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Water Quality in the Delmarva Peninsula

Delaware, Maryland, and Virginia, 1999–2001

U.S. Department of the Interior
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Circular 1228

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Front cover: Soybeans growing on well-drained farmland in New Castle County, Delaware (photograph by David Usher, U.S. Geological Survey).

Back cover: Left, collecting a ground-water sample for radon analysis (photograph by David Hudson, U.S. Geological Survey); center, collecting a ground-water sample for age-dating (photograph by Deborah Bringman, U.S. Geological Survey); right, documenting land use at a ground-water site (photograph by Deborah Bringman, U.S. Geological Survey).

Water Quality in the Delmarva Peninsula, Delaware, Maryland, and Virginia, 1999–2001

By Judith M. Denver, Scott W. Ator, Linda M. Debrewer, Matthew J. Ferrari, Jeffrey R. Barbaro, Tracy C. Hancock, Michael J. Brayton, and Mark R. Nardi

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Contents

National Water-Quality Assessment Program iv
What kind of water-quality information does the NAWQA Program provide? v
Introduction to this Report vi
Summary of Major Findings 1
- Stream and River Highlights 1
- Ground-Water Highlights 2

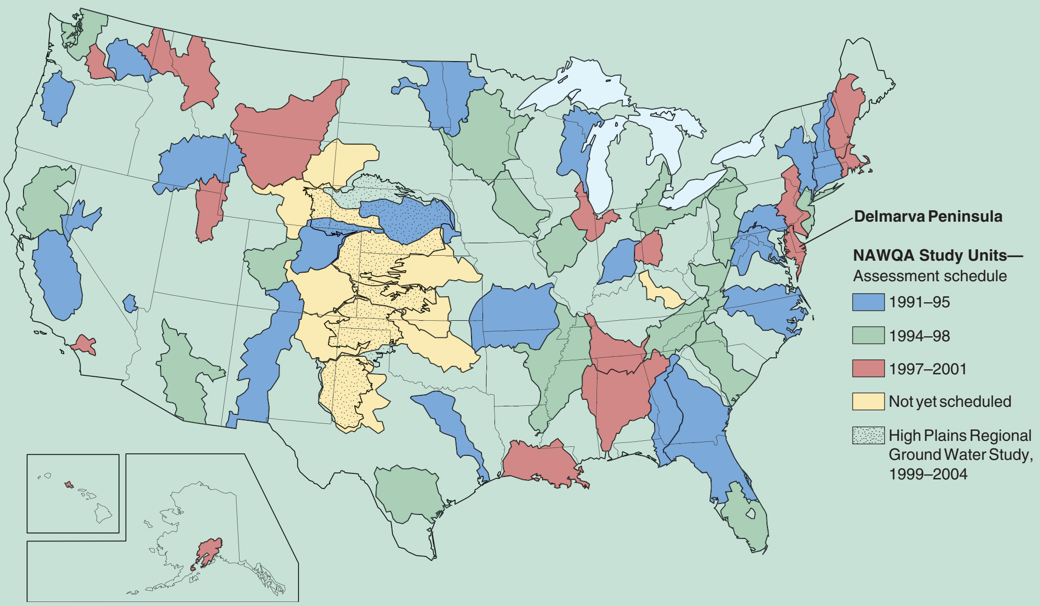
Introduction to the Delmarva Peninsula 3
- Land Use 3
- Hydrogeology and Water Use 3
- Ground-Water Quality 4
- Surface-Water Quality 5

Major Findings 6
- Nutrients in Ground Water and Streams 6
  - Nitrate is widespread in the surficial aquifer, including deeper parts used for drinking water 6
  - Nutrient concentrations in streams reflect human sources 9
- NATIONAL PERSPECTIVE—Nutrient concentrations on the Delmarva Peninsula are among the Nation’s highest. 10
- Pesticides in Ground Water and Streams 12
  - Herbicides are frequently detected in the surficial aquifer 12
  - What is a pesticide degradate? 14
  - Pesticides are commonly detected in streams 16
  - Delmarva Peninsula NAWQA study contributes to understanding of water quality in the Chesapeake Bay 17
- NATIONAL PERSPECTIVE—Herbicide concentrations in streams and ground water in agricultural areas on the Delmarva Peninsula are similar to those in other intensively farmed areas where corn and soybeans are grown. 18
- Other Ground-Water Quality Issues 19
  - Volatile organic compounds are detected in ground water 19
  - Radon occurs in water throughout the surficial aquifer 19
  - Dissolved iron is present in ground water from poorly drained areas 20
  - Arsenic is common in ground water at low concentrations 20
  - Reconnaissance for Arsenic in a Poultry-Dominated Basin on the Delmarva Peninsula 21

Study Unit Design 22
References Cited 24
Glossary 26
Appendix—Water-Quality Data from the Delmarva Peninsula in a National Context 27

National Water-Quality Assessment Program

The quality of the Nation's water resources is integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and also suitable for industry, irrigation, and habitat for fish and wildlife. Recognizing the need for long-term, nationwide assessments of water resources, the U.S. Congress has appropriated funds since 1991 for the USGS to conduct the **National Water-Quality Assessment (NAWQA) Program**. Scientists in the NAWQA Program work with partners in government, research, and public-interest groups to assess the spatial extent of water-quality conditions, the way water quality changes with time, and the effects of human activities and natural factors on water quality. This information is useful for guiding water-management and protection strategies, research, and monitoring in different hydrologic and land-use settings across the Nation.



In 1991, NAWQA began evaluating the quality of streams, ground water, and aquatic ecosystems in more than 50 major river basins and aquifer systems across the Nation, referred to as "Study Units." As indicated on the map, timing of the assessments varies within the Program's rotational design: about one-third of all Study Units are intensively investigated for 3 to 4 years, with trends assessed every 10 years.

In 2001, the NAWQA Program entered its second decade of investigations, and an intensive reassessment of water conditions was begun to determine trends, based on 10 years of comparable monitoring data collected at many of the streams and ground-water sites. The next 10 years of study also will fill critical gaps in characterizing water-quality conditions and increase understanding of processes that control water-quality conditions, which will better establish critical links among sources of contaminants, their transport through the hydrologic system, and the potential effects of contaminants on ecological health and on the quality of drinking water.

The Delmarva Peninsula assessment is one of two special studies activated in 1999 for the purpose of piloting study techniques for use in NAWQA's second decade of investigations. Specifically, the Delmarva Peninsula assessment piloted techniques for (1) monitoring trends in ground-water quality, (2) evaluating transport of agricultural chemicals to streams, and (3) assessing the effects of agricultural chemicals from corn, soybean, and small grain production on shallow ground water and surface water. The Delmarva Peninsula assessment builds upon monitoring data that the NAWQA Program collected previously in the peninsula from 1987 through 1991, as part of pilot studies conducted before full Program implementation in 1991. These data provided a baseline characterization of pesticides, nutrients, and trace elements in ground water and at surface water during base flow.

What kind of water-quality information does the NAWQA Program provide?

Water-quality assessments by a single program cannot possibly address all of the Nation's water-resources needs and issues. Therefore, it is necessary to define the context within which NAWQA information is most useful.

- Total resource assessment—NAWQA assessments are long-term and interdisciplinary, and include information on water chemistry, hydrology, land use, stream habitat, and aquatic life. Assessments are not limited to a specific geographic area or water-resource problem at a specific time. Therefore, the findings describe the general health of the total water resource, as well as emerging water issues, thereby helping managers and decision makers to set priorities.

- Source-water characterization—Assessments focus on the quality of the available, untreated resource and thereby complement (rather than duplicate) Federal, State, and local programs that monitor drinking water. Findings are compared to drinking-water standards and health advisories as a way to characterize the resource.

- Compounds studied—Assessments focus on chemical compounds that have well-established methods of investigation. It is not financially or technically feasible to assess all the contaminants in our Nation's waters. In general, the NAWQA Program investigates those pesticides, nutrients, volatile organic compounds, and metals that have been or are currently used commonly in agricultural and urban areas across the Nation. A complete list of compounds studied is on the NAWQA Web site at *water.usgs.gov/nawqa*.

- Detection relative to risk—Compounds are measured at very low concentrations, often 10 to 100 times lower than Federal or State standards and health advisories. Detection of compounds, therefore, does not necessarily translate to risks to human health or aquatic life. However, these analyses are useful for identifying and evaluating emerging issues, as well as for tracking contaminant levels over time.

- Multiple scales—Assessments are guided by a nationally consistent study design and uniform methods of sampling and analysis. Findings thereby pertain not only to water quality of a particular stream or aquifer, but also contribute to the larger picture of how and why water quality varies regionally and nationally. This consistent, multiscale approach helps to determine if a water-quality issue is isolated or pervasive. It also allows direct comparisons of how human activities and natural processes affect water quality in the Nation's diverse environmental settings.

Introduction to this Report

"The Delmarva NAWQA study provides us with a timely report and assessment of water-quality trends for nutrients and pesticides in our ground-water and surface-water resources and reminds us all that much more needs to be done to protect and improve the water resources of Delaware."

Kevin C. Donnelly
Director, Division of Water Resorces,
Delaware Department of Natural Resources and Environmental Control

This report contains the major findings of a 1999–2001 assessment of water quality in ground water and streams in the Delmarva Peninsula. It is one of a series of reports by the NAWQA Program that present major findings on water resources in 51 major river basins and aquifer systems across the Nation.

In these reports, water quality is assessed at many scales—from local ground-water flow paths to regional ground-water networks and in surface water—and is discussed in terms of local, State, and regional issues. Conditions in the Delmarva Peninsula are compared to conditions found elsewhere and to selected national benchmarks, such as those for drinking-water quality and the protection of aquatic organisms.

This report is intended for individuals working with water-resource issues in Federal, State, or local agencies, universities, public-interest groups, or the private sector. The information will be useful in addressing a number of current issues, such as source-water protection, pesticide registration, human health, drinking water, hypoxia and excessive growth of algae and plants, the effects of agricultural land use on water quality, and monitoring and sampling strategies. This report also is for individuals who wish to know more about the quality of water resources in areas near where they live, and how that water quality compares to other areas across the Nation.

Other products describing water-quality conditions in the Delmarva Peninsula are available. Detailed technical information, data and analyses, methodology, models, graphs, and maps that support the findings presented in this report can be accessed from *http://md.water.usgs.gov/delmarva*. Other reports in this series and data collected from other basins can be accessed from the national NAWQA Web site (*http://water.usgs.gov/nawqa*).

Summary of Major Findings

Stream and River Highlights

The concentrations of nitrogen, phosphorus, and pesticides in streams and rivers of the Delmarva Peninsula reflect the predominance of agriculture and the soil and aquifer conditions that promote transport of agricultural chemicals to streams. Other sources of nutrients and pesticides include septic systems, sewage, and urban and suburban chemical applications. Ground water discharged from the surficial aquifer is a primary source of water and nitrate in streams. Pesticides and phosphorus are contributed to streams primarily in runoff during storms; soluble pesticides also move to streams through ground water. Contaminated streams and rivers affect downstream estuarine waters by contributing excessive nutrients that can lead to eutrophication (blooms of algae and other nuisance plants) and hypoxia (areas of low dissolved oxygen), resulting in fishkills and loss of other living resources. Concentrations of nitrogen, phosphorus, and herbicide compounds in stream waters of the Delmarva Peninsula are similar to those in other intensively agricultural areas of the Nation.

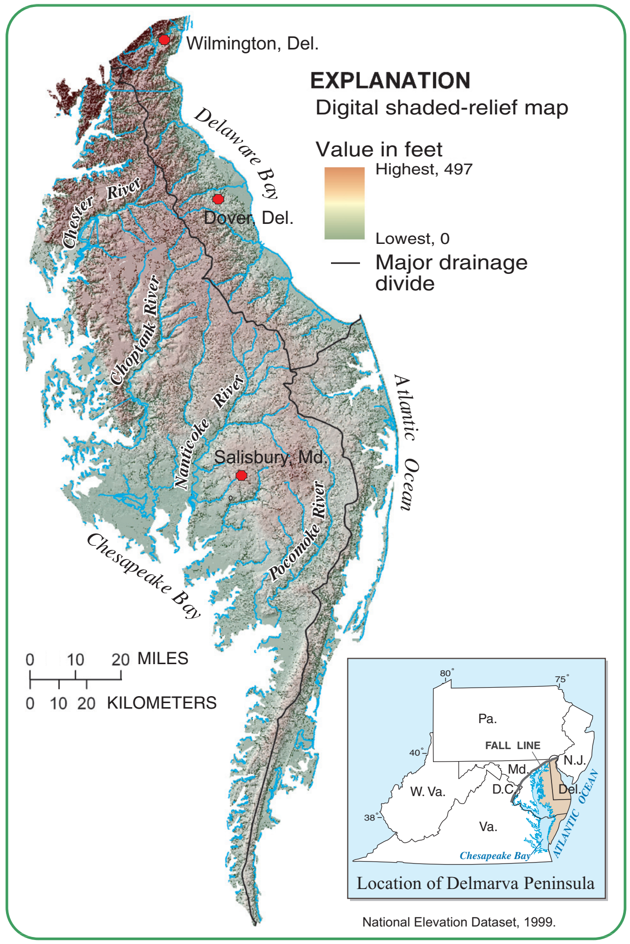
- Nitrate concentrations were greater than 3 mg/L (**milligrams per liter** as nitrogen) in about one-half of the headwater streams during base flow in the spring. Nitrate concentrations in streams generally increased with increasing agricultural intensity in upstream watersheds, particularly in areas with permeable, well-drained, and well-oxygenated sediments (p. 9).

- Phosphorus is transported to streams and rivers primarily with sediment in overland runoff during storms. Concentrations of phosphorus were typically less than 0.1 mg/L at base flow in well-drained areas but were as high as 3 or 4 mg/L at base flow in poorly drained areas (p. 11).

- Pesticides, primarily herbicides, are detectable throughout the year in streams of the peninsula, commonly occurring in mixtures of multiple compounds. At least five different compounds were detected in water from each of 23 streams sampled during base flow in the spring. Concentrations in streams generally were higher than in ground water (p. 16).

Major influences on water quality in streams and rivers

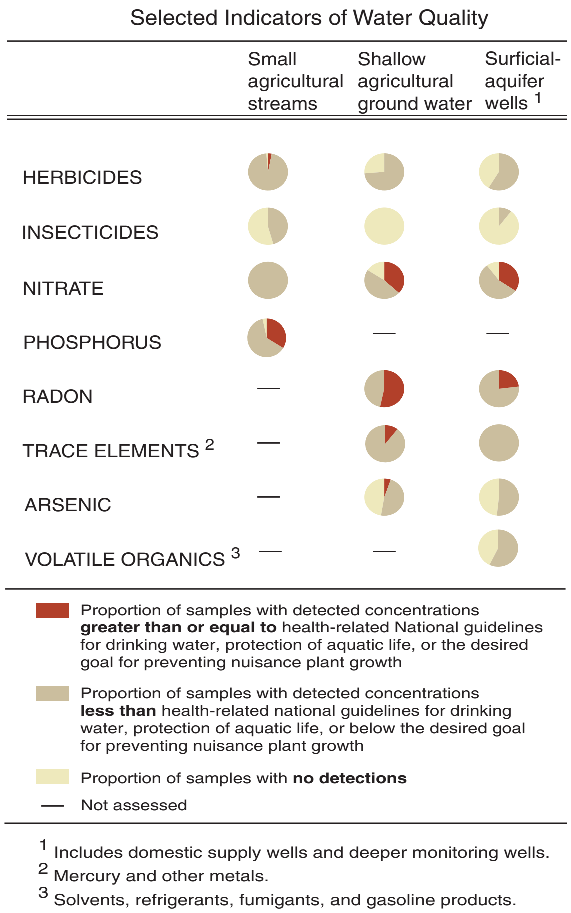
- Agriculture in watersheds
- Ground-water discharge of nitrate and pesticides
- Overland runoff of phosphorus, sediment, and pesticides during storms



The Delmarva Peninsula covers about 6,000 square miles and includes most of Delaware and parts of Maryland and Virginia east of the Chesapeake Bay. Located entirely in the Coastal Plain Physiographic Province, it has a broad central upland with flat to gently rolling topography, flanked by low plains that slope toward surrounding water bodies. Two major estuaries and the Atlantic Ocean surround the peninsula.

- Concentrations of herbicides are highest in the spring, after agricultural applications. Instream concentrations of individual compounds rarely exceeded concentrations known to be harmful to aquatic plants and animals, although such concentrations have not been established for many compounds (p. 16).

- The most commonly detected pesticides in streams were the herbicides used on corn, soybeans, and small grain crops, including atrazine, metolachlor, and alachlor. These also are among the most heavily used herbicides on the peninsula. Non-crop pesticides also were detected, but less frequently. These include the herbicides prometon (a weed killer used along rights-of-way) and pronamide (commonly used on ornamental shrubs) (p. 16).



Ground-Water Highlights

The surficial aquifer that blankets the Delmarva Peninsula is particularly susceptible to contamination from human activities because soils and aquifer sediments are relatively permeable and the water table is shallow. This aquifer is an important source of drinking water, recharge to underlying confined aquifers, and base flow to streams. Nearly half of the peninsula is used for agriculture, and chemicals applied for crop production are commonly detected in ground water. Concentrations of nitrate and herbicide compounds in ground water of the Delmarva Peninsula are among the highest in the Nation. Other chemicals associated with urban and suburban land uses, including compounds from fuels and solvents, also are detectable in ground water in those areas.

- Nitrate is widespread in the surficial aquifer, including parts of the aquifer used for drinking water. Concentrations of nitrate exceeded 10 mg/L, the Federal standard for drinking water, in about one-third of 29 samples from wells in the part of the aquifer used for domestic water supply (median well depth 45 feet); the median concentration was 5.5 mg/L. In 30 samples from deeper parts of the aquifer used for public water supply in Delaware (median well depth 80 feet), concentrations were similar (median 5.2 mg/L), although concentrations exceeded 10 mg/L in only one sample (p. 6).
- Concentrations of nitrate in ground water are highest beneath areas with well-drained, permeable soils, where dissolved-oxygen concentration also is high (greater than 1 mg/L) and lowest beneath areas with poorly drained soils, where dissolved-oxygen concentration is low (less than 1 mg/L), regardless of overlying land use (p. 7–8).
- Decreases in nitrate with depth in the surficial aquifer reflect changes in nitrogen fertilizer use over time rather than losses from degradation of nitrate to other chemical forms. Deeper water is commonly older, and nitrate concentrations reflect lower historical rates of fertilizer application. Nitrate is stable in oxygenated ground water and can persist along ground-water flow paths for decades (p. 7).
- Between 1988 and 2001, nitrate concentrations increased an average of about 2 mg/L in parts of the surficial aquifer used for domestic water supply (median well depth 45 feet) but were unchanged in shallower ground water beneath agricultural areas (median well depth 22 feet) (p. 9).
- Pesticides are widespread in the surficial aquifer underlying the Delmarva Peninsula, typically at concentrations less than 1 µg/L (**microgram per liter**). Commonly used herbicides (metolachlor, atrazine, and alachlor and their degradates) were most frequently detected; insecticides and fungicides were rarely detected (p. 12).
- A wide variety of pesticides and their degradates were present in water from the surficial aquifer used for drinking in urban and agricultural areas. In total, 19 different compounds were detected in water from public-supply wells, and 27 different compounds were detected in water from the part of the surficial aquifer used for domestic supply (p. 13).
- Volatile organic compounds (VOCs) are common in the surficial aquifer. Measured concentrations were typically below 1 µg/L (microgram per liter), and none were higher than Federal standards for the protection of drinking water where those standards exist. VOCs were much less frequently detected in domestic wells in rural areas than in public-supply wells in more populated areas (p. 19).

Major influences on ground-water quality

- Agricultural, suburban, and urban land-use activities in well-drained areas with permeable sediments
- Sandy sediments and dissolved oxygen in the surficial aquifer, which promote the transport of nitrate and pesticides in ground water

Introduction to the Delmarva Peninsula

The Delmarva Peninsula, a primarily rural lowland along the Atlantic Coast in the Eastern United States, contains most of Delaware and parts of Maryland and Virginia (fig. 1). The climate is humid and subtropical, with an average annual rainfall of 44 inches. The entire peninsula lies within the Coastal Plain Physiographic Province, which generally is a flat, seaward-sloping lowland with areas of moderate topographic relief. In 2000, about 1.1 million people lived on the peninsula; the population is increasing rapidly in the urban area south of Wilmington, Del., and near resorts along the Atlantic coastline.

Land Use

Agriculture is the dominant land use on the peninsula, covering about 48 percent of the land (fig. 1). Although plant nurseries and sod and dairy farms are common in some areas, agricultural land is used primarily to grow corn and soybeans for poultry feed. More than 600 million broiler chickens were produced on the peninsula in 2000 (Delmarva Poultry Industry, Inc., 2002). Other crops include small grains, potatoes, vegetables, and fruit. Woodlands, commonly interspersed with agricultural areas, make up about one-third of the land area. **Wetlands** are common in riparian and coastal zones and in inland forested areas and depressions. Only about 7 percent of the peninsula is classified as urban, primarily south of Wilmington, Del. (population of about 350,000), and in small towns. The largest cities are Dover, Del. (population of about 32,000), and Salisbury, Md. (population of about 24,000).

Hydrogeology and Water Use

A wedge of sand, gravel, silt, clay, and shells underlies the Delmarva Peninsula. These sediments thicken from 0 ft (feet) to the north to more than 8,000 ft along the Atlantic Coast

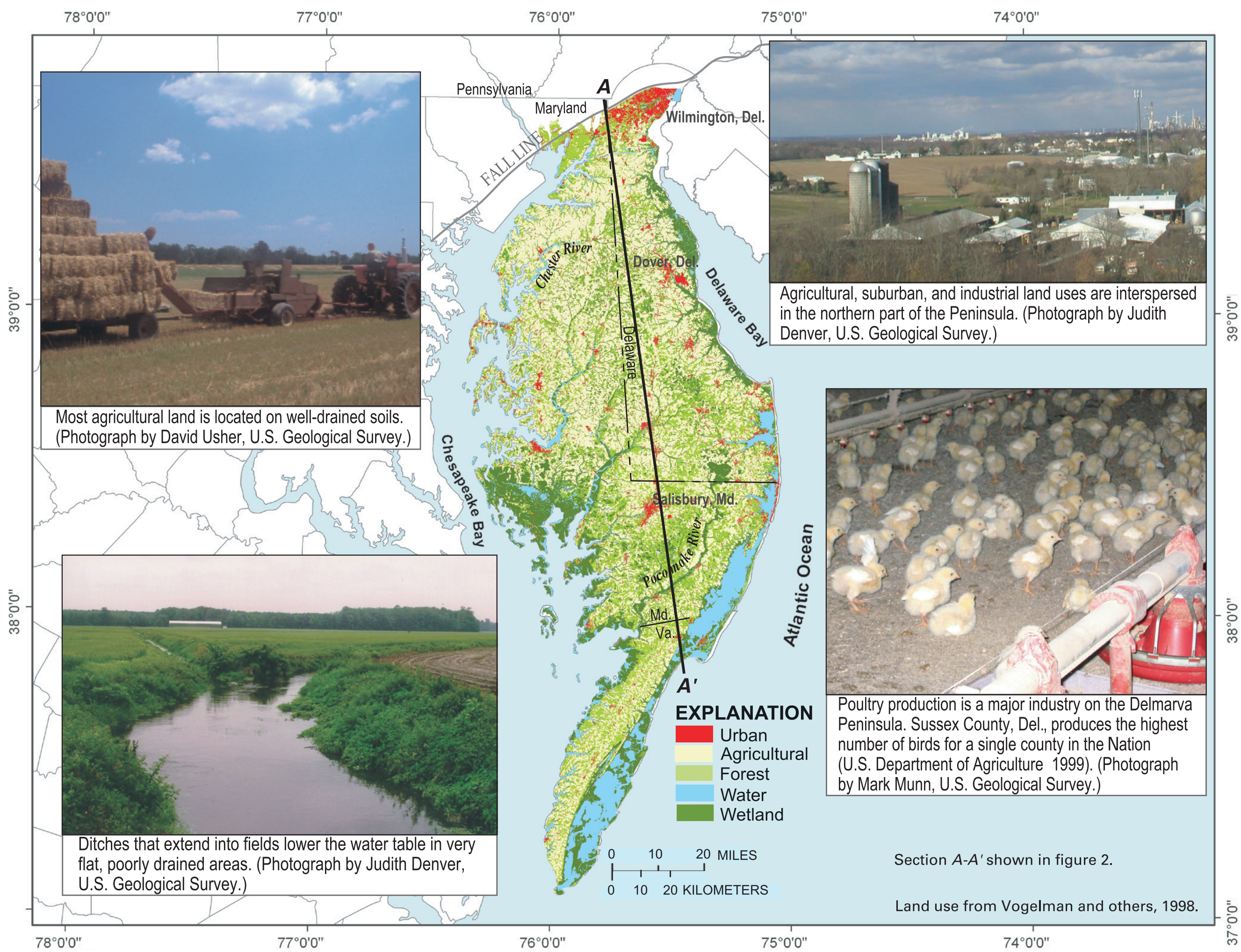


Figure 1. The Delmarva Peninsula is primarily rural, with small towns and residences interspersed among agricultural and forested land. Major areas of urban growth are to the north and along the Atlantic coastline.

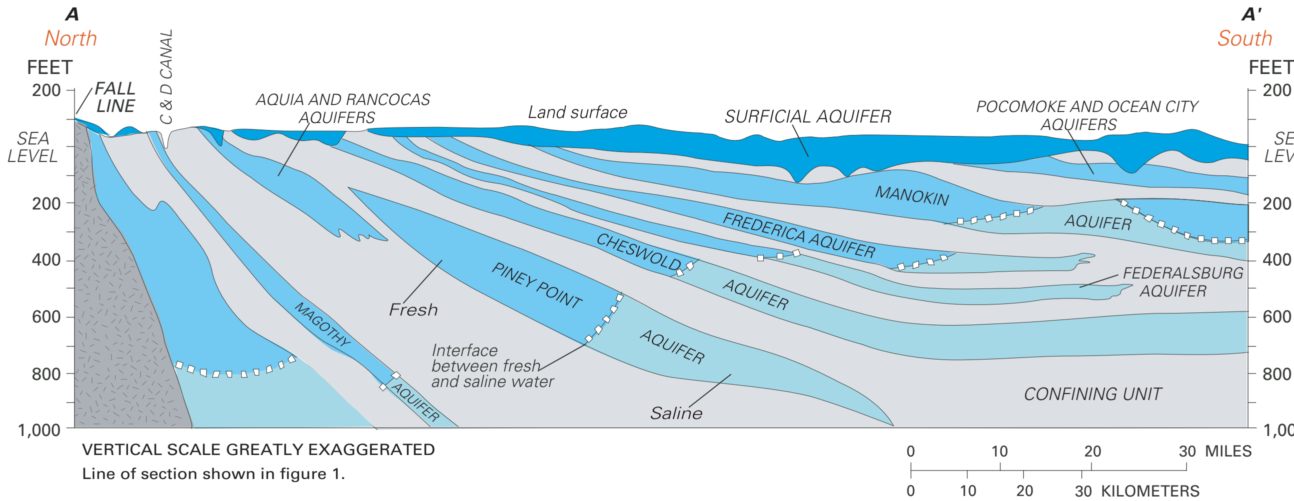


Figure 2. Sediments underlying the Delmarva Peninsula form an alternating series of confined aquifers and associated confining units, overlain by an extensive surficial aquifer that is under water-table conditions (modified from Shedlock and others, 1999).

of Maryland and form an alternating series of **confined aquifers** and confining units, overlain by an extensive unconfined **surficial aquifer** (fig. 2). Most public water supply comes from either the confined aquifers or relatively thick parts of the surficial aquifer. The surficial aquifer also provides water to individual homes and small public-supply systems in rural areas (fig. 3). In the northern part of the peninsula, rivers of the adjacent Piedmont Physiographic Province are a major source of public and industrial water supply.

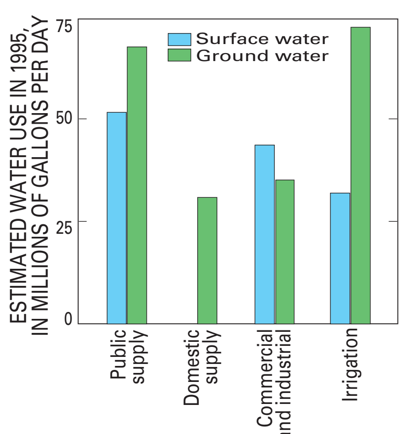


Figure 3. Ground water is the major source of water used on the Delmarva Peninsula and the sole source used for rural domestic supply. In the most populated part of the peninsula to the north, streams that originate in the adjacent Piedmont Physiographic Province also are a source of drinking-water supply.

The **recharge** area for the surficial aquifer includes most of the land surface of the Delmarva Peninsula. Most **ground-water** recharge occurs during the winter and spring, when precipitation and infiltration into soils are greatest. Water in the surficial aquifer typically flows along relatively short flow paths (distances of several hundred feet to less than a few miles) toward **discharge** areas in streams and estuaries or moves downward as recharge to confined aquifers. Water from the surficial aquifer typically reaches discharge areas in less than 50 years (Dunkle and others, 1993).

Streams on the peninsula generally become tidal within 10 miles of their **headwaters**. The largest nontidal **watershed** area is 113 mi^2 (square miles), although most streams drain less than 10 mi^2. Streams on the peninsula receive most of their flow from ground-water discharge (Bachman and others, 1998). Streamflow generally is greater in the winter and spring, when ground-water discharge is greatest and evapotranspitation is least, when compared to summer and fall. Streamflow peaks during storms, when it is augmented by overland **runoff** (fig. 4).

Ground-Water Quality

Land-use activities can contaminate shallow ground water used for drinking water. Certain chemicals that are applied to the land surface in quantities greater than crops, lawns, or golf courses can use move easily through permeable surficial soils and sediments to the **water table** and can contaminate shallow ground water. Other sources of ground-water contamination include leaking storage tanks, septic systems, and chemical spills. Under natural conditions (defined as those with no chemical input from human activity), water in the surficial aquifer contains chemicals derived from rainfall, soils, and aquifer sediments. Because soils and sediments in most areas of the peninsula do not dissolve easily, concentrations of chemical constituents occurring naturally in ground water are typically only slightly higher than the low concentrations in rainfall. Concentrations of chemicals from human sources commonly exceed concentrations of those that occur naturally in water in the surficial aquifer of the Delmarva Peninsula.

Crop and poultry production have widespread effects on ground-water quality. Inorganic fertilizers contain nitrogen and phosphorus that can enter the ground-water system. Poultry manure, commonly applied to fields to supply nitrogen to crops, contributes large amounts of nitrogen and phosphorus and trace amounts of arsenic, pharmaceuticals, and other chemicals used as feed amendments. Agricultural **herbicides** also have been frequently detected in ground water on the Delmarva Peninsula (Koterba and others, 1993; Blaier and Baxter, 2000).

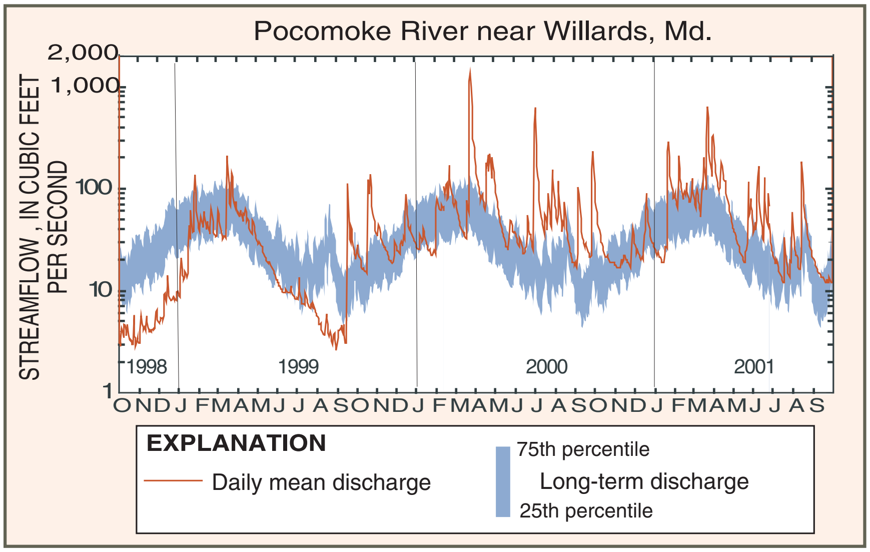


Figure 4. Streamflow varies seasonally on the Delmarva Peninsula, the highest flows typically occurring in the winter and spring when the water table is high and shallow ground-water discharge to streams is greatest. Lowest flows typically occur in the summer and fall, when the water table is lower and there is more evapotranspiration. Streamflow is augmented by overland runoff during storms. During the study period, streamflow was generally at or below normal through 1999 and at or above normal during 2000 and 2001.

Agricultural management practices intended to reduce the transport of chemicals from inorganic fertilizer, manure, and **pesticides** through changes in planting methods, application practices, and chemical formulations have been implemented over the last few decades. Many of the **nutrients** and pesticides currently in the water of the surficial aquifer were applied several decades ago, before these improvements. The new management practices should help to reduce concentrations of nutrients and pesticides in ground water and their transport to **surface water**. Improvements in water quality may not be apparent for years or even decades, however, because of the slow movement of chemicals through the ground-water system.

Urban activities also may affect shallow ground-water quality. Individual household and community septic systems potentially discharge nutrients, bacteria, household chemicals, and pharmaceuticals to the surficial aquifer. Local concerns also include chemical spills, leaking fuel-storage tanks, and use of fertilizers and pesticides on lawns, golf courses, and along roadways.

Surface-Water Quality

Streams contain chemicals from ground water and overland runoff. Ground-water discharge is a primary source of nitrate in surface water and also is a source of low concentrations of pesticides (Bachman and others, 1998; Shedlock and others, 1999). Nitrogen, phosphorus, pesticides, and other chemicals also are transported directly to surface water through overland runoff and in effluent from sewage-treatment plants and industrial discharges.

Hydrologic conditions can affect surface-water quality. Water quality in streams and rivers varies in response to changes in hydrologic conditions that are affected by weather patterns; therefore, information on precipitation and streamflow is important for assessing water quality (fig. 4). When precipitation and runoff are below average, concentrations of chemicals in streams are due primarily to the discharge of ground water to the streams; concentrations of constituents that attach to soil particles and streambed sediments, such as phosphorus and selected organic contaminants and trace elements, are lower than average. During high flows caused by runoff, however, when sediment transport is greatest, concentrations of chemicals that attach to sediment particles are higher than average. High flows caused by runoff also can dilute the concentrations of chemicals from ground water and effluent discharges.

Degraded water quality in streams can affect estuaries that are important for recreation and the local economy. Excessive nitrogen and phosphorus in streams and estuaries can cause accelerated growth of aquatic plants and algae that block sunlight from the water column, a process called **eutrophication**. Eutrophic conditions contribute to the loss of submerged vegetation, which is needed to provide habitat for ecologically and economically important species and to produce dissolved oxygen in the water column. The excessive **algae** and plant material subsequently decay, reducing dissolved oxygen needed by fish and other aquatic life; fishkills are not uncommon during eutrophic conditions. In addition to excessive nutrients and eutrophication, pesticides and other organic contaminants from industrial sources and fuels also are of concern because of their potential toxic effects on aquatic biota (Phillips and Caughron, 1997).

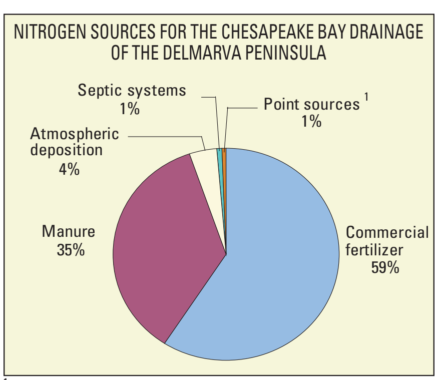
The peninsula provides important habitat for wildlife and supports large populations of migratory birds. (Photograph by Mark Nardi, U.S. Geological Survey.)

Major Findings

Nutrients in Ground Water and Streams

The primary sources of nutrients on the Delmarva Peninsula are inorganic fertilizer and manure (accounting for more than 95 percent), although other sources may be substantial in certain areas (fig. 5). **Atmospheric deposition** contributes an additional 4 percent. Estimated nitrogen contributions from the atmosphere to the peninsula were 15 million pounds in 1997, for example (National Atmospheric Deposition Program, 2003a,b). Atmospheric deposition may be a particularly important source of nutrients for plant growth in forested areas, where other nutrient sources are limited. Septic systems also contribute nutrients to ground water; previous studies on the peninsula, however, have found that septic systems generally contribute lower concentrations of nitrate to shallow ground water than do agricultural sources (Denver, 1989; Hamilton and others, 1993). Sewage-treatment plants also are nutrient sources for streams, but most treatment-plant discharges are to tidal waters surrounding the peninsula.

Nitrogen inputs from inorganic fertilizer have increased considerably over the past several decades, whereas the input of phosphorus has decreased. Nutrient inputs from manure, primarily poultry, also have recently decreased, although they still contribute substantially to total nutrient input (fig. 6).



[1] Includes discharge from sewage-treatment plants.

Figure 5. Nitrogen sources on the Delmarva Peninsula are primarily agricultural. (Data from Brakebill and Preston, 1999.)

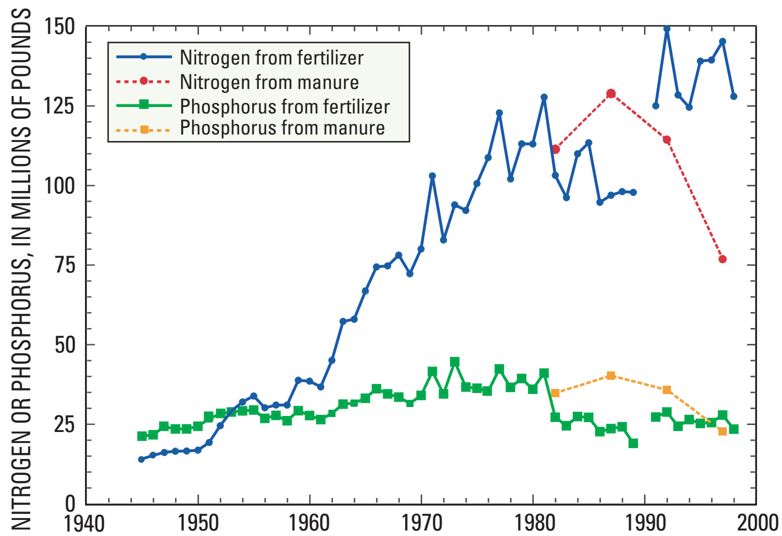


Figure 6. Nitrogen inputs from inorganic agricultural fertilizer applications on the peninsula have increased since the mid–1940s; phosphorus inputs have decreased. Manure also is a major source of nitrogen and phosphorus. (Data from Alexander and Smith, 1990; Battaglin and Goolsby, 1994; David Lorenz, U.S. Geological Survey, written commun., 2002.)

Nitrate is widespread in the surficial aquifer, including deeper parts used for drinking water

Concentrations of nitrate are typically above the natural background level of 0.4 mg/L (Hamilton and others, 1993) in shallow ground water (about 20 to 25 ft below land surface) beneath farmland. (Although laboratory results were reported as “nitrite plus nitrate,” concentrations of nitrite generally were negligible; therefore, these results are reported as “nitrate” [as nitrogen] in this report.) Specifically, the **median** concentration of nitrate in samples from 29 wells in agricultural areas was 5.4 mg/L, and the maximum was 37 mg/L (fig. 7). Water in about one-third of the wells exceeded the Primary Maximum Contaminant Level of 10 mg/L (U.S. Environmental Protection Agency, 2002b). Nitrate at concentrations greater than 10 mg/L may cause methemoglobinemia, a life-threatening illness in infants. Shallow ground water beneath farmlands is not commonly used for drinking-water supply; however, contaminated shallow ground water can move downward into the surficial aquifer over time and affect the quality of deeper ground water that is used for drinking. Elevated concentrations of nitrate in deeper parts of the surficial aquifer indicate that such movement does occur; the distribution of nitrate in the part of the aquifer used for domestic supply in rural areas (median well depth 45 ft) is similar to that in the shallow ground water beneath farmland. Specifically, median nitrate concentration in the surficial aquifer typically used for domestic supply in rural areas (as indicated by data from 29 wells, 16 of which were monitoring wells and 13 of which were domestic wells) was 5.5 mg/L, and the maximum was 27 mg/L. Concentrations of nitrate in one-third of the domestic-well samples exceeded 10 mg/L. The median nitrate concentration in 30 public-supply wells in Delaware, located closer to urban areas and generally deeper than rural domestic

These findings are supported by the Study Unit Design described on pages 22 and 23.

wells (median of about 80 ft below land surface), also was about 5 mg/L; and the maximum concentration was 11 mg/L and in only 1 well exceeded the drinking-water standard. (See "Study Unit Design" on pages 22–23 for more information about well networks.)

Elevated concentrations of nitrate in water from the surficial aquifer used for domestic supply are of particular concern because many homeowners are not aware of possible risks. Unlike public-supply wells, domestic wells are not monitored regularly. In addition, many homeowners in recently established residential areas that rely on domestic wells are not aware that chemicals leached from previous agricultural or other activities can remain in shallow ground water for decades.

Median concentrations of nitrate are generally highest in water from the surficial aquifer where dissolved-oxygen concentrations are greater than 1 mg/L (fig. 7). Nitrate is stable in the presence of dissolved oxygen. Dissolved oxygen typically is present in ground water in areas with well-drained soils and well-aerated aquifer sediments (known as "oxidizing conditions"), which are common in the central upland area of the peninsula where much of the land is agricultural. In areas with poorly drained and organic-rich soils, such as along coastal lowlands and interior wetlands, dissolved-oxygen concentrations are low or zero in the soil zone and underlying aquifer (known as "reducing conditions"). In these areas, dissolved nitrate is converted to nitrogen gas (is denitrified) by bacteria that use nitrate to obtain energy for growth, so that ammonia and organic nitrogen are the most common forms of nitrogen in the ground water.

Although most poorly drained areas on the peninsula are forested, some are used for agriculture, such as parts of southern Delaware and adjacent Maryland. Farmers excavate ditches to lower the water table and drain land that would otherwise be too wet to farm. Nitrate concentrations are typically lower in ground water underlying these areas—because of the reducing conditions—than in areas with adequate natural drainage (Hamilton and others, 1993).

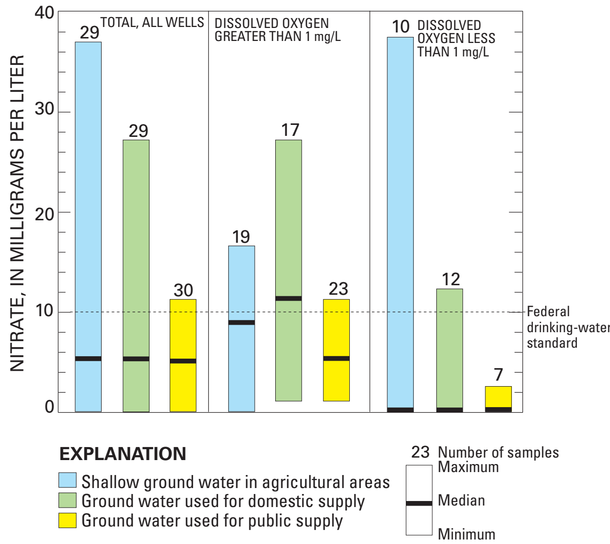


Figure 7. Concentrations of nitrate are typically well above the estimated natural background concentration (0.4 mg/L) in the surficial aquifer. The median concentration of nitrate in oxygenated areas exceeds the Federal drinking-water standard of 10 mg/L in ground water used for domestic supply.

Concentrations of nitrate are lowest in the deepest parts of the surficial aquifer, such as in areas used for public supply in Delaware (fig. 7, fig. 8). Water pumped from the public-supply wells generally reached the aquifer more than 15 years ago (median recharge date 1985), when fertilizer applications were smaller. In addition, large-yield public-supply wells can draw water from large areas, which may include less agricultural land and more areas associated with lower nitrogen sources such as forests, wetlands, and urban areas. Nitrate concentrations in shallow, near-surface ground water in agricultural areas (within 30 ft of the land surface) generally reflect more recent activities on the land (median recharge date 1994).

Nitrate concentrations increase in shallow, near-surface ground water with increasing amounts of overlying agriculture. Nitrate concentrations in shallow, near-surface ground water are affected by nearby land use when underlying aquifer sediments are oxygenated. Where dissolved oxygen is low or absent, nitrate is generally low or absent in underlying ground water, regardless of overlying land use (fig. 9). Extremely high nitrate concentrations in some samples may be related to local point sources, such as manure piles, rather than regional land use.

Nitrate concentrations can vary horizontally and vertically because of ground-water flow paths and land use in recharge areas. Water infiltrating through soils and recharging the surficial aquifer carries chemicals from the land surface in the area where the recharge originates (fig. 10). Over

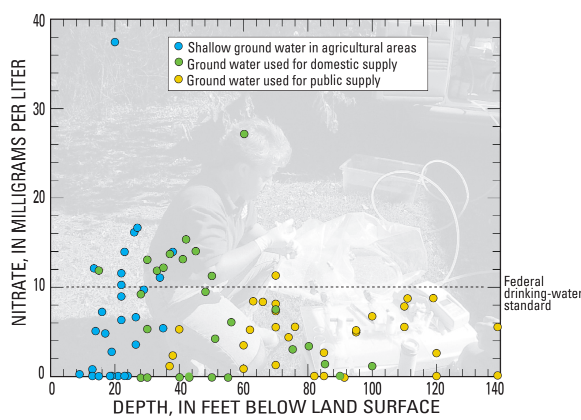


Figure 8. Concentrations of nitrate commonly exceed 10 mg/L in the surficial aquifer at depths less than 50 ft, where many domestic wells obtain water. Concentrations are generally less than 10 mg/L at greater depths, where most public-supply wells are completed.

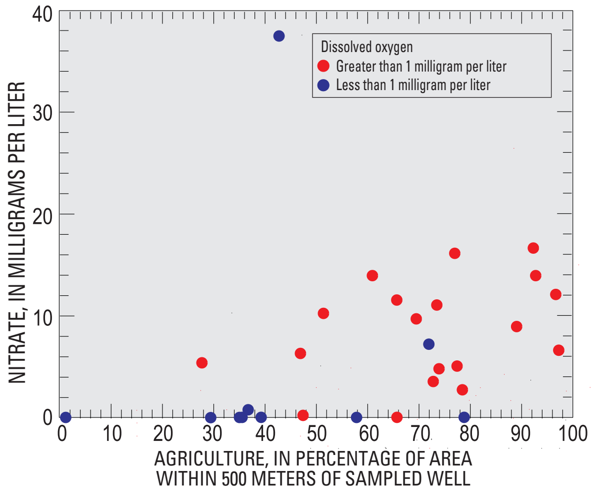


Figure 9. Nitrate concentrations are typically higher in well-oxygenated areas (dissolved oxygen greater than 1 mg/L) where nitrate is stable than in areas where dissolved-oxygen concentrations are lower (less than 1 mg/L). With some exceptions, nitrate concentrations increase with increasing proportions of overlying agriculture.

time, these chemicals are carried along ground-water flow paths to deeper parts of the ground-water system and eventually discharge to streams. As a result, nitrate concentrations in ground water beneath a forested area may increase with depth if deeper water was derived from an **upgradient** agricultural area; likewise, nitrate in water from deep wells in urban areas may represent a different land use upgradient from the well. Because of the variability of land use in recharge areas and the presence or absence of dissolved oxygen in ground water, nitrate concentrations are variable at different depths of the surficial aquifer underlying areas of different land use.

Nitrate concentrations have increased since 1988 in parts of the surficial aquifer used for domestic supply but did not change in shallow, near-surface ground water underlying agricultural areas. Nitrate in ground water used for domestic supply (median well depth 45 ft) in oxygenated parts of the surficial aquifer (dissolved oxygen greater than 1 mg/L) increased by an average of about 2 mg/L, between 1988, and 2001, to a median of greater than 10 mg/L, the Federal **drinking-water standard** (fig. 11). In oxygenated shallow ground water underlying agricultural areas (median well depth 22 ft), however, the median nitrate concentration in ground water did not change significantly, remaining below 10 mg/L.

Agricultural management practices have been implemented over the last few decades to decrease the movement of nutrients to ground water and streams—the success of which may help explain stable concentrations in the shallow, near-surface ground water. Such improvements may not be apparent for years or even decades in deeper parts of the surficial aquifer because of the relatively slow movement of ground water. In poorly oxygenated areas, nitrate concentrations were consistently low in both the shallow and deep parts of the aquifer.

Concentrations of other nutrient species are generally lower than concentrations of nitrate in Delmarva Peninsula ground water. Concentrations of dissolved phosphorus in ground water of the surficial aquifer rarely exceeded 0.1 mg/L (see Appendix,

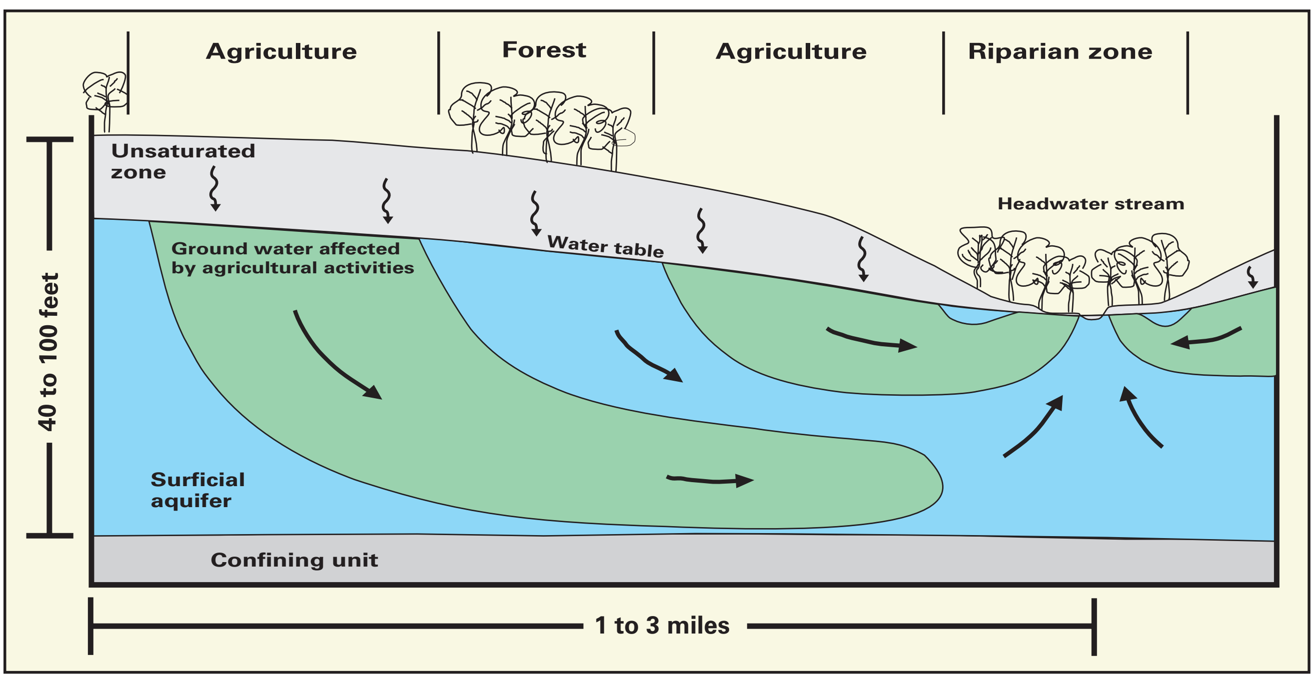


Figure 10. Patterns in the distribution of agricultural chemicals in the surficial aquifer are determined by land use in aquifer recharge areas and ground-water flow paths. Water that contains chemicals from agriculture and other human activities will eventually discharge to local streams and rivers.

p. 29) despite relatively large applications of phosphorus in inorganic fertilizer and manure (fig. 6). This finding is, in large part, explained by the chemical properties and mobility of phosphorus. Specifically, phosphorus readily attaches to soil particles under oxidizing conditions; it does not dissolve and move readily to the ground-water system. Ground water is therefore typically not vulnerable to contamination by phosphorus. Under reducing conditions (where dissolved oxygen is absent), however, phosphorus does dissolve more readily and is present in shallow ground water at concentrations greater than 0.1 mg/L. Concentrations of ammonia and organic nitrogen also are relatively low (less than 1 mg/L) in the surficial aquifer because these forms of nitrogen are readily converted to nitrate in well-drained and oxygenated soils. Ammonia and organic nitrogen are more prevalent in ground water under reducing conditions.

Nutrient concentrations in streams reflect human sources

Throughout the Delmarva Peninsula, nitrate concentrations in streams were elevated above 0.6 mg/L, the estimated concentrations of nitrate from natural sources and atmospheric deposition in streams of the Northeastern United States (Clark and others, 2000). Nearly all (94 percent) of the headwater streams on the peninsula contained nitrate concentrations greater than 0.6 mg/L during **base flow** in the spring. About half contained more than 3 mg/L. (See "Study Unit Design," p. 22–23, for more information on the design of the headwater stream network.) Nitrate concentrations in large agricultural streams on the Delmarva Peninsula also were often greater than those that might be expected from natural sources (Ator and others, in press). (See p. 10.)

Nitrate concentrations in streams of the peninsula reflect the influence of agriculture and other human sources. Although nitrate may be derived from various sources, concentrations in headwater streams on the Delmarva Peninsula generally increase with increasing proportions of agriculture in contributing watersheds (fig. 12). Concentrations typically are highest in areas with permeable, well-drained soils, aquifer, and streambed sediments. Areas with poorly drained soils often contain organic-rich sediments and other conditions that promote **denitrification**, which can reduce the concentrations of nitrate entering streams. Water in streams from some watersheds with predominantly poorly drained soils, however, still has elevated concentrations of nitrate because of interspersion of land-use and soil-drainage characteristics in the watershed (fig. 12).

Nitrate concentrations were similar in streams and ground water because ground-water discharge to streams is substantial. Ground-water discharge is estimated to constitute more than one-half of the flow to most streams on the Delmarva Peninsula (Bachman and others, 1998). As a result, the median concentration of nitrate in streams during base flow in the spring was similar to that in ground water (fig. 13). Some nitrate in ground water can be lost through chemical transformations (denitrification) as it passes through the **riparian** zone and the streambed into surface water, and aquatic plants and algae in the stream may use nitrogen and phosphorus compounds for growth (biotic uptake). Streambed sediments on the Delmarva Peninsula, however, are commonly sandy with low organic-matter content so that denitrification does not significantly decrease the nitrate content in ground-water discharge in many areas (Böhlke and Denver, 1995; Speiran, 1996).

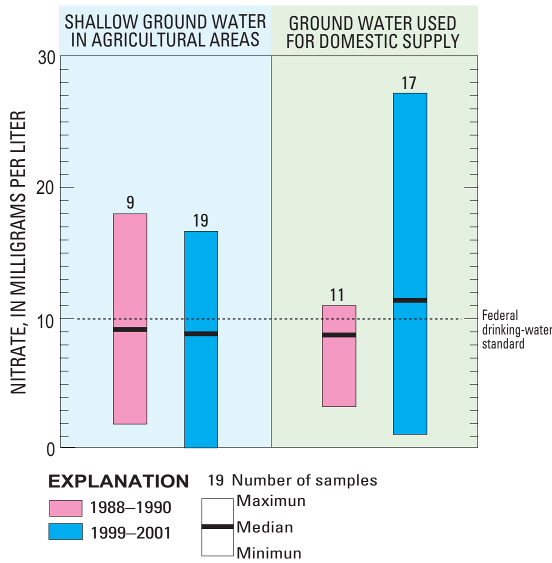


Figure 11. Concentrations of nitrate were unchanged between 1988 and 2001 in shallow ground water in agricultural areas; however, concentrations increased by an average of about 2 mg/L in deeper parts of the surficial aquifer used for domestic water supply. This increase is apparent only in well-oxygenated areas of the aquifer; concentrations in poorly oxygenated areas were consistently low.

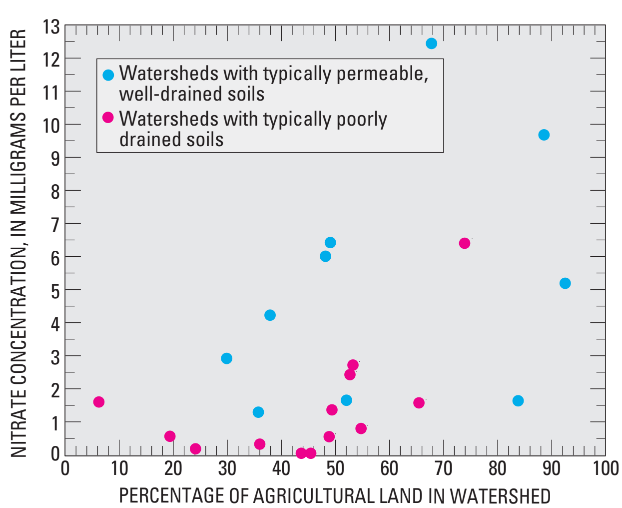
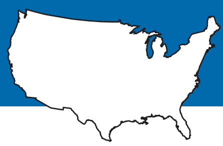


Figure 12. Nitrate concentrations generally increased with increasing percentage of agriculture in the contributing watershed in headwater streams during spring base flow.



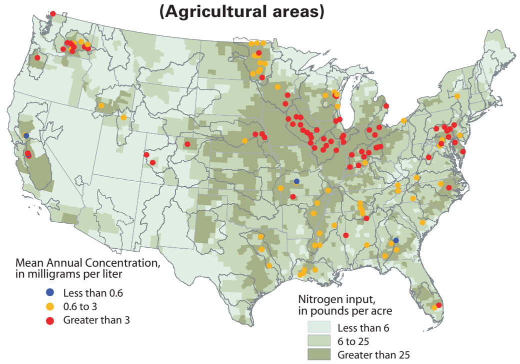
Nutrient concentrations on the Delmarva Peninsula are among the Nation's highest

Concentrations of nitrogen and phosphorus in streams and shallow ground water in agricultural areas of the Delmarva Peninsula are comparable to some of the highest measured in intensively agricultural areas of the Midwest and other parts of the Nation. Mean flow-weighted concentrations of total nitrogen in Chesterville Branch (in the Chester River Basin) and in the upper Pocomoke River (northeast of Salisbury, Md.) for 2000 and 2001 exceeded 4 mg/L; total concentrations of nitrogen in both streams are greater than concentrations in at least 80 percent of 479 streams sampled across the Nation by the NAWQA Program since 1993, although many of these streams are in nonagricultural areas and are much larger.

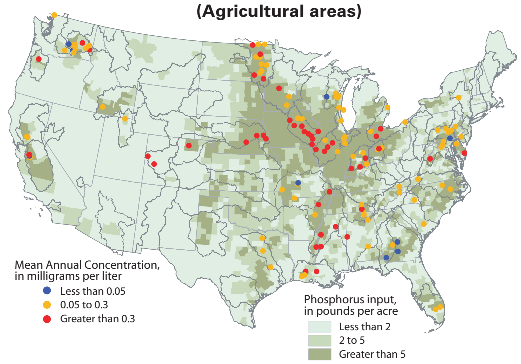
Most of the nitrogen reaching Delmarva Peninsula streams is transported through ground water in the form of nitrate. Nitrate concentrations in water from the surficial aquifer in agricultural areas of the peninsula typically exceed 5 mg/L and are among the highest (top 30 percent) measured in ground water underlying agricultural areas of the Nation. Nitrate travels relatively unaltered through sandy, oxygenated streambed sediments into streams in many parts of the Delmarva Peninsula. Phosphorus concentrations in these streams (particularly the Pocomoke River) were similarly elevated (top 40 percent) relative to streams in other parts of the Nation. Phosphorus concentrations are generally lower in ground water than in surface water because the major source of phosphorus is overland flow from agricultural fields.

The relatively high nutrient concentrations in streams and ground water of the peninsula result from intensive application of fertilizers (including manure) in agricultural areas as well as from hydrogeologic and soil conditions. Estimated nitrogen and phosphorus inputs to the peninsula from commercial fertilizer, manure, and atmospheric deposition are comparable to those in the Midwest, the Central Valley of California, and other areas of intensive agriculture. When not used by crops or other terrestrial plants, these nutrients are effectively transported with little transformation or other losses through the typically permeable soils to shallow ground water and streams. Excessive nutrients can make water unfit for human consumption and can cause eutrophication and other ecological problems in streams and estuaries.

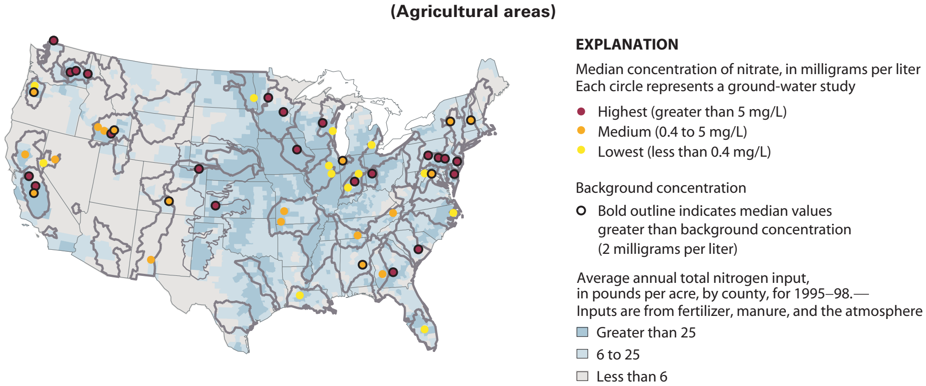
Total N in streams, 1993–2001 (Agricultural areas)



Total P in streams, 1993–2001 (Agricultural areas)



NITRATE concentrations in shallow ground water (Agricultural areas)



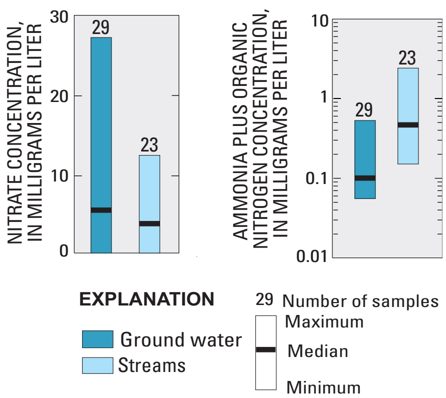


Figure 13. Although ground water from the surficial aquifer is the primary source of water to small streams during base flow, concentrations of nitrogen species often differ in surficial ground water and small streams during such conditions. Nitrate concentrations were typically higher in ground water (represented by water from the part of the surficial aquifer used for domestic drinking-water supplies), whereas concentrations of ammonia plus organic nitrogen, which are less soluble forms of nitrogen, were typically higher in streams.

Ammonia and organic nitrogen were higher in surface water than in ground water (fig. 13). Specifically, the median concentration of ammonia plus organic nitrogen in ground water was about 0.1 mg/L, whereas the median concentration in streams was about 0.5 mg/L. Ammonia and organic nitrogen are produced in streams from the decay of leaves and other natural debris, resulting in generally higher concentrations of these chemicals in stream water than in ground water.

Phosphorus is generally present at low concentrations in most Delmarva Pennsula streams and typically increases during storms. Concentrations of phosphorus in Delmarva streams during base flow were typically less than 0.1 mg/L, the recommended level to prevent excessive plant growth in freshwater streams (U.S. Environmental Protection Agency, 1986). Concentrations were as high as 3 or 4 mg/L, however, during base flow in some streams in poorly drained areas with abundant organic matter and low dissolved-oxygen concentrations.

Concentrations of phosphorus generally increase during storm runoff and may exceed 1 mg/L in streams throughout the peninsula. For example, concentrations of sediment and total phosphorous increased with increasing streamflow at Chesterville Branch from storm runoff; concentrations of nitrate and other compounds that are carried primarily through ground water decreased because of dilution by storm runoff (fig. 14) (Ator and others, in press).

Nutrient concentrations in agricultural streams on the Delmarva Peninsula vary seasonally. Nitrate concentrations in surface water typically are greatest during the winter and least in the summer. For example, from 1999 through 2001, concentrations of nitrate in the Pocomoke River reached a maximum of 5 mg/L as N in January but were lowest in June and July (fig. 15). This seasonality can be explained by hydrologic conditions and biologic uptake. Specifically, during winter and spring, the water table is highest, and shallow ground water containing nitrate contributes a larger proportion of base flow. In addition, biotic uptake of nitrate is relatively low because of cool temperatures. As a result, concentrations of nitrate in stream water are high (fig. 15). Lower nitrate concentrations in the Pocomoke River during the dry season (summer and fall) most likely reflect a greater proportion of flow from the underlying confined aquifer, which contains no nitrate. In addition, biotic uptake of nitrate is at its peak in the warmer, drier summer months.

Base-flow nitrate concentrations are expected to increase in Delmarva streams and downstream estuaries in the coming years. As water with elevated concentrations of nitrate currently in the surficial aquifer upgradient from surface-water discharge areas is transported to streams (fig. 10), an increase in nitrate concentrations in stream base flow—and therefore in the total load of nitrate reaching downstream estuaries—is likely. Increased biotic uptake may partially mitigate nitrate concentrations in some streams, although the increased plant growth may contribute to eutrophication or other ecological problems.

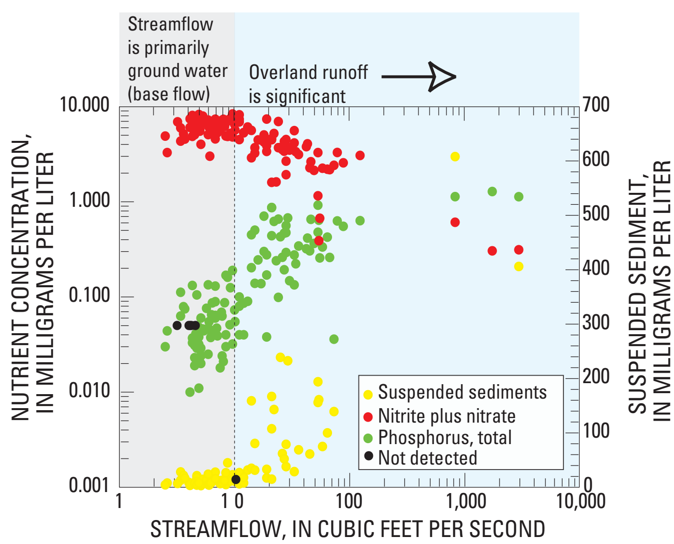


Figure 14. Changes in nutrient concentrations with streamflow reflect different modes of transport for nitrate and phosphorus to Chesterville Branch. The marked increase in suspended-sediment concentrations indicates that overland runoff becomes significant in the watershed when flow reaches about 10 cubic feet per second. Phosphorus is relatively insoluble, and the highest concentrations are associated with sediment during high flow. Nitrate, however, is fairly soluble. Decreasing nitrate concentrations with increasing flow indicate that nitrate moves to Chesterville Branch primarily through ground water.

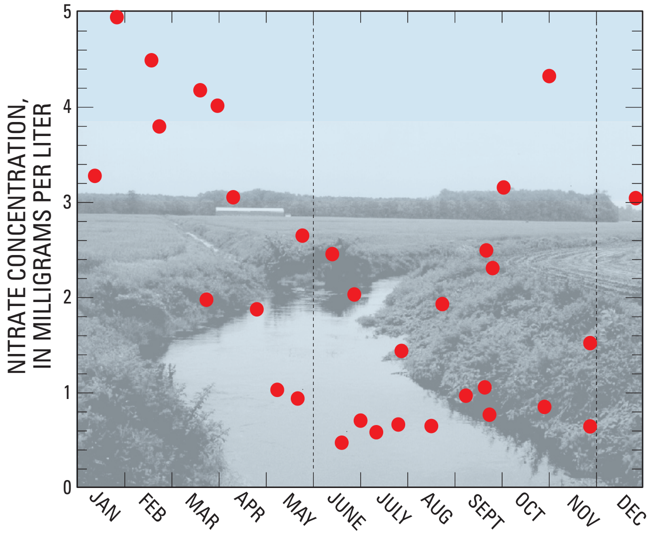
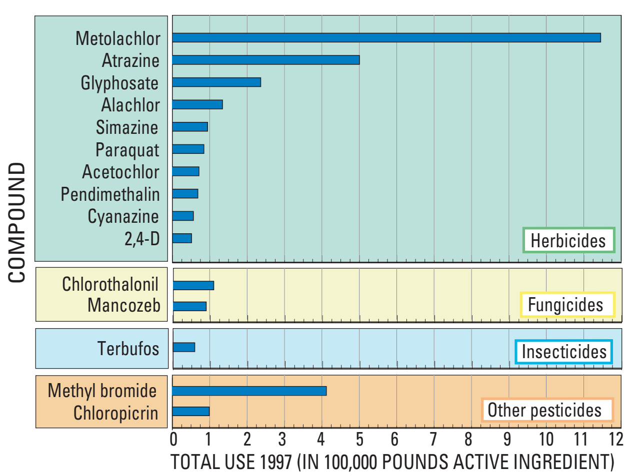


Figure 15. Nitrate concentrations were typically lowest in the Pocomoke River during June and July and highest during January and February during the sampling period from 1999 through 2001. Higher concentrations during the winter reflect greater discharge of water from the surficial aquifer, whereas lower concentrations during the summer reflect the increased proportion of discharge from the underlying confined aquifer, plus biotic uptake.

Pesticides in Ground Water and Streams

Approximately 3.8 million pounds of pesticides was applied in 1997 on the Delmarva Peninsula solely for agricultural purposes, mostly on corn (1.6 million pounds) and soybeans (997,000 pounds) (Gail Thelin, U.S. Geological Survey, written commun., 2002). Metolachlor, atrazine, glyphosate, alachlor, and simazine were the most widely used herbicide compounds in 1997, the last year for which summary data are currently available (fig. 16, table 1). Only 28 percent of the total agricultural pesticide applications on the peninsula are **insecticides**, fungicides, or other non-herbicides (fig. 16). Most of this use is of methyl bromide, a soil fumigant applied to tomatoes and strawberries in the Virginia part of the peninsula (Gail Thelin, written commun., 2002). Although it is applied in only a limited area, methyl bromide is applied at much higher rates than other commonly used pesticide compounds.

Figure 16. Applications of herbicides typically far exceed those of other types of pesticides in agricultural areas on the Delmarva Peninsula, as shown by total usage of the top 15 pesticides. (Data from Gail Thelin, U.S. Geological Survey, written commun., 2002.)



Pesticides also are applied annually for residential, transportation, industrial, public health, or other nonagricultural purposes. About one-fourth of pesticide applications nationally are for nonagricultural purposes (Aspelin and Grube, 1999).

Herbicides are frequently detected in the surficial aquifer

Pesticides are present at low concentrations in water from the surficial aquifer throughout the Delmarva Peninsula (fig. 17). Concentrations of individual compounds detected by NAWQA were typically less than 1 µg/L and were always below current Federal drinking-water standards and health advisories (U.S. Environmental Protection Agency, 2002a); however, standards or advisories are available for only 42 of the 119 pesticides analyzed for in this study.

Pesticides are widespread in shallow ground water underlying agricultural areas. Pesticides were detected in water samples from 25 of 29 shallow wells (median depth 22 ft) in agricultural areas. Twenty different pesticide compounds, mostly herbicides used on crops, were detected. Metolachlor and atrazine, which have been widely used since the 1970s, were the most commonly detected herbicides. Flumetsulam, imazaquin, imazethapyr, and glyphosate, which have increased in use in the last 10 years, also were detected, but less frequently. Less than 20 percent of samples contained detectable prometon or bromocil, which are applied to brush along roadways. Insecticides and fungicides used on crops also were detected less frequently.

Pesticides also are common in ground water used for domestic supply (median well depth 45 ft). Types of compounds were similar to those in shallow ground water in agricultural areas (fig. 17). Metolachlor and atrazine were the most widely detected compounds. Twelve other herbicides also were detected, including the more recently used pesticides flumetsulam, imazaquin, glyphosate, and imazethapyr. Fungicides used on crops and insecticides generally used for controlling insects around buildings were less frequently detected.

Pesticides also are present in the deeper part of the surficial aquifer used for public supply. Samples from the majority (27 of 30) of sampled public-supply wells completed in the surficial aquifer in Delaware (median depth 80 ft) contained detectable pesticides. (These samples were collected before any treatment and therefore may not represent the quality of tap water.) Thirteen different pesticides were detected. The suite of pesticides detected in the public-supply wells reflects a combination of agricultural and urban land use in aquifer recharge areas, as well as historical application rates. Although the most commonly used agricultural chemicals, metolachlor and atrazine, were the most frequently detected in water from public-supply wells, chemicals more frequently used in urban areas also were detected (fig. 17). These include chemicals used for weed control along roads, such as prometon and tebuthiuron, and those used historically for insect control around buildings, such as dieldrin and lindane. The other crop pesticides detected include the herbicides alachlor and simazine and the insecticide carbofuran. Samples from the public-supply wells were not analyzed for some of the more recently used pesticides, including flumetsulam, imazaquin, imazethapyr, and glyphosate.

Mixtures of pesticides and pesticide degradates typically are present in the surficial aquifer. Shallow ground water in agricultural areas and in parts of the aquifer used for domestic supply commonly contain mixtures of metolachlor, alachlor, atrazine, and their degradates, often in combination with other less frequently detected herbicide or insecticide compounds. More than 85 percent of water samples (67 of 78) with detectable pesticides or **degradates** contained three or more different compounds (fig. 18). Most of the chemical mixtures reflected agricultural uses. Water from public-supply wells contained similar mixtures of the most widely used crop herbicides as well as some herbicides and insecticides more commonly used in urban areas. Samples from many of the public-supply wells contained a greater total number of pesticides or pesticide degradates than the shallow agricultural and domestic wells sampled; one sample contained 15 different compounds. The potential additive or synergistic effects of low levels of multiple compounds on human health or aquatic life are unknown. Current experience and research on the environmental and toxicological effects of pesticides is usually based on exposure to individual compounds.

Degradates of some herbicides typically are present at higher concentrations than their parent compounds in the surficial aquifer. For example, median concentrations of the degradates alachlor ESA (ethanesulfonic acid) and metolachlor ESA

Table 1. Commonly used herbicides on the Delmarva Peninsula.

Herbicide	Thousands of pounds used, 1997	Crops
Metolachlor	1,145	Corn, soybeans
Atrazine	500	Corn
Glyphosate	235	Soybeans
Alachlor	134	Corn, soybeans
Simazine	94	Corn

From U.S. Department of Agriculture, 1999

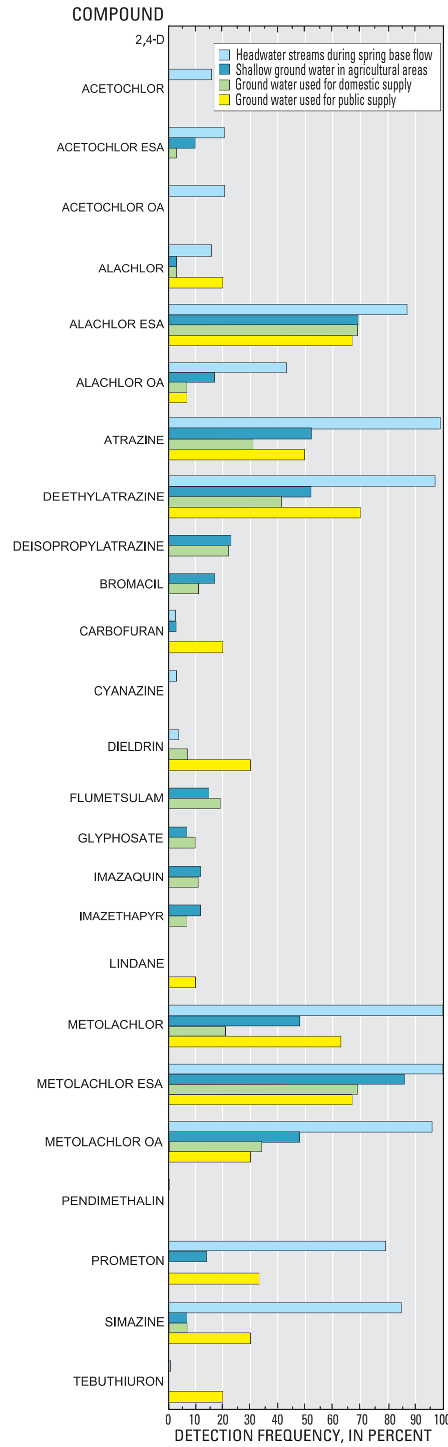
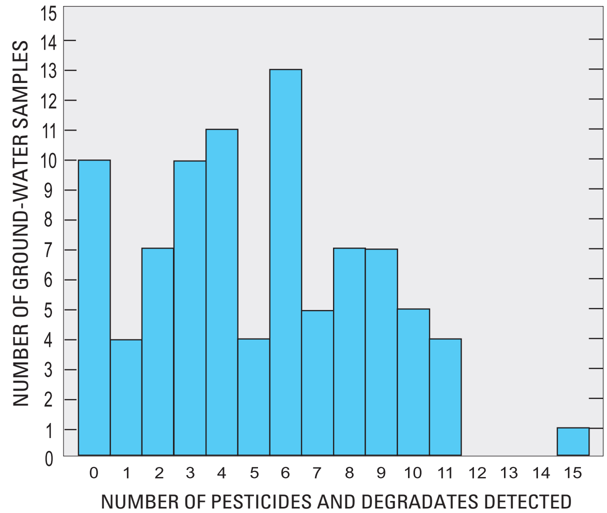


Figure 17. Although metolachlor and atrazine and their degradates are the most frequently detected compounds in ground water, pesticides associated with urban land use are more frequently detected in water from deeper parts of the aquifer in public-supply wells than in shallower parts of the surficial aquifer. Pesticides typically are detected more frequently in surface water than in ground water.

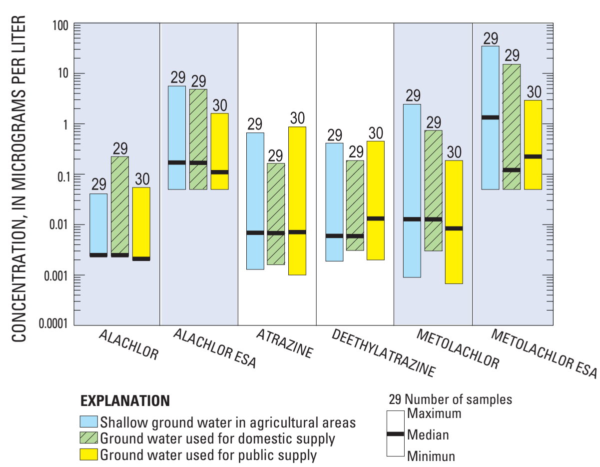
Figure 18. Multiple pesticide compounds were typically detected in individual water samples from the surficial aquifer. Three or more compounds were detected in more than 85 percent of the wells sampled.



generally are greater than 0.1 µg/L, whereas median concentrations of their parent compounds, alachlor and metolachlor, are about 10 times less (about 0.01 µg/L) (fig. 19). These two compounds are typical of most applied pesticides, only a low percentage of which reaches ground water because of adsorption onto organic matter and microbial degradation of the parent compound in the soil zone (Helling and Gish, 1986; Capel and others, 2001). In contrast, concentrations of atrazine and its degradation product, deethylatrazine, commonly occur at similar concentrations in ground water. This finding can be explained, in part, by the chemical properties of atrazine. Specifically, a combination of relatively high mobility and chemical stability in the soil zone allows atrazine to move to, and persist in, the ground-water flow system longer than metolachlor and alachlor, which have lower persistence in the soil zone and tend to break down more completely to degradates before reaching the ground-water system. Little is known about the occurrence of many other pesticide breakdown products, and even less is known about their effects on human health and aquatic life. There are no Federal standards or guidelines for these pesticide degradates.

Pesticides vary in the surficial aquifer because of land use, changes in pesticide usage over time, and physical and chemical properties that control their movement to ground water. The occurrence and concentrations of agricultural pesticides in the surficial aquifer are controlled by several factors. First, pesticide occurrence in shallow ground water varies with land use; concentrations detected in a well generally increase as the percentage of agricultural land use within 500 meters

Figure 19. Degradates of metolachlor and alachlor frequently were present in water from the surficial aquifer at higher concentrations than the parent compounds; concentrations of atrazine and its degradate, deethylatrazine, are similar.



What is a pesticide degradate?

Pesticides released into the environment break down into intermediate compounds, called degradates, and over time into simple molecules like carbon dioxide and water. The breakdown of pesticides occurs both through abiotic and biotic processes. Abiotic processes involve photochemical or chemical transformations that require sunlight or naturally occurring chemicals in soil and water. Biotic processes involve transformations by animals, plants, and microbes. Breakdown occurs primarily in the soil, but it also can occur in plants and in ground water and streams. Modification of a side carbon chain (such as in atrazine degradation) or the replacement of the halogen (chlorine) with a sulfonic acid or carboxylic acid (such as in acetochlor, alachlor, or metolachlor degradation) is commonly the first step in the breakdown of these herbicides. This first step represents only a small molecular change; however, this change may affect the toxicity, mobility, and persistence of the resulting compound compared to its parent compound.

Degradates may be short-lived in the environment or persist for years. Some may be retained in the soil, whereas others may move easily with water through the ground and to streams. A wide variety of degradates can form from a single parent compound. For example, the most widely used pesticide on the Delmarva Peninsula, metolachlor, has two commonly detected degradates, metolachlor ethanesulfonic acid (ESA) and metolachlor oxanilic acid (OA). Other common pesticides, such as atrazine, have as many as four major degradates, including the most common one, deethylatrazine; and there are many more for which analytical techniques have not been developed.

of the well increases (fig. 20). Second, types of pesticides found in the surficial aquifer strongly reflect chemical use. For example, commonly used metolachlor, alachlor, atrazine, and their degradates were the most frequently detected compounds in this study, although newer crop herbicides such as flumetsulam, imazaquin, and imazethapyr also were present in shallower parts of the aquifer where recharge has been recent (typically since the early 1990s) (fig. 17). Acetochlor was not detected in ground water on the peninsula, possibly because it has been used only since 1994. Historically used pesticides, such as carbofuran, were more frequently found in deeper and older ground water (recharged around 1985), such as that collected from public-supply wells, than in shallower, near-surface ground water recharged since 1994. Third, the frequency of detection and concentrations of selected pesticides are controlled by chemical and physical properties. For example, concentrations of herbicides and their degradates are higher in oxygen-rich environments, where soils are well drained and permeable with low organic-matter content, than in poorly drained areas with typically higher concentrations of organic matter, lower concentrations of dissolved oxygen, and a greater potential for microbial degradation in the soil zone. Glyphosate, the third most commonly used herbicide in 1997, was seldom detected, probably because it is strongly adsorbed onto soil particles.

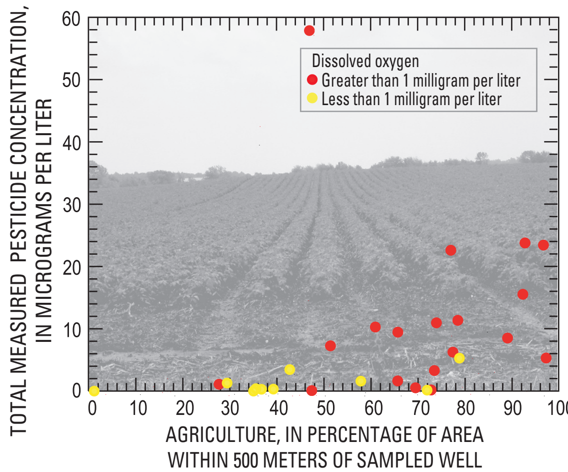


Figure 20. The total measured concentration of pesticides generally increased in shallow ground water beneath agricultural areas with increased intensity of agricultural activity in well-oxygenated parts of the surficial aquifer (dissolved-oxygen concentration greater than 1 mg/L).

Herbicides and their degradates have persisted in the surficial aquifer for more than 30 years (fig. 21). Data collected along a ground-water flow path at an agricultural study area in Fairmount, Del., show atrazine, metolachlor, and their degradates in water that recharged the aquifer as early as the mid-1960s. Degradates of both herbicides persist in the aquifer at higher concentrations than do their parent compounds. As discussed previously, most metolachlor degradation occurs in the soil zone. Although atrazine also breaks down in the soil zone, a decrease in atrazine and a corresponding increase in deethylatrazine over time implies continued degradation of atrazine as water moves through the ground-water system.

Herbicide concentrations in water from the surficial aquifer used for domestic supply have changed little over the past decade, and remain low. Although metolachlor and atrazine were detected more frequently in ground water in 2001 than in 1988 or 1990, this likely is due more to the current availability of sensitive laboratory techniques for analyzing water samples rather than to any apparent increase in concentrations within the aquifer. Twenty-three of the 29 wells sampled in 2001 to represent the ground-water resource used for domestic supply also were sampled in either 1988 or 1990 (see Study Unit Design, p. 22–23). Only one of these 23 samples contained detectable (greater than 0.007 µg/L) atrazine in 1988, and none contained detectable (greater than 0.018 µg/L) metolachlor (Koterba and others, 1993). Concentrations of atrazine exceeded 0.007 µg/L in samples from 3 of these 23 wells in 2001, and atrazine was detected at lower concentrations in samples from one other well. Similarly, samples from four wells contained detectable metolachlor in 2001, although the concentration in only one exceeded 0.018 µg/L.

Temporal trends in herbicide concentrations are similarly unclear or insignificant in shallow ground water beneath agricultural areas. Fifteen of the 29 wells sampled in 2001 to represent this resource also were sampled in either 1988 or 1990 (see Study Unit Design, p. 22–23). Concentrations of metolachlor exceeded 0.018 µg/L in only 2 of the 15 samples in 1988 or 1990, and only 3 samples contained detectable atrazine (Koterba and others, 1993). In 2001, samples from nearly one-half (7) of these 15 wells contained detectable metolachlor, although (as in 1988 and 1990) concentrations exceeded 0.018 µg/L in only 2 samples. Six of the 15 samples contained detectable atrazine, although concentrations in only 4 samples exceeded 0.007 µg/L.

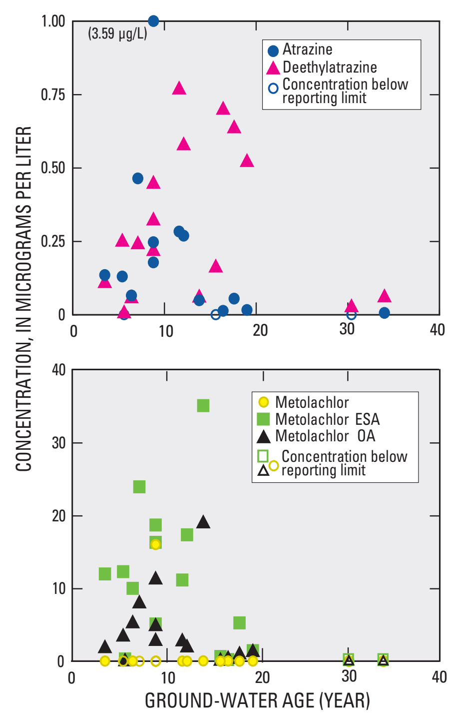


Figure 21. Concentrations of atrazine, metolachlor, and their degradates have persisted along a ground-water flow path at an agricultural study site in Fairmount, Delaware, for more than 30 years.

Pesticides are commonly detected in streams

Pesticides and their degradates are more frequently detected and generally at higher concentrations in streams than in water from the surficial aquifer (fig. 22, fig. 17). Of the 55 pesticides for which both stream and ground-water samples were analyzed, 33 were detected in streams and only 20 in ground water. Metolachlor and atrazine and their degradates were the most frequently detected in streams during spring base flow (fig. 17). Acetochlor and its degradates, which were seldom detected in ground water, also were detected more commonly in streams. Prometon and simazine, which are used for weed control along roads and other rights-of-way, also were more frequently detected in surface water.

Concentrations of pesticides and degradates were typically higher in streams during base flow than in ground water—sometimes by as much as 10 times, as indicated by the commonly used herbicides metolachlor and atrazine (fig. 22). Greater concentrations of pesticide compounds in streams than in ground water may be due to transport along short, shallow flow paths that do not allow much time for chemical changes. Also, pesticides are contributed as they are desorbed from sediments that were transported to streams during storms.

Concentrations of individual pesticides in streams rarely exceeded levels that are known to be harmful to aquatic plants and animals, although such levels are known for only 40 percent of the compounds analyzed for in this study. Also, largely unknown are the ecological effects of pesticide degradates or of mixtures of compounds.

Most pesticides detected in surface water on the Delmarva Peninsula are herbicides applied primarily for corn and soybean production, such as atrazine, metolachlor, and alachlor. The occurrence of other pesticide compounds in certain streams, however, reflects varying influences of other types of land uses. For example, the high frequency of detection of prometon, a herbicide used primarily along roads and other rights-of-way, during spring base flow indicates that non-crop sources of pesticides also may be important on the peninsula. In addition, the frequent detection of the herbicide pronamide, which is commonly used on ornamental shrubs, as well as the insecticides chlorpyrifos, carbofuran, diazinon, and carbaryl at Chesterville Branch (see Appendix, p. 27–28), suggests that applications to nursery plants may be affecting stream chemistry in some areas (Ator and others, in press).

Mixtures of pesticides are common in headwater streams. At least five pesticides or degradates were detected in each headwater stream sampled during spring base flow (fig. 23). The most common combination of pesticides detected was metolachlor, alachlor, atrazine, and their degradates, along with prometon and simazine. Many other herbicide and insecticide compounds were detected less frequently. The number of pesticide compounds in streams generally increases with increasing percentage of agriculture in contributing watersheds. In some watersheds, however, urban land use also contributes many different pesticides, and in one such watershed 17 different pesticide compounds were detected (see data point at upper left in fig. 23).

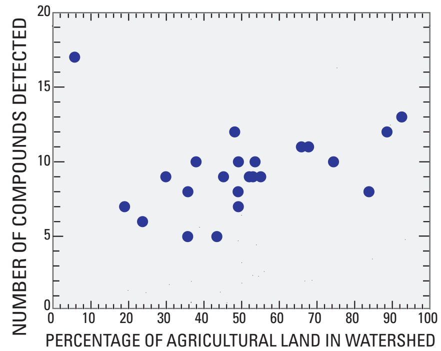
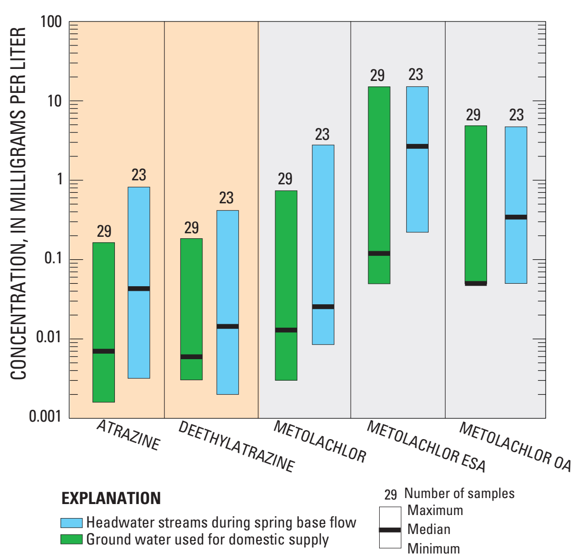


Figure 23. The number of pesticide compounds detected generally increases with increasing proportions of agriculture in contributing watersheds in headwater streams during spring base flow.

Concentrations of herbicides are generally highest during the spring and early summer, soon after periods of application. Herbicides are detectable throughout the year in streams in agricultural areas of the peninsula, in large part because of relatively continuous contributions from ground water (Shedlock and others, 1999). However, streams also receive pesticides in runoff from the land surface. Concentrations vary seasonally because pesticide-carrying runoff is most frequent and greatest in the spring when herbicides are applied, resulting in seasonally elevated pesticide concentrations. For example, in the northern Delmarva Peninsula at Chesterville Branch during the 1999–2001 sampling period, concentrations of metolachlor and atrazine, which are applied just before planting, peaked from March through May during the beginning of the growing season (fig. 24) (Ator and others, in press).

Figure 22. Concentrations of the most commonly used herbicides, atrazine and metolachlor, and their degradates were higher in stream water than in ground water (represented by wells from the part of the surficial aquifer used for domestic supply) on the Delmarva Peninsula.

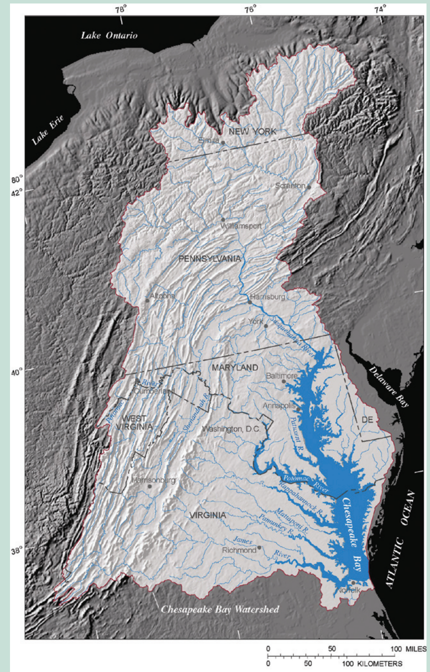


Delmarva Peninsula NAWQA study contributes to understanding of water quality in the Chesapeake Bay

The ecosystem of the Chesapeake Bay, the largest and one of the most ecologically diverse estuaries in the Nation, has been adversely affected by a combination of poor water quality and overharvesting of living resources, such as blue crabs and finfish (Phillips, 2001). About 75 percent of the land area of the Delmarva Peninsula lies within the Chesapeake Bay watershed, and the NAWQA study on the peninsula is providing critical information for understanding water quality in the bay and for implementing strategies to restore the ecosystem.

The Chesapeake Bay is affected by eutrophication (high concentrations of nutrients, leading to blooms of algae and other plants) and hypoxia (areas with low dissolved-oxygen concentrations), resulting in fishkills and loss of other living resources. Decreased water clarity resulting from algal blooms and sediment input has caused a decline in submerged aquatic vegetation, which is critical habitat for shellfish and finfish and provides food for waterfowl. Fish health also is threatened by toxic contaminants entering the system from various land uses.

On the peninsula, nutrients such as nitrogen and phosphorus and pesticides from agricultural and other human sources affect downstream waters. These contaminants are transported to the bay through overland runoff, from point sources in urban areas, and in ground-water discharge. In fact, ground-water discharge may contribute more than one-half of the load of nitrate delivered to the bay (Bachman and others, 1998). Hydrologists in the Delmarva Peninsula Study Unit coordinated with other USGS scientists working in the bay watershed to better quantify the time that elapses between ground-water recharge and discharge (ground-water residence times). Water-quality data



collected in rivers and the Chesapeake Bay show that nutrient and pesticide compounds, including pesticide degradates, that are present in rivers are present at similar or slightly lower concentrations in the bay. Resource managers use this information to help target and implement actions to reduce the amount of contaminants entering the bay.

Local differences in geology, topography, and soils affect the movement of pesticides to streams. Although pesticides are transported to streams from fields by both overland runoff and the ground-water system throughout the peninsula, each of these processes may be more or less important in different areas. In flat areas, such as the south-central part of the peninsula, overland runoff is rare, and pesticides are probably transported to streams primarily through the ground-water system. Topographic relief is generally greater in the northern part of the peninsula, and overland runoff during storms is probably more frequent. Pesticide compounds

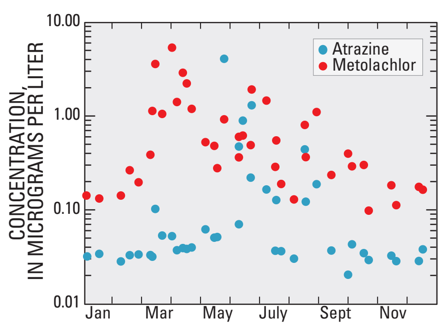


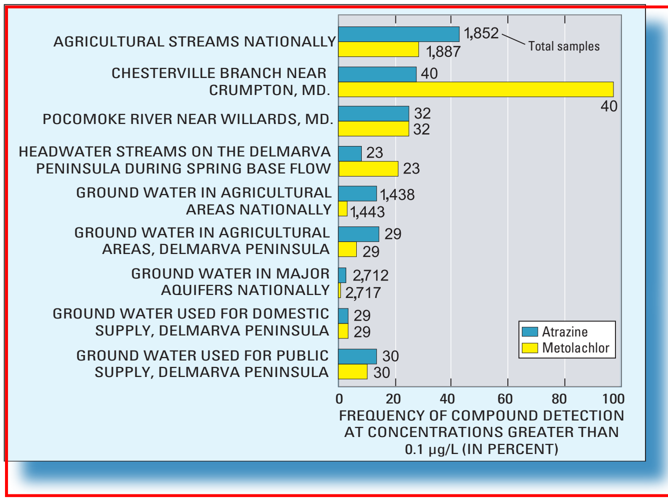
Figure 24. Although atrazine and metolachlor were detectable throughout the year in Chesterville Branch (a stream draining an agricultural watershed near Kennedyville, Maryland) during the 1999–2001 sampling period, concentrations were typically highest during application periods in the spring.

(particularly degradates) also move through the surficial aquifer in these areas, however, particularly where soils and shallow sediments are sandy.

The discharge of pesticides (which is the amount being transported in a stream per unit time) increases as streamflow increases. At Chesterville Branch, for example, when streamflow is less than 10 cubic feet per second, ground water contributes most of the water and chemicals in the stream. When streamflow is greater than 10 cubic feet per second, however, discharge of metolachlor, in particular, increases as runoff from agricultural fields increases (fig. 25) (Ator and others, in press).

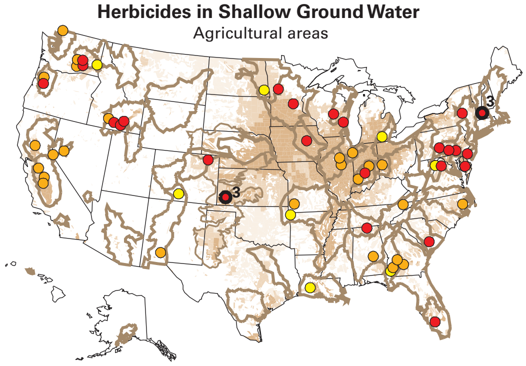
Herbicide concentrations in streams and ground water in agricultural areas on the Delmarva Peninsula are similar to those in other intensively farmed areas where corn and soybeans are grown

Herbicide concentrations in streams and shallow ground water in agricultural areas of the Delmarva Peninsula are similar to concentrations in the Upper Midwest and other heavily farmed areas of the Nation. Soils and shallow sediments in agricultural areas of the peninsula are typically sandy, permeable, and well weathered, and applied herbicides are apparently transported effectively to ground water and streams. Although herbicide application rates are higher in areas such as the Midwest, many of those areas contain relatively impermeable organic-rich soils that may more effectively retain applied herbicides. Established guidelines for the protection of aquatic life were occasionally exceeded for at least one compound in Chesterville Branch.



The occurrence of specific herbicides on the Delmarva Peninsula reflects local application rates and patterns as well as water solubility and local hydrologic, geologic, and soil conditions. Detection frequencies for atrazine in ground water of the peninsula were similar to those in other areas of the Nation, although atrazine was detected less frequently in Chesterville Branch and the upper Pocomoke River than in similar streams nationally. Metolachlor, on the other hand, was detected more frequently in surficial ground water in agricultural areas of the peninsula than in similar areas of the Nation and was measured at concentrations exceeding 0.1 µg/L in 39 of 40 samples collected from Chesterville Branch. Concentrations of metolachlor in the upper Pocomoke River were similar to those in other agricultural streams around the Nation. Metolachlor is the most heavily used herbicide on the peninsula. Moreover, metolachlor is used on both corn and soybeans, whereas atrazine is used only on corn.

Herbicides in Shallow Ground Water
Agricultural areas



EXPLANATION

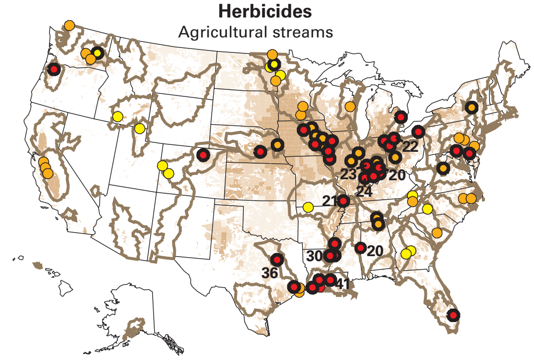
Herbicide use, in pounds per acre of agricultural land*
- Highest (greater than 0.406)
- Medium (0.090 to 0.406)
- Lowest (less than 0.090)
- No reported use

*Data available for conterminous US only

Frequency of wells with one or more herbicides in the GCMS method — Each circle represents a ground-water study
- Highest 25 percent (greater than 59.2)
- Middle 50 percent (16.2 to 59.2)
- Lowest 25 percent (less than 16.2)

Drinking-water standards or guidelines
- Bold outline indicates exceedance by one or more herbicides in the GCMS method. Number is percentage of wells that exceeded a standard or guideline.

Herbicides
Agricultural streams



EXPLANATION

Herbicide use, in pounds per acre of agricultural land*
- Highest (greater than 0.406)
- Medium (0.090 to 0.406)
- Lowest (less than 0.090)
- No reported use

*Data available for conterminous US only

Sum of herbicide concentrations in the GCMS method — 75th percentile, in micrograms per liter
- Highest 25 percent (greater than 1.070)
- Middle 50 percent (0.093 to 1.070)
- Lowest 25 percent (less than 0.093)

Aquatic-life guidelines
- Bold outline indicates exceedance by one or more herbicides in the GCMS method. Number is percentage of samples that exceeded a guideline within a one-year period. Percentages less than 20 are not labeled.

GCMS, Gas chromatography/Mass spectrometry

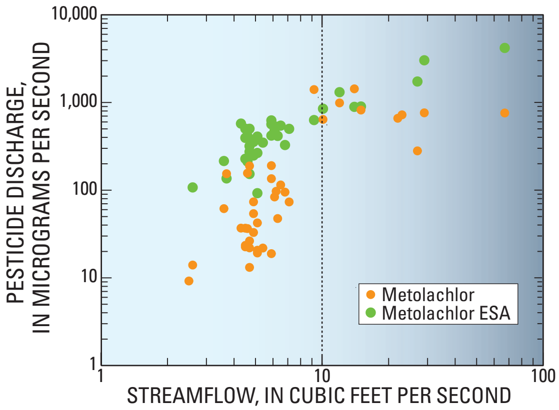


Figure 25. Discharge of both metolachlor and metolachlor ESA increases with increasing streamflow in Chesterville Branch. These compounds are probably carried to the stream primarily through ground water when streamflow is less than 10 cubic feet per second. Additional quantities of these compounds are carried in surface runoff during higher flows.

Other Ground-Water Quality Issues

Volatile organic compounds are detected in ground water

Volatile organic compounds (VOCs), such as components of fuels, lubricants, and solvents, are present in water from the surficial aquifer on the Delmarva Peninsula (fig. 26). At least one VOC was detected in each sample collected from 30 public-supply wells screened in the surficial aquifer in Delaware in 2000 (Ferrari, 2001). Water from most wells contained multiple VOCs, including four wells in which more than 10 compounds were detected. Of the 85 different VOCs for which samples were analyzed, 34 were detected at least once. Measured concentrations were typically less than 1 µg/L, which is below existing Federal standards and guidelines for the protection of drinking water (U.S. Environmental Protection Agency, 2002a,b). No standards and guidelines have been established, however, for 22 of the 34 compounds detected. The high frequency of VOC detection in the public-supply wells reflects the ready transport of organic chemicals through the sandy, permeable sediments of the surficial aquifer.

Chloroform was the most frequently detected VOC in public-supply wells (28 of 30) (fig. 26). Chloroform is used in some industrial and manufacturing processes, and it is commonly produced during the chlorination of drinking water or as a byproduct of the chlorination of wells to kill bacteria that may be introduced during drilling. The next most frequently detected VOC, tetrachloroethene, was detected in 20 of the public-supply wells. This chemical is used in some industrial and manufacturing processes as well as in dry cleaning. Methyl *tert*-butyl ether (MTBE), the third most frequently detected VOC, is widely used as an additive in reformulated gasoline to increase the octane level and reduce carbon monoxide emissions from vehicles; it was detected in 17 samples from public-supply wells on the Delmarva Peninsula.

Only nine different VOCs were detected in water from 16 of 28 wells completed in the part of the surficial aquifer used for domestic water supply (including domestic and monitoring wells). The lower number of VOCs in these wells compared to those detected in public-supply wells is expected because of fewer sources of VOCs in rural areas compared to urban areas (fig. 26). Multiple VOCs were detected in eight of the wells, with a maximum of five different compounds detected in water from one well. Concentrations generally did not exceed 0.1 µg/L and were not above any existing Federal drinking-water standards and guidelines (U.S. Environmental Protection Agency, 2002b). As in public-supply wells, chloroform was the most frequently detected compound (14 of 28 wells). The detection frequency of chloroform (50 percent) in the part of the surficial aquifer used for domestic supply is higher than the national detection frequency (30 percent) for wells in other major aquifers sampled. The next most frequently detected VOCs in the part of the surficial aquifer used for domestic supply were 1,1-dichloroethane (a solvent) and carbon disulfide (which has numerous uses).

VOCs can reach ground water from various sources, including chemical manufacturing, industrial processes (solvents, degreasers, dry cleaning), gasoline or other petroleum-based fuels, byproducts of the chlorination of drinking water, or agricultural applications (used as either pesticides or solvents for pesticides).

Radon occurs in water throughout the surficial aquifer

Radon was detected in all 63 water samples from the surficial aquifer for which it was analyzed. Radon activity exceeded 300 pCi/L (**picocuries per liter**), the proposed Federal maximum contaminant level

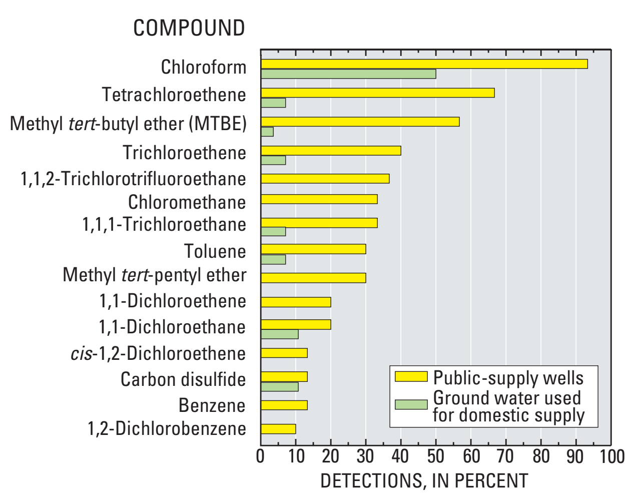


Figure 26. Volatile organic compounds (VOCs) were detected in all 30 samples from public-supply wells and in 16 of 28 wells completed in the part of the surficial aquifer used for domestic supply.

(U.S. Environmental Protection Agency, 2002a), in samples from 22 percent (6 of 27) of wells from the part of the surficial aquifer used for domestic supply but only in 1 of the 10 public-supply wells sampled for radon. Measured radon activities were as high as 1,520 pCi/L. Radon concentrations in water from the surficial aquifer on the Delmarva Peninsula are typical of those in other Coastal Plain aquifers, such as in Delaware (Bachman and Ferrari, 1995), Maryland (Bolton and Hayes, 1999; Drummond, 2001) and New Jersey (Kozinski and others, 1995) and generally are lower than those in other unconsolidated or consolidated aquifers around the Nation (see Appendix, p. 30).

Radon is a naturally occurring, colorless, odorless gas derived from the radioactive decay of uranium in rocks and soil. It has been identified as a carcinogen in humans, primarily as a cause of lung cancer. The source material for the sediments on the Delmarva Peninsula that contain uranium are rocks in adjacent areas of Pennsylvania, Virginia, and West Virginia (Lindsey and Ator, 1996).

Dissolved iron is present in ground water in poorly drained areas

High concentrations of dissolved iron are typical in poorly oxygenated ground water on the Delmarva Peninsula. Concentrations of dissolved iron were greater than 300 µg/L, the Secondary Maximum Contaminant Level for drinking water (U.S. Environmental Protection Agency, 2002a), in 24 percent of the water samples from shallow wells in agricultural areas, 31 percent of the samples from wells completed in the parts of the surficial aquifer used for domestic supply, and 17 percent of samples from public-supply wells in the surficial aquifer in Delaware. Concentrations of dissolved iron in all wells were generally below 100 µg/L in water with concentrations of dissolved oxygen greater than 1 mg/L (fig. 27). Although dissolved iron is not a human-health concern, it affects the taste of water and can stain water fixtures at high concentrations, making water treatment desirable for domestic and public water use.

Dissolved iron is derived principally from the dissolution of naturally occurring iron minerals that coat sand particles; it also may be derived from the oxidation of pyrite in sediments containing organic matter of marine origin. Reducing conditions that cause the mobility of dissolved iron are commonly present in water that recharges the surficial aquifer through poorly drained settings with fine-grained sediments, such as forested wetlands. Reducing conditions also occur near underlying confining beds where water from deeper aquifers is discharging upward and in parts of the surficial aquifer with shallow semiconfining beds.

The highest concentrations of dissolved iron in shallow ground water on the Delmarva Peninsula were found in the south-central part of the peninsula, near the Pocomoke River (fig. 1). In this area, the surficial aquifer is confined or semiconfined by fine-grained sediments with high organic-matter content that causes reducing conditions in shallow ground water. Concentrations of dissolved iron in stream water also are high in this area compared to those in well-drained watersheds. In some areas, concentrations of dissolved iron are so high in the ground water discharging to streams that iron-rich sedimentary rocks are formed in the streambeds (fig. 28).

Figure 28. Bog ore mined from the swamps in the Pocomoke River watershed was used to produce pig iron at the Nassawango Iron Furnace near Snow Hill, Maryland, between 1832 and 1850.

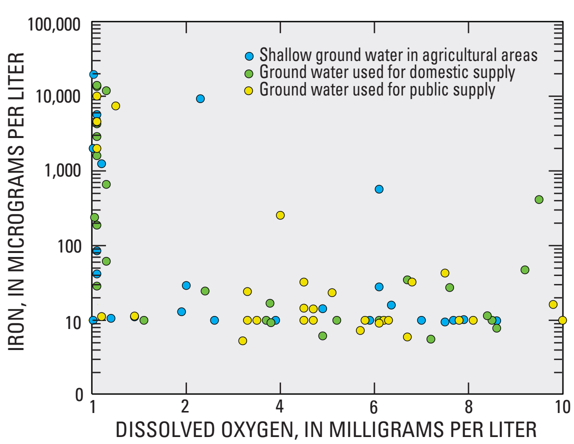


Figure 27. Concentrations of dissolved iron are often high in water from the surficial aquifer where dissolved oxygen is absent or is at very low levels.

Arsenic is common in ground water at low concentrations

Arsenic was detected in about one-half of the wells sampled in the surficial aquifer in agricultural areas and in areas used for domestic supply. Concentrations generally were low, exceeding the standard of 10 µg/L (U.S. Environmental Protection Agency, 2002b) in only one shallow agricultural well in the coastal lowlands along the western shore of the peninsula. The major natural sources of arsenic in surficial-aquifer sediments are buried organic matter and associated iron minerals of marine origin. Poultry manure applied to agricultural fields is another potential source of arsenic in shallow ground water and surface water on the Delmarva Peninsula. (See inset on next page.)

Arsenic is detected primarily as a dissolved ion under reducing conditions in ground water, conditions that typically also promote high concentrations of dissolved iron. These conditions exist in the south-central part of the peninsula near the Pocomoke River watershed. In this area, arsenic is detected in confined and semiconfined parts of the surficial aquifer where recharging ground water has passed through organic-rich marine sediments. The arsenic in this part of the surficial aquifer is believed to be primarily from natural sources in the overlying sediments.

Although arsenic occurs naturally, it is a widespread environmental contaminant and a growing concern in drinking-water supplies. The American Cancer Society recently recognized that arsenic causes cancer of the liver, lung, and skin (Heath and Fontham, 2001). In 1975, the U.S. Environmental Protection Agency established the maximum contaminant level for arsenic at 50 µg/L in drinking water; in 2001, the standard was lowered to 10 µg/L (U.S. Environmental Protection Agency, 2000), which also is the current provisional guide used by the World Health Organization (World Health Organization, 1999). Arsenic also is toxic to fish and many aquatic organisms (Canadian Council of Ministers of the Environment, 2002) and, if present in soil water, it may be taken up by plants—rendering them unsuitable for human or animal consumption (Marin and others, 1993; Krishnamurti and Naidu, 2002).

Additional Information

For more information on water quality in the surficial aquifer of the Delmarva Peninsula go to URL *http://md.water.usgs.gov/delmarva/*.

Reconnaissance for Arsenic in a Poultry-Dominated Basin on the Delmarva Peninsula

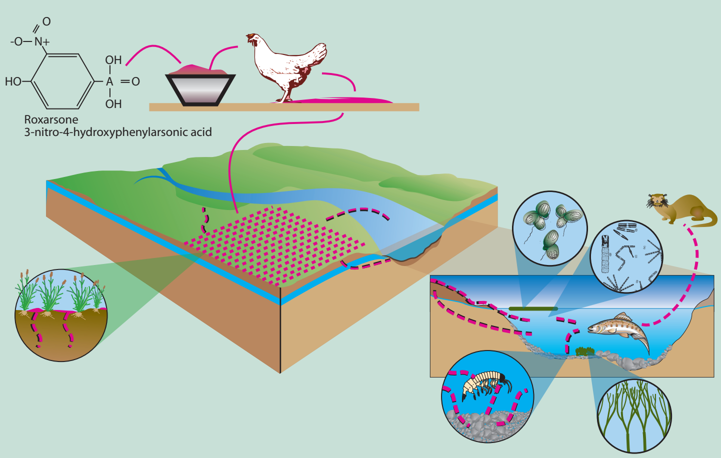
Organic arsenic feed additives are used in poultry production for increasing weight gain, improving feed efficiency and pigmentation, and controlling bacterial and parasitic disease (U.S. Food and Drug Administration, 2000). Organic arsenic compounds, such as Roxarsone (3-nitro-4-hydroxyphenylarsonic acid), do not accumulate in poultry tissue or feathers (Aschbacher and Feil, 1991) but instead are rapidly excreted, resulting in elevated concentrations of arsenic in manure (Morrison, 1969). Poultry manure applied to agricultural fields introduces arsenic into the environment and may result in increased amounts of arsenic in stream water and ground water and uptake by plants.

Results of a reconnaissance investigation in the Pocomoke River Basin (fig. 1) in an area with land application of poultry manure indicate that some of the arsenic applied to agricultural fields is released into the environment on the Delmarva Peninsula. Highest concentrations of arsenic were measured in fresh manure; aged manure and soils contained lower concentrations because arsenical feed additives, such as Roxarsone, leach rapidly from the manure into water and are transformed into inorganic forms during composting (Garbarino and others, 2003).

Arsenic concentrations were elevated above background levels (1–2 µg/L) in stormwater runoff, soil pore water, and some samples of shallow ground water beneath agricultural fields (see table, this page). Concentrations were near background levels in most stream-water and ground-water samples from the Delmarva

Solid material	Total arsenic (mg/kg)
Fresh poultry manure	27
Aged poultry manure	1.0 to 2.0
Soil	1.0 to 2.0
Streambed sediment	0.3 to 17
Ground water	**Total dissolved arsenic (µg/L)**
Deeper ground water	Less than 1.0 to 7.6
Shallow ground water	Less than 0.1 to 23
Pore water, shallow core in agricultural field	6.8 to 29
Filtered surface water (dissolved)	**Total dissolved arsenic (µg/L)**
Base flow	0.5 to 1.6
Stormflow	0.5 to 10.4
Unfiltered surface water (particulate + dissolved)	**Total arsenic (µg/L)**
Stormflow	1.16 to 9.4

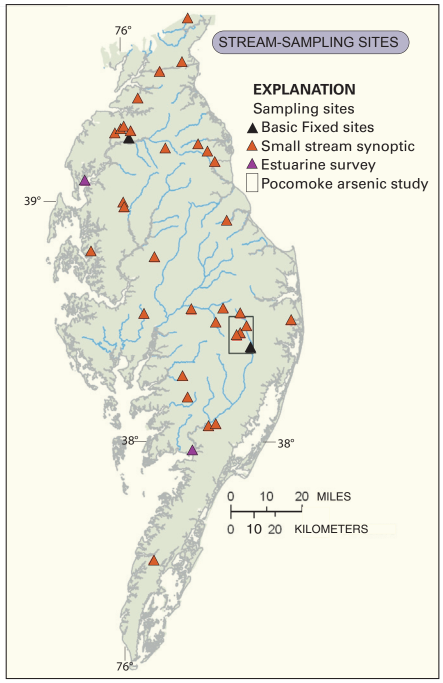
Peninsula (Welch and others, 2000; Canadian Council of Ministers of the Environment, 2002). Arsenic was detected in water samples from the deeper aquifer, which is used for domestic supplies in this area, at concentrations less than the current Federal drinking-water standard of 10 µg/L (U.S. Environmental Protection Agency, 2000). Because the deeper aquifer is confined in this area, the arsenic present is believed to be from natural sediment sources.



Land application of poultry waste organic arsenic compounds may release arsenic into the environment and may result in increased arsenic in surface water and ground water and increased uptake by plants and aquatic organisms.

Study Unit Design

Water quality in the surficial (unconfined) aquifer system and the streams that receive most of their base flow from shallow ground-water discharge was the main focus of this study. The current Delmarva Peninsula study was a continuation of a pilot NAWQA project conducted during 1987–91. Some of the pilot project's ground-water networks were resampled for this project as part of the study of trends in ground-water quality. The effects of agriculture on water quality was targeted for study because agriculture is the predominant land use on the Delmarva Peninsula. Results from this study are compared to those in other agricultural areas around the Nation.

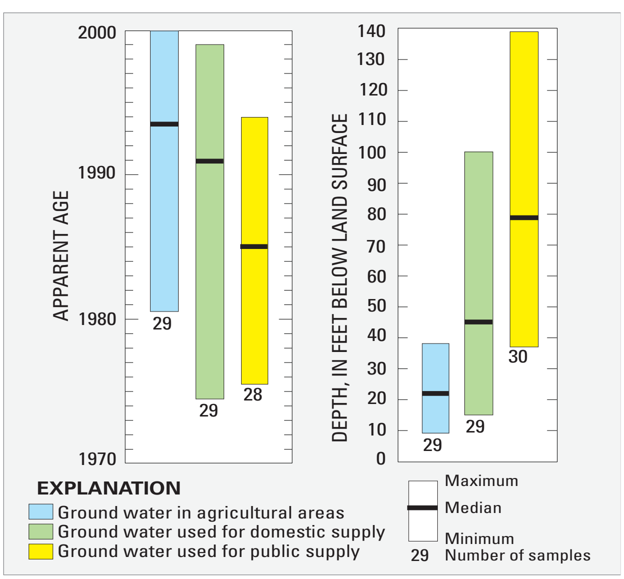


Stream Chemistry

Two **basic fixed** sites in watersheds with predominantly agricultural land use, but in different hydrogeologic settings, were sampled frequently to determine the occurrence and seasonal variability of nutrients and pesticides in surface water.

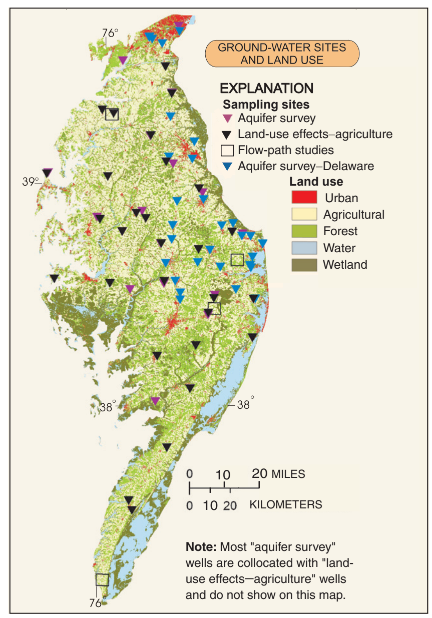
Ground-Water Chemistry

An aquifer survey was done to assess overall water quality in the part of the aquifer that is used as a source for domestic drinking water. A land-use effects study in agricultural settings was done in the shallow part of the surficial aquifer underlying areas of agricultural land use. Public-supply wells screened in the surficial aquifer were sampled as part of a collaborative source-water assessment project with the State of Delaware. The apparent age of ground water increased as well depth increased in these three networks. Four agricultural flow-path studies examined the transport and fate of nutrients in water of the surficial aquifer on a local scale.



Special Studies

A reconnaissance of arsenic in ground water, stream water, streambed sediment, soil, and aquifer material was done in the watershed upstream from the Pocomoke River fixed site. Pesticide concentrations were measured in estuarine waters downstream from the two basic fixed sites in collaboration with a study of fish health being done as part of the USGS Chesapeake Bay studies. A synoptic study of water chemistry during low streamflow in small watersheds draining mixed land uses was done in collaboration with the U.S. Environmental Protection Agency. Stream sites for this study were selected by means of an unequal probability design. With this design, chemical results from the 23 headwater streams sampled on the Delmarva Peninsula were used to provide an unbiased estimate of regional stream conditions (Ator and others, 2003).



Summary of data collection in the Delmarva Peninsula

Study component	What data are collected and why	Types of sites sampled	Number of sites sampled	Sampling frequency and period
Stream chemistry				
Basic fixed sites—agriculture	Streamflow, pesticides, pesticide degradates, nutrients, major ions, suspended sediment, specific conductance, pH, and dissolved oxygen; to describe occurrence and concentrations and to evaluate seasonal, temporal, and flow-related variations.	Streams that drain primarily agricultural watersheds.	2	Monthly, September 1999–September 2001
Ground-water chemistry				
Aquifer survey (surfical aquifer used for domestic supply)	Pesticides, pesticide degradates, nutrients, major ions, trace metals, radionuclides, bacteria, specific conductance, turbidity, pH, and dissolved oxygen; to describe water chemistry in the surficial unconfined aquifer on the peninsula.	Monitoring (16) or domestic (13) wells, selected using a random approach (Scott, 1990). Median well depth, 45 ft.	29	Once, in 2001
Aquifer survey—Delaware	Pesticides, pesticide degradates, volatile organic compounds, nutrients, major ions, radium, radon, specific conductance, turbidity, pH, and dissolved oxygen; to describe water chemistry in the surficial unconfined aquifer where used for public supply in Delaware.	Public drinking-water supply wells **(sample collected prior to any treatment)** in surficial aquifer in Delaware, selected using a random approach (Scott, 1990). Median well depth, 80 ft.	30	Once, in 2000
Land-use effects—agriculture (shallow wells underlying agriculture)	Pesticides, pesticide degradates, nutrients, major ions, specific conductance, turbidity, pH, and dissolved oxygen; to describe water chemistry in the surficial unconfined aquifer in agricultural areas of the peninsula.	Shallow monitoring (27) and domestic (2) wells, located in areas with agricultural land using a random approach (Scott, 1990). Median well depth, 22 ft.	29	Once, in 2001, and December 2002–January 2003
Flow-path studies	Pesticides, pesticide degradates, nutrients, major ions, specific conductance, pH, and dissolved oxygen; to document the movement of chemicals into and through the surficial unconfined aquifer in agricultural areas of the peninsula.	Shallow monitoring wells and streams in selected small watersheds. Various depths.	4 watersheds	Once, in 1999
Special studies				
Pocomoke arsenic study	Arsenic compounds; to determine the fate and transport of arsenic within the upper Pocomoke watershed.	Small streams, wells, soils, soil pore water, and poultry manure from several locations within the watershed.	1 watershed	Once, in 1999
Estuarine survey	Pesticides, pesticide degradates, nutrients, specific conductance, turbidity, pH, and dissolved oxygen; to evaluate the transport of chemicals from flowing streams to tidal estuaries and to support ongoing studies of fish health.	Tidal estuaries, downstream from basic fixed sites.	2	Quarterly, 2001 and 2002
Small stream synoptic	Streamflow, pesticides, pesticide degradates, nutrients, major ions, specific conductance, pH, and dissolved oxygen; to describe the occurrence of concentrations in ground water discharging to small streams.	Small, first-order streams, randomly selected to represent various land uses (Pitchford and others, 2000; Ator and others, 2003).	23	Once, spring 2000, during base-flow conditions

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Glossary

Algae—Chlorophyll-bearing nonvascular, primarily aquatic species that have no true roots, stems, or leaves; most algae are microscopic, but some species can be as large as vascular plants.

Aquifer—A water-bearing layer of soil, sand, gravel, or rock that will yield usable quantities of water to a well.

Atmospheric deposition—The transfer of substances from the air to the surface of the Earth, either in wet form (rain, fog, snow, dew, frost, hail) or dry form (gases, aerosols, particles).

Base flow—Sustained, low flow in a stream; ground-water discharge is the source of base flow in most streams.

Basic fixed site—Site on a stream at which streamflow is measured and samples are collected for temperature, salinity, suspended sediment, major ions and metals, nutrients, and organic carbon.

Confined aquifer (artesian aquifer)—An aquifer that is completely filled with water under pressure and that is overlain by a fine-grained material that restricts the movement of water.

Degradate (degradation product)—Compounds resulting from transformation of an organic substance through chemical, photochemical, and(or) biochemical reactions.

Denitrification—A process by which oxidized forms of nitrogen such as nitrate (NO_3^-) are reduced to form nitrogen oxides or free nitrogen: commonly brought about by the action of denitrifying bacteria and usually resulting in the escape of nitrogen to the air.

Discharge—Rate of fluid flow or a constituent of flow passing a given point at a given moment in time, expressed as volume or mass per unit of time.

Drinking-water standard or guideline—A threshold concentration in a public drinking-water supply, designed to protect human health. As defined here, standards are U.S. Environmental Protection Agency regulations that specify the maximum contamination levels for public water systems required to protect the public welfare; guidelines have no regulatory status and are issued in an advisory capacity.

Eutrophication—The process by which water becomes enriched with plant nutrients, most commonly phosphorus and nitrogen. Eutrophication can cause excessive growth of aquatic plant and algae in water bodies. Decay of this biomass can result in low concentrations of dissolved oxygen in the water column.

Ground water—In general, any water that exists beneath the land surface, but more commonly applied to water in fully saturated soils and geologic formations.

Headwaters—The source and upper part of a stream.

Herbicide—A chemical or other agent applied for the purpose of killing undesirable plants. See also Pesticide.

Insecticide—A substance or mixture of substances intended to destroy or repel insects. See also Pesticide.

Median—The middle or central value in a distribution of data ranked in order of magnitude. The median also is known as the 50th percentile.

Micrograms per liter (µg/L)—A unit expressing the concentration of chemical constituents in solution as mass (micrograms) of solute per volume (liter) of water; equivalent to one part per billion in most stream water and ground water. One thousand micrograms per liter equals 1 milligram per liter.

Milligrams per liter (mg/L)—A unit expressing the concentration of chemical constituents in solution as mass (milligrams) of solute per unit volume (liter) of water; equivalent to one part per million in most stream water and ground water.

Nutrient—Element or compound essential for animal and plant growth. Common nutrients in fertilizer include nitrogen, phosphorus, and potassium.

Pesticide—A chemical applied to crops, rights-of-way, lawns, or residences to control weeds, insects, fungi, nematodes, rodents, or other “pests.”

Picocurie (pCi)—One trillionth (10^{-12}) of the amount of radioactivity represented by a curie (Ci). A curie is the amount of radioactivity that yields 3.7×10^{10} radioactive disintegrations per second (dps). A picocurie yields 2.22 disintegrations per minute (dpm) or 0.037 dps.

Recharge—Water that infiltrates the ground and reaches the saturated zone.

Riparian—Pertaining to or located on the bank of a body of water, especially a stream.

Runoff—Excess rainwater or snowmelt that is transported to streams by overland flow, tile drains, or ground water.

Surface water—An open body of water, such as a lake, river, or stream.

Surficial aquifer—The shallowest aquifer whose upper surface is the water table; the aquifer on the Delmarva Peninsula containing unconfined ground water.

Upgradient—Of or pertaining to the place(s) from which ground water originated or traveled through before reaching a given point in the aquifer.

Volatile organic compounds (VOCs)—Organic chemicals that have a high vapor pressure relative to their water solubility and which evaporate readily at normal pressures and temperatures. VOCs include components of gasoline, fuel oils, and lubricants, as well as organic solvents, fumigants, some inert ingredients in pesticides, and some byproducts of chlorine disinfection.

Watershed—The portion of the surface of the Earth that contributes water to a stream through overland runoff, including tributaries and impoundments.

Water table—The point below the land surface at which ground water is first encountered and below which the earth is saturated. Depth to the water table varies widely across the country.

Wetlands—Ecosystems whose soil is saturated for long periods seasonally or continuously, including marshes, swamps, and ephemeral ponds.

Appendix—Water-Quality Data from the Delmarva Peninsula in a National Context

Concentrations and detection frequencies of the most commonly detected constituents, constituents that exceed a drinking-water standard or aquatic-life guideline, or constituents that are of regulatory or scientific importance, are presented below. Plots of other pesticides, nutrients, VOCs, and trace elements assessed in the Delmarva Peninsula are available at our Web site at:

http://water.usgs.gov/nawqa/graphs

These summaries of chemical concentrations and detection frequencies from the Delmarva Peninsula are compared to findings from 51 NAWQA Study Units investigated from 1991 to 2001 and to water-quality benchmarks for human health, aquatic life, fish-eating wildlife, or prevention of nuisance plant growth. These graphical summaries provide a comparison of chemical concentrations and detection frequencies between (1) surface- and ground-water resources, (2) agricultural, urban, and mixed land uses, and (3) shallow ground water and aquifers commonly used as a source of drinking water.

CHEMICALS IN WATER

Concentrations and detection frequencies, Delmarva Peninsula, 1999–2001

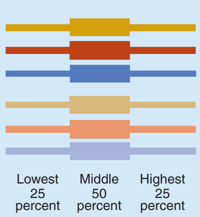
◆ Detected concentration in Study Unit

66 38 Frequencies of detection, in percent. Detection frequencies were not censored at any common reporting limit. The left-hand column is the study-unit frequency and the right-hand column is the national frequency

-- Not measured or sample size less than two

12 Study-unit sample size. For ground water, the number of samples is equal to the number of wells sampled

National ranges of detected concentrations, by land use, in 51 NAWQA Study Units, 1991–2001—Ranges include only samples in which a chemical was detected



National water-quality benchmarks

National benchmarks include standards and guidelines related to drinking-water quality, criteria for protecting the health of aquatic life, and the desired goal for preventing nuisance plant growth due to phosphorus. Sources include the U.S. Environmental Protection Agency and the Canadian Council of Ministers of the Environment

| Drinking-water quality (applies to ground water and surface water)

| Protection of aquatic life (applies to surface water only)

| Prevention of nuisance plant growth in streams

* No benchmark for drinking-water quality

** No benchmark for protection of aquatic life

For example, the graph for atrazine shows that detections and concentrations in the Delmarva Peninsula generally are (1) detected in surface water more frequently than in ground water; (2) at greater concentration in streams in agricultural areas than in shallow ground water from agricultural areas; (3) very seldom found at concentrations above the USEPA drinking-water standard or criteria for protection of aquatic life.

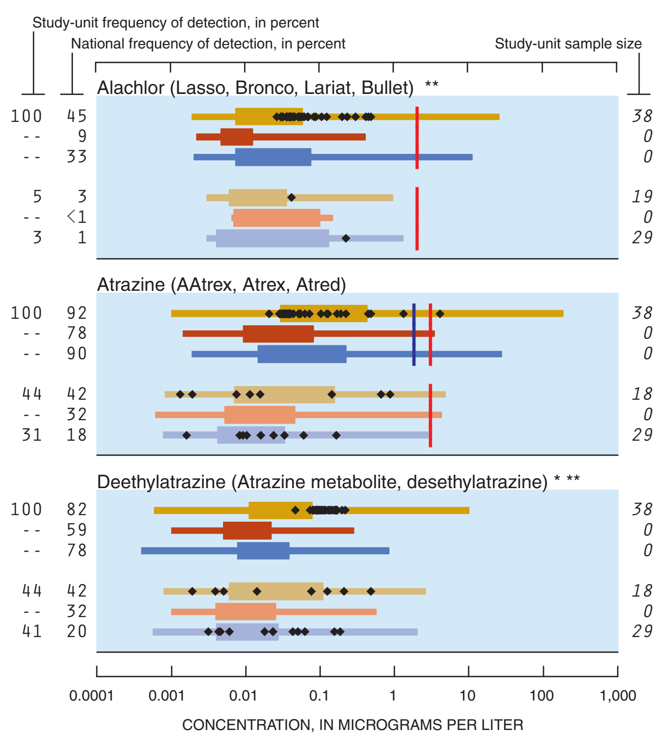
NOTE to users:

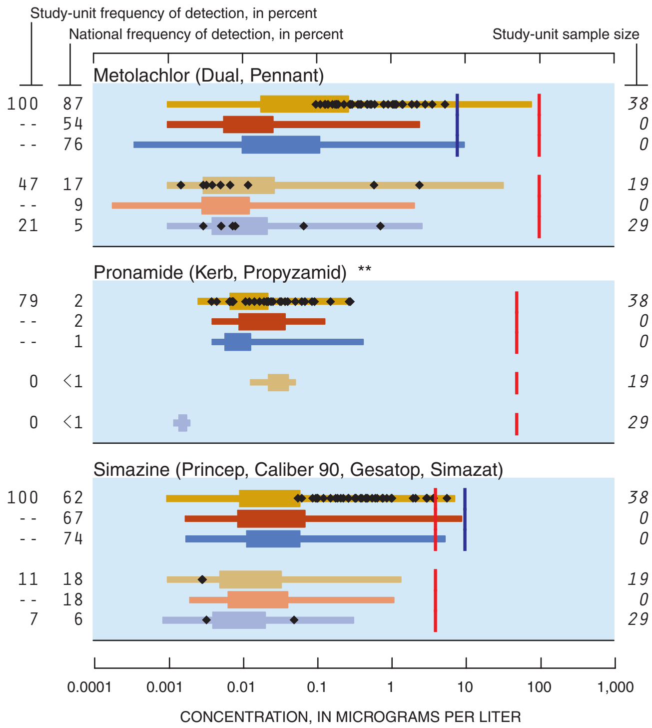
- The analytical detection limit varies among monitored chemicals, thus frequencies of detections are not comparable among chemicals.
- It's important to consider the frequency of detection along with concentration. For example, herbicides were detected more frequently in surface water and generally in the higher percentile of detections than nationwide.

Quality-control data for these analytes indicate relatively frequent low-level contamination of samples during sample processing for analysis. Results for these analytes cannot, therefore, be presented using the generalized methods that were applied to other analytes in this Appendix. Analysis of results for analytes potentially affected by contamination requires special statistical treatment beyond the scope of this report. For more information about these analytes and how to interpret data on their occurrence and concentrations, please contact the appropriate NAWQA Study Unit.

Trace elements in ground water: aluminum, barium, boron, cadmium, chromium, cobalt, copper, lithium, nickel, strontium, zinc
SVOCs in bed sediment: phenol, bis(2-ethylhexyl)phthalate, butylbenzylphthalate, di-*n*-butylphthalate, diethylphthalate
Insecticides in water: *p,p'*-DDE

Pesticides in water—Herbicides





Other herbicides detected

Acetochlor (Harness Plus, Surpass) * **
Butylate (Sutan +, Genate Plus, Butilate) **
Cyanazine (Bladex, Fortrol)
2,6-Diethylaniline (metabolite of Alachlor) * **
EPTC (Eptam, Farmarox, Alirox) * **
Linuron (Lorox, Linex, Sarclex, Linurex, Afalon) *
Metribuzin (Lexone, Sencor)
Napropamide (Devrinol) * **
Pendimethalin (Pre-M, Prowl, Weedgrass Control, Stomp, Herbadox) * **
Prometon (Pramitol, Princep, Gesagram 50, Ontracic 80) **
Trifluralin (Treflan, Gowan, Tri-4, Trific, Trilin)

Herbicides not detected

Chloramben, methyl ester (Amiben methyl ester) * **
Benfluralin (Balan, Benefin, Bonalan, Benefex) * **
DCPA (Dacthal, chlorthal-dimethyl) **
Ethalfluralin (Sonalan, Curbit) * **
Molinate (Ordram) * **
Pebulate (Tillam, PEBC) * **
Propachlor (Ramrod, Satecid) **
Propanil (Stam, Stampede, Wham, Surcopur, Prop-Job) * **
Tebuthiuron (Spike, Tebusan)
Terbacil (Sinbar) **
Thiobencarb (Bolero, Saturn, Benthiocarb, Abolish) * **
Triallate (Far-Go, Avadex BW, Tri-allate) *

Pesticides in water—Insecticides

Insecticides detected

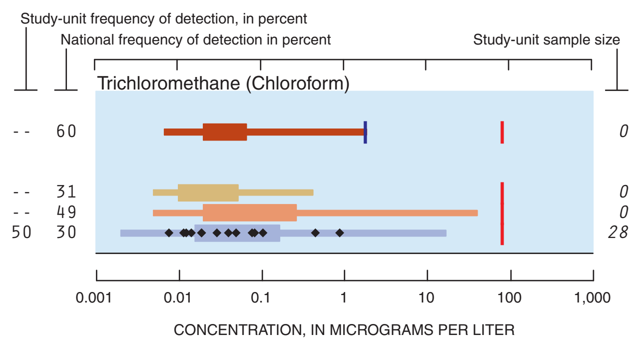
Carbaryl (Carbamine, Denapon, Sevin)
Carbofuran (Furadan, Curaterr, Yaltox)
Chlorpyrifos (Brodan, Dursban, Lorsban)
Diazinon (Basudin, Diazatol, Knox Out)
Dieldrin (Panoram D-31, Octalox)
Malathion (Malathion)

Insecticides not detected

Azinphos-methyl (Guthion, Gusathion M) *
Disulfoton (Disyston, Di-Syston, Frumin AL, Solvirex, Ethylthiodemeton) **
Ethoprop (Mocap, Ethoprophos) * **
Fonofos (Dyfonate, Capfos, Cudgel, Tycap) **
alpha-HCH (alpha-BHC, alpha-lindane) **
gamma-HCH (Lindane, gamma-BHC, Gammexane)
Methyl parathion (Penncap-M, Folidol-M, Metacide, Bladan M) **
Parathion (Roethyl-P, Alkron, Panthion) *
cis-Permethrin (Ambush, Astro, Pounce) * **
Phorate (Thimet, Granutox, Geomet, Rampart) * **
Propargite (Comite, Omite, Ornamite) * **
Terbufos (Contraven, Counter, Pilarfox) **

Volatile organic compounds (VOCs) in water

These graphs represent data from 32 Study Units, sampled from 1994 to 2001



Other VOCs detected

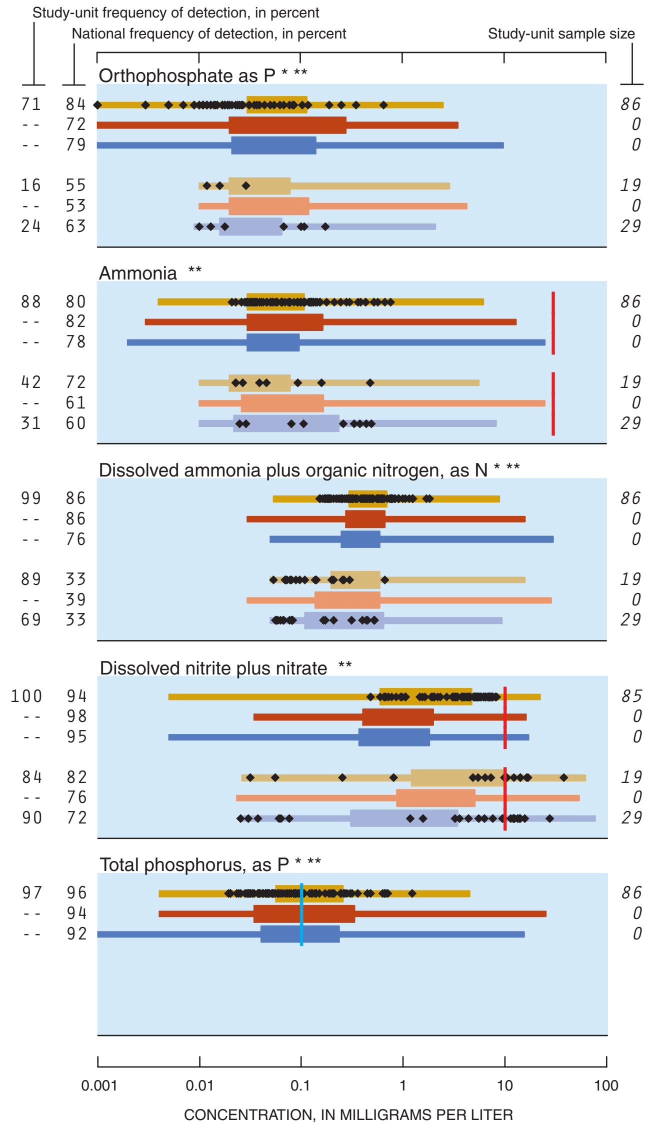
Carbon disulfide * **
1,4-Dichlorobenzene (*p*-Dichlorobenzene, 1,4-DCB)
1,1-Dichloroethane (Ethylidene dichloride) * **
Methyl *tert*-butyl ether (MTBE) **
Methylbenzene (Toluene)
Tetrachloroethene (Perchloroethene)
1,1,1-Trichloroethane (Methylchloroform) **
Trichloroethene (TCE)

VOCs not detected

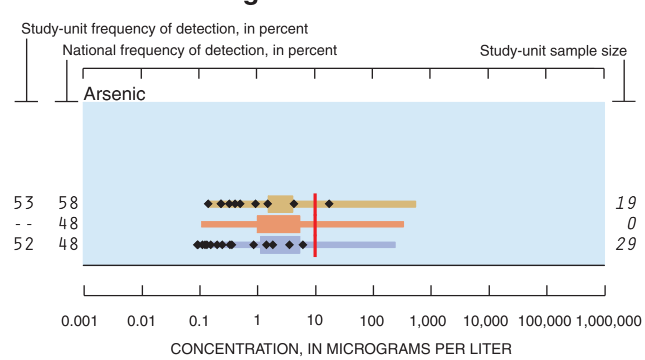
Acetone (Acetone) * **
Benzene
Bromobenzene (Phenyl bromide) * **
Bromochloromethane (Methylene chlorobromide) **
Bromodichloromethane (Dichlorobromomethane) **
Bromoethene (Vinyl bromide) * **
Bromomethane (Methyl bromide) **
2-Butanone (Methyl ethyl ketone (MEK)) **
n-Butylbenzene (1-Phenylbutane) * **
sec-Butylbenzene ((1-Methylpropyl)benzene) * **
tert-Butylbenzene ((1,1-Dimethylethyl)benzene) * **
3-Chloro-1-propene (3-Chloropropene) * **
1-Chloro-2-methylbenzene (*o*-Chlorotoluene) **
1-Chloro-4-methylbenzene (*p*-Chlorotoluene) **
Chlorobenzene (Monochlorobenzene)
Chloroethane (Ethyl chloride) * **
Chloroethene (Vinyl chloride) **
Chloromethane (Methyl chloride) **

1,2-Dibromo-3-chloropropane (DBCP, Nemagon) **
Dibromochloromethane (Chlorodibromomethane) **
1,2-Dibromoethane (Ethylene dibromide, EDB) **
Dibromomethane (Methylene dibromide) * **
trans-1,4-Dichloro-2-butene ((Z)-1,4-Dichloro-2-butene) * **
1,3-Dichlorobenzene (*m*-Dichlorobenzene)
Dichlorodifluoromethane (CFC 12, Freon 12) **
1,2-Dichloroethane (Ethylene dichloride)
1,1-Dichloroethene (Vinylidene chloride) **
trans-1,2-Dichloroethene ((E)-1,2-Dichlorothene) **
cis-1,2-Dichloroethene ((Z)-1,2-Dichloroethene) **
Dichloromethane (Methylene chloride)
1,2-Dichloropropane (Propylene dichloride) **
2,2-Dichloropropane * **
1,3-Dichloropropane (Trimethylene dichloride) * **
trans-1,3-Dichloropropene ((E)-1,3-Dichloropropene) **
cis-1,3-Dichloropropene ((Z)-1,3-Dichloropropene) **
1,1-Dichloropropene * **
Diethyl ether (Ethyl ether) * **
Diisopropyl ether (Diisopropylether (DIPE)) * **
1,2-Dimethylbenzene (*o*-Xylene) **
1,3 & 1,4-Dimethylbenzene (*m*-&*p*-Xylene) **
Ethenylbenzene (Styrene) **
Ethyl methacrylate (Ethyl methacrylate) * **
Ethyl *tert*-butyl ether (Ethyl-t-butyl ether (ETBE)) * **
Ethylbenzene (Phenylethane)
2-Ethyltoluene (*o*-Ethyltoluene) * **
1,1,2,3,4,4-Hexachloro-1,3-butadiene (Hexachlorobutadiene)
1,1,1,2,2,2-Hexachloroethane (Hexachloroethane) **
2-Hexanone (Methyl butyl ketone (MBK)) * **
Iodomethane (Methyl iodide) * **
Isopropylbenzene (Cumene) * **
p-Isopropyltoluene (*p*-Cymene, 1-Isopropyl-4-methylbenzene) * **
Methyl acrylonitrile (Methacrylonitrile) * **
Methyl methacrylate (Methyl-2-methacrylate) * **
4-Methyl-2-pentanone (Methyl isobutyl ketone (MIBK)) * **
Methyl-2-propenoate (Methyl Acrylate) * **
Naphthalene
2-Propenenitrile (Acrylonitrile) **
n-Propylbenzene (Isocumene) * **
1,1,2,2-Tetrachloroethane **
1,1,1,2-Tetrachloroethane (1,1,1,2-TeCA) **
Tetrachloromethane (Carbon tetrachloride)
Tetrahydrofuran (Diethylene oxide) * **
1,2,3,4-Tetramethylbenzene (Prehnitene) * **
1,2,3,5-Tetramethylbenzene (Isodurene) * **
Tribromomethane (Bromoform) **
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113, CFC 113) * **
1,2,4-Trichlorobenzene
1,2,3-Trichlorobenzene (1,2,3-TCB) *
1,1,2-Trichloroethane (Vinyl trichloride) **
Trichlorofluoromethane (CFC 11, Freon 11) **
1,2,3-Trichloropropane (Allyl trichloride) **
1,2,3-Trimethylbenzene (Hemimellitene) * **
1,2,4-Trimethylbenzene (Pseudocumene) * **
1,3,5-Trimethylbenzene (Mesitylene) * **
tert-Amyl methyl ether (TAME) * **

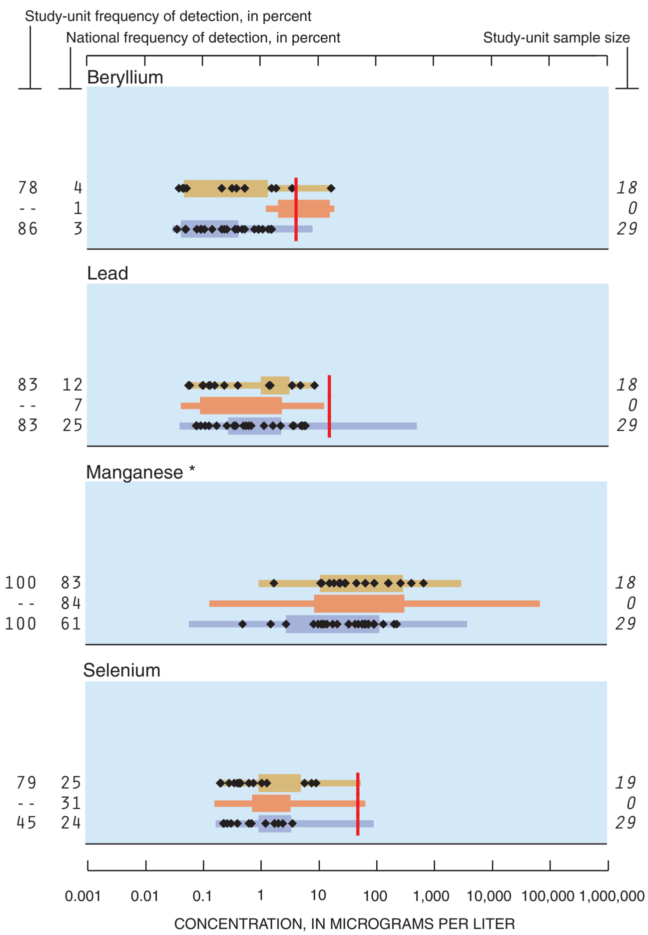
Nutrients in water

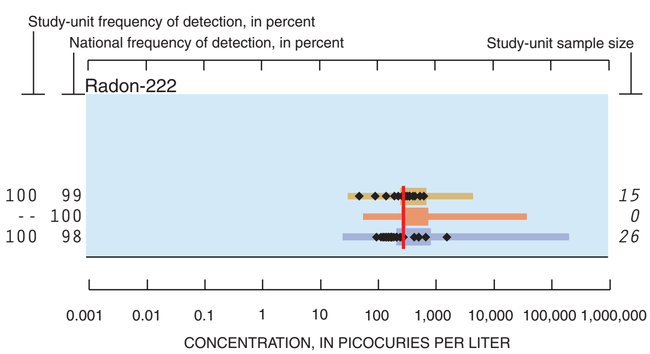


Trace elements in ground water



Trace elements in ground water





Other trace elements detected

Antimony
Molybdenum
Thallium
Uranium
Vanadium *

Trace element not detected

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- Natural Resources Conservation Service

U.S. Environmental Protection Agency
- National Exposure Research Laboratory
  - Landscape Ecology Branch
- Office of Research and Development
  - Mid-Atlantic Integrated Assessment
- Region III

State and Local Agencies

Accomac/Northhampton Planning District
Delaware Department of Agriculture
Delaware Department of Natural Resources and Environmental Control
Delaware Department of Health and Social Services
Delaware Geological Survey
Maryland Department of the Environment
Maryland Department of Natural Resources
Virginia Department of Environmental Quality
Virginia Department of Health

Universities

University of Delaware
University of Maryland

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