits*—Continued

Environmental subunit	Study name	Number of samples	Nitrate concentration, in milligrams per liter as nitrogen							
			Minimum value	Value at indicated percentile					Maxi-mum value	Value at long-term monitoring site during synoptic studies
				10	25	50 (median)	75	90		
Appalachian Mountain carbonate agricultural	Well synoptic	30	0.10	2.2	5.3	9.0	11	14	18	5.1
	Long-term monitoring site	16	5.1	5.4	6.0	6.4	7.3	7.9	7.9	--
	Subunit synoptic[1]	15	.88	1.8	2.8	3.1	5.0	5.9	6.8	5.1
	Focused synoptic[1]	10	1.3	1.8	4.3	5.6	6.6	8.8	11	5.8
Appalachian Mountain sandstone and shale agricultural	Well synoptic	22	<.05	.05	.05	.64	6.1	8.9	13	1.9
	Long-term monitoring site	26	1.3	1.9	3.3	3.8	5.2	7.8	8.2	--
	Subunit synoptic[1]	13	.50	.80	1.0	2.7	3.6	4.4	5.7	3.4
	Focused synoptic[1]	4	3.1	3.1	3.2	3.4	3.6	3.9	3.9	3.4
Appalachian Mountain sandstone and shale forested	Well synoptic	7	<.05	.05	.05	.05	.13	.16	.16	.58
	Long-term monitoring site	15	.41	.41	.56	.68	.98	1.2	1.2	--
	Subunit synoptic[1]	15	.10	.11	.15	.26	.56	.61	.82	.78

[1] Number of samples does not include the sample collected at the long-term monitoring site.
[2] Nitrate values do not include samples collected at the point sources.

In the Piedmont Physiographic Province, median nitrate concentrations in ground water are significantly higher in the carbonate agricultural subunit compared to the crystalline agricultural subunit (fig. 15, table 8). The Piedmont carbonate agricultural subunit had the highest median nitrate concentration, 11 mg/L, of any of the ground-water synoptic areas studied (table 8), and 60 percent of the wells sampled had nitrate concentrations that exceeded the USEPA maximum contaminant level of 10 mg/L. The Piedmont carbonate agricultural subunit had the highest median nitrate concentration of 66 areas studied across the country in 20 NAWQA study units. The general causes for the high concentrations of nitrate in ground water in the carbonate agricultural area include 1) nonpoint-source inputs of nitrogen (table 2) that are higher in this subunit than in any other subunit and that exceed the removal rate for any crop grown in the area, and 2) the soil and bedrock that allows rapid leaching of nitrate from the land surface to the ground water.

The median concentration of nitrate in ground water in the Piedmont crystalline agricultural subunit, although significantly lower than the median concentration in the Piedmont carbonate agricultural subunit, was 8.2 mg/L (fig. 13, table 8), and more than 25 percent of the wells sampled exceeded the maximum contaminant level of 10 mg/L. These concentrations indicate that, although the bedrock is noncarbonate, leaching of nitrate into the ground water is a greater concern in this subunit than in the Ridge and Valley sandstone and shale agricultural subunit. The high concentrations of nitrate in ground water are related to the high manure application rates (table 2); however, other factors also influence the concentrations of nitrate in ground water in this area. The topography and land-use patterns in the Piedmont crystalline area indicate that the contributing recharge area to a well may be limited to the immediate surrounding land use (fig. 4). With the agricultural activity extending all the way to the hilltops, a well in an agricultural setting is likely to have all of the recharge to that well coming from agricultural land without mixing with water recharged from other land-use types. The high concentrations of dissolved oxygen in water from these wells also indicates that denitrification generally is not occurring in aquifers of the Piedmont crystalline subunit.

The median base-flow concentration of nitrate in surface water in the Piedmont carbonate agricultural subunit is significantly higher than in the Piedmont crystalline agricultural subunit (fig. 15, table 8). The carbonate agricultural subunit also has a higher range of concentrations. Similar results were seen in the well samples, but the differences were more pronounced in the surface-water samples. The relatively low concentrations of nitrate in surface water in the Piedmont crystalline agricultural subunit are most likely due to uptake of nitrate by vegetation in the forested riparian zones as described earlier and the lower input of nitrogen from point and nonpoint sources.

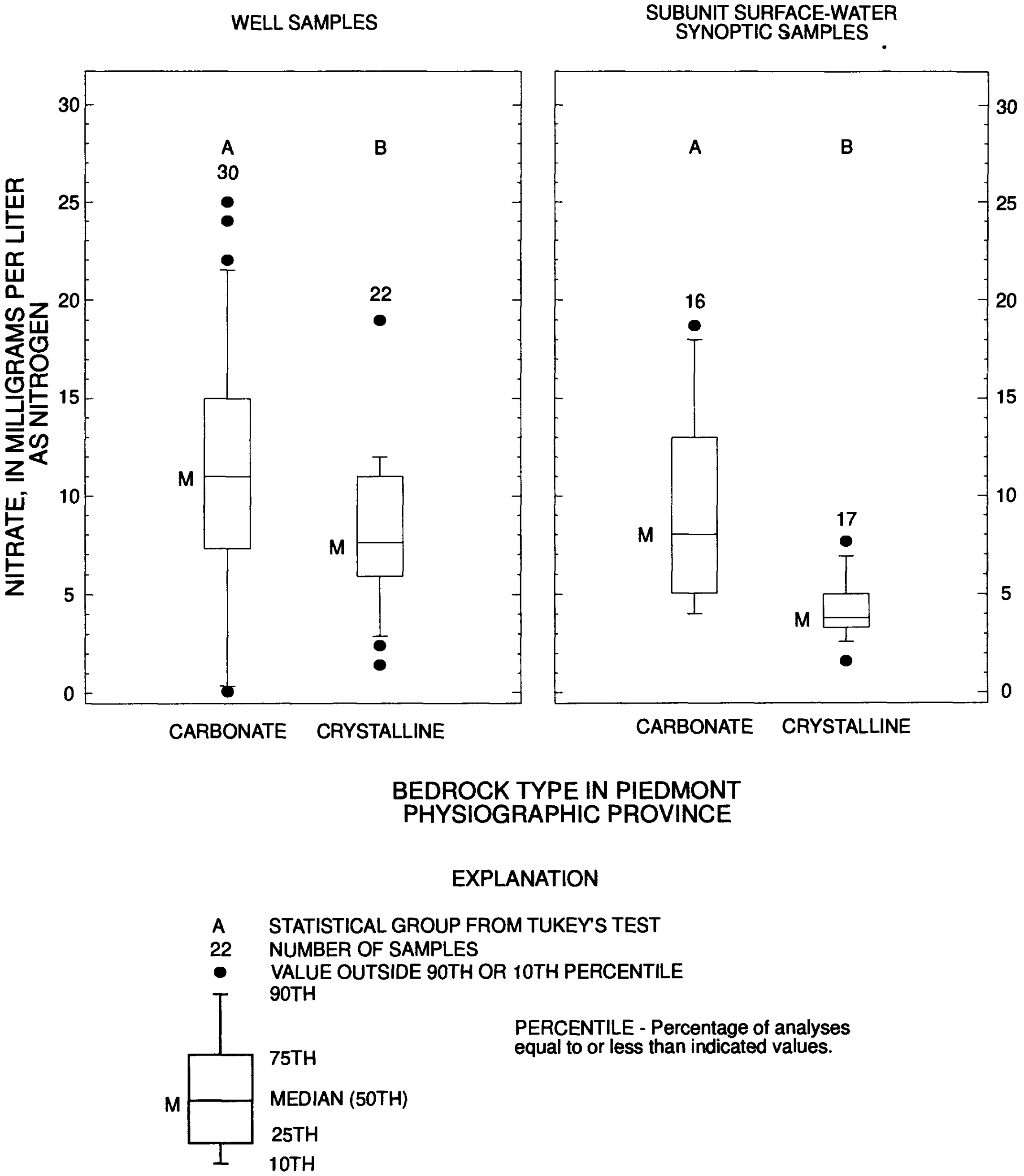


Figure 15. Distribution of nitrate concentrations in subunit surface-water synoptic studies and well synoptic studies in agricultural areas of the Piedmont Physiographic Province underlain by carbonate and crystalline bedrock, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

Land Use

Another factor that affects the spatial distribution of nitrate concentrations is land use within the basin or in the area that contributes to a well. Nitrate concentrations can be associated with land use because nitrogen inputs are similar within a specific land-use category and nitrogen inputs commonly differ among land-use categories. The data collected in areas that differ in land use were used to illustrate the effect of land use on spatial variation in nitrate concentration.

The comparison of nitrate concentrations in the sandstone and shale agricultural and sandstone and shale forested subunits of the Appalachian Mountain Section of the Ridge and Valley Physiographic Province shows statistically significant differences for both ground-water and surface-water samples (fig. 16, table 8). The only sources of nitrogen in forested areas are atmospheric deposition and decomposing vegetation, whereas agricultural areas have those sources plus others such as manure applications, fertilizer applications, and septic systems (table 6). Where hydrogeologic and nitrogen transport processes are the same, the nitrate sources control the concentration of nitrate in ground water and surface water.

A comparison of nitrate concentrations between carbonate agricultural and carbonate urban areas within the Great Valley Physiographic Section again shows higher median concentrations in the agricultural areas than in the urban areas (fig. 17, table 8). These differences are statistically significant for the ground-water samples at a confidence level of more than 95 percent, and the differences for the surface-water sample sets are significant at a 90-percent confidence level. Nitrate sources in an urban area include atmospheric deposition, fertilizers applied to lawns and recreation areas, septic systems, and possibly other sources such as leaking sewer lines. Point-source discharges to the urban streams also contribute to the nitrate concentrations detected in those streams. As previously discussed, the urban carbonate surface-water synoptic samples were partially influenced by agricultural land in the headwaters of those basins, otherwise the differences between the agricultural and urban areas would be greater.

Manure Application

The comparisons between land use and nitrate concentration show that agricultural areas generally have the highest nitrate concentrations; however, all agricultural areas are not the same. Three carbonate agricultural areas are compared to determine how the application rate of manure within a given basin affects the resulting nitrate concentrations in that basin. The concentrations from ground-water samples collected in these three areas are not significantly different; however, it is difficult to relate this information to manure application rates because of the difficulty of defining contributing areas to a well, particularly in an area underlain by carbonate bedrock. This analysis will, therefore, focus on the surface-water synoptic sampling, where the basin boundaries can be defined and manure application rates can be determined for each basin.

The carbonate agricultural surface-water synoptic study area with the highest median manure application rate is the Piedmont carbonate agricultural subunit (table 7), and this subunit also has the highest median nitrate concentration. The carbonate agricultural surface-water synoptic study area with the lowest median manure application rate is the Appalachian Mountain carbonate agricultural subunit (table 7), and this subunit has the lowest median nitrate concentration (fig. 18). The nitrate concentrations in the Piedmont carbonate agricultural subunit were significantly higher than in the Appalachian Mountain subunit, but not significantly higher than in the Great Valley subunit, which had the second highest manure application rate. To further examine the relation between nitrate concentration in a basin and the manure application rate in the basin, a Spearman's

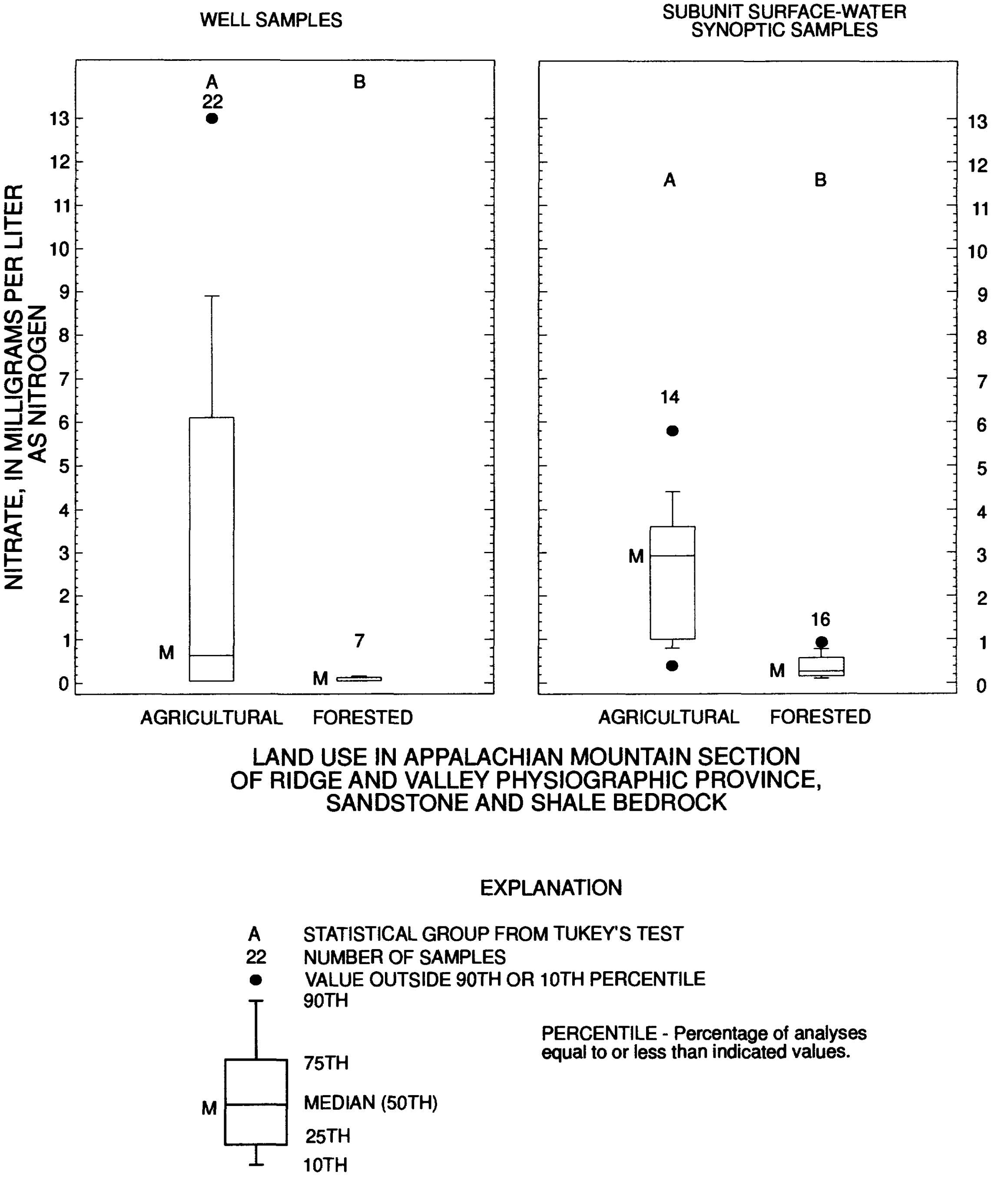


Figure 16. Distribution of nitrate concentrations in subunit surface-water synoptic studies and well synoptic studies in an agricultural and a forested area of the Appalachian Mountains Physiographic Section underlain by sandstone and shale, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

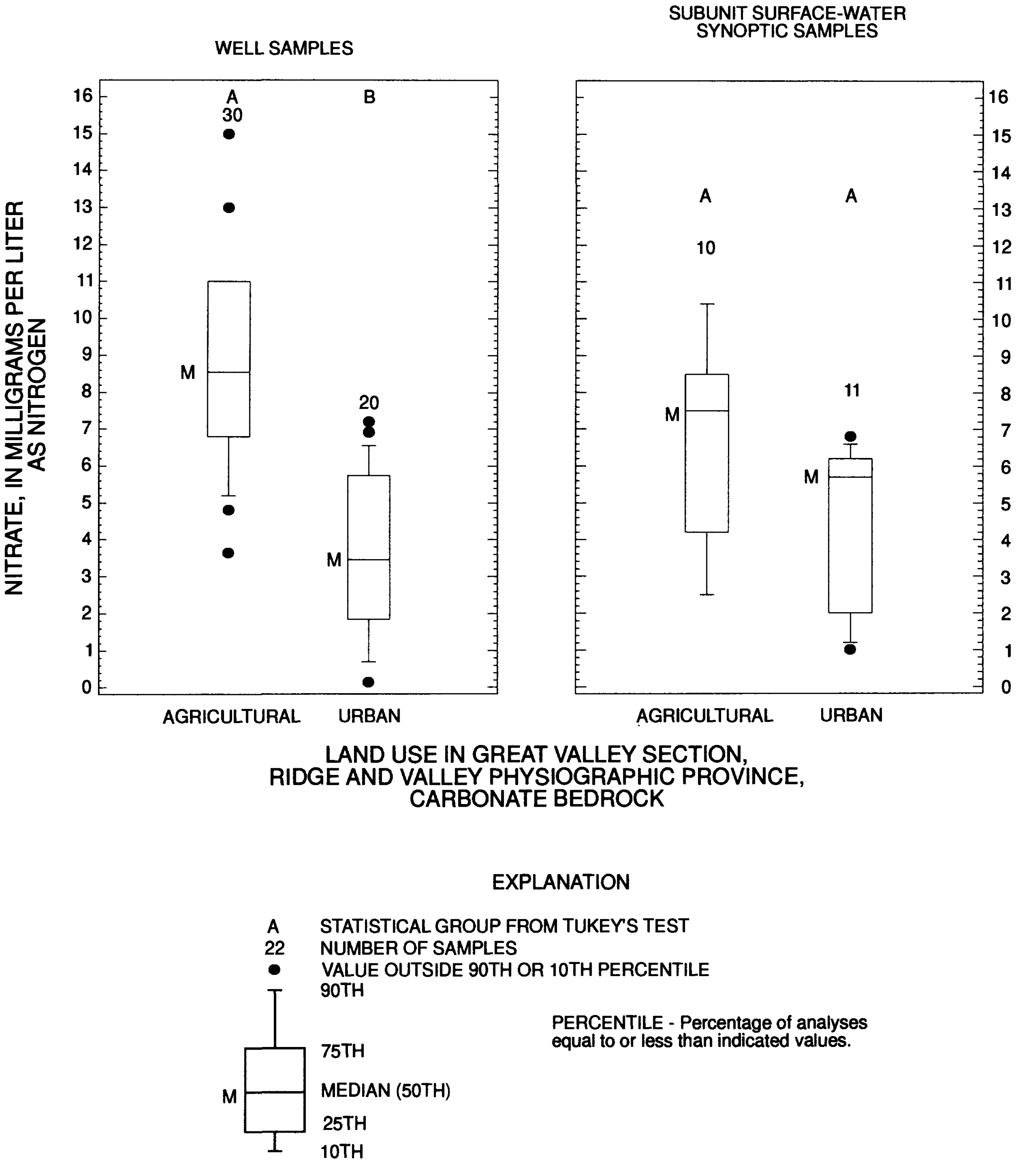


Figure 17. Distribution of nitrate concentrations in subunit surface-water synoptic studies and ground-water synoptic studies in an agricultural and an urban area of the Great Valley Physiographic Section underlain by carbonate bedrock, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

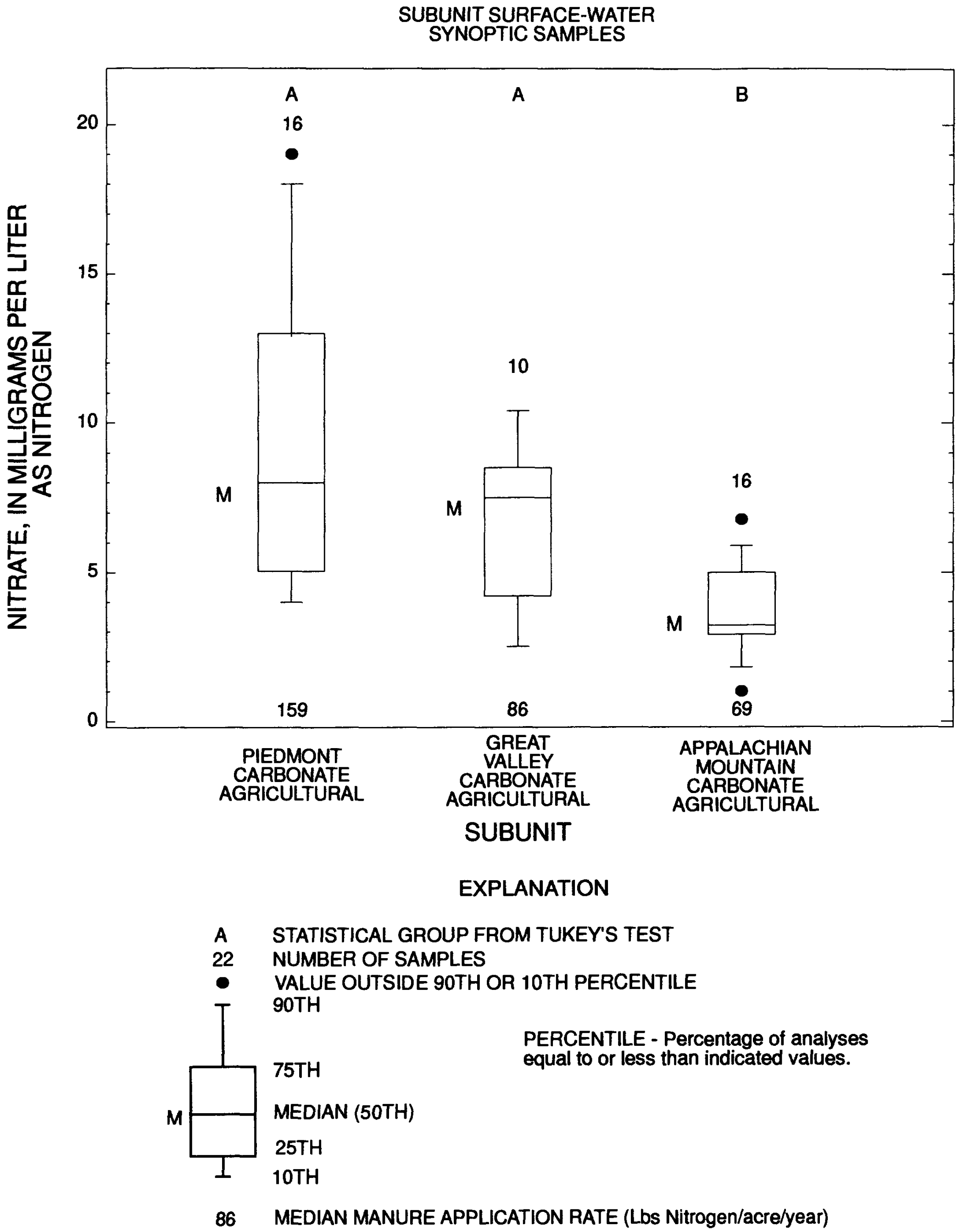


Figure 18. Distribution of nitrate concentrations in subunit surface-water synoptic studies and manure application rates in subunits representing agricultural areas underlain by carbonate bedrock, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland.

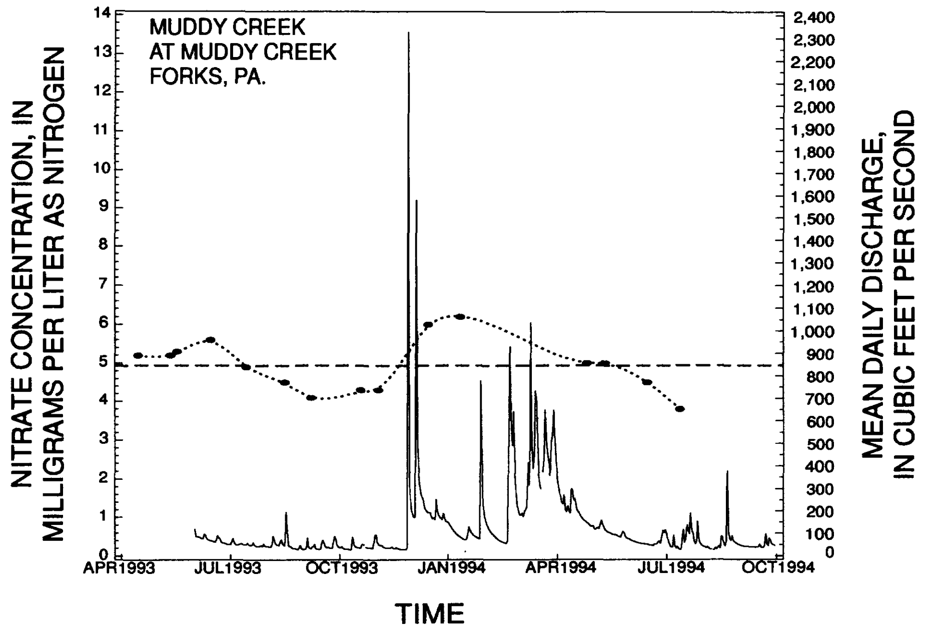
correlation was conducted for the subunit synoptic basins in the three carbonate agricultural subunits. The correlation conducted for the 41 agricultural basins within these three subunits showed a statistically significant relation between nitrate concentration and manure application rate. The Spearman's correlation coefficient (rho) was 0.685 and the probability (or p-value) was 0.0001 illustrating that, although bedrock type and land use may be factors that affect nitrate concentrations, the manure application rate can have a large effect on nitrate concentrations within agricultural areas of similar bedrock type. The data analysis indicates that the manure application rate may be the most important factor controlling nitrate concentrations in surface water for agricultural basins underlain by carbonate bedrock in the Lower Susquehanna River Basin.

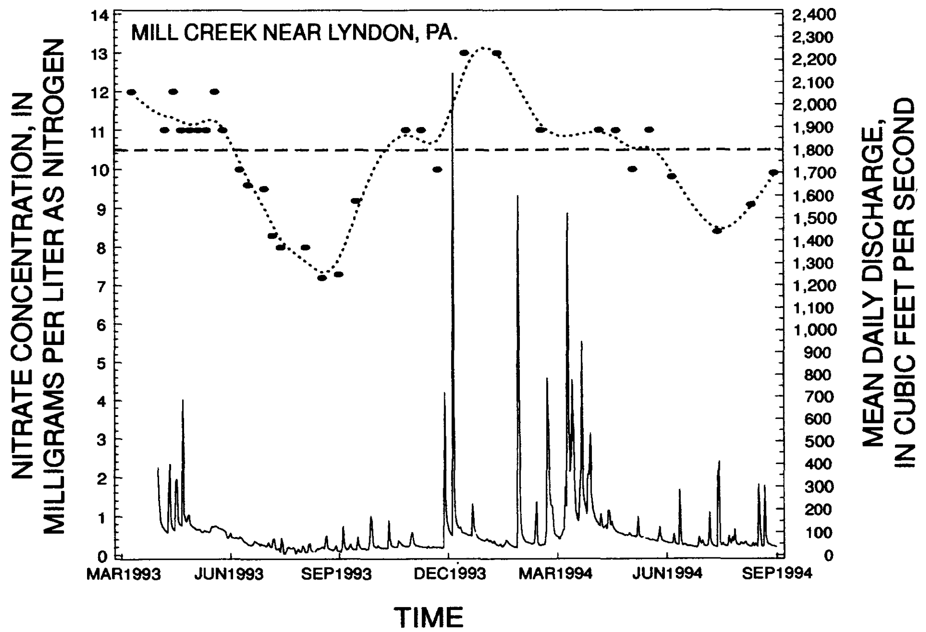
Factors Affecting Temporal Variations in Nitrate Concentrations

The base-flow nitrate concentrations at seven long-term monitoring sites were examined to determine temporal variations. The purpose of the sampling at these long-term sites was to evaluate seasonal trends in the base-flow nitrate concentration. Relations between flow and concentration for a single hydrologic event and long-term trends could not be evaluated with the data collected.

Seasonal Variations in Nitrate Concentrations

Temporal variations in nitrate concentration were evident at all seven long-term monitoring sites. Mean daily discharge exhibits seasonal patterns that vary from year to year; however, discharge is generally decreasing through the summer months (fig. 19). Nitrate concentration also shows seasonal patterns (fig. 19). The streams generally exhibited a pattern in which concentrations were increasing from the late summer through the middle of winter, then decreasing from the mid-winter through the summer period. In general, concentrations in samples collected between December and June are greater than the median concentration, and concentrations between June and December are less than the median concentration. All of the sites also showed a small increase in nitrate concentration in the late spring to early summer time period in at least one of the years.



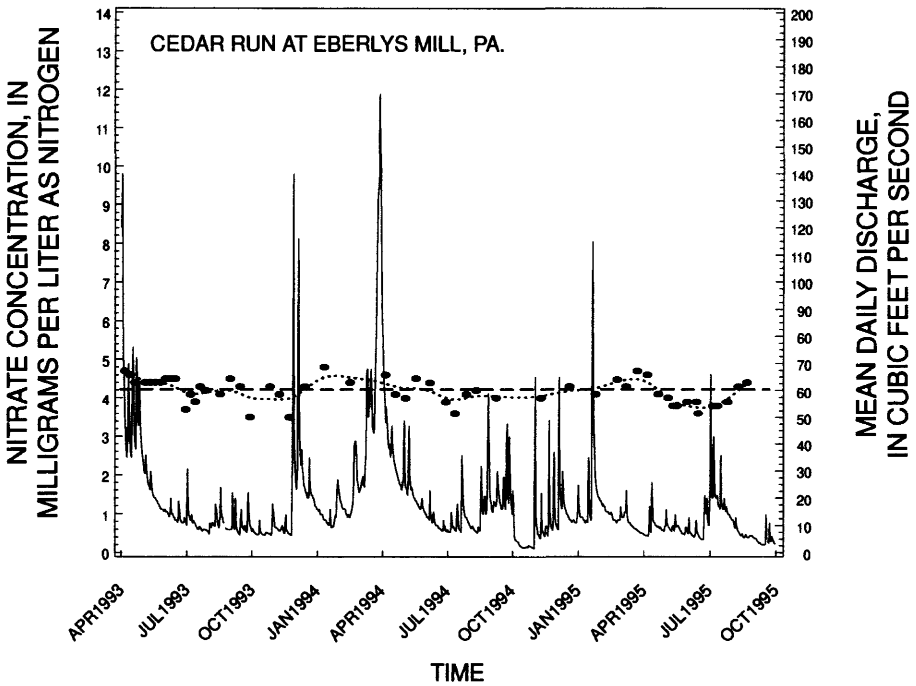


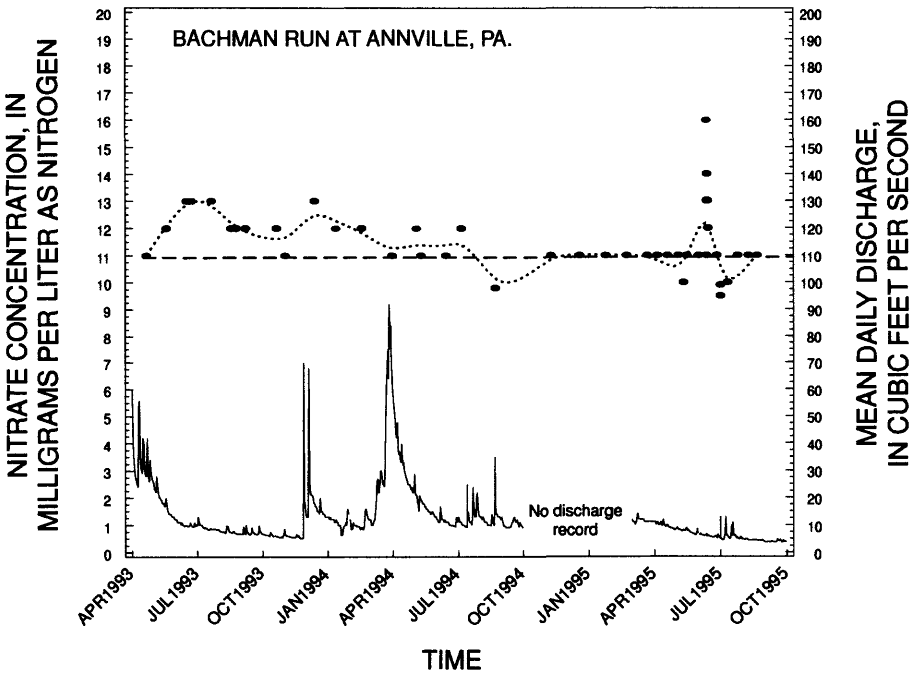
EXPLANATION

- MEAN DAILY DISCHARGE
- SMOOTH LINE OF NITRATE CONCENTRATION*
- MEDIAN BASE FLOW NITRATE CONCENTRATION
- NITRATE CONCENTRATION IN BASE FLOW SAMPLES

* The formula for calculating the smooth line fit is described in Reinsch (1967).

Figure 19. Nitrate concentrations and discharge hydrographs for the seven long-term monitoring sites.



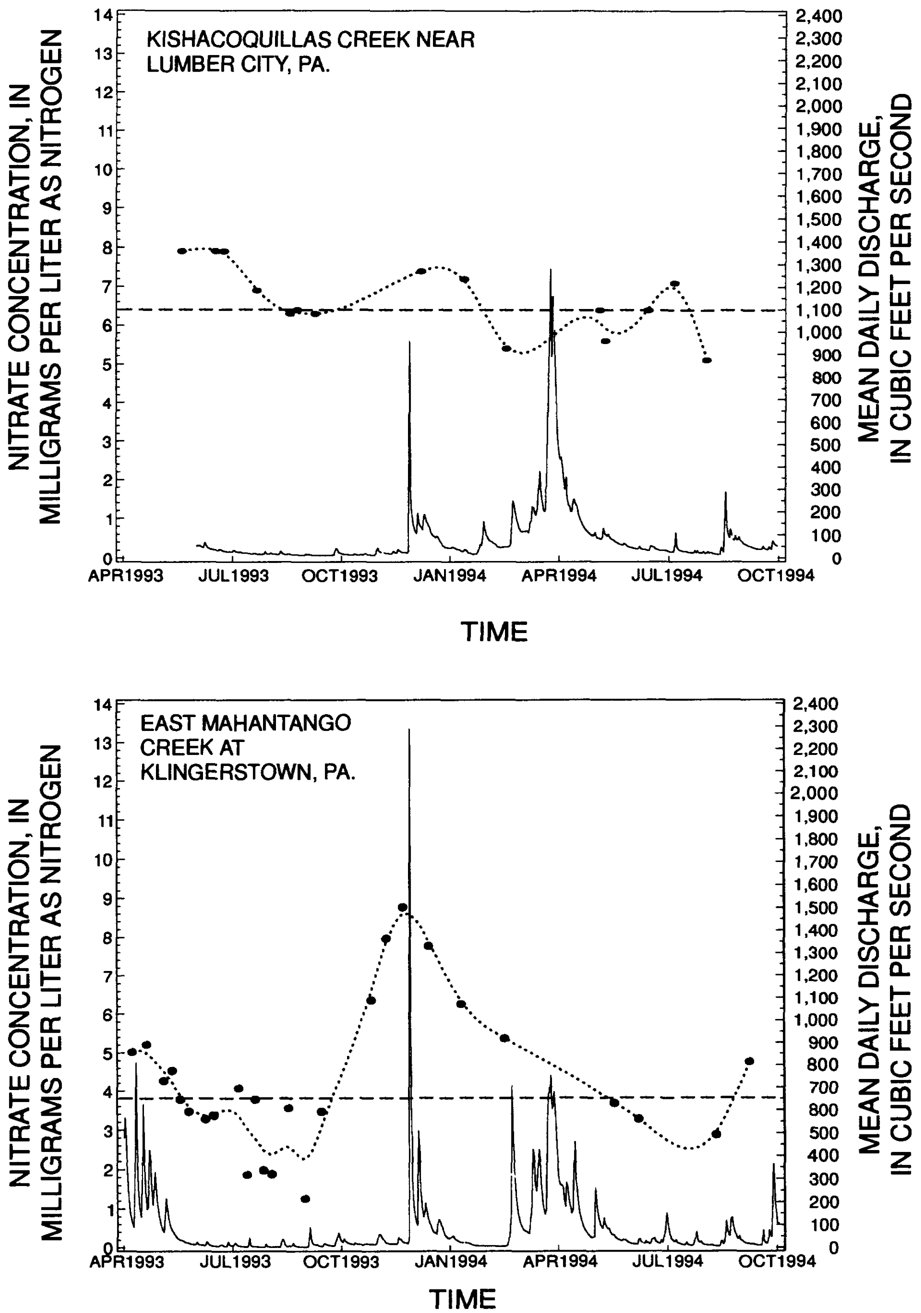


EXPLANATION

- MEAN DAILY DISCHARGE
- SMOOTH LINE OF NITRATE CONCENTRATION*
- MEDIAN BASE FLOW NITRATE CONCENTRATION
- NITRATE CONCENTRATION IN BASE FLOW SAMPLES

* The formula for calculating the smooth line fit is described in Reinsch (1967).

Figure 19. Nitrate concentrations and discharge hydrographs for the seven long-term monitoring sites—Continued.

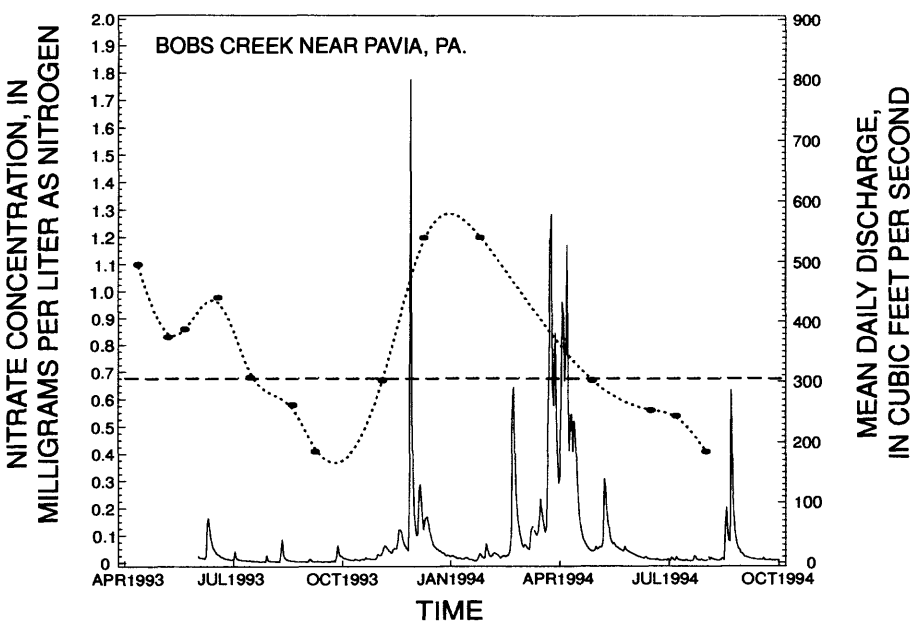


EXPLANATION

- MEAN DAILY DISCHARGE
- SMOOTH LINE OF NITRATE CONCENTRATION*
- MEDIAN BASE FLOW NITRATE CONCENTRATION
- NITRATE CONCENTRATION IN BASE FLOW SAMPLES

* The formula for calculating the smooth line fit is described in Reinsch (1967).

Figure 19. Nitrate concentrations and discharge hydrographs for the seven long-term monitoring sites—Continued.



EXPLANATION

————	MEAN DAILY DISCHARGE
··············	SMOOTH LINE OF NITRATE CONCENTRATION*
– – – – – –	MEDIAN BASE FLOW NITRATE CONCENTRATION
•	NITRATE CONCENTRATION IN BASE FLOW SAMPLES

* The formula for calculating the smooth line fit is described in Reinsch (1967).

Figure 19. Nitrate concentrations and discharge hydrographs for the seven long-term monitoring sites—Continued.

Relations Between Stream Discharge and Nitrate Concentration

The initial step in interpreting this temporal variation in nitrate concentration was an analysis of the relation between stream discharge and nitrate concentration. This was conducted to determine if the discharge volume affected nitrate concentrations during base flow. Scatterplots showing the relation between concentration and log of discharge showed a linear relation with a positive slope for some sites and no relation for other sites (fig. 20). A Spearman's correlation used to determine the statistical significance of the relations indicated statistically significant relations for six of the seven long-term monitoring sites (table 9). This is an indication that some of the temporal variation in nitrate concentration at these six sites may be related to seasonal variations in flow. The samples collected at Kishacoquillas Creek show a poor correlation between discharge and nitrate concentration.

A USDA-ARS research study on a small watershed within the East Mahantango Creek Basin (Schnabel and others, 1993) has shown that nitrate concentrations are strongly related to stream discharge because of the changes in source areas for base flow. Much of the water discharged from the ground during wet periods comes from the shallow layer of the aquifer that has higher nitrate concentrations, and water discharged during dry periods is more influenced by the deeper layers of the aquifer. Water in these deeper layers originates from the forested upland areas and has lower nitrate concentrations. Because the USDA-ARS research was conducted within the East Mahantango Creek Basin, hydrologic controls such as the layering of the ground-water system are a likely explanation for the variation seen in the samples collected at the East Mahantango site (fig. 19). The temporal variation at the other sites may also be influenced by similar hydrologic conditions; however, these other areas do not have detailed study sites where this has been demonstrated.

Because of the relation between streamflow and nitrate concentration, plots of flow-adjusted nitrate concentration were made by plotting residuals from a LOWESS smoothing technique (Helsel and Hirsh, 1992). These flow-adjusted concentration plots were very similar to figure 19 and new patterns were not seen. The correlations between nitrate concentrations and streamflow (table 9) for the six streams where a good relation existed had values of Spearman's rho between 0.34 and 0.81. This indicates that, although a relation exists between flow and concentration for these sites, the variation in flow does not account for all of the variation in concentration. The seasonal increases in concentration preceded the increases in flow in many of the streams (fig. 19), suggesting that factors other than flow probably affect the seasonal variations.

Relations Between the Nitrogen Cycle and Temporal Variations in Nitrate Concentrations

Five factors that are directly or indirectly related to the nitrogen cycle may affect the variation in nitrate concentrations. These factors are 1) the timing of applications of manure and fertilizer, 2) the uptake of nitrate by plants, 3) the time for nitrate to travel from recharge at the ground surface and discharge to the stream, 4) the characteristics of the aquifer that the water is traveling through, and 5) the temporal variation of in-stream biological activity. Although this sampling program was not designed to specifically evaluate these factors, the data provide some information for a preliminary analysis.

Application of manure and fertilizer before planting is probably the cause of the small increase in nitrate concentrations seen in early summer in the long-term sampling basins. Some agricultural land is located in all of the long-term basins, including the urban and forested basins. Nitrogen from manure and fertilizer may move rapidly through the system and cause an increase in base-flow nitrate concentrations until the crops began to utilize more of the nitrogen. The plants use the available nitrogen through the summer,

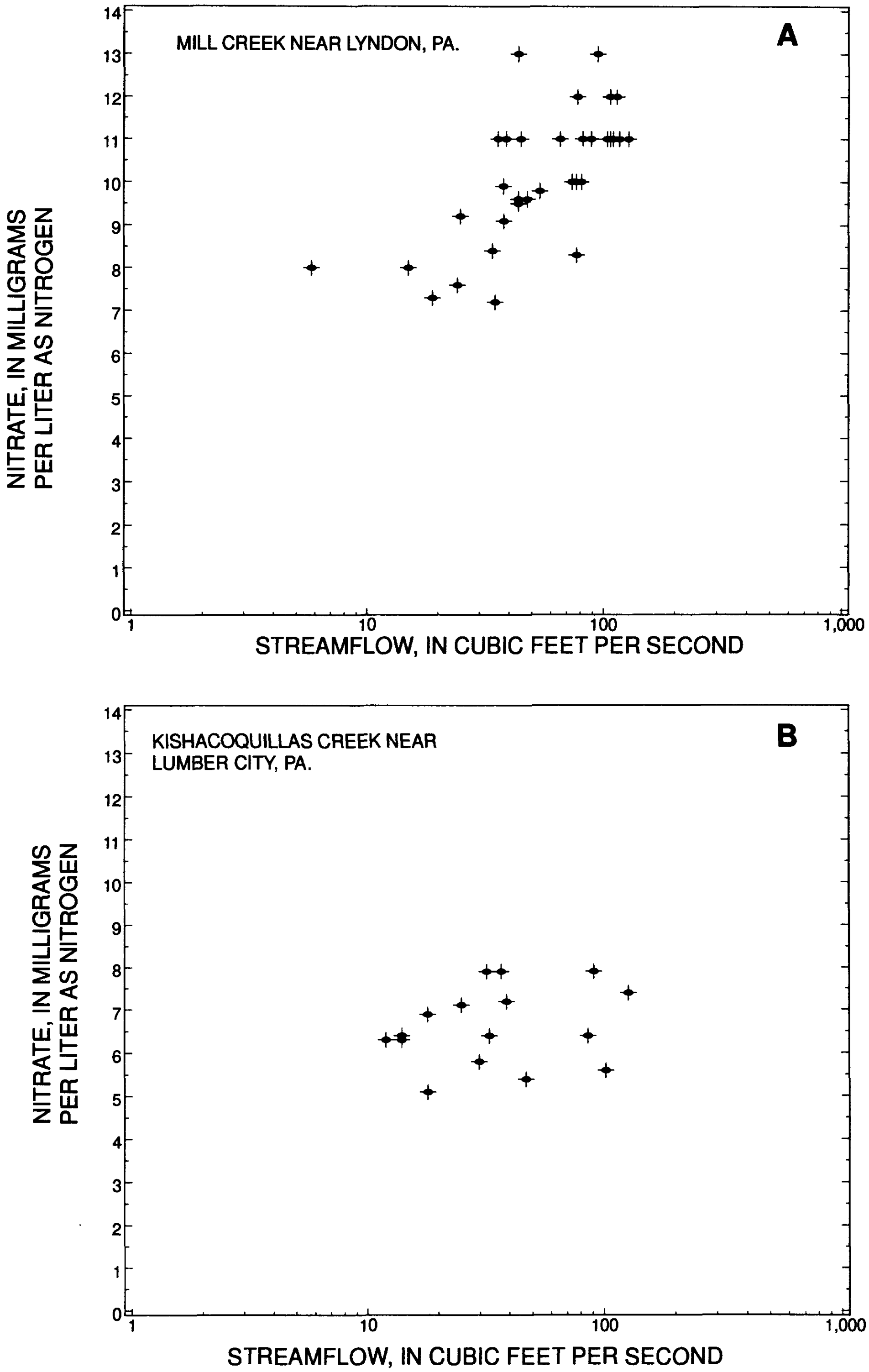


Figure 20. Examples of A) positive slope log-linear relation and B) no relation of nitrate concentration to stream base flow at selected long-term monitoring sites.

Table 9. *Summary of regression between nitrate concentration and log of streamflow for the seven long-term monitoring sites, Lower Susquehanna River Basin study unit, Pennsylvania and Maryland*

[shaded areas represent statistically significant correlations]

Environmental subunit	Site number	Name and location	Number of samples	Spearman's rho	Probability
Piedmont crystalline agricultural	01577300	Muddy Creek at Muddy Creek Forks, Pa.	16	0.81	0.0001
Piedmont carbonate agricultural	01576540	Mill Creek near Lyndon, Pa.	34	.72	.0001
Great Valley carbonate agricultural	01573095	Bachman Run at Annville, Pa.	48	.38	.0084
Great Valley carbonate urban	01571490	Cedar Run at Eberlys Mill, Pa.	54	.34	.0125
Appalachian Mountain carbonate agricultural	01564997	Kishacoquillas Creek at Lumber City, Pa.	16	.27	.3080
Appalachian Mountain sandstone and shale agricultural	01555400	East Mahantango Creek at Klingerstown, Pa.	26	.68	[illegible]
Appalachian Mountain sandstone and shale forested	01559795	Bobs Creek near Pavia, Pa.	15	.75	[illegible]

causing stable or decreasing concentrations of nitrate in stream base flow. Summer is also the dry time of the year, and nitrate would not tend to leach from the soil. In the fall, when leaves die and crops are harvested, the plant uptake would cease or decrease considerably. The fall also has more precipitation, which would cause any accumulations of nitrate in the soil to be leached and transported to the ground-water system. Nitrate in the ground water discharges to the stream, causing the increase in base-flow concentrations observed during the late fall and early winter. As nitrate is flushed from the ground-water system, the concentrations begin to decrease through the spring until the cycle begins again.

The time for the water to move through the ground-water system is another factor to consider in interpreting the temporal variation in base-flow nitrate concentration. The movement of water and nitrate to the streams from fields and aquifers is not instantaneous. If a large volume of water moves rapidly through a shallow aquifer system during the wet parts of the year, the response in the stream would be rapid. Nitrate concentrations in the stream could also lag behind the activities on the land surface near the stream because of the ground-water traveltime. For example, the high nitrate concentrations in the winter may be from fertilizer applied during the previous spring that took 6 to 9 months to move through the system. The traveltime may be in months or years. A flow model constructed for an area in the Piedmont Physiographic Province underlain by crystalline bedrock estimated maximum ground-water traveltimes of 11 years for the fractured bedrock but only 6 months for the alluvium on the hillsides (McFarland, 1994). A USDA-ARS model supports rapid movement of ground water through the shallow layers, particularly during wet periods of the year in the Appalachian Mountain sandstone and shale subunit (Schnabel and others, 1993). The data collected for this study cannot be used to determine conclusively the ground-water traveltime and its affect on temporal variation of nitrate in stream base flow.

Biological activity also could be a factor affecting the temporal variation of nitrate in the streams. Nitrate uptake by algae in streams increases during the summer months and decreases during the winter. Increasing algal activity during the summer could cause a decrease in nitrate concentrations, and decreasing algal activity could cause nitrate concentrations to increase over the winter, as observed at the long-term sampling sites. Bacteria in the soil can cause both denitrification of nitrate to nitrogen gas and mineralization of organic nitrogen into nitrate. Biological activities are temperature dependant. Although a detailed analysis of biological processes is beyond the scope of this report, indications are that these processes may have been a factor in the temporal variations observed.

Nitrate Loads and Yields from Subunits

Base-flow loads and yields for nitrate were estimated from the data collected at the long-term monitoring sites. Because the period of record and number of samples were not adequate to use robust modeling or regression techniques to estimate loads (Cohn and others, 1992), a simpler load estimation was conducted. This estimation was done for the 1994 water year (Oct. 1, 1993, to Sept. 30, 1994), the year in which the most complete streamflow records were available. Annual base flow was calculated for each stream. Annual base flow was multiplied by the 10th percentile, median, and 90th percentile of base-flow nitrate concentrations to obtain low, medium, and high estimates for annual base-flow nitrate load (table 10). The base-flow yield was calculated by dividing the annual base-flow load by the surface area of the stream basin and used to make comparisons between basins with unequal drainage areas.

The estimates of base-flow yield for nitrate show that differences among yields are similar to differences among concentrations. Agricultural areas underlain by carbonate bedrock that had the highest concentration also had the highest estimated nitrate yield of any of the subunits. The crystalline agricultural subunit had the next highest yield, followed by the carbonate urban and the sandstone and shale agricultural area. The lowest yield was from the sandstone and shale forested subunit.

The base-flow load and yield data were qualified in four ways. First, the nitrate concentrations detected at the long-term monitoring sites were compared to the nitrate concentrations in the synoptic samples collected in the same subunit to determine if the long-term monitoring site was a representative site for that subunit. Secondly, the nitrate concentrations at the long-term monitoring site were compared to the nitrate concentrations in the focused synoptic samples to determine what factors affect nitrate concentrations within that basin. A third method of qualifying the load and yield data was to calculate high, medium, and low estimates of loads and yields by using the 90th percentile, the median, and the 10th percentile of nitrate concentrations to show the range for the site. Finally, the base-flow yields at these sites were compared with yields at sites in similarly defined settings using data from an analysis of nutrients in the Chesapeake Bay watershed (Langland and others, 1995).

Long-term Monitoring Basins Compared to Subunit Synoptic Studies

To determine how well the long-term monitoring site represented conditions in the subunit, the sample collected at the long-term monitoring site during the subunit surface-water synoptic study was compared to the rest of the samples collected in the subunit during that study (table 8). These samples were compared because they were collected under the same conditions. If the nitrate concentration in the sample collected at the long-term monitoring site was between the 25th and 75th percentile of the other samples collected in the subunit, the long-term monitoring site was considered to be a good representative site for that subunit.

Table 10. *Base-flow loads and yields estimated for long-term monitoring basins in the Lower Susquehanna River Basin study unit and yields from similar basins within the Chesapeake Bay watershed*

[lb N/acre/yr, pounds of nitrogen per acre per year; --, no data available]

NAWQA Subunit and comparable Chesapeake Bay study area	Data collected for Lower Susquehanna NAWQA project							Data from Chesapeake Bay loads database[1]			
	Number of basins	Annual base-flow load (tons of nitrogen)			Base-flow yield (lb N/acre/yr)			Number of basins	Base-flow yield (lb N/acre/yr)		
		Low[2]	Medium[3]	High[4]	Low[2]	Medium[3]	High[4]		Minimum	Median	Maximum
Crystalline agricultural	1 (Muddy Creek)	418	505	612	18	22	27	53	3.1	6.1	12
Carbonate agricultural	1 (Mill Creek)	514	675	772	30	39	44	58	3.7	16	31
Carbonate agricultural	1 (Bachman Run)	111	124	146	45	50	59	58	3.7	16	31
Carbonate urban	1 (Cedar Run)	73.2	81.7	88.5	18	20	22	0	--	--	--
Carbonate agricultural	1 (Kishacoquillas Creek)	406	481	593	22	26	32	58	3.7	16	31
Sandstone and shale agricultural	1 (East Mahantango)	102	203	418	7.1	14	29	50	3.7	9.8	31
Sandstone and shale forested	1 (Bobs Creek)	12.7	21.1	37.2	2.4	4.0	7.0	31	1.2	2.1	6.5

[1] Data are from Langland and others (1995).
[2] Calculated using 10th percentile of concentrations at long-term monitoring site.
[3] Calculated using the median concentration at long-term monitoring site.
[4] Calculated using 90th percentile of concentration at long-term monitoring site.

Comparisons of the subunit surface-water synoptic study to the long-term monitoring sites showed that five of the long-term monitoring sites accurately represent the subunits. Samples collected at the long-term sites on Mill Creek, Muddy Creek, and East Mahantango Creek had nitrate concentrations equal to or slightly higher than the median nitrate concentration of samples collected at the synoptic sites in the respective subunit. At the long-term site on Cedar Run, the nitrate concentration was slightly lower than the median nitrate concentration of the samples collected in the urban subunit synoptic study. These long-term monitoring sites are probably representative of their subunits. For Bobs Creek, even though the nitrate concentration at the long-term site exceeded the concentrations at all but one of the synoptic sites, the variation in concentrations at all of the sites is less than 0.8 mg/L, so the estimations of loads and yields for this site are also representative of the forested subunit.

Samples collected at two of the long-term monitoring sites were not representative of the subunits. At the long-term site on Kishacoquillas Creek, the sample collected had a nitrate concentration slightly higher than the 75th percentile of the synoptic samples (table 8) collected in that subunit. This site may provide a high estimate for loads and yields. The nitrate concentration in the sample collected at Bachman Run during the subunit synoptic sampling exceeded the concentrations in all but one of the other sites in that subunit. This indicates that loads and yields calculated from this site will likely overestimate the loads and yields that could be expected in that subunit.

Long-term Monitoring Basins Compared to Focused Synoptic Studies

Of the seven long-term monitoring sites, six had samples collected at upstream tributaries within the basin (table 8) to determine the factors that contribute to the nitrate concentrations detected at the long-term site. Focused synoptic samples were examined to determine what factors contribute to the concentrations detected at the long-term monitoring sites. A sample was collected at the long-term monitoring station during the basin synoptic study to allow comparisons of data collected under similar conditions (table 8). This will further qualify the load and yield estimates for the long-term sites by identifying unusual or anomalous nitrate sources within the basin that may be affecting loads or yields.

In the Muddy Creek Basin, the synoptic samples had very little variation in nitrate concentrations. This shows that Muddy Creek upstream of the long-term monitoring site is homogeneous with respect to the distribution of nitrate concentrations, and the nitrate load and yield estimates were probably not influenced by a single tributary or nitrogen source.

In the Mill Creek Basin, nitrate concentrations were more variable than the concentrations in Muddy Creek. Two of the headwaters sites that originate in crystalline forested parts of the basin had very low nitrate concentrations. Five point sources that discharge into Mill Creek were sampled at the discharge point, and although four had nitrate concentrations similar to the concentrations in the stream, one of the discharges had a concentration of 34 mg/L. The flow from this source was about 1 ft^3/sec. Because of the extremely high concentration of the effluent, this point source had a considerable effect on the stream concentrations at the point where it entered the stream and probably affected concentrations at the long-term monitoring site. Other tributaries sampled in the Mill Creek Basin had nitrate concentrations that varied from 4.6 to 13.0 mg/L. The load and yield estimate for this basin may be influenced by the low concentrations in the headwaters sites and the high concentrations in the point source; however, this is probably typical for streams in this area (table 8).

In the Bachman Run Basin, the nitrate concentrations increase from low concentrations (0.57 mg/L) in the forested headwaters to the highest concentration (11 mg/L) at the long-term monitoring site. This progressive increase in nitrate concentration corresponds to the progressive downstream increases in agricultural land use. A minor point-source discharge to a headwaters tributary of Bachman Run had very little affect on the nitrate concentrations at the long-term site. The load and yield estimates for Bachman Run were not affected by a single point source or tributary.

In the Cedar Run Basin, the nitrate concentrations are affected by agricultural and urban land use. Tributaries that originate in the agricultural part of the basin have the highest nitrate concentrations and, in the opposite situation from Bachman Run, nitrate concentrations decrease downstream as the percentage of agricultural land decreases. Tributaries that are in urban areas have lower concentrations of nitrate. Many urban streams sampled follow this pattern, where a small amount of agricultural land in the basin may be the source of much of the nitrate in the basin. This combination of urban and agricultural land use may help explain the high load and yield estimates in Cedar Run. Although several of the urban streams sampled for the subunits synoptic study had point-source discharges, there were no point-source discharges to Cedar Run.

In the Kishacoquillas Creek Basin, nitrate concentrations were variable. The two tributaries that originate on the forested ridge had the lowest concentrations. A large spring issuing from carbonate rocks in the middle of the valley had the highest concentration. Other tributaries had nitrate concentrations that were similar to the concentration detected at the long-term site. The distribution of nitrate concentrations seen in the Kishacoquillas Creek Basin was typical of streams in the Appalachian Mountain carbonate agricultural subunit.

In the East Mahantango Creek Basin, very little variation was seen in nitrate concentrations between the tributary streams and the long-term monitoring site. Four sites were sampled within the East Mahantango Creek Basin at or above the fixed station at Klingerstown, and all of the samples were within 0.5 mg/L of the concentration detected at the long-term site indicating that the nitrate concentrations at the long-term site are a result of equal contributions of nitrate from the tributaries.

Range of Concentrations, Loads, and Yields Within Long-term Basins

The range of concentrations (table 8) is a major factor that affects the ranges of estimates for base-flow loads and yields at the long-term monitoring site. Sites such as Bachman Run and Cedar Run, where nitrate concentrations had little variation throughout the year, also had a narrow range of load and yield estimates. The narrow range in concentrations allows more confidence in the loads and yields than if concentrations would have been highly variable. The larger basins such as Muddy Creek, Mill Creek, and East Mahantango Creek had large variations in concentrations and load estimates, probably due to the greater range of conditions that occur in a larger basin. Estimates of concentration, load, and yield of nitrate for Kishacoquillas Creek do not vary greatly. Concentration, load, and yield estimates for Bobs Creek were variable; however, because the concentrations were small at this site, the variation did not make a large change in the values for load or yield.

Comparison of Base-Flow Yields to Other Studies

Langland and others (1995) studied nutrient loads and yields for the Chesapeake Bay Basin. That study used physiography, bedrock type, and land use to classify basins similar to the NAWQA study described here. Langland's work showed that agricultural basins underlain by carbonate bedrock had the highest base-flow yields of nitrate, and forested basins underlain by sandstone and shale had the lowest base-flow yields of nitrate. The base-flow yields from these similarly defined basins in the Chesapeake Bay Basin (hereafter referred to as Bay sites or basins) are presented for comparison (table 10). The yields for the Bay basins were calculated using a multiple regression model (Cohn and others, 1992), although the loads and yields for the basins in this study were not calculated with this method. Therefore, data collected in this study were compared to data from Langland and others (1995) to assess and qualify the accuracy of these simplified estimates of nitrate yields.

The comparison shows that the yield estimates for the long-term sampling sites are nearly twice as high as the median yields computed for the Bay sites. Most of the differences are probably due to the different methods used to calculate the yields, extremely high base flows that occurred at all sites during 1994, and differences in site selection and basin characteristics.

The flow data used to calculate yields for the NAWQA long-term sites were from water year 1994, which was a wetter than normal year. Water discharge from the Lower Susquehanna River Basin was 42 percent greater than normal (Durlin and Schaffstall, 1996). This factor has a direct influence on the yield data, particularly because the calculation is based on the annual base flow. The database for the Bay site calculations was a compilation of existing data that had been previously collected and was based on multiple years of data collection, including wet, dry, and normal years. The comparison of a wet year to normal and dry years would be expected to result in notably higher loads and yields.

Basin classification for this study and the study by Langland and others (1995) was based on physiography, bedrock type, and land use; however, the two studies had slightly different criteria for assigning land-use categories. Site-selection methods were also different. The NAWQA basins were specifically selected on the basis of land use, whereas the Bay basins were assigned land-use categories after the data were collected. The data for the Bay sites were collected for numerous reasons, some unrelated to land use. The criteria used to classify the land use for the Chesapeake Bay sites was that basins with greater than 50 percent agricultural land were agricultural, and basins with greater than 75 percent forested land were forested. The agricultural basins in the Chesapeake Bay study where base-flow nitrate yields could be calculated ranged from 57 percent to 60 percent agricultural land use. The agricultural basins in the NAWQA study range from 59 percent to 83 percent agricultural land use. The median basin size was larger for the Chesapeake Bay sites, which probably makes these sites represent more diverse land-use practices.

Bachman Run, the smallest long-term basin with the highest percentage of agricultural land, had the highest base-flow nitrate yield. This basin has waters with high nitrate concentrations compared to other sites in the Great Valley carbonate agricultural subunit. Kishacoquillas Creek, with 59 percent agricultural land, had yields that are closer to the yields at the carbonate agricultural Chesapeake Bay sites. Manure application rates, previously shown to be directly correlated with base-flow concentration, are probably greater in the long-term basins because they are located in some of the most intense agricultural areas in the Chesapeake Bay watershed.

Although differences exist between the yields at the NAWQA sites and the Bay sites, the NAWQA basins, with their smaller size and targeted land use, probably represent their subunits well, except for Bachman Run, which has unusually high yields. High base flow in 1994 probably accounts for much of the difference in the calculated yields. The Chesapeake Bay basins are less targeted to the specific land use, and the yields represent a variety of hydrologic conditions.

CONCLUSIONS

This analysis and interpretation of nitrate concentrations in ground water and stream base flow in the Lower Susquehanna River Basin focused on ground water-surface water interaction, spatial distribution and temporal variation in nitrate concentration, and spatial variation in nitrate loads and yields. The following conclusions were made on the basis of the data analysis and interpretation.

The comparison of nitrate concentrations in ground water to the nitrate concentrations in surface water showed that different factors control nitrate concentration in ground water compared to surface water in different environmental subunits of the basin.

- Nitrate concentrations commonly were higher in ground water than surface water for the carbonate agricultural and crystalline agricultural subunits. The topographic position of wells in relation to the agricultural land use leads to high concentrations of nitrate in ground water relative to surface water. The mixture of different land uses within surface-water basins, riparian forest buffers, and in-stream or near-stream biological processes lower the concentration of nitrate in surface water relative to ground water.

- Nitrate concentrations were commonly higher in surface water than in ground water in carbonate urban subunits. Small amounts of agricultural land within the urban basins and point sources of nitrogen in the urban basins lead to high nitrate concentrations in surface water relative to ground water.

- Nitrate concentrations were higher in surface water than ground water in sandstone and shale agricultural and sandstone and shale forested subunits. The fact that much of the contributing areas for the wells in the sandstone and shale subunit was forested land lead to lower concentrations in ground water relative to surface water, regardless of the land use immediately next to the wells. Denitrification in the aquifer, which could also cause nitrate concentrations to be lower in well samples than in surface-water samples, was evident in the water samples collected in wells in the sandstone and shale subunits.

Analysis of the spatial distribution of nitrate in wells showed a large variability among the subunits studied.

- Ground-water nitrate concentrations were highest in the Piedmont carbonate agricultural subunit, where well water nitrate concentrations exceed the U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level (MCL) in more than half the well waters sampled. The Appalachian Mountain and Great Valley carbonate agricultural subunits and the Piedmont crystalline agricultural subunit also had ground-water nitrate concentrations that exceed the MCL in about 30 percent of the wells sampled.

- Nitrate concentrations in water from wells in the carbonate urban, sandstone and shale agricultural, and sandstone and shale forested subunits seldom exceed the MCL.

Comparisons of nitrate concentrations in water in various geologic settings showed that ground-water quality may vary in areas underlain by different bedrock types.

- Nitrate concentrations were higher in ground water in carbonate agricultural areas than in sandstone and shale agricultural areas, but the concentrations in surface water were not significantly different. Nitrogen inputs were similar in these two areas.

- In the Piedmont Physiographic Province, nitrate concentrations were significantly higher in the carbonate agricultural subunit than in the crystalline agricultural subunit for both surface water and ground water. This may be because manure application rates were far greater in the carbonate subunit than in the crystalline subunit.

Comparisons of water quality showed statistically significant differences in nitrate concentrations among various land-use settings. The application rate of nitrogen to the land was one of the factors that controlled nitrate concentrations.

- In the Appalachian Mountain Physiographic Section, nitrate concentrations were significantly higher in both surface water and ground water in the sandstone and shale agricultural subunit than in the sandstone and shale forested subunit.

- In the Great Valley Physiographic Section, nitrate concentrations were higher in both ground water and surface water in the carbonate agricultural subunit than in the carbonate urban subunit.

- The amount of manure applied to the land was related to nitrate concentrations. Median nitrate concentrations in surface water were highest in carbonate agricultural areas with the highest manure application rates and lowest in carbonate agricultural areas with the lowest application rates. More detailed analysis for 41 surface-water basins showed a strong correlation between the manure application rate and the nitrate concentration. The manure application rate may be the most important factor controlling nitrate concentrations in surface water for agricultural basins underlain by carbonate bedrock in the Lower Susquehanna River Basin.

Temporal variation of nitrate concentrations were observed at the seven long-term monitoring sites to determine seasonal patterns in the nitrate.

- Nitrate concentrations were highest in the winter and lowest in the summer.

- Several explanations could be responsible for this seasonal pattern, including plant growth cycles, seasonal precipitation, seasonal uptake of nitrate by algae in streams, and hydrologic controls on nitrate concentration.

- Analysis of the seasonal pattern was not conclusive because the traveltime for ground water through the hydrologic system and discharge to the stream is unknown.

Base-flow nitrate loads and yields estimated from the seven environmental subunits indicate the relative contribution of nitrate from the subunits to the Susquehanna River and Chesapeake Bay. Yield estimates based on the National Water Quality Assessment (NAWQA) data compare favorably to the yields calculated from the previous studies conducted in the Chesapeake Bay Basin. Although the yields for the NAWQA sites were consistently higher because of variation in basin size, site-selection methods, and flow conditions, the following conclusions are consistent for both studies:

- Agricultural areas underlain by carbonate bedrock had the highest yields of any subunit. Carbonate agricultural areas comprise about 12 percent of the Lower Susquehanna River Basin. Carbonate agricultural subunits are providing a disproportionately large amount of the nitrate that enters the Lower Susquehanna River Basin when compared with other subunits.

- The sandstone and shale agricultural and crystalline agricultural areas also had high yields of nitrate and comprise 14 percent and 10 percent of the lower basin, respectively.

- Areas of agricultural land use have the most effect on nitrate concentrations and loads in the main stem of the Susquehanna River.

- The carbonate urban subunit has a high nitrate yield but comprises a very small percentage of the basin and, therefore, has less effect on the nitrate load in the main stem of the Susquehanna River.

- Nitrate yields are low in the sandstone and shale forested subunits, but these areas comprise a large part of the basin (34 percent) and affect the nitrate load in the main stem. Although streams draining this area are likely to dilute the concentrations in the mainstem of the river, much of the overall load in the river will come from forested areas.

REFERENCES CITED

Battaglin, W.A., and Goolsby, D.A., 1995, Spatial data in geographic information system format on agricultural chemical use, land use, and cropping practices in the United States: U.S. Geological Survey Water-Resources Investigations Report 94-4176, 87 p.

Berg, T.M., Edmunds, W.E., Geyer, A.R., Glover, A.D., Hoskins, D.M., MacLachlan, D.B., Root, S.I., Sevon, W.D., and Socolow, A.A., comps., 1980, Geologic map of Pennsylvania: Pennsylvania Geological Survey, 4th ser., scale 1:250,000, 2 sheets.

Chichester, D.C., 1996, Hydrogeology of, and simulation of ground-water flow in, a mantled carbonate-rock system, Cumberland Valley, Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 94-4090, 39 p.

Cohn, T.A., Caulder, D.L., Gilroy, E.J., Zynjuk, L.D., and Summers, R.M., 1992, The validity of a simple statistical model for estimating fluvial constituent loads—An empirical study involving nutrient loads entering Chesapeake Bay: Water Resources Research, v. 289, no. 9, p. 2,353-2,363.

Day, R.L., Richards, P.L., and Brooks, R.L., 1996, Chesapeake Bay riparian forest buffer inventory: University Park, Pa., Pennsylvania State University, 113 p.

Durlin, R.R., and Schaffstall, W.P., 1994, Water resources data, Pennsylvania, water year 1993, vol. 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Report PA-93-2, 361 p.

____1996, Water resources data, Pennsylvania, water year 1994, vol. 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Report PA-94-2, 418 p.

____1997, Water resources data, Pennsylvania, water year 1995, vol. 2, Susquehanna and Potomac River Basins: U.S. Geological Survey Water-Data Report PA-95-2, 518 p.

Firestone, M.K., 1982, Biological denitrification, *in* Stevenson, Frank J. ed., Nitrogen in agricultural soils: American Society of Agronomy, Inc., p. 289-326.

Fishel, D.K., and Lietman, P.L., 1986, Occurrence of nitrate and herbicides in ground water in the Upper Conestoga River Basin, Pennsylvania: U.S. Geological Survey Water-Resources Investigations Report 85-4202, 8 p.

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water Resources Investigations, book 5, chap. A1, 545 p.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment program: Occurrence and distribution assessment: U.S. Geological Survey Circular 1112, 33 p.

Hainly, R.A., and Loper, C.A., 1997, Water-quality assessment of the Lower Susquehanna River Basin, Pennsylvania and Maryland—Sources, characteristics, analysis, and limitations of nutrients and suspended-sediment data, 1975-90: U.S. Geological Survey Water-Resources Investigations Report 97-4209, 136 p.

Haycock, N.E., and Burt, T.P., 1993, Role of floodplain sediments in reducing the nitrate concentration of subsurface run-off—A case study in the Cotswolds, UK: Hydrological Processes, v. 7, p 287-295.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical Methods in Water Resources: New York, Elsevier Science Publishing Company, Inc., p. 217-218.

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.

Langland, M.J., and Fishel, D.K., 1996, Effects of agricultural best-management practices on the Brush Run Creek headwaters, Adams County, Pennsylvania, prior to and during nutrient management: U.S. Geological Survey Water-Resources Investigations Report 95-4195, 80 p.

Langland, M.J., Lietman, P.L., and Hoffman, Scott, 1995, Synthesis of nutrient and sediment data for watersheds within the Chesapeake Bay drainage basin: U.S. Geological Survey Water-Resources Investigations Report 95-4233, 121 p.

Legg, J.O., and Meisinger, J.J., 1982, Soil Nitrogen Budgets, *in* Stevenson, Frank J. ed., Nitrogen in agricultural soils: American Society of Agronomy, Inc., p. 289-326.

Lynch, J.A., 1990, Spatial and temporal variability in atmospheric deposition overview—A Pennsylvania prospectus *in* Conference on Atmospheric Deposition in Pennsylvania—A Critical Assessment, University Park, Pa., 1989, Proceedings: University Park, Pa., Pennsylvania Department of Environmental Resources, Bureau of Air Quality Control and U.S. Department of Agriculture Forest Service, p. 50-62.

Maizel, M.S., Muehlbach, G., Baynham, P., Zoerkler, J., Monds, D., Welle, P., and Iivari, T., 1995, Potential for nutrient loadings from septic systems to ground and surface water resources and the Chesapeake Bay: Natural Resources Conservation Service, the Pennsylvania Association of Conservation Districts, and the National Center for Resource Innovations, Chesapeake, Inc., 30 p.

Malone, T.C., Boynton, W., Horton, T., and Stevenson, C., 1993, Nutrient loadings to surface waters: Chesapeake Bay case study *in* Uman, M.F., ed., 1993, Keeping pace with science and engineering--case studies in environmental regulation: National Academy of Engineering, p. 8-38.

McFarland, E.R., 1994, Relation of land use to nitrogen concentration in ground water flow in the Patuxent River Basin, Maryland: U.S. Geological Survey Water-Resources Investigations Report 94-4170, 20 p.

McKee, J.E., and Wolf, H.W., 1963, Water quality criteria: The Resources Agency of California, State Water Quality Control Board, Publication no. 3-A, 300 p.

Mitchell, W.B., Guptill, S.C., Anderson, K.E., Fegeas, R.G., and Hallam, C.A., 1977, GIRAS - a geographic information and retrieval and analysis system for handling land use and land cover data: U.S. Geological Survey Professional Paper 1059, 16 p.

Patton, C.J., and Truitt, E.P., 1992, U.S. Geological Survey nutrient preservation experiment--Nutrient concentration data for surface-, ground-, and municipal-supply water samples and quality-assurance samples: U.S. Geological Survey Open-File Report 95-141, 140 p.

Reinsch, C.H., 1967, Smoothing by spline functions: Numerische Mathematik, v. 10, p. 177-183.

Risser, D.W., and Siwiec, S.F., 1996, Water-quality assessment of the Lower Susquehanna River Basin, Pennsylvania and Maryland—Environmental setting: U.S. Geological Survey Water-Resources Investigations Report, 94-4245, 135 p.

Rupert, M.G., 1996, Major sources of nitrogen input and loss in the Upper Snake River Basin, Idaho and Western Wyoming: U.S. Geological Survey Water-Resources Investigations Report 96-4008, 15 p.

Schnabel, R.R., Urban, J.B., and Gburek, W.J., 1993, Hydrologic controls in nitrate, sulfate, and chloride concentrations: Journal of Environmental Quality, v. 22, p. 589-596.

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.

Serotkin, N., ed., 1994, The agronomy guide 1995-1996: University Park, Pa., Pennsylvania State University, p. 19-30.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Sisterson, D.L., 1990, Detailed SO_x-S and NO_x-N Budgets for the United States and Canada (Appendix A): *in* Relationships between Atmospheric Emissions and Deposition/Air Quality, National Acid Precipitation Assessment Program Science and Technology Report 8, Acidic Deposition: State of Science and Technology, 10 p.

Siwiec, S.F., Hainly, R.A., Lindsey, B.D., Bilger, M.D., and Brightbill, R.A., 1997, Water-quality assessment of the Lower Susquehanna River Basin, Pennsylvania and Maryland—Design and implementation of water-quality studies, 1992-95: U.S. Geological Survey Open-File Report 97-583, 121 p.

Sloto, R.A., and Crouse, M.Y., 1996, HYSEP—A computer program for streamflow hydrograph separation and analysis: U.S. Geological Survey Water-Resources Investigations Report 96-4040, 46 p.

Susquehanna River Basin Study Coordinating Committee, 1970, Susquehanna River Basin study, Supplement B--Project Summary.

Tukey, J.W., 1977, Exploratory data analysis: Reading, Mass., Addison-Wesley Pub., 506 p.

U.S. Bureau of the Census, 1992, Census of population and housing, 1990: Washington, D.C., Summary tape file 3 on CD-ROM [machine-readable data files].

U.S. Department of Agriculture, 1972, General soil map of Pennsylvania: Soil Conservation Service, scale 1:750,000.

____1994, 1993-1994 Annual Report and Statistical Summary: Pennsylvania Agricultural Statistics Service report no. PASS-115, 90 p.

____1995a, 1994-1995 Annual Report and Statistical Summary: Pennsylvania Agricultural Statistics Service report no. PASS-117, 123 p.

____1995b, Weekly Crop and Weather Roundup, April 16, 1995: Pennsylvania Agricultural Statistics Service, 2 p.

____1995c, Weekly Crop and Weather Roundup, April 23, 1995: Pennsylvania Agricultural Statistics Service, 2 p.

____1995d, Weekly Crop and Weather Roundup, May 21, 1995: Pennsylvania Agricultural Statistics Service, 2 p.

____1995e, Weekly Crop and Weather Roundup, May 28, 1995: Pennsylvania Agricultural Statistics Service, 2 p.

____1995f, Weekly Crop and Weather Roundup, October 8, 1995: Pennsylvania Agricultural Statistics Service, 2 p.

____1995g, Weekly Crop and Weather Roundup, October 15, 1995: Pennsylvania Agricultural Statistics Service, 2 p.

U.S. Department of Commerce, 1995, Climatological Data Annual Summary, Pennsylvania 1995, Ashville, N.C., Volume 100 no. 13, 27 p.

____1951-80, Climatological data - Pennsylvania: National Oceanic and Atmospheric Administration.

U.S. Environmental Protection Agency, 1996, Drinking water regulations and health advisories: Washington, D.C., EPA 822-R-96-001, 11 p.

Viessman, W., Knapp, J., Lewis, G., and Harbaugh, T., 1977, Introduction to hydrology: New York, Harper & Row, 704 p.

Wilcoxon, F., 1945, Individual comparisons by ranking methods: Biometrics, 1, p. 80-83.

Wilk, M.B., and Chen, H.J., 1968, A comparative study of various tests for normality: Journal of the American Statistical Association, 63, p. 1,343-1,372.