# Water-Quality Assessment of the Delmarva Peninsula, Delaware, Maryland, and Virginia: Results of Investigations, 1987–91

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# FOREWORD

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

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

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

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

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

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

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

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

Robert M. Hirsch
Chief Hydrologist

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## CONVERSION FACTORS AND VERTICAL DATUM

| Multiply | By | To obtain |
|---|---|---|
| | **Length** | |
| inch (in.) | 25.4 | millimeter |
| foot (ft) | 0.3048 | meter |
| mile (mi) | 1.609 | kilometer |
| | **Area** | |
| acre | 0.4047 | hectare |
| square mile ($mi^2$) | 2.590 | square kilometer |
| | **Mass** | |
| pound, avoirdupois (lb) | 0.4536 | kilogram |
| pounds per acre | 1.121 | kilograms per hectare |
| ton, short (2,000 lb) | 907.2 | kilogram |
| | **Flow rate** | |
| million gallons per day (Mgal/d) | 0.04381 | cubic meters per second |

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

$$°F = 1.8 \times ( °C) + 32$$

**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.

**Other abbreviated units of measure**: Specific conductance is expressed in microsiemens per centimeter (µS/cm) at 25 °C. Concentrations of chemical constituents in water are expressed in milligrams per liter (mg/L), or micrograms per liter (µg/L). Radioactivity is expressed in picocuries per liter (pCi/L).

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## ABSTRACT

A regional ground-water-quality assessment of the Delmarva Peninsula was conducted as a pilot study for the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. The study focused on the surficial aquifer and used both existing data and new data collected between 1988 and 1991. The new water samples were analyzed for major ions, nutrients, radon, volatile organic compounds, and a suite of herbicides and insecticides commonly used on corn, soybeans, and small grains. Samples also were collected from wells completed in deeper, confined aquifers and from selected streams, and analyzed for most of these constituents. The study employed a multi-scale network design. Regional networks were chosen to provide broad geographic coverage of the study area and to ensure that the major hydrogeologic settings of the surficial aquifer were adequately represented. Local-scale well networks were installed in several of the major hydrogeologic settings to study changes in ground-water quality along flow paths in the surficial aquifer.

Both the existing data and the data from samples collected during the study showed that agricultural activities had affected the quality of water in the surficial aquifer over most of the Peninsula. Water from most wells completed in the surficial aquifer in areas underlain by agricultural land had a distinct chemical signature. These waters had a chemical composition dominated by calcium, magnesium, and nitrate ions, indicating that they had been significantly affected by leaching of fertilizers and lime applied to the fields. The data showed no significant contamination by volatile organic compounds, radon, or trace elements in either the surficial aquifer or any of the confined aquifers.

Nitrate was detected at concentrations above 3.0 milligrams per liter in water from the surficial aquifer in most areas of the Peninsula. The concentration of nitrate exceeded the U.S. Environmental Protection Agency's Maximum Contaminant Level of 10 milligrams per liter (as nitrogen) in about 20 percent of the samples. The highest nitrate concentrations were found in shallow ground water below agricultural fields, but concentrations above 3.0 milligrams per liter were detected at all levels of the surficial aquifer at many locations in the study area. In contrast, concentrations of nitrate were generally less than 1.0 milligrams per liter in samples from wells in the confined aquifers.

The spatial distribution of nitrate in the shallow ground-water system is related to ground-water-flow patterns and characteristics of the landscape, mainly land use, drainage patterns, soils, and geology. The highest median concentrations of nitrate, for example, are in an area of the Peninsula referred to as the well-drained upland. This area has the highest percentage of agricultural lands and

well-drained soils in the Peninsula, and also has the longest ground-water-flow paths. Relatively high concentrations of nitrate are found in water from the surficial aquifer in other areas of the Peninsula, but the lower percentage of agricultural lands in these other areas yields lower median nitrate concentrations relative to the median concentration in the well-drained upland.

Very low concentrations of herbicides (generally below U.S. Environmental Protection Agency Maximum Contaminant Levels) were found in water from shallow wells near agricultural fields. The concentrations of these compounds were generally below 1 microgram per liter. Although herbicide detections were common in shallow parts of the ground-water system, pesticides generally were not found in deeper parts of the surficial-aquifer system used for water supply, and were found in only one sample from the confined aquifers. The most commonly detected compounds were metolachlor, atrazine, simazine, alachlor, and cyanazine, which are herbicides commonly used on crops in the study area. Desethylatrazine, a degradation product of atrazine and simazine, was also commonly detected. Trace concentrations of insecticide were found in only two samples. Most of the pesticide detections are in waters that were probably recharged after the late 1960's, when these compounds were first widely used on crops in the study area.

The spatial distribution of herbicides in shallow ground water, like that of nitrate, is related to land use and ground-water-flow patterns. Most of the pesticide detections were in samples from wells near farm fields. Metabolites of the triazine herbicides were detected in samples from wells in several of the local-scale well networks. Neither the metabolite data nor the depth-distribution data on pesticides, however, shed much light on the potential for pesticides to migrate to deeper parts of the ground-water system over time.

Both elevated nitrate concentrations and trace concentrations of herbicides were found in nontidal streams under base-flow conditions. Nitrate concentrations in surface waters are related to land-use patterns and differences in soil types, but no seasonal patterns were observed in the nitrate data from the regional surface-water network. Surface waters from well-drained watersheds commonly contained higher concentrations of nitrate and other ions from agricultural chemical sources than surface waters from watersheds in poorly drained areas. Pesticide concentrations in surface water showed seasonal patterns and were less related to land use and soil patterns than nitrate concentrations. Concentrations of the parent compounds of the triazine herbicides were highest in streams during late spring base-flow periods, after pesticides were applied to the fields. Desethylatrazine concentrations in streams did not show as much seasonal variation as the parent compounds and remained at concentrations similar to those found year round in shallow ground water. This similarity indicates that ground water is the primary source of the desethylatrazine in surface water, and that the higher concentrations of the parent compounds of triazines in the spring base flow are derived from other sources, such as bed sediment, soil water, or ground water within a few feet of the water table under agricultural fields.

## INTRODUCTION

Since 1986, the U.S. Congress has appropriated funds annually for the U.S. Geological Survey (USGS) to develop and conduct a National Water-Quality Assessment (NAWQA) Program (Hirsch and others, 1988). The NAWQA program is designed to describe the status and trends in the quality of the Nation's ground-water and surface-water resources and to link assessment of status and trends with an understanding of the natural and human factors that affect the quality of the water (Gilliom and others, 1995).

The Delmarva Peninsula of Delaware, Maryland, and Virginia was one of seven pilot project areas chosen to test and refine concepts and approaches for the NAWQA program. The Delmarva pilot project started in 1986 and was one of three that focused mainly on regional assessment of ground-water quality. Because of the high percentage of agricultural land on the Peninsula, one of the primary objectives of the project was to document the occurrence and distribution of agricultural chemicals, primarily nitrate and pesticides, in the ground-water system. A second objective was to relate patterns in the distribution of nitrates and pesticides to regional differences in landscape characteristics and hydrogeologic setting. In 1991, the project was expanded to include a survey of surface-water quality during base-flow periods to study relations between ground-water and surface-water quality.

This report summarizes the results of investigations conducted between 1987 and 1991 for the Delmarva Peninsula pilot NAWQA project. The report includes a description of the study area, the design of the water-quality networks and sampling strategy, the study results, and a discussion of the implications and limitations of the results. The report also includes a complete bibliography of published results and data from the pilot project.

## Description of Study Area

The Delmarva Peninsula (fig. 1) is a coastal lowland drained by a series of short tidal streams. The Peninsula covers about 6,000 $mi^2$ (square miles) and includes most of the State of Delaware and the parts of Maryland and Virginia east of the Chesapeake Bay. It is bordered on the east by Delaware Bay and the Atlantic Ocean. Most of the Peninsula is within the Atlantic Coastal Plain Physiographic Province and is characterized by flat to gently rolling topography. The Peninsula has a broad central upland with altitudes ranging from 50 to 100 ft above sea level. The upland areas are flanked by low plains that slope toward the coastlines. The coastal areas along Chesapeake and Delaware Bays are fringed by major tidal wetlands that extend inland along the banks of the tidal rivers. The Atlantic coastline is fringed by barrier beaches, tidal lagoons, and marshes. The extreme northern part of the Peninsula is in the Piedmont Physiographic Province and was not considered part of the study area.

The study area is mostly a rural setting and had an estimated population between 600,000 and 700,000 (U.S. Bureau of the Census, 1986; U.S. Bureau of the Census, 1995) during the study period. Several small cities have populations between ten and twenty-five thousand, but most towns have populations of less than a few thousand. During the summer, however, the seasonal population of the major beach resorts along the Atlantic Coast can exceed several hundred thousand people.

The climate of the study area is temperate. Precipitation (rain and snow) averages about 45 inches per year (in/yr) and varies seasonally from 3–4 inches per month in the spring to more than 5 inches per month in late summer (National Oceanographic and Atmospheric Administration, 1977). Temperatures on the Peninsula range from an average of about 2 degrees Celsius (°C) in January and February to 25 °C in July and August.

## Land Use

Agriculture is the most prevalent land use (about 48 percent) in the study area (Hamilton and others, 1993). Most of the agricultural land is used to grow soybeans and corn, which are used for poultry feed. Large poultry farms are found all across the Peninsula, which is one of the leading production areas of broiler chickens in the United States. Corn and soybeans are often grown in an annual rotation with each other, as well as winter wheat, and other small grains (U.S. Department of Agriculture, 1991). Other crops include hay (for other livestock), potatoes, vegetables, and fruit (for fresh markets and processing). Dairy farms, plant nurseries, and sod farms are also found in the Peninsula.

Woodlands constitute about 31 percent of the land area and commonly are interspersed with agricultural areas (Hamilton and others, 1993). The size of agricultural fields and the degree of interspersion of fields with woodlands are related to local differences in soil, geomorphic features, and hydrologic characteristics. The well-drained areas are characterized by large agricultural fields, with woodlands confined to riparian zones along natural stream valleys. The poorly drained areas are characterized by smaller agricultural fields


**Figure 1.** Location of the Delmarva Peninsula study area.

interspersed with woodlands, many of which are seasonally saturated palustrine wetlands (Phillips and others, 1993).

Wetlands comprise about 13 percent of the study area. Most of the areas that border Chesapeake Bay, Delaware Bay, and the Atlantic Ocean are fringed with tidal and nontidal marshes. Tidal marshes and tidal swamps extend along the flanks of the tidal rivers, in some cases for distances more than 10 miles upstream from the mouth. The Peninsula also contains a large number of freshwater depressional wetlands, mainly in poorly drained, forested parts of the central upland. Riparian wetlands are common in valleys of the freshwater sections of the streams. Although they contain wetlands, the barrier beaches along the Atlantic coastline are classified as barren lands and comprise about 1 percent of the study area.

Urban and residential lands comprise only about 7 percent of land use in the study area. Small towns and rural residential communities are rather evenly distributed throughout the Peninsula.

## Surface Drainage

Most of the Delmarva Peninsula (roughly two-thirds) is in the Chesapeake Bay drainage area. The remaining areas drain to Delaware Bay or to tidal waters along the Atlantic Ocean. The Peninsula has no integrated surface drainage network, but rather is drained by a series of streams that have their headwaters in the central upland of the Peninsula and become tidal within 10 miles of their headwaters. As a result, tidal rivers extend for a considerable distance into the interior of the Peninsula. This incursion of tidal waters into the interior of the Peninsula, coupled with the gently rolling topography, results in a surface drainage network composed of many small basins. The drainage area of the largest nontidal watershed is less than 113 $mi^2$ and most watersheds are less than 10 $mi^2$ in area.

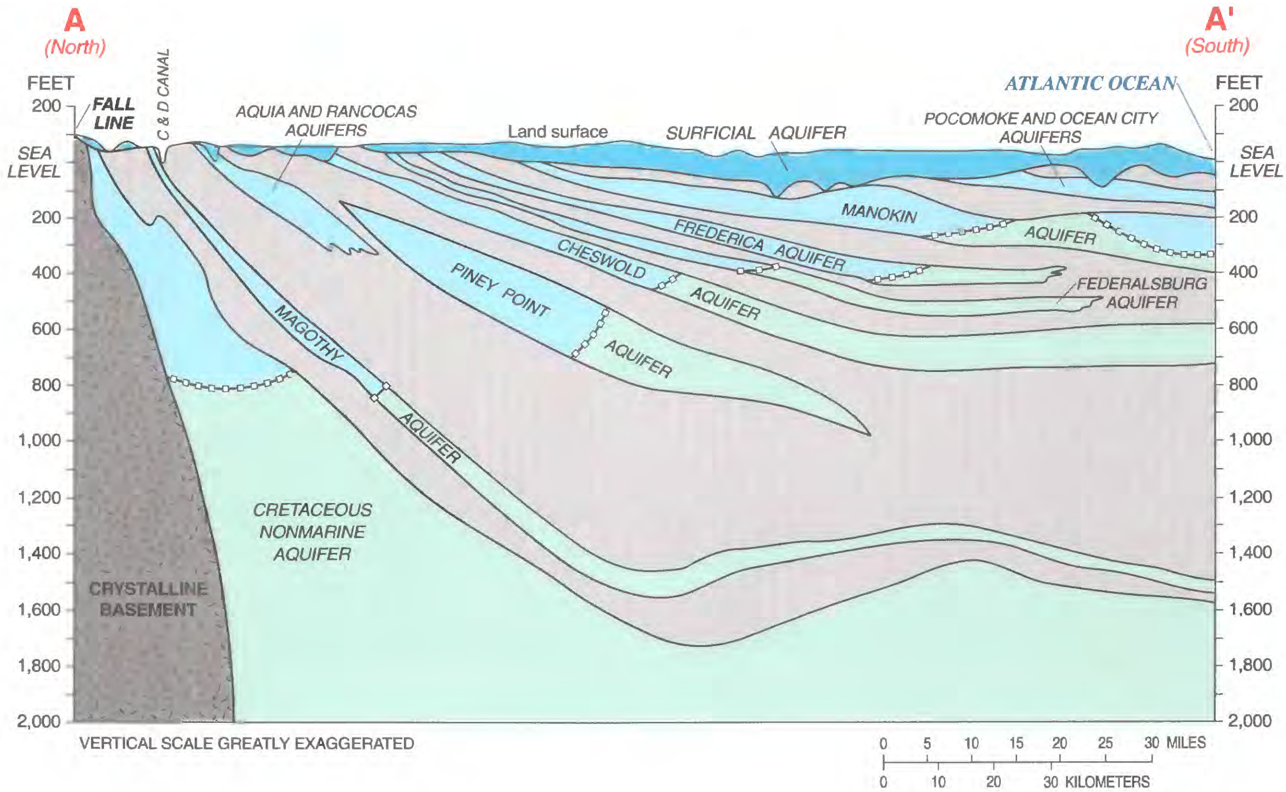
Ditching is common in the study area, especially in poorly drained areas. Some areas have extensive networks of ditches in agricultural fields that drain to larger ditches connected to natural drainageways. In many of these areas, the natural stream channels have been straightened and deepened, especially through some of the broader riparian wetlands.

## Hydrogeologic Framework

The Delmarva Peninsula is underlain by a wedge of unconsolidated sediments that thickens to the south and east of the Fall Line (fig. 2). The thickness of these sediments ranges from virtually zero at the Fall Line to more than 8,000 ft along the Atlantic Coast of Maryland. These sediments consist primarily of sand, silt, clay, gravel, and shells. With the exception of carbonates in the form of shell material, the sediments are composed mostly of quartz and other minerals that are generally resistant to weathering (Cushing and others, 1973).

Cushing and others (1973) divided these deposits into a complex aquifer system consisting of a series of nine confined sand aquifers (fig. 2) in Maryland and Delaware. Some of these aquifers are further subdivided in Maryland (Wheeler and Wilde, 1989; Achmad and Wilson, 1993) and in Delaware (Talley, 1976; Bachman and Ferrari, 1995). In Virginia, Harsh and Laczniak (1990) identified a compatible series of six confined aquifers and associated confining units. In most of the study area, the confined aquifers are overlain by an extensive surficial aquifer that is under water-table conditions. In the central part of the Peninsula, however, the surficial aquifer is a multi-layered aquifer system. The sands that make up the bulk of the surficial aquifer are overlain by silts and clays, which in turn are overlain by a relatively thin layer of wind-blown sand (generally less than 20 ft thick). In this setting, the water table is in the wind-blown sand deposits and the sands below the silts and clays are under confined conditions. In the northern part of the study area, the deposits that comprise some of the confined aquifers crop out, and thus are under water-table conditions in some localities.

The surficial aquifer was the focus of the Delmarva NAWQA pilot study because it is used extensively as a source of water supply and because it is a source of recharge to the underlying confined aquifers. Most of the water supply in the Peninsula is obtained from the ground-water system. The confined aquifers are the major sources of public water supply, except in the central part of the Peninsula, where the surficial aquifer is used. Most individual homes or groups of homes in rural areas obtain their water from




**EXPLANATION**




**Figure 2.** Hydrogeologic section across the Delmarva Peninsula (modified from Cushing and others, 1973).

private domestic wells. The surficial aquifer is the main source for most private domestic wells and many irrigation wells all over the Peninsula. About one-half of the 170 million gallons per day (Mgal/d) pumped from wells on the Peninsula is withdrawn from the surficial aquifer (Hamilton and others, 1993).

Annual recharge to the surficial aquifer is about 16 in/yr (Johnston, 1976). Water-table depths in the surficial aquifer generally range from 0 to about 20 ft in most areas (Hamilton and others, 1993), but depths of 30 ft or more are found in some well-drained areas with deeply incised streams. The depth to ground water at a given site can vary several feet seasonally because of changes in precipitation and evapotranspiration.

### Acknowledgments

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Robert Kellogg and Samuel Rives of the Economic Research Service, U.S. Department of Agriculture, provided valuable insights on agricultural practices in the study area.

Many property owners kindly granted permission to the study team to sample their domestic and irrigation wells, and some property owners also provided other information useful to the study, such as local agricultural practices.

Other USGS personnel who made significant contributions include Roger J. Starsoneck, the principal field technician on the study team and Herbert J. Freiberger, who assembled the liaison committee and provided invaluable assistance in coordinating its activities.

## DESIGN OF STUDY

This regional assessment of ground-water quality was done by assembling and analyzing a data set consisting of data collected during the study and carefully screened existing data (available through 1987). The new data consisted of analyses of ground-water samples from several different networks of wells and a regional stream network. These networks were designed to allow for assessment of water-quality patterns at several different spatial scales (Koterba and others, 1991, Shedlock and others, 1993).

The well networks developed for this multi-scale sampling design (table 1) were used primarily to assess water-quality conditions in the surficial aquifer. A network of existing wells was used to assess water quality in confined aquifers used for water supply. Before the new networks were designed, a preliminary assessment of ground-water quality was made from data available through 1987 (Hamilton and others, 1991). The results of this preliminary assessment were used to design sampling networks for acquisition of new data. Available data were also examined before the surface-water network was designed. The surface-water network included streams in both well-drained and poorly drained basins.

**Table 1.** Water-quality-sampling network name, sampling period, well type, network design features, and sampling objectives in the Delmarva NAWQA pilot study

[Modified from Bachman and Phillips, 1996; National Water-Quality Assessment (NAWQA) Program; –, no data available]

| Network type name | Sampling period | Well type | Network design features | Sampling objective |
|---|---|---|---|---|
| Regional, areal | Summer 1988 | Private; monitoring | 67 wells at 35 sites distributed throughout the study area, randomly selected, and with both a shallow and a deep well at most sites. | To describe and assess the quality of water in the surficial aquifer throughout the Peninsula. |
| Regional, confined-aquifer | Summer 1989 to Spring 1990 | Private; monitoring | 36 wells at 35 sites distributed among 10 confined aquifers; 2 to 3 sites along inferred flow paths in most aquifers. Some aquifers have 5 to 6 wells. | To describe and assess the quality of water in the freshwater part of the confined-aquifer system. |
| Targeted, peninsula-wide transects | Summer 1989 | Monitoring | 38 sites distributed along 5 east-west trending transects across the Peninsula, with 2 to 5 sites in each hydrogeomorphic region crossed by a transect. 5 to 10 wells (at 5 to 8 sites) sampled along each transect. | To describe and assess the quality of water in the surficial aquifer and in different hydrogeomorphic regions in the study area. |
| Targeted, local watershed | 1988-91 Seasonal | Monitoring | 158 sites distributed among 7 small watersheds in different hydrogeomorphic regions. Wells are distributed among different agricultural and forested settings and along shallow ground-water-flow paths. 7 to 33 wells and 2 to 7 stream sites sampled in each watershed; 4 to 8 wells (at 4 to 5 sites) and 1 to 3 stream sites sampled seasonally in each watershed. | To describe and assess the quality of water in local shallow-flow systems in different hydrogeomorphic regions, and to assess temporal variations in water quality and the effect of land use on water quality. |
| Regional, stream survey | 1990-91 Seasonal | – | Base-flow samples were collected from 47 sampling sites during each of four seasons. | To relate stream chemistry to hydrologic landscape characteristics and season, and to provide an estimate of nitrogen loading from base flow to the estuarine tributaries of the Chesapeake Bay. |

The data collected were analyzed to determine the range of chemical composition and patterns in water quality in two categories: (1) natural ground water (water not affected by human activity) and (2) water affected by human activity. Nitrate and pesticides (commonly used herbicide, insecticide, and fungicide compounds) were selected as indicators of human activities because these constituents are commonly introduced into the ground-water system by agricultural and residential activities (the dominant human activities in the study area).

Water samples were collected for the Delmarva NAWQA project by the USGS between 1988 and 1991. The ground-water samples from the regional networks were analyzed for dissolved constituents including major ions, nutrients, dissolved organic carbon, selected trace elements, radon, gross-alpha radiation, volatile organic compounds, commonly applied herbicides, and selected insecticides (table 2). Ground-water samples from the local-scale networks and surface-water samples were analyzed for major ions, dissolved organic carbon, nutrients, and commonly applied herbicides and selected degradation products of the triazine herbicides. Alkalinity, specific conductance, dissolved oxygen, and pH of all water samples were measured or analyzed in the field. Most of the samples from the local-scale

**Table 2.** Water-quality analyses by type, analyte, and constituents and properties

[From Koterba and others, 1991]

| TYPE | ANALYTE (S) | CONSTITUENTS AND PROPERTIES |
|---|---|---|
| Field measurements | Physical and chemical properties | pH, specific conductance, dissolved oxygen, alkalinity, and bicarbonate. |
| Inorganic constituents | Major ions and metals and trace elements | Calcium, magnesium, potassium, sodium, chloride, fluoride, bromide, sulfate, silica, aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, vanadium, and zinc. |
| Nutrients | Nitrogen | Ammonium, nitrate plus nitrite, nitrite, Kjeldahl nitrogen (ammonium plus organic). |
| | Phosphorus | Soluble-reactive phosphorus. |
| | Carbon | Dissolved organic carbon (includes natural and synthetic). |
| Radiochemicals and isotopes | Radionuclides | Gross-alpha, gross-beta, radon-222, and tritium. |
| | Ratios of stable isotopes | Deuterium/protium and oxygen 18/oxygen 16. |
| Organic compounds | Pesticides | More than 20 different herbicides including *S*-triazine- and chlorophenoxy-acid-based compounds. More than 15 different insecticides including carbamate-based compounds. |
| | Volatile organic compounds | Approximately 40 compounds, including simple (multi-) halogenated alkanes, alkenes, and aromatics. Some of these may be used in agricultural areas. |

ground-water networks and selected samples from wells in the regional networks were analyzed for concentrations of chlorofluorocarbon compounds and tritium, which indicate the residence time of the water in the aquifer system. Selected ancillary data, including local land use, soil type, and lithologic and gamma logs, were also documented for each well site.

A quality-assurance (QA) program was developed to ensure that unbiased procedures would be used for data collection and that any erroneous data would be eliminated. The QA program was also designed to determine the effect of the sampling design on the measurement of selected water-quality constituents. QA samples were geographically distributed throughout the study area and were collected during all sampling periods. Specific aspects of the QA program are described in detail in Koterba and others (1991).

## Subdivision of Study Area into Hydrogeomorphic Regions

To address regional patterns in ground-water quality, the project area was divided into seven subregions (fig. 3), referred to as hydrogeomorphic regions (HGMR's). The HGMR's represent different hydrologic settings in the surficial aquifer (Hamilton and others, 1991; Shedlock and others,

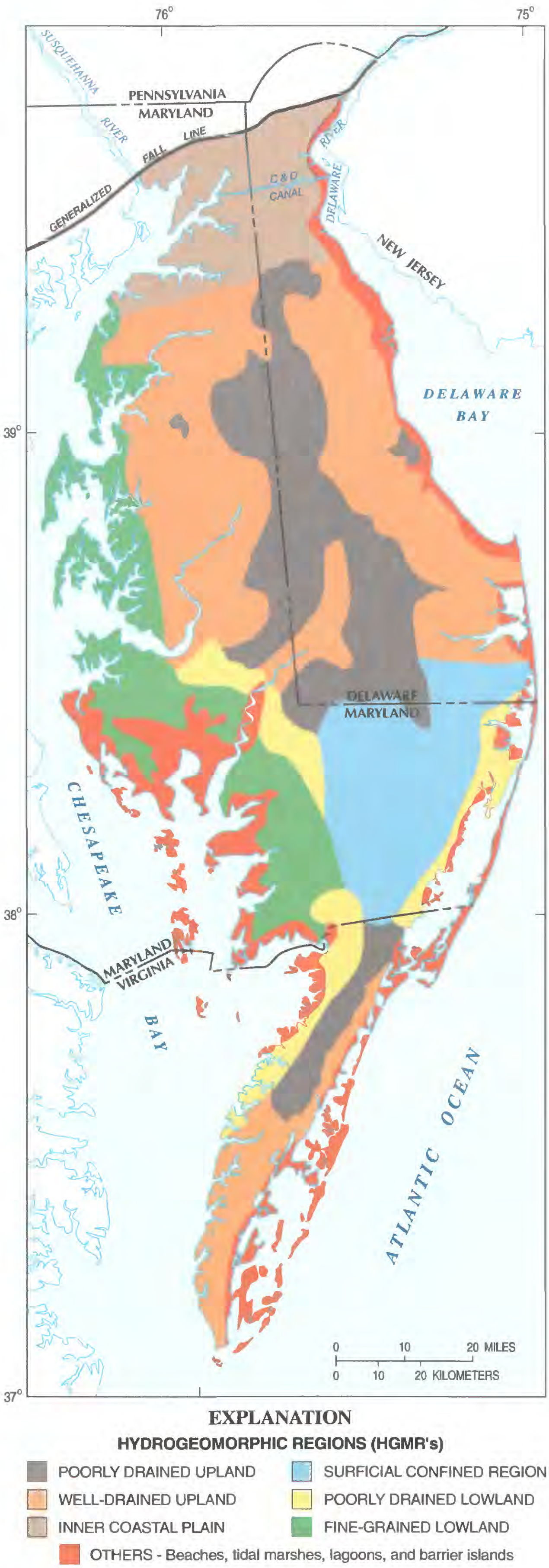



**Figure 3.** Hydrogeomorphic regions in the surficial aquifer the Delmarva Peninsula (from Hamilton and others, 1993).

1993; Phillips and others, 1993). Each HGMR has a characteristic set of geologic and geomorphic features, drainage patterns, soils, and land-use patterns. An HGMR consists of hundreds of small watersheds that, in aggregate, represent a distinct hydrologic landscape with characteristic patterns of ground-water flow and ground-water quality.

The HGMR map was used for regional data analysis, and as a basis for understanding and transferring interpretations of local-scale water-quality patterns to the regional-scale patterns. The delineation of the HGMR's was based on interpretation of county maps of soils and geology, USGS topographic maps, and 1:250,000-scale land-use and land-cover data. Characteristics of each HGMR are summarized in table 3.

## Compilation and Selection of Available Data

A preliminary assessment of ground-water-quality conditions in the study area, based on data available through 1987, is presented in Hamilton and others (1991). This report includes maps describing regional water chemistry and the spatial distribution of selected chemical constituents, and summary statistics and graphical summaries of selected chemical constituents. Analyses of waters from 193 wells sampled between 1944 and 1987 were selected from the historical data for inclusion in the project data set. Required physical information for the wells included site characteristics and well construction data, especially depth to and length of well screens. Required chemical information included the availability of analytical data for major cations and anions and a charge balance error for the analysis of less than 10 percent.

For the study of surface-water quality at base-flow conditions, existing data on selected physical characteristics (soils, slopes, and land use) of 78 watersheds were analyzed to classify them as either well-drained or poorly drained. This classification was used to design a sampling network that assessed the quality of stream base flow in both types of watersheds. Results of this analysis are presented in Phillips and Bachman (1996), and Bachman and Phillips (1996).

**Table 3.** Characteristics of hydrogeomorphic regions (HGMR's) on the Delmarva Peninsula

[Hamilton and others, 1991; Phillips and others, 1993; Owens and Denny, 1979; ft, feet]

| HGMR | CHARACTERISTICS |
|---|---|
| *Poorly drained upland* | Northern part of region: hummocky, low relief, depressions contain wetlands. |
| | Southern part of region: flat, with broad seasonally flooded wetlands. |
| | Poorly drained forested areas containing wetlands are interspersed with moderately well- to well-drained agricultural areas. |
| | Streams flow through shallowly incised valleys with low gradients. Ditching to promote soil drainage is common in drainage headwaters. |
| | Water table generally within 10 ft of land surface. |
| | Surficial aquifer thickness ranges from about 25 ft in the north to more than 100 ft in the south. |
| | Ground-water-flow paths range from several hundred feet to about 1 mile in the northern part to over 1 mile in the southern part. |
| | Soils and surficial aquifer sediments are generally sandy. |
| | Poor drainage is related to shallow stream incision and high water table, rather than to fine-grained sediments. |
| *Well-drained upland* | Relatively flat to gently rolling with a high degree of stream incision. |
| | Nontidal streams are mostly short, steep tributaries that drain the narrow interfluves between tidal rivers. |
| | Most of the upland land area is used for agriculture. |
| | Wooded areas are generally confined to narrow riparian zones. |
| | Wetlands are generally associated with riparian zones. |
| | Sediments in the surficial aquifer are primarily sand and gravel and range from about 20 to 40 ft thick in the north to more than 100 ft thick in the south. |
| | Depth to the water table ranges from 10 to 30 ft below land surface beneath topographic highs to land surface in riparian discharge areas. |
| | Ground-water-flow paths range from about one-half mile to several miles. |
| *Inner Coastal Plain* | Gently rolling with a high degree of stream incision. |
| | Nontidal streams are mostly short, steep tributaries that drain the narrow interfluves between tidal rivers. |
| | Most of the upland is used for agricultural or residential development, and wooded areas are confined to narrow riparian zones. |
| | Wetlands are generally associated with the riparian zones. |
| | The sands comprising the surficial aquifer in this region are thin and overlie subcropping sands or confining beds of several older Coastal Plain aquifers. |
| | Stream valleys are commonly incised into the older units and the surficial sandy deposits do not form an areally extensive aquifer, so flow paths are relatively short. |
| | Shallow ground-water-flow systems in the surficial sediments commonly extend into confined aquifers where they are close to the surface. |

**Table 3.** Characteristics of hydrogeomorphic regions (HGMR's) on the Delmarva Peninsula–Continued

| HGMR | CHARACTERISTICS |
|---|---|
| *Surficial confined* | Flat sandy plain with low dune ridges that rise several feet above the surrounding landscape. |
| | Stream incision is shallow and ditching to promote soil drainage is widespread. |
| | Large tracts of forest are interspersed with agricultural fields of the plains. |
| | Broad forested riparian zones and swamps are adjacent to major drainageways. |
| | The surficial aquifer is geologically heterogeneous, consisting of a major sand unit 80 to 100 ft thick overlain by 0 to 40 ft of complexly layered clay, silt, sand, and peat, which itself is overlain by 4 to 20 ft of sand with some peaty sand, silt, and clay lenses at the base. |
| | The complex set of fine-grained sediments acts as a confining bed over much of the region. |
| | The water table is generally less than 10 ft below land surface and occurs in the upper sand unit. |
| | Ground-water-flow paths in the upper unit are relatively shallow and generally less than 1,000 ft long. In the lower unit, regional flow paths are up to several miles long. |
| *Poorly drained lowland* | Poorly drained lowlands adjacent to tidal marshes and lagoons. |
| | Although sandy, soils are poorly drained because of a shallow water table (less than 10 feet below land surface), flat water-table gradients, and minimal stream incision. |
| *Fine-grained lowland* | Includes the broad low-lying areas that fringe the Chesapeake Bay about 5 to 10 ft above sea level. |
| | Sediments are very fine-grained and of low permeability. |
| | The water table is generally 1 to 10 ft below land surface. |
| *Others* | Unvegetated areas such as beaches; tidal wetlands and barrier islands. |

## Sampling Networks for Collection of New Water-Quality Data

Five networks were established as part of a multi-network sampling design (fig. 4; table 1). The areal, confined, and stream survey networks were designed to provide data for regional descriptions and assessments of water quality. The transect and local-watershed networks were designed to target specific HGMR's and study-area features that could affect ground-water quality, particularly in the surficial aquifer. About 230 wells were identified or installed and sampled in the study area over the course of the project. The stream survey network included 47 sites geographically distributed throughout the Maryland and Delaware parts of the study area (Bachman and Phillips, 1996). No streams in Virginia were included in the stream survey network because of the very small drainage areas of the freshwater portions of streams in that part of the study area.

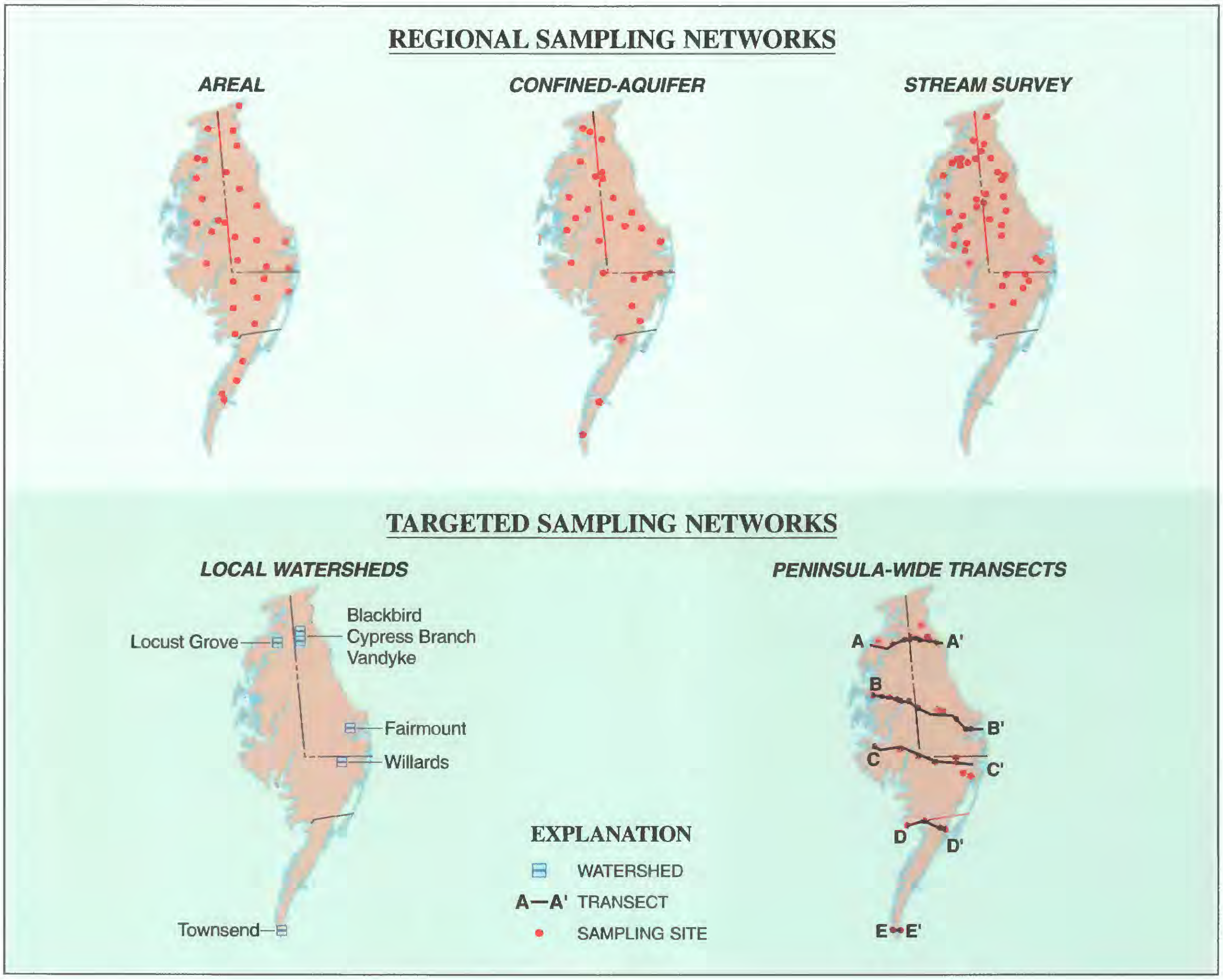



**Figure 4.** Sampling-site locations for each of the five water-quality networks of the Delmarva Peninsula National Water-Quality Assessment pilot project. (Some locations have more than one well.)

## QUALITY OF GROUND WATER

Water in the surficial aquifer generally is characterized by low pH, low alkalinity, and low dissolved-solids concentrations (Hamilton and others, 1991). The dilute and acidic nature of the water in this aquifer is caused by the low pH of the rainfall and snowmelt in the study area as well as the mineralogy of the soils and aquifer materials, which are composed mainly of quartz, feldspar, and clay minerals. In addition, the aquifer materials are nearly devoid of carbonate minerals, except in coastal areas underlain by marginal marine sediments and in areas where the confined aquifers subcrop or outcrop in the northern part of the study area. Elevated concentrations of nitrate (above 5 mg/L) were found to be prevalent in the surficial aquifer, and represent the most significant water-quality concern for this aquifer.

Water in the confined aquifers was found to be much less acidic, and have higher hardness and dissolved-solids concentrations than water from the surficial aquifer. Natural water-quality problems in the confined aquifers included high concentrations of dissolved iron, excessive hardness, and the presence of saline water downdip in each aquifer, which limits the use of these aquifers for water supply. Elevated concentrations of nitrate are not a problem in most parts of the confined-aquifer system (Hamilton and others, 1991).

A principal goal of the Delmarva NAWQA project was to evaluate the effects of agricultural activity on water quality in the surficial aquifer. To determine the effects of agriculture and other human activities on natural water quality, it was necessary to distinguish between water samples whose chemical composition had been significantly affected by human activity from those not affected or only minimally affected. This was

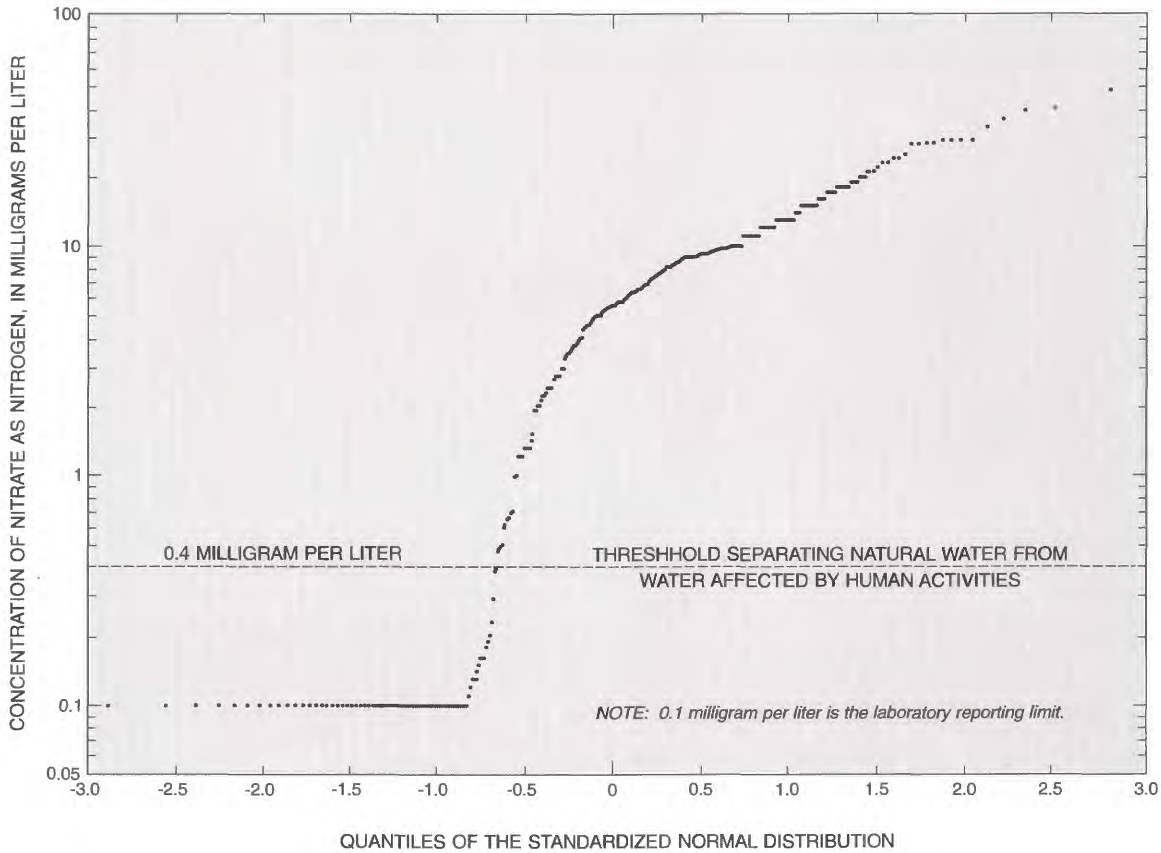



**Figure 5.** Probability distribution of nitrate concentrations in water collected from wells completed in the surficial aquifer in the Delmarva Peninsula, 1976-90 (from Hamilton and others, 1993).

accomplished by constructing a probability plot of nitrate concentrations in samples from 296 wells in the completed surficial aquifer (fig. 5). Nitrate was chosen as the indicator of human activity because it is introduced into the ground-water system in both agricultural areas (by application of fertilizer and manure) and residential areas (from septic-tank effluent and lawn and garden fertilizers). On the basis of the probability plot, a threshold nitrate concentration indicative of human activity was defined to be 0.4 mg/L (Hamilton and others, 1993). About 74 percent of the samples (219) were considered to be affected by human activity. The 77 unaffected samples were used to examine regional patterns in natural or nearly natural ground-water chemistry. This method of sorting did not consider the effects of redox conditions on the presence or absence of nitrate in ground water.

Analysis of the chemical composition of ground-water samples from the study area shows that natural ground water can be distinguished from ground water affected by human activities on the basis of patterns in major-ion chemistry (Hamilton and others, 1993). These patterns also can be used to distinguish between the types of human activities that have affected water quality. A summary of the chemical characteristics of water affected by natural, agricultural, and residential activities is shown in table 4.

## Chemistry of Natural Ground Water

The chemistry of natural ground water in the study area is controlled by the chemistry of the rain and snowmelt, dissolution of minerals in the aquifer sediments, oxidation and reduction reactions, cation exchange, and mixing of fresh water with brackish or saline waters. Mineral dissolution is the major source of dissolved constituents in shallow ground water. Concentrations

**Table 4.** Summary of the chemical characteristics of natural water and water affected by agricultural or residential activities in the surficial aquifer of the Delmarva Peninsula, 1976-90

[Modified from Hamilton and others, 1993; Analysis includes water samples collected from wells in the existing network and the National Water-Quality Assessment areal and transect networks; samples affected by agriculture and residential areas were determined by use of 1:250,000-scale land-use data (U.S. Geological Survey, 1979a, 1979b, 1979c, 1980a, 1980b, and 1980c); total number of analyses is in parentheses ( ); µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; for more information on p-value and statistical tests, see Hamilton and others, 1993]

| | PROPERTIES | | | DISSOLVED CONSTITUENTS | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | pH (standard unit) | Specific conductance (µS/cm) | Alkalinity (as calcium carbonate mg/L) | Calcium (mg/L) | Magnesium (mg/L) | Calcium plus magnesium (mg/L) | Sodium (mg/L) | Potassium (mg/L) | Iron (µg/L) | Silica (mg/L) | Barium (µg/L) | Strontium (µg/L) | Sulfate (mg/L) | Chloride (mg/L) | Nitrate (as nitrogen mg/L) |
| **Natural Ground Water** | | | | | | | | | | | | | | | |
| Median value or concentration | 5.76 (77) | 115 (77) | 26 (77) | 4.8 (77) | 1.7 (77) | 6.9 (77) | 9.4 (77) | 1.1 (77) | 1,800 (77) | 24 (77) | 37 (49) | 57 (49) | 6.6 (77) | 9.1 (77) | 0.1 (77) |
| **Ground Water Affected by Agricultural Activities** | | | | | | | | | | | | | | | |
| Median value or concentration | 5.25 (185) | 170 (185) | 6.0 (185) | 9.0 (185) | 5.0 (185) | 15 (185) | 7.9 (185) | 2.6 (185) | 16 (185) | 15 (185) | 120 (85) | 140 (85) | 6.0 (185) | 14.0 (185) | 8.2 (185) |
| **Ground Water Affected by Residential Activities** | | | | | | | | | | | | | | | |
| Median value or concentration | 5.35 (34) | 163 (34) | 6.0 (34) | 7.8 (34) | 4.1 (34) | 12 (34) | 9.3 (34) | 2.6 (34) | 2 (34) | 18 (34) | 110 (18) | 105 (18) | 7.5 (34) | 16.0 (34) | 7.1 (34) |
| ***p*-value for Mann-Whitney Statistical Test** | | | | | | | | | | | | | | | |
| Summary statistic | .448 | .876 | .093 | .716 | .199 | .358 | .009 | .424 | .819 | .080 | .452 | .452 | .040 | .427 | .172 |

of total dissolved constituents are generally low (less than 200 mg/L) because the soils, sands, and silts of the surficial aquifer consist primarily of relatively insoluble quartz and feldspars (Hamilton and others, 1993). In some areas with sediments of marine origin, water chemistry is also affected by the addition of calcium, magnesium, and bicarbonate ions from the dissolution of shell material. Near the coasts and along tidal rivers, saline or brackish water can intrude into the surficial aquifer, elevating the concentration of chloride ions. Chloride ion concentration in natural waters (except in areas affected by saline water) is generally around 6 mg/L or below, and is derived from precipitation (Denver, 1986).

Four natural-water types, defined on the basis of major-ion chemistry, are present in the surficial aquifer of the Delmarva Peninsula including calcium bicarbonate type, sodium bicarbonate type, sodium chloride type, and calcium sodium sulfate type (fig. 6; Hamilton and others, 1993). The natural characteristics of waters are easily changed and concealed by human activities because of the naturally dilute chemistry of the waters. Table 5 provides a summary description of natural water types identified on the Peninsula.

Several hydrochemical water types have been identified in the confined aquifers of the Delmarva Peninsula (Back, 1966). In the updip sections of most of these aquifers, the water grades from a mixed chemical type in the surficial aquifer to a calcium bicarbonate type. With increasing depth in each aquifer, the calcium bicarbonate water grades into a sodium bicarbonate type. Further downdip in each aquifer, the sodium bicarbonate waters grade into brackish and saline waters (sodium chloride type) that are unsuitable for water supply (Cushing and others, 1973). All of the sampled wells completed in the confined aquifers in this study produced water from zones of calcium bicarbonate type, sodium bicarbonate type, or dilute mixed water types similar to those found in the surficial aquifer.

**Table 5**. Natural water types and their distribution and characteristics in the surficial aquifer on the Delmarva Peninsula

[From Hamilton and others, 1991]

| WATER TYPE | DISTRIBUTION AND CHARACTERISTICS |
|---|---|
| Sodium bicarbonate | Dominant in the central part of the Peninsula, where the surficial aquifer is within the Beaverdam Formation, a medium to coarse quartz sand with variable amounts of fine-grained sand and gravel. The major ions in this ground-water type are derived primarily from atmospheric precipitation and the dissolution of silicate minerals, principally feldspars. |
| Calcium bicarbonate | Dominant in the northern part of the Peninsula, where the surficial aquifer is thin and shallow ground water comes in contact with underlying marine sediments. The surficial aquifer is within the fluvially derived Pensauken Formation, a fine- to medium-grained quartz sand with varying amounts of coarse sand and gravel. The underlying marine units are predominantly quartzose and contain shell material. Water chemistry is controlled by atmospheric precipitation, dissolution of silicate materials, and dissolution of shell material. |
| Sodium chloride | Observed in shallow ground water near saline and brackish water bodies. Results from the intrusion of brackish water into the surficial aquifer. |
| Calcium sodium sulfate | Present in sediments associated with estuarine environments, forested wetlands, and marshy parts of streams dominated by fine-grained sediments. Generally present in areas with relatively short flow paths, which results in minimal dissolution of silicate minerals. Water chemistry is controlled primarily by degradation of organic matter in the sediments and commonly is associated with reducing conditions, although components from silicate mineral dissolution and atmospheric precipitation are also present. |

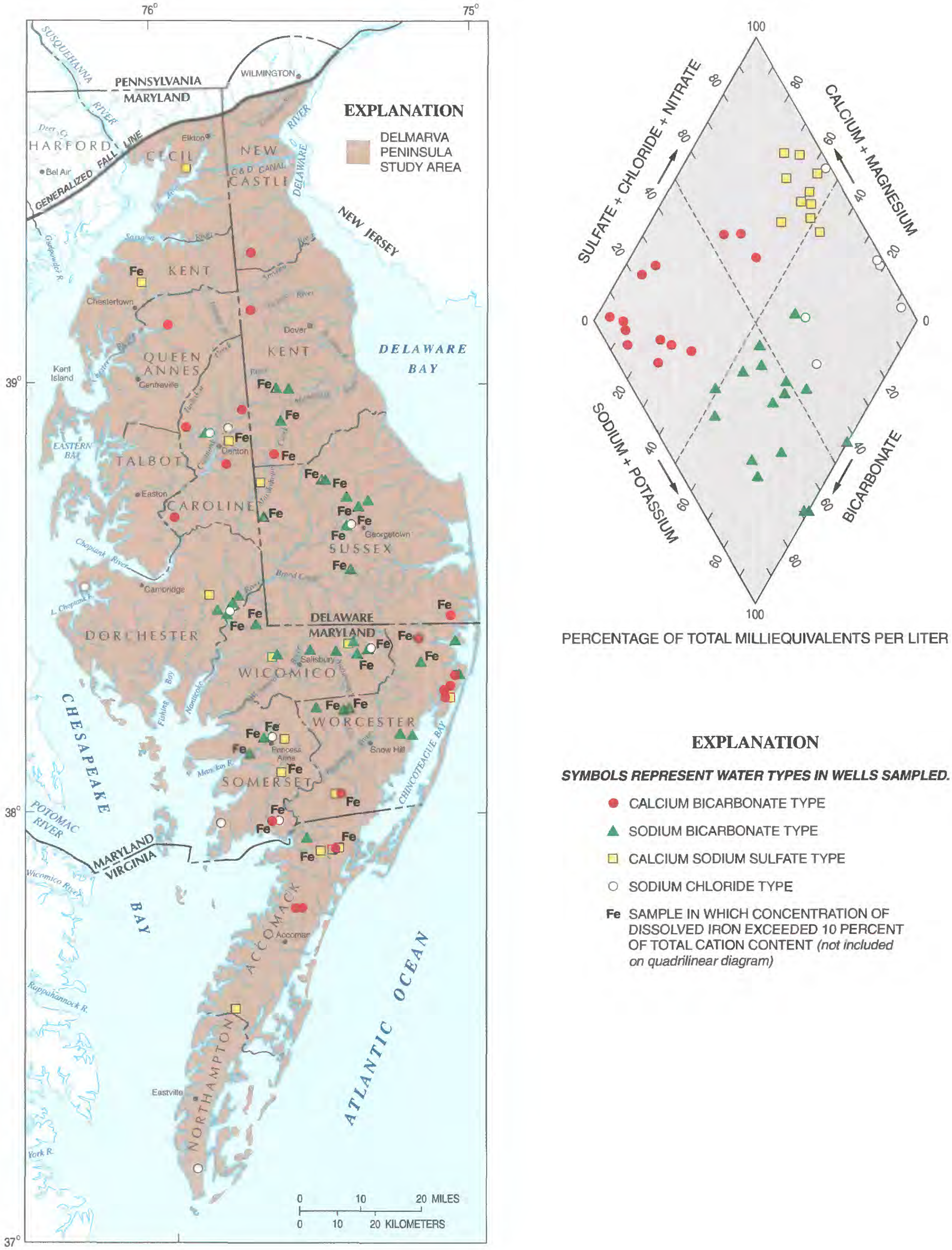



**Figure 6.** Distribution of natural water types in wells completed in the surficial aquifer in the Delmarva Peninsula, 1980-90 (from Hamilton and others, 1993).

In parts of the surficial aquifer system with well-drained recharge areas, dissolved oxygen is commonly present throughout the flow system. Reducing conditions in the surficial aquifer exist in areas recharged through poorly drained soils and in areas where organic matter is associated with fine-grained deposits. Most natural waters on the Delmarva Peninsula are associated with poorly drained recharge areas (Hamilton and others, 1993). These areas, which are commonly forested and contain wetlands, are unsuitable for agriculture or residential development, and are not exposed to the human activities that affect water quality.

Dissolved iron is a major component of natural ground waters associated with reducing conditions. Concentrations of dissolved iron on the Delmarva Peninsula commonly exceed the U.S. Environmental Protection Agency's (USEPA) Secondary Maximum Contaminant Level (SMCL) of 0.3 mg/L. In fact, the median concentration (1.8 mg/L) is above the SMCL (table 4). Natural sources of iron are found along both long and short ground-water-flow paths. Along the longer flow paths, iron is leached from iron oxyhydroxide coatings on mineral grains in the aquifer. Dissolved iron is also derived from oxidation of pyrite. This process is probably most prevalent in settings with short flow paths common to areas containing organic sediments with small, finely disseminated grains of pyrite. Waters in this setting usually have pH values below 4.5, which promotes the dissolution of pyrite.

Dissolved aluminum was found at concentrations ranging from less than the detection limit (0.010 mg/L) to 0.101 mg/L in samples from wells in the regional networks. The higher concentrations of aluminum tend to be found in poorly drained areas characterized by short ground-water-flow paths (Phillips and Shedlock, 1993; Bachman, 1994; Bachman and Phillips, 1996). These settings are most commonly associated with wetlands and riparian zones along streams.

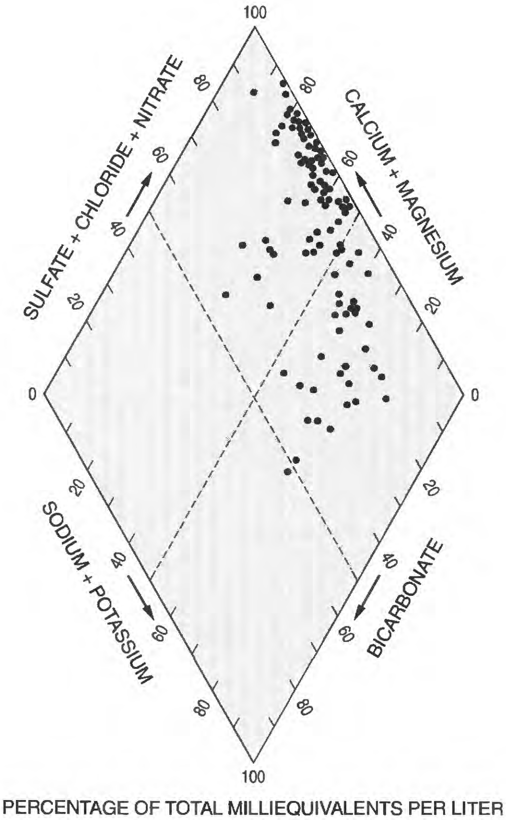
### Effects of Human Activities on the Chemistry of Ground Water

Agriculture is the dominant human activity that affects water quality in the study area. Agricultural practices with the most influence on the major-ion chemistry of ground water include the applications of lime, fertilizer, and manure to the major crops, namely, corn, soybeans, and small grains. Ions leached to ground water as a consequence of these applications include calcium and magnesium from lime, nitrogen and phosphorus from manure and inorganic fertilizer, and potassium and chloride from potash (Denver, 1989). In areas where well-drained soils overlie oxic aquifer conditions, nitrogen fertilizers, which are generally applied in reduced forms, are oxidized to nitrate and leached through the soil zone into the ground-water system.

The dissolved constituents in ground water affected by agriculture are dominated by nitrate, calcium, and magnesium from fertilizer, manure, and lime applications (fig. 7). Potassium and chloride, which are components of potash fertilizer, are also elevated above their concentrations in natural ground water. The dominance of these ions in the water is a chemical signature indicative of leaching of agricultural chemicals into shallow ground water. Alkalinity is commonly lower in water affected by agricultural activity because bicarbonate ion is consumed in the oxidation of ammonium to nitrate (Denver, 1986). The phosphorus present in some fertilizers is strongly sorbed onto soil particles and not readily leached into ground water.

The chemical signature of water affected by agricultural activity is readily identifiable in ground water throughout the Peninsula where agricultural land overlies well-drained soils (Hamilton and others, 1993). The agricultural chemical signature is recognizable because of the naturally low concentrations of dissolved ions in the aquifer beneath sandy upland recharge areas. Sandy recharge areas are common in the well-drained upland, poorly drained upland, and Inner Coastal Plain HGMR's. Natural water in these regions is usually calcium bicarbonate or sodium bicarbonate type. The agricultural chemical signature is not obvious in ground waters where agricultural land use overlies fine-grained sediments, such as in the surficial confined HGMR. In this region, the natural water type (calcium sodium sulfate) is not distinct from agriculturally affected waters and reducing conditions in the aquifer commonly inhibit the conversion of nitrogen species to nitrate.

Ground water in residential parts of the study area commonly has a chemical signature in which sodium, chloride, sulfate, and nitrate are the dominant ions. Effluent from domestic septic systems and the application of lawn fertilizers affect the major-ion chemistry of ground water by elevating concentrations of nitrate (Hamilton and




**EXPLANATION**

• CHEMICAL ANALYSIS OF GROUND WATER AFFECTED BY AGRICULTURAL ACTIVITIES

**Figure 7.** Chemistry of water affected by agricultural activities collected from wells completed in the surficial aquifer in the Delmarva Peninsula, 1976-90 (from Hamilton and others, 1993). (Only samples with complete chemical analyses were plotted.)

others, 1993). Sodium and chloride are also elevated in septic-system effluent, as a result of salt in the human diet, while sulfate levels are elevated by the oxidation of organic materials. Neither sulfate nor sodium is commonly present at elevated concentrations in ground water affected by agriculture, although many of the other ionic components attributable to agricultural activities are also common in waters affected by residential land use (table 4).

## Patterns in Concentrations of Selected Constituents in Ground Water

Regional patterns in the distribution of nitrate and pesticides in ground water vary in relation to differences in hydrogeomorphic characteristics of the Delmarva Peninsula. The processes that affect the transport and transformation of these constituents, however, are similar from one hydrogeomorphic region to another (Shedlock and others, 1993; Koterba and others, 1993). Differences in the observed concentrations and spatial patterns in chemical constituents in ground water are primarily related to differences in land use, soil characteristics, aquifer configuration, and hydrogeochemical conditions. The water-quality patterns were studied along several local-scale flow paths in networks installed in areas representing major geomorphic and hydrologic settings of the Peninsula (Hamilton and others, 1993; Denver, 1993; Shedlock and others, 1993). The understanding of the physical and chemical processes affecting the distribution of nitrates and pesticides in ground water derived from the local-scale studies was applied to interpretation of regional water-quality patterns.

The investigation of spatial water-quality patterns focused chiefly on the distribution of agricultural chemicals in the ground-water system because agriculture is the most widespread land use on the Peninsula. Regionally, agricultural lands are located predominantly on well-drained soils, whereas most forests, the second most prominent land cover, are on poorly drained soils (Phillips and Blomquist, 1991). Exceptions to these patterns exist where poorly drained, but coarse-textured, soils have been ditched to lower the water table and improve drainage for farming. This practice is extensive in the surficial confined HGMR and common in the poorly drained upland HGMR (fig. 3).

Chemicals from agricultural sources are potentially present throughout flow paths associated with recharge areas that coincide with agricultural lands. Inspection of historical and recent aerial photography indicated that patterns of forested and agricultural land have been consistent in the study area for the last 30 to 40 years. Corn, soybeans, and small grains have been the major crops produced in this region since the 1960's, when expansion of the poultry industry created a market for their use as feed. Ground-water residence times in the surficial aquifer indicate that some waters in the middle and distal parts of the shallow ground-water-flow systems are 30 to 50 years old (Dunkle and others, 1993).

### Occurrence and Distribution of Nitrate

Hamilton and others (1993) found that nitrate concentrations range from below detection limits to greater than 40 mg/L in water from the surficial aquifer. Elevated concentrations of nitrate were detected in nearly all areas of the Peninsula and at nearly all depths in the surficial aquifer system. The distribution of nitrate in ground water varies among the HGMR's and is related to differences in the regional patterns of oxic and anoxic conditions in the aquifer, as well as the distribution of agricultural, forested, and residential land.

Nitrate exceeded the USEPA Maximum Contaminant Level (MCL) for drinking water (10 mg/L as nitrogen) in about 33 percent of the 185 analyses of water from the surficial aquifer in agricultural areas (Hamilton and others, 1993). Nitrate con-centrations also were elevated above the back-ground level of 0.4 mg/L in water associated with residential recharge areas. In fact, the median concentration of nitrate in water from wells in residential areas (7.1 mg/L) was only slightly lower than the median concentration in water from wells in agricultural areas (8.2 mg/L) (table 4). Although the median values are similar, less than 15 percent of the samples from wells in residential areas exceeded the MCL of 10 mg/L, compared to 33 percent for agricultural areas.

High nitrate concentrations are found in the surficial aquifer because nitrate applied in excess of crop uptake is easily leached into ground water through the sandy, permeable soils common to agricultural areas of the Peninsula. Most of the nitrate that enters ground water remains in the system as long as oxic conditions are maintained in the aquifer along the ground-water-flow path, a common condition along entire flow paths that originate beneath well-drained soils.

Concentrations of nitrate in water in the surficial aquifer show a strong correlation with HGMR's. Hamilton and others (1993) found significant differences among the median values of nitrate concentrations for water samples from different HGMR's. Water from wells in the well-drained upland had the highest median nitrate concentrations (8.9 mg/L), followed by those in the poorly drained uplands (4.4 mg/L), surficial confined region (1.1 mg/L), and the poorly drained and fine-grained lowlands (0.1 mg/L). This pattern agrees with the findings of Bachman (1984), who observed that nitrate concentrations were significantly higher in areas with well-drained soils, where oxic conditions dominate the aquifer system, than in areas with poorly drained soils, where oxic and anoxic conditions are interspersed to varying degrees. The median concentrations of nitrate in ground water from the local-scale networks tend to follow the regional trends seen in their respective HGMR's (figs. 8A and 8B). The median concentrations of nitrate are somewhat higher in waters from wells in the local-scale networks because well placement is biased more towards agricultural land use in the local-scale networks than in the regional well networks.

Changes in nitrate concentration in ground water also seem to be related to changes in nitrogen fertilizer application rates over time (Hallberg and Keeney, 1993; Böhlke and Denver, 1995). Figure 9 shows that nitrate concentrations in ground water in the Locust Grove local-scale network have increased in waters recharged since the 1960's at a rate similar to the rate of increase in fertilizer usage for the region. In general, concentrations of nitrate in ground water are highest in water from shallow wells located in or immediately downgradient from well-drained agricultural fields (Dunkle and others, 1993). Older ground waters (those recharged before the 1970's) have lower concentrations of nitrate than younger ground waters from the same flow paths. This pattern is illustrated in cross sections from the Fairmount and Locust Grove local-scale networks (fig. 10) and was also observed in water from local-scale networks in the poorly drained upland in northern Delaware and the well-drained upland at the southern tip of Virginia (Hamilton and others, 1993).

In contrast to patterns observed in the local-scale networks, regional analysis of nitrate data indicated no statistically significant relation between depth below land surface and the con-centration of nitrate in ground water in the surficial aquifer (Hamilton and others, 1993) (fig. 11). Concentrations of nitrate greater than 10 mg/L as nitrogen are sometimes found near the base of the surficial aquifer along ground-water-flow paths in which oxic conditions are maintained. One of the wells in the Fairmount local-scale network, screened at 80 ft below land surface but not along the cross section in figure 10, had water with a nitrate concentration of 40 mg/L (Denver, 1989). In most of the local-scale networks, however, nitrate seems to generally decrease with depth below farm fields. The lack of a statistically significant relation between depth and nitrate concentrations in the regional scale is at least in part due to the fact that commercial fertilizers and manures have been applied to agricultural lands in the study area and have been leaching into the surficial aquifer for

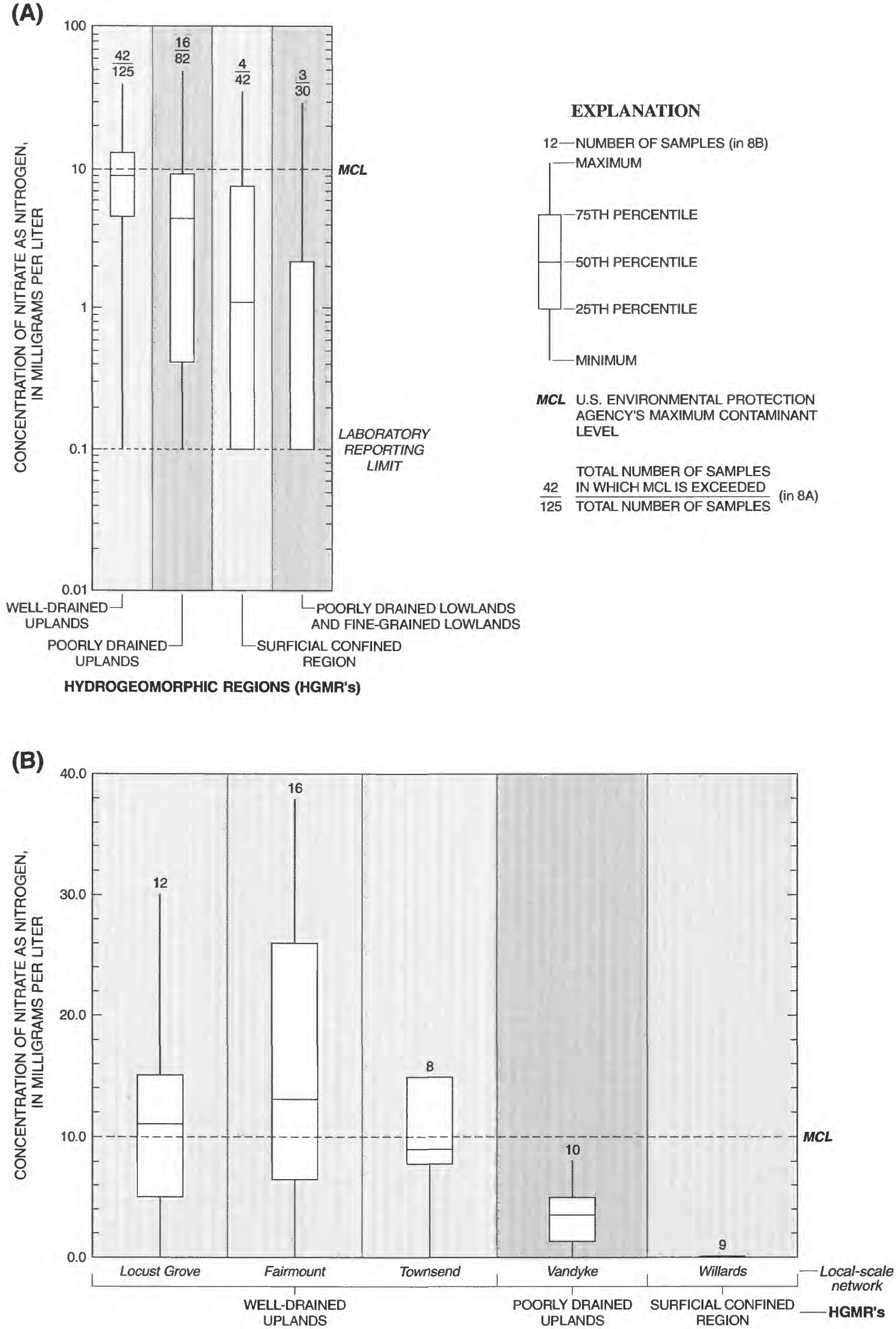



**Figure 8.** Distribution of nitrate concentrations in ground water collected from wells in **(A)** the surficial aquifer and **(B)** local-scale networks, grouped by hydrogeomorphic region (from Hamilton and others, 1993).

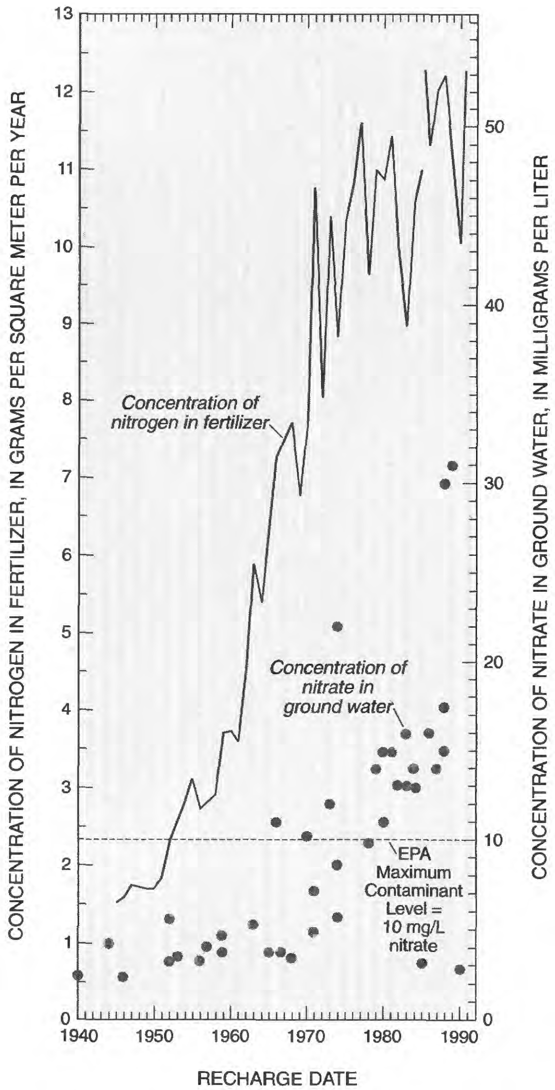



**Figure 9.** Comparison of nitrate concentration in ground water to load of nitrogen applied as fertilizer in area of Locust Grove local-scale network (modified from Böhlke and Denver, 1995).

many decades. Differences in flow rates and residence times in the surficial aquifer across the Peninsula may also contribute to the lack of a relation between depth and nitrate concentrations.

Nitrate concentrations in ground water are not necessarily correlated with the overlying land use at the site of the well sampled. For example, nitrate concentrations in ground water can be higher at depth beneath forested areas than in adjacent areas with interspersed forested and agricultural land use. This apparent anomaly occurs where the forested area is downgradient in the shallow ground-water-flow system from an agricultural area in which ground water with high nitrate concentration is recharging the surficial aquifer. Thus, the concentration of nitrate at any depth in the surficial aquifer depends more on the land use associated with the recharge area for that part of the shallow ground-water-flow system than on the land use immediately surrounding the well site. This relation was seen in water samples from several well clusters in both the regional and local-scale networks. In some areas, ground water that is recharged through agricultural fields upgradient of forested areas flows beneath the water recharged in downgradient forested areas (fig. 12). The water recharged in the agricultural areas has nitrate concentrations much higher than those in the overlying water recharged beneath the forested land. Water from wells completed at intermediate depths in the surficial aquifer in such forested areas may have concentrations of nitrate above 5 mg/L, a value well above concentrations observed in natural ground water below forested areas. This general pattern is shown on figure 10 for the Fairmount local-scale network, and was also observed at the Townsend local-scale network, where a broad, forested riparian zone is in the downgradient part of the flow path near a stream (Hamilton and others, 1993).

The flow-path studies in the local-scale networks and the regional data indicate that over time, waters with high concentrations of nitrate have moved from shallow to deep parts of the surficial aquifer. These waters will eventually discharge to local streams, wetlands, tidal rivers, or other tidal water bodies along the major coastlines of the Peninsula. Age-dating work by Dunkle and others (1993) and Böhlke and Denver (1995) and simulation studies by Reilly and others (1994) suggest that it may take as long as 30 years for some of these high-nitrate waters to reach their discharge areas.

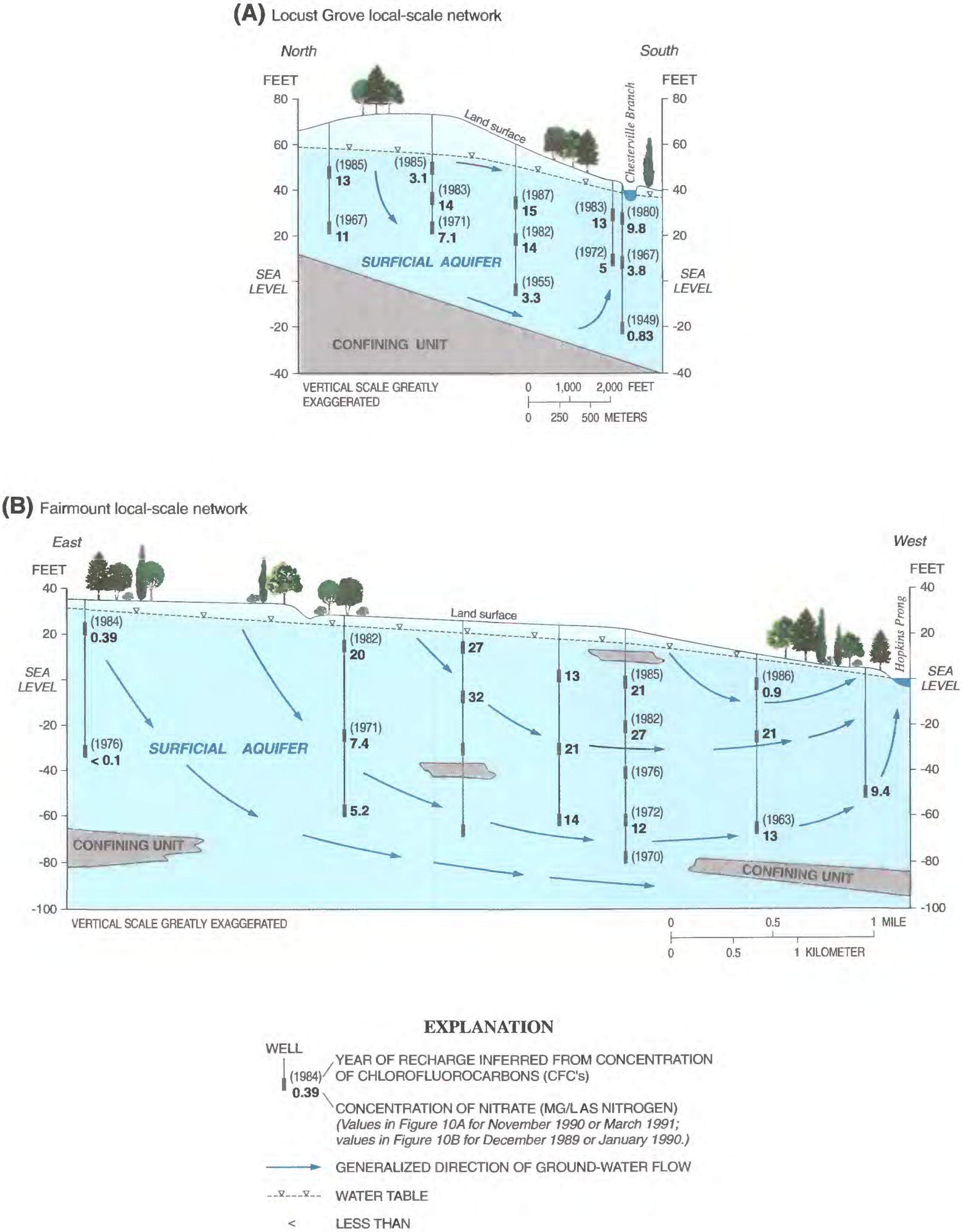



**Figure 10.** Cross sections of the **(A)** Locust Grove and **(B)** Fairmount local-scale networks showing chlorofluorocarbon (CFC)-modeled recharge years, nitrate concentrations (in milligrams per liter as N), and general ground-water-flow paths (from Dunkle and others, 1993).

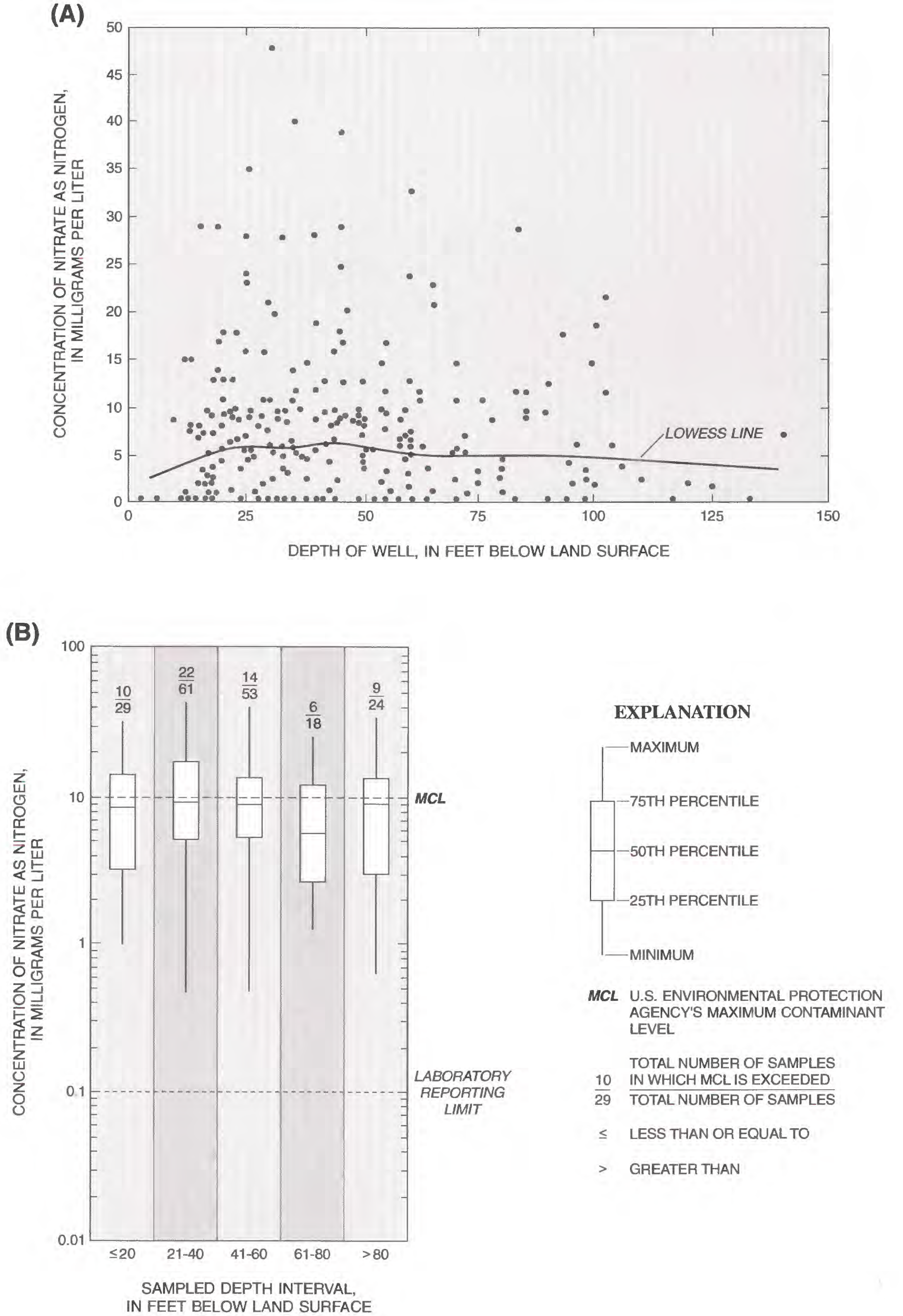



**Figure 11.** Nitrate concentrations and depth of wells in the surficial aquifer in the Delmarva Peninsula, 1976-90: **(A)** scatter diagram; **(B)** percentile diagram (from Hamilton and others, 1993).

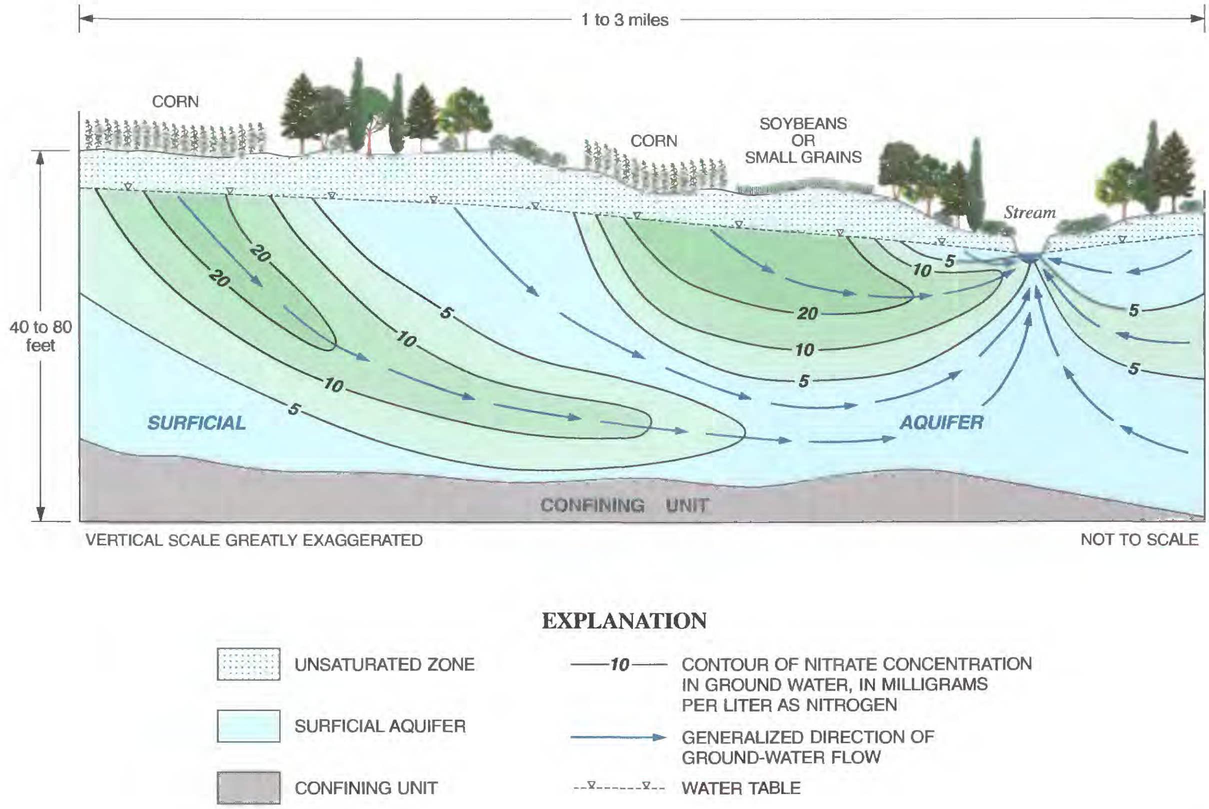
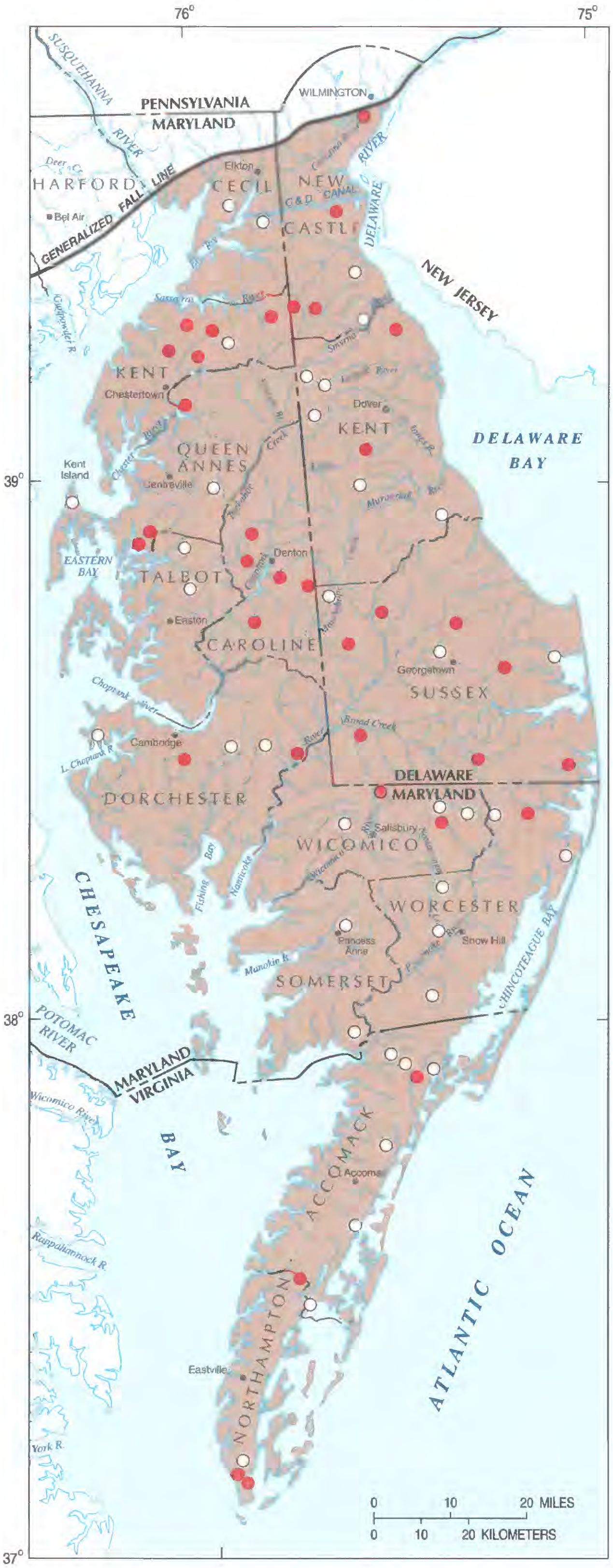



**Figure 12.** Relation between land use and nitrate concentrations in ground water in shallow flow systems in the surficial aquifer in the Delmarva Peninsula.

### Occurrence and Distribution of Pesticides

Pesticide residues, primarily herbicides, were detected in shallow ground water throughout the Delmarva Peninsula (Koterba and others, 1993) (fig. 13). The most frequently detected pesticides were the herbicides that are among the most widely and intensively used in the study area (figs. 14 and 15a). Atrazine was the most frequently detected, followed by cyanazine, simazine, alachlor, metolachlor, and dicamba. These herbicides are used in the production of corn, soybean, or small grain crops, which have been the major crops in the study area since the 1960's. Insecticides, such as carbofuran, were seldom detected. Multiple residues (two or more pesticides) were detected in 19 of the 35 samples in which pesticides were detected. Desethylatrazine, a common metabolite (breakdown product) of atrazine and simazine, was detected in waters from the local-scale networks at concentrations and frequencies similar to that of atrazine. Concentrations of commonly detected pesticides ranged from the detection levels of about 0.01 micrograms per liter (µg/L) to about 5 µg/L. Only two samples had concentrations of any single pesticide compound exceeding 10 µg/L and only four of the detections in the regional sampling networks were at concentrations above the USEPA Health Advisory Level (HAL) or MCL for that compound (fig. 15).

The spatial distribution of pesticides in ground water is related primarily to the distribution of agricultural land and herbicide-usage patterns on the most common crops. Ground water with detectable pesticides commonly had an agricultural chemical signature, in which calcium, magnesium, and nitrate were the major chemical constituents, although all waters with this signature did not always contain pesticide residues (Koterba and others, 1993). In general, pesticides have not been in use as long as nitrogen fertilizers, manures, or




**EXPLANATION**

○ WELL SITE FOR AREAL, TRANSECT, OR SUBCROP WELL IN WHICH WATER SAMPLE CONTAINED NO DETECTABLE PESTICIDES

● WELL IN WHICH WATER SAMPLE CONTAINED ONE OR MORE DETECTABLE PESTICIDES

**Figure 13.** Locations of wells sampled for pesticides and wells with pesticide detections (from Koterba and others, 1993). (Some locations have more than one well.)

septic systems (the major sources of nitrate in the ground water of the study area). Pesticides are seldom found in waters whose recharge age predates the early-to-mid 1970's, when the commonly detected herbicides gained widespread use (Koterba and others, 1993).

Concentrations and detections of pesticides were generally greatest in samples from wells completed in shallow parts of the surficial aquifer, with 90 percent of the detections in the regional-sampling network from wells screened within 35 ft of the overlying water table. The probability of detecting a pesticide residue is inversely correlated to the depth of the well screen below the water table. No correlation was evident, however, between pesticide detection and depth to the water table. Pesticides were not generally found in parts of the aquifer used for water supply, as these wells are commonly screened near the base of the aquifer, at depths greater than 35 ft below the water table. The pesticides detected and the range of concentrations detected were similar in ground water from the regional and local-scale networks.

As was the case with nitrate, the detection of pesticide residues in the surficial aquifer is related to HGMR's in the study area. Koterba and others (1993) found a higher percentage of pesticide detections in water samples from wells in upland HGMR's than samples from wells in the lowland HGMR's. This difference is related to variations in soils among the HGMR's. These variations affect land-use patterns as well as the persistence and mobility of pesticides. Agricultural and residential land use and the pesticide-usage practices associated with each are most pervasive in areas of the Peninsula with well-drained soils, which are most commonly found in the upland HGMR's. Furthermore, well-drained soils are generally sandy and have a low organic matter content, conditions that are least likely to inhibit pesticide mobility. Water recharging the aquifer leaches relatively quickly through the soil zone under these conditions. Once pesticide residues have left the soil zone, the opportunity for their degradation greatly decreases (Helling and Gish, 1986). In contrast, poorly drained soils, which occur mainly in lowland HGMR's and to varying degrees in the upland HGMR's, commonly contain the greatest amounts of silt, clay, and organic matter. These soils are most likely to impede the movement of water and retain pesticides in the soil zone, where most pesticides degrade by interactions with soil microorganisms.

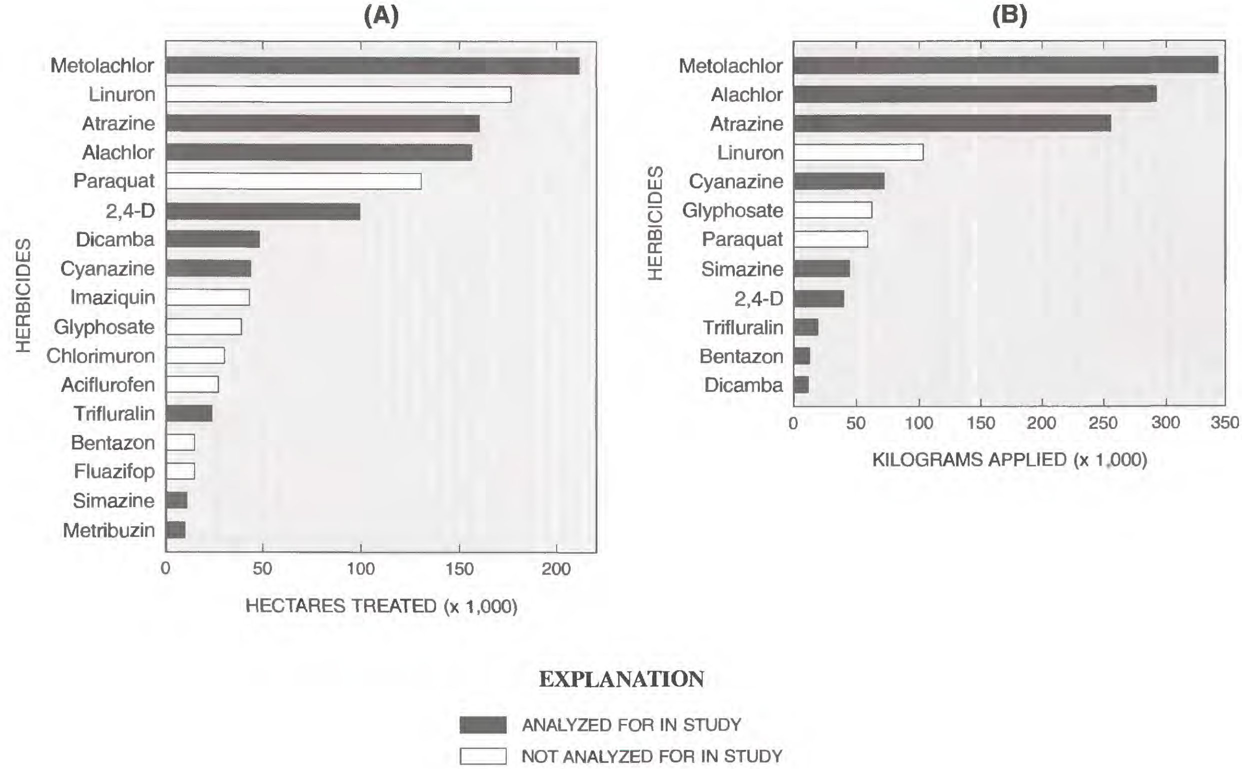



**Figure 14.** Herbicide use (1987) in **(A)** hectares treated and **(B)** kilograms applied in the Delmarva Peninsula (modified from Koterba and others, 1993).

Pesticides commonly used on local crops were detected in ground water from each of the local-scale networks. The networks in which they were detected most frequently and at the highest concentrations, the Fairmount and Locust Grove networks, are both located within the well-drained upland HGMR (fig. 3). Of the other three networks, one is in the poorly drained upland and another in the surficial confined HGMR. The remaining local-scale network is in the well-drained upland near Townsend, Virginia, but pesticide use in this area differs significantly from that in other areas because of the higher percentage of cropland in vegetables in this network.

All of the commonly detected herbicides were detected at least once in ground waters from the Locust Grove and Fairmount local-scale networks, with atrazine and desethylatrazine detected most frequently and at the highest concentrations. Atrazine concentrations ranged from the detection level (0.01 µg/L) to 2.0 µg/L at Fairmount and 0.53 µg/L at Locust Grove. Age-dates for ground water (Dunkle and others, 1993) indicate that atrazine persists in the surficial aquifer at the Locust Grove network for about 10 years and at Fairmount for about 17 years. The oldest waters in which desethylatrazine was detected were recharged in the mid-1970's, a timeframe that corresponds to the beginning of the widespread use of atrazine in the study area, as seen in the regional data.

Where atrazine and its metabolites were measured in ground water in the local-scale networks, the proportion of atrazine metabolites to atrazine increased with residence time in the aquifer. In fact, only metabolites were present in samples of waters with the longest residence times (Bachman and others, 1992; Denver and Sandstrom, 1991). Such a pattern in the Locust Grove local-scale network is shown in figure 16.

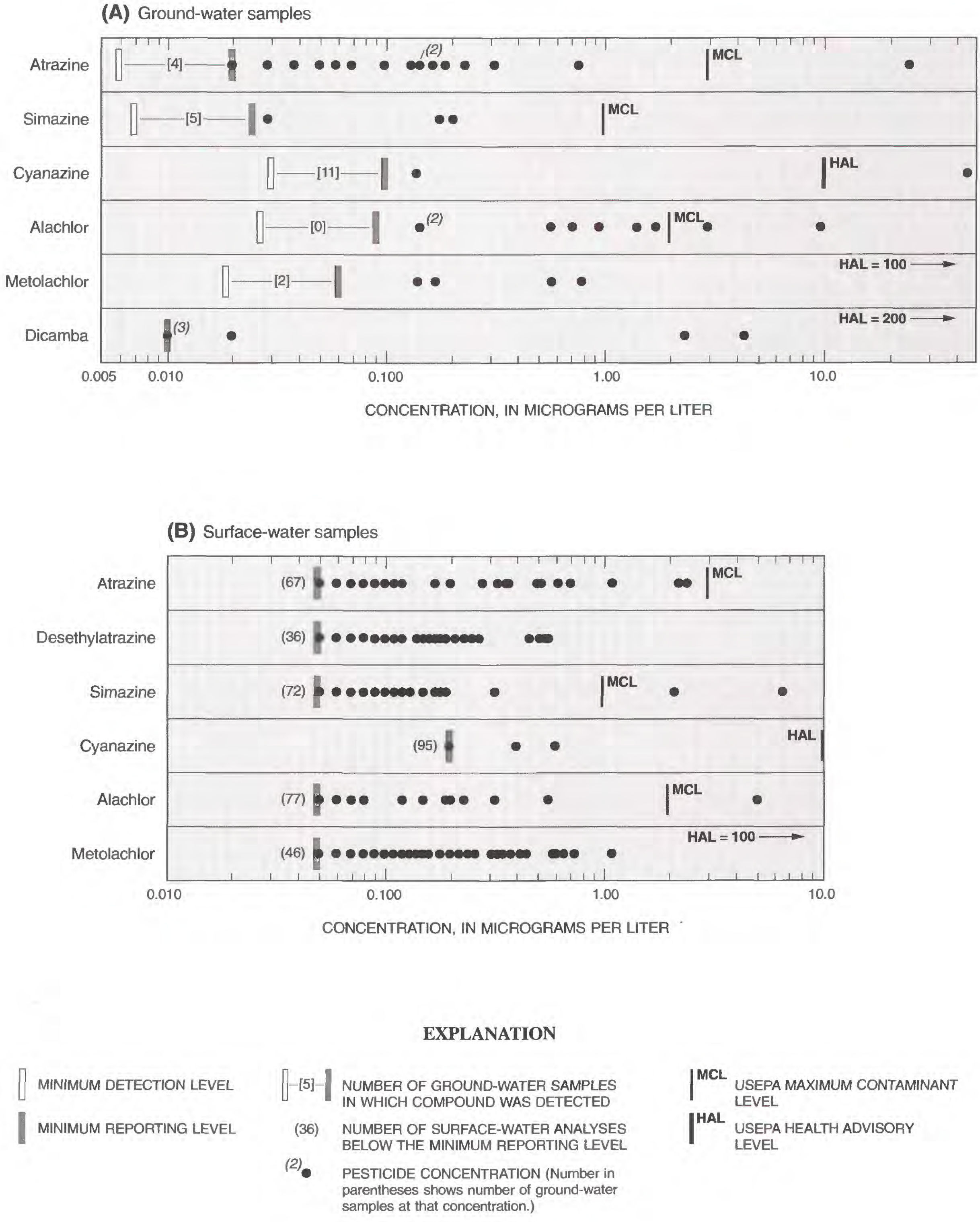



**Figure 15.** Minimum detection and reporting levels, sample concentrations, and health-related water-quality criteria for pesticides commonly detected in **(A)** ground water and **(B)** surface water in the Delmarva Peninsula (ground-water data plot modified from Koterba and others, 1993).

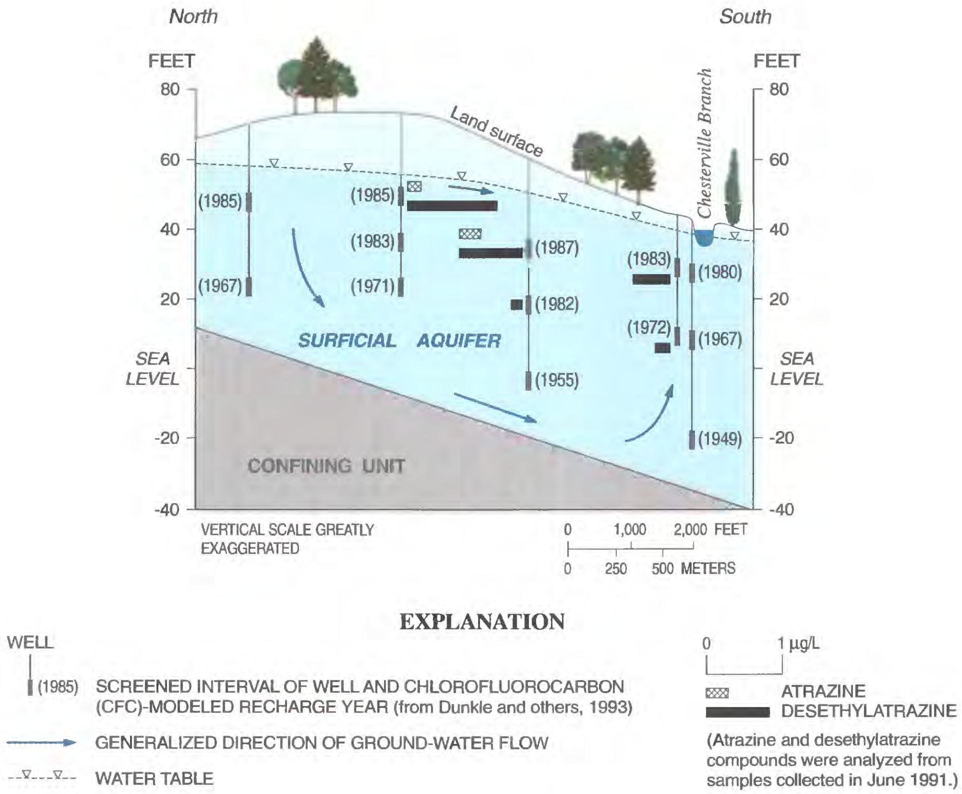



**Figure 16.** Cross section of Locust Grove local-scale network showing general flow paths in the surficial aquifer, and the relation between atrazine and desethylatrazine concentrations and chlorofluorocarbon (CFC)-modeled recharge years.

While most of the desethylatrazine is probably formed by degradation of atrazine in the soil zone, some degradation may have occurred in the ground-water system. This process may be acting in ground water from the Fairmount local-scale network, where higher concentrations of desethyl-atrazine are found at intermediate depths of the aquifer than at shallower depths (Denver and Sandstrom, 1991). Research at other sites where atrazine is applied indicates that this trend is most likely caused by a combination of atrazine degradation within the aquifer and preferential transport of desethylatrazine over atrazine (McMahon and others, 1992; Perry, 1990; Adams and Thurman, 1991).

Differences in persistence and mobility among the pesticides that were commonly detected in ground water can affect the relative frequency of their occurrence and their concentrations in the surficial aquifer. Although metolachlor and alachlor are as, or more, widely used than atrazine (fig. 14), atrazine is detected with a greater frequency in ground water. This pattern is probably related to the differences in solubilities and half-lives of these compounds, which cause atrazine to persist in the environment for a longer period than the other commonly applied pesticides (table 6). Atrazine is moderately soluble in water and has a relatively long half-life in soils. In contrast, alachlor and metolachlor have greater solubilities, but relatively short half-lives. These differences result in atrazine being available in the soil zone in greater quantities for a longer periods of time, and therefore, more likely to leach into ground water. Thus, pesticide occurrence in ground water from the study area is related to land use and associated pesticide usage, soil properties, and the physical and chemical properties of the pesticides applied.

### Occurrence of Volatile Organic Compounds, Gross–Alpha Radiation, Radon, and Trace Elements

All of the samples from the regional networks in the surficial aquifer and the samples from the shallowest well in each of the confined aquifers were analyzed for a suite of volatile organic compounds, and for gross–alpha radiation, radon, and selected trace elements, such as cadmium, arsenic, and selenium. In the laboratory reports, volatile organic compounds (VOC's) were detected

**Table 6.** Solubility, persistence, and sorption characteristics of the pesticides commonly detected on the Delmarva Peninsula

[Values for solubility from Farm Chemicals Handbook (1991); values for metolachlor and simazine from Wauchope and others (1991); values for other herbicides from Rao and Hornsby (1989) and Perry and others (1988); mg/L, milligrams per liter; °C, degrees Celsius; $T_{1/2}$, half-life; $K_{OC}$, sorption coefficient normalized to organic carbon content of sorbent (soil or sediment), in liters per kilogram sorbent (L/kg); –, no data available]

| Pesticide | Solubility (mg/L at 25 °C) | Solubility (mg/L at 20 °C) | Persistence ($T_{1/2}$, days) | Sorption ( $K_{OC}$ L/kg) |
|---|---|---|---|---|
| Alachlor | 240 | – | 15- 70 | 170 |
| Atrazine | 33 | – | 60-365 | 100 |
| Cyanazine | 171 | – | 14- 20 | 190 |
| Dicamba | 4,500 | – | 5- 94 | 2 |
| Metolachlor | – | 530 | 15- 90 | 200 |
| Simazine | – | 3.5 | 18-365 | 130 |

at trace levels (below MCL's) in 18 percent of the 120 samples analyzed. In order of frequency of detection, the compounds that were found in the samples include: chloroform, methylene chloride, benzene, toluene, tetrachloroethylene, 1,2-dichloroethane, and trichloroethane. Only six samples had detections of more than one volatile organic compound. Three of the samples with multiple detection of VOC's contained benzene and were from wells in urban or residential sites where minor contamination of the aquifer from gasoline or other petroleum products could be expected. Subsequent checking of both field data and analytical quality-assurance data suggested that many of the single compound detections of contaminants were introduced into the samples during collection or laboratory analysis, including most of the detections for chloroform and methylene chloride.

All of the samples from the regional ground-water networks, including all samples from the confined aquifers, were analyzed for radon. The median concentration (or activity) of radon was 180 pCi/L (picocuries per liter) for samples from the surficial aquifer, and 190 pCi/L for samples from the confined aquifers. Maximum concentrations were 2,400 pCi/L for the surficial aquifer and 1,300 pCi/L for the confined aquifers. The concentration of radon was greater than 1,000 pCi/L in only 3 samples from all the networks and equaled or exceeded 500 pCi/L in only 14 samples. No recognizable geographic or hydrogeologic patterns were observed in the radon concentration data and in no sample was the MCL for gross-alpha radiation exceeded.

With the exception of one sample with cadmium at the MCL, there were no exceedances of MCL's for other trace elements of concern. In about 18 percent of the samples however, trace levels of either cadmium, arsenic, or selenium were detected. As was the case with the radon data, there were no recognizable hydrogeologic or geographic patterns in the trace-element data. The low concentrations and detection frequencies of these trace elements are consistent with the pre-dominance of oxic conditions in the surficial aquifer on the Delmarva Peninsula. Most of the minerals that release many of these trace elements are relatively insoluble under oxic conditions.

## QUALITY OF STREAM BASE FLOW

Ground-water discharge (base flow) provides between 48 and 88 percent of total streamflow in the study area (Bachman, 1994). The regional stream survey shows that the range of chemical composition of base flow (fig. 17) is similar to that of ground water in the study area (Bachman and Phillips, 1996; Phillips and Bachman, 1996; Denver and others, 1993). Base flow is a mixture of ground waters contributed from flow paths of different lengths transporting waters of different ages and recharge areas in the contributing watershed. Thus, the chemical composition of base flow can be used in a general manner to assess overall water quality in an area over time. Limitations that must be kept in mind include the residual effects of past stormwater runoff events and the fact that surface-water quality can be modified by instream biological processes and changes in redox state.

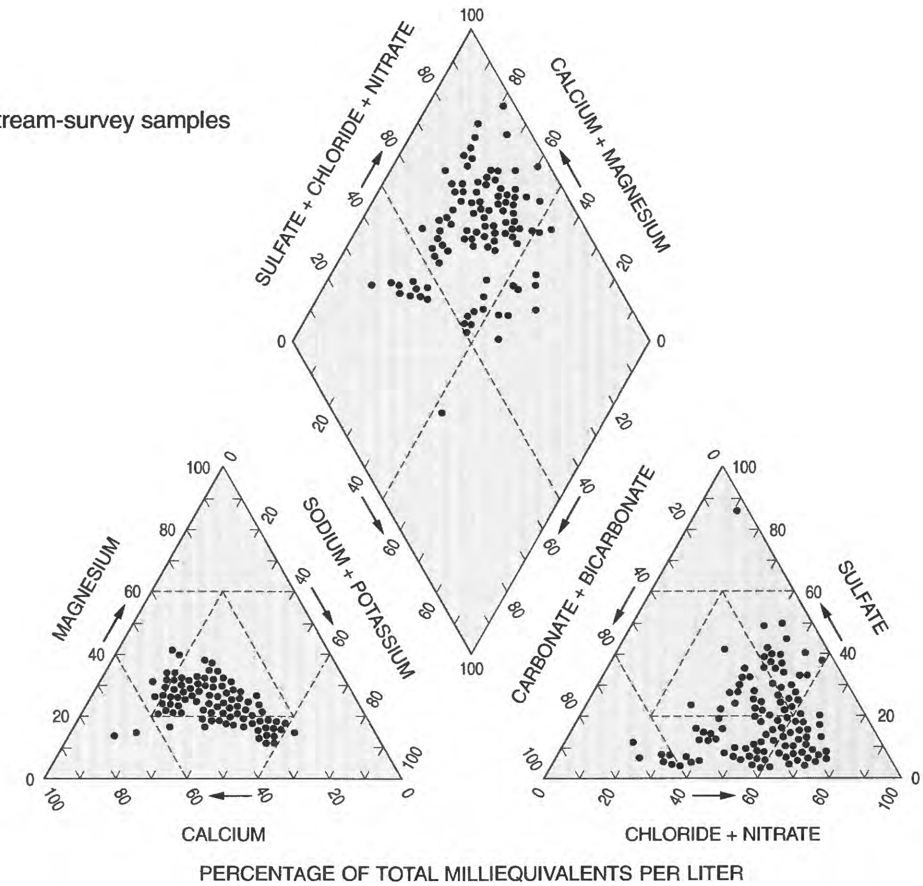
### Occurrence and Distribution of Nitrate

Areal patterns in nitrate concentrations in surface water are related to differences in land use, soils, and hydrogeology within the drainage areas contributing to the stream at the sampling location (Phillips and Blomquist, 1991). Most watersheds in the study area are characterized by multiple land uses, but most can be categorized by their dominant land use. Watersheds classified as well-drained are most common in the well-drained upland and Inner Coastal Plain HGMR's (fig. 3; Phillips and Bachman, 1996). In these regions, agricultural land use and oxygenated aquifer conditions are generally dominant, and poorly drained areas with reducing conditions in the underlying aquifer are limited to narrow forested riparian zones. Poorly drained watersheds are most common in the poorly drained upland, surficial confined, poorly drained lowland, and fine-grained lowland HGMR's. In these regions, there is a significantly higher proportion of poorly drained aquifer-recharge areas and forested land than in well-drained basins. Reducing conditions are generally prevalent in the aquifers in these watersheds and oxidizing conditions are confined to small, well-drained areas. A comparison between nitrate concentrations in stream base-flow samples and the percentage of agricultural land use in watersheds within different HGMR's is shown in figure 18.

In well-drained watersheds, surface water commonly contains higher concentrations of ions from agricultural sources (including calcium, magnesium, potassium, chloride, and nitrate), and often has a higher specific conductance (table 7) and pH than surface water from poorly drained watersheds (Denver and others, 1993). In areas with a thick surficial aquifer, such as the well-drained uplands HGMR, most ground water flowing towards stream discharge areas passes under the riparian zone and flows directly into the stream, effectively bypassing potential reducing conditions in the sediments of the riparian zone (Phillips and others, 1993). The result is that nitrate in ground water discharging to streams in well-drained watersheds does not always pass through potential zones of denitrification, and thus nitrate concentrations in surface water generally correlate with the percentage of agricultural land use in a watershed (fig. 18). The concentrations of nitrate in surface water from well-drained watersheds are commonly lower than the concentrations in ground water because of mixing of waters from older and younger flow paths that contain different nitrate concentrations related to changes in nitrogen application rates over time. Some of the nitrate in surface water may also be consumed or denitrified by biological processes.

In well-drained watersheds in the Inner Coastal Plain HGMR, stream channels are commonly incised through the sandy surficial aquifer into deeper formations of marine origin. Water typically enters streams from short, shallow ground-water-flow paths in this region and may be affected by reducing conditions associated with both marine sediments in the aquifer and riparian-zone sediments. In this setting, nitrate carried in ground water from well-drained recharge areas can be denitrified before it discharges to surface water (Böhlke and Denver, 1995). Data for stable isotopes of nitrogen and carbon in the ground and surface waters of one of the areas studied by Böhlke and Denver indicate that denitrification in the aquifer is related to the geochemical environment of the aquifer sediments rather than to interactions of the waters with soils or vegetation in the riparian zone. This is shown by the very low nitrate concentrations in water from streams in the Inner Coastal Plain HGMR compared to water from streams in basins with similar percentages of agricultural land in the well-drained upland HGMR (fig. 18).

**(A)** Stream-survey samples




**(B)** Regional ground-water samples

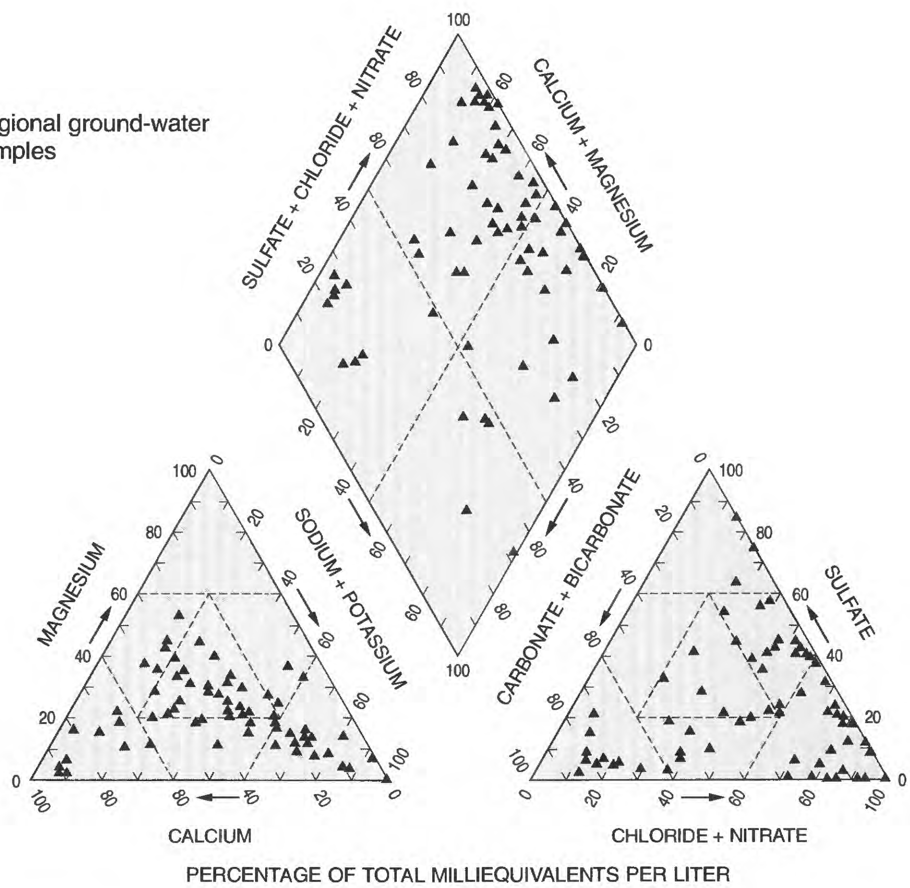



**Figure 17.** Comparison of the chemical compositions of **(A)** stream-survey samples and **(B)** regional ground-water samples collected by the Delmarva NAWQA Project from 1988-91 (from Bachman and Phillips, 1996).

**Table 7.** Median concentrations of selected chemical constituents in water samples collected from well-drained and poorly drained basins in the stream-survey network of the Delmarva NAWQA Project, Spring 1991

[Modified from Phillips and Bachman, 1996; National Water-Quality Assessment (NAWQA) Program; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; <, less than; for more information on p-value and statistical tests, see Hamilton and others, 1993]

| | Median concentrations in samples from well-drained basins greater than median concentrations in samples from poorly drained basins | | | | | | | Median concentrations in samples from well-drained basins less than median concentrations in samples from poorly drained basins | | | | Median concentrations in samples do not differ by basin type | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Constituent or property | Calcium (mg/L) | Magnesium (mg/L) | Potassium (mg/L) | Chloride (mg/L) | Alkalinity (mg/L) | Nitrate (as nitrogen mg/L) | Specific conductance (µS/cm) | Aluminum (mg/L) | Dissolved organic carbon (mg/L) | Sodium (mg/L) | Silica (mg/L) | Sulfate (mg/L) | pH |
| **Well-drained basins** | | | | | | | | | | | | | |
| Median concentration | 12 | 5.3 | 2.9 | 18 | 15 | 4.3 | 160 | 0.020 | 2.3 | 6.3 | 9.7 | 12 | 6.4 |
| **Poorly drained basins** | | | | | | | | | | | | | |
| Median concentration | 6.9 | 2.5 | 1.9 | 10 | 12 | 1.7 | 110 | .090 | 5.6 | 8.3 | 17 | 13 | 6.3 |
| ***p*-value for Mann-Whitney statistical test** | | | | | | | | | | | | | |
| Summary statistic | .018 | <.010 | .030 | .013 | <.01 | .012 | .015 | .016 | .040 | .063 | <.010 | .61 | .17 |

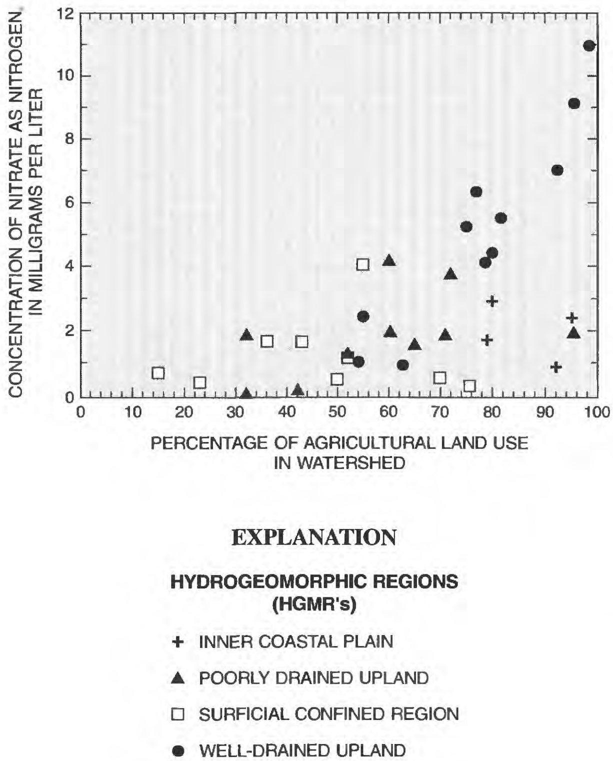



**Figure 18.** Relation between nitrate concentrations in stream base flow and percentage of agricultural land use in watersheds within the major hydrogeomorphic regions of the Delmarva Peninsula.

In poorly drained watersheds, surface water contains aluminum, dissolved organic carbon, sodium, and silica at concentrations higher than the respective concentrations of these constituents in surface waters from well-drained basins (Bachman and Phillips, 1996). The high proportion of forested land in the poorly drained watersheds results in water chemistry that is predominantly affected by natural processes, in particular those associated with reducing conditions (Denver and others, 1993). Because of the high degree of interspersion of land uses, streamwater in watersheds classified as poorly drained is often derived from both well-drained and poorly drained landscapes. Nitrate ions present in base flow are commonly contributed by ground-water discharge originating in locally well-drained parts of the watershed.

The interspersion of land use within a watershed can result in seasonal changes in water chemistry. Base-flow discharges are about an order of magnitude higher during winter and early spring (when precipitation rates are highest) than they are during the late spring and summer growing season (Bachman and Phillips, 1996). During periods of high base flow, shallow ground-water-flow paths contribute most actively to streamflow in both poorly and well-drained basins. In poorly drained watersheds, shallow flow paths commonly originate in near-stream and headwater wetland areas that are generally forested. Acidic waters with low specific conductance, low concentrations of silica, and high concentrations of aluminum, sulfate, and dissolved organic carbon are contributed to streamflow in this setting. In areas where well-drained agricultural land is dominant, shallow ground-water-flow paths can contribute ground water with high nitrate concentrations and an agricultural chemical signature to surface waters (Denver and others, 1993). This pattern is most common in the headwaters of well-drained watersheds, but can also affect water chemistry in predominantly poorly drained basins because of the interspersion of multiple land uses and agricultural ditching.

During periods of low base flow (the growing season and droughts), streamflow is maintained by discharge from long, deep ground-water-flow paths. During such periods, flow rates are low, and headwater areas, ditches, and wetlands are commonly dry; therefore, surface-water chemistry reflects land uses in upland parts of the landscape closest to watershed divides. These waters are generally older than waters from shallower flow paths and commonly contain higher concentrations of silica and sodium (from silicate mineral dissolution). If the land use in upland-recharge areas is different from the land use closer to the stream, the effect of human activities on waters in deeper flow paths may differ from the effect of these activities on waters in shallow flow paths (Denver and others, 1993). In addition, because deeper flow paths provide older water to streams, land use when the water originally recharged the aquifer may have been different from the land use during the period of this study. As a result, the chemistry of ground water discharging to streams can reflect a mixture of historical rather than current land-use practices in a watershed (Böhlke and Denver, 1995).

### Occurrence and Distribution of Pesticides

Potential sources of pesticides to surface waters include ground-water discharge, runoff from agricultural fields, and atmospheric transport. Dissolved pesticides carried in ground water can potentially enter surface water through direct discharge at the ground-water/surface-water interface. Studies in other areas, however, have shown that overland runoff during storm events that occur shortly after pesticide application is the primary source of most pesticides in surface water (Glotfelty and others, 1984; Squillace and Thurman, 1992; Kolpin and Kalkhoff, 1993).

Commonly reported herbicide residues in stream base-flow samples from the study area included atrazine, simazine, desethylatrazine, metolachlor, alachlor, and prometone.

Concentrations of pesticide residues in base-flow samples were similar to those in ground water, and generally ranged from the minimum reporting level to a maximum of about 6 µg/L (fig. 15). Metolachlor and alachlor were more frequently detected in surface water than ground water. Detections of higher concentrations of these residues in surface water from local-scale network sites were closely related to preceding storm events.

For streams at which seasonal measurements were made, concentrations of herbicides were highest in the spring (Bachman and others, 1992). Desethylatrazine concentrations, which were highest in base flows from well-drained basins, were consistent year round, indicating the principal contribution of this metabolite is through direct ground-water discharge. This is shown in figure 16 for the Locust Grove local-scale network, which shows the concentrations of desethylatrazine in surface water to be near that of ground water approaching the discharge area to Chesterville Branch.

It is not known how concentrations of pesticides and their metabolites in surface water will change over time. It is possible that they will modestly increase as ground waters with higher concentrations of agricultural chemicals (those recharged since the 1970's) reach the streams.

## SUMMARY AND CONCLUSIONS

A regional assessment of ground-water quality in the Delmarva Peninsula was conducted by using data available through 1987 supplemented by data collected between 1988 and 1991 from several different networks of wells. These networks were designed to investigate ground-water-quality patterns in different hydrologic settings at different spatial scales. The study focused on the areally extensive surficial aquifer, but also included samples from several wells completed in each of the confined aquifers used for water supply on the Peninsula. Several synoptic surveys of the quality of stream base flow also were conducted to investigate relations between surface-water quality and ground-water quality.

The chemical character of water in the surficial aquifer is affected by agricultural activities over most of the Delmarva Peninsula, but waters in confined aquifers have not been significantly affected by agricultural chemicals. The effect of agriculture on water quality is indicated by the areal extensiveness of shallow ground waters with an agricultural chemical signature, and the significant percentage of detections of dissolved nitrate in ground water at concentrations above the U.S. Environmental Protection Agency's Maximum Contaminant Level. The agricultural influence is also demonstrated by the frequent detection in shallow ground water of trace concentrations of herbicides used on the major crops grown in the study area. Insecticides were detected in only a few samples from the shallow aquifers, and pesticides were detected in only one sample from the confined aquifers.

Historical differences in the usage of fertilizers and pesticides in the Delmarva Peninsula are reflected in the ground-water-quality patterns. For example, commercial fertilizers and manure have been applied at much higher rates for longer periods of time than the herbicides used on the common crop types. As a result, nitrate concentrations in water affected by agricultural activities range from several milligrams per liter to several tens of milligrams per liter while herbicide concentrations in these waters are near detection levels at concentrations of tenths and hundredths of a microgram per liter. In addition, elevated concentrations of nitrate are found in a greater percentage of shallow ground-water samples and at greater depths in the surficial aquifer than the detections of trace concentrations of herbicides. Furthermore most of the ground waters with high concentrations of agricultural chemicals were recharged after 1970, based on estimates of ground-water recharge dates inferred from chlorofluorocarbon analyses. This ground-water-quality pattern is consistent with estimates of agricultural chemical use which show significant increases in the rates of application of commercial fertilizer and manure in the 1970's relative to the 1950's and 1960's. In addition, the pesticides found in the shallow ground water began to be used more universally in the study area in the 1970's.

Data from several local-scale studies of water-quality variations along ground-water-flow paths indicate that the spatial distribution of nitrate in the shallow ground-water system is related to ground-water-flow patterns and characteristics of the landscape, mainly land use, drainage patterns, soils, and geology. The highest median concentrations of nitrate, for example, are in a region of the study area referred to as the well-drained upland. This area has the highest percentage of agricultural lands and well-drained soils of all areas of the Delmarva Peninsula, and it also has the longest ground-water-flow paths. Elevated nitrate concentrations are found in other regions of the Peninsula, but the lower percentage of agricultural lands and well-drained soils in these areas yields lower median nitrate concentrations relative to those in the well-drained upland.

The spatial distribution of herbicides in the shallow ground water is related to land use and ground-water-flow patterns. Most of the detections of herbicides were in samples of water with an agricultural chemical signature from wells near farm fields. Virtually no herbicides were detected in parts of the ground-water system used for water supply, namely, the deeper parts of the surficial aquifer and the confined aquifers. Metabolites of the triazine herbicides were detected in samples from wells in several of the local-scale well networks. Neither the metabolite data nor the depth-distribution data on pesticides, however, give much indication of the potential for pesticides to migrate to deeper parts of the ground-water system over time.

Elevated concentrations of nitrate and trace levels of herbicides were found in nontidal streams under base-flow conditions. Desethylatrazine, a metabolite of atrazine and other triazine herbicides, was found at trace levels in both stream base flow and ground water. Nitrate concentrations seem to be related to land-use patterns and soils, and show no demonstrable seasonal patterns. The concentrations of herbicides, on the other hand, were significantly higher during late spring base-flow periods, after application on the fields.

These results have several important implications for environmental management and future water-quality assessment and monitoring in the Delmarva Peninsula. First, the surficial aquifer contains large volumes of ground water with elevated concentrations of nitrate in nearly all areas of the Peninsula. In some regions, these elevated concentrations are found at all depths of the surficial aquifer. These high-nitrate ground waters seem to be the principal sources of nitrate to streams under base-flow conditions. Age-dating of ground water in the surficial aquifer indicates that it may take 10 to 30 years before some of these high-nitrate ground waters discharge to streams or other surface-water bodies. Therefore, in some parts of the study area, ground water with elevated nitrate concentrations will continue to discharge to surface water even if application rates for fertilizers and manure are significantly reduced. This strongly suggests that water-quality-monitoring programs designed to evaluate the effectiveness of best-management practices on nutrient loading in streams should consider both surface- and ground-water quality.

This study also demonstrated the value of using isotopic and other geochemical data to perform regional ground-water-quality assessments. Data on major ion concentrations, isotopic data, and other constituents collected in this study showed that the shallow ground-water system in the Delmarva Peninsula contains a geochemical record of past land-use practices. These techniques offer the potential for observing temporal trends in ground-water quality and for evaluating the effectiveness of different land practices on ground-water quality. Such methods also offer great potential for improving the knowledge of how ground-water-flow systems and ground-water-quality patterns influence surface-water-quality patterns.

Finally, the results of this study demonstrate the value of a multi-scale network design for regional water-quality assessment. The regional networks provided information on the geographic distribution of water-quality constituents over the study area and the statistical relations among water quality, natural landscape features, and human activities. Information from the local networks allowed for more detailed investigation of relations among water quality, features of the ground-water-flow system, landscape features, and human influences such as agricultural practices and residential development patterns. The local-scale information was also helpful in assessing bias in the regional data sets. The multi-scale approach led to a better understanding of the processes influencing water-quality patterns in the Delmarva Peninsula and a better information base upon which to design future assessments of spatial and temporal trends in water quality.

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