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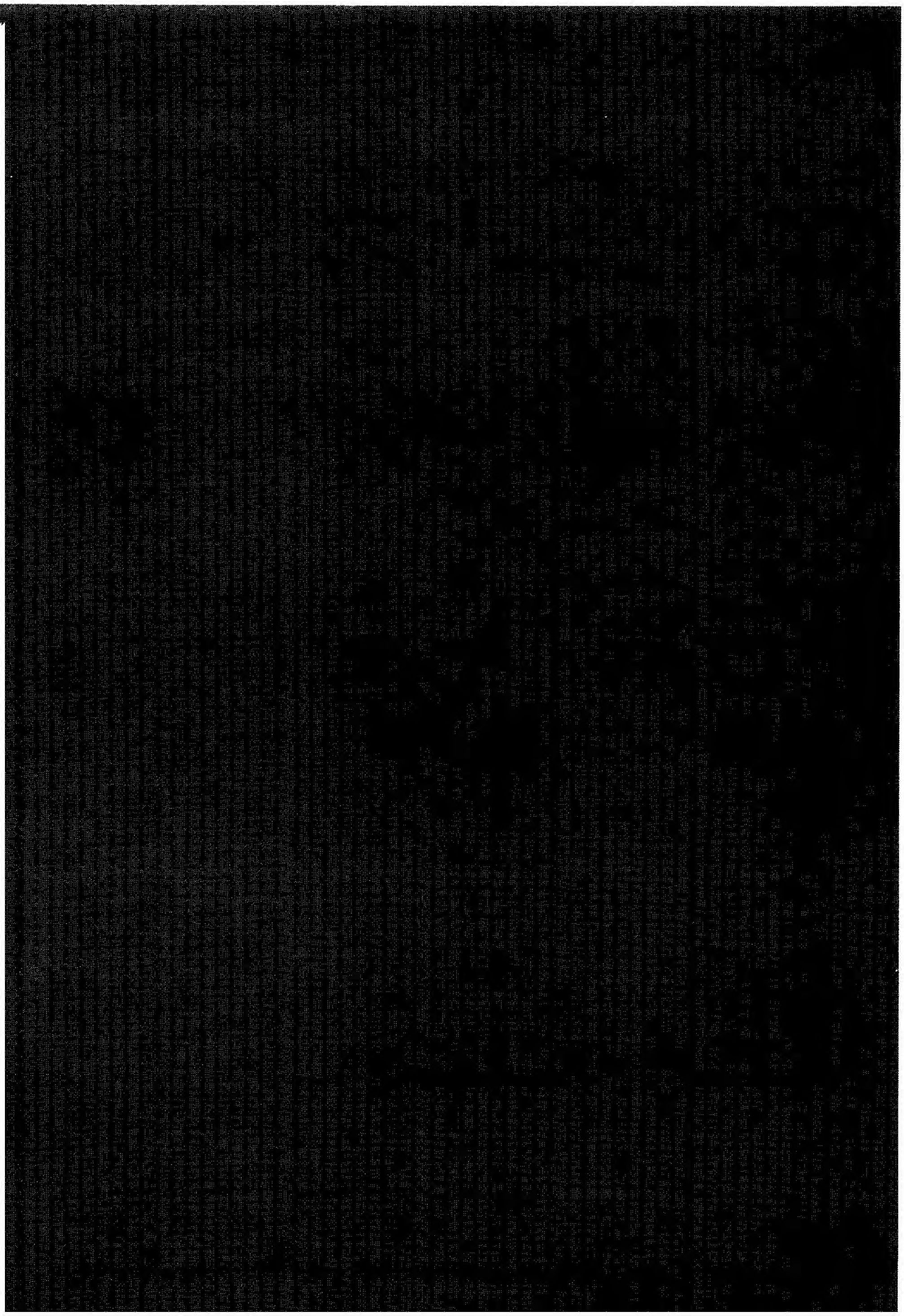

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Prepared in cooperation with the Maryland Department of the Environment

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Ground-Water Flow, Geochemistry, and Effects of Agricultural Practices on Nitrogen Transport at Study Sites in the Piedmont and Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

By E. Randolph McFarland

Prepared in cooperation with the Maryland Department of the Environment

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

Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
acre	0.4047	hectare
square mile (mi^2)	2.590	square kilometer
foot per day (ft/d)	0.3048	meter per day
inch per year (in/yr)	25.4	millimeter per year
square foot per day (ft^2/d)	0.09290	square meter per day
pounds per acre per year [(lb/acre)/yr]	1.121	kilograms per hectare per year
gallon per minute (gal/min)	0.06309	liter per second
cubic foot per second (ft^3/s)	0.03005	liter per second

Water temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$F = 1.8(°C) + 32$$

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, formerly called Sea Level Datum of 1929.

Water-quality units: Chemical concentrations, water temperature, and specific conductance are given in metric units. Chemical concentration is expressed in milligrams per liter (mg/L). Specific conductance is expressed in microsiemens per centimeter at 25 degrees Celsius (µS/cm). This unit is equivalent to micromhos per centimeter at 25 degrees Celsius (µmho/cm), formerly used by the U.S. Geological Survey.

Ground-Water Flow, Geochemistry, and Effects of Agricultural Practices on Nitrogen Transport at Study Sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

By E. Randolph McFarland

Abstract

The effects of agricultural practices on nitrogen transport were assessed at two 10-acre study sites in the Patuxent River Basin, Maryland, from 1986 to 1992. Nitrogen load was larger in ground water than in surface runoff at both sites. Denitrification and (or) long traveltimes of ground water at the study site in the Piedmont Province resulted in lower concentrations of nitrate than at the site in the Coastal Plain Province. The study period was brief compared to the traveltimes of nitrogen in ground water of several decades. Therefore, the effects of agricultural practices were observed only in parts of both sites.

At the Piedmont site, nitrate concentration in two springs was 7 milligrams per liter 2 years after corn was grown under no-till cultivation and decreased to 3.5 milligrams per liter during 4 years while cultivation practices and crops included no-till soybeans, continuous alfalfa, and contoured strips alternated among corn, alfalfa, and soybeans. Nitrogen load in ground water decreased from 12 to 6 pounds per acre per year.

At the Coastal Plain site, the concentration of nitrate in ground water decreased from 10 milligrams per liter after soybeans were grown under no-till cultivation for 2 years to 9 milligrams per liter after soybeans were grown under conventional till cultivation for 3 years. No-till cultivation in 1988 resulted in a greater nitrogen load in ground water [12.55 (pounds/acre)/year], as well as greater ground-water recharge and discharge, than conventional till cultivation in 1991 [11.51 (pounds/acre)/year], even though the amount and timing of precipitation for both years were similar.

INTRODUCTION

Degradation of water quality in the Chesapeake Bay drainage basin has been attributed in part to farming practices (Chesapeake Implementation Committee, 1988). Surface runoff from farmland erodes soil and transports fertilizers, pesticides, and animal wastes to streams. Consequently, loads of nutrients, sediment, and toxic substances in streams and rivers that discharge to the Bay are increasing. In an effort to improve water quality in the Bay, Federal and State agencies are promoting agricultural practices that conserve soil and minimize the application of agricultural chemicals and animal wastes. Government programs encourage farmers to adopt agricultural "best management practices" (BMP's), some of which include planting of cover crops, manure management, terracing, crop rotation, contour plowing, strip cropping, and conservation tillage (U.S. Department of Agriculture, 1985). Some BMP's are intended to improve the efficiency of applied chemical fertilizers, pesticides, and manure by altering the types, amounts, and timing of application and cropping. Other BMP's are designed to conserve soil and retain applied chemicals and manure by increasing infiltration of precipitation into the soil, thereby reducing surface runoff and erosion.

Precipitation that infiltrates the land surface percolates downward through the soil and recharges the ground water. Sediment and chemicals that sorb to sediment are filtered by soil; however, dissolved chemicals can be transported to ground water. Concentrations of certain chemicals in ground water, most notably nutrients (nitrogen, phosphorus, and potassium) that originate from chemical fertilizers and manure, can be increased above natural concentrations by farming practices. Other chemicals, such as pesticides, which are used in farming and would not be present naturally in ground water, are sometimes added. Although the rate of transport of some chemicals could be slowed in soil, agricultural practices that increase infiltration also increase the potential for higher concentrations of nutrients and pesticides in ground water because the amount of chemicals removed by surface runoff is less.

Some of the water in streams and rivers does not originate as surface runoff, but is supplied by discharge of ground water as base flow. Thus, an agricultural practice intended to preserve surface-water quality by diverting chemicals to ground water could be ineffective because the chemicals will eventually enter streams in ground-water discharge. In addition, increased infiltration and recharge could steepen hydraulic gradients and increase rates of ground-water flow and chemical transport to receiving streams.

In 1986, the U.S. Geological Survey (USGS), in cooperation with the Maryland Department of the Environment, began an investigation to determine the effects of particular agricultural practices on nitrogen transport in ground water. Collection of ground-water hydrologic and chemical-quality data began in August 1986 at two study sites in small rural subbasins of the Patuxent River Basin in Maryland, a major tributary of Chesapeake Bay. One study site was located in the Piedmont Physiographic Province, hereafter referred to as the "Piedmont site," and the other study site was located in the Coastal Plain Physiographic Province, hereafter referred to as the "Coastal Plain site." Both study sites were initially instrumented for a related project, conducted by the USGS and the Maryland Department of the Environment, to study nonpoint-source contamination of surface water in the Patuxent River Basin (Summers, 1986).

Nitrogen, one of the chemicals that has increased in ground water as a result of farming in Maryland and other parts of the country, was chosen for study because nitrogen significantly affects the quality of water in Chesapeake Bay (Fisher, 1989; Officer and others, 1984; Ryther and Dunstan, 1971). Excess nitrogen in the Bay results in eutrophic conditions that are deleterious to aquatic ecosystems. Nitrogen transport is difficult to control because nitrogen generally is mobile in the subsurface environment. In addition, excess nitrogen in ground water degrades the quality of drinking water from water-supply wells through increased health hazards posed by nitrosamines, some of which are mutagens (Dyer and others, 1984) or carcinogens and methemoglobinemia or blue-baby disease (Shuval and Gruener, 1972; U.S. Environmental Protection Agency, 1977).

The two study sites have different geologic and hydrologic characteristics. Therefore, the effects of agricultural practices on ground water underlying the sites could differ. The different effects provide a comparison of transport of nitrogen by ground water under different hydrogeologic conditions.

Many diverse agricultural practices are currently (1994) in use under different hydrogeologic conditions throughout the Chesapeake Bay drainage area. Moreover, farmers typically change their cropping and cultivation practices for a particular field from year to year, depending on changes in weather and economic conditions. "Best management practice" is a relative term. Some of the first BMP's to be developed for reducing runoff and erosion, such as conservation tillage, have been in increasingly widespread use for several years to decades and are considered to be an improvement over centuries-old agricultural practices. Other BMP's have not yet been as widely implemented because of higher costs or more recent development.

Relations of agricultural practices to water quality are complex. The diversity of agricultural practices in use in the Chesapeake Bay drainage basin can produce effects that can differ spatially and temporally. Because of different hydrologic conditions, a practice that is effective in one area can be ineffective in another. Weather conditions and previous land use, which also can differ greatly over time and space, also affect the hydrologic conditions observed at a particular location at a given time. Despite these complexities, an evaluation of the effectiveness of different agricultural practices for protecting and improving water quality can be approached by determining the effects of different practices under different hydrologic conditions.

Purpose and Scope

This report describes the flow and geochemistry of ground water and the transport of nitrogen at two study sites in the Patuxent River Basin in Maryland. Ground-water data are presented for the period from August 1986 through June 1992.

Characteristics of aquifers, directions and rates of ground-water flow, and relations among different components of flow through the study sites are described. Ground-water flow is simulated by use of numerical models. Model boundaries and calibration procedures are described. Simulated ground-water flow is compared to measured precipitation and surface runoff and to other unmeasured flow components, including evapotranspiration and storage and interflow in the unsaturated zone.

The chemical composition of ground water at the study sites is described. Possible chemical-weathering reactions and solute-transport processes are examined to account for the observed major-ion composition of the water. Chemical transformation reactions among nitrogen species are described to account for the distribution of nitrogen species in ground water.

Nitrogen concentrations in surface runoff, soil water, and ground water are analyzed to determine the effects of agricultural practices and other factors on nitrogen transport at the study sites. Spatial and temporal distributions of nitrogen concentration are examined to infer controls on nitrogen transport, and nitrogen loads in surface runoff and ground water are estimated by using nitrogen-concentration and flow data. Changes in nitrogen concentration and load in surface runoff and ground water are related to changes in agricultural practices.

Description of Study Sites

The two sites selected for the study are in the Patuxent River Basin in Maryland (fig. 1). The Patuxent River is 110 mi long and drains an area of about 930 mi^2 from central Maryland to the western shore of Chesapeake Bay. The climate throughout the basin is humid-temperate, with warm summers and mild winters. Annual precipitation is about 43 in. The basin spans two distinctly different physiographic provinces—the Piedmont and the Coastal Plain. The Fall Line separates the Piedmont Province to the northwest from the Coastal Plain Province to the southeast.

Physiography

The headwaters of the Patuxent River are in the Piedmont Physiographic Province. Within the Patuxent River Basin, the Piedmont Province is generally characterized by rolling terrain. Residual soils from 0 to more than 100 ft thick overlie bedrock that consists of igneous and metamorphic rocks of late Proterozoic and early Paleozoic age.

The Coastal Plain Physiographic Province has well-drained soils and is characterized by rolling terrain with deeply incised stream valleys in the northwestern part and gently rolling-to-level terrain in the southeastern part. The Coastal Plain Province contains southeastward-dipping strata of unconsolidated to partly consolidated sediments of Cretaceous, Tertiary, and Quaternary age that unconformably overlie Piedmont rock.

The hydrogeology of the two provinces is diverse. Ground water in the Piedmont Province is present in fractures in bedrock and in pores in weathered residuum developed over the bedrock. Ground water in the Coastal Plain Province is present in pores in the sediments; thick sequences of porous and permeable strata form regional aquifers, and impermeable strata form confining units between the aquifers.

The Piedmont study site is in a small (about 10 acre) drainage basin (fig. 2) on the property of the University of Maryland Forage Farm in Howard County. The land surface is concave. The study site is bounded by a topographic divide to the north and east. The surface relief across the site is approximately 70 ft. Surface soil is loam and gravelly loam of the Manor Series on the slopes and silt loam and gravelly silt loam of the Chester Series on the divide (Matthews and Hershberger, 1968).

The Coastal Plain study site is defined by a small (about 10 acre) drainage basin on the property of the Jefferson Patterson State Park in Calvert County (fig 3). The land surface is flat. The study site is bounded by a topographic divide to the east and the Patuxent River to the west. The surface relief is about 50 ft. The surface soil is silt loam of the Matapeake and Mattapex Series and fine sandy loam of the Woodstown Series (Matthews, 1971).

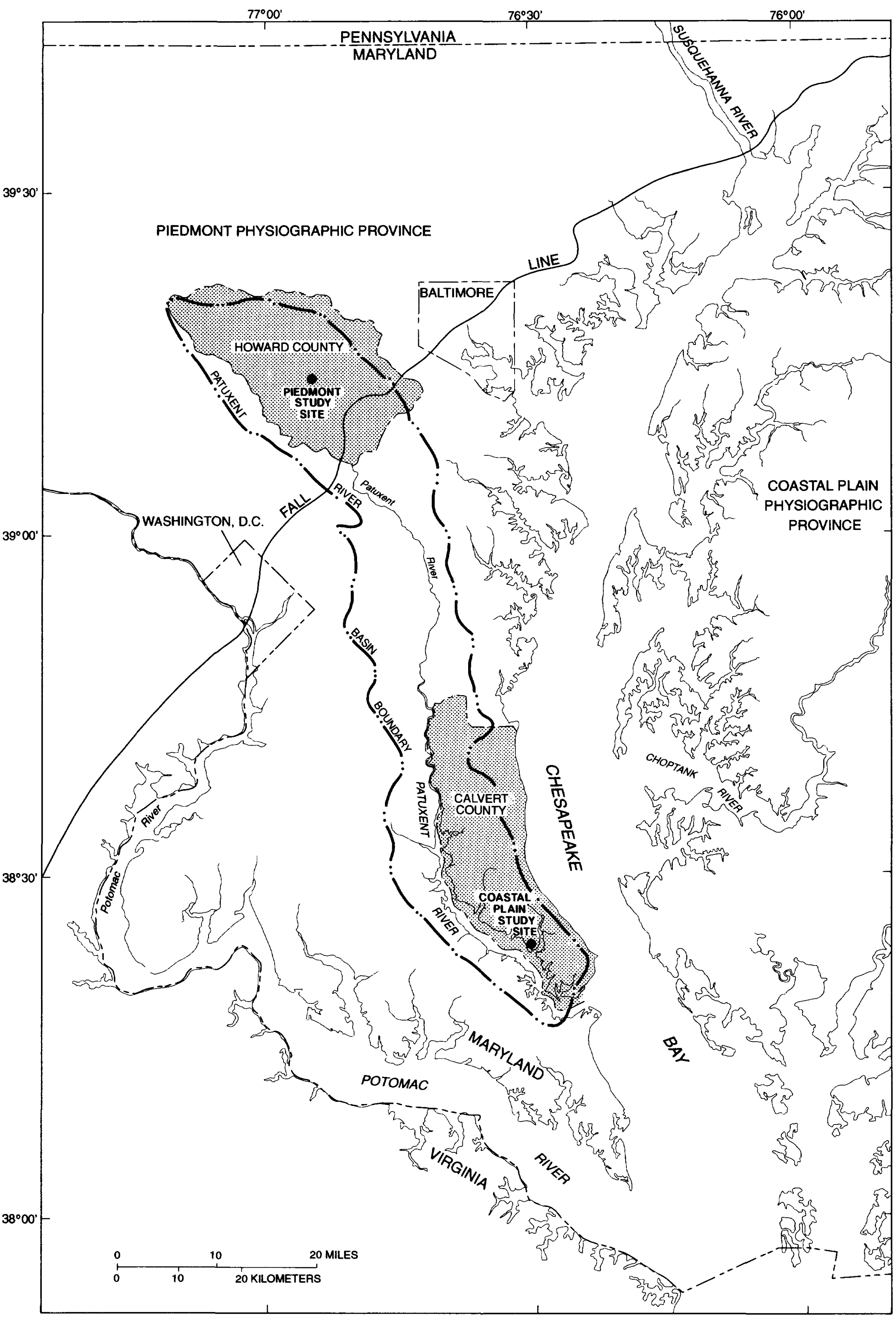

Figure 1. Location of Piedmont and Coastal Plain study sites in the Patuxent River Basin, Maryland.

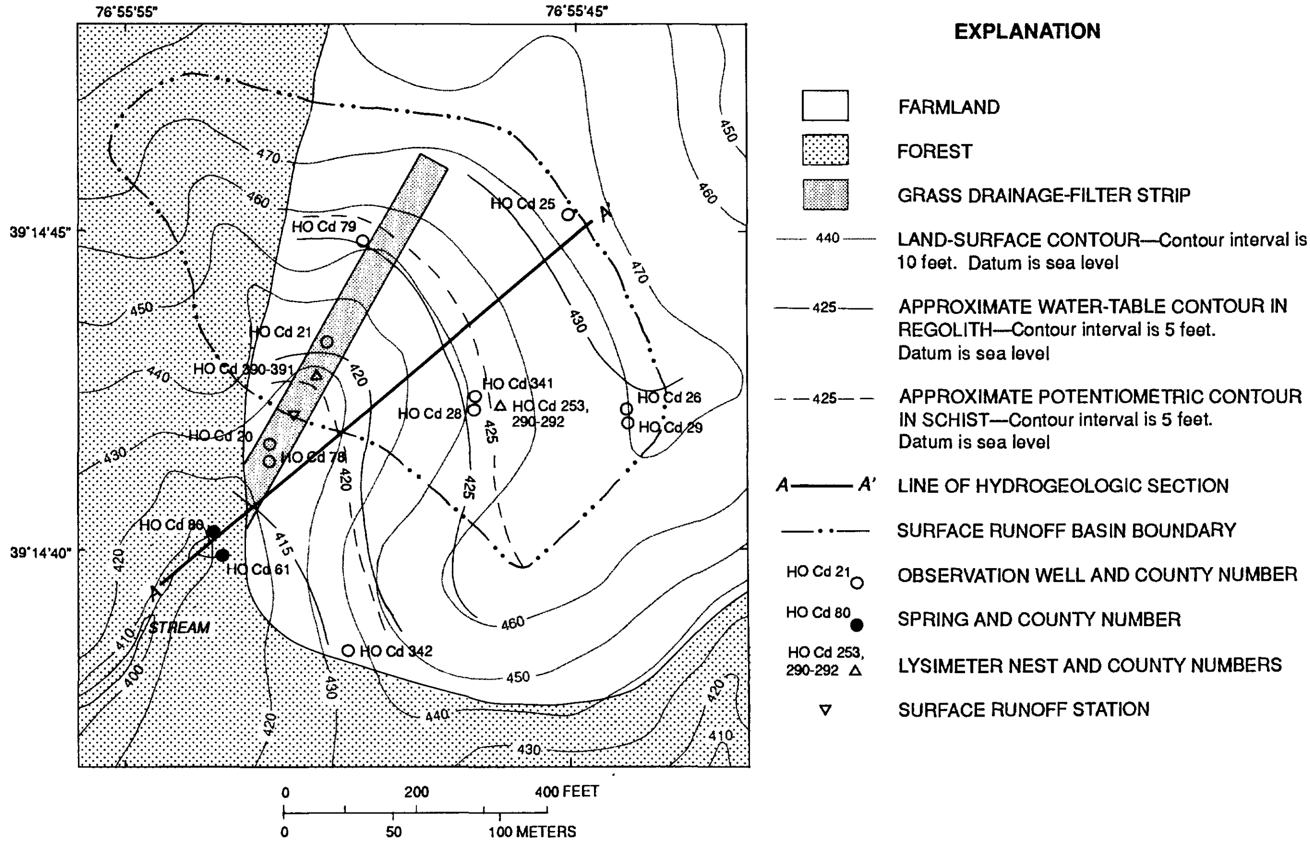

Figure 2. Topography, ground-water levels, instrumentation, and land use at the Piedmont study site in the Patuxent River Basin, Maryland.

Agricultural Practices

In consultation with local county extension agents, who visit many farms in the region, the land owners planned and implemented agricultural practices at the study sites to meet the needs of the farming operations (table 1). Neither site was irrigated. Amounts of nitrogen applied to the sites were estimated from available records. Nutrients were applied at both sites only as chemical fertilizer and not as manure.

Changes in agricultural practices at the study sites were made during the study to meet the changing needs of the farming operations; such changes are typical of most farms in the region. The approach taken in this study differed from another approach commonly followed in which hydrologic processes are characterized on the basis of data collected during a long period (5 to 10 years) during which little or no change in agricultural practices takes place. Although a high degree of experimental control is obtained by using the long-term approach, it is not representative of what happens at most farms. This study was designed to observe the effects on ground water of agricultural practices typically implemented extensively throughout a region.

Piedmont Site

The Piedmont site (fig. 2) is entirely cultivated. A grass drainage-filter strip was maintained at the site throughout the study period to reduce erosion. The site is bordered by other farm fields to the north and east and by forest to the south and west.

Because the study site is located on the University of Maryland research farm, relatively detailed records of agricultural practices are maintained (F.L. Walbert, University of Maryland, written commun., 1991). Corn, soybeans, and alfalfa were grown at different times before and during the study period. Generally larger amounts of nitrogen fertilizer were applied to corn than to other crops (table 1).

Before the study, "no-till" corn was grown during 1985. No till, which is a form of conservation tillage in which crops are planted without disturbing the land surface or altering soil structure by plowing as with conventional tillage, is intended to reduce surface runoff and erosion (U.S. Environmental Protection Agency, 1987). No-till soybeans were grown during the 1986 to 1987 season (table 1). Nitrogen fertilizer was not applied to the soybeans at the site in 1986. Soybeans are legumes that obtain much of their required nitrogen from the atmosphere. Additionally, residual nitrogen probably was present in the soil because approximately 68 lb/acre of nitrogen fertilizer had been applied during 1985 when no-till corn was grown. Nitrogen that had been applied to corn could have been retained in the soil by a cover crop of barley that was planted after the corn was harvested. In 1987, about 30 lbs/acre of nitrogen was applied to the site. The soybeans were harvested both years by combining, which removes the beans but leaves the roots and cut stalks intact and spreads the remaining plant debris over the land surface. Decomposition of the plant debris reincorporates nitrogen into the soil.

Table 1. Agricultural practices at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

[lb/acre, pound per acre; do., ditto]

Year	Crop	Cultivation method	Approximate nitrogen fertilizer application (lb/acre)
		Piedmont site	
1986	Soybeans..	No-till	0
1987	...do	...do	30
1988	Alfalfa......	Continuous................	12
1989	...do	...do	0
1990	Corn	Contoured strips........	30
	Alfalfa......	...do	0
	Corn	...do	30
1991	Soybeans..	...do	0
	Corn	...do	30
	Soybeans..	...do	0
1992	Corn	...do	30
	Soybeans..	...do	0
	Corn	...do	30
		Coastal Plain site	
1986	Soybeans..	No-till	[1]10
1987	...do	...do	[1]10
1988	...do	...do	[1]10
1989	.. do	Conventional till	[1]10
1990	...do	...do	[1]10
1991	...do	...do	[1]10
1992	...do	No-till	[1]10

[1]Estimated.

During the 1988 to 1989 season, continuous (grown throughout the year) alfalfa was grown to treat an infestation of Johnson grass weed. Alfalfa can tolerate an herbicide that is used to kill Johnson grass. The alfalfa was planted in 1988 after conventionally tilling the site and applying about 12 lbs/acre of nitrogen. No additional nitrogen was applied during 1989 because alfalfa is a legume that derives nitrogen from the atmosphere. Alfalfa was intermittently removed from the site by mowing and collecting the clippings.

During 1990, the site was divided into three strips oriented parallel to topographic contours along which planting and other cultivation operations were conducted. Contouring is a progressive BMP that is intended to reduce soil erosion and contaminant transport (U.S. Environmental Protection Agency, 1987). In addition, corn, alfalfa, and soybeans were alternated on the contoured strips from 1990 to 1992; this rotation made more efficient use of the nitrogen in the soil. During 1990, alfalfa in two of the strips (2 and 4 acres) was plowed under, and no-till cultivation of corn was begun. The intervening center strip (3 acres) remained in alfalfa. During 1991, the alfalfa in the center strip was plowed under, and no-till cultivation of corn was begun. In the two adjacent strips, no-till soybeans followed the previous year's corn. During 1992, the center strip was planted with no-till soybeans and the two adjacent strips were planted with no-till corn. About 30 (lbs/acre)/yr of nitrogen was applied to strips planted in corn. No nitrogen was applied to strips planted in soybeans and alfalfa. Nitrogen was reincorporated into the soil by the decomposition of plant remains after harvest. In addition, about 80 lbs/acre of nitrogen could have been released by plowing under the alfalfa prior to planting corn (Pennsylvania State University, 1987).

Coastal Plain Site

The Coastal Plain site (fig. 3) is entirely cultivated. A 50-ft-wide buffer strip of small trees and undergrowth was maintained throughout the study period between the cultivated area and the shore of the Patuxent River. The site is bordered by other farm fields to the north, south, and east and by several farm buildings in a farmyard to the east.

The farmyard probably does not have a major effect on conditions at the study site. No animals were kept in the farmyard or buildings before and during the

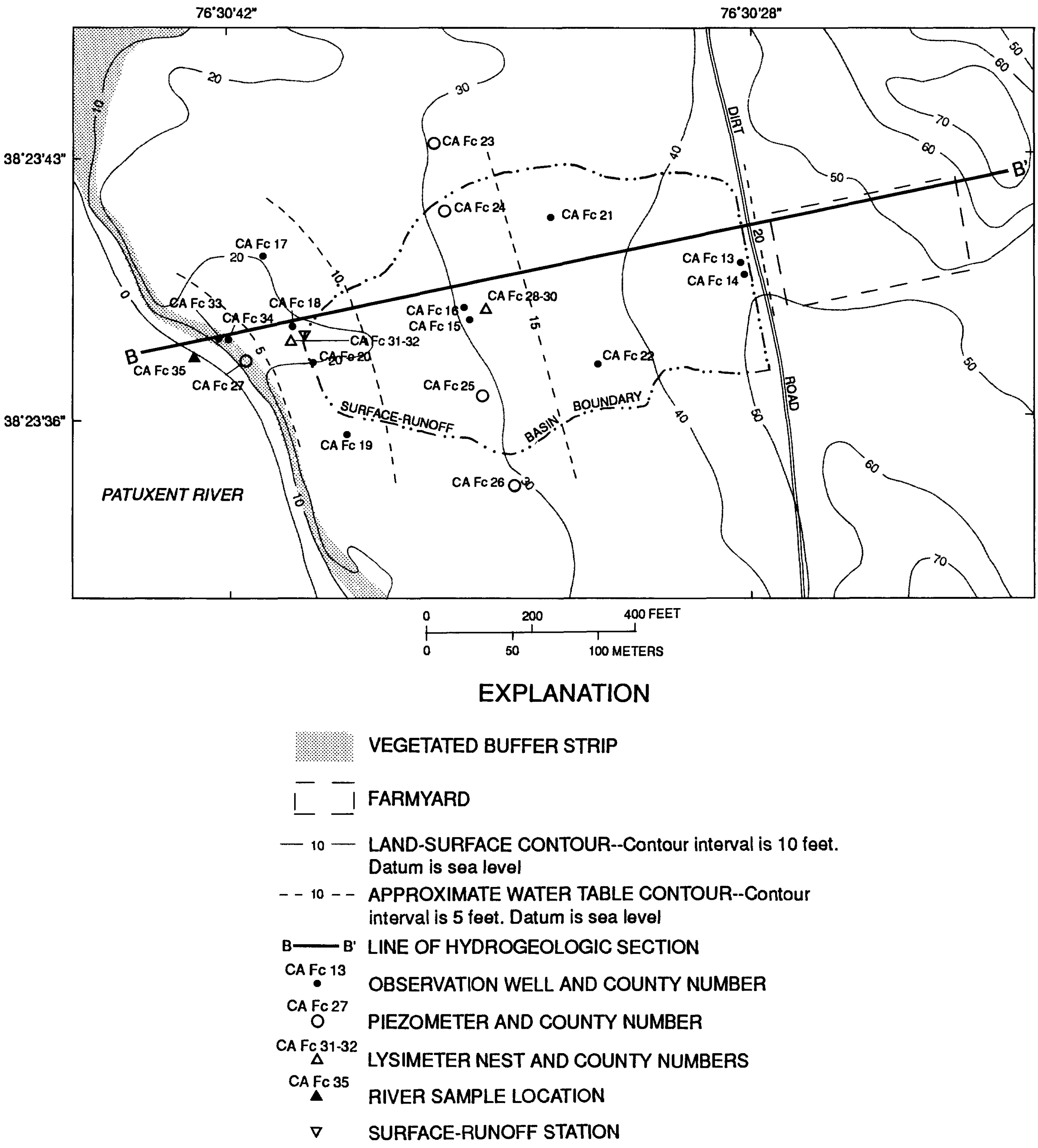

Figure 3. Topography, water-table configuration, and instrumentation at the Coastal Plain study site in the Patuxent River Basin, Maryland.

beginning of the study; the buildings were primarily vacant and received little use. A road grade at the upslope end of the site separates the site from the farmyard (fig. 3) and diverts any surface runoff in the farmyard to the east and away from the site. Also, the shallow aquifer under unconfined conditions does not extend beneath the farmyard (see section on "Hydrogeologic Frameworks").

Because the Coastal Plain site is on park land that is leased to a tenant farmer, information on agricultural practices is less detailed than at the Piedmont site, but agricultural practices before and during the study period also changed less than at the Piedmont site. Soybeans were grown throughout the study period at the Coastal Plain site, but methods of cultivation changed over time (table 1). In addition, no-till and conventionally tilled soybeans were grown at the site for a decade or more prior to the study, and a winter cover crop of wheat or rye was planted during some of those years (S.L. Boyer, U.S. Geological Survey, written commun., 1988). Corn also could have been grown, however, in part of the study site as recently as 1982.

Soybeans were grown using no-till cultivation during 1986–88 and 1992 and using conventional tillage during the 1989 to 1991 seasons (table 1). Specific amounts of nitrogen fertilizer applied during this period are not known. Because historical records, including those for 1979 and 1984, indicate consistent application of 10 (lbs/acre)/yr of nitrogen fertilizer to soybeans throughout the park (S.L. Boyer, U.S. Geological Survey, written commun., 1988), similar amounts are assumed to have been applied at the site during the study period (table 1). Historical records indicate, however, that 45 (lbs/acre)/yr or more could have been applied to corn in part of the site as recently as 1982.

Methods of Investigation

Hydrologic instrumentation was initially installed at both study sites for a related project, in which nonpoint-source pollution of surface water in the Patuxent River Basin was studied (Summers, 1986). Data on the quantity of precipitation and the quantity and quality of surface runoff were collected by using rain gages, runoff-flow gages, and automatic runoff-water samplers.

For this study, observation wells and piezometers were installed at the study sites (table 2; figs. 2, 3) to measure water levels, nitrogen concentrations, and other chemical quality characteristics in ground water and to record aquifer characteristics. A network of wells was established at the beginning of the study and was later supplemented with additional wells. Soil-moisture tensiometers and ceramic-cup suction lysimeters were installed in the unsaturated zone above the water table to measure soil-water content changes, nitrogen and bromide-tracer concentrations, and other chemical quality characteristics.

Water-level measurements were recorded continuously from October 1986 through December 1991 by automatic recorders at selected wells and measured approximately once a month with a graduated steel tape at all wells and piezometers. Ground-water samples were collected from most of the wells approximately monthly for field analysis of pH, dissolved oxygen, specific conductance, and temperature and for laboratory analysis of nitrogen species. Additional field analyses for alkalinity and laboratory analyses for major dissolved ions and selected minor constituents were made once every 3 months for at least 1 year. Selected wells were used for aquifer pumping tests to obtain estimates of aquifer hydraulic properties. In addition, geologic and geophysical (gamma) well logs were obtained to infer the spatial configurations and compositions of the aquifers. Although cuttings were obtained during drilling, samples of aquifer materials were not collected with their structure intact. Therefore, samples of similar materials were collected with their structure intact from surface exposures at the downslope ends of the study sites and were used to infer physical properties of the aquifer materials.

At the Piedmont site (table 2; fig. 2) 10 ground-water observation wells were installed. Six wells (HO Cd 28, HO Cd 29, HO Cd 78, HO Cd 79, HO Cd 341, HO Cd 342) were cased with 3.5-in. inside-diameter PVC (polyvinyl chloride), have 5- to 10-ft-long screens in the regolith (saprolite and alluvium), and total depths that ranged from 9 to 63 ft. The remaining wells (HO Cd 20, HO Cd 21, HO Cd 25, HO Cd 26) have open holes in bedrock, that range from 96 to 143 ft deep, and were cased with 6-in. inside-diameter steel through the regolith to bedrock. All casings were grouted with bentonite. Five of the regolith wells (HO Cd 28, HO Cd 29, HO Cd 78, HO Cd 341, HO Cd 342) were equipped with automatic water-level recording devices. Stainless-steel well points were installed for sampling two springs at the downslope end of the site. Lysimeters were installed in the central part of the site at depths of 1, 5, 10, and 14 ft and at the downslope end of the site at depths of 4 and 7 ft. At each group of lysimeters, two soil-moisture tensiometers also were installed at depths of 2 and 5 ft.

At the Coastal Plain site, 12 ground-water observation wells were installed (table 2; fig. 3). Five piezometers also were installed to provide additional water-level data. All the piezometers and 10 of the wells were cased with 3.5-in. inside-diameter PVC, which ranges from 12 to 36 ft deep, screened in sand,

Table 2. Construction characteristics of observation wells, springs, lysimeters, and piezometers at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

[ft, feet; —, no data; do., ditto; >, greater than]

Station number[1]	Lithology	Sampling interval: Depth to top (ft)	Sampling interval: Depth to bottom (ft)	Range of depth to water level (ft)	Elevation of land-surface datum (feet above sea level)
Piedmont site					
Observation wells:					
HO Cd 20...	Schist...........	30	96	5– 11	425.70
HO Cd 21...	...do...........	55	96	12– 19	434.18
HO Cd 25...	...do...........	60	97	37– 47	470.90
HO Cd 26...	...do...........	106	143	42– 52	469.94
HO Cd 28...	Deep saprolite	41	46	24– 35	453.11
HO Cd 29...	...do...........	63	68	41– 50	470.34
HO Cd 78...	Alluvium........	9	19	8– 10	425.58
HO Cd 79...	Deep saprolite	43	53	23– 30	452.37
HO Cd 341..	Shallow saprolite..	25	30	24–>30	453.00
HO Cd 342..	...do...........	20	25	20– 24	436.46
Springs:					
HO Cd 80...	Alluvium........	0	2	0– 0	412.96
HO Cd 81...	...do...........	0	2	0– 0	412.40
Lysimeters:					
HO Cd 253..	Shallow saprolite..	1	1	—	456.61
HO Cd 290..	...do...........	5	5	—	456.61
HO Cd 291..	...do...........	10	10	—	456.61
HO Cd 292..	...do...........	14	14	—	456.61
HO Cd 390..	Alluvium........	4	4	—	427.89
HO Cd 391..	...do...........	7	7	—	427.89
Coastal Plain site					
Observation wells:					
CA Fc 13...	Sand, shells......	29	34	26– 31	47.44
CA Fc 14...	Sand, clay.......	25	30	26–>30	47.56
CA Fc 15...	Sand, shells......	31	36	15– 18	30.56
CA Fc 16...	...do...........	18	23	15– 19	30.75
CA Fc 17...	...do...........	27	32	12– 15	22.59
CA Fc 18...	...do...........	18	23	6– 10	15.56
CA Fc 19...	...do...........	28	33	16– 19	25.49
CA Fc 20...	...do...........	22	27	11– 14	20.62
CA Fc 21...	...do...........	28	33	17– 21	35.51
CA Fc 22...	...do...........	30	35	17– 21	36.52
CA Fc 33...	...do...........	12	14	7– 8	12.17
CA Fc 34...	...do...........	16	18	7– 8	12.01
Piezometers:					
CA Fc 23...	...do...........	24	26	15– 18	30.49
CA Fc 24...	...do...........	23	25	15– 19	31.00
CA Fc 25...	...do...........	23	25	14– 17	28.90
CA Fc 26...	...do...........	24	26	14– 17	28.69
CA Fc 27...	...do...........	10	12	9–>12	15.33
Lysimeters:					
CA Fc 28...	Sand, shells......	4	4	—	31.40
CA Fc 29...	...do...........	9	9	—	31.40
CA Fc 30...	...do...........	14	14	—	31.40
CA Fc 31...	...do...........	2	2	—	15.46
CA Fc 32...	...do...........	5	5	—	15.46

[1]Station number: HO Cd in Howard County, Maryland; CA Fc in Calvert County, Maryland.

and grouted with bentonite. CA Fc 33 and CA Fc 34 had stainless-steel points that were installed in the vegetated buffer strip at depths of 14 and 18 ft, respectively. Five wells (CA Fc 13, CA Fc 16, CA Fc 18, CA Fc 33, CA Fc 34) were equipped with automatic water-level recording devices. Lysimeters were installed in the central part of the site at depths of 4, 9, and 14 ft and at the downslope end of the site at depths of 2 and 5 ft. At each group of lysimeters, two soil-moisture tensiometers also were installed at depths of 2 and 5 ft.

Ground-water samples were collected approximately monthly from most of the wells at both study sites from August 1986 through December 1991. Water standing in the well casings was removed by pumping approximately three casing volumes prior to sampling. Sampling was discontinued from the bedrock wells at the Piedmont site after 1 year, except for a few follow-up samples, because nitrogen concentrations in these samples were consistently close to or below the detection limits of 0.2 mg/L or less.

Soil-water samples were collected approximately monthly except during dry periods when the lysimeters were unable to obtain an adequate volume of water. A vacuum was applied to each lysimeter by using a small hand pump, which induced soil water to flow through the porous ceramic cup and to accumulate inside the lysimeter. Samples were collected generally within 1 to 2 days of applying the vacuum.

Ground- and soil-water samples were collected and analyzed in the field according to procedures outlined in "the National Handbook of Recommended Methods for Water-Data Acquisition" (U.S. Geological Survey, 1977). Field measurements included temperature, pH, specific conductance, alkalinity, and dissolved oxygen. Samples for nitrogen analysis were collected by passing 250 mL of water through a cellulose-nitrate filter with 0.45 μm pores into an opaque polyethylene container, preserved with 13 mg of mercuric chloride, placed on ice, and shipped by airfreight to the USGS National Water Quality Laboratory (NWQL) in Denver, Colo. Colorimetry was used (Skougstad and others, 1979) to analyze for such dissolved nitrogen species, as nitrate, nitrite, ammonium, and organic nitrogen. Additional analyses for major ions were made quarterly for 1 year from samples collected at most of the wells.

Automatic water-level-recorder data and steel-tape water-level readings were computer processed at the USGS office in Towson, Md. Water-quality data were computer processed at the NWQL and at the Towson, Md., office. All data were processed and stored in the USGS National Water Information System computer data base and have been published in USGS annual data reports for Maryland (U.S. Geological Survey, 1990).

Transmissivities and horizontal hydraulic conductivities of the aquifers at both study sites were estimated using aquifer-test data. Time-drawdown data were analyzed by using the method of Cooper and Jacob (1946), and by variations of the method of Theis (1935) for nonsteady flow to an aquifer under leaky-confined conditions (Hantush, 1960) in schist at the Piedmont site, and for delayed yield from storage in an aquifer under unconfined conditions (Boulton, 1963) in regolith at the Piedmont site and sand at the Coastal Plain site. Most of the wells had shallow depths and small diameters; both limited the rate at which water could be withdrawn. The performance of available pumping equipment further limited the duration and withdrawal rate at all the wells tested to 2 hours or less and 1 gal/min, respectively.

Because undisturbed samples of aquifer materials were not collected during drilling, samples of similar materials were collected with their structures virtually intact from surface exposures at the downslope ends of the study sites and were analyzed for physical properties, including porosity and grain-size distribution. The surface exposures are in steeply eroded areas in alluvium near the springs at the Piedmont site and in sand along the shore of the Patuxent River at the Coastal Plain site. The materials appeared to be relatively unweathered compared with surface soils and resembled well cuttings in color and texture. The aquifer samples were collected by inserting a thin-walled tube into the aquifer material. Porosity was determined by using the method of Vomocil (1965), and grain-size distribution was determined by sieving.

Bromide-tracer tests were performed at locations where lysimters were installed at both study sites to determine rates of solute transport through the unsaturated zone. About 4 lb of solid sodium bromide was applied manually to the land surface over an area of about 100 ft^2 centered on the location of the lysimeters. Bromide concentration was analyzed by using a bromide-ion specific electrode in several soil-water samples collected before application and in most soil-water samples collected after application.

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GROUND-WATER FLOW

Analysis of solute transport in ground water at the study sites required an accurate understanding of the ground-water flow systems (Reilly and others, 1987). Furthermore, an understanding of the regional flow system in which the study sites are located was needed to understand the local flow systems in the immediate vicinity of the study sites. Areas where water enters and leaves the flow systems were identified to determine boundaries on the systems, and the internal geometries of the systems were defined to estimate the spatial distributions of flow. The resulting conceptualizations of the flow systems were quantitatively represented by numerical ground-water flow models, which were used in analyzing nitrogen transport.

Hydrogeologic Frameworks

Characteristics of ground-water flow systems in the Patuxent River Basin differ between the Piedmont and the Coastal Plain Physiographic Provinces. Different hydrologic conditions between the study sites result from these different characteristics.

Piedmont

In the Piedmont, bedrock is overlain by as much as 100 ft or more of regolith. In central Maryland, the regolith typically ranges from 20 to 40 ft in thickness and is thinner beneath valleys and thicker beneath hilltops (Richardson, 1980). Regolith generally consists of two components: —a granular residual layer of saprolite (derived from weathering of underlying bedrock) and thin, discontinuous alluvial deposits (Heath, 1984). Saprolite is widely distributed throughout the Piedmont, whereas alluvium is generally restricted to areas adjacent to streams (Harned, 1989). Saprolite is generally less permeable than alluvium. Within a few feet of the land surface, porous and permeable surface soil grades downward from the root zone of plants into clay-rich, impermeable saprolite. The saprolite grades into bedrock through a transition zone, which can form the most permeable part of the flow system (Nutter and Otton, 1969). The thickness of the transition zone depends on the parent bedrock; greater thickness is associated with more schistose rock types.

Although the water table can be positioned in bedrock, the saturated zone more typically extends upward into the regolith (LeGrand, 1967). Thus, an unsaturated zone and saturated zone are within the regolith, and the saturated zone includes part of the regolith, as well as the bedrock. Ground water is present in regolith in pores between grains and in bedrock in fractures. Because saprolite is derived from bedrock, the hydraulic conductivity of saprolite on a regional scale of many square miles generally is similar to its parent rock and can range from 0.001 to 1 ft/d (Heath, 1984). Hydraulic conductivity can be anisotropic, depending on such structures as foliation and (or) folds (Harned, 1989). The porosity of saprolite (20–30 percent), however, generally is much higher than that of bedrock (0.01–2 percent) on a regional scale. The hydraulic conductivity of saprolite can be low because pores are not well connected (Ligon and Wilson, 1972).

Regolith serves as a reservoir that supplies water to an interconnected network of bedrock fractures that transmit water to discharge zones (Heath, 1984). Much of the ground water in storage is in regolith. A comparatively small volume of water flows in fractures, but flow velocity through fractures can be fast (Harned, 1989).

Because of its limited availability, ground water in the Piedmont generally is used only for domestic and small municipal supplies. Some shallow bored wells draw water from regolith, but more commonly, wells are drilled into and draw water from the fractured bedrock system.

Ground water in the Piedmont is recharged by precipitation that infiltrates the land surface and percolates through the unsaturated zone to the water table. The shape of the water table generally follows the land surface, and the slope of the water table and direction of ground-water flow generally follow the topographic slope (LeGrand, 1967). From the water table, water flows downward because of gravity and laterally to streams and generally does not cross topographic divides (Richardson, 1980). Ground water is unconfined in most areas (Richardson, 1980), although artesian heads can be in deeper fractures (Nutter and Otton, 1969), usually beneath discharge zones near streams. Stream base flow is supplied largely by ground-water discharge from regolith (Nutter and Otton, 1969).

Because stream networks are closely spaced in the Piedmont, many separate local ground-water flow systems are present (LeGrand, 1967). Perennial stream basins define specific ground-water flow cells that generally are separate from surrounding cells, although some deeper regional flow systems could cover larger areas (Harned, 1989). Most ground-water flow takes place within the upper 30 ft of the flow system where permeability is highest because of the regolith-bedrock transition zone and the highest density of fractures in the shallowest bedrock (Harned, 1989). The most rapid flow could be in the transition zone (Harned, 1989). The areal extent of most individual fractures in bedrock is less than a few hundred feet, although some fracture zones can extend for several miles (Richardson, 1980). Estimates of the maximum depth of water-bearing fractures are 300 ft (Richardson, 1980), 400 ft (LeGrand, 1967), and 800 ft (Heath, 1989).

The Piedmont site is underlain by pelitic schist originally described as belonging to the Wissahickon Formation, Eastern Sequence (Hopson, 1964), but since renamed as the Loch Raven schist (Dine and others, 1992). The schist is a medium- to coarse-grained, micaceous metamorphic rock of Precambrian to Lower Paleozoic age. The study site is positioned between the Clarksville and the Mayfield gneiss domes, and Cockeysville marble and pegmatite dikes are present nearby (Hopson, 1964). The possibility of pegmatite or quartz veins at the study site is indicated by angular quartz cobbles and boulders at and near the land surface.

Well logs indicate that the schist bedrock is overlain by a 30- to 106-ft-thick layer of regolith (fig. 4). The bedrock surface is irregular and does not follow the land surface. Beneath most of the study site, the regolith is fine-grained saprolite that has formed in place by chemical weathering of the schist. The saprolite is thickest in the center and upper part of the study site but thins toward the downslope end of the site. Wells were not logged with sufficient detail to delineate a transition zone between saprolite and schist. Regolith in the downslope part of the study site is permeable coarse-grained alluvium and (or) colluvium (sand, pebbles, cobbles, boulders) that was transported during erosion.

The Piedmont site is at the headwater of a small, unnamed tributary of the Patuxent River. Ground water at the site is present in regolith and schist. Although sustained surface-water flow is not sustained at the study site, surface runoff is channeled toward the downslope end of the site during brief periods of intense rainfall. The water table is within the regolith and generally follows the land surface (figs. 2, 4). The study site consists of a topographic basin that defines a ground-water flow cell that probably is separate from surrounding cells at the local scale outside of the site. Ground water flows from the topographic divide toward two small perennial springs at the southwestern downslope end of the site.

The approximate water-table position, hydraulic-head distribution, and ground-water flow direction

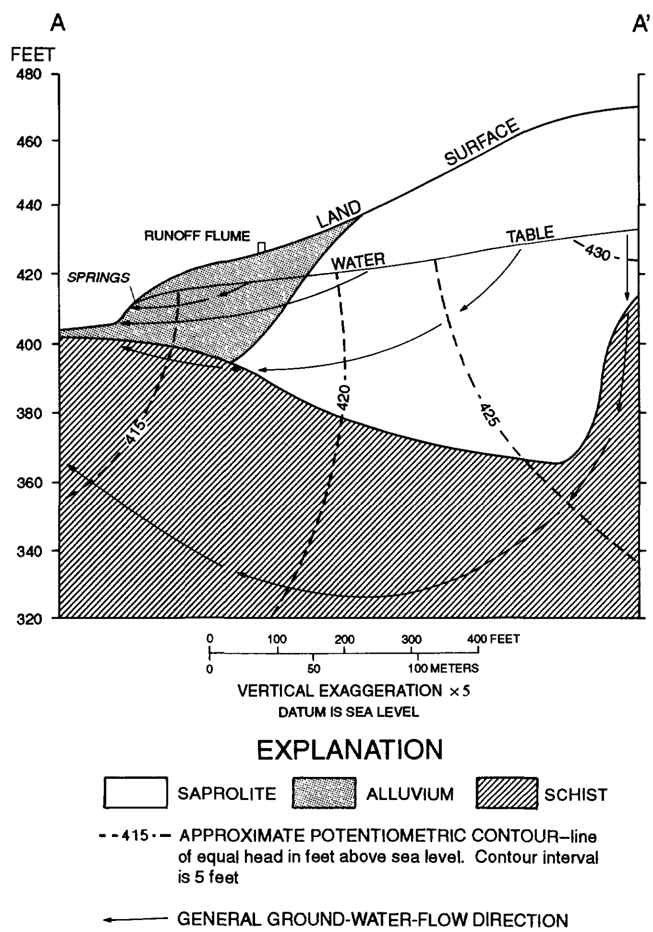

Figure 4. Hydrogeologic section across the Piedmont study site in the Patuxent River Basin, Maryland. Line of hydrogeologic section shown in figure 2.

are represented in vertical section (fig. 4) with the spatial configuration of subsurface materials; the section is vertically exaggerated. Ground-water flow is probably more complex than is represented by the section for several reasons. The water-table position and head distribution (represented by potentiometric contours) are based on water levels measured in wells. Water levels varied over time in all wells (table 2). In addition, wells completed in schist are open over large vertical intervals. Water levels in the schist wells were assumed to represent the head in the schist at the midpoint of the open interval of each well. Wells in schist, however, intersect one or more fractures through which water flows, and the distribution and hydraulic characteristics of the fractures are unknown. Therefore, water levels in schist wells integrate the different heads in individual fractures and only approximately indicate the head distribution in schist.

Hydraulic gradients (fig. 4; table 3) are predominately horizontal in regolith in the central part of the site, vertically downward from regolith into schist at the upslope part of the site, and vertically upward from schist into regolith at the downslope part of the site. The horizontal gradient in schist is less than in regolith. The vertical gradient within regolith in the center part of the site is small.

Ground water in regolith is unconfined and is recharged on site by precipitation that infiltrates the land surface and percolates through the unsaturated zone to the water table. From the water table, water flows downward because of gravity and laterally toward the springs (fig. 4).

Table 3. Approximate mean hydraulic gradients between selected wells at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

[Positive vertical gradients represent downward flow, and negative vertical gradients represent upward flow. See table 2 for explanation of station numbers.]

Direction of flow	Wells	Gradient
Piedmont site		
Horizontal in regolith . .	HO Cd 341–HO Cd 78	0.028
Vertical in regolith	HO Cd 341–HO Cd 28	−.006
Horizontal in schist. . . .	HO Cd 25–HO Cd 20	.018
Between regolith	HO Cd 29–HO Cd 26	.037
and schist.	HO Cd 78–HO Cd 20	−.045
Coastal Plain site		
Horizontal in sand	CA Fc 13–CA Fc 18	.014
	CA Fc 18–CA Fc 34	.025
Vertical in sand.	CA Fc 16–CA Fc 15	−.005
	CA Fc 33–CA Fc 34	.035

Beneath the upslope part of the study site, water flows downward from the base of the regolith into fractures in schist. Although not delineated by well logs, a transition zone between saprolite and schist is probably present at the base of the regolith. Some water that enters the transition zone could flow laterally (Harned, 1989), which would leave less water to continue downward into schist.

Ground water in schist is present almost entirely in fractures because of the low primary permeability of the schist. The amount of ground water in schist is probably small compared with the amount stored in regolith. The linear velocity of flow through individual fractures, however, could be higher than the average linear velocity through regolith. The distribution of fractures is unknown, but is likely to differ spatially because it is closely spaced along some zones and comparatively widely spaced in other areas. Surface drainage can indicate the distribution of fractures, and a possible fracture zone is indicated by the position of the small stream that originates from the springs (fig. 2). The low linear area along which the grass drainage-filter strip is maintained indicates a continuation of the zone upslope of the stream. Two wells (HO Cd 20 and HO Cd 21) were installed in schist along the fracture zone. Pumping of HO Cd 20 resulted in rapid water-level declines in HO Cd 21, which indicated that the wells are connected by fractures with small storage capacities. Other fractures and (or) fracture zones are indicated by water in the other wells (HO Cd 25 and HO Cd 26) installed in schist, but the distribution of these fractures is not indicated by topography or other easily observable features.

Flow at the springs is ground-water discharge from regolith. Additional ground water probably discharges from the site by flowing through regolith and schist beneath the land surface at the springs (fig. 4) and could flow to the land surface along the stream farther downgradient. The vertical gradient is upward from schist into regolith beneath the downslope part of the site, and some of the water in schist probably flows upward into regolith before discharging from the site.

Coastal Plain

Bedrock dips to the east beneath the Coastal Plain Physiographic Province and is overlain by a seaward thickening wedge of unconsolidated sediment. The Fall Line is the westernmost extent of this sediment and defines the boundary between the Coastal Plain and the

Piedmont (fig. 1). The thickness of the sediment wedge in Maryland ranges from 0 ft at the Fall Line to more than 8,000 ft along the Atlantic Coast (Cushing and others, 1973). Near the mouth of the Patuxent River, the sediment is about 3,000 ft thick (Overbeck, 1951).

The sediment wedge consists of a sequence of marine and nonmarine deposits that range in age from Cretaceous to Miocene (Glaser, 1971). The sediments were deposited on flood plains and deltas where streams reached the coast and then reworked by waves and ocean currents during repeated marine transgressions (Heath, 1984). Bedding strikes northeast-southwest and dips southeast at very shallow angles (generally less than 1°), although local strike rotations and dip reversals are common (Glaser, 1971). The deposits are subdivided into a sequence of geologic formations that crop out at the land surface along arcuate bands that parallel the Fall Line; the ages of the formations at the land surface decrease to the southeast. During Pleistocene time, a thin veneer of nearly flat-lying sediment was deposited over much of the sediment wedge (Glaser, 1971). In addition, because sea level fluctuated several hundred feet during Pleistocene time, major river channels were eroded through parts of the sediment wedge and then refilled with Pleistocene-age deposits.

The sediment sequence forms a geohydrologic framework of aquifers and confining units (Meng and Harsh, 1988). Permeable formations from which significant amounts of water are drawn are known as aquifers, and less permeable formations that partly restrict ground-water flow are known as confining units. Because of large thicknesses and large areal extents, Coastal Plain aquifers provide a widely used ground-water supply (Heath, 1984).

Unconfined ground water is present primarily in the Pleistocene deposits (Chapelle and Drummond, 1983). Much of the unconfined ground water flows short distances and discharges to nearby streams, but a small amount flows downward to recharge the deeper aquifers. Recharge to the deep aquifers is primarily beneath interfluves (areas of high elevation between major river valleys) (Harsh and Laczniak, 1990). Recharge is highest where the aquifers crop out or subcrop where aquifers are overlain only by Pleistocene sediments (Chapelle and Drummond, 1983). Less water enters the aquifers by downward flow across confining units than through outcrops and subcrops, but more can enter near Pleistocene channels where confining units are breached and adjacent aquifers are hydraulically connected (Harsh and Laczniak, 1990). Water also possibly enters the aquifers by upward flow from the underlying bedrock, if flow from the Piedmont extends beneath the Coastal Plain sediment wedge.

Flow through the confined aquifers is primarily lateral in the down-dip direction to the southeast and toward major discharge areas near large rivers and coastal water (Harsh and Laczniak, 1990). Because of the stratification of the sediments, horizontal hydraulic conductivity is commonly higher than vertical hydraulic conductivity. The confined aquifers discharge by upward flow across intervening confining units to the discharge areas. Discharge increases where Pleistocene channels have breached the confining units and connected the aquifers.

The Coastal Plain site is located next to the Patuxent Estuary (figs. 1, 3) on a broad terrace that borders the estuary in Calvert County (Overbeck, 1951). The Talbot Formation, which is one of three subdivisions of the Pleistocene deposits, is described as occupying near-shore areas of the Patuxent River and consisting of mostly sand with some gravel and marine shells (Overbeck, 1951). The terrace is more recently mapped as containing Pleistocene lowland deposits, which consist mostly of medium- to coarse-grained sand and pebbly sand (Glaser, 1971). The thickness of the deposits throughout the Coastal Plain in Maryland ranges from 0 to 150 ft, but 20 to 30 ft is more typical.

Pleistocene deposits are underlain by Miocene-age deposits of the Chesapeake Group, which is subdivided into the Calvert, the Choptank, and the Saint Marys Formations (Overbeck, 1951). The three formations can differ in age but are lithologically similar and together consist of nearly 300 ft of clay, clayey sand and silt, and highly fossiliferous sand (Glaser, 1971). An exposure located less than 1 mi from the study site, along the shore of the Patuxent River at the mouth of Saint Leonard Creek, contains indurated fossiliferous sand belonging to the Choptank Formation (Glaser, 1971). Exposed about 0.25 mi uphill of this location is 20 ft of lowland deposits consisting of coarse-grained pebbly sand (Glaser, 1971).

Sediments beneath the Coastal Plain site probably consist of the Chesapeake Group, specifically the Choptank Formation, which is overlain by Pleistocene lowland deposits. Well logs indicate that a 30-ft-thick layer of quartz sand overlies a layer of clay that extends beneath the entire site (fig. 5). The top surface of the clay generally is parallel to the land surface. Clay also is mixed or finely interbedded with sand at depths of 5 to 10 ft below the land surface throughout the site and at depths of 10 to 20 ft beneath the center of the site. Parts of the sand that are deeper than 15 to 30 ft contain abundant calcareous fossil bivalve shells and are cemented with calcite, indicating that the lower part of the sand could belong to the Chesapeake Group.

Ground water is present in the sand. Although surface-water flow is not sustained at the study site, surface runoff is channeled toward the downslope end of the site during brief periods of intense rainfall. The upper and lower parts of the sand probably are divided between Pleistocene lowland deposits and the Chesapeake Group, respectively, but the entire volume of sand functions hydraulically as an aquifer under unconfined conditions. The water table is planer in shape and slopes toward the Patuxent River (fig. 3), following the land surface and top surface of the clay but at a shallower angle and intersects the clay at the upgradient end of the study site (fig. 5).

The clay that underlies the entire site probably belongs to the Chesapeake Group, which because of its large proportion of clay, is not considered to be an aquifer that could be used as a regional water supply (Overbeck, 1951) and is a confining unit to the underlying Piney Point–Nanjemoy aquifer (Chapelle and Drummond, 1983). The clay truncates the saturated zone within the sand at the Coastal Plain site (fig. 5) and bounds the upgradient end of the sand aquifer. Exploratory borings for a geotechnical study of building construction in the farmyard area intersect the clay (M.A. Smolek, Jefferson Patterson Park, written commun., 1990). A continuous saturated zone in the sand was not found to overlie the clay in the borings east of the study site. Discontinuous, thin saturated zones, however, could exist for brief periods during recharge.

The approximate position of the water table, hydraulic-head distribution, and ground-water flow direction are represented in vertical section (fig. 5) with the spatial configuration of subsurface materials; the section is vertically exaggerated. The water table and head distribution (represented by potentiometric contours) are based on water levels measured in wells. Ground-water flow is probably more complex than is represented by the section because a range of water levels was measured in each well during the study period (table 2).

The hydraulic gradient within the sand is primarily horizontal (table 3) and steepens toward the Patuxent River (figs. 3, 5). The vertical gradient within the sand is small, except near the shore where it increases downward. The vertical gradient between the sand and underlying clay is unknown because no wells were installed to measure water levels in the clay. The clay probably is relatively impermeable compared with the sand, however, and restricts vertical flow to or from the underlying confined Piney Point-Nanjemoy aquifer.

Ground water in sand is unconfined. From the water table, water flows primarily laterally away from the upgradient edge of the saturated zone and toward the Patuxent River where it discharges (fig. 5). Point measurements of submarine ground-water discharge rates at

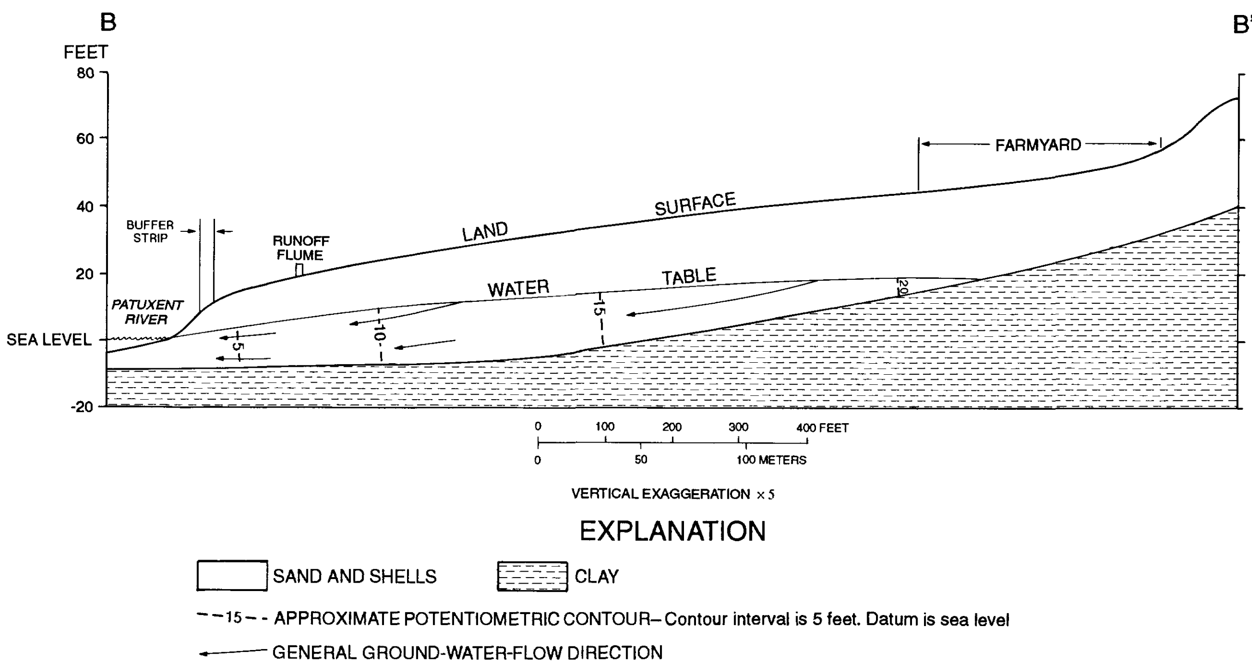

Figure 5. Hydrogeologic section across the Coastal Plain study site in the Patuxent River Basin, Maryland. Line of hydrogeologic section shown in figure 3.

the Coastal Plain site (Zimmerman, 1990) and at other similar locations along the shore of Chesapeake Bay (Simmons and others, 1990) indicate that the discharge area could extend more than 100 ft from the shore on the basis of a discharge rate equal to the estimated recharge rate of 7 in/yr (see section "Simulation of Ground-Water Flow").

Because the study site is next to the Patuxent River, which is a regional discharge zone, unconfined ground water probably does not flow downward through the clay to recharge the underlying confined Piney Point–Nanjemoy aquifer. Although flow through the clay was not determined at this site, the regional setting indicates that ground water more likely flows upward from the confined aquifer through the clay and into the unconfined aquifer before discharging into the Patuxent River. Data collected outside but near the study site indicate, however, that upward flow from the confined aquifer also is unlikely in this area. Water levels in Maryland Water-Level Network observation wells CA Fd 51, CA Fe 22, and SM Df 66, which were completed in the underlying Piney Point–Nanjemoy aquifer within 10 mi of the study site, averaged close to or below sea level during the period of study (U.S. Geological Survey, 1990). In addition, a model-simulated potentiometric surface of the Piney Point–Nanjemoy aquifer for 1990 is approximately at sea level near the study site (Chapelle and Drummond, 1983). The apparently small hydraulic gradient between the Piney Point–Nanjemoy aquifer and the Patuxent River precludes the potential for upward flow near the study site.

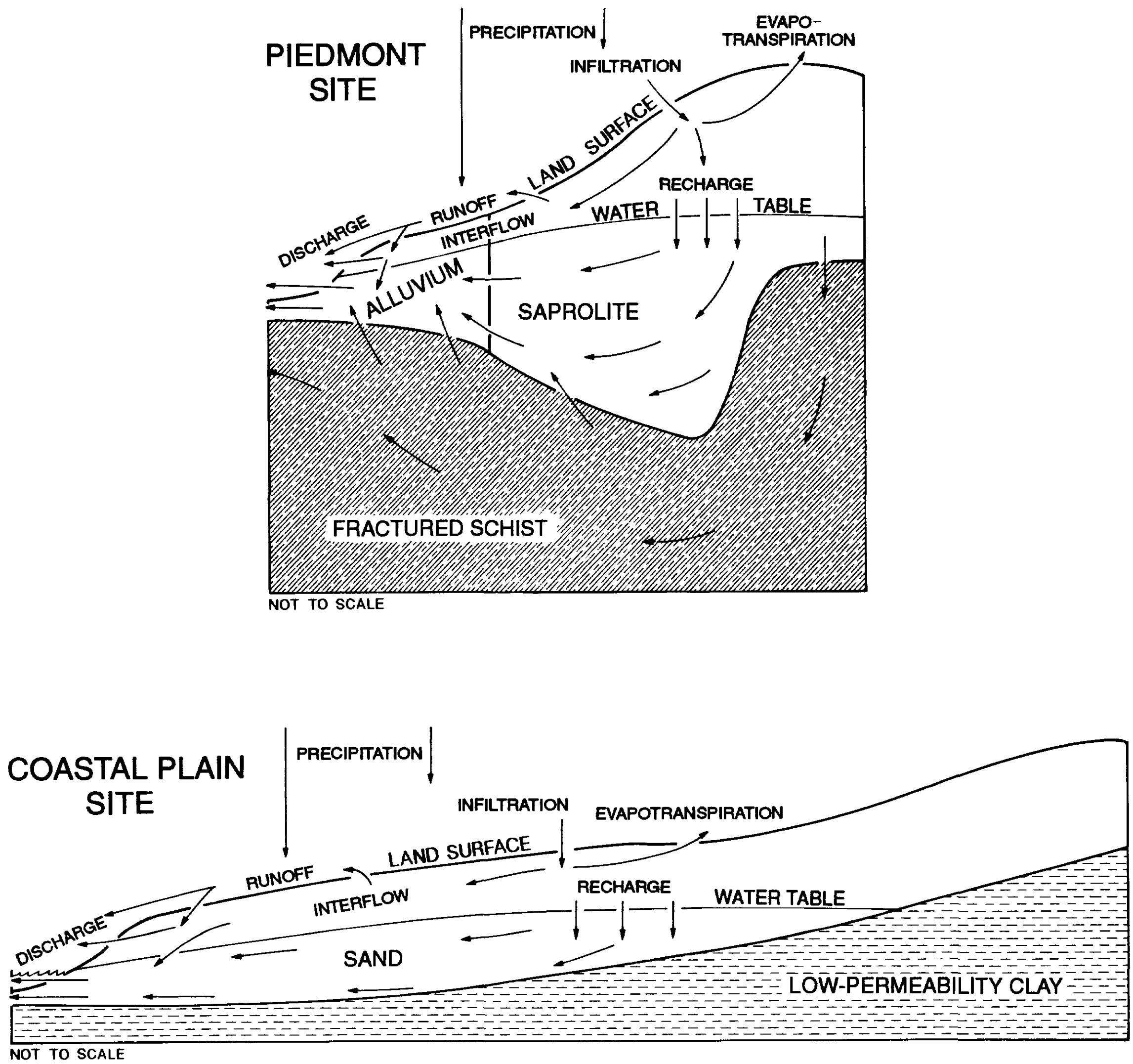

Figure 6. Conceptualized ground-water-flow systems at the study sites in the Patuxent River Basin, Maryland.

Recharge/Discharge Relations

Flow through the study sites is divided into different components (fig. 6). Most precipitation infiltrates the land surface, although occasionally the infiltration capacity of the soil is exceeded, and surface runoff is produced. Part of the water that infiltrates the surface is returned to the atmosphere by evapotranspiration. The remainder either flows through the unsaturated zone as interflow (some of which may resurface to produce runoff), percolates through the unsaturated zone to the water table to recharge the unconfined aquifer, or is stored in the unsaturated zone as soil moisture.

Water-level data show seasonal trends that indicate cycles of recharge and discharge at both study sites (figs. 7, 8). Ground water discharges continuously from the downgradient ends of the study sites and are replaced by precipitation that infiltrates the land surface and percolates through the unsaturated zone to the water table (fig. 6). Recharge is indicated by rises in the altitude of the water table, typically during the period from January to May when the rate of evapotranspiration is small. When the recharge rate exceeds the discharge rate, the excess water is stored in the aquifer, causing the water table to rise.

By June, land-surface temperatures rise, and plant growth begins to increase, both of which increase the rate of evapotranspiration. Most of the precipitation that infiltrates during the period from June to December is returned to the atmosphere or stored in the unsaturated zone. Little or no precipitation recharges the ground-water system, even though the amount of precipitation is similar to other times of the year. Ground water is released from storage and continues to discharge off-site, but is not replaced by recharge. Therefore, the water table declines.

The amount and duration of recharge at the study sites differed from year to year and between the sites. Year-to-year differences in recharge at each site could have resulted from differences in precipitation, land-surface temperature and other climatic factors, and agricultural practice. Additionally, the unsaturated zone is thinner and probably more permeable at the Coastal Plain site than at the Piedmont site, and flow velocities in the zone probably are faster and traveltimes shorter. For comparison, faster recharge than that found at either of the sites for this study was observed throughout the year in an agricultural area underlain by a karst flow system in Pennsylvania (Gerhart, 1986; Hall, 1992b), where water percolates through sinkholes and bedrock fractures enlarged by solution weathering. Storage of the water in the unsaturated zone and removal by evapotranspiration were probably larger at both study sites than in karst areas.

No recharge took place at the study sites until soil-moisture content was large, as indicated by moisture tension that is near zero (figs. 7, 8). Soil generally dried when the rate of evapotranspiration was high. When evapotranspiration decreased, [soil-moisture content increased, generally several months before recharge began. Soil-moisture contents typically change seasonally—less in deep soil than shallow soil and more beneath the base of slopes rather than further uphill (Chorley, 1978). A lag time of several months can pass after soil moisture is replenished and before recharge occurs (Ligon and Wilson, 1972).

When the rate of evapotranspiration is low, water that infiltrates the land surface nearly saturates (about 80 percent) the upper soil layers, creating a wetting front (Chorley, 1978). Water percolates downward through the unsaturated zone under the influence of gravity and also from wet areas to dry areas under the influence of a moisture-tension gradient. The wetting front moves downward under the tension gradient in a manner similar to the rise of capillary water from the water table. Behind the wetting front, water is retained by the field capacity of the soil where the downward force of gravity is equal to the moisture tension. Additional infiltration pushes the water already present farther downward.

When the rate of evapotranspiration is high, much of the water that infiltrates the land surface is returned to the atmosphere, and little or no water percolates to the water table. Soil near the land surface becomes dryer than deeper soil; this difference results in an upward moisture-tension gradient that induces flow toward the land surface. Consequently, a vertical gradient divide can form between zones of upward and downward flow (Dennehy and McMahon, 1987). This gradient produces a stagnation point of no flow. Although data from the study sites were not adequate to indicate divides, multiple gradient divides could be produced by alternating periods of infiltration and evapotranspiration, and the resulting distribution of hydraulic head in the unsaturated zone can be complex.

Not all the water that infiltrates and is not removed by evapotranspiration recharges ground

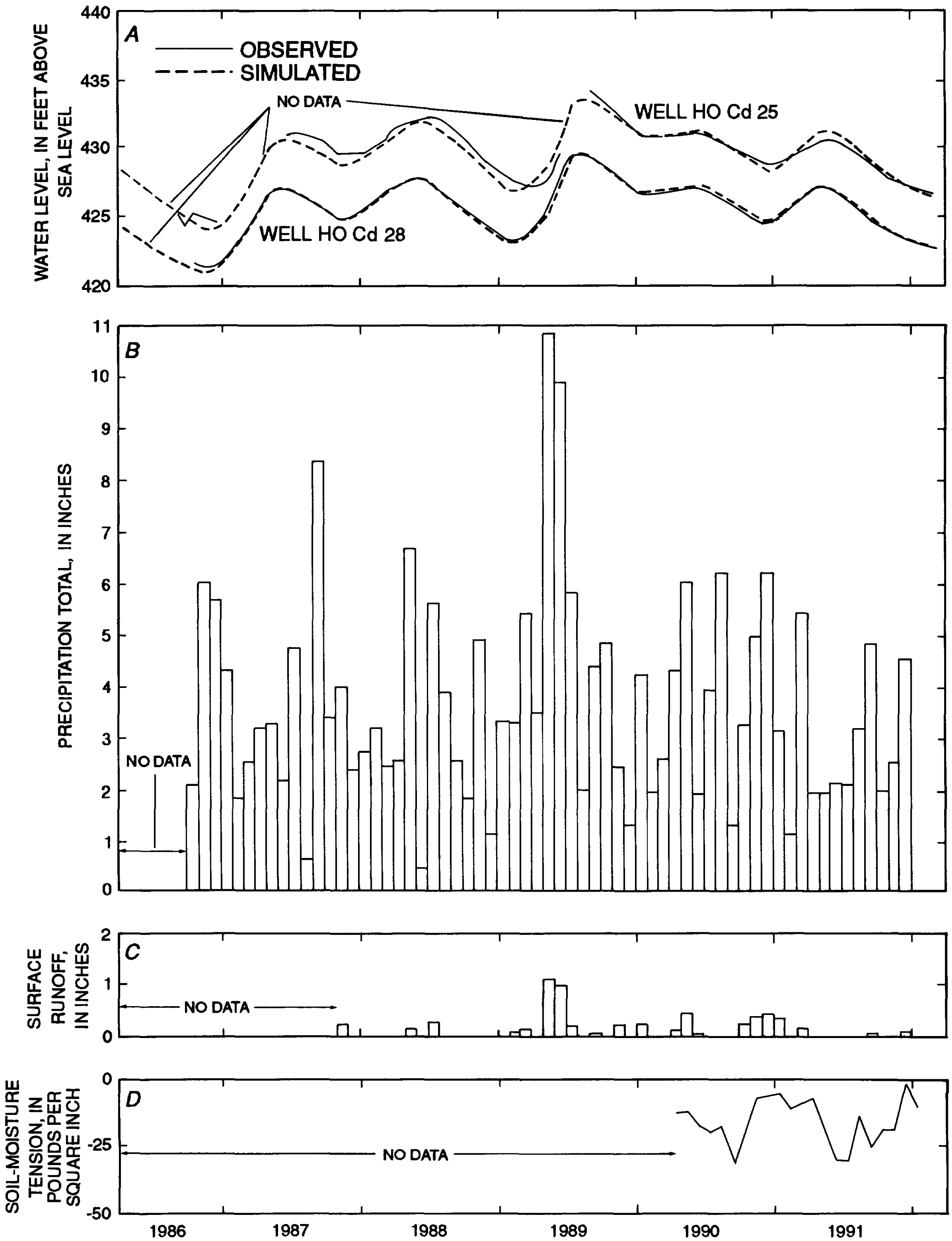

Figure 7. Observed and simulated water levels in selected wells (*A*), total monthly precipitation (*B*), total monthly surface runoff (*C*), and monthly mean soil-moisture tension (*D*), at the Piedmont study site in the Patuxent River Basin, Maryland.

water. Percolating water commonly encounters one or more impermeable soil layers, such as the B soil horizon underlying the study areas, where it slows and saturates the soil above the layer, creating a perched water table (Chorley, 1978). Much of the perched water can flow laterally as interflow without intersecting the

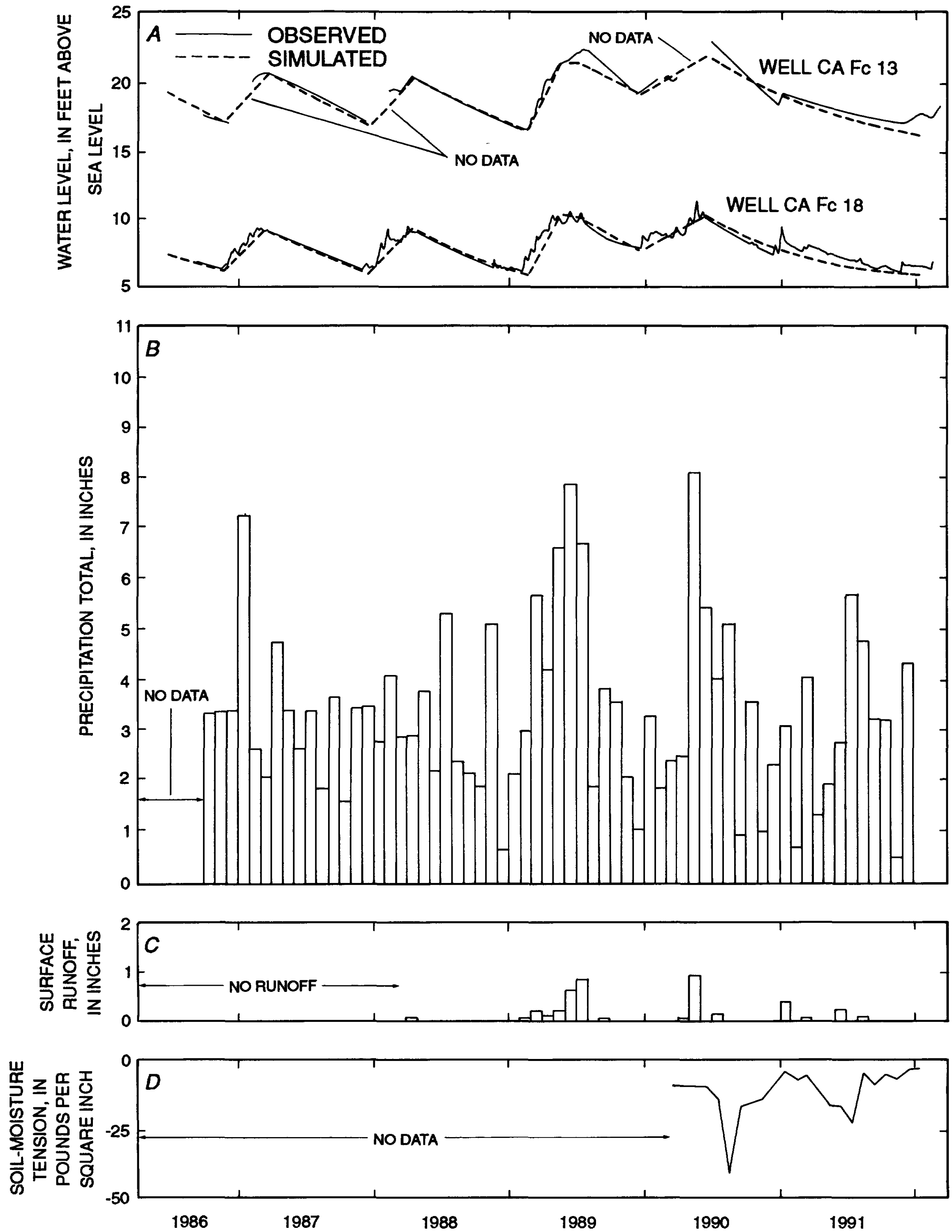

Figure 8. Observed and simulated water levels in selected wells (*A*), total monthly precipitation (*B*), total monthly surface runoff (*C*), and monthly mean soil-moisture tension (*D*), at the Coastal Plain study site in the Patuxent River Basin, Maryland.

permanent water table to recharge ground water (fig. 6). As much as 62 percent of the total precipitation on the land surface can move through the subsurface as interflow (Dunne, 1978). Interflow also takes place in macropores, such as root holes and animal burrows, without the soil being fully saturated.

The amount of water that percolates to the water table generally is less than that in interflow and can take from months to years to reach the water table (Chorley, 1978). Because water reaches the water table during recharge by being displaced downward by infiltration at the land surface, recharge water can be considerably older than that which is infiltrating. Unsaturated flow traveltimes are probably slower at the Piedmont site than at the Coastal Plain site, and recharging water at the Piedmont site is probably older than that at the Coastal Plain site.

Interflow can discharge directly to streams for up to several weeks after infiltration (Chorley, 1978). Interflow also can join flow from the permanently saturated ground-water zone in discharge areas near streams (fig. 6). Thus, some part of the subsurface discharge to the springs at the Piedmont study site and to the Patuxent River at the Coastal Plain study site probably is interflow.

Toward the base of slopes, interflow can rise under artesian pressure and continue across the land surface as runoff. Because precipitation is rarely of sufficient intensity to exceed the infiltration capacity of soil, most surface runoff is resurfaced interflow (Chorley, 1978). Concave topography, such as streamhead hollows, converges interflow to a limited contributing area at the base of the slope, resulting in a high antecedent soil-moisture content that promotes rapid resaturation of the soil and resurfacing of interflow. At both study sites, surface runoff is primarily toward the downslope ends of the sites and probably originates largely from interflow (fig. 6). Also, interflow was intercepted by the outer sides of the runoff flumes, which is similar to shallow cutoff trenches, and was channeled to the surface at the downslope ends of the flumes. Thus, at the study sites, amounts of water equal to or greater than ground-water recharge probably flow through as interflow.

Most of the water in surface runoff at the study sites probably does not leave the sites from the land surface. Instead, water collects in the level areas below the runoff flumes, reinfiltrates the land surface, and joins interflow and (or) flow from the permanently saturated ground-water zone before discharging from the study sites (fig. 6). Occasionally, runoff discharges directly to the small stream at the Piedmont site and to the Patuxent River at the Coastal Plain site, as indicated by small channels at the downslope ends of the sites. Most of the water, however, leaves the sites through the subsurface.

Simulation of Ground-Water Flow

Saturated ground-water flow at the study sites was quantitatively represented by mathematical-numerical models that were developed on the basis of the conceptual frameworks described in the preceding sections. Quantitative representation serves two purposes—analysis of the hydraulic characteristics and spatial distribution of flow within the shallow ground-water flow system at each of the study sites and determination of temporal changes in ground-water flow. Temporal changes could be related to agricultural practices, as well as to changes in precipitation and other climatic factors, and can be used to calculate nitrogen loads in ground water. The models were used to examine the spatial and temporal routings of water in aquifers and other surface and subsurface pathways through the study sites. Saturated ground-water flow was simulated by using MODFLOW, which is a modular three-dimensional finite-difference ground-water flow model (McDonald and Harbaugh, 1988).

Ground-water flow is described by a partial differential equation that cannot be solved exactly except for very simple systems. The finite-difference model consists of a series of algebraic equations that approximately describe ground-water flow between specified aquifer subsections or cells. A grid of square cells scaled to 40 ft per side was superimposed on a topographic map of each site to divide the aquifers into discrete cells (figs. 9, 10). The hydraulic characteristics of the aquifers, any sources or sinks of water other than flow from adjacent cells, and an initial approximation of hydraulic head are specified for each cell. The model area is defined by boundaries along which conditions of flow or head are specified. By using iterative calculations, a computer program of the model simultaneously solves the series of equations for the hydraulic head and the rate and volume of ground-water flow in each aquifer cell. The strongly implicit procedure was used to solve the equations.

Model Designs and Boundary Conditions

Ground-water flow systems at the study sites are complex. Conceptual models of the hydrogeologic frameworks at the sites were used to define boundary conditions, however, and their use allows the flow systems to be translated into simple forms for mathematical simulation. At both study sites, the model area was defined by lateral and vertical hydrologic boundaries by using the conventions of Franke and others (1987).

Piedmont Site

The ground-water flow model for the Piedmont site contains two layers—an upper to represent regolith under unconfined conditions and a lower to represent schist under confined conditions. Most of the upper regolith layer represents saprolite. Part of the upper layer corresponding to the downslope end of the study site represents alluvium (fig. 9), however, a zone surrounding the alluvium represents a mixture or gradation zone consisting partly of alluvium and partly of saprolite. At the study site, a transition zone could be present at the base of the regolith between saprolite and schist (see section "Hydrogeologic Frameworks"); well-log data, however, are inadequate to delineate a transition zone as a distinctly separate part of the regolith, and the presence and hydraulic properties of a transition zone are unknown. Therefore, a transition zone was not represented separately from regolith as an additional layer in the model.

The Piedmont study site consists of a topographic basin that defines a ground-water flow cell, which probably is separate from surrounding cells outside of the site. Ground water flows from the topographic divide toward two springs (see section "Hydrogeologic Frameworks"). Accordingly, a no-flow boundary was specified on the northern and eastern sides of the model area, corresponding to the topographic divide, which was assumed to coincide with a water-table divide (fig. 9). The shape of the water table at the study site generally follows the land surface, and the position of the water-table divide probably remains fixed because aerial recharge is the only stress applied to the flow system. No-flow boundaries also were specified on the southern and western sides of the model area along flow lines that were inferred from the observed shape of the water table (fig. 2). Water moves along the flow lines, but cannot cross them.

Ground water discharges from the Piedmont site at and beneath the two springs at the head of a small stream (see section "Hydrogeologic Frameworks"). Flow from the site converges on the stream in a radial direction toward the springs. Accordingly, a constant head was specified in the model for the cell corresponding to location of the springs at the

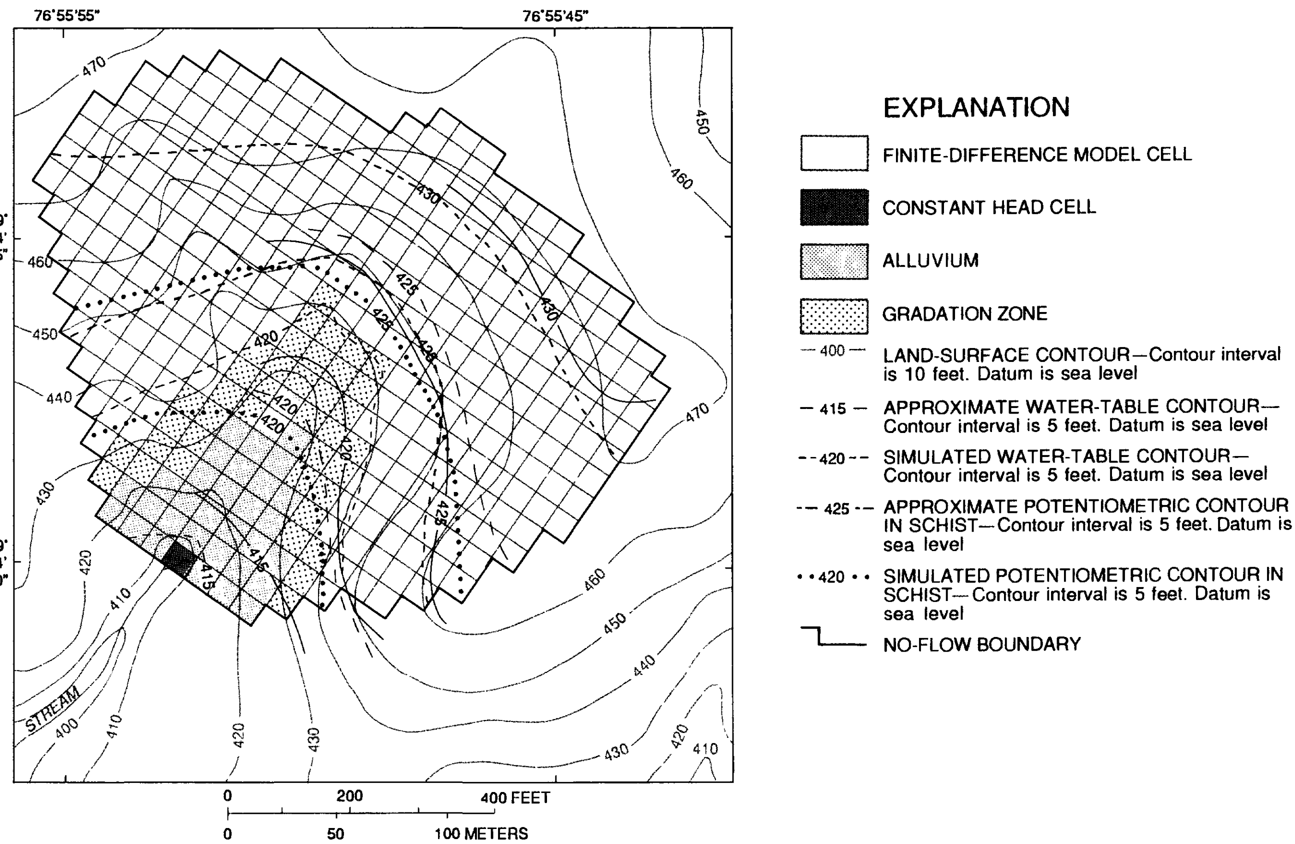

Figure 9. Grid and boundaries of ground-water-flow model and observed and simulated steady-state water-table contours and potentiometric surface contours at the Piedmont study site in the Patuxent River Basin, Maryland.

southwestern corner of the model area. On the basis of the approximate altitude of the springs and on the difference in head between regolith and schist at the downgradient end of the site, constant heads of 413 and 415 ft above sea level were specified for the upper regolith layer and lower schist layer, respectively. The volume and rate of flow through the cell can fluctuate.

The altitude of the top of the aquifer under unconfined conditions in the flow model was designated by the water table, which was simulated as a free surface in regolith that can fluctuate except at the constant-head cell in which the springs are located. Horizontal flow in the unconfined aquifer was simulated as a single layer in regolith. The altitude of the base of the regolith layer was designated by the regolith/schist contact, as indicated by well logs for cells that correspond to well locations. The base of the regolith layer for other cells was interpolated between the wells. The underlying second layer represents the confined schist aquifer and is bounded at its base by a no-flow boundary. The thickness of the schist layer was considered to be 60 ft, which is the approximate penetration of the wells drilled in schist.

All ground water that enters the model area is simulated as recharge at the water table in regolith. From the water table, ground water can flow laterally through regolith and downward into schist. Water also can subsequently flow upward from schist into regolith. All ground water leaves the model area by flowing from regolith and schist through the constant-head cell corresponding to the location of the springs.

Coastal Plain Site

The ground-water flow model for the Coastal Plain site contains one layer representing sand under unconfined conditions. The upgradient edge of the aquifer at the site is bounded along the line of intersection between the water table and the top of the clay layer (fig. 5). Ground water flows primarily laterally and discharges into the Patuxent River (see section "Hydrogeologic Frameworks"). Accordingly, a no-flow boundary was specified along the eastern side of the model area corresponding to the intersection of the water table and the top of the clay layer (fig. 10). Although the saturated zone at the site continues into the clay, the clay probably has a lower hydraulic conductivity than the sand, and flow between the sand and clay is negligible. Therefore, water was simulated in the model as not flowing to or from the clay into the sand. No-flow boundaries also were specified on the northern and southern sides of the model area along flow lines inferred from the observed water table because water cannot cross lines of flow.

Ground water discharges from the Coastal Plain site into the Patuxent River (see section "Hydrogeologic Frameworks"). Accordingly, a head-dependent flux boundary was specified along the western side of the model area corresponding to the shore of the river (fig. 10). The simulated volume and rate of discharge across the boundary can fluctuate and is a function of the simulated difference in head between the aquifer and the river and of the specified conductance of riverbed material along the boundary. Cells representing the river were assigned a head value of 0 ft above sea level (the approximate altitude of the shore of the river along the boundary). Because of tides, the actual river stage fluctuates by a small amount compared to the difference in head across the site, and the tidal effect on flow was assumed to be negligible.

The altitude of the top of the layer under unconfined conditions in the flow model was designated by the water table, which was simulated as a free surface in sand that can fluctuate. Horizontal flow in the unconfined aquifer was simulated as a single layer in sand. The altitude of the base of the sand layer was designated by the sand/clay contact, as indicated by well logs for cells that correspond to well locations. The base of the sand layer for other cells was interpolated between the wells. Because the hydraulic conductivity of the underlying clay probably is less than that of the sand and unconfined ground water at the study site does not appear to flow into or out of the regional flow system (see section "Hydrogeologic Frameworks"), the sand layer in the model is bounded at its base by a no-flow boundary, and no additional layers were included to represent deeper aquifers.

All ground water that enters the model area is simulated as recharge at the water table in sand. From the water table, ground water can flow laterally through the sand, but not downward into clay. Water also cannot flow upward from clay into sand. All ground water leaves the model area by flowing through sand along the head-dependent flux boundary corresponding to the shore of the Patuxent River.

Model Calibration

After lateral and vertical boundaries were defined, hydrologic data were input to the model computer code, and the computer program was executed to output data that represented the ground-water flow system at each

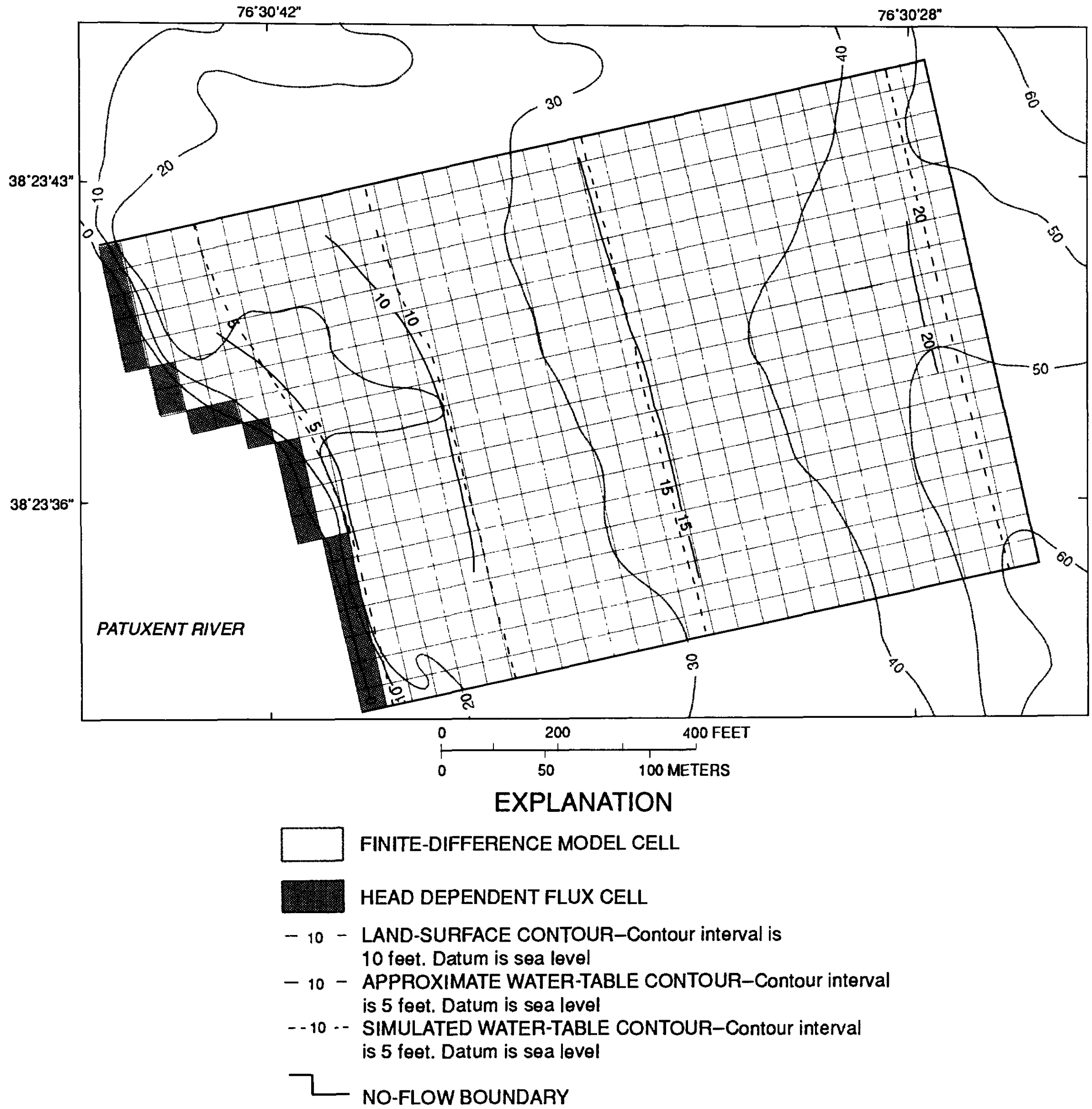

Figure 10. Grid and boundaries of ground-water-flow model and observed and simulated steady-state water-table contours and potentiometric surface contours at the Coastal Plain study site in the Patuxent River Basin, Maryland.

study site. To the extent possible, input data were based initially on field-measured values. Measured values were not available for all inputs required by the model, however, values for unmeasured inputs had to be selected from within realistic ranges on the basis of the types of aquifer materials at the study sites and published data for the region. In addition, the field-measured values are only estimates made at the point of measurement and are possibly not appropriate effective values to represent the flow system mathematically at the scale at which the models are constructed (Cooley and Naff, 1990). Therefore, some inputs were adjusted during repeated executions of the model program on the basis of how well the inputs probably represented the flow system at the scale of the study sites. No further adjustments to the inputs were made when simulated heads were approximately equal to water levels measured at corresponding areal locations at the study sites. The resulting "calibration" values for the model inputs were compared with available field measurements and published data.

The degree of uncertainty in the model inputs was evaluated by determining the sensitivity of the model representation of the flow system to changes in the value of each input. The model program was repeatedly executed while each input was changed from the calibration value by fixed increments. The inputs were then ranked according to their relative magnitudes of effect.

Ground-water flow at the study sites was simulated under steady-state and transient conditions. Steady-state simulations provide static representations of the flow system in which conditions of flow do not change over time and were performed first to analyze hydraulic characteristics and the spatial distribution of flow. Transient simulations provide dynamic representations of the flow system in which flow conditions change over time in response to changes in storage and applied stresses and were performed next to determine changes in ground-water flow during the period of study. The same boundaries on the model areas, as described above, were used for both types of simulations, but different calibration procedures were required.

Steady-State Simulations

The hydraulic characteristics and spatial distribution of flow within the shallow ground-water flow system at each of the study sites was analyzed by performing steady-state simulations. Mathematical representations of steady-state ground-water flow generally consist of systems of equations that relate values for hydraulic head, volumetric flow rate, and hydraulic conductivity or transmissivity. If two of the values are known, then the equations can be solved for the third value. Field-based measurements or estimates were made for all three values but with different sources and degrees of error associated with each.

Hydraulic head usually is estimated from measurements of water levels in wells open to an aquifer. Generally, water levels can be accurately measured to within a hundredth of a foot. Wells open at different depths at a single areal location, however, often exhibit different water levels because of vertical hydraulic gradients in the aquifer. In contrast, model-simulated hydraulic head for a single layer represents a vertically averaged value (Cooley and Naff, 1990) and does not differ with depth through the layer. If vertical gradients in the aquifer are high, then accurate simulation may require the aquifer to be divided into more than one layer. Conversely, if vertical gradients are low relative to horizontal gradients, then the aquifer can be simulated as a single layer in which average head is estimated from water levels but could differ from actual head by several feet or more.

At the Piedmont site, vertical gradients between regolith and schist are similar in magnitude to horizontal gradients (see section "Hydrogeologic Frameworks"). Therefore, separate model layers were used to represent regolith and schist. Water levels measured in wells open to regolith and schist were used to estimate the average head in the upper and lower layers, respectively. Vertical gradients within parts of the regolith and schist probably exist, and water levels in some wells will differ from the average head in each layer (particularly in schist because heads are likely to be distributed irregularly in fractures).

At the Coastal Plain site, gradients are primarily horizontal in the sand, and because unconfined ground water does not appear to flow through the underlying clay and into or out of deeper confined aquifers (see section "Hydrogeologic Frameworks"), one model layer was used to represent the sand. Water levels measured in wells open to sand were used to estimate the head in the single model layer.

The volumetric flow rate at both study sites is equal to the rate of recharge because recharge is the only source of water to the sites. Net annual groundwater recharge at each site was estimated by using hydrograph-separation techniques (Pettyjohn and Henning, 1979) on streamflow data from nearby streamflow-gaging stations in similar hydrologic settings. Fixed-interval, sliding-interval, and local-minimum methods gave similar estimates of recharge rate. When using these methods, two things need to be assumed—the ground- and surface-water divides coincide for the drainage area above the gage and the volume of stored ground water shows no net change for the period. The estimates represent net recharge and do not include water that is removed from the aquifer by evapotranspiration.

The closest streamflow-gaging station to the Piedmont site is the Middle Patuxent River at Simpsonville, Md., which at the time of the analysis had only 1 complete year of records (1988). Analysis of the data resulted in a recharge rate of about 8 in/yr. The closest streamflow-gaging station to the Coastal Plain site is the St. Marys River at St. Marys City, Md., with records from 1986 to 1988. Analysis resulted in recharge rates of about 7 in/yr. These rates are averages over areas that are approximately 100 times larger than the study sites, parts of which could have different land use and subsurface hydrologic properties and could receive different amounts of precipitation than the study sites. Therefore, recharge at the study sites

Table 4. Physical and hydraulic properties of aquifer materials measured at study sites in the Piedmont and the Coastal Plain Physiographic Provinces in the Patuxent River Basin in Maryland, published for the Physiographic Provinces, and used in calibrated ground-water-flow models

[mm, millimeter; —, no data]

Properties measured	Piedmont site			Coastal Plain site	
	Saprolite	Alluvium	Schist	Sand	Cemented sand
Grain-size distribution measured at site (percent):					
Larger than 2 mm	—	10–27	—	0 -2	—
0.063–2 mm	—	61–64	—	64 -99	—
Smaller than 0.063 mm	—	9–29	—	1 -36	—
Porosity (percent)					
Measured at study site	—	36–55	11	45 -52	35
Published values	[a]20–[b]52	—	[a].01–[b]5	—	—
Horizontal hydraulic conductivity (feet per day)					
Measured at study site	.01–.18	3.0–5.8	—	2.4–10.1	—
Published values	[e].003–[d]20	—	—	—	—
Calibration value	.18	12.6	—	3.9	—
Transmissivity (feet squared per day)					
Measured at study site	—	—	2.2–13.5	—	—
Published values	—	—	[e]12–[b]4,600	—	—
Calibration value	—	—	10.8	—	—
Specific storage					
Published values	[b]0–[b]29	—	[b]0–[e].17	—	—
Calibration value	7	7	.004	.1	—

[a]Heath, 1984. [b]Nutter and Otton, 1969. [c]LeGrand, 1967. [d]Harned, 1989. [e]Richardson, 1980.

could differ from the estimated rates by several inches per year.

Values for transmissivity are input to the flow model to represent aquifers under confined conditions. For aquifers under unconfined conditions, the saturated thickness and, hence, the transmissivity differ with changes in the position of the water table. Therefore, values of horizontal hydraulic conductivity are input to the model to represent aquifers under unconfined conditions. Transmissivity is then calculated in the computer code by multiplying hydraulic conductivity by the saturated thickness that results from the position of the water table.

Horizontal hydraulic conductivity of regolith at the Piedmont site and sand at the Coastal Plain site and transmissivity of schist at the Piedmont site were estimated by analysis of aquifer-test data (table 4). Time-drawdown data were analyzed by using both the method of Cooper and Jacob (1946) and variations of the method of Theis (1935) by Hantush (1960) and Boulton (1963) (see section "Methods of Investigation"). The methods generally are based on the following assumptions: the aquifers are of infinite horizontal extent; they are uniform in thickness, homogeneous, and isotropic; and water flows through pores. Although water in schist at the Piedmont site flows through fractures, the volume of schist beneath the site probably is large compared to the volume of the fractures, and the schist is assumed to approximate a porous medium. At best, the assumed conditions are probably only approximated within the zone of influence from pumping at both study sites.

How well the aquifer-test results represent the study sites for simulation of ground-water flow is uncertain. At least some of the aforementioned analytical assumptions are probably unrealistic at the study sites. In addition, the analytical methods involve graphical techniques that are subject to the judgment of the analyst. Furthermore, the test data are limited. The shallow depths and small diameters of the wells and the limitations of available pumping equipment restricted the duration and withdrawal rate at the wells to 2 hours or less and 1 gal/min, respectively. As a result, pumping the wells in the aquifers under unconfined conditions may not have produced an adequate stress over a sufficient period to induce pore drainage, and data from wells open to the schist at the Piedmont site probably show the effects of flow through only a small number of fractures. Therefore, the aquifer tests probably indicate conditions only within the proximity of the wells. The hydraulic properties of the aquifers are probably heterogeneous and are appropriately represented mathematically with effective values for the scale at which the models are developed, a scale that could differ from the aquifer-test results by an order of magnitude or more.

Of the three values that are related by mathematical representations of steady-state ground-water flow, hydraulic head and volumetric flow rate (as recharge) probably were estimated more accurately by field-based measurements than by hydraulic conductivity and transmissivity. To simulate ground-water flow at the study sites, therefore, recharge rates were specified as the values estimated by hydrograph separation, while hydraulic conductivities of the unconfined aquifers (and transmissivity of schist at the Piedmont site) were adjusted during repeated executions of the model program. No further adjustments to the hydraulic properties were made when simulated heads in each model layer approximately equaled water levels measured at corresponding areal locations at the study sites (figs. 9, 10). A range of water levels was measured at each well during the period of study; that range was compared to simulated heads. Because simulated heads do not differ vertically within a single model layer, they do not precisely equal measured water levels at all corresponding areal locations.

Hydraulic properties of an aquifer can differ in different directions, and horizontal hydraulic conductivity and transmissivity can be either isotropic or anisotropic. Horizontal isotropy was assumed initially for all model layers at both study sites. Several different degrees of anisotropy were assumed during subsequent adjustments of hydraulic conductivity and transmissivity, but were found not to be required to produce simulated heads to approximate measured water levels. Therefore, isotropic conditions were specified for the final calibration values, and hydraulic conductivity and transmissivity are constant in the horizontal direction in all model layers.

Recharge, hydraulic conductivity, and transmissivity can differ spatially within the model area. As previously discussed, the possible range of recharge rates probably is smaller than that of hydraulic conductivities and transmissivities. Therefore, recharge was specified to be aerially uniform, and the magnitude and spatial distribution of hydraulic conductivity and transmissivity were changed aerially where necessary within realistic ranges for simulated heads to approximate measured water levels.

Piedmont Site

Part of the upper model layer represents alluvium (fig. 9), which was specified to have a higher hydraulic conductivity than saprolite on the basis of the relative difference in values of hydraulic conductivity from aquifer tests (table 4). A zone next to the alluvium was specified to have an intermediate hydraulic conductivity and represents a mixture or gradation zone that consists partly of saprolite and partly of alluvium. The transmissivity of schist in the lower model layer was specified to be aerially uniform. The value for transmissivity is based on the assumption that the schist has the same hydraulic conductivity as saprolite and that the thickness of the fractured water-bearing zone in schist is 60 ft, which is the approximate length of the open interval of the wells in schist. Calibration values for hydraulic conductivity and transmissivity are relatively close to the aquifer-test results (table 4) as compared with the degree of uncertainty in the results.

Two layers were specified in model simulation because water flows vertically between regolith and schist (see section "Model Designs and Boundary Conditions"). Therefore, a model input to represent conditions of vertical flow is required. Although horizontal hydraulic conductivity and transmissivity are input to the model computer code, the vertical hydraulic conductivity of each layer is not specified explicitly. Instead, vertical leakance is specified to represent the conductance of water between model layers. Vertical leakance is based on a thickness-weighted average of the vertical hydraulic conductivities of adjacent layers. Measured values from the Piedmont site are not available on which to base vertical leakance, however, and a value initially was selected from within a realistic range and adjusted during calibration.

A vertical leakance between the regolith and schist layers of 0.0008 per day resulted in simulated differences in head between the two layers that approximate measured water-level differences between regolith and schist. If the thickness between the layers is taken to be 60 ft, which is approximately the vertical distance between the midpoints or nodes in the upper and lower layers, then the average vertical hydraulic conductivity is 0.048 ft/d, which is one to three orders of magnitude less than the horizontal conductivity. Vertical hydraulic conductivity is commonly less than horizontal hydraulic conductivity in many hydrogeologic settings.

Ground water is discharged from the model area by flowing through the constant-head cell corresponding to the location of the springs (see section "Model Designs and Boundary Conditions"). The amount of flow is determined by the head value, which was specified to be the altitude of the springs, and no additional data were required.

Coastal Plain Site

The composition of the sand aquifer under unconfined conditions at the Coastal Plain site is relatively uniform compared to regolith at the Piedmont site. Therefore, hydraulic conductivity of the sand layer was specified in the flow model to be aerially uniform (table 4). The calibration value for hydraulic conductivity is relatively close to the aquifer-test results as compared with the degree of uncertainty in the results.

Only one layer was specified in model simulation because vertical flow into, out of, or within the aquifer under unconfined conditions at the Coastal Plain site was assumed to be negligible (see section "Model Designs and Boundary Conditions"). Therefore, representation of ground-water flow is mathematically reduced to two dimensions in the horizontal direction, vertical flow is set to zero, and a model input to represent conditions of vertical flow is not required.

Ground water is discharged across a head-dependent flux boundary specified along the western side of the model area (fig. 10), corresponding to the shore of the Patuxent River (see section "Model Designs and Boundary Conditions"). The amount of flow is determined by the simulated difference in head between the aquifer and the river and the specified conductance of riverbed material. The river was assigned a head value of 0 ft above sea level (the approximate altitude of the shore of the river along the boundary). The conductance of the riverbed material depends on the geometric configuration of the riverbed (length, width, and thickness within each model cell) and hydraulic conductivity according to the following relation:

$$C = \frac{KLW}{M},$$

where

C is conductance,
K is hydraulic conductivity,
L is length,
W is width, and
M is thickness.

Because of the large size of the Patuxent River relative to the model cells, the riverbed was assumed to overlie the aquifer entirely throughout each of the cells along the boundary; the thickness and hydraulic conductivity of the riverbed are unknown. Riverbed conductance cannot be determined directly without field measurements of river seepage and associated head differences. Therefore, an initial arbitrary conductance value was chosen from within a realistic range and adjusted during calibration.

A riverbed conductance of 18.5 ft^2/d resulted in simulated heads that approximate measured water levels. Assuming that the riverbed entirely overlies the aquifer throughout each of the cells along the boundary, the length and width of the riverbed in each cell are both 40 ft. If the riverbed were 10 ft thick, then it would have a vertical hydraulic conductivity of about 0.1 ft/d. If the riverbed were only 1 ft thick, then vertical hydraulic conductivity would be 0.01 ft/d. Relatively small hydraulic conductivities such as these could be expected in the bed of the estuary because of a high percentage of organic material and fine-grained sediments.

Sensitivity Analysis

The degree of uncertainty in model inputs was evaluated by determining the sensitivity of simulated heads to each input. The model program was repeatedly executed while each value of each input was changed in fixed increments by up to an order of magnitude above and below the calibration value. The root-mean-square error was calculated from differences between simulated heads and measured water levels for each execution and plotted with the multiplication factor used to change the model input value incrementally (fig. 11). A curve was then fitted through the points that resulted from the change of each input.

All the curves pass through a point with a multiplication factor of 1, which represents the calibration

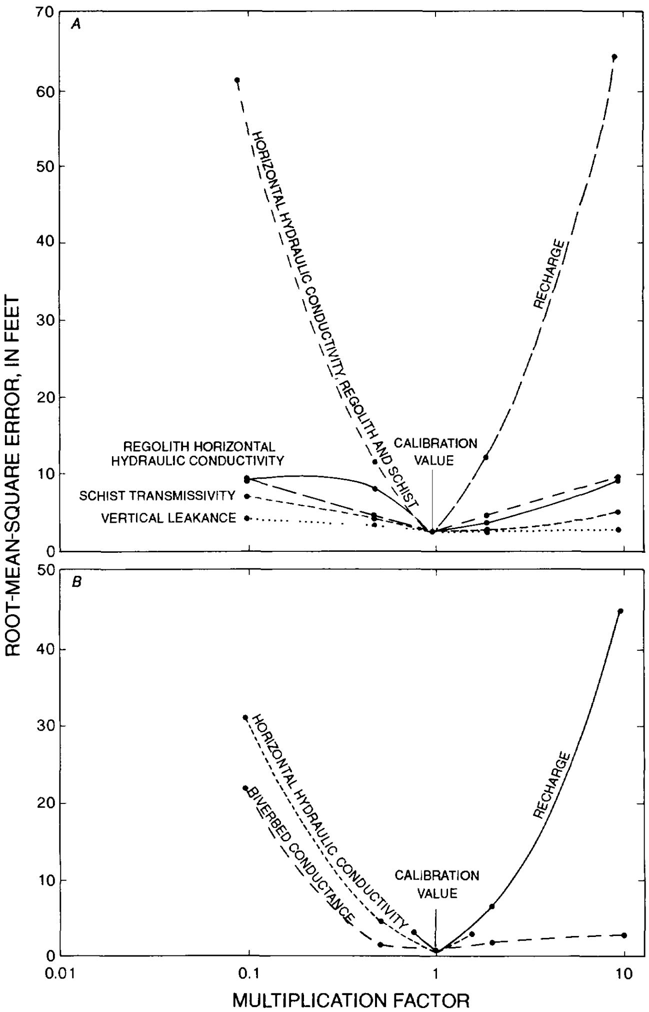

Figure 11. Sensitivity of simulated water levels to changes in values of hydraulic properties input to ground-water flow models of the Piedmont (*A*) and Coastal Plain (*B*) study sites in the Patuxent River Basin, Maryland.

value. The root-mean-square error is least at the calibration value because the calibration value produced the smallest difference between simulated heads and measured water levels. The calibration value for recharge rate is the value estimated by hydrograph separation. The other inputs are or are related to hydraulic conductivity and were adjusted for simulated heads to approximate measured water levels.

Changes of inputs that produced large differences between simulated heads and measured water levels plot as steep curves. The results of the model are strongly dependent on the degree of certainty with which these inputs were estimated. Changes of inputs that produced small differences between simulated heads and measured water levels plot as flat curves. The degree of certainty with which these inputs were estimated is unimportant because they do not strongly affect model results.

For the Piedmont site, the calibration value for the transmissivity of schist was specified, assuming that the horizontal hydraulic conductivity of schist is equal to that of saprolite. Because the horizontal hydraulic conductivity of regolith and the transmissivity of schist are related, similar differences result in the field. Therefore, transmissivity values input to the model were changed together, as well as separately, to represent the effect of the conductive property of the entire two-layer flow system (fig. 11). Reducing regolith hydraulic conductivity and schist transmissivity below their calibration values together created a greater effect than reducing them separately. Increasing the values together produced a lesser effect than decreasing together and produced a similar effect as increasing separately.

Increasing the conductive property of the flow system in the model flattens hydraulic gradients and the water table and lowers heads. The constant-head cell located at the springs imposes a lower limit on heads. Decreasing the conductive property steepens gradients and the water table and raises heads, which do not have an upper limit.

Varying values for the rate of recharge in the model of the Piedmont site produced a curve that mirrors the combined regolith hydraulic conductivity/schist transmissivity curve (fig. 11). Increasing the volumetric flow rate is equivalent to decreasing conductivity, which results in the same effect described in the preceding paragraph.

As indicated by steep curves (fig. 11), model results are equally dependent on input values for recharge rate and combined regolith hydraulic conductivity/schist transmissivity, and the degree of certainty with which these values were estimated is equally important for the model to represent the flow system at the Piedmont site accurately. When considered separately, regolith hydraulic conductivity has a slightly greater effect than schist transmissivity, but both are less than their combined effect.

The input value for vertical leakance between the regolith and schist layers in the model of the Piedmont site has a small effect. Because measured values of vertical leakance were not available, a value had to be selected arbitrarily from within a realistic range. The degree of certainty with which vertical leakance was estimated is unimportant, however, because vertical leakance does not strongly affect model results.

The constant-head specified for the cell corresponding to the location of the springs at the Piedmont site sets the head in the layer throughout the cell equal to the altitude of the springs. Flow through the cell is a function solely of the difference in head between the cell and adjacent cells. To evaluate the effects of these assumptions on simulated heads, flow through the cell was altered to a head-dependent flux, which is a function of the specified conductance of bed material in the springs and the difference in head between the cells. Measured values of bed-material conductance were not available but high values, 10,000 ft^2/d or higher, were required to produce simulated heads equal to those produced by using a constant-head boundary. Decreasing conductance to 1,000 ft^2/d slightly increased the difference between simulated heads and measured water levels, but the effect was less than that which resulted from changing the other inputs.

For the Coastal Plain site, the curve produced by changing values for recharge rate is a mirror image of the hydraulic conductivity curve (fig. 11), similar to the Piedmont site. As before, increasing the volumetric flow rate is equivalent to decreasing conductivity, and model results are equally dependent on the degree of certainty with which recharge rate and hydraulic conductivity were estimated for the model to represent the flow system at the Coastal Plain site accurately.

The range of input values for hydraulic conductivity in the model of the Coastal Plain site was limited at the upper end, and recharge rate was limited at the lower end. These limitations were imposed because cells in the upgradient part of the model area went dry. The saturated thickness is lowest at the upgradient end of the model layer, and changing the inputs beyond these ranges caused some model cells to go dry if enough water were not supplied by recharge or if hydraulic conductivity were too high, which allowed water to flow out of the cells too quickly. Because no part of the aquifer at the Coastal Plain site was observed to go dry during the study period, dewatering of model cells is not realistic. Further, because some cells went dry corresponding to well locations, no heads were simulated with which to calculate the root-mean-square error. Therefore, values for hydraulic conductivity and recharge rate were not extended beyond the point at which cells would run dry.

Riverbed conductance in the model of the Coastal Plain site has the least effect of the model inputs. Measured values of riverbed conductance were not available, and a value had to be selected arbitrarily from within a realistic range. The degree of certainty with which riverbed conductance was estimated is less significant than the other inputs, however, because riverbed conductance does not as strongly affect model results.

The effect of changing the input value of riverbed conductance is small for values above the calibration value but larger for values below the calibration value. Increasing riverbed conductance in the model flattens the hydraulic gradient between the model layer and the river and lowers heads in the layer. The head of the river imposes a lower limit on heads in the layer. With an infinitely large conductance, the head-dependent flux boundary would become a constant-head boundary along which the head in the layer would be equal to the head of the river. Decreasing riverbed conductance without an upper limit steepens the gradient and raises heads.

For both study sites, steady-state simulation of ground-water flow was calibrated by using field-based estimates of recharge rate, which can differ from values that accurately represent the study sites by several inches per year. Steady-state simulations provide static representations of the flow system in which conditions of flow do not change over time. Estimates of hydraulic conductivity also were obtained from field data but can differ from values that accurately represent the study sites by an order of magnitude or more. Therefore, hydraulic conductivity and the other related model inputs were adjusted for simulated heads to approximate measured water levels. Because recharge rate and hydraulic conductivity have equal effects on model results, recharge rate is the better input on which to base calibration of the models because of its smaller range.

Transient Simulations

Transient simulations provide dynamic representations of the flow system in which flow conditions change over time in response to changes in storage and applied stresses. Recharge is the only stress on the aquifers simulated in the models of the study sites. Transient simulations were performed after the steady-state simulations to determine changes in ground-water flow during the period of study. Changes in flow could be related to agricultural practices, as well as changes in precipitation and other climatic factors, and can be used to calculate nitrogen loads in ground water. The same boundaries on the model areas were used but different calibration procedures were required.

Ground-water flow is represented by transient simulations for the periods March 1986 through February 1992 at the Piedmont site and June 1986 through January 1992 at the Coastal Plain site. The simulation periods are divided into 18 stress periods at the Piedmont site and 11 stress periods at the Coastal Plain site. Recharge differs among stress periods but is constant during each stress period, which is divided into one or more time steps for which conditions of flow are calculated. All time steps used in these models represent 1 month. Stress periods range from one to several monthly time steps.

Mathematical representations of transient ground-water flow generally consist of systems of equations that relate values for hydraulic head, volumetric flow rate, and hydraulic conductivity or transmissivity (as with steady-state flow) and values for storage. Also, changes in flow through time are dependent on the initial head, which must be specified at the beginning of the simulation period.

Prior simulation of steady-state flow provides a framework in which mathematical relations that can be extended to transient simulation are established. Transient-simulated hydraulic head is a vertically averaged value for each layer and is estimated from water levels, as in steady-state simulation but can change in time in response to changes in flow through the layer and into or out of storage (see section "Recharge/Discharge Relations"). Volumetric flow rate (as recharge) also can change over time. Hydraulic conductivity and transmissivity, however, are properties of the aquifers that do not change over time (except in cases of large withdrawls or recharge, neither of which are applicable here). Calibration values of hydraulic conductivity and transmissivity from the steady-state simulations were assumed to be appropriate effective values to represent the aquifers mathematically and, therefore, were used in the transient simulations.

Transient simulations represent changes in ground-water flow that result from changes in recharge, and recharge rates must be specified for each stress period. Estimates of recharge rate from hydrograph-separation methods formed the basis for calibration of the steady-state simulations but represented only average values for the gaged basins closest to the study sites. Recharge estimates were not available for different times during the study period. To perform transient simulations, therefore, the hydraulic conductivities of the layers representing aquifers under unconfined conditions, as well as the transmissivity of the layer representing schist under confined conditions at the Piedmont site, were specified as the steady-state calibration values, whereas the value of the recharge rate for each stress period was adjusted during repeated executions of the model program. Initial head was specified as that produced by the calibrated steady-state simulations. Calibration of transient simulations was complete when output data from heads that approximately equaled water levels measured at corresponding locations and times in each model layer were produced (figs. 7, 8). Simulated heads do not differ vertically within layers, and do not precisely equal measured water levels at all corresponding locations and times (see section "Steady-State Simulations").

When recharge rates at the study sites exceed discharge rates, excess water is stored in the aquifers, and water levels rise (figs. 7, 8). When recharge is less than discharge, water levels decline as ground water is released from storage (see section "Recharge/Discharge Relations"). The amount of water that goes into or out of storage per unit change in head is represented in the model program by input values of specific yield for layers under unconfined conditions (regolith for the Piedmont site, sand for the Coastal Plain site) and of the storage coefficient for layers under confined conditions (schist for the Piedmont site). Because of aquifer-test limitations (see section "Steady-State Simulations"), time-drawdown data are inadequate to provide estimates of specific yield and storage coefficient. Values had to be selected arbitrarily from within realistic ranges (table 4) and were adjusted during repeated executions of the model program for simulated heads to approximate measured water levels.

Recharge rate and storage had to be determined by adjusting input values, but both affected simulated heads. During periods of rapid water-level decline, however, recharge rate was assumed to equal zero and, with hydraulic conductivity and transmissivity specified, simulated heads depended only on storage. Therefore, storage was adjusted first for simulated heads to approximate measured water levels during periods of water-level decline, and recharge rate was set to zero. Recharge rates then were adjusted during periods of water-level rise and, as in the steady-state simulations, were aerially uniformly distributed.

As in steady-state simulation, the degree of uncertainty in the inputs for transient simulation was evaluated by determining the sensitivity of simulated heads to each input. Water-level measurements were not available for all locations and times corresponding to transient simulated heads, however, root-mean-square errors could not be calculated from differences between simulated heads and measured water levels. Therefore, only sensitivity effects were determined. Differences between simulated heads and measured water levels were qualitatively examined after repeatedly executing the model program and changing each input value by fixed increments. Similar to steady-state simulations, the effects of changing input values in transient simulations of both study sites are greatest for recharge rate and hydraulic conductivity and least for vertical leakance for the Piedmont site and riverbed conductance for the Coastal Plain site. The effect of changing storage, which is included only in transient simulation, but not in steady-state simulation, is intermediate between the other inputs for both study sites. Changing storage of the regolith and schist layers together in the Piedmont site model produced the same effect as changing the storage of the regolith layer separately. Changing storage of the schist layer separately produced little effect because the volume of water flowing through and stored in the schist layer is small compared with the regolith layer (see section "Flow Through the Aquifers").

For both study sites, steady-state simulations provided approximate effective values of hydraulic conductivity and related model inputs; these values which were used in transient simulations to determine differences in recharge during different parts of the study period. In the steady-state simulations, however, recharge was specified from hydrograph-separation estimates, which can differ from values that accurately represent the study sites by several inches per year, and upon which the accuracy of the models is dependent to represent the volume of ground water flowing through the study sites. Therefore, model simulation is useful mostly for determining the spatial distribution of ground-water flow through the study sites, and, in the case of transient simulations, determining differences in the amount of recharge during different parts of the study period.

Distribution of Flow

Data that were input to and output from the ground-water flow model simulations of the study sites and additional field data were used to determine the spatial and temporal distributions of flow in aquifers, as well as on the land surface and through the unsaturated zone at the study sites. Simulated rates and amounts of water that flows into, through, and out of the aquifers and amounts of water stored in the aquifers were calculated. Amounts of time required for ground water to flow through different parts of the study sites were compared. Simulated recharge was compared with measured total amounts of water that enter the study sites in the form of precipitation and with amounts leaving the study sites, including measured surface runoff and unmeasured evapotranspiration and interflow in the unsaturated zone.

Flow Through the Aquifers

In steady-state simulations, conditions of flow do not change over time, and the amount of water stored in the aquifers shows no net changes. Therefore, the rates at which water was specified to enter the simulated flow systems as recharge equal the rates at which water leaves as discharge (table 5). Because two layers were used in the model of the Piedmont site to represent regolith and schist, steady-state flow is divided into two components—one through regolith and the other through schist. Only one layer, which represents sand, was used in the Coastal Plain site model, and flow is not divided into more than one component.

Table 5. Simulated ground-water flow rates and amounts at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

[in/yr, inch per year; in., inch. Positive storage values represent water taken into storage, and negative storage values represent water released from storage.]

Flow component	Steady-state simulation flow rate (in/yr)	Transient simulation amount (in.)				
		1987	1988	1989	1990	1991
Piedmont site						
Net recharge...	8.00	9.43	7.19	11.26	5.72	6.70
Regolith into schist.	2.34	2.27	2.41	2.50	2.35	2.27
Schist into regolith.	2.03	1.81	2.10	2.04	2.17	2.03
Discharge from regolith.	7.69	7.78	7.93	8.50	7.55	7.32
Discharge from schist.	.30	.28	.32	.33	.31	.28
Storage in regolith.	.00	1.19	-1.05	2.30	-2.01	-.86
Storage in schist.	.00	.18	-.01	.13	-.13	-.04
Coastal Plain site						
Net recharge...	7.00	4.74	6.32	9.00	7.14	1.98
Discharge.....	7.00	6.02	6.04	6.88	7.23	4.79
Storage.......	.00	-1.28	.28	2.12	-.09	-2.81

All ground water enters the Piedmont site model as recharge at the water table in the regolith layer under unconfined conditions. From the water table, ground water flows laterally through the regolith layer, and some water flows downward into the schist layer under confined conditions. Most of the water in the schist layer flows back into the regolith layer, however, and only a small amount (0.30 in/yr) remains to discharge out of the flow system from the schist layer (table 5). Therefore, most of the water that enters the flow system at the Piedmont site as recharge probably leaves as discharge from regolith, but about one-fourth of the water could initially flow through schist. All ground water leaves the model by flowing from the regolith and schist layers through the constant-head cell corresponding to the location of the springs.

All ground water enters the Coastal Plain site model as recharge at the water table in the sand layer under unconfined conditions. From the water table, ground water flows laterally through the sand layer and leaves the model by flowing through the head-dependent flux boundary corresponding to the shore of the Patuxent River.

In transient simulations, recharge rates change in time, thereby changing the amounts of water that flow through, discharge from, and are stored in the model layers. Flow amounts in the form of recharge, discharge, and storage in the models were calculated from the transient simulations for the years 1987 to 1991 (table 5).

During years when recharge in the model of the Piedmont site was larger than discharge (1987, 1989), the excess water was stored (table 5). In years when more water discharged than entered as recharge (1988, 1990, 1991), water was released from storage. Regolith serves as the primary storage reservoir at the Piedmont site, and little water is stored or released from schist. The amount of recharge differs from year to year more than the amount of discharge from either regolith or schist; the differences are accounted for by changes in storage, primarily in regolith. The exchange of water between regolith and schist remains constant from year to year.

In the model of the Coastal Plain site, excess water was stored in the sand layer during those years when recharge was larger than discharge (1988, 1989) and released from storage when recharge was less than discharge (1987, 1990, 1991) (table 5). Similar to the Piedmont site, the amount of recharge differs from year to year more than the amount of discharge; the differences are accounted for by changes in storage.

Ground-water flow-model data and other data were analyzed to estimate the amount of time required for water to flow through the aquifers at the study sites. Average horizontal linear velocities of ground water, calculated from model-calibration values of hydraulic conductivity, measured hydraulic gradients, and estimated porosities, were used to estimate traveltimes of ground water flowing the entire length of the study sites (table 6). On the basis of published values (table 4), a porosity of 40 percent was used for all granular materials, and 2 percent was used for schist. Because different aquifer materials in regolith at the Piedmont site have different hydraulic conductivities, flow velocities and traveltimes through different parts of regolith were calculated separately and were added to equal the total traveltime through regolith. Traveltime through schist was calculated separately.

Traveltimes of ground water flowing through the entire length of the study sites represent the maximum amount of time the water remains in the aquifers beneath the sites, as well as the amount of time required for flow to displace the entire volume of water in the aquifers. Water that enters the aquifers at any point other than the upgradient ends of the sites, however, will have a shorter flow path and a shorter traveltime. Therefore, mean residence times also were calculated (table 6) by dividing the simulated volume of water in the aquifers by the simulated volumetric flow rates.

Table 6. Horizontal ground-water flow velocities, flow-path lengths, and traveltimes and residence times at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

[ft/yr, feet per year; ft, feet; —, not calculated]

Aquifer material	Average horizontal linear velocity (ft/yr)	Maximum flow path length (ft)	Maximum traveltime (year)	Mean residence time (year)
Piedmont site				
Saprolite	4.6	350	76	23
Gradation zone between saprolite and alluvium.	138	100	.7	3.0
Alluvium	322	150	.5	1.3
Schist	59	650	11	6.2
Undifferentiated	—	—	—	25
Coastal Plain site				
Sand	40	1,100	27	9.7

Ground-water volumes were calculated by multiplying saturated thicknesses of aquifers represented in model layers in steady-state flow simulations by the model areas and estimated aquifer porosities. Volumetric flow rates were assumed to equal steady-state recharge rates. Initially, volumes of water in regolith and schist at the Piedmont site were calculated separately and added to calculate the mean residence time of the undifferentiated regolith/schist flow system, but flow is partitioned among different materials in different parts of the aquifer (table 5). Therefore, for comparison, mean residence times of ground water at the Piedmont site also were calculated separately for different parts of the aquifer as a result of dividing the ground-water volumes by the flow rates through each part (table 6).

Ground-water traveltimes and mean residence times represent two divergent views of the ground-water flow system, neither of which probably describes the flow system with complete accuracy. Traveltimes can be used to represent the age of ground water flowing from one end of the aquifer to the other without mixing in a linear horizontal manner described as "piston" flow. In this view, only 6 percent of the water in regolith (traveltime of 77 years), but 45 percent of the water in schist (traveltime of 11 years), flowed out of the Piedmont site during the 5-year study period as a result of being displaced by recharge from the upgradient end of the aquifer at the study site. At the Coastal Plain site (traveltime of 27 years), 19 percent of the water in the aquifer flowed out of the site in 5 years.

Recharge enters the aquifers at both study sites aerially over the entire water-table surface and not just at the upgradient ends of the aquifers at the sites. Mean residence times represent the age of ground water if it were to mix completely by dispersion throughout the aquifer before discharging, regardless of the location at which the recharge entered the aquifer. Accordingly, 20 percent of the water in the undifferentiated regolith/schist aquifer at the Piedmont site (residence time of 25 years) flowed out of the site during the 5-year study period, and 52 percent flowed out of the Coastal Plain site (residence time of 9.7 years). Residence times and flow rates through different aquifer materials at the Piedmont site, which also were used to calculate cumulative residence times through different parts of the aquifer, indicate that 22 percent of ground water flowed out of the site in 5 years. Of all recharge to the aquifers during the 5-year study period, only 20 to 22 percent of the water at the Piedmont site and 52 percent of the water at the Coastal Plain site have since been discharged.

Ground water probably does not flow at either site in a manner similar to piston flow, nor is ground water completely mixed by dispersion throughout the entire aquifer before discharging. From the water-table surface, water moves along flow lines of different length depending on the distance to the downgradient end of the site (figs. 4, 5). The velocity at which the water moves and, hence, the amount of time since the water entered the aquifer, depend on the hydraulic gradient and properties of the aquifer materials, both of which can change with position along the flow line. Water from adjacent flow lines also can be mixed by dispersion. Thus, the spatial distribution of the age of ground water can be complex.

To examine possible ground-water age distributions at the study sites, steady-state flow-model data were analyzed by using particle-tracking procedures. Flow paths through the model layers were calculated from model data by using a computer program called MODPATH (Pollock, 1989). Points of elapsed traveltime were plotted along flow paths and then contoured to represent schematically the age distribution of ground water at the study sites (fig. 12). Ground water appears to be stratified at both study sites. Water that recharged the aquifers during the 5-year study period remains close to the water table, whereas older ground water is deeper.

Ground-water age, which is indicated by particle-tracking analysis, increases with depth in the models of both study sites (fig. 12). In the model of the Piedmont site, however, the vertical age profile is partly inverted toward the downgradient end of the model area, where water in the schist is younger than some of the water in the regolith. Flow velocity at the Piedmont site is considerably higher in schist than in saprolite (table 6) because schist has a low porosity and water flows quickly through fractures. Water that enters schist can flow a longer distance in a given amount of time than water that remains in saprolite. Thus, water in schist can overtake water in saprolite, and as a result, water that flows from schist back into regolith at the downgradient end of the site can be younger than shallower water that remains in regolith (fig. 12). Similarly, the age of ground water in deep Coastal Plain aquifers in Virginia was determined from concentrations of chlorofluorocarbon compounds to be older than the ground water in underlying basement rocks (Nelms and Ahlin, 1993) possibly because linear flow velocity in the fractured rocks is higher than in overlying sediments.

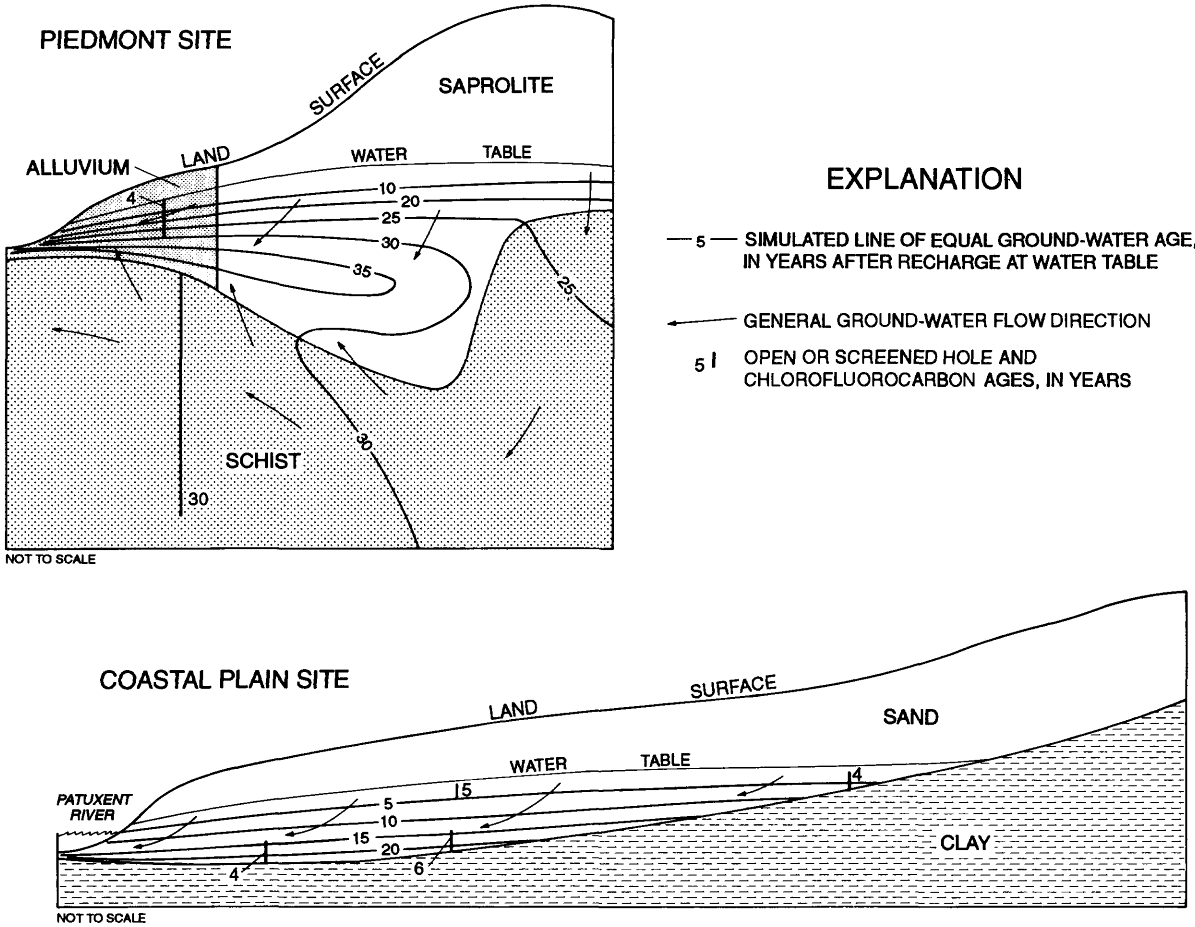

Figure 12. Simplified distributions of ground-water age at study sites in the Patuxent River Basin, Maryland, determined by particle-tracking analysis and chlorofluorocarbon recharge ages.

Additional estimates of the age of ground water in different parts of the aquifers were made by analyzing a small number of ground-water samples for tritium, which is a radioactive isotope of hydrogen with a half-life of about 12 years, and chlorofluorocarbons (CFC's or freons); both are environmental tracers. The natural concentration of tritium in water, ranged globally from 5 to 20 tritium units (TU), equal to 1 part in 10^{18} before atmospheric nuclear testing began in 1953; after nuclear testing, the concentration increased by several orders of magnitude (Freeze and Cherry, 1979). Therefore, ground water with tritium concentrations less than 5 TU probably was recharged before 1953.

CFC compounds have been steadily increasing in the atmosphere and in other parts of the environment as the use of these compounds has become widespread during the last few decades. Busenberg and Plummer (1992) developed a technique to collect ground-water samples for CFC analysis. This technique allows CFC concentrations to be related to the amount of time that has elapsed since the water entered the water table as recharge. Although the technique analyzed for freon–11 (trichlorofluoromethane) and freon–12 (dichlorodifluoromethane), freon–11 concentrations could have been affected by the use of this compound in agricultural chemicals, an effect that has been indicated in other rural areas (L.N. Plummer, U.S. Geological Survey, oral commun., 1992). Therefore, only freon–12 concentrations were used to interpret ages.

Tritium and CFC results indicate young ages for unconfined ground water at both study sites. All tritium analyses ranged from 20 to 30 TU and are interpreted to have been recharged after 1953, with the exception of water in schist that has 3.9 TU and could have been recharged before 1953. CFC results indicate that unconfined ground water at both study sites is recharged within 4 to 6 years and that water in schist at the Piedmont site, within 30 years (fig. 12). CFC recharge ages, however, are accurate only to plus or minus 2 years.

Particle-tracking analyses and tritium and CFC results provide only approximate estimates of the age of ground water. Water from adjacent flow lines is mixed by an unknown amount by dispersion, depending on the hydraulic properties of aquifer materials. Mixing by dispersion is not accounted for by the particle-tracking analyses but probably makes the ground-water age distribution more uniform throughout the aquifers. Paths of water molecules through pores or fractures differ in length on a microscopic scale. In addition, hydraulic properties can be heterogeneous on a small scale, and flow velocities can differ over small areas. Thus, a given volume of water in the aquifer will consist of molecules with different traveltimes. The extent of mixing increases in the downgradient direction as water molecules are dispersed along their flow paths. At the downgradient ends of the study sites, ground water is discharged through a relatively small area compared with the size of the water table, and mixing of water of different ages from the entire water table is probably most pronounced (Duffy and Lee, 1992).

At the Piedmont site, tritium and CFC results in schist agree reasonably well with the particle-tracking analysis (fig. 12). The CFC recharge age of 4 years for water in alluvium, however, is considerably younger than that indicated by the particle-tracking analysis, which indicates a range of ages up to 35 years. Most of the water for the CFC sample could have been drawn from the shallow part of the alluvium and mixed little with deeper, older water. Stratification of ground-water solutes at the Piedmont site (see section "Ground-Water Geochemistry") indicates that vertical mixing is limited in much of the aquifer, even in discharge at the downgradient end of the site. Flow through schist is localized in fractures, and that localization also could restrict the amount of mixing with shallower water in alluvium in the discharge area.

At the Coastal Plain site, CFC results indicate relatively young ages of ground water throughout the aquifer (fig. 12). Particle-tracking analysis, however, indicates older ages than does CFC recharge for ages of ground water near the base of the aquifer, and ground water probably is older at the base of the aquifer than near the water table where the water first enters the saturated zone. Although care was taken during CFC sample collection to avoid contamination, water samples from the base of the aquifer could have been contaminated by contact with the present-day atmosphere. If the water level was drawn below the top of the screened interval of the well during sampling, then the water could have been exposed to the atmosphere in the well as it trickled down the inside surface of the screen before entering the pump. Alternatively, pumping the wells at the base of the aquifer could have induced vertical mixing of water of different ages. Because of the time-consuming collection techniques required for the CFC samples, considerably larger amounts of water were pumped for the CFC samples than were routinely pumped for collecting ground-water samples (which was usually only enough to purge the well casing). Young shallow water could have been drawn into the deeper wells by prolonged pumping. The same problem apparently did not result when sampling the schist well at the Piedmont site, possibly because the water originated primarily from fractures in the schist.

Flow Through the Study Sites

The amounts of recharge used in the transient simulations of ground-water flow were compared with measured amounts of precipitation and surface runoff from 1987 to 1991 to determine the flow of water through the study sites (table 7). The total amount of water that entered the study sites was in the form of precipitation. Accordingly,

$$P = RO + ET + IF + RE + dSM,$$

where

P is precipitation,
RO is runoff of surface water,
ET is evapotranspiration,
IF is interflow in the unsaturated zone,
RE is recharge to ground water, and
dSM is change in soil-moisture content.

Flow through the study sites is divided into different components (fig. 6, see section "Recharge-Discharge Relations"). Precipitation initially infiltrates the land surface, and only rarely exceeds the infiltration capacity to produce surface runoff strictly. Part of the water that infiltrates the surface is returned to the atmosphere by evapotranspiration (ET). Remaining water either flows through the unsaturated zone as interflow, some of which may resurface to produce runoff; percolates through the unsaturated zone to the water table to recharge the aquifer under unconfined conditions; or is stored in the unsaturated zone as soil moisture.

Data on precipitation and surface runoff at both study sites were obtained from a related study of non-point-source pollution in the Patuxent River Basin (Summers, 1986; see section "Methods of Investigation"). Surface runoff was generally observed during only the most intense storms (figs. 7, 8), and most often

Table 7. Agricultural practices and amounts of water flowing through study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

[in., inches; do., ditto; <, less than]

Year	Agriculture practice	Measured precipitation (in.)	Measured surface runoff		Simulated ground-water recharger		Unmeasured evapotranspiration, interflow, and change in soil moisture storage	
			Amount (in.)	Percent of precipitation	Amount (in.)	Percent of precipitation	Amount (in.)	Percent of precipitation
Piedmont site								
1987	No-till soybeans..........	40.92	0.25	0.61	9.43	23.04	31.24	76.34
1988	Continuous alfalfa........	38.08	.39	1.02	7.19	18.88	30.50	80.09
1989	. . .do..................	56.99	2.66	4.67	11.26	19.76	43.07	75.57
1990	Contoured strip crops......	46.73	1.84	3.94	5.72	12.24	39.17	83.82
1991	. . .do..................	34.76	.56	1.61	6.70	19.28	27.50	79.11
Coastal Plain site								
1987	No-till soybeans..........	39.91	<.01	.01	4.74	11.88	35.17	88.12
1988	. . .do..................	35.71	.02	.06	6.32	17.70	29.37	82.25
1989	Conventional till soybeans .	48.26	2.19	4.54	9.00	18.65	37.07	76.81
1990	. . .do..................	40.05	1.18	2.95	7.14	17.83	31.73	79.23
1991	. . .do..................	35.14	.86	2.45	1.98	5.63	32.30	91.92

when the land surface was clear of vegetation. The volumetric flow rate of surface runoff was measured during most storms, but because of equipment limitations or malfunctions, not all runoff was measured.

Measured surface runoff was less than 3 in/yr, or 5 percent of precipitation, at both study sites during the study period (table 7). Other data collected within a mile of the Piedmont site (Angle and others, 1984) indicate that surface runoff was a small part of precipitation (0.2–4.4 percent). Because most surface runoff at the study sites was measured, the contribution of surface runoff to the total amount of flow through the study sites probably was small. In addition, much of the surface runoff reinfiltrated the land surface in the level area below the runoff flumes (see section "Recharge/Discharge Relations") and left the sites through the subsurface. A larger amount of the total water entering both study sites recharged ground water than ran off and ranged from about 6 to 11 in/yr, or 12 to 23 percent of precipitation at the Piedmont site, and 2 to 9 in/yr, or 6 to 19 percent at the Coastal Plain site (table 7).

The largest components of flow through the study sites were not measured and include evapotranspiration and storage and interflow in the unsaturated zone (table 7). Evapotranspiration in Maryland (Rasmussen and Andreasen, 1959) and in Delaware (Johnston, 1976) can be more than 60 percent of precipitation but also differs significantly aerially, as well as during the year and from year to year. The remaining 15 to 25 percent of precipitation at the study sites is either stored in or flows through the unsaturated zone as interflow. The limited soil-moisture tension data that were collected (figs. 7, 8) indicate the timing of percolation, but are not adequate to determine changes in the amount of water stored in the unsaturated zone. Measured surface runoff is primarily interflow that resurfaced under confining pressure at the downslope ends of the study sites (see section "Recharge/Discharge Relations"), but total interflow was not measured.

Year-to-year changes in amounts of the different flow components generally appear to correspond with changes in precipitation (table 7), although the unmeasured components are more constant than recharge and surface runoff. Apparently, recharge and surface runoff consist primarily of precipitation in excess of that removed by evapotranspiration and (or) stored in the unsaturated zone.

Changes in the amounts of the different flow components that resulted from changes in agricultural practice are probably relatively small compared with changes that resulted from differences in the amount and timing of precipitation. At the Piedmont site, precipitation was less in 1988 when alfalfa was planted than in the previous year when soybeans were planted (table 7). The amounts of the other flow components also decreased, with the exception of surface runoff which increased slightly. The site was plowed before alfalfa was planted, and that plowing could have promoted surface runoff (U.S. Environmental Protection Agency, 1987). Also, runoff during 1988 was primarily in May and July, when larger amounts of precipitation fell than during the same months the previous year, and occurred shortly after the site had been plowed.

Precipitation at the Piedmont site increased substantially in 1989 from the previous year, while alfalfa continued to be grown. Although all flow components increased, the unmeasured components increased more than recharge or surface runoff. Much of the additional precipitation during 1989 was in May and June, when evapotranspiration could be higher than at other times of year. In addition, the continuous cover of alfalfa possibly resulted in more evapotranspiration than would have resulted from other crops that are harvested seasonally. Precipitation then decreased for the next 2 years (1990–1991), while contoured strip crops were grown. All flow components also decreased, with the exception of recharge in 1991, which increased slightly. More precipitation fell toward the end of 1990 than during the same part of the previous year; and this increase could have resulted in more recharge during the early part of 1991.

Similar to the Piedmont site, precipitation, as well as the other components of flow, at the Coastal Plain site also increased substantially in 1989 from the two previous years (table 7). During this period, agricultural practice changed from no-till soybeans to conventional-till soybeans. The no-till method is intended to produce less runoff than conventional tillage but also could result in larger infiltration and recharge (U.S. Environmental Protection Agency, 1987). Instead of plowing the soil as with conventional tillage, a layer of crop debris is left on the undisturbed soil surface, a technique that is intended to slow runoff velocity and to promote infiltration. In 1989, recharge and surface runoff increased, however, probably because of the increase in precipitation. In addition, changes in recharge and surface runoff generally correspond to changes in precipitation throughout the study period. Any effect on surface runoff and recharge in 1989 caused by the change in tillage methods is unclear.

Some effects on surface runoff and recharge at the Coastal Plain site from no-till cultivation during 1988 possibly are comparable to conventional tillage during 1991. Surface runoff was lesser and recharge was more during no-till in 1988 than during conventional tillage in 1991, even though amounts of precipitation were approximately equal both years (table 7). Also, amounts of precipitation during the preceding years (1987, 1990) were similar. Surface runoff possibly decreased and recharge increased under no-till from that which results under conventional tillage, given the same amount of precipitation.

In addition to different tillage practices, differences in the timing of precipitation between 1988 and 1991 also could have affected surface runoff and recharge at the Coastal Plain site. Differences in monthly precipitation between 1988 and 1991 averaged less than 2 in., indicating that differences in the timing of precipitation between the 2 years generally were not large. Precipitation during the winter and early spring, however, when most recharge occurs because evapotranspiration is low, was over 3 in. more in 1988 than during the same period in 1991 (fig. 7). Precipitation in 1991 was more by a similar amount during late spring, summer, and early fall, resulting in nearly equal total amounts for both years, but evapotranspiration probably was high and possibly resulted in less recharge. The effects of no-till compared with conventional tillage in this instance must be viewed cautiously because the timing of precipitation and possibly other unmeasured factors, such as antecedent soil moisture and climate (air temperature, humidity, sunlight, and wind speed and direction), could have differed between 1988 and 1991 and also affected runoff and recharge.

GROUND-WATER GEOCHEMISTRY

Samples of ground water and soil water collected at both study sites and a sample of the Patuxent River at the Coastal Plain site were analyzed for physical properties and concentrations of chemical constituents (table 8). Concentration data were analyzed to determine the major-ion composition of water. Positive cation equivalents were within 5 percent or less of negative anion equivalents in all samples, indicating that the analyses accounted for all major dissolved constituents. Differences in specific conductance are assumed to reflect differences in total dissolved solids. Samples of surface runoff were not analyzed for major-ion concentration or specific conductance, but because most surface runoff probably is resurfaced interflow from the unsaturated zone (see section "Recharge/Discharge Relations") and, therefore, had extended contact with the soil, the dissolved-ion composition of runoff probably is similar to that of soil water. Additional material in the form of suspended sediments probably, however, is usually in runoff water.

Chemical reactions and solute-transport processes that could produce the observed major-ion compositions were inferred and were compared between the study sites. Concentrations of different forms of nitrogen in ground water, soil water, and surface runoff were examined along with other chemical data to determine transformation reactions among nitrogen species.

Major-Ion Composition

The concentrations of major ions in ground water and soil water differ between the two study sites and within different parts of the Piedmont site (fig.13; table 8). At the Piedmont site, there are two types of major-ion composition of ground water. Calcium and magnesium make up a slightly larger part of the total cations in soil water and water in shallow saprolite and alluvium than in water in deep saprolite and schist. Among the anions, chloride, as well as nitrate (table 9), is most concentrated in soil water and water in alluvium, less concentrated in water in shallow saprolite, and least concentrated in water in deep saprolite and schist. Conversely, bicarbonate is generally less concentrated in shallow saprolite and alluvium than in deep saprolite and schist. Thus, the major-ion composition of ground water at the Piedmont site grades from a calcium magnesium chloride nitrate-type water in soil and shallow saprolite and alluvium to a mixed-cation bicarbonate-type water in deep saprolite and schist (fig. 13).

Specific conductance, pH, and concentrations of dissolved oxygen, sulfate, iron, manganese, and sulfide also differ with depth at the Piedmont site (table 8). Iron, manganese, and sulfide concentrations and pH generally are lower and dissolved-oxygen concentration higher in water in regolith than in schist. Sulfate concentration and specific conductance are higher in soil water and water in alluvium and schist and lower in water in saprolite.

The median temperatures of water discharging from the springs at the Piedmont site were about 2°C

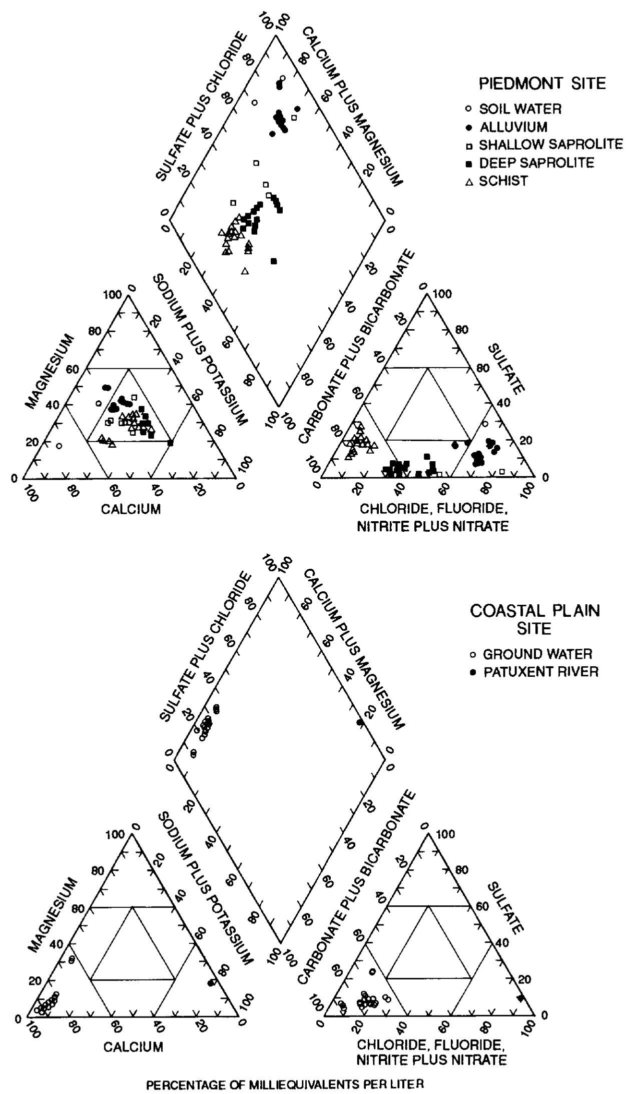

Figure 13. Distribution of major ions in ground-water samples from the study sites in the Patuxent River Basin, Maryland.

less than elsewhere at the site (table 8). Although water temperatures of the springs were close to that measured at nearby well HO Cd 78 during most of the study, several considerably lower temperatures were measured at the springs during 1990, resulting in the low median temperatures. The low temperatures during 1990 indicated that the source of water to the springs could have changed. Measurements of other chemical constituents in ground water at the springs during 1990, however, did not depart from trends that were apparent before and after 1990, so the cause of the low temperatures remains unclear. Although not measured, a consistently low daily air temperature at the site during 1990 could have resulted in low water temperatures of the springs.

Table 8. Physical properties and concentrations of selected chemical constituents in ground water and soil water at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland, and in the Patuxent River from August 1986 through August 1991

[ft, feet; µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; do., ditto; –, no data; <, less than. The number of analyses is that which was performed on all properties and constituents. A greater number of analyses was performed on some properties or constituents. Ranges are not shown where the median is below the analytical detection limit.]

Station number	Lithology	Range of depth below water table (ft)	Minimum number of field analyses	Specific conductance (µS/cm)		pH (standard units)		Water temperature (°C)		Dissolved oxygen (mg/L)	
				Median	Range	Median	Range	Median	Range	Median	Range
Piedmont site											
Observation wells:											
HO Cd 20	Schist	19– 91	15	102	78– 130	6.9	6.3–7.5	12.0	9.0–14.0	0.4	<0.1– 1.4
HO Cd 21	...do.	36– 84	15	94	62– 114	6.9	6.6–7.5	12.0	9.5–14.5	.4	<.1– 1.4
HO Cd 25	...do.	13– 60	4	74	57– 214	6.7	6.0–7.9	13.3	11.0–18.4	1.4	.8– 3.4
HO Cd 26	...do.	54–101	3	101	85– 182	8.4	8.1–8.7	13.0	11.0–15.0	1.5	1.2– 1.8
HO Cd 28	Deep saprolite	6– 22	38	28	20– 72	5.9	5.6–6.5	12.6	9.0–19.4	6.4	.2–11.8
HO Cd 29	...do.	13– 27	25	24	19– 32	5.7	5.4–6.4	12.5	9.0–18.1	8.2	1.5–10.8
HO Cd 78	Alluvium	0– 11	54	92	71– 105	5.5	4.3–7.2	12.3	9.5–16.6	8.8	4.9–10.9
HO Cd 79	Deep saprolite	13– 30	36	37	31– 42	5.6	3.4–5.9	12.9	11.0–21.6	8.0	4.9– 9.4
HO Cd 341	Shallow saprolite	0– 6	21	52	32– 82	5.5	4.1–5.8	13.0	12.0–19.3	8.9	4.3–15.7
HO Cd 342	...do.	0– 5	29	76	59– 96	6.0	5.6–6.4	12.0	11.0–20.1	8.1	5.0–10.4
Springs:											
HO Cd 80	Alluvium	0– 2	36	123	101– 147	5.6	5.2–6.1	10.5	5.0–15.0	9.0	7.2–13.8
HO Cd 81	...do.	0– 2	31	99	86– 128	5.8	5.4–6.2	10.2	6.0–15.0	8.4	4.9–11.9
Lysimeters:											
HO Cd 253	Shallow saprolite	—	12	375	117– 923	—	—	—	—	—	—
HO Cd 290	...do.	—	1	349	78–1,116	7.2	—	—	—	—	—
HO Cd 291	...do.	—	1	157	145– 300	7.1	—	—	—	—	—
HO Cd 292	...do.	—	20	147	81– 198	—	—	—	—	—	—
HO Cd 390	Alluvium	—	16	208	135– 321	—	—	—	—	—	—
HO Cd 391	...do.	—	19	299	124– 351	—	—	—	—	—	—

Table 8. Physical properties and concentrations of selected chemical constituents in ground water and soil water at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland, and in the Patuxent River from August 1986 through August 1991–Continued

[ft, feet; µS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; do., ditto; —, no data; <, less than. The number of analyses is that which was performed on all properties and constituents. A greater number of analyses was performed on some properties or constituents. Ranges are not shown where the median is below the analytical detection limit.]

Station number	Minimum number of laboratory analyses	Calcium, as Ca (mg/L)		Magnesium, as Mg (mg/L)		Sodium, as Na (mg/L)		Potassium, as K (mg/L)		Bicarbonate, as HCO_3 (mg/L)		Sulfate, as SO_4 (mg/L)		Chloride as Cl (mg/L)	
		Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Piedmont site—Continued															
Observation wells:															
HO Cd 20	4	6.9	5.3– 7.8	3.4	2.7–3.9	5.5	5.2–5.9	2.6	2.0– 2.6	51	29– 58	8.3	4.6–15	1.5	1.4– 3.7
HO Cd 21	4	5.7	4.5– 7.1	3.1	2.7–4.0	4.8	4.3–5.1	2.6	2.1– 9.3	43	35– 68	8.0	4.0–12	1.6	1.3– 1.7
HO Cd 25	4	3.8	3.2– 4.2	2.2	1.8–2.4	4.4	4.3–4.4	2.2	1.9– 4.1	24	24–127	5.5	4.0– 7.5	1.1	1.0– 1.2
HO Cd 26	3	9.7	8.9–10	2.3	2.1–2.4	4.6	4.5–4.9	3.3	1.2– 4.4	83	43– 97	8.6	7.4– 9.0	1.1	1.0– 1.2
HO Cd 28	4	1.1	1.1– 1.8	.9	.8–1.0	1.3	1.2–1.4	1.2	.8– 7.8	10	7.0– 20	.7	<.2– .9	1.2	1.1– 1.3
HO Cd 29	4	1.0	1.0– 1.1	.6	.5– .6	1.2	1.2–1.3	1.0	.9– 1.1	7.1	4.8– 10	<.2	—	1.2	1.1– 1.4
HO Cd 78	4	4.5	4.1– 5.4	3.6	3.1–4.2	3.5	3.3–3.7	1.6	1.4– 2.1	11	5.2– 16	4.0	3.4– 5.5	8.7	8.1–13
HO Cd 79	4	1.8	1.6– 2.1	1.2	1.0–1.3	1.7	1.6–1.9	1.3	1.1– 1.4	12	10– 15	<.2	—	1.0	.9– 1.1
HO Cd 341	2	2.8	2.6– 3.0	2.5	1.7–3.3	2.9	2.6–3.2	1.5	1.3– 1.7	9.5	7.8– 11	<.2	—	8.4	2.9–14
HO Cd 342	3	5.8	5.1– 5.9	2.5	2.4–2.5	2.7	2.6–2.8	4.8	1.5– 7.9	18	17– 18	<.2	—	4.4	4.3– 4.9
Springs:															
HO Cd 80	5	7.6	6.9– 8.4	6.3	5.7–6.7	2.8	2.6–2.9	1.5	1.4–11	7.8	5.6– 9.1	7.7	7.5– 9.6	9.8	9.5–11
HO Cd 81	4	6.1	6.0– 6.7	3.9	3.7–4.0	3.5	3.4–3.8	1.9	1.0– 2.1	10	9.9– 12	3.2	3.0– 5.2	8.2	7.8– 8.5
Lysimeters:															
HO Cd 253	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
HO Cd 290	1	33	—	4.7	—	1.3	—	5.2	—	143	—	20	—	12	—
HO Cd 291	1	16	—	9.1	—	4.9	—	2.9	—	98	—	27	—	4.1	—
HO Cd 292	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
HO Cd 390	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
HO Cd 391	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Station number	Silica, as SiO_2 (mg/L)		Iron, as Fe (mg/L)		Manganese, as Mn (mg/L)		Sulfide, as S (mg/L)		Total organic carbon (mg/L)	
	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Piedmont site—Continued										
Observation wells:										
HO Cd 20	25	15 –29	1.7	1.3 –2.5	0.11	0.072–0.17	<0.5	—	0.8	0.8– 2.3
HO Cd 21	23	17 –27	1.6	1.1 –1.7	.074	.047– .15	<.5	—	1.3	.9– 2.7
HO Cd 25	20	13 –25	.35	.26 –1.1	.095	.069– .11	<.5	—	2.6	1.3– 3.3
HO Cd 26	3.7	3.0– 7.6	.006	.005– .006	.012	.010– .028	<.5	—	2.0	.4– 2.2
HO Cd 28	9.6	8.6– 9.8	.030	.008– .23	.072	.043– .10	<.5	—	.8	<.1–13
HO Cd 29	7.4	7.0– 7.6	.008	.006– .009	.006	.005– .013	<.5	—	<.1	—
HO Cd 78	13	12 –13	<.01	—	.004	.003– .006	<.5	—	<.1	—
HO Cd 79	11	10 –11	.017	.010– .29	.045	.026– .11	<.5	—	<.1	—
HO Cd 341	8.6	8.0– 9.3	.005	.005– .008	.071	.060– .083	<.5	—	1.6	.7– 2.5
HO Cd 342	14	14–15	.008	.008– .009	.007	.005– .008	<.5	—	1.7	.8– 2.7
Springs:										
HO Cd 80	9.4	8.9– 9.8	<.01	—	.023	.017– .086	<.5	—	13	2.9–33
HO Cd 81	14	13–14	<.01	—	<.01	—	<.5	—	1.1	.7– 2.1
Lysimeters:										
HO Cd 253	—	—	—	—	—	—	—	—	—	—
HO Cd 290	26	—	.009	—	.018	—	—	—	.8	.4– 1.2
HO Cd 291	37	—	.016	—	.56	—	—	—	.5	.5– .9
HO Cd 292	—	—	—	—	—	—	—	—	.8	—
HO Cd 390	—	—	—	—	—	—	—	—	—	—
HO Cd 391	—	—	—	—	—	—	—	—	—	—

Table 8. Physical properties and concentrations of selected chemical constituents in ground water and soil water at study sites in the Piedmont and Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland, and in the Patuxent River from August 1986 through August 1991—Continued

[μS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; do., ditto; —, no data; <, less than. The number of analyses is that which was performed on all properties and constituents. A greater number of analyses was performed on some properties or constituents. Ranges are not shown where the median is below the analytical detection limit.]

Station number	Lithology	Range of depth below water table (ft)	Minimum number of field analyses	Specific conductance (μS/cm)		pH (standard units)		Water temperature (°C)		Dissolved oxygen (mg/L)	
				Median	Range	Median	Range	Median	Range	Median	Range
				Coastal Plain Site							
Observation wells:											
CA Fc 13	Sand, shells ...	0– 8	67	608	488– 733	7.1	7.1–8.2	15.0	13.0–25.0	6.0	3.5– 7.9
CA Fc 14	Sand, clay.....	0– 4	20	578	514– 668	7.1	6.7–7.4	15.0	12.5–19.3	7.8	5.7– 9.5
CA Fc 15	Sand, shells ...	13–21	44	552	481– 655	7.3	6.6–7.6	14.6	13.0–20.0	7.0	4.9– 9.0
CA Fc 16	...do.........	0– 8	56	574	494– 690	7.3	6.5–8.0	14.2	10.1–20.0	7.4	3.4– 9.0
CA Fc 17	...do.........	12–20	39	580	505– 638	7.2	6.1–7.5	14.6	13.0–19.0	6.6	5.3– 8.9
CA Fc 18	...do.........	8–17	58	589	491– 700	7.1	6.5–7.9	14.0	10.7–20.0	6.9	1.9–10.2
CA Fc 19	...do.........	9–17	32	562	492– 609	7.2	6.9–7.6	14.1	13.0–17.3	4.0	.3– 7.3
CA Fc 20	...do.........	8–16	37	588	491– 665	7.2	6.6–7.9	14.2	12.0–19.0	6.9	1.9– 8.7
CA Fc 21	...do.........	7–16	35	455	379– 585	7.3	6.9–7.7	14.5	13.0–20.0	5.8	2.2– 7.8
CA Fc 22	...do.........	9–18	32	576	480– 690	7.2	6.7–7.9	14.4	13.0–20.0	6.6	5.0– 8.6
CA Fc 33	...do.........	4– 7	28	683	585– 810	7.2	6.6–7.7	12.0	7.0–18.4	2.0	.5– 5.0
CA Fc 34	...do.........	8–11	21	680	553– 735	7.2	6.8–7.6	12.6	6.0–18.5	3.8	.9– 6.2
Lysimeters:											
CA Fc 28	Sand, shells ...	—	30	236	184– 399	—	—	—	—	—	—
CA Fc 29	...do.........	—	35	415	269– 682	—	—	—	—	—	—
CA Fc 30	...do.........	—	48	570	446– 888	—	—	—	—	—	—
CA Fc 31	...do.........	—	23	669	410–2,150	—	—	—	—	—	—
CA Fc 32	...do.........	—	32	403	271–1,300	—	—	—	—	—	—
River:											
CA Fc 35	—	—	1	23,700	—	8.2	—	28.0	—	8.4	—

Station number	Minimum number of laboratory analyses	Calcium, as Ca (mg/L)		Magnesium, as Mg (mg/L)		Sodium, as Na (mg/L)		Potassium, as K (mg/L)		Bicarbonate, as HCO_3 (mg/L)		Sulfate, as SO_4 (mg/L)		Chloride, as Cl (mg/L)	
		Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Coastal Plain site—Continued															
Observation wells:															
CA Fc 13	10	110	94–130	6.8	4.9–10	10	8.5–11	4.0	2.8– 6.9	321	300–378	18	12–24	14	10 –17
CA Fc 14	2	78	77– 80	24	24 –24	3.7	3.6– 3.8	9.6	9.1–10	300	282–321	35	34–36	6.8	6.2– 7.3
CA Fc 15	4	105	100–110	4.4	4.1– 4.5	8.9	8.7– 9.1	3.3	2.8– 3.6	266	184–285	18	16–21	18	18 –18
CA Fc 16	5	110	110–110	4.2	4.0– 4.3	9.0	8.8– 9.5	2.9	2.8– 3.5	276	195–318	18	16–20	18	18 –21
CA Fc 17	4	120	110–120	3.4	3.3– 3.5	7.8	7.5– 8.0	1.1	.9– 1.1	282	248–306	24	22–25	19	18 –20
CA Fc 18	6	116	110–120	3.4	3.1– 4.0	6.9	6.2– 7.8	.9	.8– 1.1	293	179–310	29	24–33	18	14 –20
CA Fc 19	4	110	110–110	4.4	4.3– 4.5	6.7	6.6– 6.9	1.7	1.4– 1.9	273	207–285	33	33–35	14	14 –15
CA Fc 20	4	120	110–120	2.8	2.7– 3.0	7.3	7.1– 7.6	1.2	1.0– 1.3	278	255–310	26	24–33	17	16 –18
CA Fc 21	5	84	77– 94	4.4	1.9– 5.0	7.2	6.6– 7.4	2.1	1.2– 3.1	195	133–226	23	19–60	18	15 –20
CA Fc 22	6	110	100–120	5.6	5.2– 5.8	9.3	8.6– 9.6	5.0	4.0– 5.6	286	256–322	19	16–21	17	16 –19
CA Fc 33	1	130	—	3.1	—	5.0	—	.4	—	318	—	22	—	16	—
CA Fc 34	1	130	—	3.4	—	6.3	—	.5	—	356	—	24	—	15	—
Lysimeters:															
CA Fc 28	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CA Fc 29	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CA Fc 30	5	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CA Fc 31	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—
CA Fc 32	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—
River:															
CA Fc 35	1	180	—	560	—	4,500	—	170	—	84	—	1,200	—	7,900	—

Table 8. Physical properties and concentrations of selected chemical constituents in ground water and soil water at study sites in the Piedmont and Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland, and in the Patuxent River from August 1986 through August 1991—Continued

[μS/cm, microsiemens per centimeter; °C, degrees Celsius; mg/L, milligrams per liter; do., ditto; —, no data; <, less than. The number of analyses is that which was performed on all properties and constituents. A greater number of analyses was performed on some properties or constituents. Ranges are not shown where the median is below the analytical detection limit.]

Station number	Silica, as SiO_2 (mg/L)		Iron, as Fe (mg/L)		Manganese, as Mn (mg/L)		Sulfide, as S (mg/L)		Total organic carbon (mg/L)	
	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Coastal Plain site—Continued										
Observation wells:										
CA Fc 13	22	19 –23	<0.01	—	<0.01	—	—	—	0.5	<0.1–21
CA Fc 14	8.3	8.0– 8.6	<.01	—	<.01	—	—	—	2.8	2.7– 3.0
CA Fc 15	16	16 –17	<.01	—	<.01	—	—	—	<.1	—
CA Fc 16	17	16 –17	<.01	—	<.01	—	—	—	<.1	—
CA Fc 17	16	16 –17	<.01	—	<.01	—	—	—	<.1	—
CA Fc 18	21	14 –27	<.01	—	<.01	—	—	—	.2	.1– 1.0
CA Fc 19	22	21 –25	.011	.009–.019	<.01	—	—	—	.8	.2– 1.0
CA Fc 20	16	15 –22	<.01	—	<.01	—	—	—	.3	.2– 1.8
CA Fc 21	16	15 –25	<.01	—	<.01	—	—	—	1.0	.2– 3.4
CA Fc 22	18	18 –19	<.01	—	<.01	—	—	—	.8	.5– .9
CA Fc 33	11	—	<.01	—	<.01	—	—	—	3.9	2.9– 6.7
CA Fc 34	21	—	<.01	—	<.01	—	—	—	10	—
Lysimeters:										
CA Fc 28	—	—	—	—	—	—	—	—	1.5	1.2– 1.9
CA Fc 29	—	—	—	—	—	—	—	—	1.3	1.3– 2.4
CA Fc 30	—	—	—	—	—	—	—	—	2.9	2.6– 4.2
CA Fc 31	—	—	—	—	—	—	—	—	4.0	3.5– 4.5
CA Fc 32	—	—	—	—	—	—	—	—	1.5	1.1– 1.7
River:										
CA Fc 35	1.8	—	<.01	—	.030	—	—	—	—	—

At the Coastal Plain Site, the composition of ground water is a calcium bicarbonate-type water through the aquifer (fig. 13). Concentrations of calcium and bicarbonate ions are an order of magnitude higher than concentrations of chloride, sulfate, and nitrate; two orders of magnitude higher than magnesium, sodium, and potassium; and five orders of magnitude higher than iron and manganese (tables 8, 9). Specific conductance, pH, and dissolved-oxygen concentration are uniform throughout the aquifer, except for samples from wells CA Fc 19, CA Fc 33, and CA Fc 34, with lower dissolved oxygen. The specific conductance of soil water has a large range, which encompasses that of ground water. The specific conductance of the Patuxent River is two orders of magnitude higher than ground water. The composition of the river water is a sodium-chloride type and also differs from ground water (fig. 13). This water type results from the exchange of water in the estuary with the Atlantic Ocean.

Chemical Evolution of Ground Water

The chemical composition of water results from chemical reactions between the water and materials with which it comes in contact. Upon falling to the land surface at the study sites, precipitation, which is dilute, comes in first contact with chemicals that originate from agricultural practices, including ionic salts from fertilizers, and from atmospheric deposition. Upon infiltrating the surface, the composition of the water is altered by chemical-weathering reactions with minerals in the subsurface.

At the Piedmont site, the composition of soil water probably results primarily from contact with agricultural chemicals applied to the land surface. Concentrations of chemicals and specific conductance in soil water generally are high as a result of the dissolution of ionic salts in fertilizer, but the concentrations and specific conductance are decreased by dilution as the water percolates to the shallowest part of the water table in alluvium (table 8). Shallow ground water is more dilute than soil water because flow through the unsaturated zone to the water table is driven by increases in soil-moisture content (see section "Recharge/Discharge Relations"). The proportions of ions do not change appreciably (fig. 13), however, indicating that reaction in the alluvium between the water and subsurface minerals is minor. In saprolite, water that percolates deeper to the water table is further diluted, but the major-ion composition of water also changes. Concentrations of sodium, potassium, and bicarbonate decrease less than those of calcium, magnesium, sulfate, and chloride, indicating that the water is reacting with subsurface minerals (fig. 13). The chemical composition continues to change in water that flows deeper into schist, and chemical concentrations increase in schist because the reactions produce ions, but the water is no longer diluted.

Schist at the Piedmont site consists of silicate minerals (muscovite, biotite, quartz, feldspar, garnet) and other minerals (calcite, pyrite). Regolith consists of partly weathered schist. The silicate minerals are observed in drill cuttings and outcrops of regolith and schist. Calcite and pyrite are reported as accessory minerals (Hopson, 1964) and are indicated by field evidence, such as rhombohedral solution cavities in vein quartz and hydrogen-sulfide odor from water in schist.

Several chemical-weathering reactions that could contribute to the composition of ground water at the Piedmont site have been documented in the Piedmont Province in Maryland (Cleaves and others, 1970). In schist, hydrolysis of silicate minerals probably consumes hydrogen ions and produces dissolved alkali and alkaline-earth cations (calcium, magnesium, sodium, potassium, depending on mineral composition), silica, and bicarbonate. Calcite reacts with hydrogen ions, yielding calcium and bicarbonate ions to ground water. Iron and manganese are produced by hydrolysis of biotite and garnet and also by pyrite weathering. Pyrite weathering also produces hydrogen ions, can produce sulfide and (or) sulfate ions, and consumes oxygen. Hydrogen ions produced by pyrite weathering are probably consumed by further weathering of silicates and calcite, and hydrogen-ion consumption buffers the pH of ground water. Much of the iron and manganese that is weathered from biotite, garnet, and pyrite in schist reacts with dissolved oxygen to precipitate in solid oxide phases. The concentration of dissolved oxygen is low in water in schist, however, possibly from having been consumed by reaction with iron and manganese and with some unreacted iron and manganese that remains in solution (table 8).

Water in saprolite at the Piedmont site differs from that in schist in that ionic concentrations and specific conductance in water in saprolite are low and dissolved-oxygen concentration is high (table 8). Water in saprolite follows a shorter flow path than water in schist. Pyrite, calcite, feldspar, and garnet in schist have probably weathered from saprolite, and their dissolved products have been flushed from the saprolite by ground-water flow. Nonreactive minerals, such as quartz and mica, and products of weathering, such as clays and iron oxides, remain in the saprolite but contribute few ions to water.

At the Coastal Plain site, the concentrations of major ions in soil water were not determined, but similar to the Piedmont site, soil-water composition probably results primarily from agricultural chemicals applied at the land surface. Unlike the Piedmont site, however, the specific conductance of soil water at the Coastal Plain site generally is less than that of ground water (table 8).

Subsurface minerals at the Coastal Plain site consist primarily of quartz sand and calcium carbonate in the form of fossil shells and cement. Lesser amounts of silicate minerals (clay, mica, feldspar) are in the fine-grained sediments. Quartz is nonreactive and does not contribute appreciable quantities of solutes to ground water. Calcium carbonate (in the form of calcite or aragonite) is reactive, however, and dissolves readily in ground water to produce calcium and bicarbonate ions. Dissolution of calcium carbonate probably is the primary chemical weathering reaction resulting in the major-ion composition of ground water at the Coastal Plain site. Smaller concentrations of other ions are produced by silicate-mineral weathering and (or) originate from agricultural practices and atmospheric deposition. The total quantity of ions produced, and hence the specific conductance, is higher than that in soil water (table 8).

Unlike the Piedmont site, the concentrations of ions in ground water at the Coastal Plain site do not change appreciably with depth (table 8). The unsaturated zone through which water is diluted downward is thinner at the Coastal Plain site. Also, a thick layer of chemically nonreactive residuum, such as the saprolite at the Piedmont site, is not present. Calcium carbonate, which affects ground-water composition at the Coastal Plain site, is present throughout most of the subsurface, but schist at the Piedmont site is 20 ft or more below the water table. In addition, chemical weathering at the Piedmont site includes oxidation-reduction reactions that depend on the presence of oxygen, which changes with depth, whereas dissolution of calcium carbonate at the Coastal Plain site does not change with depth.

Speciation of Nitrogen in Water

Samples of ground and soil waters and surface runoff at both study sites were analyzed for nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), and organic nitrogen (table 9). All nitrogen transported in ground and soil waters was assumed to be dissolved, and ground- and soil-water samples were analyzed only for dissolved nitrogen. More than one-half of the organic nitrogen in the surface-runoff samples was in particulate form, however, and concentrations of dissolved and suspended organic nitrogen were added to give total organic nitrogen in runoff. The single water sample collected from the Patuxent River at the Coastal Plain site had a small concentration of total dissolved nitrogen (0.5 mg/L), most of which was organic nitrogen, although additional organic nitrogen was probably present in particulate form.

The concentration of nitrogen in water at the study sites differs among the different nitrogen species (table 9). Nitrate is the predominant form of dissolved nitrogen in ground and soil waters at both sites. Concentrations of organic nitrogen are generally an order of magnitude smaller, and ammonium and nitrite are at least two orders of magnitude smaller. A notable exception is water in schist at the Piedmont site, in which nitrate concentrations are consistently an order of magnitude or more smaller than the rest of the site. In surface runoff at both sites, organic nitrogen is the predominant form of nitrogen and is at higher concentrations than in ground water and soil water.

Dissolved nitrogen can change form during several processes. Plants use photosynthesis to absorb solar energy and to incorporate inorganic nitrogen (nitrate and ammonium), applied as fertilizer or naturally in the soil, into their tissue as organic nitrogen. Leguminous plants, such as soybeans and alfalfa, also derive organic nitrogen from atmospheric nitrogen gas. Upon the death of the plants, solar energy is no longer absorbed, and plant tissue decomposes because the tissue is thermodynamically unstable. Organic nitrogen tends to react to form inorganic nitrogen species but can remain in disequilibrium because of slow reaction rates. Bacteria, however, can catalyze the reactions to derive metabolic energy in a two-step process called mineralization (Klein and Bradford, 1979). In the first step, ammonification, either aerobic bacteria (which survive only in the presence of oxygen) or anaerobic bacteria (which survive only in the absence of oxygen) can convert organic nitrogen into ammonium (NH_4^+).

Table 9. Concentrations of nitrogen species in ground water, soil water, and surface runoff at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland, from August 1986 through August 1992

[ft, feet; mg/L, milligrams per liter; <, less than; —, no data; do., ditto. the number of analyses is that which was performed on all species. A greater number of analyses were performed on some species. Ranges are not shown where the median is below the analytical detection limit. Concentrations are of dissolved species except for organic nitrogen in runoff which is of suspended plus dissolved.]

Station number	Lithology	Range of depth below water table (ft)	Minimum number of analyses	Nitrate (mg/L)		Nitrite (mg/L)		Ammonium (mg/L)		Organic nitrogen (mg/L)	
				Median	Range	Median	Range	Median	Range	Median	Range
Piedmont site											
Observation wells:											
HO Cd 20	Schist	19– 91	27	<0.1	—	<0.01	—	0.04	0.01 –0.32	0.2	<0.2– 0.7
HO Cd 21	...do.	36– 84	28	<.1	—	<.01	—	.02	<.01 - .09	.3	<.2– .9
HO Cd 25	...do.	13– 60	9	.2	<.1– .73	<.01	—	.04	<.01 - .30	.2	<.2– 1.0
HO Cd 26	...do.	54–101	9	<.1	—	<.01	—	.03	<.01 - .06	.2	<.2– .9
HO Cd 28	Deep saprolite	6– 22	47	.54	.37– .99	<.01	—	.02	<.01 - .23	.2	<.2– 1.4
HO Cd 29	...do.	13– 27	35	.68	.58– .93	<.01	—	.02	<.01 - .06	.2	<.2– 1.3
HO Cd 78	Alluvium	0– 11	55	3.2	2.4– 3.9	<.01	—	<.01	—	.2	<.2– 1.3
HO Cd 79	Deep saprolite	3– 30	39	1.6	.85– 2.0	<.01	—	<.01	—	<.2	—
HO Cd 341	Shallow saprolite.	0– 6	25	2.1	1.2– 4.6	<.01	—	<.01	—	<.2	—
HO Cd 342	...do.	0– 5	34	3.0	.77– 4.3	<.01	—	<.01	—	.3	<.2– .6
Springs:											
HO Cd 80	Alluvium	0–0	44	4.0	1.3– 8.6	<.01	—	.01	<.01 - .04	.4	<.2– 1.3
HO Cd 81	...do.	0–0	38	3.9	2.1– 5.4	<.01	—	<.01	—	.3	<.2– 1.2
Lysimeters:											
HO Cd 253	Shallow saprolite	—	19	3.1	<.1–79	<.01	—	.02	<.01 - .14	.5	<.2– 1.2
HO Cd 290	...do.	—	34	2.7	.19–47	<.01	—	<.01	—	.3	<.2– .9
HO Cd 291	...do.	—	29	11	2.1–17	<.01	—	.01	<.01 - .10	.5	.2– 2.1
HO Cd 292	...do.	—	29	15	1.3–19	<.01	—	.01	<.01 - .15	.5	<.2– 1.2
HO Cd 390	Alluvium	—	20	.1	<.1– 3.6	<.01	—	<.01	—	<.2	—
HO Cd 391	...do.	—	23	2.5	.90– 5.3	<.01	—	.01	<.01 - .05	.3	<.2– .8
Runoff:											
—	—	—	55	.51	.07– 7.6	.01	.005–.22	.07	.004–4.8	3.2	.7-39

Table 9. Concentrations of nitrogen species in ground water, soil water, and surface runoff at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland, from August 1986 through August 1992—Continued

[ft, feet; mg/L, milligrams per liter; <, less than; —, no data; do., ditto. the number of analyses is that which was performed on all species. A greater number of analyses were performed on some species. Ranges are not shown where the median is below the analytical detection limit. Concentrations are of dissolved species except for organic nitrogen in runoff which is of suspended plus dissolved.]

Station number	Lithology	Range of depth below water table (ft)	Minimum number of analyses	Nitrate (mg/L)		Nitrite (mg/L)		Ammonium (mg/L)		Organic nitrogen (mg/L)	
				Median	Range	Median	Range	Median	Range	Median	Range
Coastal Plain site											
Observation wells:											
CA Fc 13	Sand, shells	0– 8	68	8.4	5.7– 9.6	<0.01	—	0.02	<0.01– 0.11	0.5	<0.2– 1.4
CA Fc 14	Sand, clay	0– 4	21	8.3	7.2– 9.9	<.01	—	<.01	—	.7	.2– 2.3
CA Fc 15	Sand, shells	13–21	48	9.8	9.1–12	<.01	—	.01	<.01– .08	.5	<.2– 1.4
CA Fc 16	...do.	0– 8	66	10	8.9–12	<.01	—	.02	<.01– .12	.5	<.2– 1.6
CA Fc 17	...do.	12–20	44	8.6	6.5– 9.8	<.01	—	.02	<.01– .07	.4	<.2– 1.5
CA Fc 18	...do.	8–17	71	7.9	1.3–15	<.01	—	.02	<.01– .07	.5	<.2– 2.2
CA Fc 19	...do.	9–17	36	5.9	2.6– 9.9	<.01	—	.02	<.01– .24	.4	<.2– 1.3
CA Fc 20	...do.	8–16	43	8.8	3.4–10	<.01	—	.02	.01– .07	.6	.2– 2.2
CA Fc 21	...do.	7–16	41	8.9	2.3–10	<.01	—	.01	<.01– .08	.5	<.2– 1.8
CA Fc 22	...do.	9–18	40	10	8.0–12	<.01	—	.02	<.01– .08	.5	<.2– 1.4
CA Fc 33	...do.	4– 7	31	2.7	<.1– 8.2	.09	.01–.29	.02	<.01– .08	.3	<.2– .9
CA Fc 34	...do.	8–11	24	5.6	1.2– 9.5	.02	.02–.02	.02	<.01– .31	.5	<.2– 1.3
Lysimeters:											
CA Fc 28	Sand, shells	—	41	2.9	<.1–21	<.01	—	.02	<.01– .18	.4	<.2– 4.0
CA Fc 29	....do.	—	37	.63	<.1–26	<.01	—	.01	<.01– .10	.3	<.2– 2.4
CA Fc 30	...do.	—	51	3.9	.05–13	<.01	—	.02	<.01– .12	.4	<.2– 1.8
CA Fc 31	...do.	—	23	6.6	<.1–18	<.01	—	.02	<.01– .11	.5	.2– 1.3
CA Fc 32	...do.	—	30	.75	<.1–13	<.01	—	.01	<.01– .06	.3	<.2– 1.0
Runoff:											
--	—	—	27	.10	<.02– 1.3	.008	.002–.067	.06	.02– .40	2.7	1.6–45

If dissolved oxygen is absent, then ammonium ions from mineralizing plant tissue can accumulate in ground and soil waters or can be adsorbed onto solid particles. If dissolved oxygen is present, then ammonium reacts with the oxygen (becomes oxidized) in the second mineralization step, nitrification, to form nitrite, hydrogen ions, and water as follows:

$$2\,NH_4^+ + 3\,O_2 \rightarrow 2\,NO_2 + 4\,H^+ + 2\,H_2O.$$

Many aerobic bacteria, including Nitrosomonas, can catalyze the reaction (Ehrlich, 1990; Firestone, 1982).

Nitrite is an unstable transition product in most instances and is quickly oxidized in a second reaction to form nitrate as follows:

$$2\,NO_2^- + O_2 \rightarrow 2\,NO_3^-.$$

Other aerobic bacteria, including Nitrobacter, can catalyze this reaction (Ehrlich, 1990; Firestone, 1982).

At both study sites, most of the nitrogen in water at the land surface is initially in an organic form that is released from decaying plant tissue. The organic nitrogen is transported by percolation through the unsaturated zone and by surface runoff. In the unsaturated zone, most of the organic nitrogen is mineralized and oxidized to form nitrate within a few feet or less from the land surface. Ammonium is initially formed and can be partially removed from solution by adsorption onto solid particles. Most of the ammonium that is not adsorbed, however, is converted to nitrate.

Nitrate can remain chemically stable in ground water under aerobic conditions, but under anaerobic conditions, nitrate can undergo denitrification to form nitrogen gas (N_2). Bacteria in ground water derive metabolic energy by catalyzing oxidation-reduction reactions, in which electrons are transferred from electron donors, most commonly organic matter, to one or more electron acceptors that yield the most energy. Oxygen yields more energy than other electron acceptors until its concentration becomes depleted, at which point bacteria will use nitrate and produce nitrogen gas, as follows:

$$4\,NO_3^- + 5\,\underset{\text{(carbohydrate)}}{HCHO} \rightarrow 2\,N_2 + 5\,CO_2 + 4\,OH^- + 3\,H_2O.$$

If sufficient organic matter is not available, then bacteria can use reduced inorganic species (manganese, ferrous iron, or sulfide) as electron donors, if present at adequate concentrations, and multiple electron donors can be used in an aquifer (Korom, 1992). The concentration of N_2 in ground water possibly will not increase appreciably above that in equilibrium with the atmosphere (approximately 16 mg/L at 12°C) if excess N_2 produced by denitrification is able to diffuse out of the aquifer (Korom, 1992), but the extent of N_2 diffusion generally is unknown.

Nitrate also can be reduced to ammonium (NH_4^+) in environments similar to those in which denitrification occurs, but relations between the two processes are not well known (Korom, 1992). Once N_2 is formed, however, it resists further reaction because of the strong triple bond between nitrogen atoms, and N_2 can be removed from ground water by diffusion. Ammonium, however, can remain dissolved in ground water and, if transported into an aerobic environment, can be oxidized back into nitrate.

Decreased concentrations of nitrate in parts of the aquifers at both study sites could be the result of denitrification and (or) reduction of nitrate to ammonium. Ammonium concentrations are low compared with the range of nitrate concentration (table 9), however, and denitrification is, therefore, the more likely process lowering concentrations. Spearman's rho rank correlation coefficients (Iman and Conover, 1983) show that with more than 99-percent certainty (alpha less than 0.005), nitrate concentration at both study sites correlates with dissolved-oxygen concentration (fig. 14). Lower dissolved-oxygen concentrations could promote denitrification at the study sites. Nitrate concentrations generally are lower at the Piedmont site than at the Coastal Plain site for a given dissolved-oxygen concentration, and the amount of denitrification could be larger at the Piedmont site.

Nitrate and dissolved-oxygen concentrations in ground water at the Piedmont site generally decrease with depth—from the shallowest water in alluvium, through deeper water in saprolite, and into the deepest water in schist (tables 8, 9)—and could indicate denitrification in deep ground water. Total organic carbon concentrations generally differ little throughout the site, but concentrations of iron, manganese, and sulfide are highest in water in schist (table 8) and could be electron donors. Denitrification can be associated with pyrite weathering (Korom, 1992), as follows:

$$5\,FeS_2 + 14\,NO_3^- + 4\,H^+ \rightarrow 7\,N_2 + 10\,SO_4^{2-} + 5\,Fe_2^+ + 2\,H_2O,$$

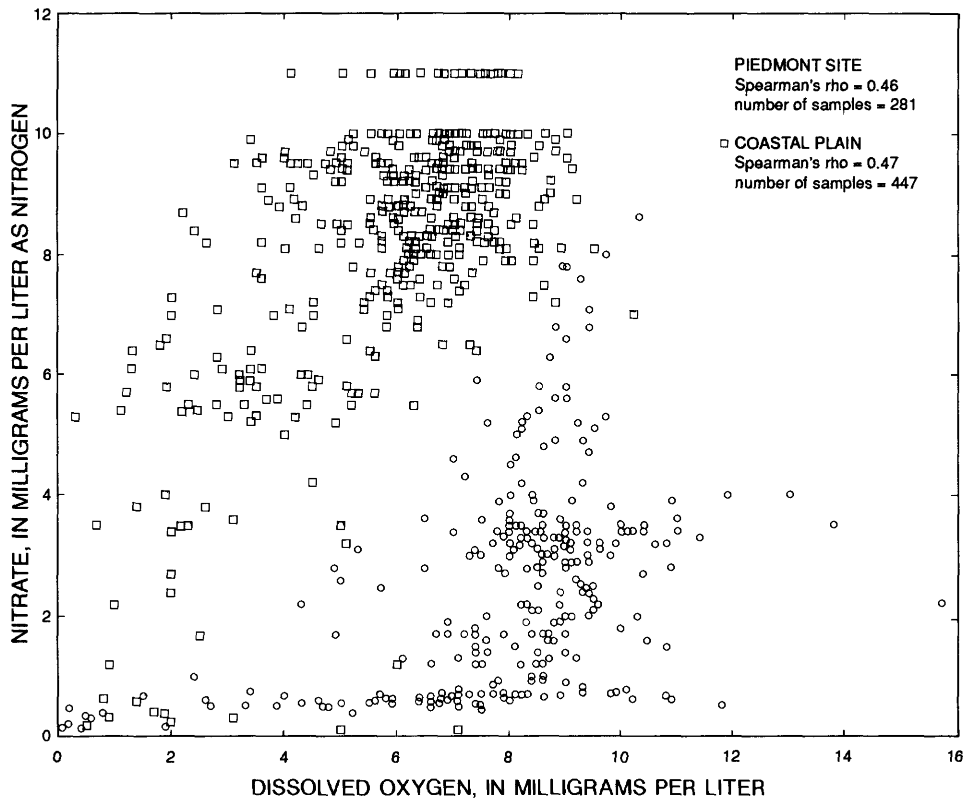

Figure 14. Relation between nitrate and dissolved-oxygen concentrations in ground water at the study sites in the Patuxent River Basin, Maryland.

which is catalyzed by the bacteria *Thiobacillus denitrifican*, and which can account for iron and sulfate concentrations in water in schist that are higher than in shallower ground water (see section "Chemical Evolution of Ground Water"). Denitrification in water in schist would produce N_2; one sample of water in schist (well HO Cd 20), however, had 19 mg/L of dissolved N_2, which is only slightly higher than 17 mg/L analyzed in a sample of water from alluvium (well HO Cd 78) collected at the same time. The concentrations of both samples are close to the concentration in equilibrium with air of 16 mg/L at 12°C. Additional N_2 formed by denitrification in schist could have diffused out of water in the aquifer.

At the Coastal Plain site, the lowest concentrations of nitrate and dissolved oxygen are in water samples from wells CA Fc 19, which is the only well screened partly in clay underlying the sand aquifer, and from wells CA Fc 33, and CA Fc 34, both of which are located in the vegetated buffer strip near the shore of the Patuxent River (tables 8, 9). Concentrations of N_2 were not analyzed in water samples from these wells to compare with other parts of the aquifer.

Water samples from well CA Fc 19 could consist partly of water from the clay. Most of the major-ion concentrations in samples from this well are similar to those throughout the site. These samples, however, have the highest concentrations of iron, which could be from glauconite in the green marine clay and which could be an electron donor for denitrification. Although the volume of water that flows between the clay and overlying sand is probably minimal (see section "Hydrogeologic Frameworks"), some water could flow slowly from the sand into and through the underlying clay, where iron concentration increases from glauconite weathering and nitrate concentration decreases from denitrification.

Water samples from wells CA Fc 33 and CA Fc 34 have the highest concentrations of total organic carbon at the Coastal Plain site (table 8). Aquifer materials beneath the vegetated buffer strip in which the wells are located consist of dark-brown sand that appears to contain more organic matter than in other parts of the site. The water table is shallow enough beneath the buffer strip that organic matter in the plant root zone extends downward into the saturated ground-water zone. Some nitrogen could be temporarily routed out of the aquifer by direct plant uptake, but would not be permanently removed so long as plant material is not removed from the buffer strip. Maintenance of the buffer strip, however, allows organic matter to accumulate in the soil, which can be an electron donor for denitrification when concentrations of dissolved oxygen are sufficiently low.

Shallow ground water beneath the vegetated buffer strip at the Coastal Plain site (well CA Fc 33) has a lower nitrate concentration than deeper ground water (well CA Fc 34) (table 9). Similarly, nitrate concentrations in ground water beneath forested areas downgradient of farm fields in other parts of the Coastal Plain are often lower near the water table than at greater depth (Hamilton and Shedlock, 1992). Although decreased nitrate concentrations at the water table in these settings have been attributed to denitrification and (or) plant uptake, shallow ground water that percolates through soils covered with forest vegetation probably does not contain as much nitrogen as deeper ground water from agricultural areas upgradient. Therefore, nitrate is not removed from ground water by denitrification beneath the forest, but is only displaced downward by nitrogen-poor recharge through the forest soil.

Unlike the forested areas cited previously, the buffer strip at the Coastal Plain site occupies a smaller area than the cultivated area upgradient (fig. 3), and the amount of recharge moving directly through the buffer strip is small compared with the volume of ground water originating from the cultivated area. In addition, concentrations of nitrate and dissolved oxygen in that beneath the strip are lower throughout the entire thickness of the aquifer than in that beneath the cultivated area upgradient. Therefore, decreased nitrate concentrations in ground water beneath the buffer strip probably result primarily from denitrification. In addition, significant quantitates of nitrite were detected at only two wells—CA Fc 33 and CA Fc 34 (table 9). Depletion of dissolved oxygen could have interrupted nitrogen mineralization to leave unreacted nitrite.

Sampling locations with the highest nitrate and dissolved-oxygen concentrations at both study sites show seasonal and (or) yearly changes in the concentrations. The concentration changes are small, however, compared with the total concentrations and do not appear to be clearly related to possible denitrification. Concentrations of dissolved N_2 samples collected from a small number of wells averaged 18 mg/L at both sites, an amount that is only slightly above the concentration in water in equilibrium with the atmosphere of about 16 mg/L at 12°C. Additional N_2 formed by denitrification could have diffused out of water in the aquifers, however. The cutoff point at which dissolved-oxygen concentration is high enough for the cessation of denitrification differs among bacteria (Korom, 1992). One organism is known to denitrify at dissolved-oxygen concentrations as high as 6.9 mg/L, although most bacteria probably require considerably lower concentrations; consequently, the seasonal and yearly changes probably do not result from denitrification. Nitrate concentration also can differ in response to changes in the amount of nitrogen that is transported to the aquifers in recharge. At sampling locations that do not have an appreciably decreased dissolved-oxygen concentration, changes in nitrate concentration over time probably result primarily from changes in the amount of nitrogen transported to the aquifers.

EFFECTS OF AGRICULTURAL PRACTICES ON NITROGEN TRANSPORT

Nitrogen concentrations in surface runoff, soil and ground waters, and other hydrologic data were analyzed to characterize nitrogen transport at the study sites and to determine the effects of agricultural practices on nitrogen transport. Spatial and temporal distributions of nitrogen concentration were examined to infer effects on transport. Nitrogen-concentration data were used with flow data to estimate nitrogen loads in surface runoff and ground water. Changes in nitrogen concentration and load in surface runoff and ground water were related to changes in agricultural practices.

Surface Runoff

Data on nitrogen concentration in surface runoff were analyzed to determine the effects of agricultural practices on nitrogen concentrations in runoff and to establish numerical relations between nitrogen concentration and runoff flow rate. Nitrogen loads in surface runoff were estimated from nitrogen-concentration/flow-rate relations and were compared among years where agricultural practices differed.

Nitrogen is quickly transported from the study sites in surface runoff. Although nitrogen in ground

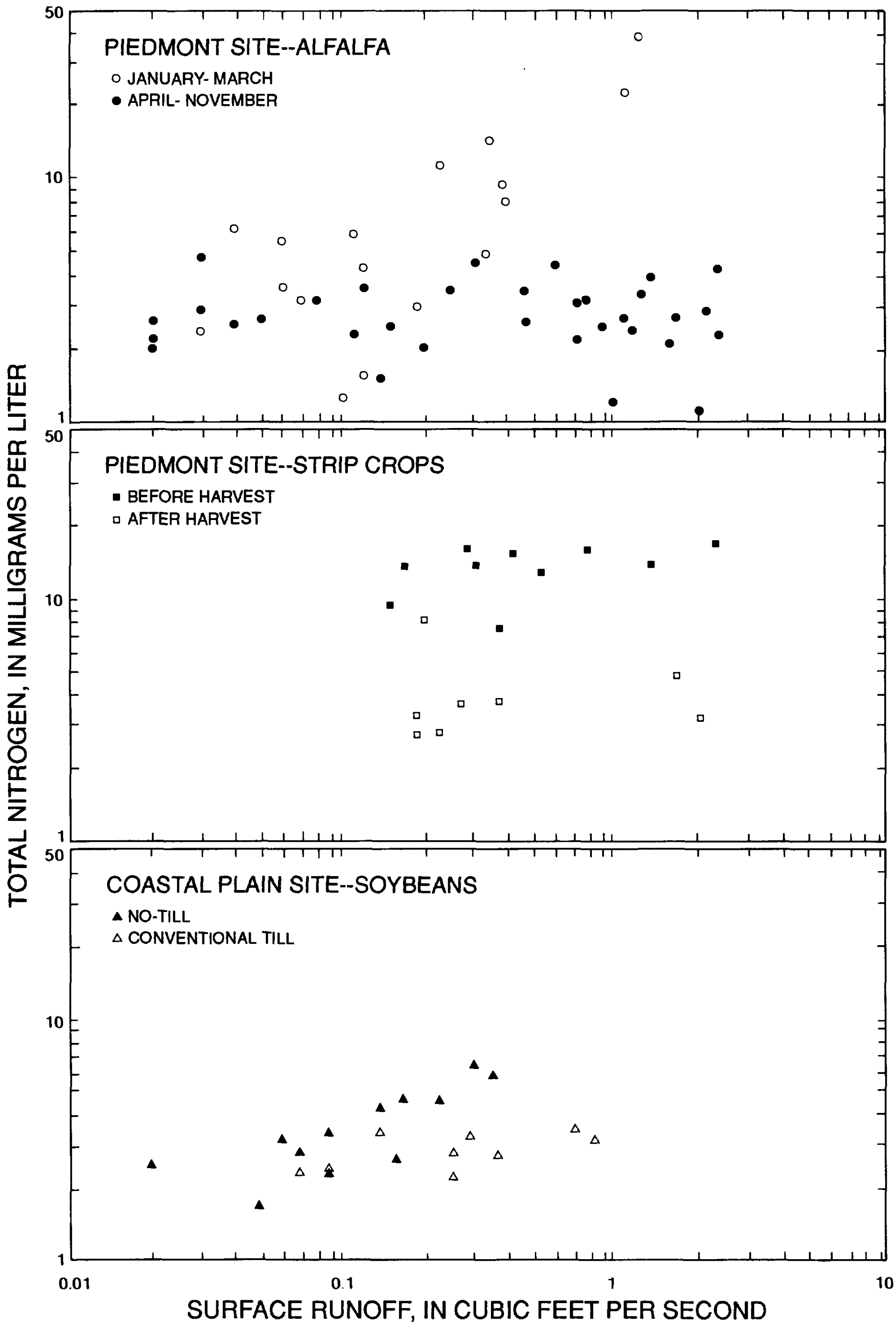

Figure 15. Relation between total nitrogen concentration and surface runoff for crop types at the study sites in the Patuxent River Basin, Maryland.

and soil waters is present primarily in the form of nitrate, a significant part of the nitrogen in surface runoff is present as organic nitrogen, ammonium, and (or) nitrite (table 9), which were added to nitrate to indicate the total concentration of nitrogen in runoff. Total nitrogen concentration in surface runoff differs between the two study sites, among periods of different agricultural practice at each study site, and with the discharge rate during some periods of agricultural practice.

At the Piedmont site, samples of surface runoff were not collected while soybeans were cultivated by using no-till during the 1986–1987 season, and no runoff occurred during the strip-crop growing season in 1991. From 1988 through early 1991, nitrogen concentration in surface runoff appeared to change as a function of flow during some periods (fig. 15). While alfalfa was grown continuously during the 1988–1989 season, nitrogen concentration increased as the rate of flow increased during the winter months (January through March 1988 and 1989) but appeared to remain constant and did not change with flow rate during the nonwinter months (April through November; no samples were collected in December). Alfalfa was dormant during the winter and could have partially died from frost to contribute nitrogen in runoff. Also, if the ground were frozen, then possibly less water infiltrated and more water transported nitrogen in runoff. At other times of the year, surface runoff transported only a small amount of nitrogen that was not either taken up by the alfalfa or transported in the subsurface.

While strip crops were grown at the Piedmont site, nitrogen concentration in surface runoff appeared to increase slightly with flow rate before the 1990 harvest but generally remained at a lower concentration after harvest in late 1990 and early 1991 (fig. 15). Concentrations were higher during the growing season, probably as a result of applying fertilizer to corn and (or) plowing under part of the alfalfa, but decreased after the growing season when fertilizer was no longer applied.

At the Coastal Plain site, nitrogen concentrations in surface runoff were higher during no-till cultivation of soybeans (1986–88) than during conventional tillage of soybeans (1989–91) (fig. 15). Also, nitrogen concentration appears to have increased with flow rate to a greater extent during no-till than conventional-till. Compared with corn, relatively little fertilizer was applied to the soybeans during either period because soybeans obtain most of the nitrogen they require from the atmosphere. Nitrogen concentrations in surface runoff could be higher during no-till cultivation because more nitrogen is available as particles of crop debris that are left on the land surface. Although nitrogen concentration was higher during no-till cultivation, the amount of nitrogen transported in surface runoff generally is expected to be larger under conventional tillage because plowing of the soil reduces infiltration and increases the volume of surface runoff water (U.S. Environmental Protection Agency, 1987). The amount of nitrogen that is transported in surface runoff cannot be determined from concentration data alone, however, because the amount of flow can change. For example, a large amount of less concentrated runoff can transport more nitrogen than a small amount of more concentrated runoff. Therefore, nitrogen loads must be calculated to indicate amounts of nitrogen transported by surface runoff during periods of different agricultural practices.

Nitrogen loads in surface runoff at both study sites were calculated. Few samples of surface runoff

Table 10. Statistical relations between surface-runoff flow rate and nitrogen concentration for periods of different agricultural practices at the study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

[mg/L, milligrams per liter; *p*, probability that regression does not indicate a relation; do., ditto;—, no data]

Years	Agricultural practice	Timing of sample collection	Number of samples	Mean total nitrogen concentration (mg/L)	Correlation coefficient	Log-linear regression		
						Slope	Intercept	*p* value
				Piedmont site				
1988–89	Continuous[1] alfalfa . .	January–March	18	8.2	0.78	0.64	1.25	0.0004
1988–89	. . .do.	April–November . . .	34	2.8	—	—	—	—
1990	Contoured strip crops .	Before harvest.	10	13.6	.41	.14	1.17	.20
1990	. . .do.	After harvest	8	4.0	—	—	—	—
				Coastal Plain site				
1986–88	No-till soybeans	Entire period	11	3.8	.94	.42	.96	.001
1989–91	Conventional till soybeans.	. . .do.	12	2.8	.59	.17	.56	.04

[1]Grown throughout the year.

were collected because of infrequent runoff periods at both study sites, and surface runoff was not sampled during all runoff events or with high frequency during most events. Because a large number of runoff flow rates, however, were measured during sampled and unsampled events, flow-rate data were used to estimate—nitrogen concentrations and calculate nitrogen loads that correspond to each flow measurement.

For periods during which nitrogen concentration appeared to change with flow, measured surface-runoff nitrogen concentrations and corresponding flow rates were transformed to log values and were used to calculate linear regression equations between concentration and flow rate for each of the periods of different agricultural practice (table 10). Flow rates measured without corresponding samples were then substituted into the regression equations to solve for nitrogen concentration and to calculate nitrogen load. A bias in the regression/estimated concentration can result when the value is retransformed from log space to linear space (Cohn and others, 1989) but probably is not of consequence in this case because only one drainage area is included. For periods at the Piedmont site during which nitrogen concentration did not appear to change with flow (April through November under alfalfa and after harvest of strip crops), nitrogen load was calculated by multiplying the flow volume by the mean concentration for the period (table 10).

Flow rates and nitrogen concentrations in surface runoff from contoured strip crops before harvest at the Piedmont site resulted in a small correlation coefficient and high p value. Estimates of nitrogen load resulting from the regression equation, however, were at least as accurate as would have been produced by using the mean concentration.

Nitrogen loads were summed for each year for comparison (table 11). Because most of the flow was measured, calculated nitrogen loads should adequately indicate major differences among different years.

Nitrogen load in surface runoff at both study sites was least in 1988 (table 11) but increased substantially the following year. Nitrogen load in surface runoff at the Piedmont site continued to increase through 1990 while nitrogen load decreased at the Coastal Plain site. During 1991, nitrogen load in surface runoff decreased from the previous year at both study sites. Data are inadequate to calculate nitrogen loads in runoff during 1987.

Nitrogen load in surface runoff increased from 1988 to 1989 at both study sites (table 11), corresponding to a large increase in precipitation and runoff volume (table 7). Alfalfa was grown at the Piedmont site during 1988 and 1989, and the increase in nitrogen load in surface runoff was probably the result of the increased volume of runoff caused by increased precipitation. In 1990, contoured strips of corn were planted at the Piedmont site; the corn crop required a large

Table 11. Agricultural practices and calculated annual nitrogen loads in surface runoff and ground water at study sites in the Piedmont and the Coastal Plain Physiographic Provinces, Patuxent River Basin, Maryland

[(lb/acre)/yr, pounds per acre per year; —, not calculated; do., ditto]

Year	Piedmont site			Coastal Plain site			
	Agricultural practice	Nitrogen load [(lb/acre)/yr]		Agricultural practice	Nitrogen load [(lb/acre)/yr]		
		Surface runoff	Ground water[1]		Surface runoff	Ground water from cultivated area[1]	Ground-water discharge to Patuxent River[1]
1987	No-till soybeans	—	—	No-till soybeans	—	12.37	—
1988	Continuous[2] alfalfa...	.25	12.25	...do.............	.01	12.55	—
1989	...do..............	1.80	9.23	Conventional till soybeans.	1.97	13.25	2.43
1990	Contoured strip crops .	2.96	7.13	...do.............	1.07	15.34	7.42
1991	...do..............	.55	5.64	...do.............	.07	11.51	8.36

[1]Nitrogen loads in ground water resulted from agricultural practices during and prior to the period of study (see section "Saturated Zone").
[2]Grown throughout the year.

application of fertilizer (table 1). Nitrogen concentration increased (fig. 15), and as a result, nitrogen load increased further from the previous year even though the volume of runoff decreased. Because the volume of runoff was smaller (table 7), nitrogen load in 1991 was smaller than in 1990, even though corn continued to be grown. Also, only one contoured strip was planted in corn during 1991, whereas two strips were planted in corn during 1990, so less fertilizer was applied.

Between 1988 and 1989, precipitation and surface-runoff volume increased at the Coastal Plain site (table 7), and nitrogen load in runoff also increased (table 11). At the same time, agricultural practice changed from no-till soybeans to conventional-till soybeans. During 1990 and 1991, precipitation and surface-runoff volume and nitrogen load decreased from those of 1989, while conventional tillage continued. No-till is intended to result in smaller runoff volumes and, hence, smaller nitrogen loads than conventional tillage because the layer of crop debris left on the undisturbed soil surface can slow runoff velocity and promote infiltration (U.S. Environmental Protection Agency, 1987). Surface-runoff volume and nitrogen load, however, increased in 1989, probably at least partly because of the increase in precipitation. Any effect on runoff volume and nitrogen load caused by the change from no-till to conventional tillage is unclear.

Precipitation at the Coastal Plain site during 1988 under no-till cultivation was approximately equal to that during 1991 under conventional tillage, and no-till cultivation possibly resulted in a smaller volume of surface runoff than conventional tillage, given the same amount of precipitation (see section "Flow Through the Study Sites"). At a given surface-runoff flow rate, nitrogen concentration in runoff is higher under no-till cultivation than conventional tillage (fig. 15) possibly because more nitrogen is available at the land surface under no-till as particles of crop debris. Therefore, no-till cultivation apparently results in higher nitrogen concentrations than conventional tillage but possibly smaller runoff volumes and nitrogen loads for a given amount of precipitation. Differences in nitrogen load in surface runoff during different agricultural practices, however, are minor compared with the larger nitrogen loads in ground water (table 11; see section "Saturated Zone").

Unsaturated Zone

Soil-water nitrogen and bromide-tracer concentration data were analyzed to determine solute-transport processes, average vertical velocities, and average traveltimes in the unsaturated zone at the study sites. Data from time-series concentration hydrographs were examined. Relative degrees of vertical percolation and horizontal interflow, as well as effects from agricultural practices, were inferred.

Nitrogen Transport

Nitrogen that is not transported from the study sites in surface runoff is transported by infiltration at the land surface and moves into the unsaturated zone. Nitrate is the predominant form of dissolved nitrogen in soil water at both study sites (table 9). Changes in nitrate concentration in soil water over time differ between the study sites, and between the upslope and downslope sampling locations at each site (fig. 16). Concentrations of other forms of nitrogen in soil water are low and remain relatively constant.

At all sampling locations, farming practices (plowing, planting, chemical application) had to be stopped in an area of about 100 ft^2 directly over the lysimeters after installation. Farm equipment had to be diverted several feet around lysimeter sample-collection tubes that protruded from the land surface. Therefore, the supply of nitrogen to the lysimeters by vertical percolation from the land surface was effectively stopped, and as a result, nitrate concentrations in water from some lysimeters decreased after installation. Nitrogen also was transported horizontally, however, by interflow in the unsaturated zone (see section "Recharge/Discharge Relations") and was still in some lysimeters even though the source of the nitrogen directly above the lysimeters had stopped.

At the Piedmont site, nitrate concentration in soil water sampled at the upslope location (lysimeters HO Cd 253, HO Cd 290, HO Cd 291, HO Cd 292) decreased at depths below land surface of 1 ft (lysimeter HO Cd 253) and 5 ft (HO Cd 290) within about 1 year after installation, and remained low for another year and a half (fig. 16). Nitrate concentration at 10 ft (lysimeter HO Cd 291) was more variable and at 14 ft (lysimeter HO Cd 292) increased during the first year and a half and generally remained high thereafter. Subsurface materials at the Piedmont site have a high clay content. Water is probably frequently perched above impermeable clay layers, and flow can be directed

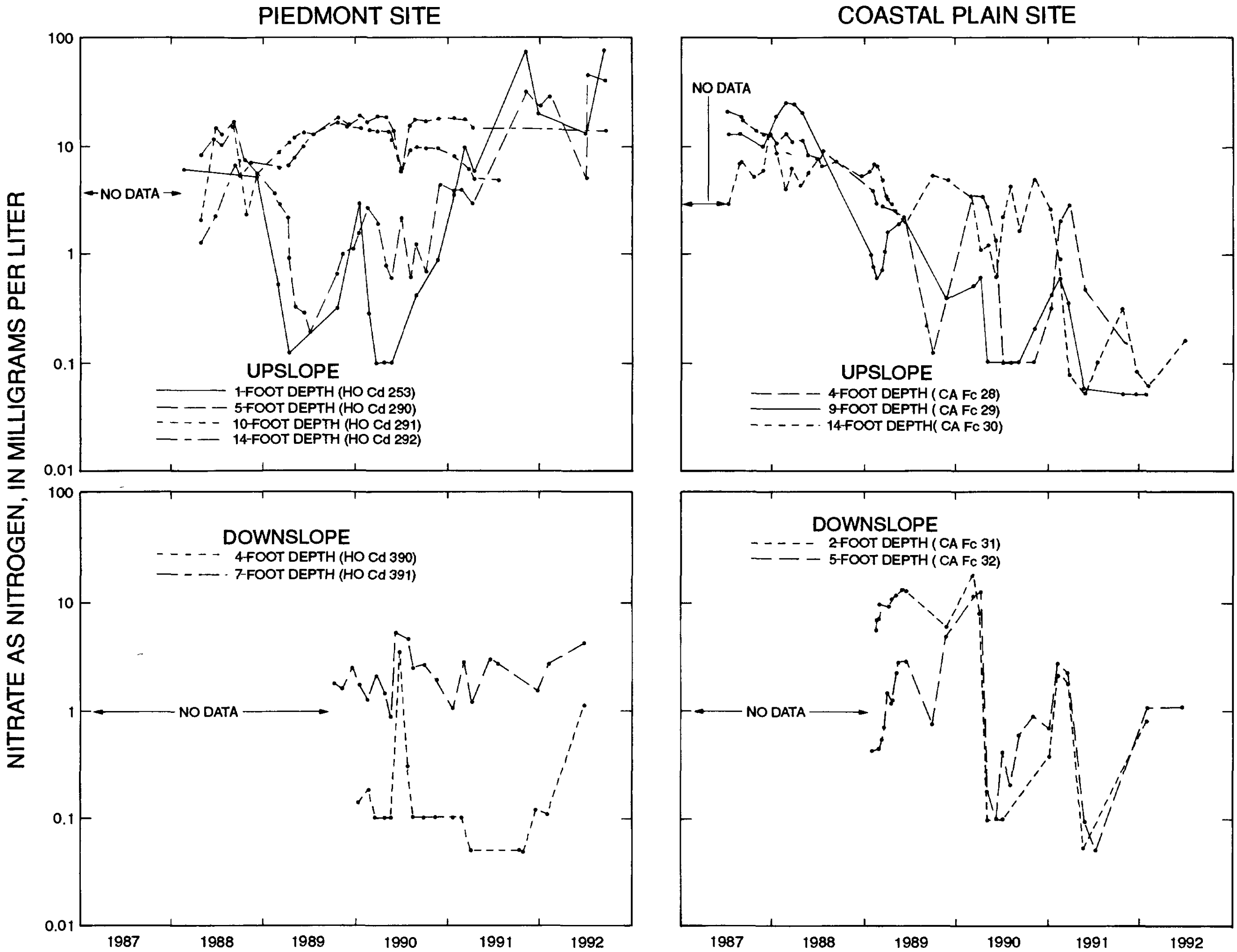

Figure 16. Concentrations of dissolved nitrate in soil water over time for upslope and downslope locations at the study sites in the Patuxent River Basin, Maryland.

through secondary pore spaces (macropores) that increase interflow and decrease vertical percolation. Therefore, nitrogen transport through the unsaturated zone at the Piedmont site could have a significant horizontal component, and nitrogen in deep soil water could originate from the land surface upslope of the sampling location.

Because agricultural practice directly above the lysimeters ceased at installation and nitrate concentration in soil water as deep as 5 ft below land surface at the upslope location at the Piedmont site decreased to near zero a year later, the approximate vertical transport rate in shallow soil was 5 ft/yr. Because nitrate concentration in deeper soil water generally remained high for several more years, transport at depths below 5 ft could be partly horizontal. The depth to the water table is approximately 25 ft at this location, and nitrogen could take several years to be transported from the land surface to the water table. Similarly, solute-transport times through unsaturated micaceous saprolite in the Piedmont Province in South Carolina were indicated by a tritium tracer to be about 6 years from the land surface to the water table at a depth of 66 ft (Ligon and others, 1980). In contrast, times of less than 2 years were estimated at a site in the Piedmont Province in Pennsylvania (Hall, 1992a), which is underlain by a karst flow system where water percolates through sinkholes and bedrock fractures enlarged by solution weathering.

Nitrate concentration in soil water at depths of 1 and 5 ft (lysimeters HO Cd 253 and HO Cd 290) at the upslope sampling location at the Piedmont site began to increase about 2 years after initially decreasing (fig. 16). At the same time, agricultural practice changed from continuous alfalfa to contoured strips of corn, and nitrogen load in surface runoff increased. Although agricultural activity was not resumed directly over the lysimeters, the supply of nitrogen to shallow soil water could have been renewed by nitrogen-laden shallow interflow or surface runoff that infiltrated over the lysimeters after the alfalfa had been plowed under and fertilizer had been applied to the corn.

At the downslope soil-water sampling location at the Piedmont site (lysimeters HO Cd 390 and HO Cd 391), nitrate concentration in soil water was generally low (fig. 16). This location was positioned in a grass drainage-filter strip that was maintained in the center of the site throughout the study period to reduce erosion (fig. 2). Surface runoff with nitrogen concentrations that were considerably higher than soil water beneath the grass strip regularly flowed across the strip (table 9). Apparently, the grass removed some nitrate from water that percolated through soil beneath the strip. The grass was routinely mowed during harvesting and other activities at the site, which could have resulted in removal of nitrogen from the strip.

Soil water at a depth of 7 ft beneath the grass drainage-filter strip at the Piedmont site (lysimeter HO Cd 391) had higher nitrate concentrations than shallower soil water (lysimeter HO Cd 390) (fig. 16). Some soil water beneath the strip could have originated from horizontal interflow in the unsaturated zone that did not percolate through the grass. Surface runoff was primarily interflow that resurfaced at the downslope end of the site (see section "Recharge/Discharge Relations"), and interflow probably was largest at the downslope location. Thus, the removal of nitrogen from soil water by the grass strip could have been limited to a shallow depth beneath the strip.

Nitrate concentration in soil water at both depths sampled beneath the grass drainage-filter strip at the Piedmont site increased slightly in 1990 and again in 1992 (fig. 16). A contoured strip of corn, which requires heavy applications of fertilizer, was planted during these years next to the part of the filter strip where the lysimeters were located and could have contributed to the concentration increase. Nitrate concentration remained low in 1991, when soybeans were grown and no fertilizer was applied in this contoured strip, and corn was grown farther away in another contoured strip upslope.

At the Coastal Plain site, nitrate concentration in soil water at the upslope location (lysimeters CA Fc 28, CA Fc 29, CA Fc 30) decreased at all depths sampled within about 2 years after lysimeter installation (fig. 16). Subsurface materials at the Coastal Plain site have a larger sand content than at the Piedmont site. Water is less frequently perched above impermeable clay layers, and flow can be uniformly distributed in primary pore spaces where vertical percolation is greater than interflow. Therefore, nitrogen transport through the unsaturated zone at the Coastal Plain site could be primarily vertical, and nitrogen in soil water at all depths originates primarily from the land surface directly above the lysimeters.

Because agricultural activity directly above the lysimeters ceased after installation, and nitrogen concentration in soil water as deep as 14 ft below the land surface at the upslope location at the Coastal Plain site had decreased to near zero 2 years later, the approximate vertical transport rate is 7 ft/yr. The depth to the water table fluctuated from 15 to 19 ft at this location, and much of the nitrogen could have reached the water table within 2 years. For comparison, average vertical transport rates of chloride tracer in the unsaturated zone in unconsolidated sediments at a site in the Coastal Plain Province in South Carolina ranged from 3 to 62 ft/yr (Dennehy and McMahon, 1987).

Nitrate concentration in soil water at depths of 4 and 9 ft (lysimeters CA Fc 28 and CA Fc 29) at the upslope sampling location at the Coastal Plain site briefly increased twice after initially decreasing (fig. 16). Both increases coincided with the onset of recharge in the early part of the year; the recharge may have leached small residual amounts of nitrogen from the soil. Similarly, at a study site in the Coastal Plain Province in South Carolina, percolation resulted in small increases in the concentration of chloride tracer after most of the chloride had been transported away from the measurement point (Dennehy and McMahon, 1987). At the same time that the nitrate increases were observed in this study, agricultural practice changed from no-till to conventional-tilled soybeans. Although agricultural activity was not resumed directly over the lysimeters, the supply of nitrogen to shallow soil water could have been renewed. Nitrogen-laden shallow interflow or surface runoff possibly infiltrated over the lysimeters after crop debris that accumulated on the land surface during 2 years of no-till cultivation had been plowed under.

Nitrate concentration in soil water at a depth of 14 ft (lysimeter CA Fc 30) at the upslope sampling location at the Coastal Plain site generally remained high for about 2 years after the concentration in shallower soil water had decreased (fig. 16). Soil water at a depth of 14 ft is periodically within 1 ft of the water table at the upslope location; at these times, the soil water probably is in the saturated capillary zone. Thus, nitrogen in some soil-water samples at 14-ft depth could originate from the saturated zone below the water table (phreatic zone), as well as from percolation from the land surface.

At the downslope location (lysimeters CA Fc 31 and CA Fc 32) at the Coastal Plain site, nitrate concentration in soil water decreased at both depths sampled within about 1.5 years after lysimeter installation and subsequently increased by small amounts with the onset of recharge during the following years (fig. 16). This sampling location is positioned within 5 ft of the area of surface runoff near the runoff flume. Interflow that is associated with runoff probably is larger than elsewhere at the site and can extend laterally beyond the runoff flume and transport some nitrogen to soil water from upslope of the sampling location. Nitrogen transport through the unsaturated zone probably is primarily vertical throughout most of the site, except in the area of surface runoff and interflow at the downslope end of the site.

Most of the nitrogen in water that infiltrated at the downslope location at the Coastal Plain site before the lysimeters were installed was transported deeper than 5 ft below the land surface in about 1.5 years. The average vertical transport rate is, therefore, at least 3 ft/yr. The depth of the water table fluctuated from 5 to 9 ft at this location, and much of the nitrogen could have reached the water table within about 1.5 years.

Bromide-Tracer Transport

Soil-water bromide-tracer concentration data were analyzed similarly to nitrate-concentration data to determine solute-transport processes, average vertical velocities, average traveltimes, and the relative degrees of vertical percolation and horizontal interflow through the unsaturated zone at the study sites. Similar to the nitrate findings, changes in bromide-tracer concentration in soil water over time differ between the study sites and between the upslope and downslope sampling locations at each site (fig. 17). Although the source of nitrogen directly above the lysimeters was stopped at the time of installation, sodium bromide was applied to the land surface directly above the lysimeters after installation. Subsequent infiltration and percolation transported bromide to most of the lysimeters within a few months. Water that entered lysimeters by horizontal interflow, however, originated from outside the application area and did not transport bromide to the lysimeters.

At the Piedmont site, bromide concentration in soil water sampled at the upslope location increased after application of the tracer at depths of 1 and 5 ft (lysimeters HO Cd 253 and HO Cd 290) (fig. 17). The larger increase at 5 ft than at 1 ft could be a result of a concentrated mass of bromide being transported in a macropore that intersected the 5-ft lysimeter but bypassed the 1-ft lysimeter. Alternatively, the maximum concentration at 1 ft possibly occurred between sample-collection times. Bromide concentration at 10 ft (lysimeter HO Cd 291) increased only slightly during the half a year after application, after which no samples could be collected from this lysimeter. Bromide concentration at 14 ft (lysimeter HO Cd 292) remained below the detection limit of 1 mg/L for almost 2 years after application. Similar to nitrogen, bromide appears to be transported by vertical percolation quickly through shallow soil at the Piedmont site. Transport through deep soil is slower in the vertical direction, where flow could be largely horizontal, and deep soil water could originate from the land surface outside of the bromide application area and upslope of the sampling location. Most of the bromide in water that infiltrated at the upslope location at the Piedmont site was transported deeper than 5 ft below the land surface in about 2 years, and the average vertical transport rate in shallow soil is, therefore, at least 2 ft/yr, a rate that is similar to that calculated for nitrate. Vertical transport is slower at greater depths because flow is primarily horizontal.

At the downslope location (lysimeters HO Cd 390 and HO Cd 391) at the Piedmont site, bromide concentration increased after application but less quickly than at the upslope location (fig. 17). Some of the sodium bromide applied at the land surface initially could have been removed by surface runoff at the downslope location, resulting in less bromide transported in soil water. Most of the bromide in water that infiltrated at the downslope location at the Piedmont site was transported deeper than 7 ft below the land surface in about 2 years, and the average vertical transport rate in shallow soil is, therefore, at least 3 ft/yr. Unlike bromide, nitrogen could be partly attenuated in the drainage-filter strip at the downslope location by being taken up by grass, which is then removed by mowing and collection of clippings.

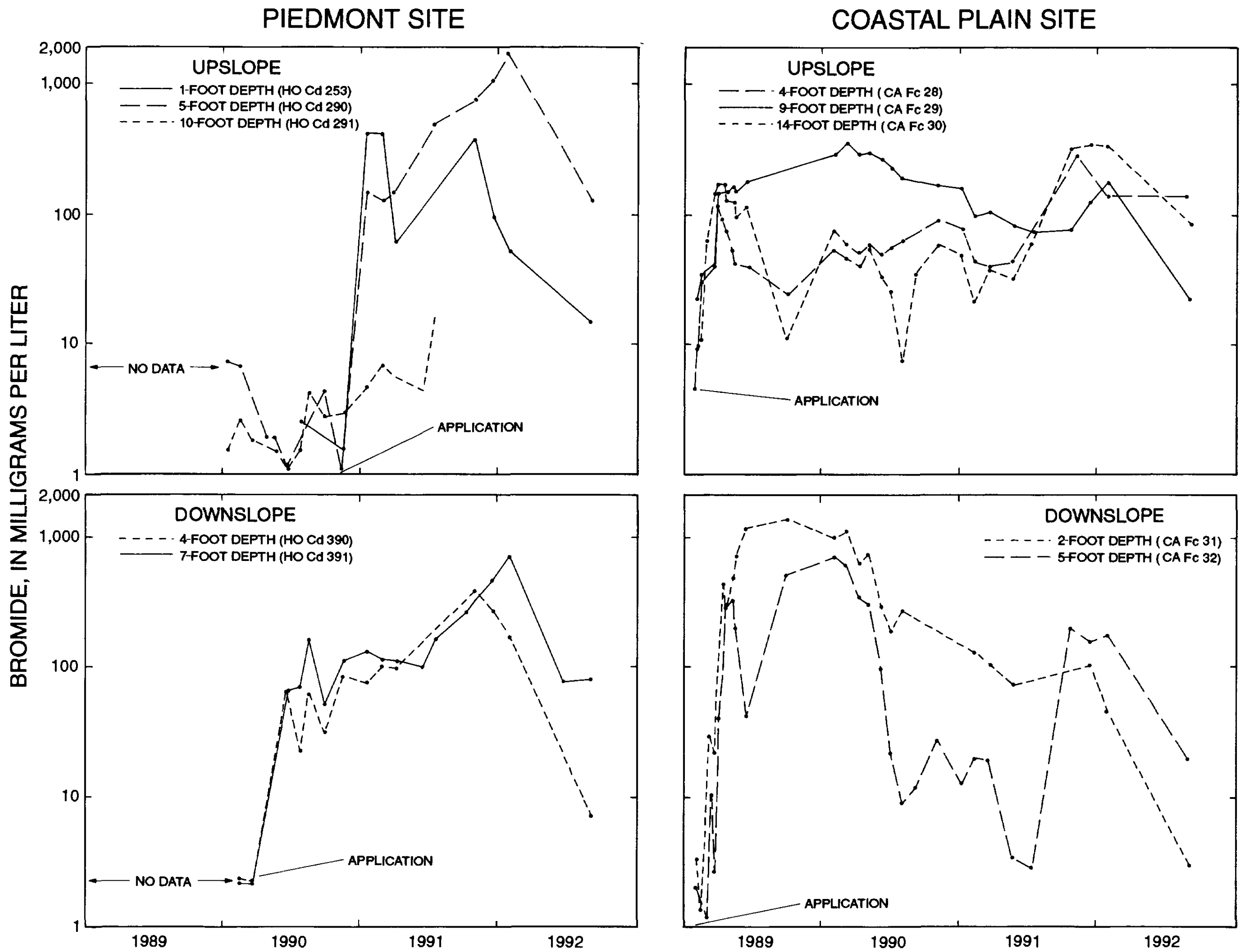

Figure 17. Concentrations of bromide tracer in soil water over time for upslope and downslope locations at the study sites in the Patuxent River Basin, Maryland.

At the Coastal Plain site, bromide concentration in soil water at the upslope location (lysimeters CA Fc 28, CA Fc 29, and CA Fc 30) changed more irregularly over time than elsewhere at either study site (fig. 17). Although concentrations initially increased after application at all depths sampled, they subsequently decreased during the next year at depths of 4 ft (lysimeter CA Fc 28) and 14 ft (lysimeter CA Fc 30) while continuing to increase at the intervening depth of 9 ft (lysimeter CA Fc 29). Concentration at depths of 4 and 14 ft then changed over a small range while concentration at 9 ft gradually decreased, and concentration at all depths increased once more about 2 years after application. The changes in bromide concentration probably result only from vertical transport directly beneath the application area, rather than horizontal transport from outside the immediate area, because bromide originates only from the land surface directly over the lysimeters and unsaturated flow is primarily vertical.

The irregular change of bromide concentration during the study period in soil water at the upslope location at the Coastal Plain site could result from changes in vertical transport rates and direction. Vertical flow in the unsaturated zone can be upward toward the land surface during periods of high evapotranspiration rates, as well as downward when evapotranspiration rate is low, and is zero at vertical hydraulic-gradient divides (see section "Recharge/Discharge Relations"). Although the uniform nitrate-concentration decrease during 1987–88 (fig. 16) indicates that vertical transport rate was constant, sodium bromide was not applied until later in 1989. Precipitation, recharge, and surface runoff increased appreciably during 1989 from the previous 2 years (table 7) and could have coincided with changes in unsaturated flow. In this case, nitrogen transport rates could be more variable than is indicated by the nitrate-concentration decrease during 1987–88.

Unsaturated flow at the Coastal Plain site also could have been artificially affected by the addition of sodium from sodium bromide, which can cause smectite clays to swell and reduce the hydraulic conductivity of the soil (Drever, 1988). Although the smectite content of the soil at the site is unknown, shrinkage cracks of more than 1 in. wide have been observed at some locations on the land surface at the site after prolonged dry periods, indicating that some smectite could be in the soil. High sodium concentrations did not decrease hydraulic conductivity in the unsaturated zone in unconsolidated sediments at a site in the Coastal Plain Province in South Carolina where sodium chloride tracer was used (Dennehy and McMahon, 1987). If sodium decreased hydraulic conductivity at the site described in this report, however, then the changes in bromide concentration are spurious and do not represent naturally occurring solute transport through the unsaturated zone at the site. Unfortunately, the available information is inadequate to determine the extent to which changes in transport rates and directions, reduction of hydraulic conductivity by sodium, and (or) possibly other factors could have affected bromide concentration.

At the downslope location (lysimeters CA Fc 31 and CA Fc 32) at the Coastal Plain site, bromide concentration in soil water at both depths sampled increased after application (fig. 17), subsequently decreased within about 1.5 years after application, and remained low thereafter. Most of the bromide in water that infiltrated at the downslope location was transported deeper than 5 ft below the land surface in about 1.5 years. Similar to nitrogen, the average vertical transport rate of bromide is, therefore, at least 3 ft/yr, and because the depth of the water table is about 7 ft, much of the bromide could have reached the water table within 2 years.

Saturated Zone

Ground-water nitrate-concentration data were analyzed to determine the effects of different agricultural practices on nitrate concentration, as well as different traveltimes through the aquifers, dispersive mixing, and denitrification. Nitrogen loads in ground water, which estimated from nitrogen concentrations and discharge volumes calculated in simulations of ground-water flow as part of this study, were compared among years having different agricultural practices and to nitrogen loads in surface runoff.

Water that did not flow from the study sites as surface runoff or interflow in the unsaturated zone entered the saturated ground-water zone as recharge at the water table (fig. 6). Changes in nitrogen concentration in ground water during the study period at both study sites resulted from changes in the amounts of nitrogen being transported to the aquifers in recharge. Nitrogen that resulted from recent agricultural practices is transported most quickly to ground water beneath the downgradient part of the study sites, where the unsaturated zone is thinnest. Recharge further upgradient took longer to percolate through the larger thickness of unsaturated zone. Therefore, the nitrogen concentration near the water table further upgradient resulted from earlier agricultural practices. After recharge, additional time was required for ground water to flow downgradient from the water table, and the nitrogen concentration in ground water below the water table resulted from still earlier agricultural practices.

Nitrogen concentration in ground water was partly altered from that which initially resulted from recharge. Nitrate concentration was decreased by denitrification in some parts of the aquifers where dissolved-oxygen concentration was sufficiently low (see section "Speciation of Nitrogen in Water"). In addition, the extent of dispersive mixing increased in the downgradient direction, and ground water of different ages and nitrogen concentrations became increasingly mixed toward the downgradient ends of the study sites (see section "Flow Through the Aquifers"). Consequently, the nitrogen concentration of ground water that discharged from the downgradient ends of the study sites resulted from the mixing of water of different ages that entered the aquifer at different locations upgradient. Some of the nitrogen in discharge resulted from recent agricultural practices and was transported quickly to shallow ground water beneath the downgradient part of the sites. Deeper ground water from farther upgradient also discharged, however, with a different nitrogen concentration than shallow ground water that resulted from earlier agricultural practices. Thus, nitrogen concentration in ground-water discharge was a composite that resulted from agricultural practices at different times over several decades.

For the entire ground-water system at each study site to be affected by a single agricultural practice, the practice would have to be implemented for several decades or more. For this study, therefore, different parts of the ground-water system at each study site were examined and compared to infer the effects of specific agricultural practices on nitrogen transport.

Nitrate is the dominant form of dissolved nitrogen in ground water at both study sites (table 9). Concentrations of other forms of nitrogen in ground water are low and remain constant. Mean monthly ground-water nitrate concentrations were calculated from nitrate concentrations in ground-water samples collected at sampling locations in different parts of each study site (fig. 18). Seasonal Kendall statistics (Helsel and Hirsch, 1992) were calculated from mean monthly concentrations to analyze temporal trends in nitrate concentration in the different parts of each site. The tau values are analogous to correlation coefficients in that they range from -1 to 1 and indicate the strengths of monotonic trends but are unique because seasonal (in this case monthly) variability is compensated for. All the indicated trends were detected with more than 95 percent certainty (significance level, less than 0.05). The trend slopes are estimates of the magnitudes of the trends.

In addition to nitrate-concentration trends, nitrogen loads in ground-water discharge also were calculated for both study sites (table 11) to compare among years having different agricultural practices and to nitrogen loads in surface runoff. Mean monthly concentrations of total nitrogen in ground-water discharge were calculated from concentrations of nitrogen species in ground water and were multiplied by monthly discharge volumes calculated by ground-water flow models of the study sites (see "Simulation of Ground-Water Flow") to calculate monthly nitrogen loads in ground-water discharge. Monthly nitrogen loads were summed for each year for comparison.

Piedmont Site

Nitrate concentration in ground water at the Piedmont site was generally higher at the springs (HO Cd 80 and HO Cd 81) than elsewhere at the site but decreased during the study period by about 4 mg/L (fig. 18). Nitrate concentration in ground water was higher in alluvium (well HO Cd 78) and shallow saprolite (well HO Cd 341, HO Cd 342) than in deep saprolite (wells HO Cd 28, HO Cd 29, HO Cd 79), but increased slightly during the study period. Nitrate concentration in water in schist (wells HO Cd 20, HO Cd 21, HO Cd 25, HO Cd 26) was less than elsewhere at the site and remained constant. For comparison, the mean nitrate concentration from the USGS National Water Information System data base for ground water collected throughout the Piedmont in the Patuxent River Basin is about 3 mg/L, although some of the wells sampled are considerably deeper than those sampled in this study. Other forms of nitrogen in ground water throughout the Piedmont are at low concentrations.

Much of the ground water at the Piedmont site is in deep saprolite and schist and has a low nitrate concentration, possibly as a result of denitrification (see section "Speciation of Nitrogen in Water"). Alternatively, low nitrate concentrations in ground water in deep saprolite and schist could be the result of smaller fertilizer applications in the past than during the period of this study. Water may take several decades to move through the deepest part of the flow system (see section "Flow Through the Aquifers"). Although agriculture has probably been practiced at the land surface for hundreds of years, fertilizer applications were increased nationwide recently during the early 1970's with the intent of increasing crop yields. If ground water in deep saprolite and schist infiltrated when applications of fertilizers at the Piedmont site were comparatively small, then the infiltrating water could have contained less nitrogen than was in infiltrating water during this study. Although chemical evidence indicates that denitrification also could occur to some extent in water in deep saprolite and schist, available information is inadequate to separate the relative effects of denitrification and small pre-1970 fertilizer application rates on nitrate concentration in deep saprolite and schist.

The increase in nitrate concentration in ground water deep saprolite (fig. 18) indicates a decrease in denitrification and (or) an increase in the nitrate concentration in recharge resulting from agricultural practices. Water takes several years to percolate from the land surface to the water table, however, (see section "Unsaturated Zone"), and another decade or more to travel beneath the study site through saprolite; as a result, most of the nitrate in deep saprolite probably resulted from agricultural practices from a decade or more ago and not from practices during the study period.

Nitrate concentration in water at the springs at the Piedmont site changed more than elsewhere at the site (fig. 18) and probably resulted from changes in the amount of nitrogen being transported to the aquifer in recharge. From 1988 to 1990, nitrate

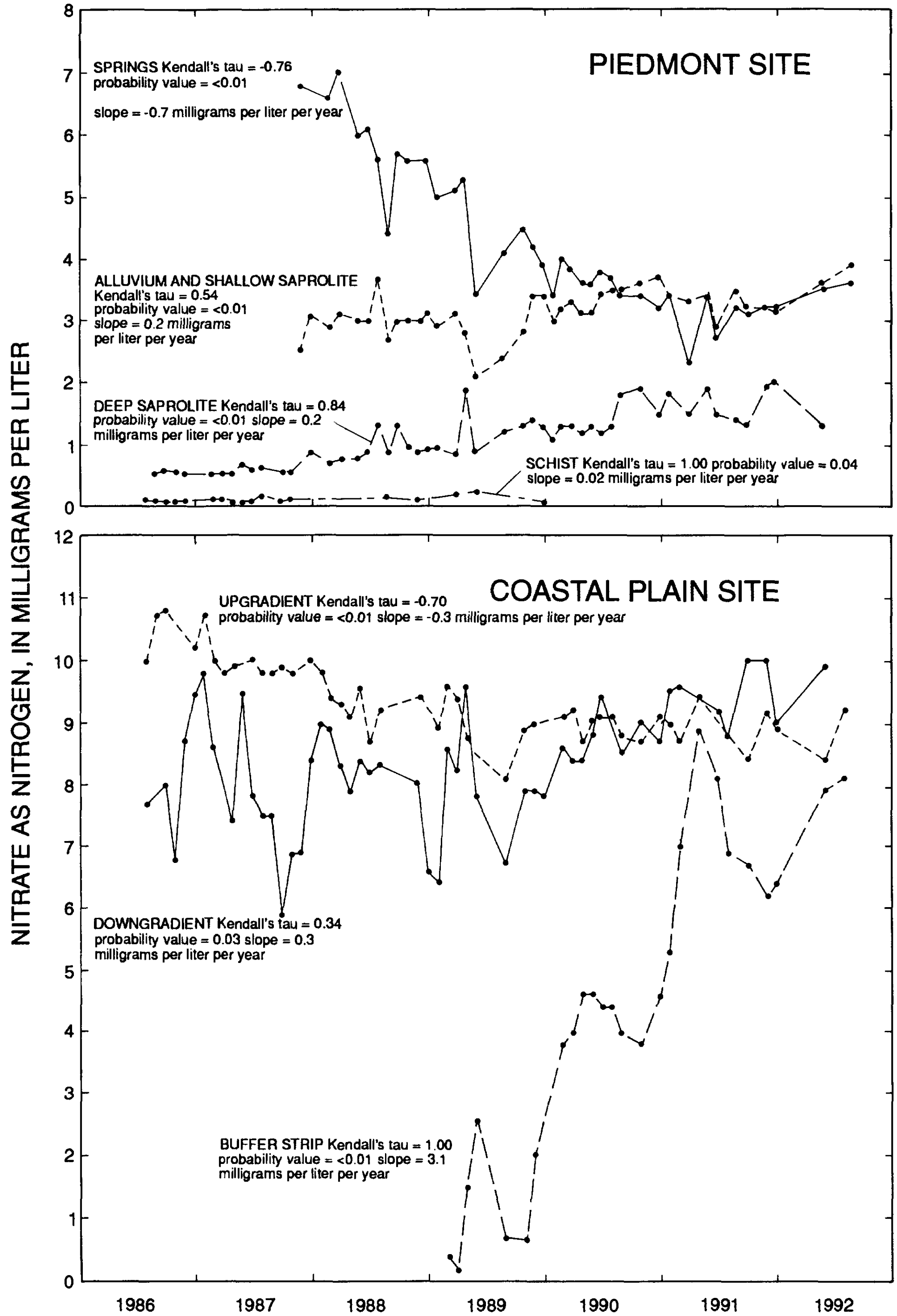

Figure 18. Monthly mean nitrate concentrations and seasonal Kendall tau, two-sided probability level, and trend-slope estimate for ground water at the study sites in the Patuxent River Basin, Maryland.

concentration in water at the springs decreased from about 7 to 3.5 mg/L. During the same period, nitrate concentration in ground water in alluvium and shallow saprolite increased slightly from about 3 to 3.5 mg/L. At estimated rates of ground-water flow (see section "Flow Through the Aquifers"), 1 to 2 years are required for ground water to flow from the sampling locations in alluvium and shallow saprolite (wells HO Cd 78 and HO Cd 342) to discharge at the springs. Therefore, water with an initially high nitrate concentration at the springs was displaced by ground water having a lower concentration from upgradient.

Because nitrate concentration is low in water in deep saprolite and schist at the Piedmont site, a relatively small amount of nitrate is transported to the springs from deep ground water. Most of the nitrate in ground water that discharged at the springs during the study period was transported quickly to shallow ground water beneath the downgradient end of the site and resulted from recent agricultural practices. Mixing of shallow ground water with deeper, less concentrated ground water probably diluted ground water at the springs at a fairly constant rate. Therefore, changes in nitrate concentration over time at the springs resulted primarily from changes in recent agricultural practices because the effects of earlier practices were reduced.

The initially high nitrate concentration in ground water at the springs at the Piedmont site could be the result of heavy application of fertilizer required for no-till corn, which was grown before the study as recently as 1985 (F.L. Walbert, University of Maryland, written commun., 1988). Nitrate concentration could potentially have been higher except that ground water at the springs probably was diluted by mixing with deeper, less concentrated ground water from upgradient.

Nitrate concentration at the springs decreased (fig. 18) after soybeans which received little fertilizer were grown during the 1986–87 season and while continuous alfalfa (which accumulates nitrogen in a deep root system) was grown during the 1988–89 season. In 1990, two-thirds of the alfalfa was plowed under, and the site was divided into three contoured strips in which planting alternated each year among alfalfa, corn, and soybeans. Strips planted in corn require heavy applications of fertilizer that, together with the plowed-under alfalfa, could result in an increase in nitrate concentration in ground water. Alternating the strips with other crop types, however, is intended to use residual amounts of nitrogen in the soil and to prevent nitrogen from being leached to ground water (U.S. Environmental Protection Agency, 1987). Also, the total area in which corn was grown and fertilizer applied was only about one-half the area of the entire site.

Nitrate concentration in ground water at the springs and in alluvium and shallow saprolite at the Piedmont site remained approximately the same in 1992 as that which resulted in 1990 from growing soybeans and continuous alfalfa, (fig. 18) even though strip crops had been grown and fertilizer applications had been increased for 2 years. Alternating different crops among the strips could have used nitrogen in the soil as intended and limited the amount transported to ground water, but high nitrate concentrations that resulted from no-till corn before the study period persisted for 4 years after the practice had ceased. Any increase in nitrate concentration in ground water as a result of strip-crop corn probably would have been apparent by 1992, but as long as 4 years could be needed from when the corn strips were first planted, or until 1994, for an increase to be detected.

To calculate nitrogen load in ground-water discharge from the Piedmont site, nitrogen concentrations in ground water at the springs were used to calculate mean monthly nitrogen concentrations. Because nitrogen concentrations in water in schist are low and flow out of the Piedmont site from schist is a small amount of the total ground-water-flow volume (table 5), most of the nitrogen in ground water is transported from the site in discharge from regolith. Therefore, discharge volumes that were calculated by model simulation (table 5) from only regolith, not from schist, were multiplied by the mean monthly nitrogen concentrations to calculate nitrogen load in ground-water discharge.

Nitrogen load in ground-water discharge from the Piedmont site steadily decreased from about 12 to 6 (lbs/acre)/yr during the study period (table 11), even though discharge volume increased from 1988 to 1989 before decreasing during the rest of the study period (table 5). Nitrogen load during the period was primarily a function of nitrogen concentration, which was initially high as a result of no-till corn grown before the beginning of this study but has since decreased while soybeans, alfalfa, and contoured strip crops were grown (fig. 18).

Throughout the study period, nitrogen load in ground-water discharge remained greater than that in surface runoff, even though the latter changed considerably (table 11). Subsurface transport of nitrate (leaching associated with recharge) is often the most important component of nitrogen transport (Legg and Meisinger, 1982). Surface-runoff nitrogen load, however, probably does not represent removal of nitrogen from the study site because much of the surface runoff reinfiltrates the land surface in the flat area below the runoff flume (see section "Recharge/Discharge Relations"). Nitrogen in surface runoff can be added to that leaving the site in ground-water discharge and (or) can leave the site in interflow in the unsaturated zone.

Estimates of nitrogen load in ground water from other locations in the Piedmont Province in Maryland are not available. Roughly comparable amounts to loads in ground water of from 5 to 8 (lb/acre)/yr of nitrogen, however, are removed in stream base flow, which originates as discharge of ground water to streams from the nearby Susquehanna River Basin in Pennsylvania, which drains a similar area in the Piedmont and Appalachian Physiographic Provinces (Susquehanna River Basin Commission, 1990).

In contrast to the findings at the Piedmont site, much larger nitrogen loads in ground water that range from about 100 to 200 (lb/acre)/yr were estimated for an agricultural site in part of the Piedmont Province in Pennsylvania, which is underlain by a karst flow system (Hall and Risser, 1992). Large applications of nitrogen, primarily as manure, are associated with intensive animal production at the Pennsylvania site and range from 120 to 830 (lb/acre)/yr. Resulting ground-water nitrate concentrations are from 11 to 82 mg/L. In addition, large volumes of ground-water flow in the karst system were estimated on the basis of a recharge rate of 19 in/yr. Heavy applications of nitrogen and heavy ground-water flows resulted in higher ground-water nitrate concentrations and nitrogen loads than at the Piedmont site. Thus, effects of agriculture on ground water in the Piedmont Province can differ, depending on the nature of agricultural practice and hydrogeologic characteristics in a particular area.

Coastal Plain Site

At the Coastal Plain site, nitrate concentrations in ground water generally ranged from 6 to 10 mg/L throughout the site but changed differently during the study period in different parts of the site (fig. 18). During the first part of the study period, nitrate concentration in ground water in the upgradient part of the site (wells CA Fc 13, CA Fc 14, CA Fc 15, CA Fc 16, CA Fc 21, and CA Fc 22) was about 10 mg/L and was higher than at the downgradient end of the site (wells CA Fc 17, CA Fc 18, and CA Fc 20), which was about 8 mg/L. Well CA Fc 19 is excluded because it is screened partly in clay that underlies the sand aquifer under unconfined conditions, and that configuration could affect the nitrogen concentration of ground-water samples (see section "Speciation of Nitrogen in Water"). During the study period, nitrate concentration in the upgradient part of the site decreased slightly by about 1 mg/L, whereas nitrate concentration at the downgradient end of the site increased by a similar amount. Nitrate concentration in ground water beneath the vegetated buffer strip (wells CA Fc 33 and CA Fc 34) was close to zero midway through the study period but increased substantially during the rest of the period. Nitrate concentration in ground water throughout the site was similar at about 9 mg/L by the end of the study period.

Most nitrate concentrations in ground water collected by USGS personnel throughout the Coastal Plain in the Patuxent River Basin are from deep aquifers under confined conditions and are lower than in the aquifer under unconfined conditions at the Coastal Plain site. More than 15 percent of the wells sampled largely from aquifers under unconfined conditions in the Delmarva Peninsula, which makes up a large part of the Coastal Plain Province in Maryland, however, have nitrate concentrations higher than 10 mg/L (Hamilton and Shedlock, 1992).

Agricultural practices at the Coastal Plain site affected nitrate concentration in ground water differently than at the Piedmont site. Unlike the Piedmont site, little or no nitrate was removed by denitrification from ground water in the upgradient part of the Coastal Plain site. Ground water that entered the aquifer toward the downgradient end of the site contained nitrate resulting from recent agricultural practices but mixed with ground water from upgradient, which had either a higher or lower nitrate concentration that resulted from earlier agricultural practices. As a result, nitrate concentration in ground water at the downgradient end of the site was a composite that resulted from agricultural practices from as long ago as 27 years (see section "Flow Through the Aquifers") and could not be directly attributed to a particular agricultural practice from a specific time.

Ground water underlying the cultivated area at the Coastal Plain site flowed beneath the vegetated buffer strip before discharging into the Patuxent River. Nitrate concentration in ground-water discharge was probably reduced from that in the cultivated area by denitrification beneath the buffer strip (see section "Speciation of Nitrogen in Water"). Nitrate concentration beneath the buffer strip increased since wells were installed in the strip in 1989 (fig. 18). Dissolved-oxygen concentration similarly increased during the period, and the amount of denitrification appeared to have decreased as the water became more oxygenated. An increased supply of oxygen could have resulted from increased flow rates. Recharge increased substantially during 1989 from the 2 previous years (table 5), resulting in higher water levels (fig. 8), steeper hydraulic gradients, and higher ground-water-flow velocities. Therefore, the amount of denitrification beneath the buffer strip could change with flow conditions.

Because of mixing and denitrification at the downgradient end of the Coastal Plain site, nitrate concentration in ground water in the upgradient part of the site was probably most directly attributable to recent agricultural practices. The nitrate concentration at the water table resulted from the most recent agricultural practices and below the water table, from earlier practices. Because most of the nitrate that originated from the land surface is transported to the water table within 2 years (see section "Unsaturated Zone"), changes in agricultural practice could have affected nitrate concentration at the water table in 1 year or less. If flow rates and dispersive mixing were sufficiently high, then nitrate concentration below the water table also could have been affected.

Nitrate concentration in ground water at all depths sampled in the upgradient part of the Coastal Plain site (wells CA Fc 13, CA Fc 14, CA Fc 15, CA Fc 16, CA Fc 21, CA Fc 22) decreased slightly (about 1 mg/L) during the study period (fig. 18). Soybeans, which received little fertilizer, were grown throughout the period but the method of cultivation changed from no-till between 1986 and 1988 to conventional tillage between 1989 and 1991. The amount of nitrogen in soybean plant material at the land surface probably was similar from year to year, but the change in tillage practice could potentially alter the amount, manner, and rate at which nitrogen was released from the plant material, the rate of infiltration and percolation, and the amount of nitrogen transported to ground water (U.S. Environmental Protection Agency, 1987).

No-till cultivation possibly results in more nitrogen being transported to ground water than does conventional tillage. Although no-till cultivation possibly reduces surface-runoff volume and nitrogen load from conventional tillage (see sections "Flow Through the Study Sites" and "Surface Runoff"), the amount of nitrogen transported to ground water can potentially increase because of increased infiltration and ground-water recharge.

Nitrate concentration in ground water in the upgradient part of the Coastal Plain site was only slightly higher during no-till soybean cultivation than during conventional-till soybean cultivation. In addition, differences in amounts of nitrogen transported to ground water between the two periods cannot be inferred solely from nitrate concentrations in ground water because the volume of recharge also can differ. For example, a large amount of less concentrated recharge can transport more nitrogen than a small amount of more concentrated recharge. Although recharge volume generally changed with the amount of precipitation, recharge volume was larger during no-till cultivation in 1988 than during conventional tillage in 1991, even though precipitation during both years was similar (table 5). Larger recharge in 1988 could be the result of no-till cultivation, although the timing of precipitation and (or) other unmeasured soil and climatic factors also could affect recharge (see section "Flow Through the Study Sites").

Even with estimates of recharge volume, nitrogen load into the aquifer in recharge water cannot be calculated directly because nitrate concentration in recharge water is unknown. Nitrate concentration in recharge water cannot be assumed to equal the nitrate concentration in the aquifer because solute concentrations are diluted downward with increasing moisture contents from the unsaturated zone downward to the saturated zone (see section "Unsaturated Zone"). If the recharge volume that results from no-till is larger than that from conventional tillage (given equal amounts of precipitation), however, then the higher nitrate concentration in ground water that also resulted during no-till indicates that nitrogen load in recharge could be larger than during conventional tillage. Alternatively, the lower nitrate concentrations during conventional tillage could have resulted from dilution from the large amount of precipitation during 1989.

Nitrate concentration in ground water at the downgradient end of the Coastal Plain site is a composite of agricultural practices from as long ago as 27 years and is less clearly attributable to specific agricultural practices than nitrate concentration in ground water in the upgradient part of the site. The mean residence time of ground water at the site was calculated to be 9.7 years (table 6), assuming that water is uniformly mixed throughout the entire volume of the aquifer before discharging. Ground water is actually only partly mixed by dispersion, and water that enters the aquifer toward the downgradient end of the site is discharged sooner than water that enters at the upgradient end (see section "Flow Through the Aquifers"). The average age of ground-water discharge is probably less than is indicated by the mean residence time, and probably more than one-half of the discharge water entered the aquifer within the 5-year study period. Therefore, nitrate concentration at the downgradient end of the site could be primarily affected by recent agricultural practices but also is still partly affected by earlier practices.

Nitrate concentration in ground water at the downgradient end of the Coastal Plain site at the beginning of the study period was generally lower than at the upgradient end of the site (fig. 18) and was a composite that resulted from a combination of agricultural practices before the study period. No-till and conventionally tilled soybeans were grown at the site for a decade or more before the beginning of the study, with a winter cover crop of wheat or rye planted during some years (S.L. Boyer, U.S. Geological Survey, written commun., 1988). Corn also was grown in at least part of the site as recently as 1982, and the corn crops probably required large fertilizer applications that could have resulted in heavy concentrations of nitrate in ground water.

During the first one-half of the study period, no-till cultivation of soybeans could have resulted in increased amounts of nitrogen being transported to the aquifer. Ground water that entered the aquifer in the upgradient part of the site began to flow downgradient to displace less concentrated ground water at the downgradient end of the site. Also, ground water that entered the aquifer toward the downgradient end of the study site mixed with and was diluted by less concentrated ground water. As a result, nitrate concentration in ground water at the downgradient end of the site (wells CA Fc 17, CA Fc 18, CA Fc 20) increased during the study period (fig. 18). After agricultural practice at the site changed from no-till cultivation of soybeans to conventional tillage of soybeans, nitrate concentration in ground water in the upgradient part of the site was lower than during no-till, but nitrate concentration at the downgradient end of the site was higher because of mixing, and nitrate concentration in ground water in both parts of the site by the end of the study period was similar at about 9 mg/L.

To calculate nitrogen load in ground-water discharge from the Coastal Plain site, nitrogen concentrations in ground water at the downgradient end of the cultivated part of the site and beneath the vegetated buffer strip were used separately to calculate mean monthly nitrogen concentrations. Discharge volumes calculated in model simulation were multiplied by the mean monthly nitrogen concentrations to calculate nitrogen loads in ground-water discharge leaving the cultivated area upgradient of the buffer strip and entering the Patuxent River downgradient of the buffer strip (table 11).

Nitrogen load in ground-water discharge from the cultivated area at the Coastal Plain site steadily increased from about 12 to 15 (lb/acre)/yr from 1987 to 1990 (table 11). Discharge volume also increased during the period (table 5). Similarly, nitrogen load from the cultivated area decreased to less than 12 (lb/acre)/yr during 1991 (table 11), while discharge volume also decreased (table 5). Because changes in nitrate concentration in ground water at the downgradient end of the site were small, nitrogen load from the cultivated area was primarily a function of discharge volume, which changed yearly in response to volumes of recharge and storage in the aquifer (see section "Flow Through the Aquifers").

Estimates of nitrogen load in ground water from other locations in the Coastal Plain Province in Maryland are not available, but roughly comparable amounts to these loads of from 9 to 19 (lb/acre)/yr of nitrogen were removed in subsurface drainage from farmland in the Coastal Plain Province in North Carolina where soybeans and corn were annually alternated (Jacobs and Gilliam, 1983).

No-till cultivation of soybeans at the Coastal Plain site resulted in slightly increased nitrate concentrations in ground water in the upgradient part of the study site but also possibly resulted in larger nitrogen loads from the cultivated area than from conventional tillage. Although the amount of precipitation was relatively equivalent in 1988 and 1991, no-till cultivation in 1988 possibly resulted in larger recharge than did conventional tillage in 1991 (see section "Flow Through the Study Sites"). If so, then the resulting increase in discharge volume during no-till cultivation in 1988 produced a larger nitrogen load from the cultivated area of 12.55 (lb/acre)/yr than the 11.51 (lb/acre)/yr during conventional tillage in 1991, even though nitrate concentration at the downgradient end of the site was less during no-till.

Nitrogen load in ground-water discharge to the Patuxent River from the Coastal Plain site increased each year from the previous year during the period from 1989 to 1991 (table 11), even though discharge volume decreased in 1991 (table 5). Because changes in nitrate concentration in ground water were high beneath the vegetated buffer strip, nitrogen load to the Patuxent River was primarily a function of nitrate concentration, which increased during the period probably as a result of decreased amounts of denitrification.

Differences between nitrogen load in ground-water discharge from the cultivated area and that to the Patuxent River indicate the amount of nitrogen removed by denitrification beneath the buffer strip, which decreased toward the end of the study period. Denitrification could have decreased in response to an increased supply of oxygen that resulted from increased flow rates following a large volume of recharge during 1989 (table 5). Therefore, the amount of nitrogen-load decrease beneath the buffer strip in ground-water discharge to the Patuxent River could change with flow conditions.

Throughout the study period, nitrogen load in ground-water discharge from the cultivated area and that to the Patuxent River remained larger than nitrogen load in surface runoff, even though the latter changed considerably (table 11). Surface-runoff nitrogen load, however, probably does not represent removal of nitrogen from the study site because much of the surface runoff reinfiltrates the land surface in the level area below the runoff flume (see section "Recharge/Discharge Relations"). Nitrogen in surface runoff can be added to that which leaves the site in ground-water discharge to the Patuxent River and (or) can leave the site in interflow in the unsaturated zone.

SUMMARY AND CONCLUSIONS

Degradation of water quality in Chesapeake Bay from eutrophication caused by excess nitrogen has been attributed, in part, to farming operations. Some agricultural practices that are being promoted to alleviate water-quality problems in the Bay, however, possibly do not address nitrogen transport in ground water. To determine the effects of particular agricultural practices on nitrogen transport in ground water, hydrologic data were collected from 1986 to 1992 at two study sites of about 10 acres in the Patuxent River Basin in Maryland, a major tributary of Chesapeake Bay. One site is in the Piedmont Physiographic Province, and the other site is in the Coastal Plain Physiographic Province. Changes in agricultural practices at the sites during the study period were typical for the region. At the Piedmont site, agricultural practices included no-till cultivation of soybeans during the 1986–87 season, continuous alfalfa during the 1988–89 season, and contoured strip crops alternated among corn, alfalfa, and soybeans during the 1990 to 1992 seasons. At the Coastal Plain site, agricultural practices included no-till cultivation of soybeans during the 1986 to 1988 and 1992 seasons, and conventional tillage of soybeans during the 1989 to 1991 seasons. Only chemical fertilizer, and not manure, were applied at both sites, and neither site was irrigated.

The hydrogeologic frameworks of both study sites were characterized. Surface-water flow was not sustained at the sites. Surface runoff occurred at both sites only during brief periods of intense rainfall. The Piedmont site is located at the headwater of a small, unnamed tributary of the Patuxent River. Ground water at the Piedmont site is recharged at the water table at depths from 0 to 50 ft in regolith. Ground water flows horizontally and vertically through pore spaces in regolith and through fractures in schist bedrock before discharging at two springs at the head of a small perennial stream at the downgradient end of the site. The Coastal Plain site is located on a broad terrace next to the Patuxent estuary. Ground water at the Coastal Plain site is recharged at the water table at depths from 0 to 31 ft in sand. Ground water flows primarily horizontally through pore spaces in sand but probably not vertically into or out of underlying clay before discharging into the estuary. Recharge at both sites occurred primarily during the first one-half of each year when the rate of evapotranspiration was small. Ground water that was stored in the aquifers during recharge was discharged during the remainder of the year. Water that flows horizontally through the unsaturated zone can flow out of the study sites as interflow without reaching the water table as recharge. Surface runoff at the study sites consisted primarily of interflow that resurfaced toward the downslope ends of the sites. Much of the surface runoff reinfiltrated the land surface in level areas at the downslope ends of the study sites and flowed out of the sites through the subsurface.

Ground-water flow at both study sites was simulated by applying numerical ground-water flow models. Long-term average recharge rates, estimated by hydrograph separation of flow data from streams draining similar areas nearby, were 8 in/yr for the Piedmont site and 7 in/yr for the Coastal Plain site. Ground-water flow models of the study sites were calibrated under steady-state conditions on the basis of estimated recharge rates. Calibration values for aquifer hydraulic conductivity were comparable to aquifer pumping-test estimates and were used in transient simulations to estimate year-to-year differences in recharge during the study period. Recharge at both study sites varied by several inches per year between

1987 and 1991. Discharge varied less, and differences between recharge and discharge went into or came out of storage in the aquifers. At the Piedmont site, most of the ground water discharges from regolith under unconfined conditions and little from schist under confined conditions. About one-fourth of ground water, however, flows from regolith into schist at the upgradient end of the study site and back into regolith at the downgradient end of the study site before discharging. Changes in ground-water storage took place primarily in regolith, and little water was stored in schist. Ground-water flow at the Coastal Plain site was simulated as taking place entirely through sand under unconfined conditions and not through the underlying clay.

The times required for ground water to flow through the aquifers at both study sites were estimated. Calculated ground-water traveltimes and mean residence times ranged from about one to several decades but do not adequately represent the age distribution of water in the aquifers at the study sites. Particle-tracking analyses of simulated ground-water flow indicate ages of up to two to three decades for ground water in the deep parts of the aquifers but do not account for mixing caused by dispersion, which makes the age distribution more uniform. Tritium and chlorofluorocarbon recharge ages calculated from a limited number of ground-water samples at both study sites indicate ages of 4 to 6 years with the exception of water in schist at the Piedmont site; that water could be 30 years old. The accuracy of some of the age determinations was possibly affected by flow to the wells during pumping for sample collection.

Simulated recharge was compared with other components of flow through the study sites. Precipitation changed by several inches per year at both study sites from 1987 to 1991. Recharge ranged from about 6 to 11 in/yr, or 12 to 23 percent of precipitation, at the Piedmont site, and from 2 to 9 in/yr, or 6 to 19 percent, at the Coastal Plain site. Surface runoff was less than 3 in/yr, or 5 percent of precipitation, throughout the study period at both sites. Probably about 60 percent of precipitation was returned to the atmosphere by evapotranspiration, and another 15 to 25 percent was either stored in or flowed through the unsaturated zone as interflow. Year-to-year changes in the different flow components generally corresponded to changes in precipitation, and changes as a result of different agricultural practices were probably less. No-till cultivation of soybeans at the Coastal Plain site in 1988, however, possibly resulted in larger recharge and smaller surface runoff than during conventional tillage of soybeans in 1991, even though precipitation both years was similar.

The major-ion composition of ground water at both study sites results from dissolution of both ionic salts in applied agricultural chemicals and minerals in aquifer materials. At the Piedmont site, the composition of soil water and shallow ground water is a calcium magnesium chloride nitrate-type water, resulting from the application of agricultural chemicals. The composition of deep (several tens of feet below land surface) ground water at the Piedmont site is a mixed-cation bicarbonate-type water that also contains iron, manganese, and sulfide but little dissolved oxygen and is produced from dissolution of silicate minerals, pyrite, and calcite. At the Coastal Plain site, the calcium–bicarbonate type water present throughout the aquifer is produced by dissolution of calcium carbonate from fossil shells.

Nitrogen in surface runoff, soil water, and ground water at both study sites originates from plant material and applied fertilizer. A substantial part of the nitrogen in surface runoff is in organic form from plant material, but nitrogen in soil water and ground water is primarily in the form of nitrate because organic nitrogen is mineralized by bacteria within a few feet of the land surface. Because of limited supplies of dissolved oxygen and the presence of suitable electron donors, bacteria probably convert some nitrate to nitrogen gas by denitrification in parts of the aquifers at both study sites, including deep regolith and schist at the Piedmont site and beneath the vegetated buffer strip at the Coastal Plain site.

Relations between surface-runoff flow rate and nitrogen concentration during periods of different agricultural practice were used to infer the effects of the practices on nitrogen concentration and to calculate nitrogen loads in surface runoff with log-linear regression equations. Surface-runoff nitrogen load generally changed from year to year with runoff volume. Fertilization of contoured strips of corn at the Piedmont site during 1990, however, resulted in higher runoff nitrogen concentrations and, hence, a larger nitrogen load than resulted from the cultivation of alfalfa the previous year, even though runoff volume was less. In addition, conventional tillage of soybeans at the Coastal Plain site during 1991 possibly resulted in larger surface-runoff volume and, hence, a larger nitrogen load than resulted from no-till cultivation of soybeans in 1988, even though precipitation was about the same in both years, but differences in nitrogen loads in runoff at both sites were minor compared with larger nitrogen loads in ground water.

Changes in nitrate and bromide-tracer concentrations in soil water during the study period were used to determine solute-transport rates and directions through the unsaturated zone at the study sites. In the upslope part of the Piedmont site, solutes are transported vertically by percolation through the upper 5 ft of the unsaturated zone in 2 years or less. Vertical transport is slower at greater depth, and transport could be primarily horizontal in interflow above impermeable clay layers and (or) through macropores. Solutes could take several years to be transported from the land surface to the water table. In the downslope part of the Piedmont site, some nitrogen could be removed from water percolating through a grass drainage-filter strip. At the Coastal Plain site, solutes were transported primarily vertically by percolation through the unsaturated zone to the water table in 2 years or less.

Changes in nitrate concentration in ground water at the study sites result from changes in the amounts of nitrogen transported in recharge from different agricultural practices, as well as different traveltimes through the aquifers, dispersive mixing, and denitrification. Nitrate concentration in ground water was generally less at the Piedmont site than at the Coastal Plain site. Denitrification is more likely in a large part of the aquifer at the Piedmont site. In addition, because of long traveltimes at the Piedmont site, low concentrations in much of the site could have resulted from agricultural practices several decades before the study period when small amounts of fertilizer were applied. Higher concentrations at the Coastal Plain site probably resulted mostly from practices within the past several years and were largely unaffected by dentrification. At both study sites, effects of agricultural practices on nitrate concentration were observed in different parts of the flow systems, but because of long traveltimes, effects on the entire systems could not be discerned within the timeframe of the study.

Ground-water nitrogen-concentration data were used with discharge volumes calculated by ground-water flow models to estimate nitrogen loads in ground water at the study sites. Nitrogen loads in ground water were considerably larger than those in surface runoff throughout the study period at both study sites. In addition, most of the nitrogen in runoff was transported into the subsurface, as runoff infiltrated at the downslope ends of the sites.

At the Piedmont site, ground water in the upgradient part of the site contained nitrate that resulted from agricultural practices from several decades before the study period and could be partly removed by denitrification. Shallow ground water at the springs contained nitrate that originated from recent agricultural practices within the past several years but was probably diluted by mixing with less concentrated ground water from upgradient. Large nitrate concentrations of about 7 mg/L at the springs at the beginning of the study probably resulted from large fertilizer applications required for the no-till corn crops planted in the years before the study. Nitrate concentrations at the springs decreased to about 3.5 mg/L while no-till soybeans, continuous alfalfa, and contoured strip crops of corn, alfalfa, and soybeans were grown during the study period.

Nitrogen load in ground-water discharge from the Piedmont site decreased from about 12 to 6 (lbs/acre)/yr because nitrogen load was primarily a function of nitrate concentration. Contoured strips planted in corn require heavy applications of fertilizer that potentially could result in increased amounts of nitrogen transported to ground water. Nitrate concentration at the springs, however, and nitrogen load in ground-water discharge remained low after strip crops had been grown for 2 years. Alternating the strips among different crop types could limit the amount of nitrogen transported to ground water. Also, the total amount of fertilizer applied to the site was reduced.

At the Coastal Plain site, no-till cultivation of soybeans during the first one-half of the study period resulted in nitrate concentrations of about 10 mg/L in the upgradient part of the aquifer. Conventional tillage of soybeans during the second one-half of the study period resulted in slightly lower concentrations of about 9 mg/L. Ground-water recharge volumes (relative to the amount of precipitation) and nitrogen loads in recharge also were possibly greater from no-till cultivation than from conventional tillage because more nitrogen was released to infiltrating water under no-till. At the downgradient end of the site, lower nitrate concentrations of about 8 mg/L at the beginning of the study were a composite that resulted from earlier (up to 27 years ago) agricultural practices but increased to about 9 mg/L during the study period because of mixing with more concentrated recharge.

Nitrogen load in ground water from the cultivated part of the Coastal Plain site was primarily a function of ground-water discharge because changes in nitrate concentration were relatively small. No-till cultivation of soybeans during the first part of the study period, however, possibly resulted in larger ground-water recharge and discharge volumes (relative to the amount of precipitation). If so, the nitrogen load from the cultivated area of 12.55 (lb/acre)/yr during 1988 was larger as a result of no-till than the 11.51 (lb/acre)/yr during 1991 that resulted from conventional tillage of soybeans, even though nitrate concentration at the downgradient end of the site was less under no-till cultivation. Nitrate concentration and nitrogen load in ground water are decreased, probably by denitrification, as the water flows from the cultivated part of the site beneath a vegetated buffer strip before discharging into the Patuxent River. The amount of denitrification decreased during the study period, however, possibly because a large amount of recharge in 1989 increased ground-water flow velocities and the supply of dissolved oxygen.

This study provides examples of some possible effects of particular agricultural practices on nitrogen transport at the study sites and during the specific study period. Agricultural practices and hydrologic conditions in the Chesapeake Bay drainage area are diverse. Effects of the agricultural practices described in this study, as well as of other practices, could differ for constituents other than nitrogen, such as pesticides, and could differ at different locations and times. Effects of all commonly used agricultural practices, as well as more innovative practices that have development potential, need to be determined under a wide range of hydrologic conditions for a large number of constituents before agriculture in the Chesapeake Bay drainage area can be managed to protect and improve water quality.

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