Factors Affecting Spatial and Temporal Variability in Nutrient and Pesticide Concentrations in the Surficial Aquifer on the Delmarva Peninsula

Scientific Investigations Report 2005–5257

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By Linda M. Debrewer, Scott W. Ator, and Judith M. Denver

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U.S. Department of the Interior
DIRK KEMPTHORNE, Secretary

U.S. Geological Survey
Mark D. Myers, Director

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Foreword

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity and quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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Conversion Factors and Vertical Datum

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
Flow rate		
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
cubic foot per second (ft^3/s)	8.02	gallon per minute (gal/min)
Mass		
pound, avoirdupois (lb)	0.4536	kilogram (kg)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8×°C)+32$$

Vertical datum: In this report, vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD 29) and (where noted) to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above or below sea level.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Factors Affecting Spatial and Temporal Variability in Nutrient and Pesticide Concentrations in the Surficial Aquifer on the Delmarva Peninsula

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Abstract

Water quality in the unconfined, unconsolidated surficial aquifer on the Delmarva Peninsula is influenced by the availability of soluble ions from natural and human sources, and by geochemical factors that affect the mobility and fate of these ions within the aquifer. Ground-water samples were collected from 60 wells completed in the surficial aquifer of the peninsula in 2001 and analyzed for major ions, nutrients, and selected pesticides and degradation products. Analytical results were compared to similar data from a subset of sampled wells in 1988, as well as to land use, soils, geology, depth, and other potential explanatory variables to demonstrate the effects of natural and human factors on water quality in the unconfined surficial aquifer. This study was conducted as part of the National Water-Quality Assessment Program of the U.S. Geological Survey, which is designed (in part) to describe the status and trends in ground-water quality and to provide an understanding of natural and human factors that affect ground-water chemistry in different parts of the United States. Results of this study may be useful for water-resources managers tasked with addressing water-quality issues of local and regional importance because the surficial aquifer on the Delmarva Peninsula is a major source of water for domestic and public supply and provides the majority of flow in local streams.

Human impacts are apparent in ground-water quality throughout the surficial aquifer. The surficial aquifer on the Delmarva Peninsula is generally sandy and very permeable with well-oxygenated ground water. Dissolved constituents found throughout various depths of the unconfined aquifer are likely derived from the predominantly agricultural practices on the peninsula, although effects of road salt, mineral dissolution, and other natural and human influences are also apparent in some areas. Nitrate occurred at concentrations exceeding natural levels in many areas, and commonly exceeded 10 milligrams per liter (as nitrogen). In addition to land use in the aquifer recharge area, concentrations of nitrate in ground water are related to regional patterns in soil drainage that affect underlying aquifer redox conditions. Over the peninsula, nitrate concentrations are not related to recharge date of the water, but are positively correlated with depth in shallow wells screened beneath agricultural areas. Nitrate concentrations increased in oxic areas (dissolved oxygen greater than 1 milligram per liter) of the deeper part of the surficial aquifer used for domestic supply by an average of about 2 milligrams per liter between 1988 and 2001, although no changes were apparent in shallower parts of the aquifer over that same period. Water in the surficial aquifer generally flows from land-surface recharge to surface-water discharge areas in less than 30 years. As a result, the entire flow system in the surficial aquifer has likely been affected by human activities on and near the land surface over the past several decades.

Pesticide compounds occurred widely at low levels throughout the surficial aquifer. The most commonly used herbicides (metolachlor, alachlor, and atrazine) were the most commonly detected. These pesticides primarily occurred in ground water in the form of degradation products. The widespread occurrence of these and other pesticide compounds reflects their abundant use as well as chemical properties and aquifer characteristics that allow their movement into ground water. Mixtures of pesticides are common. Most samples contained at least 3 different compounds; several samples contained as many as 11. Pesticide concentrations in the surficial aquifer are relatively high beneath recharge areas with well-drained soils in the shallow part of the aquifer and in oxic environments throughout the surficial aquifer. Concentrations are generally below existing drinking-water standards, although standards are not available for all of the pesticide compounds detected. Temporal trends in pesticide concentrations are difficult to determine from available data. Although pesticides were more frequently detected in 2001 than in 1988, this increased frequency of detection is likely due to improved sampling and analytical methods that report detections at lower levels, and may not be indicative of actual changes in pesticide concentrations in the surficial aquifer since 1988.

Introduction

Water-resources managers need a thorough understanding of the natural and human factors affecting the spatial and temporal variability in water quality to address water-resource issues of regional and local importance. Water from the unconfined surficial aquifer on the Delmarva Peninsula (fig. 1) is widely used for domestic and public supplies. Ground water also provides a significant part of the annual flow in local streams. The presence of pesticides, nutrients, and other anthropogenic chemicals in the aquifer has been well documented for the past several decades. Sources of these compounds from agriculture and other human activities are widespread on the peninsula. The well-drained soils and permeable well-weathered sediments of the surficial aquifer, typical of many areas of the peninsula, promote the movement of pesticides from the land surface into shallow ground water. Once these chemicals enter the surficial aquifer, they can travel along flow paths to deeper parts of the aquifer used for drinking water, and, eventually to discharge areas of local streams.

Dissolved nutrients (primarily nitrate) are widespread in the surficial aquifer on the Delmarva Peninsula. Miller (1972) reported nitrate concentrations in parts of the surficial aquifer in Delaware approaching 10 mg/L[1] (milligrams per liter) as early as 1971; 10 mg/L is the Maximum Contaminant Level (MCL) for drinking water established by the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 2004). Nitrate is primarily attributed to agricultural applications of nutrients through fertilizer and manure and to wastewater disposal (Miller, 1972; Bachman, 1984a; Denver, 1986; Andres, 1986; Hamilton and others, 1993). Nitrogen is often applied as ammonia or in organic forms, but it is rapidly converted to nitrate in the well-oxidized water typical of much of the surficial aquifer. In agricultural areas, nitrate is commonly the dominant anion in water of the surficial aquifer (Hamilton and others, 1993). Nitrate concentrations are typically highest beneath areas with well-drained soils near urban or agricultural land and are lower or absent beneath areas with poor drainage, regardless of land use (Bachman, 1984a; Hamilton and others, 1993). Elevated nitrate concentrations are not limited to shallow depths within the surficial aquifer; concentrations greater than 10 mg/L have been measured in water near the base of the aquifer, at depths approaching 100 ft (feet) (Denver, 1989). Although phosphorus is also an important nutrient and component of fertilizers and human and animal waste, it is relatively insoluble, and is rarely detected in the surficial aquifer (Denver, 1986; Hamilton and others, 1993).

Water in some parts of the surficial aquifer on the Delmarva Peninsula contains dissolved pesticides as well as nutrient compounds. Herbicides commonly used on corn and soybeans, such as alachlor, atrazine, metolachlor, and simazine, have been detected in ground water of the surficial aquifer since the 1980s (William F. Ritter, University of Delaware, written commun.,1987; Denver, 1993; Koterba and others, 1993; Ator and Ferrari, 1997; Blaier and Baxter, 2000; Ferrari, 2002). Samples of ground water often contain multiple pesticides; however, their individual concentrations rarely exceed 1 μg/L (microgram per liter). Although herbicides are detectable in ground water throughout the surficial aquifer, concentrations are generally greatest in shallow ground water (within 10 meters of the water table) in or near areas of application to corn, soybeans, and similar crops (Denver, 1993; Koterba and others, 1993; Blaier and Baxter, 2000). Concentrations are also typically greatest in areas where soils are permeable, well-drained, and contain little organic matter, properties that allow the movement of herbicides from the land surface to the water table (Denver, 1993; Koterba and others, 1993; Blaier and Baxter, 2000). Insecticides (carbaryl, carbofuran, dieldrin, lindane, and propoxur) and less commonly used herbicides (butylate, diphenamid, eptam, hexazinone, pebulate, and propachlor) have also been detected in ground water of the surficial aquifer, generally at much lower concentrations than the major-use herbicides (Koterba and others, 1993; Ferrari, 2002).

Nitrate and pesticides in ground water may cause health problems when consumed in drinking water. The surficial aquifer on the Delmarva Peninsula is widely used for domestic and public water supply. Drinking water containing nitrate at concentrations greater than 10 mg/L has the potential to cause methemaglobanemia, a life-threatening illness in infants. This is an issue of concern on the peninsula as many domestic wells are not routinely tested for water quality. Drinking-water standards have also been established for several pesticides. Existing standards are seldom exceeded in ground water; however, the potential additive or synergistic effects of exposure to multiple pesticide compounds are largely unknown (Denver and others, 2004).

Nitrate and pesticides in ground water of the surficial aquifer may also contribute to ecological problems on the Delmarva Peninsula. Ground-water discharge contributes more than half of the flow in streams on the Delmarva Peninsula (Cushing and others, 1973); the majority of this discharge is from the surficial aquifer (Bachman and Phillips, 1996). Excessive nitrate in surface water may lead to eutrophic conditions that are unhealthy for some aquatic biota and certain pesticides may be toxic to some aquatic organisms (Phillips and Caughron, 1997). Although hydrogeologic and soil conditions in some areas of the peninsula promote denitrification or may retard pesticide transport, about half of the first-order (headwater) streams on the peninsula contain more than 3 mg/L of nitrate during spring base flow, and more than 20 percent contain metolachlor at concentrations exceeding 0.1 μg/L (Böhlke and Denver, 1995; Speiran, 1996; Denver and others, 2004). Bachman and Phillips (1996) estimated that 40 percent of the nitrogen entering Chesapeake Bay from the Delmarva Peninsula is derived from ground-water discharge to streams.

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[1] Concentrations of nitrogen species are presented in this report as equivalent concentrations of elemental nitrogen. Nitrate concentrations also include any measurable nitrite.

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

Management strategies intended to mitigate anthropogenic effects on ground-water quality are complicated by the variable, and often unknown, traveltime required for water to move completely through the surficial aquifer. Estimates of the age of ground water in the surficial aquifer on the peninsula typically range from 10–20 years, although water recharging the aquifer along topographic divides may require as much as 30–35 years to reach discharge areas in streams (Dunkle and others, 1993; Böhlke and Denver, 1995; Speiran, 1996; Ferrari, 2002; Lindsey and others, 2003). Therefore, several decades may be needed for the effects of management strategies designed to lower the concentrations of contaminants in the surficial aquifer to be fully realized in the deeper part of the aquifer used for drinking water and in Delmarva streams. A ground-water flow model was used to estimate the effects of ground-water residence times on hypothetical management strategies for nitrate in a similar hydrogeologic setting in the Coastal Plain of southern New Jersey (Kauffman and others, 2001). The model suggests that nitrate concentrations in both streams and ground water would continue to increase for several years or decades after nitrate inputs at the land surface were reduced or fixed at a constant level. Even if inputs from human activities were immediately eliminated, decades would be required for concentrations in streams and ground water to decrease to natural levels (Kauffman and others, 2001).

Purpose and Scope

This study was conducted as part of the National Water-Quality Assessment (NAWQA) Program (Gilliom and others, 1995) of the U.S. Geological Survey (USGS), which is designed (in part) to describe the status and trends in ground-water quality and to provide an understanding of natural and human factors that affect ground-water chemistry in different parts of the United States (see Foreword). Natural and human factors affecting spatial and temporal variability in the quality of ground water (particularly concentrations of nutrients and pesticides) in the surficial aquifer on the Delmarva Peninsula are described and discussed in this report. Because agricultural land use is dominant on the peninsula, this study focuses on the effects of agriculture on shallow ground-water quality. Results are based on analyses of samples collected from two networks of wells screened in the surficial aquifer—relatively shallow wells screened beneath agricultural areas (median depth of 22 ft bls, below land surface), and typically deeper wells screened in the part of the aquifer often used for domestic drinking-water supply (median depth of 45 ft bls). Major-ion chemistry is summarized, along with the occurrence and distribution of nutrients and pesticides, and the apparent relation between water quality and land use, geology, and other potential explanatory factors. Concentrations of selected chemical constituents measured in 2001 are compared to concentrations measured in 1988 in the same set of wells to identify and quantify significant trends in ground-water quality over the intervening years.

Description of Study Area

The Delmarva Peninsula lies entirely within the Atlantic Coastal Plain Physiographic Province and includes most of Delaware and parts of Maryland and Virginia east of the Chesapeake Bay (fig. 1). The peninsula covers about 6,000 square miles and is bounded to the north by the Fall Line and the Piedmont Physiographic Province; to the west by the Chesapeake Bay; and to the east by the Atlantic Ocean and Delaware Bay. The peninsula consists of a flat to gently sloping broad central upland flanked by low plains that slope toward the coasts. The highest elevation of the central uplands of the peninsula is about 80 ft, with a maximum elevation of about 500 ft in the northernmost part of the peninsula. Tidal wetlands fringe the coastal areas along the Chesapeake and Delaware Bays. Barrier beaches, inland bays, tidal lagoons, and marshes characterize the Atlantic coastline. Surface drainage from two-thirds of the peninsula contributes to the Chesapeake Bay and the remaining areas drain to the Delaware Bay or other tidal estuaries along the Atlantic Coast.

Hydrogeologic Setting

The peninsula is underlain by a wedge of unconsolidated sediment that thickens to the south and east from 0 ft at the Fall Line to as much as 8,000 ft along the Atlantic Coast (Cushing and others, 1973). Aquifer sediments range in age from Cretaceous to Holocene, and are primarily quartz sand, clay, silt, gravel, and variable amounts of shells. Organic material is present in swamps and wetlands and in some younger geologic formations. The surficial aquifer has been referred to as the Quaternary aquifer (Cushing and others, 1973), the Pleistocene aquifer (Andres, 1986), and the Columbia aquifer (Bachman, 1984b). The sandy deposits of the surficial unconfined aquifer cover 90 percent of the study area; sediments are highly permeable across most of the peninsula and range from 20 to over 100 ft in thickness (Hamilton and others, 1993). The hydrogeologic setting ranges from well-drained regions where the surficial aquifer is thick and streams are incised to poorly drained regions where the surficial aquifer is thin or absent, topography is flat, stream channels may incise into underlying confined aquifers, and ditching practices are common to promote drainage of agricultural fields. The surficial aquifer may become locally confined by the Walston Silt and Omar Formations in the central part of the peninsula where water-table conditions are shallowest and streams are not deeply incised in the sediments (Bachman, 1984b; Hamilton and others, 1991). The surficial aquifer is underlain by a series of confined aquifers described by Cushing and others (1973) and Harsh and Laczniak (1990). Most of the confined aquifers crop out along tidal streams or subcrop below the surficial aquifer (Hamilton and others, 1991).

Most of the land surface on the Delmarva Peninsula is a ground-water recharge area. About 14 inches of water per year (32 percent of the annual average precipitation) recharges the surficial aquifer, primarily by infiltration of rainfall or snow-

melt (Johnston, 1973). Recharge mostly occurs when evapo-transpiration is at a minimum and vegetation is dormant from late fall to early spring. Depth of the water table in the surficial aquifer typically ranges from 0 to 20 ft, with depths of 30 ft or more in well-drained areas, and can vary by several feet due to seasonal changes in precipitation and evapotranspiration (Hamilton and others, 1993). The longest ground-water flow paths originate at topographic divides. Ground water flows from upland recharge areas toward discharge areas in streams, freshwater ponds and wetlands, tidal marshes, bays, and the Atlantic Ocean. The lengths of ground-water flow paths range from less than a few hundred feet to a few miles, depending on regional and local drainage conditions.

Land Use and Water Use

Land use is predominantly agricultural throughout the Delmarva Peninsula (fig. 2). Crops are mainly soybean and corn grown for poultry feed. These crops are grown in annual rotation with winter wheat and other small grains (U.S. Department of Agriculture, 1991). The most significant agribusiness is the poultry industry, which has increased over the past several decades to production levels of about 600 million broiler chickens per year on the Delmarva Peninsula (fig. 3, Delmarva Poultry Industry, Inc., 2003). The greenhouse and nursery industry has expanded on the peninsula since the early 1980s (American Farmland Trust, 2003). Dairy farms and sod farms also are common, and fruits and vegetables are grown for local and regional markets. Food processing and other small industries are located in smaller towns and cities scattered throughout the peninsula. Although agriculture remains the predominant land use, suburban development is encroaching on agricultural areas (American Farmland Trust, 2003). Urban and industrial development is greatest in northern New Castle County, Delaware; urban and suburban development is also great along the Atlantic Coast in Delaware and Maryland.

The surficial aquifer is the primary source of water for domestic and agricultural use on the Delmarva Peninsula (Denver and others, 2004). The surficial aquifer recharges underlying confined aquifers, is the dominant source of base flow to streams, and, where thick enough, is used for public drinking-water supply. In areas where the surficial aquifer is relatively thin, as in the northern part of the peninsula, confined aquifers are major sources for public-water supply (Shedlock and others, 1999).

Ground-Water Chemistry

Under natural conditions, the chemistry of water in the surficial aquifer is controlled by the chemical properties of rainfall and mineral dissolution, oxidation-reduction (redox) reactions, and residence time in the ground-water flow system. It can also be affected by saltwater intrusion near the coasts. The surficial aquifer is composed primarily of relatively

EXPLANATION

WELL NETWORKS   **LAND USE**

■ AGRICULTURAL   ▬ URBAN   ▬ FOREST
○ DOMESTIC   ▬ AGRICULTURAL   ▬ WETLAND
◆ REFERENCE
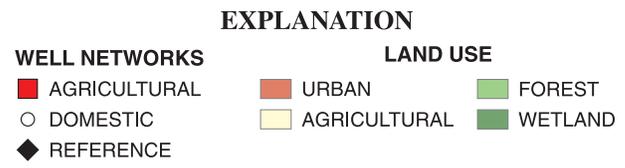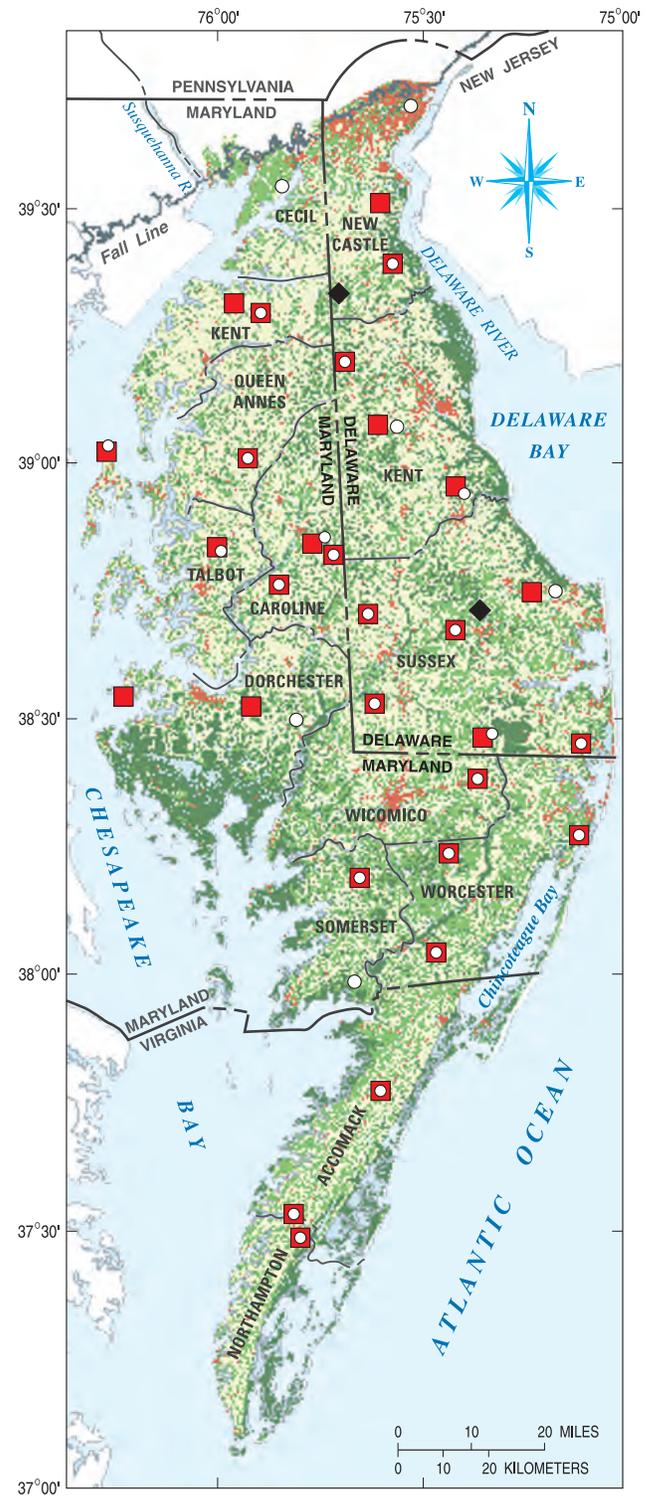
Figure 2. Land use and land cover on the Delmarva Peninsula and location of wells sampled in the study. (Land use from Volgelmann and others, 2001.)
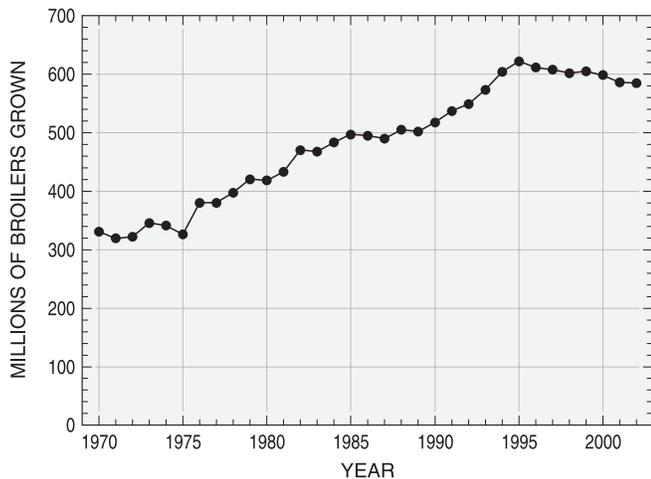
Figure 3.   Poultry production on the Delmarva Peninsula, 1970–2002. Poultry production increased from 1970 to 1995, and then declined slightly. (Data from Delmarva Poultry Industry, Inc., 2003.)

insoluble sand and gravel with low organic-matter content, resulting in relatively dilute and acidic ground water with low natural concentrations of nitrate. In a previous study of the surficial aquifer, water defined as natural had a median value of 5.8 for pH, 115 μS/cm (microsiemens per centimeter) for specific conductance, and 0.1 mg/L for the concentration of nitrate (Hamilton and others, 1993). Ground water with natural chemistry is typically limited in the surficial aquifer to that which recharges through forested areas, where the effects of anthropogenic chemicals are minimal.

Four major natural water types have been identified in the surficial aquifer of the Delmarva Peninsula (Hamilton and others, 1993). The sodium-bicarbonate water type reflects ground-water transport through sediments consisting mostly of weather-resistant quartz sand. This water type is the most dilute, with a median specific conductance of about 60 μS/cm (Denver, 1989). The other three natural water types are: calcium-bicarbonate water, which forms when ground water is in contact with shell material or other marine deposits in the sediments; sodium-chloride water, which is usually associated with saltwater intrusion and can occur near tidal areas; and calcium-sodium-sulfate water in areas dominated by fine-grained sediments with organic matter. Parts of the surficial aquifer with natural water quality also commonly have elevated concentrations of dissolved iron and bicarbonate as many areas with forested land use also contain wetlands and conditions that result in low or no dissolved oxygen in ground water. The specific conductance of natural waters is greater in these water types and where dissolved oxygen is absent than in the sodium-bicarbonate water.

Specific conductance is elevated above natural background levels in waters influenced by human sources of chemicals, such as agriculture, septic-system discharge, and road salt. Because of the dilute nature of natural waters, these human sources can create a new chemical signature in ground water. In water influenced by agriculture, the predominant land use on the peninsula, calcium and magnesium are commonly present from dolomitic lime, potassium and chloride from potash fertilizer, and nitrate from inorganic fertilizer and manure; the median specific conductance is 170 μS/cm (Denver, 1989; Hamilton and others, 1993). Water in parts of the surficial aquifer affected by agriculture is generally a calcium-magnesium-nitrate-type (Hamilton and others, 1993). Bicarbonate concentrations (and pH) are generally lower in agricultural areas than under natural conditions. Ground water affected by septic-system effluent commonly has elevated concentrations of sodium, chloride, and(or) nitrate (Denver, 1989). Road salt is another potential source of sodium and chloride. Road salt may also contribute sodium and chloride to ground water in rural and urban areas (Delaware Department of Natural Resources and Environmental Control, 2005). Because the same major ions may be elevated in waters from different sources, it is important to consider land use in understanding the sources of chemical contamination in water in the surficial aquifer.

Methods of Study

Two networks of randomly located wells were sampled in 2001 as part of a regional assessment of ground-water quality in the surficial aquifer on the Delmarva Peninsula. The networks were derived from an earlier network established in 1988 during the initial pilot phase of the NAWQA Program, the "areal" network described in Koterba and others (1990) and Shedlock and others (1993). Selected areal-network wells and additional wells were combined to create networks representative of different parts of the surficial aquifer. Water in these wells was analyzed to identify and quantify apparent spatial and temporal trends in the quality of ground water from the shallow unconfined aquifer on the peninsula, and to relate these trends to land use, hydrogeology, or other potential explanatory factors.

Network Design

The areal network was designed and sampled to assess water quality throughout the surficial aquifer of the Delmarva Peninsula (Koterba and others, 1990). To minimize bias with respect to sources of contamination, areal-network wells were selected using grid-based random sampling described in Scott (1990) and Alley (1993). The study unit was divided into 12.5- by 12.5-minute grid cells, which were aggregated to create 35 polygons of equal area. One site was randomly selected in each polygon, and suitable nearby wells were located through

a search of state and county records. Areal-network wells were originally sampled from 1988 through 1990. In this report, these samples are referred to hereafter as "areal" or "1988" samples.

The areal network included pairs of deeper and shallower wells. Existing domestic and supply wells were selected wherever possible to represent the deeper part of the surficial aquifer used for drinking water. Deep wells were installed where existing wells were not suitable for sampling (Hardy and others, 1989; Koterba and others, 1995). Shallow wells screened within a few feet of the water table were installed within one-quarter mile of each deeper well to represent the part of the aquifer likely to be most vulnerable to surficial contamination from the land use immediately surrounding the well, which, in most cases, was predominantly agricultural.

Wells from the areal network were used as the basis for developing two 29-well networks in the surficial aquifer (fig. 2; Appendix A). The "agricultural-well network" (median depth, 22 ft bls) was designed to be representative of shallow ground water beneath agricultural areas. This network includes 16 of the shallow wells from the areal network, as well as 13 that were installed or selected to replace areal network wells that were unsuitable for sampling (Lapham and others, 1995). All replacement wells were randomly selected within the same polygon as the original wells. Two additional shallow wells were also included in forested areas where anthropogenic effects on ground water are likely minimal; samples from these wells will be used to document reference conditions. A deeper (median depth, 45 ft bls) "domestic-well network" represents the part of the surficial aquifer commonly used for domestic drinking-water supply. As these wells are deeper, they represent a mixture of water from a broader area and from a wider range of land uses. Twenty-three of the deeper wells had been previously sampled in the areal network.

Agriculture, followed by forest and wetlands, is the dominant land use near wells in both networks. Land use and land cover were documented for the area within approximately 1,640 ft of each well (Appendix A). These data were derived from the USGS National Land Cover Dataset (NLCD) (Vogelmann and others, 2001). The NLCD was compiled from Landsat thematic mapper imagery from 1992 with 98-ft spatial resolution, and was coded using a modification of the Anderson land-use and land-cover classification system (Anderson and others, 1976). Although the resolution is somewhat coarse, the data were used to illustrate general patterns of land use surrounding the wells sampled for this study and the distribution of land use on the Delmarva Peninsula.

Sample Collection and Analysis

Ground-water samples were collected from 60 wells in both networks in 2001 and processed using protocols designed to obtain samples representative of the surficial aquifer, minimizing sample contamination and measurement variability (Hardy and others, 1989; Jones, 1987; Koterba

and others, 1995). Wells were purged to remove standing water in the casing (generally three well volumes) before samples were collected. Purging continued until dissolved oxygen (±0.3 mg/L), pH (±0.1 units), specific conductance (±3 percent), water temperature (±0.2°C, degrees Celsius), and turbidity (±10 percent) stabilized. Water-quality samples were collected through Teflon tubing inside a sampling chamber. A subset of samples intended for dissolved analyses was passed through a 0.45-μm (micrometer) capsule filter (for inorganic constituents) or a 0.7-μm baked glass fiber filter (for pesticides and metabolites); selected trace metals and major-ion samples were preserved with nitric acid to a pH below 2. Bottles were chilled to maintain a temperature of 4°C during shipment to the laboratory.

Samples were analyzed for concentrations of inorganic ions and compounds (major ions and trace metals), selected pesticides and pesticide degradates, and nutrients. Bicarbonate concentrations were calculated on the basis of field titrations for alkalinity (Radtke and others, 1998). Most chemical analyses were conducted at the USGS National Water-Quality Laboratory in Denver, Colorado (Fishman, 1993; Furlong and others, 2001; Garbarino, 1999; Zaugg and others, 1995). Analyses for the concentration of gaseous sulfur hexafluoride (SF_6) were done at the USGS Reston Chlorofluorocarbon Laboratory in Reston, Virginia (Busenberg and Plummer, 2000), and analyses for pesticide degradates were done at the USGS Organic Geochemistry Research Laboratory in Lawrence, Kansas (Zimmerman and others, 2000; Lee and others, 2001a,b).

Quality Control

Quality-control samples were collected to provide an estimate of sample contamination, analytical matrix effects, and measurement variability associated with the data-collection process (Koterba and others, 1995). Blanks, replicates, and spike samples were collected, preserved, and analyzed using the same methods as those used for the environmental samples. Field blanks were collected to ensure that equipment was adequately cleaned to minimize potential cross-contamination and to ensure that sample collection and processing did not result in contamination. Sequential replicate samples were collected immediately following the environmental samples using the same equipment. These samples aid in determining the variability of the chemical analyses and the consistency of sampling techniques. Selected replicates were fortified with known quantities of pesticides to determine bias as a result of matrix interference and to estimate method recoveries.

Field blanks indicate that reported concentrations may contain minimal bias due to sample contamination during collection, processing, or shipment (Appendix B). No nutrient compounds were detected in field blanks at concentrations exceeding laboratory reporting levels. Of pesticides detected in environmental samples, only metolachlor was detected in field

blanks; concentrations in field blanks were as high as 0.0228 μg/L. Metolachlor concentrations were above this level in only 4 of 60 environmental samples, although the lack of detectable metolachlor in environmental samples immediately preceding and following apparently contaminated blank samples suggests that the contamination problem may be limited and not systematic (table 1). Field blanks suggest that reported concentrations of major ions and trace elements may contain bias from sample contamination, but field blank concentrations are insignificant when compared to typical concentrations in environmental samples. Replicate analyses suggest minimal variability in laboratory and sampling technique (Appendix B). Estimated uncertainties in reported concentrations exceeded 10 percent only for nitrogen ammonia, phosphorus, atrazine degradation products, and metolachlor. Estimated uncertainties in the pesticides and degradates are based on one or two replicate sets. Median standard deviations in concentrations for replicate sets were generally low. Median recoveries for spiked pesticides ranged

from 46 percent to 155 percent (Appendix B). Reported concentrations for only 3 of the 36 pesticide and degradate compounds detected in the environmental samples may substantially differ from true environmental concentrations; carbaryl and carbofuran recoveries are biased high and deethylatrazine recoveries are biased low. These compounds have historically poor recoveries with the analytical method and have been documented in Zaugg and others (1995).

Age Dating

Recharge dates for ground-water samples were estimated on the basis of measured concentrations of SF_6 (Busenberg and Plummer, 2000) (Appendix A). SF_6 is a colorless, odorless stable gas primarily of anthropogenic origin with a small contribution from natural sources. The SF_6 method can be used to date ground water that is in equilibrium with atmospheric SF_6 during recharge and is not subsequently exposed to significant SF_6 from other sources. Industrial production of SF_6 began in

Table 1.   Metolachlor concentrations in environmental samples immediately preceding and following field blanks in 2001 and 2002 on the Delmarva Peninsula.

[Well names detailed in Appendix A; **bold** indicates the date blank sample was collected and concentration of metolachlor in the blank sample; E, estimated; <, less than]

Well name	Sampling date	Concentration	Sample type	Interpretation
Ec42-15	7/5/2001	0.6030		
	7/11/2001	**0.0228**	Blank	
Le24-11	7/11/2001	E 0.0033		Possible contamination.
KE Be 59	7/12/2001	E 0.0028		Possible contamination.
Gc14-03	7/17/2001	< 0.013		End of possible contamination.
Gc14-03	7/17/2001	< 0.013		
	7/18/2001	**0.0046**	Blank	
KE Be 46	7/18/2001	< 0.013		No contamination from blank.
Ri22-03	9/5/2001	E 0.0075		
	9/6/2001	**< 0.013**	Blank	No contamination detected.
WO Fc 46	9/6/2001	< 0.013		
CO Dd 74	11/6/2001	< 0.013		
	11/7/2001	**0.0033**	Blank	
TA Be 83	11/7/2001	< 0.013		No contamination from blank.
Ib32-08	12/17/2002	< 0.013		
	12/19/2002	**< 0.013**	Blank	No contamination detected.
Ng45-02	12/19/2002	E 0.0049		

1953 and rates of increase in the atmosphere have been documented since 1978 (Maiss and Brenninkmeijer, 1998). Once released into the environment, SF_6 has a long atmospheric half-life of about 3,200 years. Due to its rapidly increasing mixing ratio (7 percent per year), low solubility in water, high soil stability, and resistance to biodegradation and degradation under highly reducing conditions, SF_6 is a good tracer for age-dating young water (since 1970). Age-dating uncertainty is higher for water recharged since 1970 (±3 years) than for water recharged more recently in 1980 or 1990 (less than 1 and less than 0.5 years, respectively) (Busenberg and Plummer, 2000). Wells are screened over several feet of aquifer sediment; therefore, recharge date represents the average age of water withdrawn from a well.

Data Analysis

Analytical techniques were selected to identify spatial and temporal trends in the quality of unconfined ground water on the Delmarva Peninsula. Principal-components analysis (PCA, see inset) (Hamilton, 1992) was used to identify underlying patterns in pH, specific conductance, dissolved oxygen, dissolved silica and the concentrations of major ions (calcium, magnesium, sodium, potassium, chloride, sulfate, iron, and bicarbonate), and nutrients (nitrate and ammonia plus organic nitrogen) in ground water in 2001, and to provide continuous variables (principal components) summarizing those patterns. Data were censored to a common level for each compound (several compounds had multiple laboratory reporting levels) and censored values were set to one-half of the reporting level prior to PCA.

> ### PRINCIPAL COMPONENTS ANALYSIS
>
> Principal components analysis (PCA) is a mathematical transformation used to reduce multiple variables to a limited number of underlying components (Hamilton, 1992; Helsel and Hirsch, 1992). Each resulting principal component represents a subset of original variables that are well correlated with each other, but poorly correlated with other subsets. PCA generates a value called a loading, which reflects the strength of the relation between variables within a component. A small number of principal components that explain the majority of the variance in a larger number of observed variables can thus be used to simplify data analysis and interpretation. Concentrations of various chemicals in ground water are often well correlated with each other and thus are ideal candidates for PCA.

Water-quality variables were compared to land use, hydrogeology, and other potentially related environmental variables using Spearman's rank correlation and rank-transform analysis-of-variance (ANOVA) techniques (Helsel and Hirsch, 1992; Conover, 1999). All statistical tests were evaluated at the 95-percent confidence level (p=0.05). Data were censored to a common level for each compound and censored values were set to zero prior to correlation or ANOVA analyses.

Factors Affecting Spatial and Temporal Variability

The quality of water in the surficial aquifer on the Delmarva Peninsula is influenced by the availability of soluble ions from natural and human sources, and by geochemical factors that affect the mobility and fate of these ions within the aquifer. Natural precipitation on the peninsula is generally acidic and very dilute (table 2). Ground water in the surficial aquifer typically has a higher pH and specific conductance than rain, although it is still relatively dilute and acidic (table 3).

Geochemical transformations within the aquifer are largely influenced by the availability of dissolved oxygen. Ground water in the surficial aquifer is typically well-oxygenated (oxic, dissolved oxygen concentrations greater than 1 mg/L). In some poorly drained areas of the peninsula, anoxic (dissolved oxygen concentrations less than 1 mg/L) ground water is sometimes present. More than half of the samples from each network contained greater than 3 mg/L of dissolved oxygen (table 3). Iron, naturally occurring as a grain coating on aquifer sediments where dissolved oxygen is present, is desorbed from aquifer sediments and iron concentrations are typically elevated along with bicarbonate in ground water with low dissolved oxygen (Denver, 1986).

Table 2. Chemistry of wet atmospheric deposition at Wye River, Maryland, 1994–2002.

[μS/cm, microsiemens per centimeter; mg/L, milligrams per liter]

Chemical constituent	Precipitation-weighted mean concentration
Specific conductance	22.2 μS/cm
pH	4.35
Calcium	0.06 mg/L
Magnesium	0.026 mg/L
Potassium	0.018 mg/L
Sodium	0.18 mg/L
Ammonia as NH_4	0.18 mg/L
Nitrate as N	0.28 mg/L
Chloride	0.36 mg/L
Sulfate	1.74 mg/L

Source: National Atmospheric Deposition Program, 2003a.

Table 3.   Summary statistics for selected physical properties and major ions and elements in ground water of the surficial aquifer on the Delmarva Peninsula.

[μS/cm, microsiemens per centimeter; mg/L, milligrams per liter; μg/L, micrograms per liter; N, nitrogen; <, less than]

Constituent (units)	Median in natural ground water (77 samples)[1]	Agricultural-well network (29 samples)[2]			Domestic-well network (29 samples)[3]		
		Minimum	Median	Maximum	Minimum	Median	Maximum
Physical properties							
pH (standard units)	5.76	3.9	5.3	6.8	4.3	5	7.6
Specific conductance (μS/cm)	115	34	243	2,140	22	195	611
Dissolved oxygen (mg/L)		0.02	3.3	8.6	0.05	3.7	9.5
Major ions or elements							
Bicarbonate (mg/L)[4]	31.7	1	11	218	1	6	223
Calcium (mg/L)	4.8	2.2	12.1	103.3	0.9	10.2	77.6
Chloride (mg/L)	9.1	<0.2	22.9	599.6	6.2	14.2	96.7
Iron (μg/L)	1,800	<10	11.12	19,569	<10	28.7	14,001
Magnesium (mg/L)	1.7	0.70	7.2	33.9	0.2	4.2	13.6
Nitrate (mg/L as N)	0.1	<0.06	5.4	37.5	<0.05	5.5	27.2
Potassium (mg/L)	1.1	0.3	2.02	23.1	0.7	1.9	6.3
Silica (mg/L)	24	4.7	12.4	65.6	6.6	16.5	46.7
Sodium (mg/L)	9.4	2.41	9.21	269.09	2.2	9.1	82
Sulfate (mg/L)	6.6	<0.18	19.3	180.4	<0.1	5.8	59.2

[1] 1976 to 1990 (Hamilton and others, 1993).

[2] Network of shallow wells (median depth of 22 feet below land surface) in predominantly agricultural areas.

[3] Network of deep wells (median depth of 45 feet below land surface) screened in the part of the surficial aquifer used for domestic supply.

[4] Summary statistics for the concentration of bicarbonate in 25 agricultural-network wells and 28 domestic-network wells.

Regional Variability

PCA illustrates the regional influence of agriculture on water quality in the surficial aquifer of the Delmarva Peninsula as well as the local availability of certain ions from saltwater intrusion or shell material. More than 70 percent of the variability in ground-water quality throughout the aquifer (represented by the domestic-well network) is explained by three principal components that suggest that agriculture is the most important influence on ground-water quality on a regional basis, although natural sources of ions are also important, particularly in non-agricultural areas (table 4). More than 75 percent of the variability in shallow ground-water chemistry beneath agricultural areas (represented by the agricultural-well network) is similarly related to the relative importance of natural and human influences, as well as the intensity or nature of agricultural practices (table 5).

Domestic-Well Network

Agriculture is the primary regional influence on ground-water quality in the surficial aquifer on the Delmarva Peninsula. The first domestic-well network principal component (DOMPC1), which explains 38 percent of the variability in ground-water quality, represents a distinction between ground water affected by anthropogenic (primarily agricultural) influences and relatively natural ground water (table 4). Dissolved components with relatively high positive loadings for DOMPC1 that are commonly associated with agricultural influences include magnesium, nitrate, potassium, chloride, and dissolved oxygen. Nitrate is common in oxic ground water in agricultural areas; the relatively high positive loadings for potassium and chloride suggest that nitrate may be derived from inorganic fertilizer or manure applications. Also, the relatively weak loading for calcium (which has other potential

Table 4.   Loadings on the first three components from unrotated principal-components analysis[1] for ground water representing domestic drinking-water supply in the surficial aquifer of the Delmarva Peninsula and correlation of each principal component with selected well information.

[DOMPC, domestic-well network principal component; Rho, Spearman's rho (Helsel and Hirsch, 1992); oxic, oxidizing conditions (dissolved oxygen greater than 1 milligram per liter); NA, not applicable; <, less than]

Component	DOMPC1	DOMPC2	DOMPC3	Communality estimates
Magnesium	**0.7394**			0.6024
Nitrate	**0.7255**		0.5167	0.7935
Potassium	**0.7174**		0.3252	0.6593
Chloride	**0.7172**	0.4295	-0.3800	0.8432
Dissolved oxygen	**0.6481**	-0.3600	0.4366	0.7402
Silica	**-0.7290**			0.6080
pH	**-0.7213**	0.5483		0.8255
Iron	**-0.6772**			0.4929
Bicarbonate	**-0.6023**	**0.7009**		0.9002
Calcium		**0.8470**	0.3718	0.8617
Specific conductance	0.4944	**0.8498**		0.9796
Sodium	0.4462	0.3682	**-0.6212**	0.7207
Sulfate	0.5498	0.3692	-0.4772	0.6664
Ammonia plus organic nitrogen	-0.4496			0.3172
Variance explained (percent)	0.38	0.22	0.11	

Correlation with well information[2]	Rho (p-value)	Rho (p-value)	Rho (p-value)
Depth	**-0.526 (0.004)**	-0.304 (0.116)	0.055 (0.781)
Apparent recharge date	**0.468 (0.012)**	-0.134 (0.495)	-0.024 (0.904)
Agriculture	**0.414 (0.028)**	-0.118 (0.549)	0.316 (0.102)
Forest or wetlands	**-0.541 (0.003)**	0.119 (0.547)	-0.168 (0.393)
Urban	0.353 (0.065)	0.187 (0.340)	-0.215 (0.271)
Comparison among areas with different:[2]	**Rank-sum p-value (High group)**	**Rank-sum p-value (High group)**	**Rank-sum p-value (High group)**
Redox conditions[3]	**<0.001 (oxic)**	0.196 (NA)	**0.046 (oxic)**
Soil drainage[4]	0.063 (NA)	0.745 (NA)	0.745 (NA)

[1] Loadings greater than 0.60 are in **bold**; loadings less than 0.30 are omitted.

[2] Results in **bold** where p<0.05. Relation to land use indicates correlation with percentage land use within 1,640 feet of each well.

[3] Represents oxidation-reduction conditions in the surficial aquifer.

[4] Represents well-drained and poorly drained soil conditions.

Table 5.   Loadings on the first three components from unrotated principal-components analysis[1] for shallow ground water beneath agricultural areas of the Delmarva Peninsula and correlation of each principal component with selected well information.

[AGPC, agricultural-well network principal component; Rho, Spearman's rho (Helsel and Hirsch, 1992); oxic, oxidizing conditions (dissolved oxygen greater than 1 milligram per liter); well, well-drained; NA, not applicable; <, less than]

Component	AGPC1	AGPC2	AGPC3	Communality estimates
Specific conductance	**0.9519**			0.9808
Sodium	**0.9482**			0.9152
Chloride	**0.8778**	0.3069		0.8763
Magnesium	**0.7041**	0.4401	0.3843	0.8371
Bicarbonate	**0.6076**	0.3816	-0.5237	0.7890
Calcium	**0.6782**	**0.6638**		0.9219
Ammonia plus organic nitrogen	**0.6240**	**-0.6256**		0.7807
Iron	0.5483	**-0.7707**		0.9155
Silica	0.4060	**-0.7724**		0.7943
Sulfate	0.5703	-0.5702		0.7358
Dissolved oxygen		0.5781	**0.6986**	0.8421
Nitrate	-0.4018	0.3838	**0.7180**	0.8243
pH	0.4029	0.4500	-0.4310	0.5505
Potassium				0.0436
Variance explained (percent)	0.39	0.25	0.13	

Correlation with well information[2]	Rho (p-value)	Rho (p-value)	Rho (p-value)
Depth	-0.387 (0.051)	0.264 (0.193)	**0.408 (0.038)**
Apparent recharge date	-0.176 (0.391)	0.244 (0.229)	0.055 (0.788)
Agriculture	-0.076 (0.714)	0.220 (0.281)	**0.435 (0.026)**
Forest or wetlands	0.027 (0.896)	-0.163 (0.426)	**-0.421 (0.032)**
Urban	0.057 (0.784)	-0.109 (0.596)	-0.172 (0.400)
Comparison among areas with different:[2]	**Rank-sum p-value (High group)**	**Rank-sum p-value (High group)**	**Rank-sum p-value (High group)**
Redox conditions[3]	0.609 (NA)	**0.029 (oxic)**	**0.002 (oxic)**
Soil drainage[4]	0.959 (NA)	**0.006 (well)**	0.090 (NA)

[1] Loadings greater than 0.60 are in **bold**; loadings less than 0.30 are omitted.

[2] Results in **bold** where p<0.05. Relation to land use indicates correlation with percentage land use within 1,640 feet of each well.

[3] Represents oxidation-reduction conditions in the surficial aquifer.

[4] Represents well-drained and poorly drained soil conditions.

sources in water such as shell material) and high loading for magnesium (which has very limited natural sources in the surficial aquifer and is primarily derived from dolomitic lime) on DOMPC1 suggests that agricultural lime applications may be a potential source for the magnesium. The agricultural signature of DOMPC1 is similar to the chemical signature of agriculturally influenced ground water described in Hamilton and others (1993). Silica, bicarbonate, and iron, which are common major constituents in natural, particularly anoxic, ground water on the peninsula, have relatively strong negative loadings for DOMPC1 (table 4). In addition, DOMPC1 is positively correlated with agricultural intensity and apparent recharge dates; agricultural influences are more apparent (DOMPC1 is higher) in younger and shallower ground water (table 4). Estimated trends in fertilizer application (fig. 4) and the growth of the poultry industry (fig. 3) on the Delmarva Peninsula are reflected in temporal trends in DOMPC1 (fig. 5). Agricultural influences reflected in DOMPC1 generally increase with estimated recharge date until around the late 1980s; significant trends through the 1990s are less apparent (fig. 5). DOMPC1 also reflects the importance of redox conditions on the transport of chemicals to ground water. Agricultural influences reflected in DOMPC1 are significantly greater in oxic ground water than in ground water containing less than 1 mg/L of dissolved oxygen (table 4).

The second and third principal components from the domestic-well network (DOMPC2 and DOMPC3, respectively) apparently represent different natural influences on ground-water quality. DOMPC2 explains 22 percent of the variability in ground-water quality, and has relatively high positive loadings for calcium and bicarbonate (table 4). The relatively weak loading for magnesium suggests that natural shell material in aquifer sediments may be a potential source of these ions, and the strong loading for specific conductance suggests this material may be an important influence on water quality, where present. Similarly, DOMPC3 has relatively strong negative loadings for sodium, chloride, and sulfate (table 4), which suggest possible saltwater influence. The relatively strong positive loading on DOMPC3 for nitrate suggests possible human influence, although values of neither DOMPC2 nor DOMPC3 are related to land use (table 4). DOMPC2 and DOMPC3 are also not related to depth, apparent age, or soil drainage (table 4).

Agricultural-Well Network

The primary factor affecting shallow ground-water quality within agricultural areas of the Delmarva Peninsula is overall ionic strength. The first agricultural-well network principal component (AGPC1) explains 39 percent of the variability in ground-water samples from the shallow aquifer, and has high positive loadings for specific conductance, as well as many of the most frequently detected major cations and anions (table 5); several samples have high ammonia plus organic nitrogen values that are likely the result of intensive manure application near the wells (based on field observations). The weaker negative loading for nitrate and the lack of a significant correlation of AGPC1 with depth, apparent age, soil
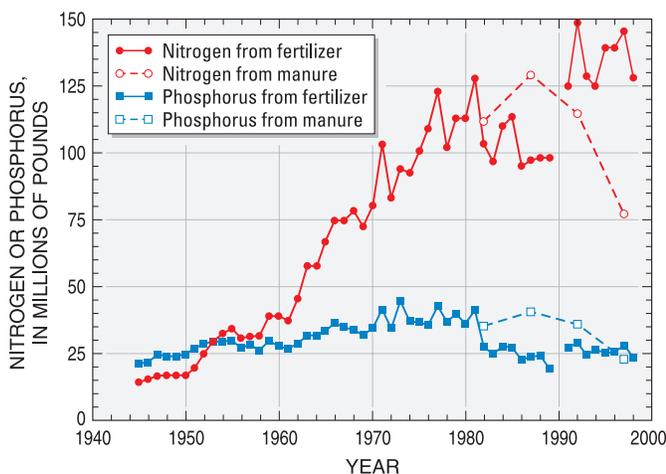
Figure 4. Estimated nutrient inputs from inorganic fertilizer and manure on the Delmarva Peninsula, 1940–2000. (Data from Alexander and Smith, 1990; Battaglin and Goolsby, 1994; David Lorenz, U.S. Geological Survey, written commun., 2002.)
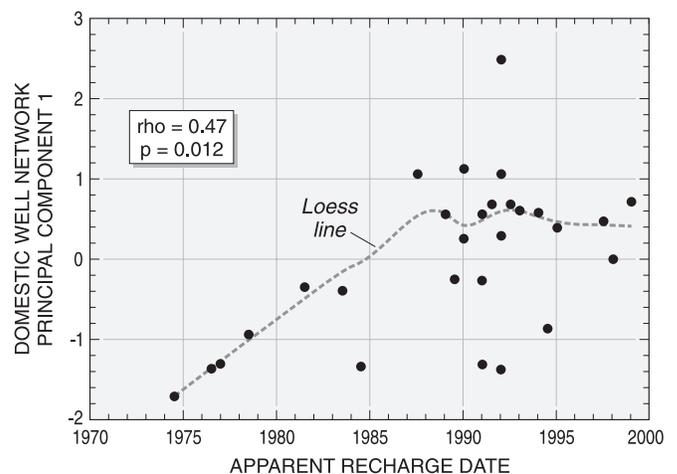
Figure 5. Relation of domestic-well principal component 1 (DOMPC1) to apparent recharge date in the deeper part of the surficial aquifer on the Delmarva Peninsula.

drainage, redox conditions, or land use suggest that many of these ions may also be derived from natural sources. As in the deeper parts of the aquifer sampled for the domestic-well network, the calcium and bicarbonate represented by AGPC1 may be derived from the dissolution of shell material in aquifer sediments; the sodium and chloride may be derived from saline intrusion (Hamilton and others, 1991).

About a quarter (25 percent) of the variability in shallow ground-water quality within agricultural areas is related to the redox condition. The second agricultural-well network principal component (AGPC2) has relatively strong positive loadings for calcium and dissolved oxygen, and relatively strong negative loadings for silica, iron, ammonia plus organic nitrogen, and sulfate (table 5), which are typical of anoxic ground water in poorly drained areas. Silica, iron, and sulfate may be derived from dissolution of minerals in estuarine or marine sediments in anoxic areas. Ammonia and organic nitrogen may be derived from natural or human sources, although these compounds would likely be converted to nitrate in the presence of dissolved oxygen. As might be expected, values of AGPC2 are highest in oxic ground water and in well-drained areas (table 5). AGPC2 is not significantly correlated with land use, apparent age, or depth.

The third factor affecting shallow ground-water quality within agricultural areas (AGPC3) of the Delmarva Peninsula may be related to the nature or intensity of agriculture. AGPC3 has relatively strong positive loadings for nitrate and dissolved oxygen, and negative loadings for pH and bicarbonate (table 5). AGPC3 is significantly correlated with agriculture, and apparently not related to urban land use (table 5). Although agricultural areas were specifically targeted in the design of the shallow well network, the areas surrounding the wells represent a range of settings, from less than 10 percent to greater than 90 percent agricultural; the other major land uses surrounding the wells are forest and wetlands. AGPC3 may represent a range of agricultural practices that affect the transport of nitrate to the surficial aquifer, as well as this range in agricultural intensity.

Nutrients in the Surficial Aquifer

Sources of nutrients in the ground-water system on the Delmarva Peninsula are both anthropogenic and natural. The major anthropogenic sources of nitrogen and phosphorus on the peninsula are inorganic fertilizer and manure applications (fig. 6). Inputs from nitrogen fertilizer applications have increased since the 1940s (fig. 4). Although data show that nutrient inputs from manure have decreased recently, they still contribute significantly to total nutrient inputs. Inputs of phosphorus from fertilizer and manure also have generally decreased in recent years (fig. 4). Other sources of phosphorus have decreased as well, such as the use of phosphate detergents and the amount of phosphorus discharged from upgraded wastewater-treatment plants (Fuhrer and others, 1999). Atmospheric deposition contributes an estimated 15 million tons of
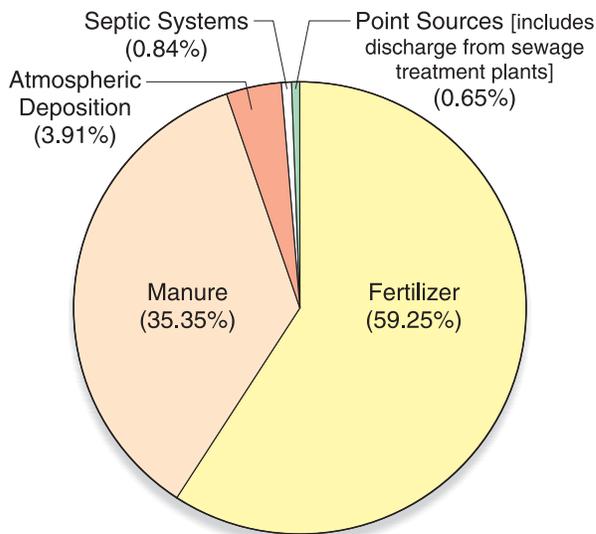
Figure 6. Estimated nitrogen sources for the Chesapeake Bay drainage area on the Delmarva Peninsula. (Data from Brakebill and Preston, 1999.)

nitrogen to Delmarva, which is less than 4 percent of the total estimated nitrogen input (National Atmospheric Deposition Program, 2003a,b). Septic systems and other point sources make up only a small percentage of the total input of nutrients on the peninsula (Brakebill and Preston, 1999).

Nitrogen

Nitrogen is applied to agricultural fields in an ammonium form in inorganic fertilizer, or in ammonium and organic forms in manure. In areas that are well-drained, most of the nitrogen present is oxidized to nitrite then rapidly to nitrate (nitrification), which is readily soluble. Excess nitrogen not taken up by plants can be leached from the soil zone into shallow ground water with infiltrating rain. Due to the rapid conversion of nitrite to nitrate, nitrite concentrations are usually negligible and nitrate is the major form of nitrogen in ground water on the peninsula (table 6). Ammonium that is not oxidized is readily adsorbed onto soil particles and generally has a low concentration in ground water. In poorly drained areas where nitrification does not occur, ammonium or organic nitrogen not held in the soil zone may be transported to ground water and are the dominant nitrogen species.

Table 6.   Summary statistics for selected nutrients in the surficial aquifer on the Delmarva Peninsula.

[mg/L, milligrams per liter; E, estimated; <, less than; N, nitrogen; P, phosphorus]

Constituent (mg/L)	Agricultural-well network			Domestic-well network		
	Minimum	Median	Maximum	Minimum	Median	Maximum
Nitrate as N[1]	<0.06	5.4	37.5	<0.05	5.5	27.2
Nitrite as N	<0.006	0.007	0.02	<0.006	<0.006	E0.043
Ammonia plus organic nitrogen as N	<0.10	<0.10	0.67	<0.10	<0.10	0.53
Ammonia as N	<0.04	<0.04	0.48	<0.04	<0.04	E0.49
Orthophosphate as P	<0.02	<0.02	0.03	<0.02	<0.02	0.18

[1] Includes nitrite.

Nitrate

Nitrate is widespread throughout the surficial aquifer on the Delmarva Peninsula. Nitrate concentrations rarely exceed 0.4 mg/L under natural conditions in ground water on the peninsula (Hamilton and others, 1993); concentrations greater than the natural background level are likely impacted by anthropogenic activity. In 2001, concentrations exceeded this level in 20 of 29 wells in both the shallow agricultural-well network and the deeper domestic-well network (fig. 7). Nitrate was not detected in the two predominantly forested reference wells.

Nitrate is the predominant nutrient detected in the surficial aquifer; median concentrations are similar in both the agricultural-well network and the domestic-well network (table 6). The median concentration was 5.4 mg/L in the 29 shallow wells beneath agricultural areas and 5.5 mg/L in the 29 wells screened in the deeper part of the surficial aquifer used for domestic water supply (fig. 8). An additional study of water from 30 public-supply wells in Delaware also showed a similar median nitrate concentration of 5.2 mg/L at greater depths in the surficial aquifer (median depth of 85 ft bls) (Ferrari, 2002). The presence of elevated nitrate concentrations at all depths of the surficial aquifer might be expected, considering that most of the water recharged the aquifer during the last 25 years (Appendix A), which is within the timeframe of consistently high nitrogen application rates on the peninsula (fig. 4).

Concentrations of nitrate were above the MCL for drinking water (10 mg/L; U.S. Environmental Protection Agency, 2004) in about one-third of the samples from both the shallow agricultural-network wells and the deeper domestic-network wells (fig. 7). Overall, the highest concentrations tended to be at the shallower depths. This pattern was also seen in a previous study on the Delmarva Peninsula in which the effects of agriculture on ground-water quality were greatest at less than 40 ft bls (Hamilton and others, 1993).
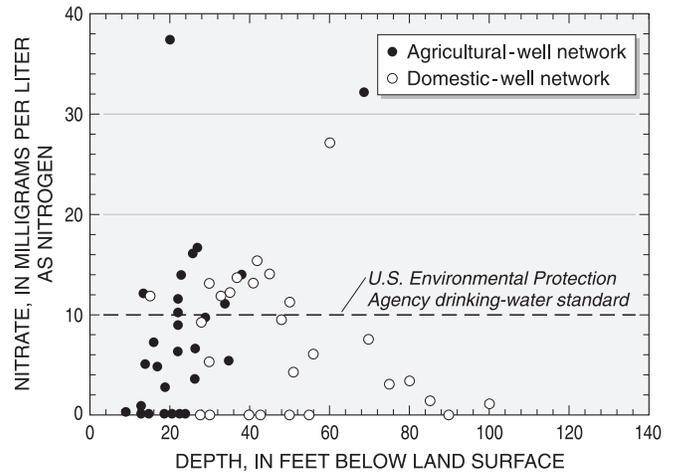
Figure 7.   Relation of nitrate concentration in ground water to sampled well depth in the surficial aquifer on the Delmarva Peninsula.

Land use and associated activities are the leading factors controlling water quality and the distribution of nitrate in the surficial aquifer on the peninsula. Nitrate concentrations are positively correlated with the percentage of agricultural land use in both the shallow and deeper parts of the surficial aquifer and negatively correlated with the percentage of forest and wetlands (table 7). In the shallower part of the surficial aquifer, represented by the agricultural-well network, nitrate concentrations also are positively correlated with depth. Elevated nitrate is present beneath other land-use settings and at all depths throughout the surficial aquifer; water recharged in upgradient agricultural areas moves horizontally along ground-water flow paths beneath forested and residential areas toward discharge areas (Denver, 1993).

EXPLANATION

- OUTLIER DATA VALUE (more than 1.5 times the IQR outside the quartile)

Data value within 1.5 times the IQR outside the quartile

INTERQUARTILE RANGE (IQR)

75th PERCENTILE (75 percent of the data values are less than this value.)

MEDIAN

25th PERCENTILE (25 percent of the data values are less than this value.)

SHALLOW GROUND WATER IN AGRICULTURAL AREAS

GROUND WATER USED FOR DOMESTIC SUPPLY

Figure 8.   Distribution of nitrate concentrations in different oxidation-reduction (redox) environments on the Delmarva Peninsula.

Median nitrate concentrations are significantly higher in oxic environments than in anoxic environments (p=0.0043 in the agricultural-well network and p=0.0004 in the domestic-well network) (fig. 8). The median concentration of nitrate is above 10 mg/L (the drinking-water standard) in the presence of dissolved oxygen in the part of the surficial aquifer used for domestic supply. In poorly drained anoxic areas, nitrate is unstable and generally denitrifies to nitrogen gas; therefore, nitrate concentrations are low and ammonia and organic nitrogen are the most common forms of nitrogen. Water withdrawn from wells may intercept both oxic and anoxic waters in different layers of aquifer sediments. As a result, some water samples with low dissolved oxygen concentrations may have high nitrate, or some waters with high dissolved oxygen concentrations may also have dissolved iron because of mixing of waters with different geochemical characteristics that are near each other in the aquifer.

Table 7.   Relation of nitrate concentrations in the surficial aquifer on the Delmarva Peninsula to potential explanatory factors.

[Analysis based on 29 samples; Rho, Spearman's rho (Helsel and Hirsch, 1992); <, less than]

Nitrate	Well network	
	Agricultural	Domestic
Correlation with well information[1]	Rho (p-value)	Rho (p-value)
Depth	**0.479 (0.009)**	-0.247 (0.197)
Apparent recharge date	0.256 (0.180)	0.235 (0.220)
Agriculture	**0.502 (0.006)**	**0.416 (0.025)**
Forest or wetlands	**-0.490 (0.007)**	**-0.515 (0.004)**
Urban	-0.042 (0.830)	0.166 (0.389)

[1] Results in **bold** where p<0.05. Relation to land use indicates correlation with percentage land use within 1,640 feet of each well.

Regionally, concentrations of nitrate in ground water are related to patterns in soil drainage that affect underlying aquifer redox conditions. The median nitrate concentration is significantly higher in the agricultural-well network below areas with well-drained soils where nitrate is stable and readily transported to the surficial aquifer than beneath areas with more poorly drained soils (fig. 9); the median concentration in well-drained soils (10.7 mg/L) is above the MCL. Overall, nitrate concentrations tend to be higher in the central uplands region of the peninsula where soils are generally well drained, agriculture is prevalent, and fertilizer use is greater than in poorly drained areas (fig. 9). Shedlock and others (1999) also found that median concentrations were significantly lower in the lowland and surficial confined regions along the fringe of the peninsula where soils are poorly drained and there is less agricultural land use. Local variability in soil drainage may explain unusually high nitrate values in poorly drained areas.

Trends in Nitrate Concentrations

Nitrate concentrations increased in oxic areas of the deeper part of the surficial aquifer used for domestic supply between 1988 and 2001 (fig. 10). Nitrate concentrations in 11 wells increased by an average of about 2 mg/L. This increase could reflect the higher amounts of nitrogen loading due to the regional increase in nitrogen fertilizer applications from the mid-to-late 1970s (represented in the areal network sampling) to the early 1990s (represented in the current resampling event). The median nitrate concentration was above the drinking water standard in oxic areas sampled in 2001 (11.4 mg/L). Although the sample size is low (a total of eight paired samples in oxic areas), the data suggest there is no
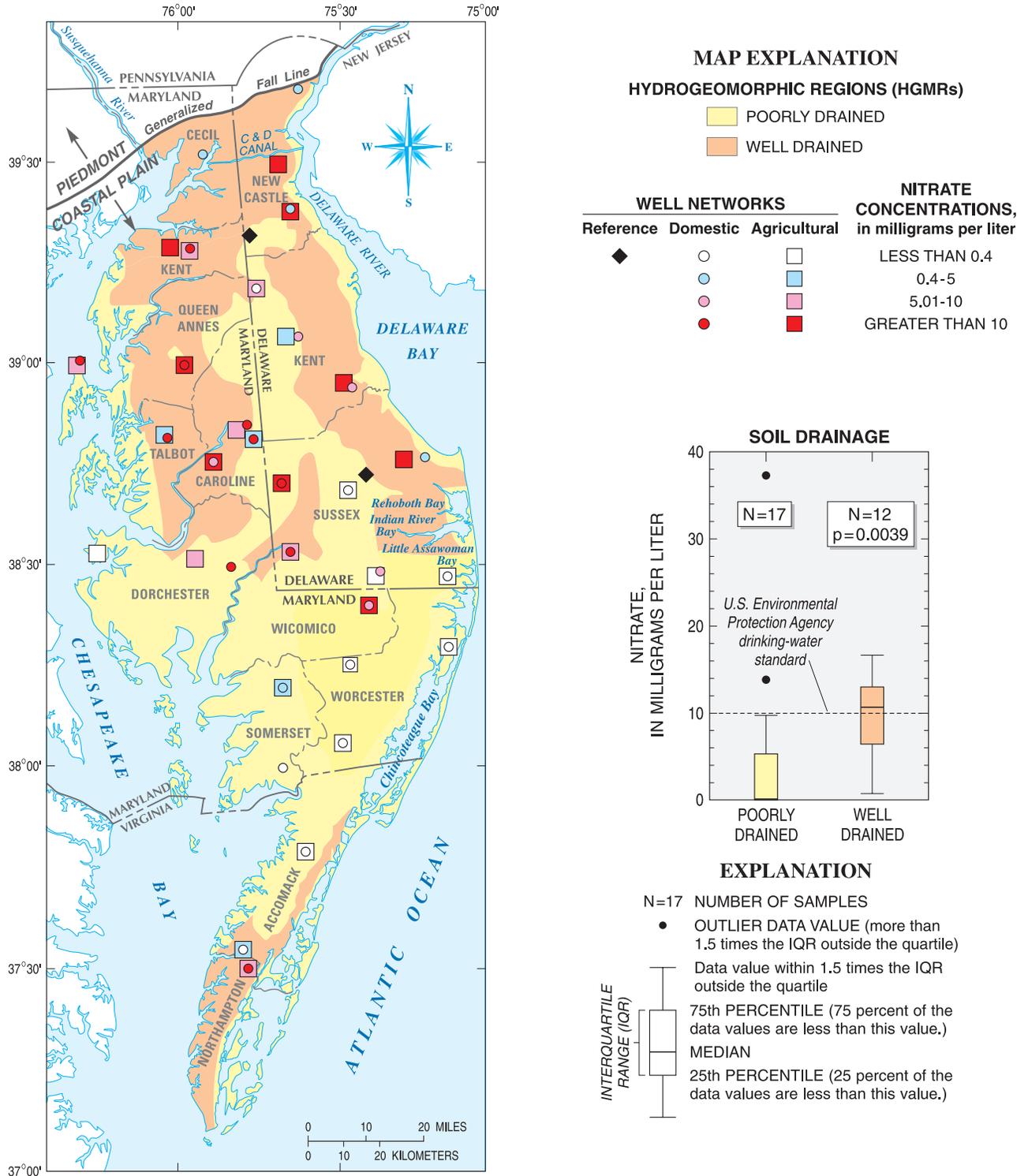
Figure 9. Soil drainage and areal distribution of nitrate concentrations in the surficial aquifer on the Delmarva Peninsula. Well drained includes well-drained uplands and inner Coastal Plain. Poorly drained includes poorly drained lowland, surficial confined region, poorly drained uplands, fine-grained lowland, and other regions (modified from Shedlock and others, 1999).
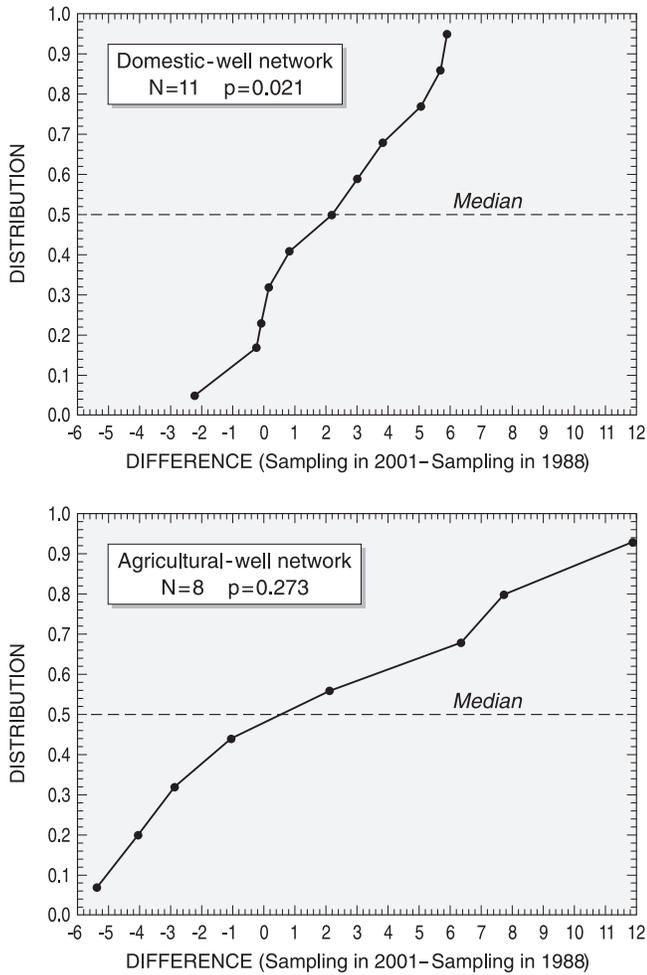
Figure 10. Distribution of measured nitrate concentrations in wells from oxic environments (dissolved oxygen greater than 1 milligram per liter) sampled in 1998 and 2001 in the domestic-well network and the agricultural-well network on the Delmarva Peninsula. Although median nitrate concentrations increased by about 2 milligrams per liter in the deeper domestic-well network, there was no significant change in the shallower agricultural-well network.

Figure 11. Distribution of ammonia plus organic nitrogen concentrations in areas of different soil drainage and dissolved oxygen concentrations in the shallow surficial aquifer on the Delmarva Peninsula. Ammonia plus organic nitrogen concentrations are greater in samples from poorly drained, oxygen-poor environments.

significant change in nitrate concentrations over time in the shallower ground water underlying agricultural areas (fig. 10). Differences in nitrate concentrations over time are small and have increased in some wells and decreased in others, which may reflect more recent local variations in nitrogen use for corn and soybean crops. Nitrate concentrations are consistently low in anoxic areas throughout the surficial aquifer.

Ammonia and Organic Nitrogen

Concentrations of ammonia and organic nitrogen are relatively low in the surficial aquifer (median less than 0.1, the laboratory reporting level) (table 6), although ammonia and organic nitrogen are the dominant forms of nitrogen in poorly drained, anoxic environments. In the shallow agricultural-well network, concentrations are higher in poorly drained, anoxic environments (p=0.012 and p=0.001, respectively) (fig. 11). Ammonia and organic nitrogen concentrations are negatively correlated with depth in the shallower part of the aquifer (table 8, fig. 12). This pattern may reflect the relatively shallow water table in poorly drained anoxic areas, where ammonia and organic nitrogen are more likely to be present than in well-drained oxygenated areas.

Table 8. Relation of ammonia plus organic nitrogen concentrations in the surficial aquifer on the Delmarva Peninsula to potential explanatory factors.

[Analysis based on 29 samples; Rho, Spearman's rho (Helsel and Hirsch, 1992); <, less than]

Nitrate	Well network	
	Agricultural	Domestic
Correlation with well information[1]	Rho (p-value)	Rho (p-value)
Depth	**-0.502 (0.006)**	-0.0003 (0.999)
Apparent recharge date	0.073 (0.707)	-0.305 (0.108)
Agriculture	**-0.393 (0.035)**	-0.191 (0.322)
Forest or wetlands	0.351 (0.062)	0.179 (0.352)
Urban	0.023 (0.906)	-0.171 (0.377)

[1] Results in **bold** where p<0.05. Relation to land use indicates correlation with percentage land use within 1,640 feet of each well.
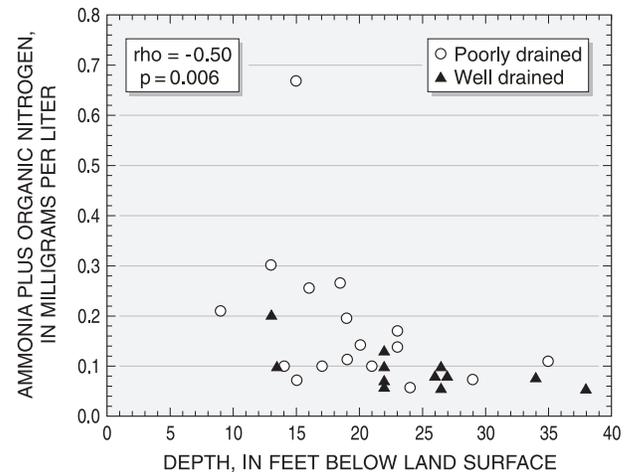

Figure 12. Relation of ammonia plus organic nitrogen concentrations in ground water to sampled well depth in the shallow agricultural-well network on the Delmarva Peninsula.

Phosphorus

Phosphorus concentrations are relatively low throughout the surficial aquifer on the peninsula; median concentrations are below the laboratory reporting level (0.02 mg/L) in the shallow agricultural-network wells and in the domestic-network wells (table 6). Concentrations exceed 0.1 mg/L in only three wells in the deeper network; dissolved oxygen is low or absent in samples from these wells.

Pesticides in the Surficial Aquifer

Pesticide compounds are used for agricultural and non-agricultural purposes on the Delmarva Peninsula. Agricultural uses of pesticides are predominantly for weed and insect control. Non-agricultural uses include turf maintenance on residential, commercial, and recreational areas; insect control for residential and commercial structures; and vegetative clearing along transportation and utility rights-of-way (Barbash and Resek, 1996).

In 1997, 151 different pesticide compounds were applied to crops on the Delmarva Peninsula, representing over 3.8 million pounds of active ingredient (Gail Thelin, U.S. Geological Survey, written commun., 2002). Over 70 percent of the pesticide compounds were herbicides used for crop production. Metolachlor, atrazine, glyphosate, and alachlor are the four most widely used agricultural herbicides; methyl bromide is widely used as a soil fumigant on the Virginia part of the Delmarva Peninsula (fig. 13, table 9). All of the pesticides commonly used on the peninsula were not included in chemical analyses done for this study (Appendix C).

Pesticide compounds were detected at low levels throughout the surficial aquifer on the Delmarva Peninsula. Detectable concentrations of pesticides or their degradates (see inset, next page) were found in 93 percent of the shallow agricultural wells and in over 83 percent of the deeper domestic wells; no pesticide residue was detected in the two reference wells (fig. 14, table 10). Metolachlor and atrazine, which have been used for over 25 years, were the most commonly detected parent pesticide compounds in the surficial aquifer. Several relatively new herbicides (flumetsulam, imazaquin, imazethapyr, and glyphosate) also were detected, but less frequently. Degradates of several pesticides, including metolachlor, alachlor, and atrazine, were among the most frequently detected compounds (table 10). Widespread detection of pesticide compounds reflects their abundant use on the peninsula as well as chemical properties (moderate to high water solubility; persistence) and the aquifer characteristics (good soil drainage) that promote movement into ground water (table 11). Concentrations were typically low (below 1 μg/L) and were always below established drinking-water standards and health advisory levels (HALs). Such guidelines have been established for only 14 of the 36 compounds detected, however (table 10).
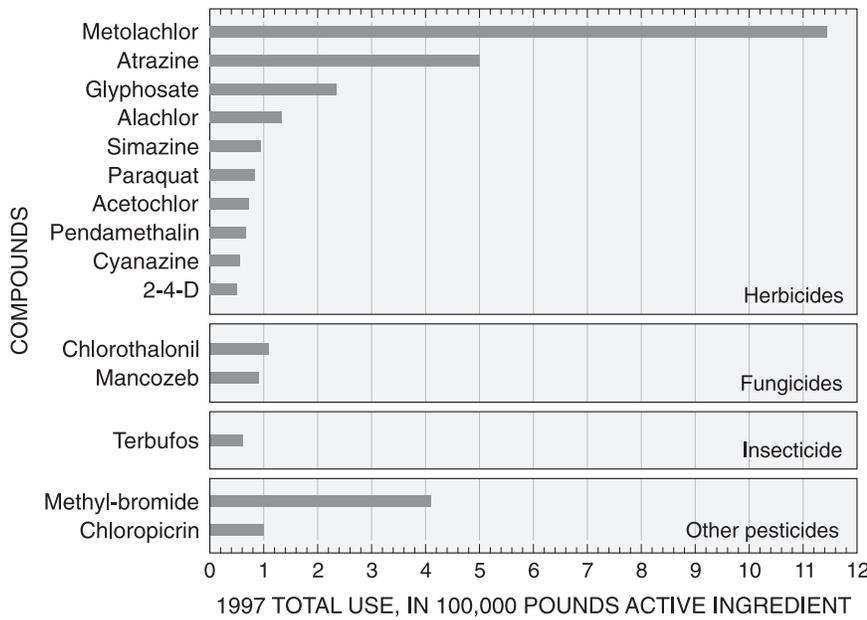
Figure 13. Estimated agricultural pesticide use on the Delmarva Peninsula, 1997. (Data from Gail Thelin, U.S. Geological Survey, written commun., 2002.)

PESTICIDE DEGRADATION PRODUCTS

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 zones, 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 chlorine with a sulfonic acid or carboxylic acid group (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 they may persist for years. Some may be bound and retained in the soil, whereas others may be more soluble and move easily through ground water. 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). Atrazine has four major degradates, the most common of which is deethylatrazine. There are many more degradates of these and other pesticides for which analytical techniques have not yet been developed.

Of the other commonly applied pesticides, glyphosate was rarely detected and methyl bromide was not detected in the surficial aquifer (only samples from the domestic-well network were tested for methyl bromide). Low detection frequencies for glyphosate might be expected as glyphosate has only been used since 1986 and chemical properties indicate that it strongly adsorbs to most soils and suspended organic and mineral matter in the aquifer (table 9). Methyl bromide is rarely detected in ground water across the Nation; it was only detected in 2 wells out of over 20,000 sampled between 1971 and 1991 (Barbash and Resek, 1996).

Metolachlor, alachlor, and atrazine compounds primarily occurred in ground water in the form of degradation products. Degradates of these pesticides were typically detected more frequently and at higher concentrations than their parent compounds in both the agricultural-well network and the domestic-well network (table 10, fig. 15). The median concentration of the ethanesulfonic acid (ESA) degradation product for metolachlor and alachlor was at least one order of magnitude higher then their parent compounds in both well networks. Alachlor oxanilic acid (OA), 2,6-Diethylaniline, and metolachlor OA also were detected but much less frequently. Alachlor and metolachlor are typical of many pesticides in that they tend to adsorb onto organic matter and quickly degrade in the soil zone, restricting movement of the parent compound into ground water. ESA and OA degradates are more soluble than the parent compounds and more likely to move into ground water (Phillips and others, 1999). Acetochlor ESA was also detected in both well networks, although its parent compound, acetochlor, was not; acetechlor has only been in use since 1994 (Meister, 2000). A relatively low amount of acetochlor was applied to corn on the Delmarva Peninsula in

Table 9. Description of commonly used and frequently detected pesticide compounds on the Delmarva Peninsula.

[USEPA, U.S. Environmental Protection Agency; ESA, ethanesulfonic acid; OA, oxanilic acid]

Compound	Use	Properties	Common degradates	Trends[1]
Metolachlor	First registered for use in the United States in 1976; broad-spectrum herbicide; used for weed control primarily in agricultural areas, on lawn and turf, ornamental plants, trees, shrubs and vines, rights-of-way, fencerows and hedgerows, and in forestry (USEPA, 1995)	Moderately persistent in soil, moderately soluble and highly persistent in water, and degrades mainly by microbial activity (Extension Toxicity Network, 1996a)	Metolachlor ESA and metolachlor OA	Between 1992 and 1997, use increased nationally by 13 percent.
Atrazine	First registered for use in the United States in 1958 (USEPA, 2003); restricted use in United States as of 1990 (Briggs, 1992); selective herbicide; used for weed control	Highly persistent in soils with low clay or organic matter; moderately to highly mobile in soils; moderately soluble in water; and degrades by chemical hydrolysis and microbial activity (Extension Toxicity Network, 1996b)	Deethylatrazine (DEA), deisopropylatrazine (DIA), deethyldeisopropylatrazine, and hydroxyatrazine	Between 1992 and 1997, use increased nationally by 3 percent.
Glyphosate	First registered for use in the United States in 1986; broad-spectrum, non-selective herbicide; used on a wide range of agricultural crops and non-crop areas where total vegetation control is needed (USEPA, 1993)	Moderately persistent in soils; strongly adsorbs to most soils, resulting in a low runoff potential; strongly adsorbed to suspended organic and mineral matter in water (Extension Toxicity Network, 1996c)	Aminomethylphosphonic acid (AMPA)	Between 1992 and 1997, use increased nationally by 107 percent.
Alachlor	First registered for use in the United States in 1969; highly restricted since 1988 and has been slowly replaced with acetochlor since 1994; selective systemic herbicide; used to control annual grasses and broadleaf weeds in corn and soybeans (USEPA, 1998; Extension Toxicity Network, 1996d)	Low persistence in soil; moderately mobile in sandy and silty soils, highly mobile and moderately persistent in water; breaks down rapidly in natural water; the degradation rate is slower in anoxic waters; degrades by microbial activity (USEPA, 1998; Extension Toxicity Network, 1996d)	Alachlor ESA, 2,6-Diethylaniline, and alachlor OA	Between 1992 and 1997, use decreased nationally by 71 percent.
Methyl bromide	Production will be eliminated by 2005; used as a soil fumigant to control nematodes, fungi, pathogens, insects, and weeds (Carpenter and others, 2000, USEPA, 2000)	Moderately persistent in soils; poorly sorbed by soils; slightly soluble in water (Extension Toxicity Network, 1996e)	Bromide ion	Between 1992 and 1997, use decreased nationally by 26 percent.

[1] Gianessi and Silvers, 2000.
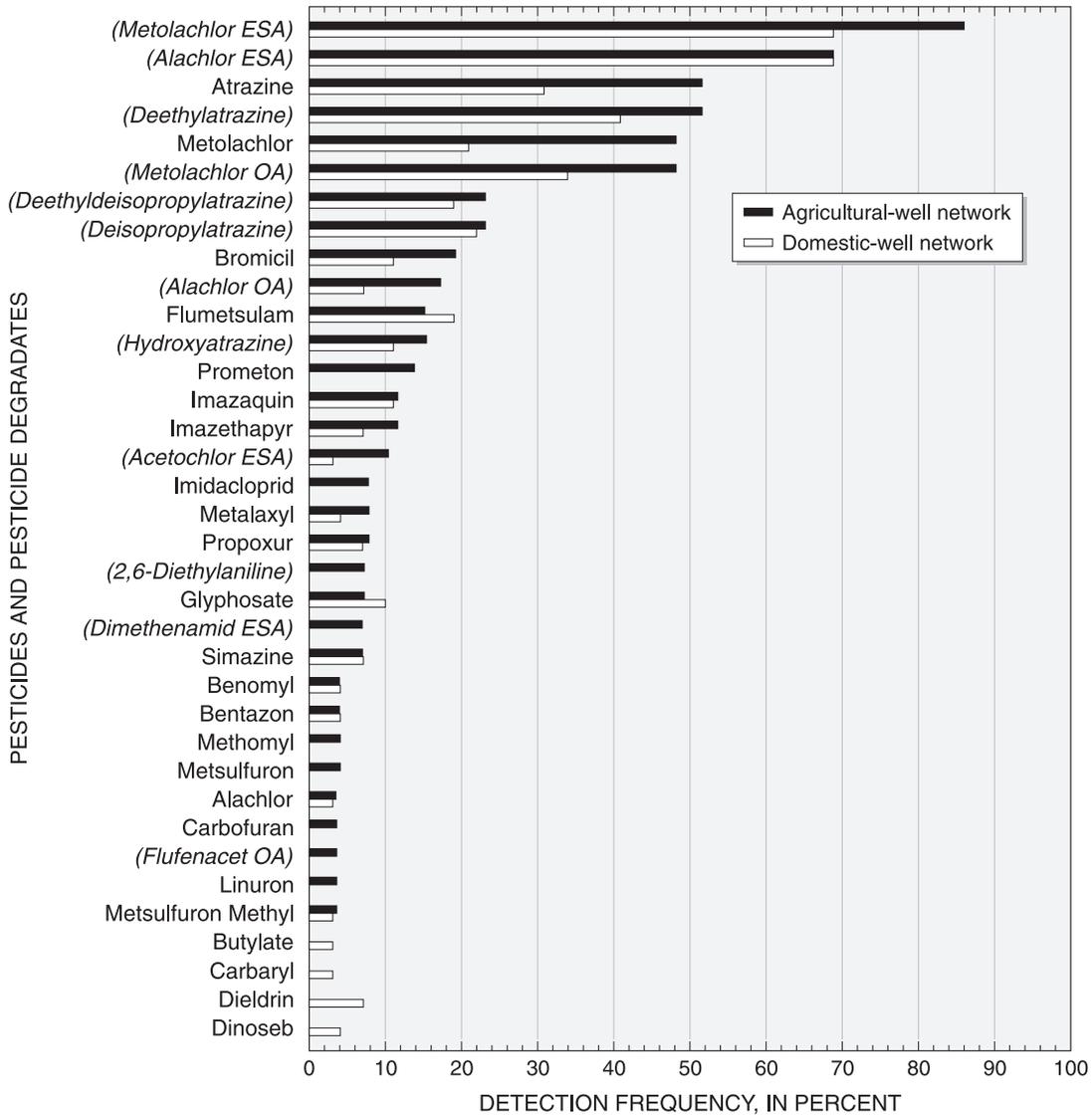
Figure 14.   Occurrence of pesticides and pesticide degradates (shown in italics and parentheses) in the surficial aquifer on the Delmarva Peninsula. (Analytical reporting levels vary among compounds and are shown in Appendix C.)

Table 10. Summary of analytical results for selected pesticides and degradates in samples from the surficial aquifer on the Delmarva Peninsula in 2001.

[n, number of samples; μg/L, micrograms per liter; %, percent; MCL, maximum contaminant level; HAL, health advisory level; E, estimated; <, less than]

Compound[1]	Use	Detection limit[1] (μg/L)	n	Per-cent detection (%)	Concentration (μg/L) Median	Concentration (μg/L) Maximum	Drinking-water standard[2] (μg/L) MCL or (HAL)
				Agricultural-well network			
Metolachlor ESA	Herbicide degradate (metolachlor)	*0.05*	29	86	1.34	35	
Alachlor ESA	Herbicide degradate (alachlor)	*0.05*	29	69	0.17	5.54	
Deethylatrazine	Herbicide degradate (atrazine)	*0.006*	29	48	<0.006	E0.413	
Atrazine	Herbicide	0.007	29	48	<0.007	0.657	3
Metolachlor OA	Herbicide degradate (metolachlor)	*0.05*	29	48	<0.05	19	
Metolachlor	Herbicide	0.013	29	45	<0.013	2.43	(100)
Deethyldeisopropylatrazine	Herbicide degradate (atrazine)	*0.01*	26	21	<0.01	E0.5758	
Deisopropylatrazine	Herbicide degradate (atrazine, cyanazine, simazine)	*0.044*	26	21	<0.044	E0.0844	
Bromacil	Herbicide	0.033	26	18	<0.033	E2.5242	(90)
Alachlor OA	Herbicide degradate (alachlor)	*0.05*	29	17	<0.05	3.48	
Hydroxyatrazine	Herbicide degradate (atrazine)	*0.008*	26	15	<0.008	E0.0971	
Flumetsulam	Herbicide	0.011	26	14	<0.011	E0.075	
Prometon	Herbicide	0.015	29	13	<0.015	0.0206	(100)
Imazaquin	Herbicide	0.016	26	11	<0.016	E0.0975	
Imazethapyr	Herbicide	0.017	26	11	<0.017	E0.0609	
Acetochlor ESA	Herbicide degradate (acetochlor)	*0.05*	29	10	<0.05	0.88	
Imidacloprid	Insecticide	0.0068	26	7	<0.0068	0.2236	
Glyphosate	Herbicide	0.1	28	7	<0.1	0.16	700
Metalaxyl	Fungicide	0.02	26	7	<0.02	0.0208	
Propoxur	Insecticide	0.008	26	7	<0.008	0.0103	
Dimethenamid ESA	Herbicide degradate (dimethenamid)	*0.05*	29	7	<0.05	0.1	
2,6-Diethylaniline	Herbicide degradate (alachlor)	*0.006*	28	7	<0.006	<0.006	
Simazine	Herbicide	0.011	29	6	<0.011	<0.011	4
Methomyl	Insecticide	0.0044	26	4	<0.0044	E0.2485	(200)
Metsulfuron methyl	Herbicide	0.025	26	4	<0.025	<0.025	
Linuron	Herbicide	0.035	29	3	<0.035	<0.035	
Carbofuran	Insecticide/nomatocide	0.02	29	3	<0.02	<0.02	40
Bentazon	Herbicide	0.011	26	4	<0.011	<0.011	(200)
Benomyl	Fungicide	0.0038	26	4	<0.0038	0.0671	
Flufenacet OA	Herbicide degradate (flufenacet)	*0.05*	29	3	<0.05	0.07	
Metribuzin	Herbicide	0.006	29	3	<0.006	0.763	(200)
Alachlor	Herbicide	0.0045	29	3	<0.0045	0.0407	2

Table 10. Summary of analytical results for selected pesticides and degradates in samples from the surficial aquifer on the Delmarva Peninsula in 2001.—Continued

[n, number of samples; μg/L, micrograms per liter; %, percent; MCL, maximum contaminant level; HAL, health advisory level; E, estimated; <, less than]

Compound[1]	Use	Detection limit[1] (μg/L)	n	Per-cent detec-tion (%)	Concentration (μg/L) Median	Concentration (μg/L) Maximum	Drinking-water standard[2] (μg/L) MCL or (HAL)
		Domestic-well network					
Metolachlor ESA	Herbicide degradate (metolachlor)	*0.05*	29	69	0.12	15	
Alachlor ESA	Herbicide degradate (alachlor)	*0.05*	29	69	0.16	4.82	
Deethylatrazine	Herbicide degradate (atrazine)	*0.006*	29	41	<0.006	E0.186	
Metolachlor OA	Herbicide degradate (metolachlor)	*0.05*	29	34	<0.05	4.85	
Atrazine	Herbicide	0.007	29	31	<0.007	0.163	3
Deisopropylatrazine	Herbicide degradate (atrazine, cyanazine, simazine)	*0.044*	27	22	<0.044	E0.0941	
Metolachlor	Herbicide	0.013	29	21	<0.013	0.735	(100)
Deethyldeisopropylatrazine	Herbicide degradate (atrazine)	*0.01*	27	19	<0.01	E0.1556	
Flumetsulam	Herbicide	0.011	27	19	<0.011	E0.0257	
Bromacil	Herbicide	0.033	27	11	<0.033	E0.2149	(90)
Hydroxyatrazine	Herbicide degradate (atrazine)	*0.008*	27	11	<0.008	E0.057	
Imazaquin	Herbicide	0.016	27	11	<0.016	E0.019	
Glyphosate	Herbicide	0.1	29	10	<0.1	0.14	700
Imazethapyr	Herbicide	0.017	27	7	<0.017	E0.1557	
Propoxur	Insecticide	0.008	27	7	<0.008	0.041	
Alachlor OA	Herbicide degradate (alachlor)	*0.05*	29	7	<0.05	2.2	
Simazine	Herbicide	0.011	29	7	<0.011	0.0497	4
Dieldrin	Insecticide	0.0048	29	7	<0.0048	0.0052	
Bentazon	Herbicide	0.011	27	4	<0.011	E0.0155	(200)
Dinoseb	Herbicide	0.012	27	4	<0.012	<0.012	7
Metalaxyl	Fungicide	0.02	27	4	<0.02	<0.02	
Carbaryl	Insecticide	0.041	29	3	<0.041	<0.041	(700)
Benomyl	Fungicide	0.0038	27	4	<0.0038	0.0065	
Acetochlor ESA	Herbicide degradate (acetochlor)	*0.05*	29	3	<0.05	1.1	
Alachlor	Herbicide	0.0024	29	3	<0.0024	0.223	2
Metribuzin	Herbicide	0.006	29	3	<0.006	0.119	(200)
Butylate	Herbicide	0.002	29	3	<0.002	0.0032	(400)

[1] *Italics* represent pesticide degradation products.

[2] U.S. Environmental Protection Agency, 2004; not all compounds have an MCL or HAL.

Table 11. Physical and chemical characteristics of commonly used pesticides on the Delmarva Peninsula.

[Values for persistence from Rao and Hornsby, 1989, and CambridgeSoft Corporation, 2004; Values for solubility and sorption from CambridgeSoft Corporation, 2004, and U.S. Department of Agriculture, 1995; $T_{1/2}$, half life; ppm, parts per million; ºC, degrees Celsius; K_{oc}, adsorption to soil organic matter; mL/g, milliliters per gram]

Compound	Persistence ($T_{1/2}$, days)	Solubility in water (ppm at 25ºC)	Sorption (K_{oc}, mL/g)
Metolachlor	15–90	530[a]	200
Alachlor	15–70	240	170
Atrazine	60–365	33	100
Glyphosate	47	12,000	24,000
Methyl bromide	55	13,400	22

[a] 20ºC.

Figure 15. Distribution of selected pesticides and pesticide degradates in the surficial aquifer on the Delmarva Peninsula. Degradates generally occur at higher concentrations than their parent compounds.

1997 (fig. 13). Acetochlor use is increasing, however, as it is being used to replace alachlor. Atrazine was detected almost as frequently and at similar concentrations as deethylatrazine in both well networks (table 10, fig. 15). Additional degradation products of atrazine (deethyldeisopropylatrazine, deisopropylatrazine, and hydroxyatrazine) also were detected in at least 15 percent of the agricultural-network wells and at least 11 percent of the domestic-network wells. A combination of relatively high mobility and chemical stability in the soil zone allows atrazine to move to, and persist in, the ground-water system longer than metolachlor or alachlor, which tend to break down more completely to degradates before reaching the ground-water system (table 11) (Denver and others, 2004). Atrazine likely degrades into other unmeasured compounds as well.

Although the parent compounds were not analyzed at the laboratory, degradation products of dimethenamid and flufenacet, herbicides used on corn and soybean crops, also were detected in the shallower agricultural-well network (table 10, fig. 14). Dimethenamid has been in use in the United States since 1993 and was the 16th most commonly used pesticide on the peninsula in 1997; flufenacet has only been in use in the United States since 1998, and use data are not available (Scribner and others, 2004).

Mixtures of pesticide compounds are commonly found in individual water samples throughout the surficial aquifer. Pesticides are frequently used in combination on crops for better control (U.S. Department of Agriculture, 1999). In addition, because of crop rotation, different chemicals are used in sequential years. Most wells sampled in the agricultural-well network (90 percent) and the domestic-well network (69 percent) contained 3 or more compounds; as many as 11

compounds were detected in several wells. The combined toxicity or synergistic effects of multiple pesticide compounds in a sample are currently unknown.

Concentrations of commonly used herbicides are related to agricultural land use and aquifer redox conditions on the Delmarva Peninsula. Analysis of total concentrations (sum of parent and degradates) of atrazine and metolachlor indicates that although pesticide and degradate compounds are detected in wells surrounded by all land-use settings throughout the peninsula, pesticide concentrations are positively correlated with the percentage of agricultural land use and are present at significantly higher concentrations in oxic environments (table 12). Pesticide concentrations are influenced by the drainage characteristics of overlying soil at shallow depths

Table 12.   Correlation of total atrazine and total metolachlor for shallow ground water beneath agricultural areas and deeper ground water representing domestic supply on the Delmarva Peninsula.

[Total concentrations are parent compound plus degradation products in molar units; Rho, Spearman's rho (Helsel and Hirsch, 1992); oxic, oxidizing conditions (dissolved oxygen greater than 1 milligram per liter); well, well-drained; NA, not applicable; <, less than]

Atrazine	Well network	
	Agricultural	Domestic
Correlation with well information[1]	Rho (p-value)	Rho (p-value)
Depth	0.334 (0.077)	-0.214 (0.266)
Apparent recharge date	**0.415 (0.025)**	**0.380 (0.042)**
Agriculture	**0.705 (<.001)**	**0.554 (0.002)**
Forest or wetlands	**-0.596 (0.001)**	**-0.564 (0.001)**
Urban	0.022 (0.909)	0.129 (0.504)
Comparison among areas with different:[1]	Rank-sum p-value (High group)	Rank-sum p-value (High group)
Redox conditions[2]	**0.005 (oxic)**	**0.001 (oxic)**
Soil drainage[3]	**0.002 (well)**	0.065 (NA)

Metolachlor	Well network	
	Agricultural	Domestic
Correlation with well information[1]	Rho (p-value)	Rho (p-value)
Depth	0.308 (0.104)	**-0.475 (0.009)**
Apparent recharge date	0.076 (0.693)	0.317 (0.094)
Agriculture	**0.689 (<.001)**	**0.545 (0.002)**
Forest or wetlands	**-0.634 (0.001)**	**-0.485 (0.008)**
Urban	0.098 (0.614)	0.123 (0.526)
Comparison among areas with different:[1]	Rank-sum p-value (High group)	Rank-sum p-value (High group)
Redox conditions[2]	**0.001 (oxic)**	**0.026 (oxic)**
Soil drainage[3]	**0.015 (well)**	0.503 (NA)

[1] Results in **bold** where p<0.05. Relation to land use indicates correlation with percentage land use within 1,640 feet of each well.

[2] Represents oxidation-reduction conditions in the surficial aquifer.

[3] Represents well-drained and poorly drained soil conditions.

in the surficial aquifer (represented by the agricultural-well network); total concentrations tend to be higher in well-drained areas (fig. 16, table 12). Despite the fact that both metolachlor and atrazine compounds occurred at all depths, total metolachlor did not occur below 60 ft in the domestic-well network (fig. 17). Total atrazine concentrations tend to be higher in younger water throughout the surficial aquifer (fig. 18).

Trends in Pesticide Detections

Temporal trends in pesticide concentrations from 1988 to 2001 in the surficial aquifer are difficult to determine due to changes in sampling and analytical procedures during the intervening years. Analytical procedures greatly improved during the 1990s, and method reporting levels decreased by as much as two orders of magnitude for some compounds (Wershaw and others, 1987; Zaugg and others, 1995; Furlong and others, 2001). Also, only whole-water (unfiltered) samples were analyzed prior to the early 1990s, and the suite of compounds was relatively small. These factors, along with inconsistent usage from year to year, make analysis of environmental trends difficult. Five pesticides were detected from 21 compounds analyzed in 1988: atrazine, metolachlor, alachlor, cyanazine, and dicamba (table 13, Appendix D). Alachlor and cyanazine were not detected in the same wells in 2001, in spite of lower laboratory reporting levels; dicamba also was not detected in the same wells in 2001, but the reporting level increased slightly. The wells that contained atrazine and metolachlor in 1988 also contained these compounds in 2001. Increased frequency of detection of pesticide compounds in the more recent samples is more likely due to better method sensitivities than to increases in pesticide concentrations over time. Pesticide concentrations remained low throughout the surficial aquifer.
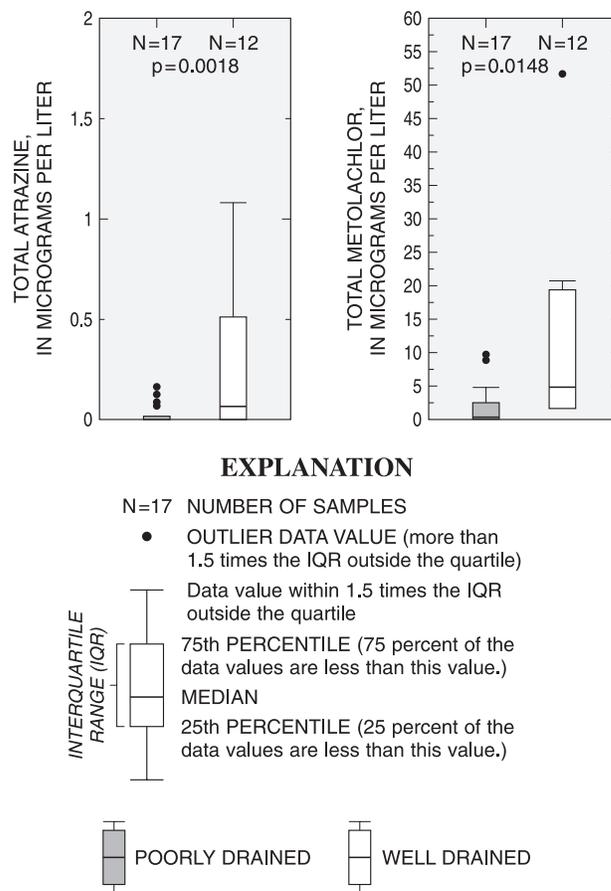
Figure 16. Distribution of selected pesticides in areas with different soil drainage in the agricultural-well network on the Delmarva Peninsula. Concentrations tend to be higher in well-drained soils. (Total atrazine refers to the sum of atrazine, deethylatrazine, hydroxyatrazine, deisopropylatrazine, and deethyldeisopropylatrazine. Total metolachlor refers to the sum of metolachlor, metolachlor ESA, and metolachlor OA. Molar sums were converted to micrograms per liter of parent compound.)
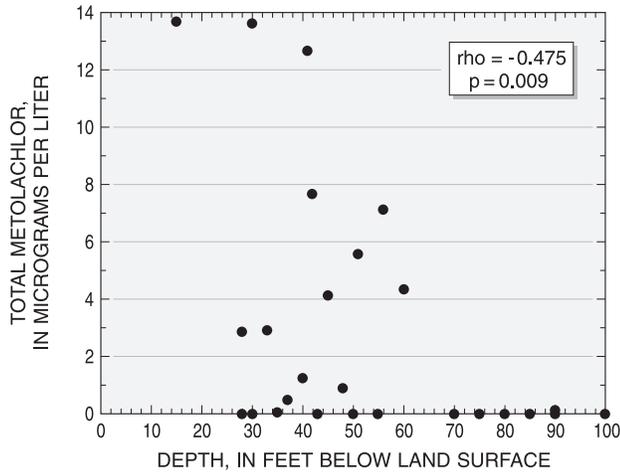
Figure 17.   Relation of total metolachlor concentrations to sampled well depth in the domestic-well network on the Delmarva Peninsula.
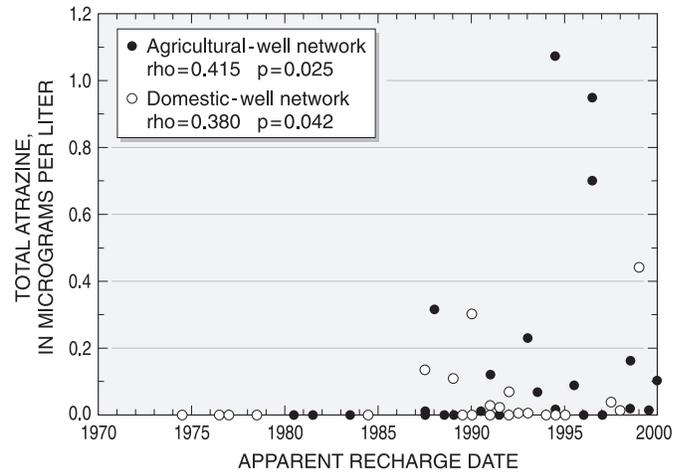
Figure 18.   Relation of total atrazine concentrations to apparent recharge date in the surficial aquifer on the Delmarva Peninsula. Concentrations tend to be higher in more recently recharged ground water.

Table 13.   Pesticide detection frequency in the areal-network wells sampled in 1988 on the Delmarva Peninsula.

[µg/L, micrograms per liter; %, percent; MCL, maximum contaminant level; HAL, health advisory level]

Compound (unfiltered)	Use	Detection limit (µg/L)	Percent detection (%)	Maximum concentration (µg/L)	Drinking-water standard[1] (µg/L) MCL or (HAL)
Agricultural-well network					
Atrazine	Herbicide	0.05	20	0.8	3
Metolachlor	Herbicide	0.15	13	0.8	(100)
Alachlor	Herbicide	0.15	7	2.0	2
Cyanazine	Herbicide	0.05	7	0.10	
Domestic-well network					
Dicamba	Herbicide	0.01	4	0.01	

[1] U.S. Environmental Protection Agency, 2004; not all compounds have an MCL or HAL.

Summary and Conclusions

Human influences are apparent in shallow ground water underlying agricultural areas as well as in deeper water used for domestic supply in the unconsolidated surficial aquifer on the Delmarva Peninsula. Dissolved constituents found throughout the unconfined aquifer are likely derived from the predominantly agricultural practices on the peninsula. In water affected by agriculture, calcium and magnesium were present from the application of lime, potassium and chloride from potash fertilizer, and nitrate from inorganic fertilizer and manure. Septic-system effluent may contribute sodium, chloride, and nitrate to ground water, although the part of the aquifer affected by septic-system effluent is likely very small relative to that affected by agriculture because of the differences in the magnitude of residential and agricultural land use. Sodium and chloride from road salt were also present in some water samples. Principal-components analysis suggests that in the deeper parts of the surficial aquifer used for domestic drinking water, the major sources of ions in ground water are anthropogenic and are primarily related to agricultural land use. Ions from other sources, including the dissolution of shells and iron minerals in the sediments and seawater intrusion, also are important, particularly in nonagricultural areas and along the coasts. Even though ions from natural sources dominate in some areas, only 5 percent of the ground-water samples collected for this study could be classified as natural and did not show some degree of anthropogenic influence.

Nitrate was widespread throughout ground water in the surficial aquifer on the Delmarva Peninsula and was the predominant nutrient detected; median concentrations were similar in both the agricultural-well network and the domestic-well network. The statistical distribution of nitrate concentrations in the surficial aquifer was nearly identical in the regional agricultural- and domestic-well networks as well as in the deeper Delaware public-supply well network (medians from 5.2 to 5.5 milligrams per liter). Nitrate was detected above the Maximum Contaminant Level (10 milligrams per liter) in about one-third of the samples from both the shallower agricultural-well network and the deeper domestic-well network. Concentrations of nitrate in ground water are not related to recharge date of the water, indicating that the entire flow system in the surficial aquifer has potentially been affected by human activities on and near the land surface. This is anticipated because nutrient inputs have been relatively high over the 35-year period during which most water currently in the surficial aquifer was recharged.

Pesticide compounds were detected at low levels throughout the surficial aquifer. Pesticides were present in 85 percent of the ground-water samples collected from the surficial aquifer for this study. Widespread detection reflects the abundant use of pesticide compounds as well as chemical properties and aquifer characteristics that allow their movement into ground water. Metolachlor, alachlor,

and atrazine and their degradates were the most commonly detected pesticide compounds. For pesticides with degradate analyses, degradation products typically were detected more frequently and at higher concentrations than parent compounds throughout the surficial aquifer. Pesticide mixtures also were common throughout the aquifer and most wells contained three or more compounds. As many as 11 different pesticide compounds were detected in several wells, representing the mix of chemicals used on the land surface.

In addition to chemical properties and aquifer characteristics, factors affecting spatial trends in ground-water quality also include natural geochemical conditions and land-use practices. Redox conditions and soil drainage affect the occurrence of nitrate and pesticides in the surficial aquifer. Geochemical transformations within the aquifer are largely controlled by the availability of dissolved oxygen. Nitrate concentrations were typically higher in oxic environments where nitrate is stable; nitrate is unstable and denitrifies in poorly drained, anoxic environments where ammonia and organic nitrogen become the dominant forms of nitrogen. As most of the surficial aquifer is under oxidizing conditions, little nitrate is removed along ground-water flow paths in the surficial aquifer. Concentrations of nitrate beneath nonagricultural land-use settings may be the result of upgradient agriculturally influenced ground water moving along deeper flow paths toward discharge areas. Pesticide concentrations in the surficial aquifer also tend to be higher beneath recharge areas with well-drained soils in the shallow part of the aquifer and in oxic environments throughout the surficial aquifer. Concentrations of nitrate and pesticides were significantly higher in the central uplands of the peninsula, which have generally well-drained soils and oxidizing aquifer conditions, and where most of the agricultural land is located.

Implementation of agricultural management practices over the past few decades may explain why there is no increase in nitrate concentrations in the shallow part of the aquifer underlying agricultural areas. Decreases in nitrate concentrations resulting from improved nutrient management practices may not be apparent in the deeper part of the surficial aquifer for years or decades due to the relatively slow movement of ground water. Results indicate that nitrate concentrations in oxic areas have increased approximately 2 milligrams per liter over the past decade in the deeper surficial aquifer; in 2001, the median nitrate concentration in this part of the aquifer was above the Maximum Contaminant Level of 10 milligrams per liter.

Temporal trends in pesticide detections are difficult to determine from the available data. Wells that contained atrazine and metolachlor in 1988 also contained these compounds in 2001. Overall, pesticides were more frequently detected in 2001 than in 1988; however, the increased frequency of detection in the more recent samples is likely due to lower detection levels rather than to increases in pesticide concentrations over time.

Degraded ground-water quality may have considerable implications for water supply and for the health of Delmarva

streams and adjacent estuaries. Nitrate concentrations above the Maximum Contaminant Level in parts of the aquifer used for domestic-water supply may be a concern as private domestic wells are not commonly subject to water-quality testing. Streams on the peninsula receive over half of their flow from ground-water discharge and the chemical composition of stream base flow on the Delmarva Peninsula is similar to that of shallow ground water. The dominant source of nitrogen discharged to the Chesapeake Bay and its tidal tributaries is from ground water. Excessive levels of nutrients (such as the nitrate contributed from ground water) in streams can lead to eutrophication (blooms of algae and other plants) and hypoxia (areas of low dissolved oxygen), resulting in fishkills and loss of other living resources. Pesticides also are common in parts of the aquifer used for domestic supply. Although pesticide detections are almost always lower than existing standards for drinking water, many pesticide compounds, including most degradation products, have as yet unknown health implications. In addition, the additive and synergistic effects of ingesting multiple pesticide compounds are unknown. Pesticides also have been measured in stream base flow; these and other organic chemicals in stream water also are of concern because of their potential toxic effects on aquatic biota.

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Appendix A.   Site information for wells sampled in the surficial aquifer on the Delmarva Peninsula.

[Wells in **bold** are trend wells sampled both in 1988 and 2001; bls, below land surface]

Well name	Well depth (ft bls)	Use of well	Recharge date	Land use[1]			
				Agriculture	Forest-wetland	Open water	Urban[2]
Agricultural-well network (median depth 22 feet below land surface)							
Ec42-15	38	Domestic	1996.5	93	1	0	7
KE Bd 42	27	Observation	1988.0	92	7	0	0
KE Be 59	26.5	Observation	1994.2	97	0	2	1
Gc14-04	34	Observation	1996.5	74	26	0	0
QA Db 45	35	Domestic	1983.5	28	18	33	22
QA Df 55	26	Observation	1991.0	77	22	0	1
Ib32-08	14	Observation	1995.5	77	15	0	8
Jc52-04	9	Observation	1995.0	47	53	0	0
TA Cc 53	26.5	Observation	1990.5	73	16	0	11
CO Db 79	22	Observation	1993.0	89	11	0	0
CO De 16	17	Observation	1988.5	74	26	0	0
Le24-11	13.5	Observation	1994.5	97	3	0	0
DO Cb 8	15	Observation	1980.5	29	37	29	4
CO Ec 36	22	Observation	1993.5	51	27	0	22
Oc21-03	23	Observation	1998.5	61	39	0	0
Oe44-01	18.5	Observation	2000.0	58	42	0	0
Ng45-02	22	Observation	1998.5	66	34	0	0
Ri22-10	23	Observation	1981.5	66	34	0	0
DO Cf 36	16	Observation	1999.5	72	4	0	24
Qc22-04	29	Observation	1994.0	69	31	0	0
WI Ch 51	20	Observation	1991.5	43	57	0	0
Rf24-08	19	Observation	1987.5	79	20	0	1
SO Be 114	19	Observation	1987.5	79	19	0	2
WO Cc 3	21	Observation	1992.0	1	99	0	0
WO Cg 78	13	Observation	1994.5	35	59	4	2
WO Fe 1	24	Observation	1991.0	39	60	0	0
66L 11	15	Observation	1989.0	36	64	0	0
64J 28	13	Observation	1996.0	37	37	0	27
64J 30	22	Observation	1997.0	47	32	1	20
Reference-well network							
Gb51-07	20	Observation	1995.0	17	76	1	6
Of12-05	13	Observation	2000.0	2	98	0	0

Appendix A.   Site information for wells sampled in the surficial aquifer on the Delmarva Peninsula.—Continued

[Wells in **bold** are trend wells sampled both in 1988 and 2001; bls, below land surface]

Well name	Well depth (ft bls)	Use of well	Recharge date	Land use[1]			
				Agriculture	Forest-wetland	Open water	Urban[2]
Domestic-well network (median depth 45 feet below land surface)							
Cd31-19	75	Observation	1998.0	3	6	3	75
CE Ce 86	85	Domestic	1991.0	60	40	0	0
KE Be 46	50	Domestic	1991.0	98	0	1	1
Gc14-03	80	Domestic	1994.5	29	62	9	0
QA Db 40	35	Domestic	1980.5	10	11	59	20
QA Df 54	42	Domestic	1989.0	76	23	0	1
Ib32-05	30	Observation	1978.5	84	14	0	2
Jc55-03	30	Domestic	1994.0	80	12	0	8
TA Be 83	37	Domestic	1991.5	79	13	0	8
CO Dd 74	15	Observation	1999.0	85	15	0	0
CO De 15	33	Observation	1995.5	73	27	0	0
Le35-11	48	Domestic	1993.0	50	28	0	22
CO Ec 25	28	Observation	1992.0	50	30	0	20
Oc21-02	45	Observation	1992.0	57	43	0	0
Oe44-02	90	Irrigation	1984.5	58	42	0	0
Nh44-08	100	Domestic	1983.5	42	57	0	0
Ri22-03	50	Stock	1974.5	69	31	0	0
DO Ch 1	41	Domestic	1990.0	78	22	0	0
22DR	60	Domestic	1987.5	81	19	0	0
WI Ch 50	70	Domestic	1981.5	46	54	0	0
Rf14-02	56	Domestic	1989.5	84	16	0	0
SO De 44	43	Observation	1991.0	49	50	0	0
SO Be 115	51	Observation	1997.5	78	20	0	2
WO Cc 2	55	Observation	1992.0	1	99	0	0
WO Cg 76	90	Observation	1977.0	37	56	4	2
WO Fc 46	43	Observation	1976.5	39	60	0	0
66L 12	28	Observation	1990.0	35	65	0	0
64J 29	40	Observation	1995.0	38	36	0	26
64J 31	30	Observation	1992.0	46	32	2	20

[1] Represents land use within 1,640 feet radius of well, based on data described in Vogelmann and others, 2001. Due to rounding, land-use percentage may not add to 100 percent.

[2] Land use includes residential, commercial, and industrial.

Appendix B.   Estimated uncertainty in reported concentrations of selected major ions, nutrients, and pesticides in the surficial aquifer on the Delmarva Peninsula.

[B_N, number of field blanks; B_{ND}, number of blanks in which compound was detected; B_{MAX}, maximum reported concentration in field blanks; S_N, number of field spikes; S_{MED}, median recovery from field spikes; %, percent; R_N, number of replicate sets; R_{NAGREE}, number of replicate sets within which compound was consistently detected or not detected; R_{UNC}, median estimated uncertainty in reported concentrations; NC, not computed because no replicate sets had consistent detected concentrations; ESA, ethanesulfonic acid; OA, oxanilic acid; --, not applicable]

Compound or ion[1]	Contamination bias			Sampling and analytical uncertainty				
	B_N	B_{ND}	B_{MAX}	S_N	$S_{MED\%}$	R_N	R_{NAGREE}	$R_{UNC\%}$[1]
Major ions (mg/L except where noted)								
Calcium	6	5	0.46	--	--	9	9	0.69
Chloride	6	2	0.30	--	--	9	9	1.22
Iron (µg/L)	6	3	28	--	--	9	8	0.40
Magnesium	6	3	0.01	--	--	9	9	0.98
Potassium	6	1	0.10	--	--	9	9	1.07
Silica	6	2	7.32	--	--	9	9	0.68
Sodium	6	3	1.77	--	--	9	9	1.68
Sulfate	6	1	0.18	--	--	9	9	1.05
Nutrients (mg/L)								
Nitrogen ammonia	6	0	--	--	--	9	9	10.50[a]
Nitrogen, nitrite	6	0	--	--	--	9	7	NC
Nitrogen ammonia + organic	6	0	--	--	--	9	8	5.89
Nitrate as nitrogen	6	4	0.06	--	--	9	9	1.82
Phosphorus, ortho	6	0	--	--	--	9	8	22.81[b]
Carbon, organic	7	4	0.39	--	--	6	6	2.61
Pesticides (µg/L)								
2,4-D	5	1	0.14	--	--	5	5	NC
2,4-D methyl ester	5	0	--	--	--	5	5	NC
2,4-DB FLTRD	5	0	--	--	--	5	5	NC
2,6-Diethylaniline	5	0	--	8	99	6	6	NC
Acetochlor	5	0	--	8	111	6	6	NC
Acetochlor ESA	1	0	--	--	--	2	2	NC
Acetochlor OA	1	0	--	--	--	2	2	NC
Acifluorfen	5	0	--	--	--	5	5	NC
Alachlor	5	0	--	8	113	6	6	NC
Alachlor OA	1	0	--	--	--	2	2	NC
Alachlor ESA	1	0	--	--	--	2	2	0.00
Aldicarb	5	0	--	--	--	5	5	NC
Aldicarb sulfone	5	0	--	--	--	5	5	NC
Aldicarb sulfoxide	5	0	--	--	--	5	5	NC
Alpha BHC	5	0	--	8	99	6	6	NC
Atrazine	5	0	--	8	101	6	6	1.78
Bendiocarb	5	0	--	--	--	5	5	NC
Benfluralin	5	0	--	8	84	6	6	NC
Benomyl	5	0	--	--	--	5	5	NC
Bensulfuron-methyl	5	0	--	--	--	5	5	NC

Appendix B. Estimated uncertainty in reported concentrations of selected major ions, nutrients, and pesticides in the surficial aquifer on the Delmarva Peninsula.—Continued

[B_N, number of field blanks; B_{ND}, number of blanks in which compound was detected; B_{MAX}, maximum reported concentration in field blanks; S_N, number of field spikes; S_{MED}, median recovery from field spikes; %, percent; R_N, number of replicate sets; R_{NAGREE}, number of replicate sets within which compound was consistently detected or not detected; R_{UNC}, median estimated uncertainty in reported concentrations; NC, not computed because no replicate sets had consistent detected concentrations; ESA, ethanesulfonic acid; OA, oxanilic acid; --, not applicable]

Compound or ion[1]	Contamination bias			Sampling and analytical uncertainty				
	B_N	B_{ND}	B_{MAX}	S_N	$S_{MED\%}$	R_N	R_{NAGREE}	$R_{UNC\%}$[1]
			Pesticides (μg/L)					
Bentazon	5	0	--	--	--	5	5	NC
Bromacil	5	0	--	--	--	5	5	NC
Bromoxynil	5	0	--	--	--	5	5	NC
Butylate	5	0	--	8	107	6	6	NC
Carbaryl	5	0	--	8	155	6	6	NC
Carbofuran	5	0	--	8	140	6	6	NC
Chlorpyrifos	5	0	--	8	100	6	6	NC
Cyanazine	5	0	--	8	104	6	6	NC
Cycloate	5	0	--	--	--	5	5	NC
Deethylatrazine	5	0	--	8	46	6	6	8.14
Deethyldeisopropylatrazine	5	0	--	--	--	5	5	26.87[b]
Deisopropylatrazine	5	0	--	--	--	5	5	21.56[a]
Diazinon	5	0	--	8	101	6	6	NC
Dicamba	5	0	--	--	--	4	4	NC
Dieldrin	5	0	--	8	109	6	6	NC
Dimethenamid ESA	1	0	--	--	--	2	2	NC
Dimethnamid OA	1	0	--	--	--	2	2	NC
Dinoseb	5	0	--	--	--	5	5	NC
Diphenamid	5	0	--	--	--	5	5	NC
Diuron	5	0	--	--	--	5	5	NC
Fenuron	5	0	--	--	--	5	5	NC
Flufenacet OA	1	0	--	--	--	2	2	NC
Flufenacet ESA	1	0	--	--	--	2	2	NC
Flumetsulam	5	0	--	--	--	5	5	NC
Fluometuron	5	0	--	--	--	5	5	NC
Fonofos	5	0	--	8	100	6	6	NC
Hydroxyatrazine	5	0	--	--	--	5	5	55.13[a]
Imazaquin	5	0	--	--	--	5	5	NC
Imazethapyr	5	0	--	--	--	5	5	9.08
Imidacloprid	5	0	--	--	--	5	5	NC
Lindane	5	0	--	8	100	6	6	NC
Linuron	5	0	--	8	121	6	6	NC
Malathion	5	0	--	8	109	6	6	NC
MCPA	5	0	--	--	--	5	5	NC
MCPB	5	0	--	--	--	5	5	NC

Appendix B.   Estimated uncertainty in reported concentrations of selected major ions, nutrients, and pesticides in the surficial aquifer on the Delmarva Peninsula.—Continued

[B_N, number of field blanks; B_{ND}, number of blanks in which compound was detected; B_{MAX}, maximum reported concentration in field blanks; S_N, number of field spikes; S_{MED}, median recovery from field spikes; %, percent; R_N, number of replicate sets; R_{NAGREE}, number of replicate sets within which compound was consistently detected or not detected; R_{UNC}, median estimated uncertainty in reported concentrations; NC, not computed because no replicate sets had consistent detected concentrations; ESA, ethanesulfonic acid; OA, oxanilic acid; --, not applicable]

Compound or ion[1]	Contamination bias			Sampling and analytical uncertainty				
	B_N	B_{ND}	B_{MAX}	S_N	$S_{MED\%}$	R_N	R_{NAGREE}	$R_{UNC\%}$[1]
			Pesticides (µg/L)					
Metalaxyl	5	0	--	--	--	5	5	NC
Metolachlor ESA	1	0	--	--	--	2	2	7.57
Metolachlor OA	1	0	--	--	--	2	2	NC
Metolachlor	5	3	0.02	8	106	6	6	48.31[a]
Metribuzin	5	0	--	8	90	6	6	NC
Metsulfuron-methyl	5	0	--	--	--	5	5	NC
p,p'-DDE	5	0	--	8	76	6	6	NC
Parathion	5	0	--	8	108	6	6	NC
Pebulate	5	0	--	8	108	6	6	NC
Pendimethalin	5	0	--	8	104	6	6	NC
Cis-permethrin	5	0	--	8	67	6	6	NC
Phorate	5	0	--	8	79	6	6	NC
Picloram	5	0	--	--	--	5	5	NC
Prometon	5	0	--	8	91	6	6	4.81
Propachlor	5	0	--	8	133	6	6	NC
Propham	5	0	--	--	--	5	5	NC
Propoxur	5	0	--	--	--	5	5	NC
Simazine	5	0	--	8	87	6	6	NC
Tebuthiuron	5	0	--	8	134	6	6	NC
Terbacil	5	0	--	8	103	6	6	NC
Terbufos	5	0	--	8	78	6	6	NC

[1] Estimated uncertainty is the median of the relative standard deviation of reported concentrations for replicate sets in which the compound was detected in all replicates. The relative standard deviation is the standard deviation divided by the mean.

[a] Estimated uncertainty above 10 percent based on one set of replicates.

[b] Estimated uncertainty above 10 percent based on two sets of replicates.

Appendix C.   Pesticides and pesticide degradates analyzed in samples from the surficial aquifer on the Delmarva Peninsula in 2001.

[Degradation products are in *italics*; CAS, Chemical Abstracts Service; µg/L, micrograms per liter; ESA, ethanesulfonic acid; OA, oxanilic acid; --, no CAS registry number available]

Organic analyte	CAS registry number®	Analytical method reporting level (µg/L)
2,4-D	94-75-7	0.021
2,4-D methyl ester	1928-38-7	0.0086
2,4-DB	94-82-6	0.016
2,6-Diethylaniline	579-66-8	0.006
2-Hydroxyatrazine	2163-68-0	0.008
3(4-Chlorophenyl)-1-methyl urea	5352-88-5	0.024
3-Hydroxycarbofuran	16655-82-6	0.0058
3-Ketocarbofuran	16709-30-1	1.5
Acetochlor	34256-82-1	0.006
Acetochlor ESA	--	0.05
Acetochlor OA	--	0.05
Acifluorfen	50594-66-6	0.0066
Alachlor	15972-60-8	0.0045
Alachlor ESA	--	0.05
Alachlor OA	--	0.05
Aldicarb	116-06-3	0.04
Aldicarb sulfone	1646-88-4	0.02
Aldicarb sulfoxide	1646-87-3	0.0082
alpha-HCH	319-84-6	0.0046
AMPA	1066-51-9	0.1
Atrazine	1912-24-9	0.007
Azinphos-methyl	86-50-0	0.05
Bendiocarb	22781-23-3	0.025
Benfluralin	1861-40-1	0.01
Benomyl	17804-35-2	0.0038
Bensulfuron-methyl	83055-99-6	0.015
Bentazon	25057-89-0	0.011
Bromacil	314-40-9	0.033
Bromoxynil	1689-84-5	0.017
Butylate	2008-41-5	0.002
Caffeine	58-08-2	0.0096
Carbaryl	63-25-2	0.028
Carbofuran	1563-66-2	0.0056
Chloramben, methyl ester	7286-84-2	0.018
Chlorimuron-ethyl	90982-32-4	0.0096

Appendix C.   Pesticides and pesticide degradates analyzed in samples from the surficial aquifer on the Delmarva Peninsula in 2001.—Continued

[Degradation products are in *italics*; CAS, Chemical Abstracts Service; μg/L, micrograms per liter; ESA, ethanesulfonic acid; OA, oxanilic acid; --, no CAS registry number available]

Organic analyte	CAS registry number®	Analytical method reporting level (μg/L)
Chlorothalonil	1897-45-6	0.035
Chlorpyrifos	2921-88-2	0.005
cis-Permethrin	54774-45-7	0.006
Clopyralid	1702-17-6	0.013
Cyanazine	21725-46-2	0.018
Cycloate	1134-23-2	0.013
Dacthal	1861-32-1	0.003
Dacthal monoacid	887-54-7	0.011
Deethylatrazine	6190-65-4	0.006
Deethyldeisopropylatrazine	3397-62-4	0.01
Deisopropylatrazine	1007-28-9	0.044
Desulfinylfipronil	--	0.004
Desulfinylfipronil amide	--	0.009
Diazinon	333-41-5	0.005
Dicamba	1918-00-9	0.012
Dichlorprop	120-36-5	0.013
Dieldrin	60-57-1	0.0048
Dimethenamid ESA	--	0.05
Dimethenamid OA	--	0.05
Dinoseb	88-85-7	0.012
Diphenamid	957-51-7	0.026
Disulfoton	298-04-4	0.021
Diuron	330-54-1	0.015
EPTC	759-94-4	0.002
Ethalfluralin	55283-68-6	0.009
Ethoprophos	13194-48-4	0.005
Fenuron	101-42-8	0.031
Fipronil	120068-37-3	0.007
Fipronil sulfide	120067-83-6	0.005
Fipronil sulfone	120068-36-2	0.005
Flufenacet ESA	--	0.05
Flufenacet OA	--	0.05
Flumetsulam	98967-40-9	0.011
Fluometuron	2164-17-2	0.031
Fonofos	944-22-9	0.0027

Appendix C.   Pesticides and pesticide degradates analyzed in samples from the surficial aquifer on the Delmarva Peninsula in 2001.—Continued

[Degradation products are in *italics*; CAS, Chemical Abstracts Service; µg/L, micrograms per liter; ESA, ethanesulfonic acid; OA, oxanilic acid; --, no CAS registry number available]

Organic analyte	CAS registry number®	Analytical method reporting level (µg/L)
Glufosinate	77182-82-2	0.1
Glyphosate	1071-83-6	0.1
Imazaquin	81335-37-7	0.016
Imazethapyr	81335-77-5	0.017
Imidacloprid	138261-41-3	0.0068
Lindane	58-89-9	0.004
Linuron	330-55-2	0.014
Malathion	121-75-5	0.027
MCPA	94-74-6	0.016
MCPB	94-81-5	0.015
Metalaxyl	57837-19-1	0.02
Methiocarb	2032-65-7	0.008
Methomyl	16752-77-5	0.0044
Metolachlor	51218-45-2	0.013
Metolachlor ESA	--	0.05
Metolachlor OA	--	0.05
Metribuzin	21087-64-9	0.006
Metsulfuron methyl	74223-64-6	0.025
Molinate	2212-67-1	0.0016
Napropamide	15299-99-7	0.007
Neburon	555-37-3	0.012
Nicosulfuron	111991-09-4	0.013
Norflurazon	27314-13-2	0.016
Oryzalin	19044-88-3	0.017
Oxamyl	23135-22-0	0.012
p,p'-DDE	72-55-9	0.0025
Parathion	56-38-2	0.01
Parathion-methyl	298-00-0	0.006
Pebulate	1114-71-2	0.0041
Pendimethalin	40487-42-1	0.022
Phorate	298-02-2	0.011
Picloram	1918-02-1	0.019
Prometon	1610-18-0	0.015
Propachlor	1918-16-7	0.01
Propanil	709-98-8	0.011

Appendix C.   Pesticides and pesticide degradates analyzed in samples from the surficial aquifer on the Delmarva Peninsula in 2001.—Continued

[Degradation products are in *italics*; CAS, Chemical Abstracts Service; µg/L, micrograms per liter; ESA, ethanesulfonic acid; OA, oxanilic acid; --, no CAS registry number available]

Organic analyte	CAS registry number®	Analytical method reporting level (µg/L)
Propargite	2312-35-8	0.023
Propham	122-42-9	0.0096
Propiconazole	60207-90-1	0.021
Propoxur	114-26-1	0.008
Propyzamide	23950-58-5	0.0041
Siduron	1982-49-6	0.016
Simazine	122-34-9	0.005
Sulfometuron-methyl	74222-97-2	0.0088
Tebuthiuron	34014-18-1	0.016
Terbacil	5902-51-2	0.0098
Terbufos	13071-79-9	0.017
Thiobencarb	28249-77-6	0.0048
Tri-allate	2303-17-5	0.0023
Tribenuron-methyl	101200-48-0	0.0088
Triclopyr	55335-06-3	0.022
Trifluralin	1582-09-8	0.009

Appendix D.   Pesticides analyzed in samples from the surficial aquifer on the Delmarva Peninsula in 1988.

[μg/L, microgram per liter; CAS, Chemical Abstracts Service]

Organic analyte	CAS registry number®	Analytical method reporting level (μg/L)
2,4,5-T	93-76-5	0.01
2,4-D	94-75-7	0.01
Dichlorprop	120-36-5	0.01
Alachlor	15972-60-8	0.1
Ametryn	834-12-8	0.1
Atrazine	1912-24-9	0.1
Carbaryl	63-25-2	0.5
Cyanazine	21725-46-2	0.1
Dicamba	1918-00-9	0.01
Methomyl	16752-77-5	0.05
Metolachlor	51218-45-2	0.1
Metribuzin	21087-64-9	0.1
Picloram	1918-02-1	0.01
Prometon	1610-18-0	0.1
Prometryn	7287-19-6	0.1
Propazine	139-40-2	0.1
Propham	122-42-9	0.05
Silvex	93-72-1	0.01
Simazine	122-34-9	0.1
Simetryn	1014-70-6	0.1
Trifluralin	1582-09-8	0.1

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