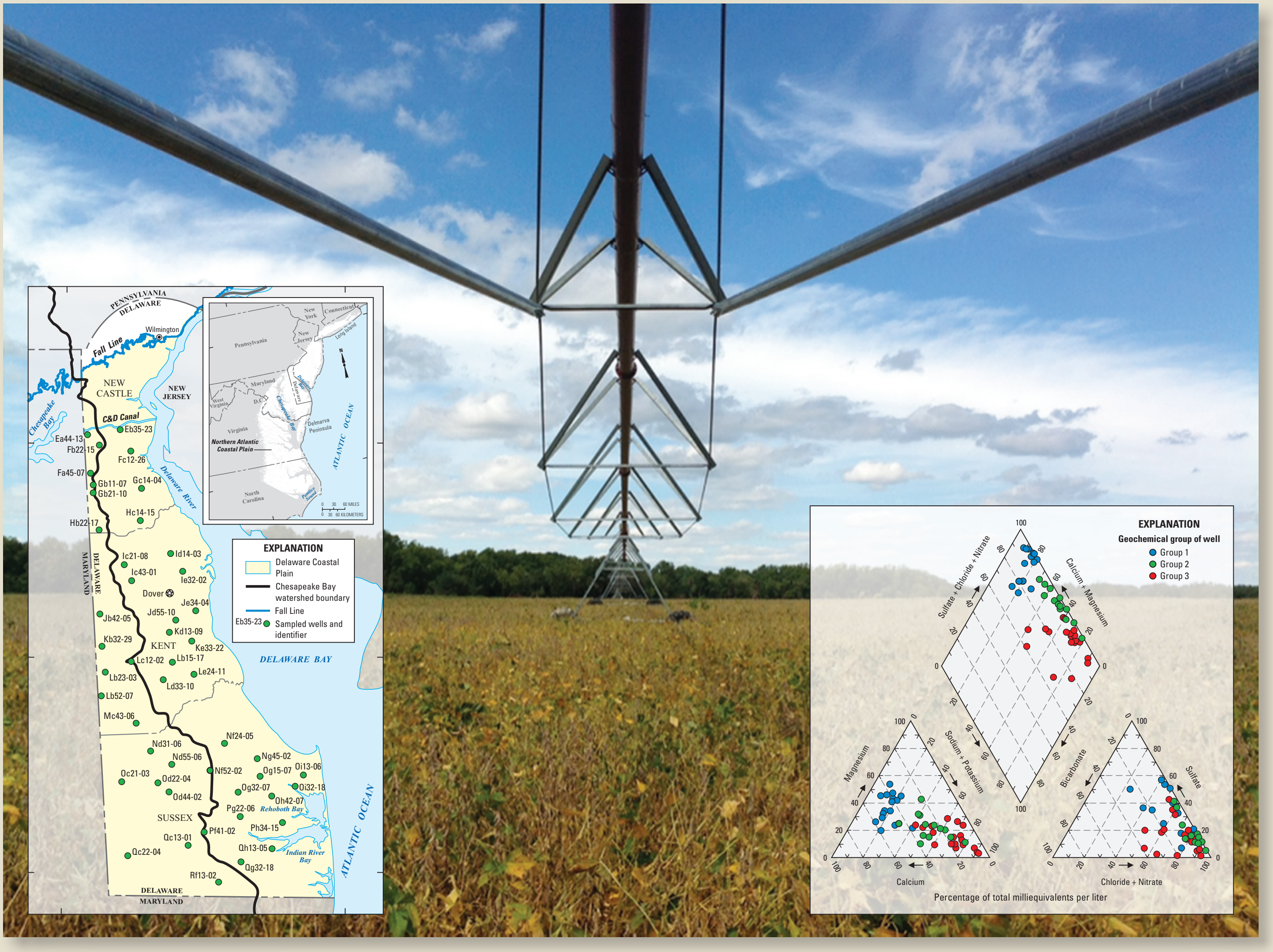
Water Quality in the Surficial Aquifer Near Agricultural Areas in the Delaware Coastal Plain, 2014



Scientific Investigations Report 2017–5054

U.S. Department of the Interior
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Cover. Map showing the Delaware Coastal Plain and location of wells (refer to figure 1); trilinear diagram of major ions within the surficial aquifer of the Delaware Coastal Plain by geochemical groups (refer to figure 6); and center-pivot irrigation system over soybean field. Photograph by John W. Clune, U.S. Geological Survey.

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By Brandon J. Fleming, Laura L. Mensch, Judith M. Denver, Roberto M. Cruz, and Mark R. Nardi

Prepared in cooperation with the Delaware Department of Agriculture

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

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Contents

Figures

Tables

Conversion Factors

Multiply	By	To obtain
	Length	
inch (in)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
acre	0.4047	hectare (ha)
acre	0.004047	square kilometer (km^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
gallon (gal)	3.785	liter (L)
	Flow rate	
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)

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

$$°F = (1.8 \times °C) + 32$$

Datums

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1988 (NGVD 88).

Horizontal coordinate information is referenced to North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Supplemental Information

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 in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

DDA	Delaware Department of Agriculture
DGS	Delaware Geological Survey
DNREC	Delaware Department of Natural Resources and Environmental Control
EPA	U.S. Environmental Protection Agency
NASS	National Agricultural Statistics Service
NRCS	Natural Resources Conservation Service
NWQL	National Water Quality Laboratory
NWIS	National Water Information System
TMDL	Total Maximum Daily Load
USDA	U.S. Department of Agriculture
USGS	U.S. Geological Survey

Water Quality in the Surficial Aquifer Near Agricultural Areas in the Delaware Coastal Plain, 2014

By Brandon J. Fleming[1], Laura L. Mensch[2], Judith M. Denver[1], Roberto M. Cruz[1], and Mark R. Nardi[1]

Abstract

The U.S. Geological Survey, in cooperation with the Delaware Department of Agriculture, developed a network of wells to monitor groundwater quality in the surficial aquifer of the Delaware Coastal Plain. Well-drained soils, a flat landscape, and accessible water in the Delaware Coastal Plain make for a productive agricultural setting. As such, agriculture is one of the largest industries in the State of Delaware. This setting enables the transport of chemicals from agriculture and other land uses to shallow groundwater. Efforts to mitigate nutrient transport to groundwater by the implementation of agricultural best management practices (BMPs) have been ongoing for several decades. To measure the effectiveness of BMPs on a regional scale, a network of 48 wells was designed to measure shallow groundwater quality (particularly nitrate) over time near agricultural land in the Delaware Coastal Plain. Water characteristics, major ions, nutrients, and dissolved gases were measured in groundwater samples collected from network wells during fall 2014. Wells were organized into three groups based on their geochemical similarity and these groups were used to describe nitrate and chloride concentrations and factors that affect the variability among the groups. The results from this study are intended to establish water-quality conditions in 2014 to enable comparison of future conditions and evaluate the effectiveness of agricultural BMPs on a regional scale.

Introduction

More than 90 percent of Delaware is underlain by the Northern Atlantic Coastal Plain Aquifer system (fig. 1). Most of the Delaware Coastal Plain has a surficial aquifer with a shallow water table and is typically composed of sandy sediments. Abundant rainfall provides aquifer recharge, but can also carry chemicals from the land surface to the water table. This aquifer is an important source of drinking water for many residents of small towns and rural households with domestic use. The surficial aquifer also provides most of the streamflow for streams that originate in the Delaware part of the Coastal Plain.

As plants grow, they extract nutrients from the soil. In order to maintain crop yields and plant health, farmers need to periodically replace these nutrients by adding either animal manure or commercial fertilizers to the soil. Most nitrogen is applied to the land in the form of organic nitrogen or ammonia in manures and commercial fertilizers. Much of the applied nitrogen is rapidly converted to nitrate by soil microbes. Nitrate dissolves in water and the amounts not used by crops can leach into the groundwater with recharge. Certain conditions increase the likelihood of nitrate moving into shallow groundwater. These conditions include the amounts and timing of nitrogen application to the land; the presence of well-drained, sandy soils that promote oxic soil and aquifer conditions (dissolved oxygen greater than 1 milligram per liter or mg/L); and a relatively high water table (Ator and Denver, 2015; Rudolph, 2015). These conditions are common in many parts of the Delaware Coastal Plain and have resulted in widespread nitrate movement into the surficial aquifer in many areas.

Nitrate, the major form of nitrogen that is soluble in water, is a common contaminant in groundwater and surface water in the Coastal Plain of Delaware (Ator and Denver, 2015). Nitrate concentrations in the surficial aquifer are commonly far greater than would be expected under natural conditions, and often high enough to affect the suitability of water for human consumption (Debrewer and others, 2007). Nitrate from groundwater is the primary source of nitrogen to many streams, which often exceed the U.S. Environmental Protection Agency (EPA) Total Maximum Daily Load (TMDL) for surface-water quality (Delaware Department of National Resources and Environmental Control, 2015). Manure and fertilizer used for agriculture are the primary sources of nitrogen applied to the land in Delaware (fig. 2). The recognition of this water-quality concern has led to the implementation of agricultural nutrient management efforts designed to maximize yields while minimizing any potentially negative effects on environmental quality.

[1] U.S. Geological Survey.

[2] Delaware Department of Agriculture.

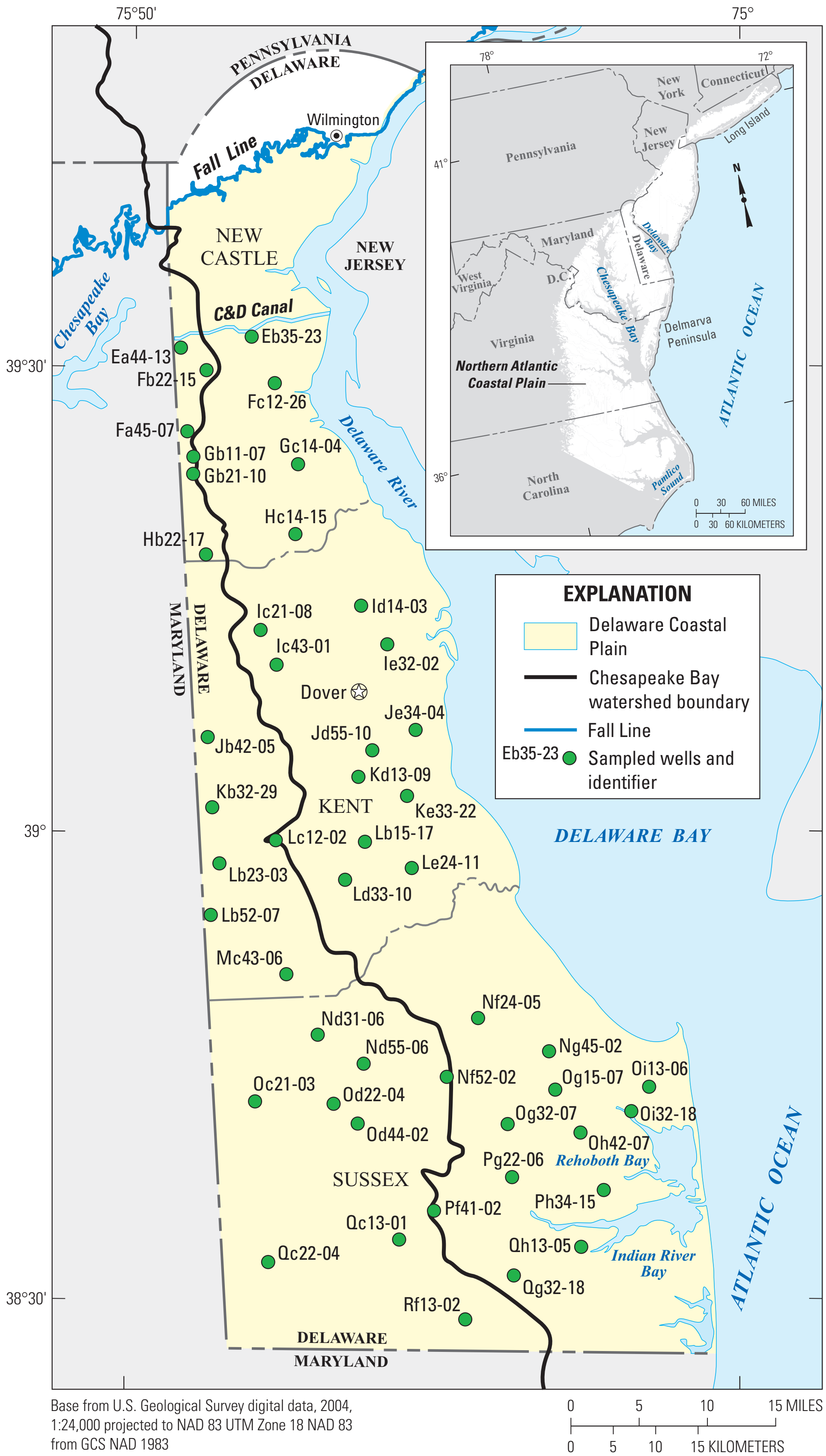

Figure 1. The Delaware Coastal Plain and location of wells.

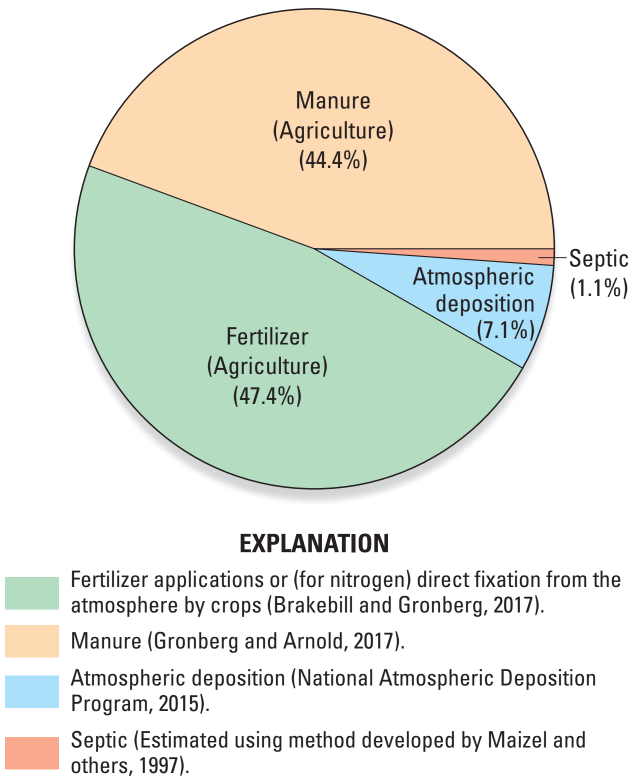

Figure 2. Nitrogen inputs to Delaware. (%, percent)

Agriculture is one of Delaware's main industries, producing over $1 billion in annual sales. With 508,000 total acres of farmland in the State, roughly 2 out of every 5 acres in Delaware are dedicated to farming. Delaware's average farm size of 200 acres is less than half the national average farm size of 438 acres, reflecting the prevalence of smaller farms. Poultry, predominantly broiler chickens, is one of the largest agricultural commodities in the State. The largest amount of farmland in the State is planted with the main crops: soybeans, corn, and wheat, with 415,000 total acres of these three crops combined (U.S. Department of Agriculture, National Agricultural Statistics Service, 2012). Produce, such as watermelons, sweet corn, lima beans, and cucumbers, also accounts for a part of the State's agricultural production.

Between 2005 and 2013, an annual average of 110,053 tons of poultry manure was applied to 49,268 acres of Delaware farmland (Delaware Department of Agriculture, 2015). That is an average of 2.23 tons of poultry manure applied per acre. Since poultry manure is composed of approximately 3 percent nitrogen (Delaware Department of Agriculture, 2012), farmers applied an annual average of 133 pounds of nitrogen per acre from poultry litter. Another major source of soil amendments used in the State is commercial fertilizer. In 2013, Delaware farmers reported applying 9,632 tons of nitrogen from commercial fertilizer on 194,898 acres of Delaware farmland (Delaware Department of Agriculture, 2015). That is an average of 99 pounds of nitrogen per acre from commercial fertilizer (U.S. Department of Agriculture, 2012). Combined, an average of about 232 pounds of nitrogen per acre annually are applied to farmland in Delaware.

Under State law (Delaware Code Title 3), every farm that applies nutrients to 10 or more acres must have a valid Nutrient Management Plan written by a Delaware certified nutrient consultant. Application of manure from poultry production is included in many Nutrient Management Plans for Delaware farms because of the value of manure as a nutrient source and its abundance. A fundamental goal of any nutrient management plan is to identify the most cost-efficient and environmentally sound way to provide plants with the optimum supply of nutrients. Success with conservation and nutrient application practices used in these plans should help to reduce concentrations of nitrate over time in Delaware waters.

A groundwater-monitoring network was established in 2014 by the U.S. Geological Survey (USGS) and the Delaware Department of Agriculture (DDA) as a tool to measure changes in water quality over time in the Delaware Coastal Plain. Temporal trends in nitrate have been evaluated in groundwater networks in different hydrogeologic settings, including the Columbia Basin in Washington (Frans and Helsel, 2005), and the California Central Valley (Burow and others, 2012). In the Mid-Atlantic region, temporal trends in nitrate and pesticides were evaluated in the Valley and Ridge carbonate aquifers and the Delmarva Peninsula (Debrewer and others, 2008). Networks in similar hydrogeologic and land-use settings in Denmark (Hansen and others, 2011) have shown improvements in groundwater quality with changes in agricultural practices. Initial data from the network established by USGS and DDA demonstrated groundwater-quality conditions near agricultural lands in the Delaware Coastal Plain in 2014. Repeated sampling of this network over time is intended to help track the effectiveness of agricultural best management practices (BMPs) aimed at reducing nitrogen transport to the water table in Delaware.

Purpose and Scope

The purposes of this report are to describe the design of an agricultural, shallow groundwater-quality monitoring network in the Delaware Coastal Plain and to present geochemical results of samples collected from the network in 2014. This study focuses on the 2014 water-quality conditions in shallow groundwater near agriculture, which is the predominant land use in Delaware. Results presented in this report are based on the analyses of samples collected at 48 shallow wells (fig. 1, table 1) in or adjacent to agricultural lands that are distributed throughout the Delaware Coastal Plain. These data allow comparison with future samples collected for a study of trends in nitrate and other chemicals in groundwater in the Delaware Coastal Plain.

Table 1. Site information for wells sampled in the surficial aquifer of the Delaware Coastal Plain, 2014.

[DNREC, Delaware Department of Natural Resources and Environmental Control; ft bls, feet below land surface; ft, feet]

Station number	Local identifier	DNREC well identifier	Latitude (decimal degrees)	Longitude (decimal degrees)	Well depth (ft bls)	Aquifer thickness (ft)
392959075435501	Fb22-15	106879	39.499834	-75.731599	23.34	67
392913075382001	Fc12-26	108632	39.487056	-75.638540	28	58
382932075221701	Rf13-02	155971	38.492083	-75.371417	12.9	19
384425075072401	Oi13-06	166167	38.740167	-75.123444	13	95
384411075150101	Og15-07	172328	38.736417	-75.250361	18.4	116
385730075321401	Ld33-10	166259	38.958361	-75.537111	17.4	80
391324075391901	Ic21-08	172352	39.223444	-75.655222	17.3	25
385956075303801	Lb15-17	172301	38.999	-75.510583	13.1	62
391814075435001	Hb22-17	172331	39.303889	-75.730472	12.3	41
392403075362101	Gc14-04	187638	39.4009	-75.605817	34	23
385817075265101	Le24-11	172300	38.971677	-75.447192	13.5	81
385129075370201	Mc43-06	155980	38.858083	-75.617167	12.8	67
384323075393201	Oc21-03	73085	38.723169	-75.658540	23	67
390634075433401	Jb42-05	172323	39.109444	-75.726194	11.1	11
391503075310401	Id14-03	155985	39.250917	-75.517722	18	15
384637075153201	Ng45-02	187640	38.777067	-75.258867	22	114
392324075445601	Gb21-10	106885	39.390111	-75.748544	14.75	61
383438075274201	Qc13-01	155972	38.577167	-75.46175	13.1	128
383221075182301	Qg32-18	166165	38.539222	-75.306472	11.8	19
384316075330501	Od22-04	155961	38.721	-75.551333	18.3	76
384201075185401	Og32-07	166198	38.700222	-75.315028	13.2	104
385830075423201	Lb23-03	172347	38.975	-75.708944	13.2	50
385515075431701	Lb52-07	166258	38.92075	-75.721444	16	51
390001075380101	Lc12-02	155982	39.000333	-75.633556	18.2	72

Description of Study Area

Most of Delaware lies on the Delmarva Peninsula within the Northern Atlantic Coastal Plain Physiographic Province (fig. 1). Topography in the Delaware Coastal Plain is relatively flat with the highest elevations located at the drainage divide between the Chesapeake Bay to the west and Delaware Bay and Atlantic Ocean to the east (fig. 1). On the Delaware Coastal Plain, land use is predominantly agriculture, forest and wetlands, and developed at 53 percent, 39 percent, and 8 percent, respectively (Masterson and others, 2016). Average annual precipitation ranges from 41 to 45 inches per year (in/yr) (Sanford and others, 2012) and is typically evenly distributed throughout the year with 3–4 inches per month.

Water Use

Total 2010 groundwater use in the Delaware Coastal Plain was 151 million gallons per day (Mgal/d), of which most (58 percent) was used for agriculture (Masterson and others, 2016; fig. 3*A*). Over the last several decades, both irrigated land (U.S. Department of Agriculture, National Agricultural Statistics Service, 2012) and the volume of groundwater withdrawn for irrigation has increased substantially (Cheryl Dieter, USGS, written commun., 2016; fig. 3*B*). Most public water supply and all domestic water use in the Delaware Coastal Plain comes from confined aquifers or relatively thick parts of the surficial aquifer. Other uses of groundwater include commercial and industrial use.

Table 1. Site information for wells sampled in the surficial aquifer of the Delaware Coastal Plain, 2014.—Continued

[DNREC, Delaware Department of Natural Resources and Environmental Control; ft bls, feet below land surface; ft, feet]

Station number	Local identifier	DNREC well identifier	Latitude (decimal degrees)	Longitude (decimal degrees)	Well depth (ft bls)	Aquifer thickness (ft)
390409075311301	Kd13-09	176048	39.069111	-75.520361	13.4	47
390205075430901	Kb32-29	155978	39.034694	-75.719056	18.1	49
384550075304001	Nd55-06	166200	38.763944	-75.511028	18.2	79
384845075211901	Nf24-05	172295	38.812444	-75.355278	13.5	121
383308075382301	Qc22-04	73089	38.552338	-75.639373	29	98
392605075452801	Fa45-07	106882	39.434834	-75.757434	22.6	45
392428075445901	Gb11-07	106884	39.407889	-75.749377	23.58	56
393210075401601	Eb35-23	108633	39.536223	-75.670763	15	53
393126075460201	Ea44-13	108634	39.524001	-75.766879	17	53
383629075245601	Pf41-02	172327	38.607944	-75.415417	12.9	123
383412075125401	Qh13-05	166166	38.569889	-75.214917	18	104
383836075183001	Pg22-06	166189	38.643361	-75.308361	16.5	89
383749075110501	Ph34-15	155953	38.630194	-75.184611	12.9	92
384250075085001	Oi32-18	172294	38.71375	-75.147167	26.8	105
384737075342701	Nd31-06	172320	38.793639	-75.574056	13.8	74
384159075310801	Od44-02	90221	38.699833	-75.518833	14.6	81
384130075125801	Oh42-07	155951	38.691639	-75.216111	13.2	107
391112075380001	Ic43-01	155984	39.186667	-75.633417	17.1	36
390252075271301	Ke33-22	172318	39.047667	-75.453611	12.6	57
391936075363201	Hc14-15	106889	39.326778	-75.608538	13.12	15
384502075235301	Nf52-02	166168	38.750556	-75.397972	12.5	105
390544075300501	Jd55-10	166262	39.095556	-75.501472	15	45
390705075263201	Je34-04	172349	39.118139	-75.442083	13	46
391232075285401	Ie32-02	172350	39.208917	-75.481611	13.5	29

Hydrogeologic Setting

The Delaware Coastal Plain is underlain by an extensive unconfined surficial aquifer that is present at the land surface in most areas (fig. 4). This aquifer supplies most of the flow to streams and rivers that incise the land surface. It generally thickens from north to south (fig. 4) and overlies the subcrop areas of a series of confined aquifers and confining beds (Denver and Nardi, 2016).

The recharge area for the surficial aquifer includes most of the land surface because of the sandy nature of the aquifer sediments. The mean annual estimated recharge ranges from about 14 to 17 in/yr, which is about one-third of the total precipitation (Sanford and others, 2012). Water in the surficial aquifer typically flows along relatively short flow paths (distances of several hundred feet to less than a few miles) towards discharge areas in streams and estuaries and reaches the discharge areas in less than 50 years (Denver and others, 2004; Sanford and others, 2012). Groundwater flow is also intercepted by pumping wells. A small amount of the recharge, less than 2 percent, moves downward into the underlying confined aquifers (Leahy and Martin, 1993).

Geologic formations with predominantly sandy surficial sediments that compose the surficial aquifer in the Delaware Coastal Plain include the Parsonsburg Sand, Sinepuxent Formation (Fm.), and parts of the Omar Fm., the Columbia Fm., the Beaverdam Fm., and the Pennsauken Fm. (Ator and others 2005; Bachman and Wilson, 1984). Other formations with mixed texture that have sandy lithology also can be part of the surficial aquifer. These formations include the Scotts Corner Fm. and Lynch Heights Fm., which occur on the eastern side and updip section of the Omar Fm. north of Indian River Bay (Ator and others, 2005; Mixon, 1985; Owens and Denny, 1979; Ramsey, 1997). These formations are of Quaternary through late Miocene age.

Aquifers that are otherwise confined that underlie the surficial aquifer may increase its thickness in areas where they subcrop beneath the surficial aquifer and are under water-table conditions. Older formations that contain aquifers and subcrop the surficial aquifer include the Tertiary age formations of the Chesapeake Group, and the Vincentown and Hornerstown Fms.; the Cretaceous age Mt. Laurel, Englishtown, and Magothy Fms., and the sandy sediments of the Potomac Group (Ator and others, 2005).

Groundwater Chemistry

The chemical constituents measured in groundwater reflect the rock types of the aquifer sediments, redox conditions in the aquifer, and chemicals applied to the land surface that are soluble in water and available to leach into the groundwater system. The surficial aquifer in the Delaware Coastal Plain is composed mostly of siliciclastic sediments in which quartz minerals are the major component (Jordan, 1964). Quartz is resistant to weathering, and under natural conditions in well-drained areas with minimal inputs of anthropogenic chemicals, the water in the surficial aquifer system is very dilute with specific conductance of less than about 60 microsiemens per centimeter at 25 degrees Celsius (µS/cm) and nitrate concentrations of less than 0.4 mg/L as N (Denver, 1989; Hamilton and others, 1993). Many of the common constituents in fertilizers that are typically applied to fields also dissolve in water and can travel to groundwater if they leach below the root zone. Plants need a variety of nutrients to grow, including nitrogen, phosphorus, potassium, magnesium, and calcium. With the exception of phosphorus, these chemicals typically contribute to the major ions in groundwater affected by agricultural activities (Hamilton and others, 1993). In well-drained soils, phosphorus is typically bound to soils and sediments and not dissolved in water (Ator and Denver, 2015).

Nitrate is widespread throughout the surficial aquifer of the Delmarva Peninsula (Debrewer and others, 2007) and nitrate concentrations in natural groundwater rarely exceed 0.4 mg/L in the surficial aquifer of the Delmarva Peninsula (Hamilton and others, 1993). Concentrations of nitrate above natural background levels are likely impacted by anthropogenic activity (Debrewer and others, 2007). Recent studies on the Delmarva Peninsula have shown that nitrate concentrations in groundwater increased about 2 mg/L as N in parts of the surficial aquifer used for domestic supply from 1988 to 2001 in response to increased nitrogen applications in previous decades (Denver and others, 2004; Ator and Denver, 2015). Headwater streams on the Delmarva Peninsula, which derive most of their flow as groundwater discharge from the surficial aquifer, also show nitrate concentrations above natural levels during base flow (Ator and Denver, 2015, Denver and others, 2004).

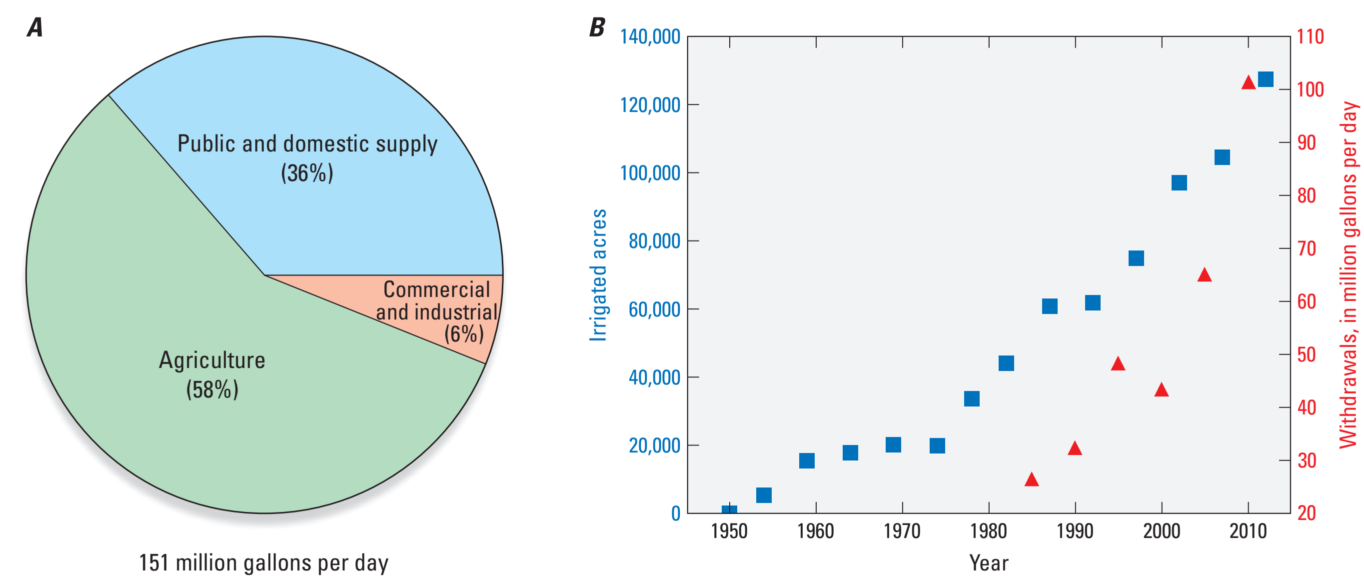

Figure 3. Groundwater use by *A*, category for the Delaware Coastal Plain 2010 (Masterson and others, 2016), and *B*, acres irrigated (U.S. Department of Agriculture, National Agricultural Statistics Service, 2012) and volume withdrawn for agricultural irrigation in the Delaware Coastal Plain (Cheryl Dieter, USGS, written commun., 2016). (%, percent)

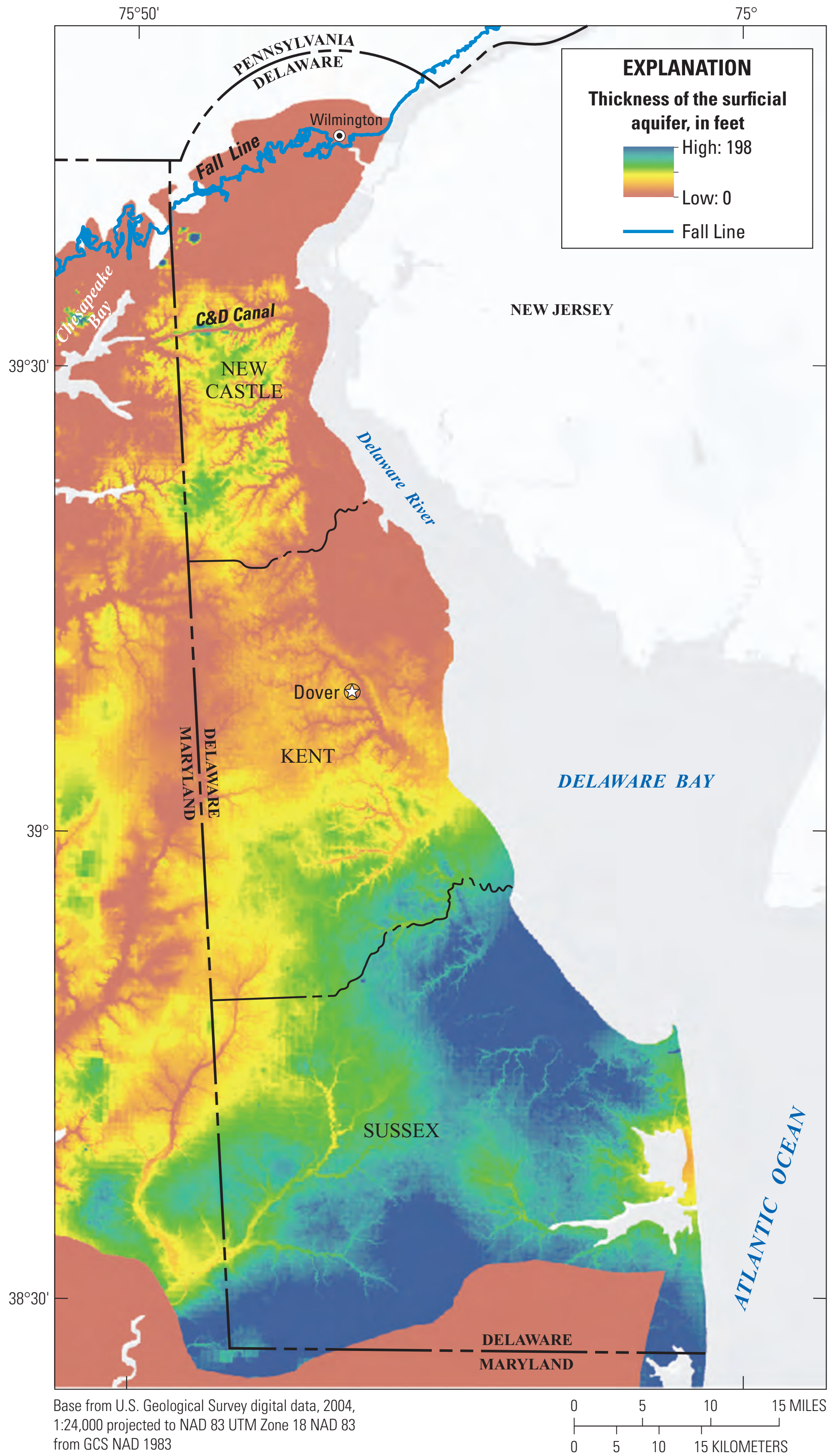

Figure 4. Thickness of the surficial aquifer in the Delaware Coastal Plain (Denver and Nardi, 2016).

Agricultural Practices, Nutrient Management, and Best Management Practices (BMPs)

Farmers use tools such as soil tests, Pre-Sidedress Nitrate Tests (PSNTs), plant tissue sample analyses, and crop yield production history to determine a crop's nutrient needs for each soil type (Haering and Evanylo, 2006). When plants receive the correct balance of nitrogen, phosphorus, and potassium throughout the growing season, they are able to use these compounds with optimal efficiency, leaving less in the soil. Providing inadequate nutrient balance not only reduces yield, but it also reduces the plant's efficiency and can lead to nutrients going unused by the crop (Plaster, 1997). A healthier plant promotes more efficient utilization of nutrients.

Nitrogen, in particular, is an essential nutrient for plants; without it, a plant cannot grow normally. Nitrogen is a major component of chlorophyll, the molecule used by plants during photosynthesis to convert sunlight energy into sugars (Plaster, 1997). Nitrogen is also an essential element of amino acids, the building blocks of protein. Delaware has predominantly sandy soils, particularly in parts of Kent and Sussex Counties (Soil Survey Staff, 2016). Sandy soils often contain low amounts of organic materials and can be deficient in nitrogen (Shober, 2015). Because of these two factors, it is especially important to provide nitrogen in its most bioavailable form, nitrate, to crops.

Delaware farmers have been using an increasing array of BMPs to reduce nutrient loading to surface water and groundwater. For example, the use of cover crops has become increasingly widespread in Delaware, taking up nutrients from the soil during the winter months to reduce nutrient leaching to the groundwater. Modified tillage practices are used to reduce the movement of sediment and nutrients away from fields.

Cover crops are grasses, legumes, or small grains planted between crop cycles to protect and improve soil health. They protect soil by reducing erosion, improving stability, and managing soil moisture. Cover crops also benefit the larger ecosystem by increasing biodiversity, attracting pollinators, suppressing weeds, and providing forage (Nolan and others, 2002). Lastly, cover crops also promote soil health by increasing organic matter, redistributing nutrients within the soil, fixing nitrogen, and removing excess nutrients (Nolan and others, 2002). Legumes such as field peas, clover, and vetch are excellent at fixing nitrogen in soil, and grass cover crops such as wheat, rye, and barley are particularly good at removing excess nutrients from soil (U.S. Department of Agriculture, Natural Resources Conservation Service, 2014).

Farmers have also altered their tillage practices in order to minimize the movement of nutrients away from their intended use locations. Tillage is the agricultural practice of cultivating or preparing soil for planting. Conventional or traditional tillage practices involve the mechanical disturbance of the top layer of soil, and the mixing of plant residues left after harvest. Conventional tillage is defined as leaving 15 percent or less crop residue on a field after harvest (Delaware Department of Natural Resources and Environmental Control, 2015). Although this practice has benefits, such as insect and weed control, conventional tillage leaves soil exposed. This can increase soil erosion and sediment runoff, and increases soil compaction, which facilitates surface-water runoff.

In contrast, conservation tillage practices involve the minimal disturbance of soil and plant residues that remain on a field after harvest. Essentially, the soil remains undisturbed after harvest and is minimally disturbed during the planting of the next crop. Conservation tillage is defined as leaving a minimum of 30 percent crop residue on a field (Delaware Department of Natural Resources and Environmental Control, 2015). To adapt to this different practice, farmers use specifically designed equipment that enables them to drill or plant seeds while minimizing the disturbance of soil and existing crop residue. This practice has many benefits, including the preservation of soil moisture; the reduction of soil erosion from wind, rain, or other forces; and an increase in the organic matter content in soil. By minimizing soil erosion, conservation tillage decreases the movement of nutrients bound with this soil off of the field in overland runoff. By increasing organic matter content in the soil, conservation tillage provides increased material to bind nutrients to the soil, minimizing the leaching of nutrients through the soil into the shallow groundwater.

In Delaware, these BMPs are being implemented in all three counties. For example, in 2015, conventional tillage was used on 11.6, 21.5, and 22.4 percent of New Castle County, Kent County, and Sussex County farmland, respectively. In contrast, conservation tillage practices were used in 81.7, 72.5, and 65.9 percent of New Castle County, Kent County, and Sussex County farmland, respectively. Cover crops were used on 24, 43, and 32.5 percent of New Castle County, Kent County, and Sussex County farmland, respectively (Delaware Department of Natural Resources and Environmental Control, 2015).

The goal of using cover crops and conservation tillage, along with estimating nutrient budgets prior to the application of fertilizer, is to minimize the amount of land-applied nutrients available to move into surface water and groundwater in Delaware.

Methods of Study

A new network of wells was designed from wells in two active groundwater-monitoring networks maintained by the DDA and the USGS in the unconfined surficial aquifer of the Delaware Coastal Plain. Wells were included in the network on the basis of depth, previously known oxic conditions, and the proximity to agricultural land use. Water from wells was analyzed to establish geochemical conditions in 2014 and identify patterns in water quality in the unconfined surficial aquifer of the Delaware Coastal Plain. Land use and soils near the wells are summarized concurrently with the groundwater-quality results, creating a snapshot of land use and water quality that will be used to compare with future conditions.

Network Design

In 1995, the DDA designed a shallow groundwater-monitoring network with the assistance of the Delaware Geological Survey (DGS) (Blaier and Baxter, 2000). The network consists of 104 dedicated monitoring wells located throughout the State south of the Chesapeake and Delaware Canal (C&D Canal, fig. 1). The wells are primarily used to monitor the State's shallow groundwater for pesticides of interest that are registered for use in the State.

With a few exceptions, the DDA pesticide monitoring wells are located on roadsides in State rights-of-way. Wells are screened in the Columbia aquifer. All wells are considered shallow, with the bottom of screen depths less than 40 feet (ft) below ground surface. Well depths range from 8.35 ft to 38.70 ft. The average completion depth for all 104 currently active monitoring wells is 16.10 ft. The monitoring wells were screened across the water-table surface at the time of drilling.

Since the network was initially designed to monitor groundwater for agricultural herbicides, all of the monitoring wells are located below the C&D Canal in the Delaware Coastal Plain, where most of the State's agricultural land is located. This requirement generally excludes land above the C&D Canal, areas within incorporated towns and cities, and areas along the coast where land is largely marsh and other wetlands.

A subset of wells from the DDA network and from an agricultural land-use network developed for the USGS National Water-Quality Assessment (NAWQA) Project were included in the new network. The existing USGS network was designed to assess water quality in the surficial aquifer of the Delmarva Peninsula (Debrewer and others, 2007; Koterba and others, 1990; Shedlock and others, 1993) as part of NAWQA. A subset of wells from the NAWQA network that are located in Delaware, and screened within oxic parts of the shallow unconfined aquifer, were selected for inclusion in the new network. In total, 8 wells from the USGS network and 40 wells from the DDA pesticide network were sampled during fall 2014 (fig. 1, table 1). Well depths ranged from 11 ft to 34 ft.

Sample Collection and Analysis

Water samples were collected using methods outlined in the USGS National Field Manual for the Collection of Water-Quality Data (U.S. Geological Survey, variously dated). The sample collection was designed to represent shallow, oxic groundwater conditions in the Delaware Coastal Plain from October through December 2014. Prior to sampling, at least three well volumes were purged using a Fultz sp300 submersible pump to remove standing water, and geochemical and physical field parameters were monitored with a YSI 6920 sonde until stable conditions were reached. For this study, stable geochemical conditions were defined as five successive 5-minute measurements of pH (± 0.1 units), water temperature (± 0.2 degrees Celsius), specific conductance (± 3 percent), dissolved oxygen (± 0.3 mg/L), and turbidity (± 10 percent). Well Pf41-02 recharged too slowly for standard purging procedures. This well was purged and allowed to recover to 90 percent of the original water level before measuring field parameters and sample collection. Samples were collected using Teflon tubing and a 0.45-micrometer capsule filter inside a clean sampling chamber. Filtered water samples for inorganics analysis were preserved using nitric acid to a pH below 2. All samples were maintained at a temperature below 4 degrees Celsius in a sealed cooler during shipment to the laboratory.

Samples from all wells were analyzed for major ions and nutrients at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado using methods described in Fishman (1993). Samples from 25 wells also were analyzed for trace atmospheric gases, including sulfur-hexafluoride, nitrogen, argon, carbon dioxide, methane, and oxygen. Gas analyses were conducted at the USGS Chlorofluorocarbon Laboratory in Reston, Virginia and recharge age determined using methods described by Busenberg and Plummer (2000). Alkalinity and bicarbonate concentrations were determined in samples with pH greater than 4.5 using field electrometric titrations on filtered samples using the inflection point method (Rounds, 2006). Where pH was below 4.5, alkalinity and bicarbonate concentrations were assumed to be zero.

Quality Control

Quality-control samples were collected to evaluate and estimate potential contamination bias and measurement variability from water-quality data-collection processes (Koterba and others, 1995). An equipment blank was collected prior to sampling; four field blanks and four replicates were collected during field activities at selected wells. Field collection procedures for quality-control samples were established using the USGS National Field Manual (U.S. Geological Survey, variously dated) in a manner consistent with procedures for the acquisition of environmental samples. This evaluation of quality-control samples included the review of analytical data, field practices, reported environmental concentrations, and timing of quality-control activities.

Age Dating

Recharge dates for groundwater samples were estimated on the basis of measured concentrations of sulfur hexafluoride (SF_6), and dissolved nitrogen, argon, carbon dioxide, methane, and oxygen (Busenberg and Plummer, 2000). Industrial production of SF_6 started in the 1950s and increasing concentrations in the atmosphere have been documented since 1978 (Maiss and Brenninkmeijer, 1998). SF_6 can be used to date groundwater that is in equilibrium with the atmosphere when it is recharged. SF_6 is a good tracer for young groundwater (recharged after 1970), however, its usefulness as a groundwater age tracer decreases for older waters. For this study, field conditions at 25 wells were suitable to sample for SF_6.

Data Analysis

Statistical methods were selected to identify patterns in shallow, oxic groundwater from unconfined wells near agricultural land use. Nonparametric Spearman correlation analysis (Helsel and Hirsch, 2002) was used to identify wells with similar geochemical characteristics based on analytical results of pH, specific conductance, dissolved oxygen, silica, chloride, bicarbonate, sulfate, magnesium, calcium, potassium, sodium, and nitrate. The Spearman correlation matrix for all wells was used as input for an agglomerative hierarchical cluster analysis using Ward's method to minimize the variance between clusters (Ward, 1963). The Python library SciKit-Learn (Pedregosa and others, 2011) was used to apply the cluster analysis. Groups of wells determined by cluster analysis were used to summarize water-quality results and describe the variability of relevant physical properties (land use, soils, and aquifer thickness). Non-parametric Kruskal-Wallis multiple comparison tests were done using the pgirmess package in the R software (Giraudoux, 2017) to determine if populations of selected constituents and land cover were significantly different by geochemical groups derived by correlation and cluster analysis. Land use and land cover from the State of Delaware (2007) and soils were documented on a well-by-well basis within an approximately 1,640-ft radius of each well through a Geographic Information System buffering and overlay procedure that extracted land-use polygons for summary. Selected water-quality constituents were compared directly to physical properties. Trilinear diagrams were constructed to illustrate major cations and ions in various water types identified within the network. Chloride to bromide mass ratios were calculated to identify possible sources of chloride in groundwater samples.

Factors Affecting Variability

The quality-control procedures included five blank samples to test for potential equipment contamination and four replicate samples to test for reproducibility of results. Detectable concentrations of ammonia, chloride, and sulfate were found in blank samples, but were within twice the respective laboratory detection limits. Manganese was detected at 0.54 micrograms per liter (µg/L) in the pre-study equipment blank, which is greater than the laboratory detection limit of 0.20 µg/L. For replicate samples, a relative percent difference (RPD) between environmental and replicate results of 20 percent was used as an indication of variability from sampling procedures for this study. A single constituent, iron, exceeded the 20-percent RPD criteria, at 6.1 µg/L for the replicate and < 4 µg/L for the environmental sample, however the mean RPD for all replicate iron samples was 8.9 percent and within the study criteria. Quality-control results show there was not significant variability or bias that would affect the interpretation of water-quality results for this study.

The quality of water in the surficial aquifer of the Delaware Coastal Plain is influenced by the availability of dissolved ions from natural and human sources, and by geochemical factors that affect the fate and transport of these ions. Dissolved oxygen concentrations can control geochemical transformations, and in the surficial aquifer, waters are typically considered oxic, with dissolved oxygen concentrations above 0.5 mg/L (McMahon and Chapelle, 2008). Understanding redox conditions is important because under oxic conditions redox-sensitive parameters (such as nitrate) are stable. In poorly drained settings in the surficial aquifer, anoxic conditions (dissolved oxygen less than 0.5 mg/L) exist, although these were avoided by design in this study. Land use and chemicals applied on the land surface play an important role in surficial groundwater quality. Soil conditions and aquifer properties also can affect recharge rates and groundwater quality. Groundwater age can influence the quality of groundwater, depending on the land use at the time recharge occurs. These and other factors combine to determine the spatial variability in groundwater quality in the surficial aquifer of the Delaware Coastal Plain.

Groundwater Age

Apparent groundwater ages of samples for which dissolved gases were measured ranged from 1 to 20 years (table 2). These results are consistent with other age tracer results in similar settings (Clune and Denver, 2012; Debrewer and others, 2008) and demonstrate that shallow wells screened just below the water table typically produce relatively young groundwater. Recently recharged groundwater, such as the groundwater observed in this study, is where expected changes in nitrate concentrations would be observed first, since it represents the start of the groundwater-flow paths to streams in the Delaware Coastal Plain.

Land Use

Agriculture, followed by forests, is typically the predominant land-cover type near the network wells. Land-cover data used in this analysis were from the State of Delaware (2007). The land-cover data for the entire State are made up of 33 classes. These data were used to summarize the land use in a 1,640-ft-radius circular buffer around each well. When summarized and grouped into four categories by well location, of the 48 wells sampled, 38 had a majority land-cover type of cropland, 6 had urban, 3 had forest, and 1 had wetland.

Table 2. Water characteristics, major ion, nutrient, and atmospheric age tracer results from groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.

[--, no data; <, less than; d, sample was diluted; i, result may be affected by interference; n, below the reporting level but at or above the detection level; r, value verified by rerun, same method; mg/L, milligrams per liter; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; mL, millimeters; fmol/kg, femtomoles per kilogram; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; SF_6, sulfur hexafluoride; pptv, parts per trillion by volume]

Station number	Local identifier	Geochemical group	Dissolved oxygen, water, unfiltered (mg/L)	pH, water, unfiltered, field, standard units	Specific conductance, water, unfiltered (µS/cm at 25 °C)	Temperature, water (degrees Celsius)	Dissolved solids dried at 180 °C, water, filtered (mg/L)	Calcium, water, filtered (mg/L)	Magnesium, water, filtered (mg/L)	Potassium, water, filtered (mg/L)	Sodium, water, filtered (mg/L)	Alkalinity, water, filtered, inflection-point titration method (incremental titration method), field (mg/L as $CaCO_3$)	Bicarbonate, water, filtered, inflection-point titration method (incremental titration method), field (mg/L)
392959075435501	Fb22-15	1	7.6	5.0	201	15.8	116	12.6	11.1	2.12	2.70	3.0	4.4
392913075382001	Fc12-26	1	8.2	5.8	259	14.1	166	19.4	11.4	1.11	8.88	23.3	28.4
382932075221701	Rf13-02	1	9.1	4.5	192	18.9	117	10.7	3.62	8.06	8.19	0.2	2.6
384425075072401	Oi13-06	1	8.8	5.8	141	17.8	89	11.5	3.39	1.46	6.86	8.8	10.9
384411075150101	Og15-07	1	9.3	4.5	658	15.6	409	56.9	23.5	5.03	18.7	0.5	2.5
385730075321401	Ld33-10	1	4.1	4.9	312	15.5	208	18.7	15.0	3.76	11.2	0.3	1.0
391324075391901	Ic21-08	1	5.9	6.0	297	16.8	189	22.4	16.8	7.99	5.72	35.9	43.8
385956075303801	Lb15-17	1	7.8	5.0	163	13.9	100	10.1	6.79	2.49	4.80	1.8	2.9
391814075435001	Hb22-17	1	7.7	4.8	114	11.6	75	9.16	3.43	1.19	2.67	0.5	1.7
392403075362101	Gc14-04	1	2.3	5.2	150	11.6	94	11.6	5.19	2.97	4.06	10.6	13.2
385817075265101	Le24-11	1	4.3	5.0	352	14.9	213	29.4 r	17.1 r	1.81 r	5.11 r	6.8	9.0
385129075370201	Mc43-06	1	5.8	5.5	335	15.2	237	35.5	9.32	3.18	8.34	14.7	18.0
384323075393201	Oc21-03	1	9.9	5.2	197	14.7	136	13.3	8.70	1.85	5.52	2.3	3.2
390634075433401	Jb42-05	1	1.2	6.0	180	14.8	139	19.5 r	3.88 r	3.27 r	6.24 r	20.7	25.3
391503075310401	Id14-03	1	9.0	5.1	414	14.8	274	32.0	20.9	1.57	9.45	4.0	5.6
384637075153201	Ng45-02	1	9.6	5.5	199	15.6	151	18.1	5.86	2.68	5.20	2.5	<0.1
392324075445601	Gb21-10	2	4.0	5.0	592	16.8	340	18.4	12.3	3.26	69.4	10.1	12.8
383438075274201	Qc13-01	2	7.6	5.1	197	17.8	120	9.85	2.85	2.67	18.0	2.5	3.7
383221075182301	Qg32-18	2	2.7	4.3	169	20.7	105 d	7.50	2.12	2.22	11.2	--	--
384316075330501	Od22-04	2	6.5	4.8	132	14.9	74	5.95	3.02	5.93	7.82	1.0	2.8
384201075185401	Og32-07	2	8.0	4.4	208	19.6	112 r	5.31 r	2.77 r	5.23 r	21.0 r	--	--
385830075423201	Lb23-03	2	<1.0	5.3	262	17.4	185	20.2	6.66	2.18	14.2	6.6	8.3
385515075431701	Lb52-07	2	6.8	5.0	109	18.0	86	5.06	3.27	1.90	6.55	3.3	4.8
390001075380101	Lc12-02	2	7.1	4.7	235	16.1	128	10.9	7.09	1.60	16.5	1.8	3.5
390409075311301	Kd13-09	2	5.6	4.8	158	13.8	102	6.02	3.63	2.77	13.9	0.8	2.3
390205075430901	Kb32-29	2	7.1	4.8	513	13.9	298	8.58 r	5.65 r	5.18 r	72.9 r	0.8	2.0
384550075304001	Nd55-06	2	10.2	4.8	95	17.0	52	5.33 r	0.826 r	1.26 r	7.28 r	0.0	1.5
384845075211901	Nf24-05	2	8.7	4.5	292	17.6	153	9.41 r	5.77 r	7.39 r	25.8 r	--	--
383308075382301	Qc22-04	2	6.4	4.8	171	13.7	104	6.07	7.09	3.00	9.37	2.3	3.6

Table 2. Water characteristics, major ion, nutrient, and atmospheric age tracer results from groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.—Continued

[--, no data; <, less than; d, sample was diluted; i, result may be affected by interference; n, below the reporting level but at or above the detection level; r, value verified by rerun, same method; mg/L, milligrams per liter; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; mL, millimeters; fmol/kg, femtomoles per kilogram; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; SF_6, sulfur hexafluoride; pptv, parts per trillion by volume]

Station number	Local identifier	Geochemical group	Bromide, water, filtered (mg/L)	Chloride, water, filtered (mg/L)	Fluoride, water, filtered (mg/L)	Silica, water, filtered (mg/L as SiO_2)	Sulfate, water, filtered (mg/L)	Ammonia, water, filtered (mg/L as nitrogen)	Nitrate plus nitrite, water, filtered (mg/L as nitrogen)	Nitrite, water, filtered (mg/L as nitrogen)	Orthophosphate, water, filtered (mg/L as phosphorus)	Total nitrogen [nitrate + nitrite + ammonia + organic-N], water, filtered, analytically determined (mg/L)	Iron, water, filtered (µg/L)	Manganese, water, filtered (µg/L)
392959075435501	Fb22-15	1	<0.030	20.3	0.04	13.8	33.5	<0.01	5.60 d	<0.001	0.006	6.02 d	4.4 n	66.0
392913075382001	Fc12-26	1	<0.030	14.2	0.02 n	13.9	38.6	<0.01	9.20 d	<0.001	0.013	10.7 d	7.8 n	0.62
382932075221701	Rf13-02	1	0.032 n	9.09	0.19	8.05	10.2	0.01	13.9 d	<0.001	0.007	14.9 d	4.5 n	40.9
384425075072401	Oi13-06	1	<0.030	13.6	<0.01	5.17	3.93	<0.01	7.53 d	<0.001	<0.004	8.03 d	<4.0	0.90
384411075150101	Og15-07	1	0.073	54.6	0.07	6.91	56.8	<0.01	41.5 d	<0.001	<0.004	46.7 d	<4.0	13.5
385730075321401	Ld33-10	1	<0.030	15.1	0.01 n	20.6	64.5	<0.01	12.3 d	<0.001	0.010	12.3 d	<4.0	451
391324075391901	Ic21-08	1	<0.030	7.72	0.03	12.3	65.3	<0.01	5.98 d	<0.001	0.031	6.30 d	<4.0	0.44
385956075303801	Lb15-17	1	<0.030	11.0	0.02	9.39	25.0	<0.01	6.85 d	<0.001	<0.004	7.37 d	<4.0	38.0
391814075435001	Hb22-17	1	<0.030	5.66	0.06	10.7	25.2	<0.01	3.00	<0.001	0.005 n	3.42	<4.0	6.74
392403075362101	Gc14-04	1	<0.030	16.4	0.03	8.95	14.6	<0.01	3.41	<0.001	0.057	3.62	6.8 n	39.5
385817075265101	Le24-11	1	0.062	26.7	0.09	12.8 r	48.0	<0.01	16.5 d	<0.001	0.006 n	16.9 d	<4.0 r	26.0 r
385129075370201	Mc43-06	1	<0.030	20.8	0.15	5.91	25.5	<0.01	22.1 d	<0.001	<0.004	22.8 d	<4.0	8.44
384323075393201	Oc21-03	1	<0.030	6.90	<0.01	15.6	14.4	<0.01	15.2 d	<0.001	0.007 n	16.5 d	<4.0	13.6
390634075433401	Jb42-05	1	<0.030	10.7	0.05	20.9 r	29.1	0.03	4.95	<0.001	0.042	5.16 d	73.3 r	40.9 r
391503075310401	Id14-03	1	<0.030	32.3	0.04	18.0	99.3 d	0.01 n	11.1 d	<0.001	0.016	11.5 d	4.3 n	21.3
384637075153201	Ng45-02	1	0.030 n	16.8	0.01 n	9.29	8.72	0.01 n	13.1 d	<0.001	<0.004	13.0 d	<4.0	1.82
392324075445601	Gb21-10	2	0.108	137 d	0.03	15.8	36.6	<0.01	6.80 d	0.003	0.007	7.26 d	<4.0	98.3
383438075274201	Qc13-01	2	<0.030	31.9	0.04	5.93	10.1	<0.01	5.12 d	<0.001	<0.004	5.54 d	<4.0	23.4
383221075182301	Qg32-18	2	<0.030	25.1	0.12	6.95	9.12	0.02	4.90	0.004	<0.004	5.08 d	77.4	20.1
384316075330501	Od22-04	2	<0.030	14.4	0.03	5.68	7.62	<0.01	5.55 d	<0.001	<0.004	6.10 d	7.4 n	14.2
384201075185401	Og32-07	2	<0.030	29.6	0.12	9.52 r	13.1	<0.01	6.89 d	<0.001	<0.004	7.22 d	<4.0	6.97
385830075423201	Lb23-03	2	<0.030	32.9	0.03	19.3	24.9	<0.01	8.44 d	0.016	0.010	8.87 d	<4.0	64.4
385515075431701	Lb52-07	2	<0.030	13.3	0.01 n	22.0	5.73	<0.01	4.05	<0.001	0.010	4.16	<4.0	24.2
390001075380101	Lc12-02	2	<0.030 i	51.7	0.06	12.3	9.45	<0.01	2.74	<0.001	<0.004	2.91	4.5 n	12.8
390409075311301	Kd13-09	2	<0.030	12.4	0.04	10.6	24.7	<0.01	4.92	<0.001	<0.004	5.09 d	<4.0	40.4
390205075430901	Kb32-29	2	<0.030 i	129 d	0.03	8.80 r	10.7	<0.01	6.77 d	<0.001	<0.004	7.04 d	<4.0 r	130 r
384550075304001	Nd55-06	2	<0.030	9.35	0.02	6.97 r	12.5	<0.01	2.21	<0.001	0.009	2.40	<4.0	36.9 r
384845075211901	Nf24-05	2	<0.030	46.4	0.12	5.79 r	12.1	<0.01	9.43 d	<0.001	<0.004	9.29 d	41.4 r	24.9 r
383308075382301	Qc22-04	2	0.036 n	13.0	0.02 n	11.6	7.11	<0.01	10.2 d	<0.001	0.007 n	10.6 d	<4.0	59.8

Table 2. Water characteristics, major ion, nutrient, and atmospheric age tracer results from groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.—Continued

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Station number	Local identifier	Geochemical group	Excess air (mL) (1 bottle)	Excess air (mL) (2 bottles)	Excess air (mL) (both)	Average excess air (mL) (average)	Estimated recharge temperature (degrees Celsius) (1 bottle)	Estimated recharge temperature (degrees Celsius) (2 bottles)	Estimated recharge temperatures (degrees Celsius) (both)	Estimated recharge temperatures (degrees Celsius) (average)	SF_6 concentration (fmol/kg) (1 bottle)	SF_6 concentration (fmol/kg) (2 bottles)	SF_6 concentration (fmol/kg) (both)
392959075435501	Fb22-15	1	4.3	4.3	4.3	4.3	12.0	12.0	12.0	12.0	3.3	3.4	3.3 to 3.4
392913075382001	Fc12-26	1	--	--	--	--	--	--	--	--	--	--	--
382932075221701	Rf13-02	1	0.0	0.0	0.0	0.0	9.2	9.2	9.2	9.2	2.2	2.1	2.1 to 2.2
384425075072401	Oi13-06	1	--	--	--	--	--	--	--	--	--	--	--
384411075150101	Og15-07	1	--	--	--	--	--	--	--	--	--	--	--
385730075321401	Ld33-10	1	--	--	--	--	--	--	--	--	--	--	--
391324075391901	Ic21-08	1	1.8	1.3	1.3 to 1.8	1.6	11.6	11.2	11.2 to 11.6	11.4	2.4	2.6	2.4 to 2.6
385956075303801	Lb15-17	1	1.4	1.4	1.4	1.4	11.5	11.5	11.5	11.5	2.4	2.5	2.4 to 2.5
391814075435001	Hb22-17	1	3.3	3.3	3.3	3.3	10.6	10.6	10.6	10.6	3.0	3.1	3 to 3.1
392403075362101	Gc14-04	1	2.9	3.5	2.9 to 3.5	3.2	9.7	10.7	9.7 to 10.7	10.2	3.2	3.2	3.2 to 3.2
385817075265101	Le24-11	1	--	--	--	--	--	--	--	--	--	--	--
385129075370201	Mc43-06	1	1.9	1.9	1.9	1.9	11.8	11.8	11.8	11.8	2.2	2.5	2.2 to 2.5
384323075393201	Oc21-03	1	2.2	2.2	2.2	2.2	12.0	12.0	12.0	12.0	2.6	2.7	2.6 to 2.7
390634075433401	Jb42-05	1	0.5	0.5	0.5	0.5	12.5	12.5	12.5	12.5	1.3	1.3	1.3 to 1.3
391503075310401	Id14-03	1	1.6	1.6	1.6	1.6	11.8	11.8	11.8	11.8	2.1	2.0	2 to 2.1
384637075153201	Ng45-02	1	1.6	1.6	1.6	1.6	13.6	13.6	13.6	13.6	2.5	2.7	2.5 to 2.7
392324075445601	Gb21-10	2	--	--	--	--	--	--	--	--	--	--	--
383438075274201	Qc13-01	2	1.2	1.2	1.2	1.2	13.5	13.5	13.5	13.5	2.2	2.2	2.2 to 2.2
383221075182301	Qg32-18	2	0.6	0.6	0.6	0.6	13.5	13.5	13.5	13.5	2.3	2.4	2.3 to 2.4
384316075330501	Od22-04	2	--	--	--	--	--	--	--	--	--	--	--
384201075185401	Og32-07	2	--	--	--	--	--	--	--	--	--	--	--
385830075423201	Lb23-03	2	1.4	1.3	1.3 to 1.4	1.4	11.7	11.8	11.7 to 11.8	11.8	2.6	2.7	2.6 to 2.7
385515075431701	Lb52-07	2	2.3	2.3	2.3	2.3	12.2	12.2	12.2	12.2	2.1	2.1	2.1 to 2.1
390001075380101	Lc12-02	2	--	--	--	--	--	--	--	--	--	--	--
390409075311301	Kd13-09	2	2.6	2.6	2.6	2.6	11.1	11.1	11.1	11.1	2.8	2.7	2.7 to 2.8
390205075430901	Kb32-29	2	--	--	--	--	--	--	--	--	--	--	--
384550075304001	Nd55-06	2	1.1	1.1	1.1	1.1	8.8	8.8	8.8	8.8	2.7	2.4	2.4 to 2.7
384845075211901	Nf24-05	2	--	--	--	--	--	--	--	--	--	--	--
383308075382301	Qc22-04	2	1.0	1.0	1.0	1.0	8.2	8.2	8.2	8.2	2.5	2.6	2.5 to 2.6

Table 2. Water characteristics, major ion, nutrient, and atmospheric age tracer results from groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.—Continued

[--, no data; <, less than; d, sample was diluted; i, result may be affected by interference; n, below the reporting level but at or above the detection level; r, value verified by rerun, same method; mg/L, milligrams per liter; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; mL, millimeters; fmol/kg, femtomoles per kilogram; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; SF_6, sulfur hexafluoride; pptv, parts per trillion by volume]

Station number	Local identifier	Geochemical group	SF_6 concentration (fmol/kg) (average)	Calculated SF_6 partial pressure (pptv) (1 bottle)	Calculated SF_6 partial pressure (pptv) (2 bottles)	Calculated SF_6 partial pressure (pptv) (both)	Calculated SF_6 partial pressure (pptv) (average)	Piston flow model SF_6 recharge age (years) (1 bottle)	Piston flow model SF_6 recharge age (years) (2 bottles)	Piston flow model SF_6 recharge age (years) (both)	Piston fow model SF_6 recharge age (years) (average)
392959075435501	Fb22-15	1	3.3	6.0	6.1	6 to 6.1	6.0	8.8	8.3	8.3 to 8.8	8.6
392913075382001	Fc12-26	1	--	--	--	--	--	--	--	--	--
382932075221701	Rf13-02	1	2.1	5.4	5.1	5.1 to 5.4	5.2	11.3	12.8	11.3 to 12.8	12.1
384425075072401	Oi13-06	1	--	--	--	--	--	--	--	--	--
384411075150101	Og15-07	1	--	--	--	--	--	--	--	--	--
385730075321401	Ld33-10	1	--	--	--	--	--	--	--	--	--
391324075391901	Ic21-08	1	2.5	5.3	5.9	5.3 to 5.9	5.6	11.9	9.4	9.4 to 11.9	10.7
385956075303801	Lb15-17	1	2.5	5.7	5.7	5.7 to 5.7	5.7	9.9	9.9	9.9	9.9
391814075435001	Hb22-17	1	3.1	5.7	5.9	5.7 to 5.9	5.8	9.9	9.4	9.4 to 9.9	9.7
392403075362101	Gc14-04	1	3.2	6.1	6.0	6 to 6.1	6.1	8.4	8.9	8.4 to 8.9	8.7
385817075265101	Le24-11	1	--	--	--	--	--	--	--	--	--
385129075370201	Mc43-06	1	2.4	5.0	5.5	5 to 5.5	5.2	12.9	10.9	10.9 to 12.9	11.9
384323075393201	Oc21-03	1	2.6	5.7	5.8	5.7 to 5.8	5.8	9.9	9.4	9.4 to 9.9	9.7
390634075433401	Jb42-05	1	1.3	3.4	3.4	3.4 to 3.4	3.4	20.5	20.5	20.5	20.5
391503075310401	Id14-03	1	2.0	4.7	4.6	4.6 to 4.7	4.7	14.5	15.0	14.5 to 15	14.7
384637075153201	Ng45-02	1	2.6	6.1	6.7	6.1 to 6.7	6.4	8.5	6.5	6.5 to 8.5	7.5
392324075445601	Gb21-10	2	--	--	--	--	--	--	--	--	--
383438075274201	Qc13-01	2	2.2	5.6	5.6	5.6 to 5.6	5.6	10.3	10.8	10.3 to 10.8	10.6
383221075182301	Qg32-18	2	2.3	6.4	6.4	6.4 to 6.4	6.4	7.3	7.3	7.3	7.3
384316075330501	Od22-04	2	--	--	--	--	--	--	--	--	--
384201075185401	Og32-07	2	--	--	--	--	--	--	--	--	--
385830075423201	Lb23-03	2	2.7	6.1	6.4	6.1 to 6.4	6.2	8.4	7.4	7.4 to 8.4	7.9
385515075431701	Lb52-07	2	2.1	4.6	4.6	4.6 to 4.6	4.6	14.9	14.9	14.9	14.9
390001075380101	Lc12-02	2	--	--	--	--	--	--	--	--	--
390409075311301	Kd13-09	2	2.8	5.6	5.6	5.6 to 5.6	5.6	10.4	10.4	10.4	10.4
390205075430901	Kb32-29	2	--	--	--	--	--	--	--	--	--
384550075304001	Nd55-06	2	2.5	5.8	5.3	5.3 to 5.8	5.5	9.9	11.9	9.9 to 11.9	10.9
384845075211901	Nf24-05	2	--	--	--	--	--	--	--	--	--
383308075382301	Qc22-04	2	2.6	5.3	5.6	5.3 to 5.6	5.5	11.9	10.4	10.4 to 11.9	11.2

Table 2. Water characteristics, major ion, nutrient, and atmospheric age tracer results from groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.—Continued

[--, no data; <, less than; d, sample was diluted; i, result may be affected by interference; n, below the reporting level but at or above the detection level; r, value verified by rerun, same method; mg/L, milligrams per liter; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; mL, millimeters; fmol/kg, femtomoles per kilogram; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; SF_6, sulfur hexafluoride; pptv, parts per trillion by volume]

Station number	Local identifier	Geochemical group	Dissolved oxygen, water, unfiltered (mg/L)	pH, water, unfiltered, field, standard units	Specific conductance, water, unfiltered (µS/cm at 25 °C)	Temperature, water (degrees Celsius)	Dissolved solids dried at 180 °C, water, filtered (mg/L)	Calcium, water, filtered (mg/L)	Magnesium, water, filtered (mg/L)	Potassium, water, filtered (mg/L)	Sodium, water, filtered (mg/L)	Alkalinity, water, filtered, inflection-point titration method (incremental titration method), field (mg/L as $CaCO_3$)	Bicarbonate, water, filtered, inflection-point titration method (incremental titration method), field (mg/L)
392605075452801	Fa45-07	3	8.8	6.0	1,290	17.0	698	36.4	21.2	3.79	185	38.4	46.9
392428075445901	Gb11-07	3	9.1	5.5	580	15.3	311 r	5.88	2.27	1.82	98.9	10	12.5
393210075401601	Eb35-23	3	4.0	6.0	1,500	17.3	791	46.2	11.1	1.97	221	37.5	45.8
393126075460201	Ea44-13	3	7.8	5.9	1,250	19.1	626	11.5	4.17	2.76	223	34.4	40.7
383629075245601	Pf41-02	3	--	4.5	358	--	203	11.1	3.47	11.0	40.2	2.3	5.2
383412075125401	Qh13-05	3	3.8	4.6	175	17.7	126	1.44	4.04	2.51	21.6	0.2	5.9
383836075183001	Pg22-06	3	2.7	4.9	114	16.4	87	1.89	1.76	2.47	13.7	2.9	4.9
383749075110501	Ph34-15	3	4.8	5.6	120	21.6	65 r	6.76	2.85	1.93	10.3	21.2	26.1
384250075085001	Oi32-18	3	8.2	5.2	189	18.8	125	3.96	5.45	2.37	20.1	3.8	5.1
384737075342701	Nd31-06	3	3.8	6.1	546	18.9	293 r	31.9	5.96	2.00	71.8	8.1	9.9
384159075310801	Od44-02	3	7.4	4.7	118	16.7	68	1.21	2.60	6.30	8.85	2.5	4.9
384130075125801	Oh42-07	3	5.3	5.1	457	18.8	248 r	9.24	4.20	4.09	65.5	6.6	8.7
391112075380001	Ic43-01	3	8.2	5.3	176	16.6	108	3.43	2.40	1.31	25.8	5.1	6.5
390252075271301	Ke33-22	3	3.8	6.2	428	13.2	227 r	27.8	11.3	3.17	35.5	63.3	77.2
391936075363201	Hc14-15	3	5.7	5.9	748	12.8	428	22.1 r	7.82 r	5.71 r	106 r	13.4	16.5
384502075235301	Nf52-02	3	5.7	6.7	470	14.4	264	15.6	4.14	1.42	75.6	73.3	89.3
390544075300501	Jd55-10	3	3.1	5.8	277	16.6	169	13.1 r	5.40 r	2.50 r	29.6 r	24.6	30.3
390705075263201	Je34-04	3	7.9	5.7	226	14.0	133	2.41 r	1.67 r	0.30 r	38.7 r	21.2	26.1
391232075285401	Ie32-02	3	5.2	6.3	1,250	13.2	704	59.5	32.9	4.22	139	121	148

Table 2. Water characteristics, major ion, nutrient, and atmospheric age tracer results from groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.—Continued

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Station number	Local identifier	Geochemical group	Bromide, water, filtered (mg/L)	Chloride, water, filtered (mg/L)	Fluoride, water, filtered (mg/L)	Silica, water, filtered (mg/L as SiO_2)	Sulfate, water, filtered (mg/L)	Ammonia, water, filtered (mg/L as nitrogen)	Nitrate plus nitrite, water, filtered (mg/L as nitrogen)	Nitrite, water, filtered (mg/L as nitrogen)	Orthophosphate, water, filtered (mg/L as phosphorus)	Total nitrogen [nitrate + nitrite + ammonia + organic-N], water, filtered, analytically determined (mg/L)	Iron, water, filtered (µg/L)	Manganese, water, filtered (µg/L)
392605075452801	Fa45-07	3	<0.060 d	334 d	0.07 n, d	7.09	65.7 d	<0.01	6.83 d	<0.001	0.006	7.38 d	<4.0	0.84
392428075445901	Gb11-07	3	<0.030	117 d	0.02	7.66	46.4	<0.01	5.42 d	<0.001	0.005	5.86 d	<4.0	25.3
393210075401601	Eb35-23	3	<0.060 d	430 d	<0.07 d	7.85	8.15 d	<0.01	4.96	0.001	0.014	5.05 d	8.6	13.7
393126075460201	Ea44-13	3	<0.060 d	336 d	0.05 n, d	3.22	25.1 d	<0.01	3.02	<0.001	0.004	2.86	<4.0	18.0
383629075245601	Pf41-02	3	0.045 n	89.7	0.14	6.57	15.9	<0.01	0.373	<0.001	<0.004	0.47	156	18.0
383412075125401	Qh13-05	3	<0.030	27.6	0.03	12.3	21.5	<0.01	1.56	<0.001	<0.004	1.73	<4.0	3.07
383836075183001	Pg22-06	3	0.037 n	22.4	0.03	9.88	5.77	<0.01	0.930	<0.001	<0.004	1.04	<4.0	1.68
383749075110501	Ph34-15	3	<0.030	12.8	<0.01	2.85	3.50	<0.01	3.33	<0.001	<0.004	3.45	<4.0	31.3
384250075085001	Oi32-18	3	0.066	21.1	0.02 n	8.09	32.9	<0.01	3.55	<0.001	<0.004	3.67	4.1 n	12.0
384737075342701	Nd31-06	3	<0.030	108 d	0.04	3.15	21.0	<0.01	1.05	<0.001	0.007	1.20	<4.0	1.24
384159075310801	Od44-02	3	0.045 n	23.8	0.05	7.53	7.56	<0.01	0.562	<0.001	<0.004	0.60	<4.0	4.40
384130075125801	Oh42-07	3	0.049 n	117 d	0.07	7.66	25.8	<0.01	0.340	<0.001	<0.004	0.41	<4.0	4.42
391112075380001	Ic43-01	3	<0.030	30.3	0.07	13.7	26.7	<0.01	1.12	<0.001	0.004 n	1.25	<4.0	4.78
390252075271301	Ke33-22	3	0.042 n	62.4	0.04	3.73	37.2	<0.01	2.15	<0.001	<0.004	2.35	<4.0	15.1
391936075363201	Hc14-15	3	<0.030 i	196 d	0.02 n, d	4.84 r	17.8 d	<0.01	2.29	<0.001	<0.004	2.48	5.4 n	1.94 r
384502075235301	Nf52-02	3	<0.030	98.9	0.05	5.86	5.23	<0.01	0.839	<0.001	0.050	0.95	<4.0	<0.20
390544075300501	Jd55-10	3	<0.030	50.2	0.03	4.77 r	25.1	0.03	1.65	<0.001	0.006 n	1.74	<4.0 r	6.38 r
390705075263201	Je34-04	3	<0.030	39.8	0.03	6.76 r	17.0	0.01 n	0.361	<0.001	<0.004	0.42	4.3	1.90
391232075285401	Ie32-02	3	<0.060 d	322 d	0.07 n, d	5.39	8.10 d	0.02 n	0.825	<0.001	0.005 n	0.91	5.2 n	7.81

Table 2. Water characteristics, major ion, nutrient, and atmospheric age tracer results from groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.—Continued

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Station number	Local identifier	Geochemical group	Excess air (mL) (1 bottle)	Excess air (mL) (2 bottles)	Excess air (mL) (both)	Average excess air (mL) (average)	Estimated recharge temperature (degrees Celsius) (1 bottle)	Estimated recharge temperature (degrees Celsius) (2 bottles)	Estimated recharge temperatures (degrees Celsius) (both)	Estimated recharge temperatures (degrees Celsius) (average)	SF_6 concentration (fmol/kg) (1 bottle)	SF_6 concentration (fmol/kg) (2 bottles)	SF_6 concentration (fmol/kg) (both)
392605075452801	Fa45-07	3	--	--	--	--	--	--	--	--	--	--	--
392428075445901	Gb11-07	3	--	--	--	--	--	--	--	--	--	--	--
393210075401601	Eb35-23	3	1.4	1.4	1.4	1.4	11.5	11.5	11.5	11.5	2.7	2.9	2.7 to 2.9
393126075460201	Ea44-13	3	--	--	--	--	--	--	--	--	--	--	--
383629075245601	Pf41-02	3	--	--	--	--	--	--	--	--	--	--	--
383412075125401	Qh13-05	3	--	--	--	--	--	--	--	--	--	--	--
383836075183001	Pg22-06	3	2.3	2.3	2.3	2.3	7.0	7.0	7.0	7.0	2.6	2.3	2.3 to 2.6
383749075110501	Ph34-15	3	--	--	--	--	--	--	--	--	--	--	--
384250075085001	Oi32-18	3	--	--	--	--	--	--	--	--	--	--	--
384737075342701	Nd31-06	3	--	--	--	--	--	--	--	--	--	--	--
384159075310801	Od44-02	3	--	--	--	--	--	--	--	--	--	--	--
384130075125801	Oh42-07	3	0.9	0.9	0.9	0.9	13.4	13.4	13.4	13.4	2.2	2.2	2.2 to 2.2
391112075380001	Ic43-01	3	2.3	2.3	2.3	2.3	9.2	9.2	9.2	9.2	2.7	2.5	2.5 to 2.7
390252075271301	Ke33-22	3	--	--	--	--	--	--	--	--	--	--	--
391936075363201	Hc14-15	3	--	--	--	--	--	--	--	--	--	--	--
384502075235301	Nf52-02	3	0.4	0.1	0.1 to 0.4	0.2	16.1	16.3	16.1 to 16.3	16.2	2.2	2.2	2.2 to 2.2
390544075300501	Jd55-10	3	2.5	2.5	2.5	2.5	13.6	13.6	13.6	13.6	2.7	2.7	2.7 to 2.7
390705075263201	Je34-04	3	--	--	--	--	--	--	--	--	--	--	--
391232075285401	Ie32-02	3	--	--	--	--	--	--	--	--	--	--	--

Table 2. Water characteristics, major ion, nutrient, and atmospheric age tracer results from groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.—Continued

[--, no data; <, less than; d, sample was diluted; i, result may be affected by interference; n, below the reporting level but at or above the detection level; r, value verified by rerun, same method; mg/L, milligrams per liter; µS/cm at 25 °C, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; mL, millimeters; fmol/kg, femtomoles per kilogram; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; SF_6, sulfur hexafluoride; pptv, parts per trillion by volume]

Station number	Local identifier	Geochemical group	SF_6 concentration (fmol/kg) (average)	Calculated SF_6 partial pressure (pptv) (1 bottle)	Calculated SF_6 partial pressure (pptv) (2 bottles)	Calculated SF_6 partial pressure (pptv) (both)	Calculated SF_6 partial pressure (pptv) (average)	Piston flow model SF_6 recharge age (years) (1 bottle)	Piston flow model SF_6 recharge age (years) (2 bottles)	Piston flow model SF_6 recharge age (years) (both)	Piston flow model SF_6 recharge age (years) (average)
392605075452801	Fa45-07	3	--	--	--	--	--	--	--	--	--
392428075445901	Gb11-07	3	--	--	--	--	--	--	--	--	--
393210075401601	Eb35-23	3	2.8	6.2	6.8	6.2 to 6.8	6.5	7.8	6.3	6.3 to 7.8	7.1
393126075460201	Ea44-13	3	--	--	--	--	--	--	--	--	--
383629075245601	Pf41-02	3	--	--	--	--	--	--	--	--	--
383412075125401	Qh13-05	3	--	--	--	--	--	--	--	--	--
383836075183001	Pg22-06	3	2.5	4.8	4.2	4.2 to 4.8	4.5	13.8	16.3	13.8 to 16.3	15.1
383749075110501	Ph34-15	3	--	--	--	--	--	--	--	--	--
384250075085001	Oi32-18	3	--	--	--	--	--	--	--	--	--
384737075342701	Nd31-06	3	--	--	--	--	--	--	--	--	--
384159075310801	Od44-02	3	--	--	--	--	--	--	--	--	--
384130075125801	Oh42-07	3	2.2	5.8	5.7	5.7 to 5.8	5.7	9.8	9.8	9.8	9.8
391112075380001	Ic43-01	3	2.6	5.3	4.9	4.9 to 5.3	5.1	11.9	13.9	11.9 to 13.9	12.9
390252075271301	Ke33-22	3	--	--	--	--	--	--	--	--	--
391936075363201	Hc14-15	3	--	--	--	--	--	--	--	--	--
384502075235301	Nf52-02	3	2.2	6.8	7.3	6.8 to 7.3	7.0	6.4	4.4	4.4 to 6.4	5.4
390544075300501	Jd55-10	3	2.7	6.0	5.9	5.9 to 6	5.9	9.0	9.5	9 to 9.5	9.2
390705075263201	Je34-04	3	--	--	--	--	--	--	--	--	--
391232075285401	Ie32-02	3	--	--	--	--	--	--	--	--	--

Soils

Soils data were extracted on an individual well basis using a similar buffer and extract methods as those used for the land-cover data. Soils data came from the Gridded Soil Survey Geographic (gSSURGO) database (Soil Survey Staff, 2016) and were downloaded from the U.S. Department of Agriculture's Geospatial Data Gateway. Surficial soils around the wells were mostly sandy with 46 of the 48 sampled wells having sand content greater than 50 percent. Soils at all wells had low clay content with none having more than 18.5 percent clay.

Well Depth and Aquifer Position

Surficial aquifer thickness at each well was determined using a simple overlay where well locations were intersected with an aquifer thickness dataset (Denver and Nardi, 2016). The dataset maps the thickness of the surficial unconfined aquifer, including from the land surface and unsaturated zone to the bottom of sediments of geologic units identified as part of the surficial aquifer. The thickness of the surficial aquifer may have impacts on groundwater-flow paths and the potential for denitrification. Wells in this study were mostly located in areas of relatively thick aquifer (table 1), with a mean thickness for all wells of 68.9 ft. The thickness range of all wells was 117 ft, with a minimum of 11 ft and a maximum of 128 ft.

Water Quality in the Surficial Aquifer

Three groups of wells with similar properties were derived using Spearman's rank correlation and cluster analysis (table 2, fig. 5*A*). A geographic pattern (fig. 5*B*) is not evident from this analysis; however, land use and geochemical properties are similar within groups. These groups are useful in describing some of the variability in groundwater quality and may facilitate more detailed statistical analysis in future studies. The patterns observed in these three groups are described below.

The major-ion composition of groundwater (table 3) in agricultural areas of Delaware consists of two end-member water types (fig. 6) that reflect the spatial variability associated with land use and land cover, practices applied on the land, soils, and aquifer properties. Overall, the predominant cations are sodium and calcium, whereas the predominant anions are chloride and nitrate, consistent with previous studies in the Coastal Plain (Ator, 2008; Ator and Denver, 2015). However, within the geochemical groups, there are strong differences between major ions in groups 1 and 3. Group 1 is a calcium-magnesium-nitrate water type (fig. 6), typically identified as an agricultural signature in the Delmarva Peninsula (Böhlke, 2002). Group 3 is a sodium-potassium-chloride water type and group 2 appears to be a mixture of groups 1 and 3 (fig. 6).

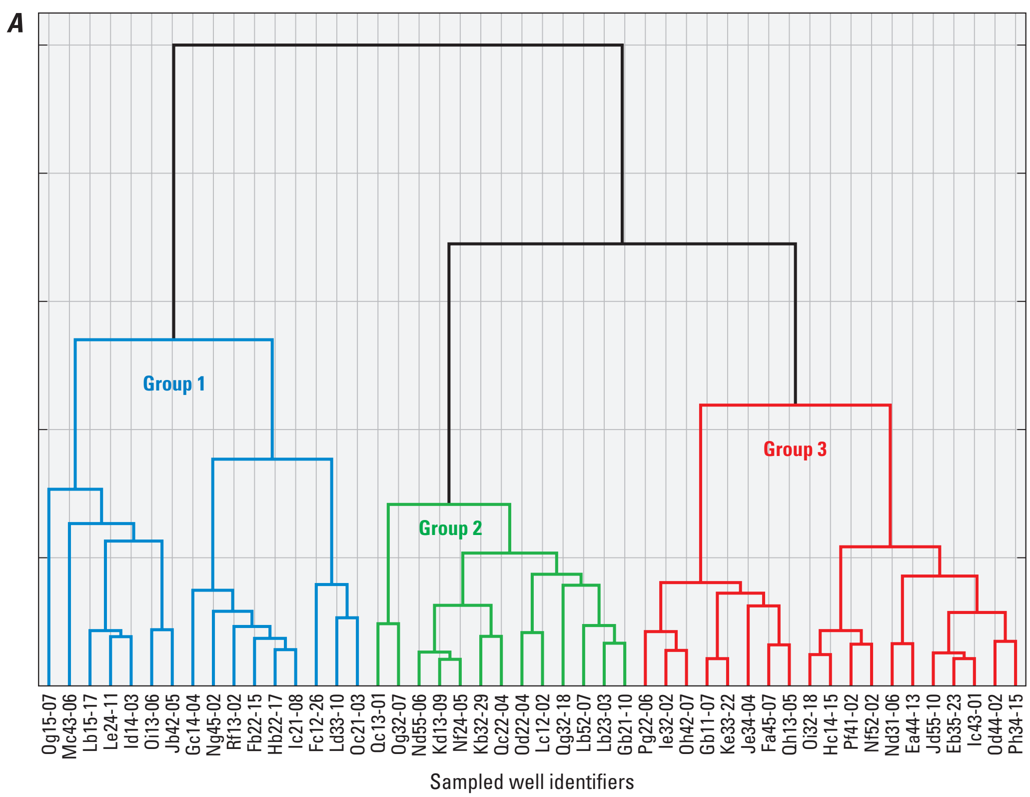

Figure 5. Results of correlation and cluster analysis, *A*, dendrogram showing the grouping of wells by correlation and cluster analysis, and *B*, the spatial distribution of geochemical groups.

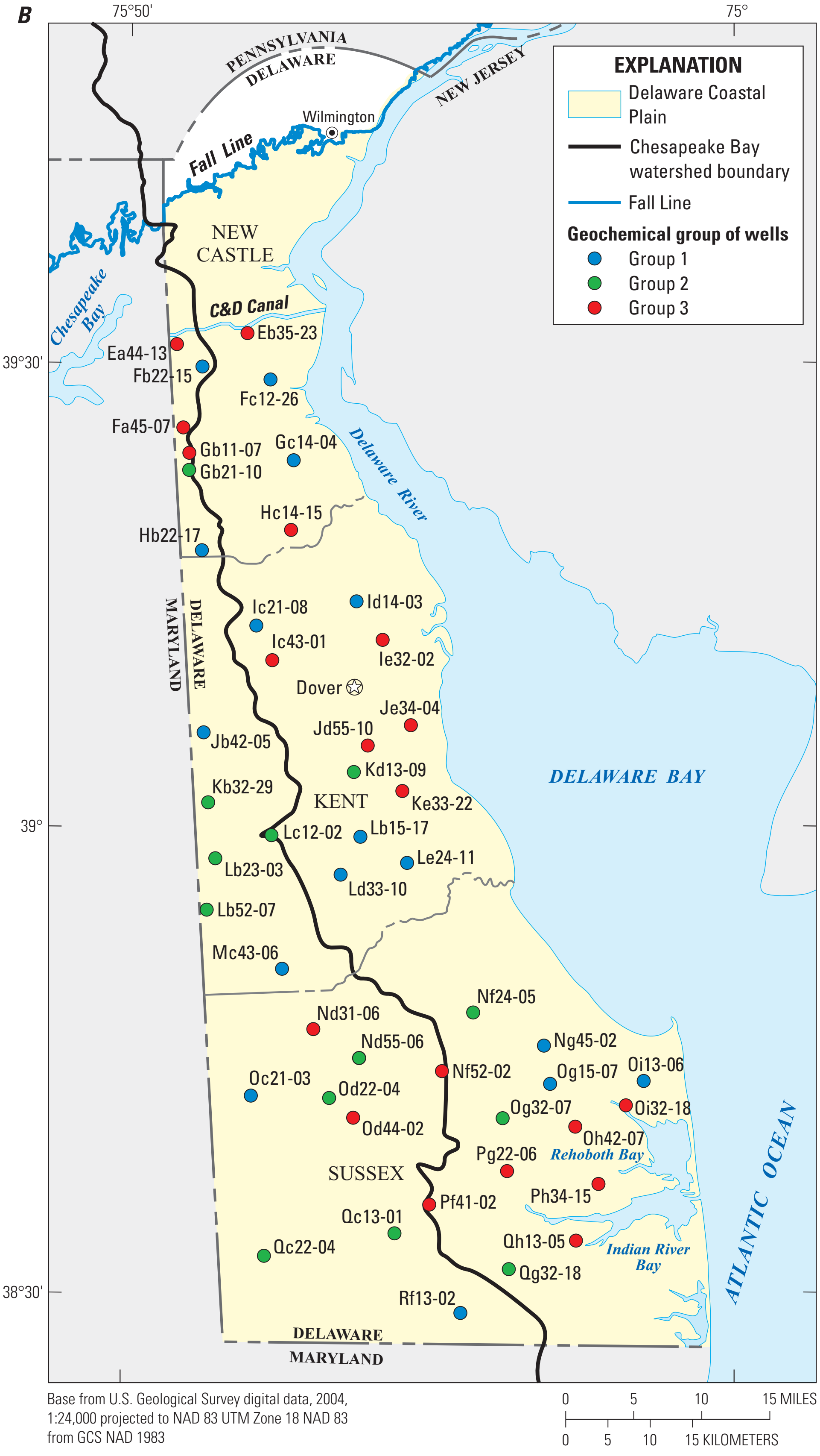

Figure 5. Results of correlation and cluster analysis, *A*, dendrogram showing the grouping of wells by correlation and cluster analysis, and *B*, the spatial distribution of geochemical groups.—Continued

Table 3. Summary statistics for selected physical properties and major ions and elements of groundwater in the surficial aquifer of the Delaware Coastal Plain, 2014.

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; N, nitrogen; <, less than]

Constituents (units)	Geochemical Group 1			Geochemical Group 2			Geochemical Group 3		
	Minimum	Median	Maximum	Minimum	Median	Maximum	Minimum	Median	Maximum
Physical properties									
pH (standard units)	4.65	5.69	6.57	4.41	5.15	6.08	4.85	5.95	7.48
Specific Conductance (µS/cm)	114	200	658	95	197	592	114	428	1,496
Dissolved Oxygen (mg/L)	1.23	7.71	9.89	1	6.78	10.24	2.67	5.68	9.06
Major ions or elements									
Bicarbonate (mg/L)	<0.1	5.00	43.80	<0.1	2.8	12.8	4.90	16.50	147.90
Calcium (mg/L)	9.157	18.39	56.85	5.06	7.50	20.25	1.21	11.11	59.53
Chloride (mg/L)	5.655	14.65	54.60	9.35	29.64	136.85	12.80	89.68	430.31
Magnesium (mg/L)	3.385	9.01	23.53	0.83	3.63	12.26	1.67	4.17	32.93
Nitrate (mg/L as N)	3.000	10.15	41.47	2.21	5.55	10.25	0.34	1.56	6.83
Potassium (mg/L)	1.111	2.59	8.06	1.26	2.77	7.39	0.30	2.50	10.98
Silica (mg/L)	5.169	11.49	20.85	5.68	9.52	21.96	2.86	6.76	13.71
Sodium (mg/L)	2.674	5.98	18.73	6.55	14.17	72.92	8.85	40.23	223.00
Sulfate (mg/L)	3.928	27.30	99.30	5.73	10.71	36.59	3.50	21.03	65.69

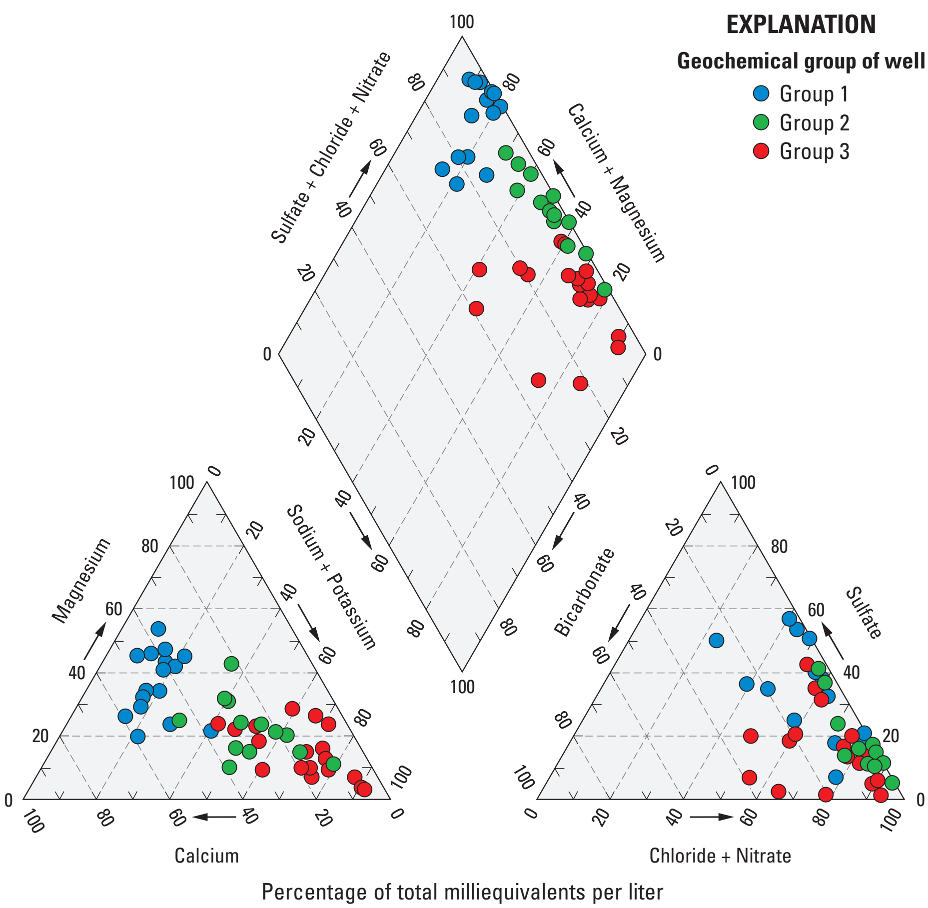

Figure 6. Trilinear diagram of major ions within the surficial aquifer of the Delaware Coastal Plain by geochemical groups.

Nitrate

Nitrate is the predominant nutrient found in the surficial aquifer of the Delaware Coastal Plain, with a median concentration of 4.95 mg/L in samples collected from the 48 wells. In the three groups of wells determined by correlation and cluster analysis, geochemical group 1 had the highest median nitrate concentration at 10.15 mg/L, exceeding the EPA drinking-water standard for public water systems of 10 mg/L (U.S. Environmental Protection Agency, 2009) (fig. 7*A*; table 3). Nitrate concentrations in group 1 were different than the nitrate concentrations in group 3 at the ($p < 0.05$) level of significance. Group 1 also had the highest median values of calcium and magnesium (figs. 7*B* and 7*C*, table 3) and differs from group 2 at the ($p < 0.05$) level of significance. Calcium and magnesium in group 3 were not different than groups 1 or 2 at the ($p < 0.05$) level of significance. Group 1 had the highest percentage of agricultural land in the 1,640-ft-radius land buffer analysis (fig. 8*A*), but was not different from groups 2 or 3 at the ($p < 0.05$) level of significance. Groundwater collected from wells in group 1 exhibited characteristics described as having an agricultural signature (calcium-magnesium-nitrate water type; fig. 6) in previous studies on the Delmarva Peninsula (Böhlke, 2002; Denver, 1989; Hamilton and others, 1993).

Group 3, which had the highest percentage of developed land near the wells (fig. 8*B*), had the lowest median nitrate concentrations (1.55 mg/L, table 3). Nitrate concentrations in the surficial aquifer have been shown to be lower in urban and developed areas compared to agricultural areas (Denver and others, 2014). The median concentration of nitrate in group 2 (5.55 mg/L) is between groups 1 and 3. The overall geochemical signature of group 2 (fig. 6, table 3) appears to be a blend of the group 1 (high nitrate, low chloride) and group 3 (low nitrate, high chloride) end members.

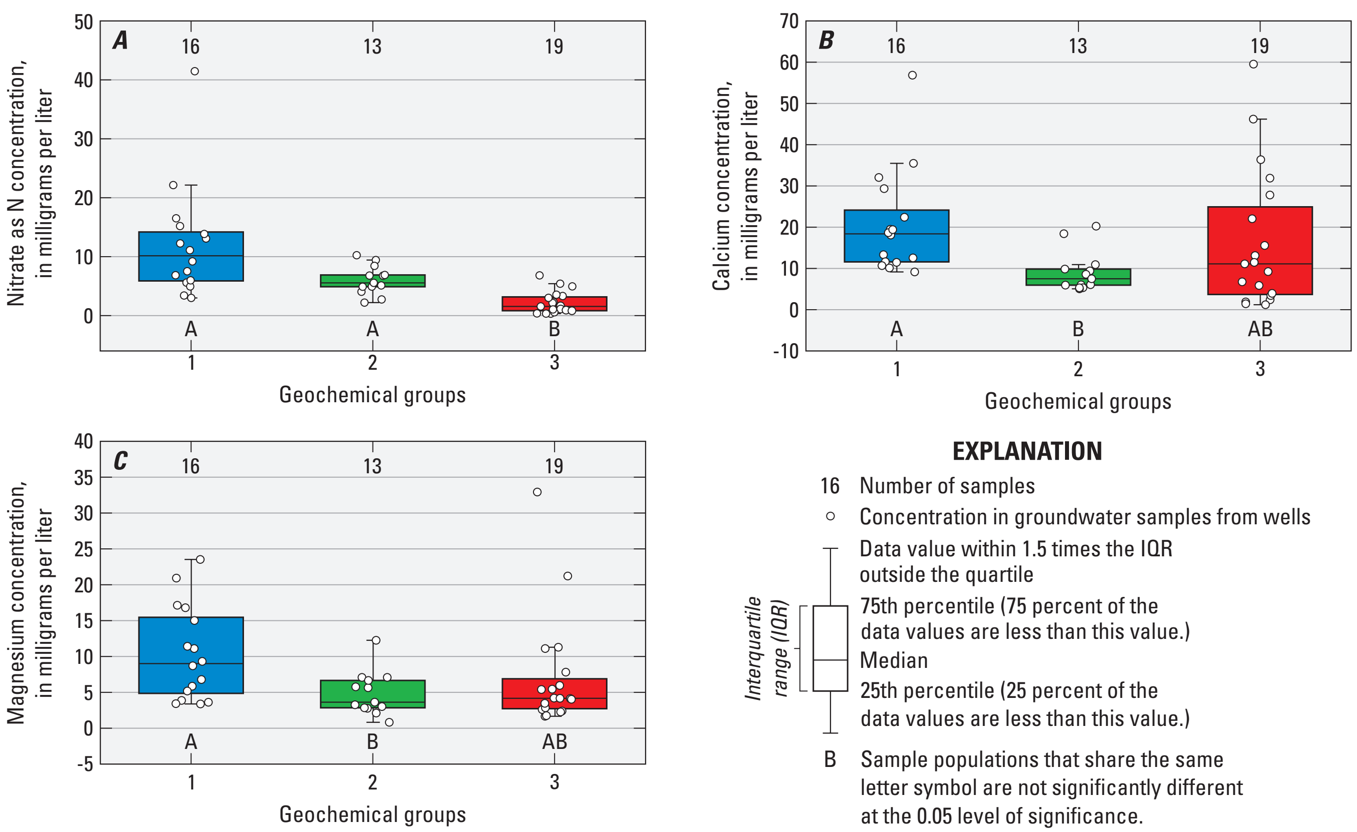

Figure 7. Boxplots of *A*, nitrate, *B*, calcium, and *C*, magnesium concentrations by geochemical groups.

Chloride

Chloride concentrations in natural groundwater are typically low (Hem, 1985), but elevated concentrations of sodium and chloride in groundwater are common in the United States (Panno and others, 2006). Common sources of chloride in groundwater are from deicing activities, commercial fertilizer, sewage and animal wastes, landfill leachate, seawater intrusion, and migration of formation brines (Mullaney and others, 2009). In Delaware, likely sources of chloride in groundwater are from deicing, potassium chloride fertilizers, and septic and animal wastes. Seawater intrusion may be a source near the coast, but because all wells in this study are at least several miles from the coast, it is unlikely that it affected the chloride concentrations in shallow groundwater that was sampled. The highest median concentrations of chloride (89 mg/L) were measured in samples collected from wells in group 3 (table 3, fig. 9*A*). These differ from chloride concentrations in group 1 at the ($p < 0.05$) level of significance. The ratio of chloride to bromide, often used to identify potential sources of chloride, was also much higher in group 3 than in groups 1 or 2, with a median value of over 2,000. Ten of the 19 wells in group 3 had chloride to bromide ratios above 2,000 (fig. 9*B*), typical of chloride with a halite source (Mullaney and others, 2009). Samples from wells in the northern part of the study area showed the highest chloride to bromide ratios and the highest chloride concentrations (fig. 9*C*). Wells in group 3 also had the highest percentage of developed land use near them (fig. 8*B*), which may be related to increased chloride from deicing activity. In general, more deicing products are used on roads in urban and suburban areas, and in Delaware, that includes more of the northern part of the Coastal Plain where ice is a greater problem. Although it is difficult to identify the exact sources of chloride, the chloride to bromide ratios in group 3 are significantly different from the chloride to bromide ratios in group 1 (fig. 9*B*).

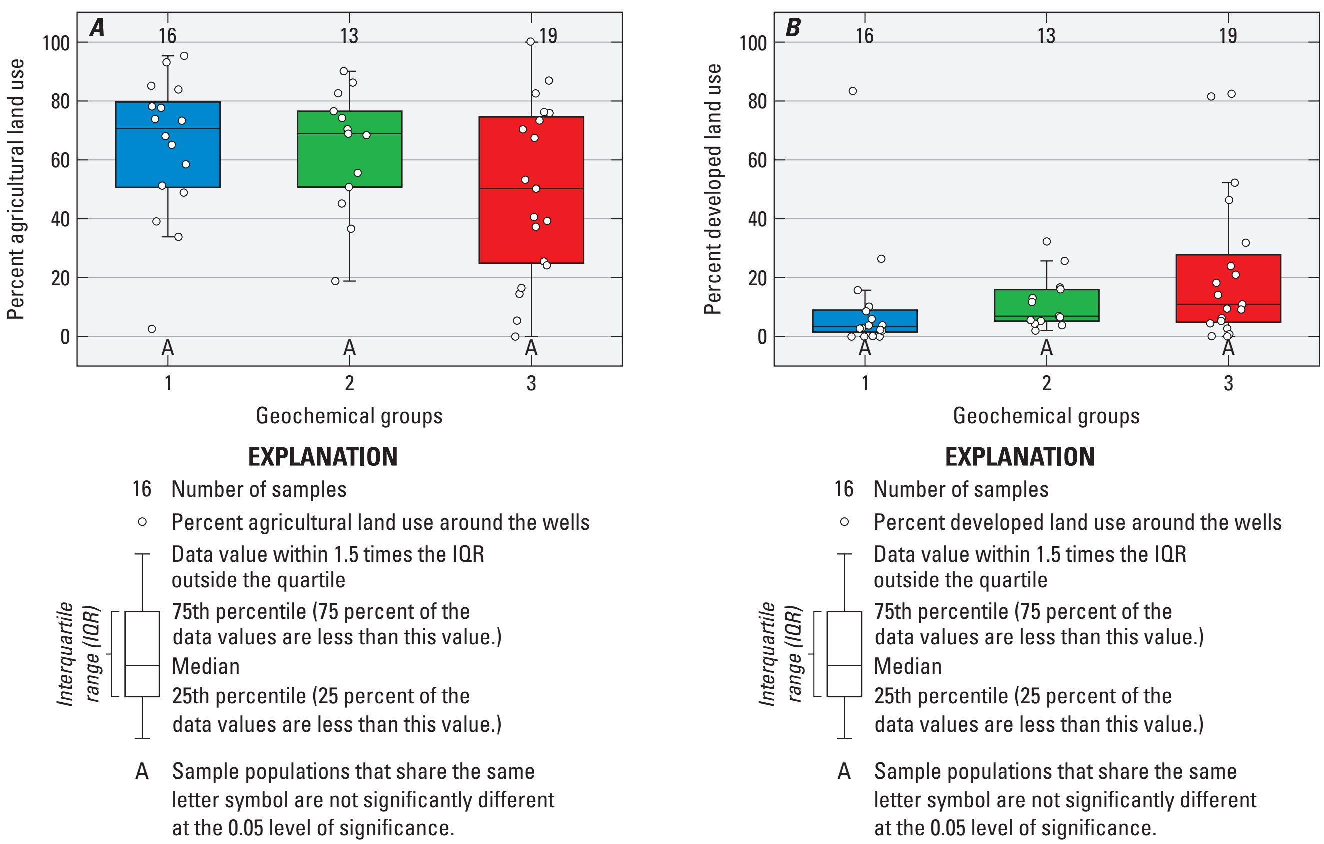

Figure 8. Boxplots of *A*, agricultural land use, and *B*, developed land use by geochemical groups.

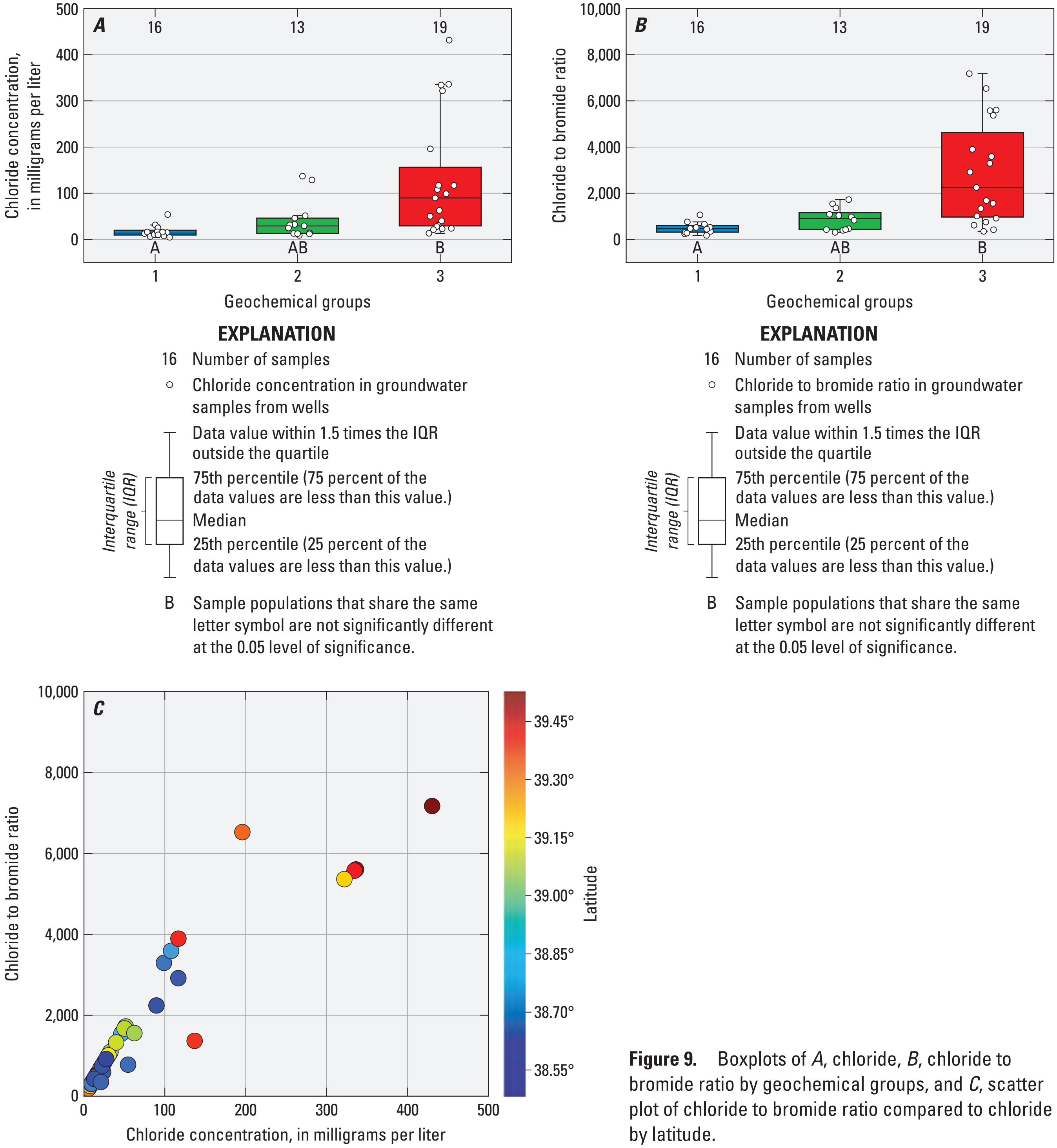

Figure 9. Boxplots of *A*, chloride, *B*, chloride to bromide ratio by geochemical groups, and *C*, scatter plot of chloride to bromide ratio compared to chloride by latitude.

Summary and Conclusions

The U.S. Geological Survey, in cooperation with the Delaware Department of Agriculture designed a network of wells to monitor groundwater quality in the surficial aquifer of the Delaware Coastal Plain. Wells in existing groundwater networks throughout the Delmarva Peninsula were selected to assess water-quality conditions over the entire Delmarva Peninsula and many water-quality parameters, including nitrate. Because of the broad nature of these existing network designs, the number of wells located in settings where nitrate is present was small, limiting the use of statistical methods to determine whether changes in nitrate concentrations are occurring over time. The network designed for this study takes advantage of what was learned about the factors affecting spatial variability in nutrients and targets those settings (shallow wells at the water table, young groundwater [recently recharged], well-drained soils, and oxic groundwater) where changes in nitrate are most likely to be observed. Forty-eight wells were identified from two existing groundwater-monitoring networks in the surficial aquifer of the Delaware Coastal Plain and sampled for water quality in 2014.

The wells sampled in 2014 were grouped based on their similarity in geochemistry using correlation and cluster analysis. These groups were effective in explaining some of the variability within the network, especially for nitrate and chloride concentrations. Although spatial patterns were not evident for nitrate, land-use patterns near wells appear to be a factor in the geochemistry of shallow groundwater. Results of this study showed that the highest median nitrate concentrations are in the group with the highest percentage of agricultural land use and the highest median chloride concentrations are in the group with the highest percentage of developed land use. There appears to be a spatial pattern in chloride concentrations, with higher values in the northern part of the study area that may be related to deicing activities. These groups of wells can be evaluated for trends independently of the entire network with future sampling, which could be useful in identifying where agricultural best management practices (BMPs) are most effective at reducing the leaching of nutrients to shallow groundwater.

The implementation of agricultural BMPs across Delaware over the last several decades has had a goal of reducing the leaching of nitrate into shallow groundwater. In the surficial aquifer of the Delaware Coastal Plain, changes in water quality that may be attributed to agricultural BMPs may only become apparent with repeated monitoring over long periods of time. The results of this study are intended to establish water-quality conditions in 2014 to allow future comparison and evaluate the effectiveness of BMPs on a regional scale.

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