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Comparison of Water Quality in Shallow Groundwater Near Agricultural Areas in the Delaware Coastal Plain, 2014 and 2019

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Acknowledgments

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
	Area	
acre	4,047	square meter (m^2)
acre	0.4047	hectare (ha)
acre	0.4047	square hectometer (hm^2)
acre	0.004047	square kilometer (km^2)
square foot (ft^2)	929.0	square centimeter (cm^2)
square foot (ft^2)	0.09290	square meter (m^2)
square inch (in^2)	6.452	square centimeter (cm^2)
section (640 acres or 1 square mile)	259.0	square hectometer (hm^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Mass	
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	metric ton (t)
ton, long (2,240 lb)	1.016	metric ton (t)
	Hydraulic gradient	
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)
	Transmissivity	
foot squared per day (ft^2/d)	0.09290	meter squared per day (m^2/d)
	Application rate	
pound per acre per year ([lb/acre]/yr)	1.121	kilogram per hectare per year ([kg/ha]/yr)

Datum

Vertical coordinate information is referenced to North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83), universe trans mercator (UTM) zone 18 North. Elevation, 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

C&D	Chesapeake and Delaware Canal
Delmarva	Peninsula of Delaware, Maryland and Virginia
DDA	Delaware Department of Agriculture
DGS	Delaware Geological Survey
DNREC	Delaware Department of Natural Resources and Environmental Control
EPA	U.S. Environmental Protection Agency
NACP	North Atlantic Coastal Plain
NASS	National Agricultural Statistics Service
NAWQA	National Water Quality Assessment
NRCS	Natural Resources Conservation Service
NWQL	National Water Quality Laboratory
NWIS	National Water Information System
OP	Orthophosphate
TMDL	Total Maximum Daily Load
USDA	U.S. Department of Agriculture
USGS	U.S. Geological Survey

Abstract

The State of Delaware has encouraged agricultural conservation practices to improve nutrient uptake by crops and to mitigate nutrient transport to groundwater in the surficial aquifer. The U.S. Geological Survey, in cooperation with the Delaware Department of Agriculture (DDA) developed a network of shallow wells near agricultural areas throughout the Delaware Coastal Plain. This network was designed to characterize water quality related to agricultural practices and to detect any recent changes in shallow groundwater quality, in particular with concentration of nitrate. The shallow well network was first sampled in 2014 and resampled in 2019. In 2019 field parameters including dissolved oxygen, pH, specific conductance, and temperature as well as major ions, nutrients, stable isotopes of water, and isotopes of nitrate isotopes were measured in groundwater samples collected between October and December. Wells were organized into three groups based on their geochemical characteristics measured in 2014, resulting in an agricultural, urban, and mixed group. Results from the 2019 sampling show little change in water quality from the 2014 sampling. Land-use factors continued to be the driving influence between groups. Groundwater moves slowly and changes in groundwater quality are likely to respond slowly to changes in conservation practices. Continued sampling of both groundwater quality in this network and monitoring land management practices are needed to detect these trends in the future.

Introduction

Delaware's surficial aquifer underlies more than 90% of the state and, is an important source of water but is sensitive to chemistry changes driven by land management (Masterson and others, 2016; Ator and Denver, 2015; Fleming and others, 2017). Groundwater from the surficial aquifer provides drinking water to rural and urban residents, irrigation for farms, baseflow to streams, and water for thermoelectric generation and industry (Dieter and others, 2018). As the dominant source of surface water within the State, the surficial aquifer also plays a critical role in controlling water quality in streams, rivers, and estuaries like the Delaware Bay and Chesapeake Bay.

Water quality within the surficial aquifer is susceptible to leaching of chemicals applied to or near the land surface because of its shallow water table, generally transmissive sandy sediments, and Delaware's abundant rainfall. These factors create a strong hydrologic connection between the land surface and the surficial aquifer (Fleming and others, 2017). Land management decisions leading to changes water chemistry in the surficial aquifer such as nutrient applications for crop growth or de-icing agents on roadways, are well reported across the greater Delmarva Peninsula (Lindsey and others, 2023; Denver, 1986; Denver, 1989; Andres., 1991; Shedlock and others, 1999; Blaier and Baxter, 2000; Denver and others, 2004; DeBrewer and others, 2008; Denver and others, 2018). Dissolved constituents in groundwater can travel through the aquifer to wells used for public and domestic drinking-water supplies. Previous sampling efforts of public-supply wells screened in the surficial aquifer detected nitrate in 90 percent of the wells sampled and the wells had a median nitrate concentration of 5.2 milligrams per liter (mg/L); detections of pesticides or pesticide derivatives were also found in many wells (Reyes, 2008). A national analysis *(*McMahon, 2012*)* of historical groundwater-quality data by the USGS National Water Quality Program (NWQP) program characterized the unconfined North Atlantic Coastal Plain on the Delmarva Peninsula as being moderately to highly susceptible to changes in nitrate concentration because of short groundwater flowpaths and generally oxic conditions.

Much of Delaware's annual streamflow is provided by groundwater discharging to streams, making groundwater the dominant source of nitrate in streams and coastal waters (Andres, 1992; Ullman and others, 2007; Ator and Denver, 2015). Nitrate is a soluble, negative ion (NO_3^-) that is easily transported through the root zone to groundwater and is unlikely to bind to soil which has a generally negative charge (Weil and Brady, 2017). Nitrate may be consumed and converted into N^2 gas by microorganisms in groundwater through a process called denitrification; however, this process is anaerobic and is generally limited to anoxic waters. In oxic groundwater, nitrate is more likely to be preserved over the flowpath and delivered to streams. Nitrate in groundwater is a concern to the State of Delaware as elevated nitrate concentrations may affect the suitability of water for human consumption (Schullehner and others, 2018; Deridder and others, 2020) and is linked to adverse environmental outcomes (Ator and Denver, 2015). Controlling groundwater quality is integral to managing surface-water quality. The surficial aquifer of Delaware contains both oxic groundwater that allows for nitrogen transport to streams and low carbon concentrations, which are related to higher baseflow nitrate values and reduced denitrification (Wherry and others, 2020). Ator and Denver (2012) estimated that baseflow nitrate fluxes represented 70% of the total nitrogen flux in Delmarva headwater streams.

Due to the detrimental impacts that high nitrate concentrations can incur on both groundwater and surface water resources, the State has a vested interest in managing groundwater quality.

The state of Delaware has and continues to invest in management practices that increase crop production while improving groundwater quality by reducing the leaching of nitrate and other ions. However, previous studies indicate that changes in nutrient management practices on the land surface, because of the slow movement of groundwater, may take decades to improve water quality of Delmarva streams (Shedlock, 1993; Sanford and Pope, 2013). In contrast, evidence of increasing concentrations of nitrate in shallow groundwater of the surficial aquifer has been related to increases in nutrient inputs on the land surface of the Delmarva Peninsula over time between 1988 to 2001-2003 prior to the implementation of nutrient management practices (Denver and others, 2018).

Previous groundwater monitoring networks in Delaware were designed to evaluate the occurrence of a broad range of contaminants in both oxic and anoxic shallow groundwater on the Delmarva Peninsula (Hamilton and others, 1993; Debrewer and others, 2007, Ator and others 2015) and in Delaware (Blaier and Baxter, 2000). These networks included, but did not focus on, young, oxic groundwater where recent land management changes had been observed. Identifying the need for a network focused on these characteristics, the USGS and Delaware Department of Agriculture (DDA) designed a shallow well network (fig. 1, Table 1) for the purpose of detecting changes in shallow groundwater quality.

The initial sampling of this network in 2014 analyzed water chemistry and was used for a correlation and cluster analysis that identified three groups based on relative concentrations of dominant ions. Group 1 (agriculture) was identified as having a “calcium, magnesium and nitrate” type water which has been related to agricultural land uses (Denver, 1989; Hamilton and others, 1993; Böhlke, 2002; Fleming and others, 2017). Group 3 (urban) is a sodium-potassium-chloride water type and was found in wells which generally had a relatively high urban land use and road density (Fleming and others, 2017). Group 2 (mixed) had a mixture of characteristics from the Agricultural and Urban Groups. The highest median nitrate concentration 10.15mg/L as N was observed in the Agricultural Group followed by the Mixed Group with a median of 5.55 mg/L and urban group with 1.56 mg/L as N. The Urban Group had the highest concentrations of chloride with a median of 89.7 mg/L with the Mixed and Agricultural groups having median chloride concentrations of 79.6 and 14.65mg/L respectively.

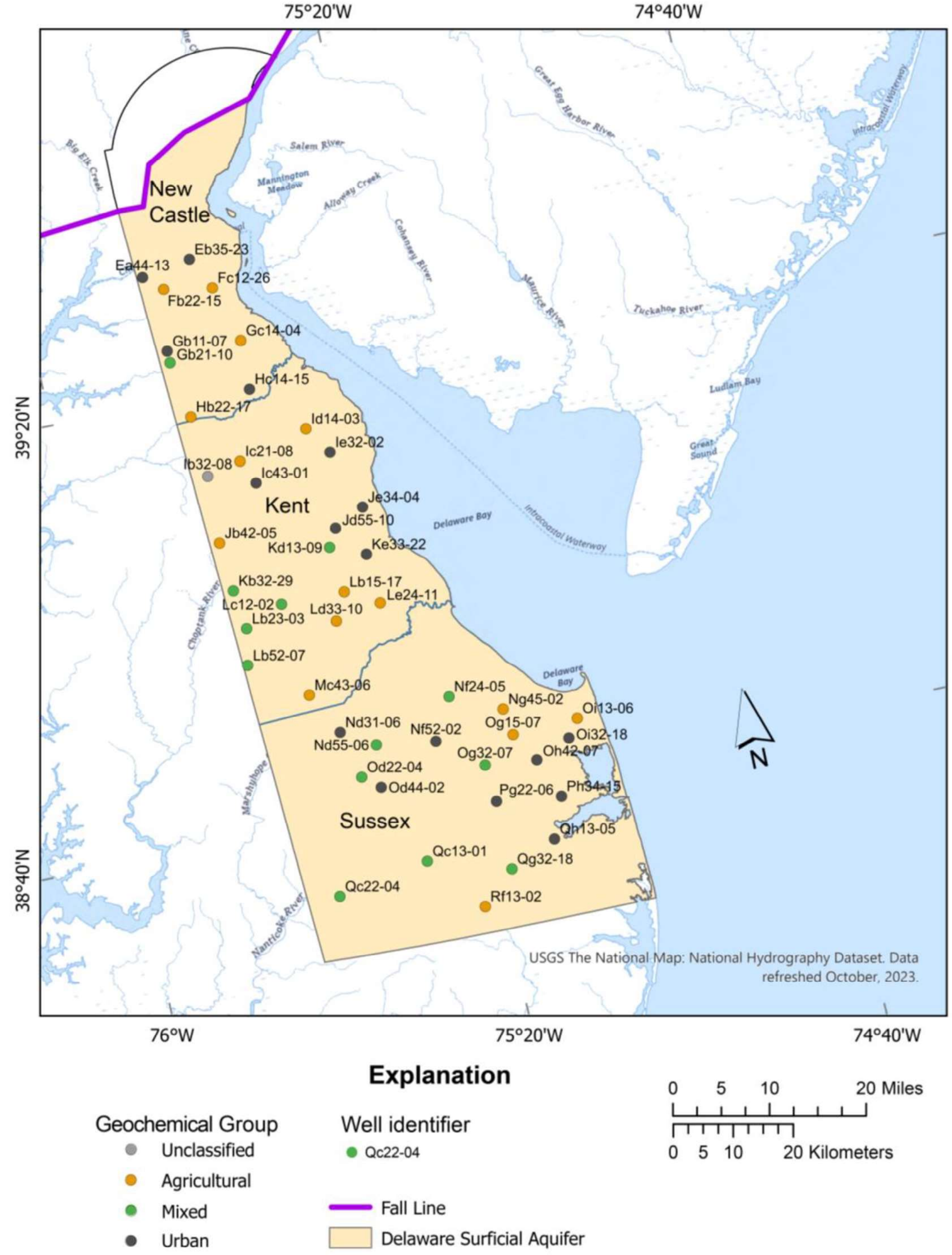

Figure 1 Locations of 46 wells sampled during the 2019 sampling event of the Delaware shallow aquifer network the Atlantic seaboard fall line demarking the piedmont and coastal plain is also shown.

Purpose and Scope

Geochemistry in shallow groundwater of the Delaware Coastal Plain is summarized in this report. Of the 46 wells sampled in 2019, 45 were previously sampled in 2014 Repeated sampling of the network provides an opportunity to begin to compare water-quality conditions over time and enhance understanding of the effectiveness of conservation practices.

In this report sources of nitrogen in groundwater are suggested and shallow groundwater quality conditions between the two sampling periods of 2014 and 2019 are compared. This study focuses on groundwater chemistry from shallow wells near agricultural areas and divides the re-sampled wells into three groups based on chemical similarities outlined in Fleming and others, 2017. Results presented include samples collected and analyzed for field parameters, nutrients, major ions, and stable isotopes of hydrogen, oxygen, and isotopes of nitrate-nitrogen.

Table 1. Site information for wells sampled in the surficial aquifer of the Delaware Coastal Plain, 2019.

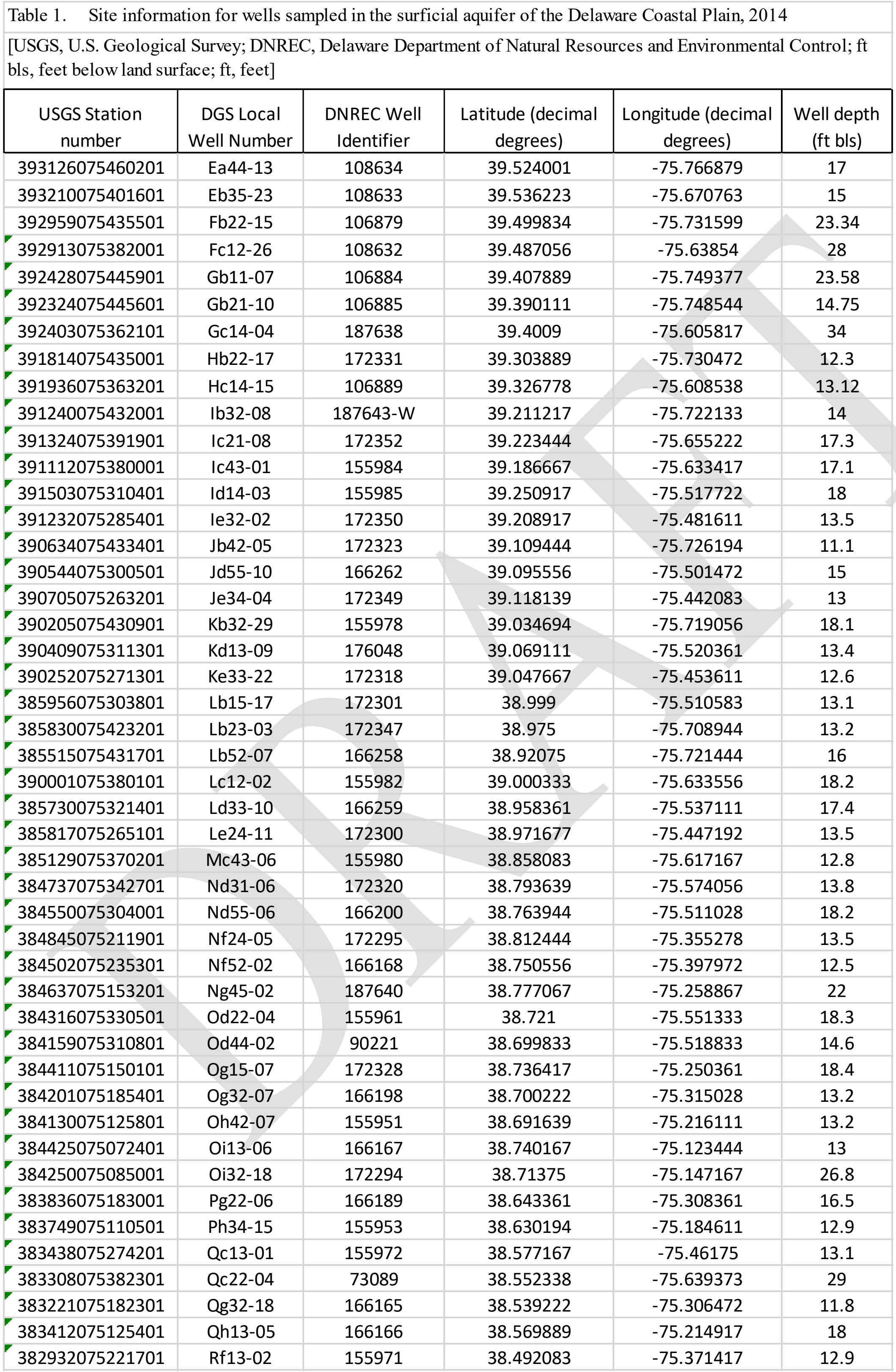

Table 1. Site information for wells sampled in the surficial aquifer of the Delaware Coastal Plain, 2014

[USGS, U.S. Geological Survey; DNREC, Delaware Department of Natural Resources and Environmental Control; ft bls, feet below land surface; ft, feet]

USGS Station number	DGS Local Well Number	DNREC Well Identifier	Latitude (decimal degrees)	Longitude (decimal degrees)	Well depth (ft bls)
393126075460201	Ea44-13	108634	39.524001	-75.766879	17
393210075401601	Eb35-23	108633	39.536223	-75.670763	15
392959075435501	Fb22-15	106879	39.499834	-75.731599	23.34
392913075382001	Fc12-26	108632	39.487056	-75.63854	28
392428075445901	Gb11-07	106884	39.407889	-75.749377	23.58
392324075445601	Gb21-10	106885	39.390111	-75.748544	14.75
392403075362101	Gc14-04	187638	39.4009	-75.605817	34
391814075435001	Hb22-17	172331	39.303889	-75.730472	12.3
391936075363201	Hc14-15	106889	39.326778	-75.608538	13.12
391240075432001	Ib32-08	187643-W	39.211217	-75.722133	14
391324075391901	Ic21-08	172352	39.223444	-75.655222	17.3
391112075380001	Ic43-01	155984	39.186667	-75.633417	17.1
391503075310401	Id14-03	155985	39.250917	-75.517722	18
391232075285401	Ie32-02	172350	39.208917	-75.481611	13.5
390634075433401	Jb42-05	172323	39.109444	-75.726194	11.1
390544075300501	Jd55-10	166262	39.095556	-75.501472	15
390705075263201	Je34-04	172349	39.118139	-75.442083	13
390205075430901	Kb32-29	155978	39.034694	-75.719056	18.1
390409075311301	Kd13-09	176048	39.069111	-75.520361	13.4
390252075271301	Ke33-22	172318	39.047667	-75.453611	12.6
385956075303801	Lb15-17	172301	38.999	-75.510583	13.1
385830075423201	Lb23-03	172347	38.975	-75.708944	13.2
385515075431701	Lb52-07	166258	38.92075	-75.721444	16
390001075380101	Lc12-02	155982	39.000333	-75.633556	18.2
385730075321401	Ld33-10	166259	38.958361	-75.537111	17.4
385817075265101	Le24-11	172300	38.971677	-75.447192	13.5
385129075370201	Mc43-06	155980	38.858083	-75.617167	12.8
384737075342701	Nd31-06	172320	38.793639	-75.574056	13.8
384550075304001	Nd55-06	166200	38.763944	-75.511028	18.2
384845075211901	Nf24-05	172295	38.812444	-75.355278	13.5
384502075235301	Nf52-02	166168	38.750556	-75.397972	12.5
384637075153201	Ng45-02	187640	38.777067	-75.258867	22
384316075330501	Od22-04	155961	38.721	-75.551333	18.3
384159075310801	Od44-02	90221	38.699833	-75.518833	14.6
384411075150101	Og15-07	172328	38.736417	-75.250361	18.4
384201075185401	Og32-07	166198	38.700222	-75.315028	13.2
384130075125801	Oh42-07	155951	38.691639	-75.216111	13.2
384425075072401	Oi13-06	166167	38.740167	-75.123444	13
384250075085001	Oi32-18	172294	38.71375	-75.147167	26.8
383836075183001	Pg22-06	166189	38.643361	-75.308361	16.5
383749075110501	Ph34-15	155953	38.630194	-75.184611	12.9
383438075274201	Qc13-01	155972	38.577167	-75.46175	13.1
383308075382301	Qc22-04	73089	38.552338	-75.639373	29
383221075182301	Qg32-18	166165	38.539222	-75.306472	11.8
383412075125401	Qh13-05	166166	38.569889	-75.214917	18
382932075221701	Rf13-02	155971	38.492083	-75.371417	12.9

Description of Study Area

The study area falls entirely in the Delaware portion of the Northern Atlantic Coastal Plain Physiographic Province. The Delaware Coastal Plain is underlain by an extensive unconfined surficial aquifer that is present at the land surface in most areas (fig. 1). Precipitation across Delaware averages between 41 and 45 in/yr and is relatively evenly distributed over time (Sanford and Pope 2012). The topography of the Delaware Coastal Plain is relatively flat and agriculture is the predominant land use. In 2019, approximately 38 percent of Delaware was classified as cropland (U.S. Department of Agriculture, 2024). Most of the agricultural activity in Delaware is located in the lower half the State.

The main crops produced in the State are corn, soybeans, and winter wheat, a majority of which is harvested to support the State’s broiler chicken industry (Delaware Department of Agriculture and USDA NASS, 2020). In 2019, Delaware farmers harvested 180,000 acres of corn, 104,000 acres of Soybeans, 50,000 acres of winter wheat (fig. 2) which supported the production of 268.8 million broiler chickens (Delaware Department of Agriculture, 2020). Irrigated land is common in Delaware; of the 180,000 acres of corn, 49.4 percent (89,000 acres) were irrigated (Delaware Department of Agriculture, 2020). Crop production in Delaware has intensified over the last 40 years, with grain yields increasing from approximately 80 bushels per acre in 1980 to 150 bushels per acre in 2019 despite acreage of fields remaining relatively stable (fig. 2). Historically, greater nutrient applications were required for increased yields, suggesting an overall increase in the mass balance of nutrients cycled in farmland (Mueller and others, 2019). The exact quantities of nutrients applied to the land surface are unknown as most estimates rely on imperfect sales data. Delaware has encouraged farming practices which improve soil health, farm profitability and water quality through conservation practices like nutrient management plans, vegetated riparian areas, manure storage facilities, drainage management, cover crops and, stream buffers.

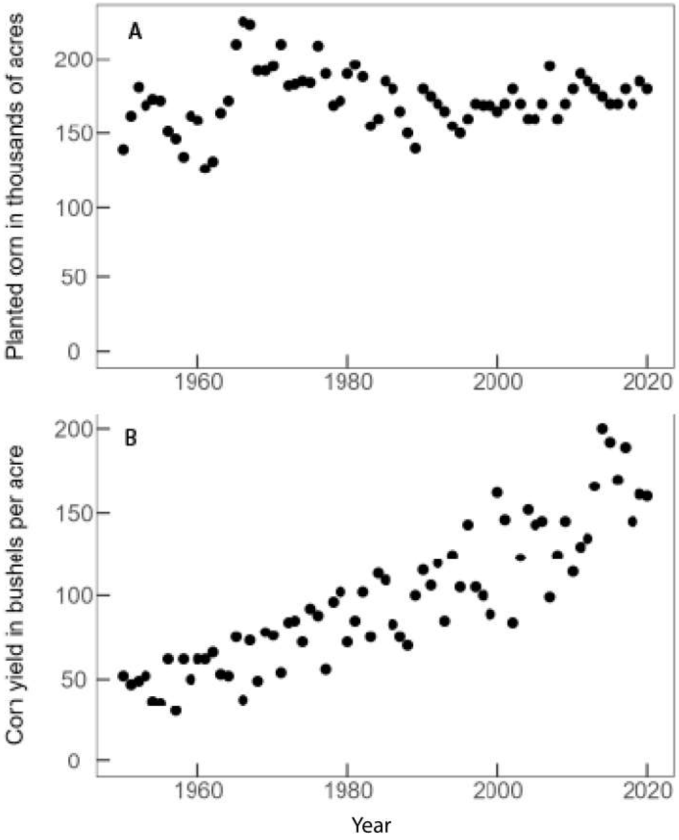

Figure 2 Delaware Corn Acreage planted (A) and yield (B) supplied by the USDA National Agricultural Statistical Service (2020)

Trends in Delaware's agricultural production are similar to national trends where farmland area is decreasing but production per unit of area is increasing (fig 2). Historically, this would have implied increasing nutrient applications as nutrients are applied to meet expected yields. Advances in both technology and genetics have improved the nutrient efficiency of major crops such as corn, soybeans and wheat which may allow for lower nutrient input for similar yields (Mueller and others, 2019). Concurrent with changing agricultural technology is the implementation and encouragement of conservation practices, also called “Better Management Practices (BMPs)”, which aim to maintain farm profitability while building soil health and nutrient retention on the field. The state of Delaware founded a nutrient management program in 1999 which focuses on improving both farm profitability and environmental outcomes through education and increasing conservation practice adoption (University of Delaware, 2023).

Water Use

In 2015, total groundwater withdrawals in the State of Delaware was 170 million gallons per day (Mgal/d) (Dieter and others, 2018), an 11.1 percent increase from the 2010 estimate of 151 Mgal/d (Masterson and others 2016). The allocation of Delaware groundwater withdrawals are summarized in figure 3 (Dieter and others, 2018).

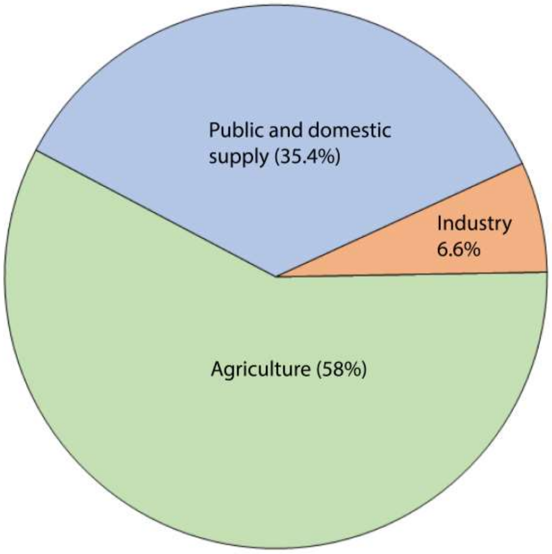

Figure 3 Percentage of groundwater withdrawals in Delaware and their general use categories as defined by Dieter and others, 2018.

Hydrogeologic setting

The unconfined surficial aquifer thickens from north to south and lies over several confining units and confined aquifers (Denver and Nardi, 2016). Flow paths within Delaware's surficial aquifer are relatively short, with a majority of estimated groundwater ages between 30 and 50 years at aquifer discharge areas to surface water (Sanford and Pope, 2012**).** Younger groundwater is present near near the surface of the aquifer, with older groundwater from upgradient recharge areas present at depth in the aquifer beneath the younger water (Ator and Denver, 2015). Flow paths in the confined aquifers are much longer, corresponding to much older groundwater ages (Sanford and Pope, 2012**).** Recharge to the surficial aquifer occurs over most of the lands surface because of the sandy nature of the overlying soil and aquifer sediment, with mean annual recharge estimated between 14 and 17 in/yr (Sanford and Pope, 2012). Recharge to the surficial aquifer can occur throughout the year and has been estimated to be relatively equally distributed between the growing and non-growing seasons (Stahl and others, 2020)**.** Within Sussex County recharge to the aquifer is possible even with the high evapotranspiration demand of summer, as groundwater levels respond to precipitation during intense rainfall events (Denver and others, 2018). Descriptions of geologic formations which compose the surficial aquifer and, lower confining units and aquifers may be found in Fleming and others (2017).

Groundwater Chemistry

Groundwater chemistry is influenced by the dissolution of minerals in aquifer sediments, inputs from the land surface, and reduction-oxidation (redox) conditions. Relatively insoluble siliciclastic sediments dominate the Delaware surficial aquifer and their dissolution results in naturally dilute groundwater with specific conductance values less than 60 µS/cm and nitrate concentrations of less than 0.4 mg/L (Denver, 1989; Ator and others, 2008; Hamilton and Others 1993). The naturally dilute nature of groundwater of the surficial aquifer is susceptible to transport of chemicals from the land surface through the soil zone during recharge events. As a result, land management practices are commonly the dominant driver of shallow groundwater quality in the surficial aquifer; for example, salt and salt-brines applied to reduce ice on roadways can dissolve and infiltrate the soil, causing an increase in groundwater concentrations of sodium and chloride ions (Fleming and others, 2017; Ator and Denver 2015). In 2014, wells sampled near urban areas and high road density also had higher specific conductance related to sodium, potassium, and chloride (Fleming and others, 2017).

In agricultural areas, soil amendments such as fertilizer, manure, and lime are applied to boost soil fertility and meet crop growing needs. Macronutrients such as nitrogen and phosphorous as well as minor nutrients such as calcium, magnesium, sulfur, and boron are commonly applied to improve soil fertility (Mid Atlantic Nutrient management handbook, 2006). Sources of nitrogen and phosphorus that are applied to cropland include commercial fertilizers and poultry litter. Historically, a majority of nitrogen delivered to cropland came from manure, but concerns related to phosphorus buildup in soil from these inputs resulted in restrictions on manure application (Natural Resource Conservation Service-Delaware, 2013). As the allowance for manure applications decreased within the state, the nitrogen required for plant nutrition was supplied through the application of commercial fertilizers. Crop fields in Delaware also receive soil acidity treatments in the form of calcium and magnesium rich limestone. The combination of the soil fertility treatments used in modern agriculture leads to groundwater chemistry being dominated by magnesium, calcium, and nitrate in areas influenced by agriculture (Denver, 1989, Hamilton and others, 1993; Böhlke 2002; Fleming and others, 2017).

Method of Study

Data were collected to support the comparison of water quality between sampling events in 2014 and 2019 in the shallow aquifer network in the State of Delaware. Of the 48 wells sampled in fall 2014, 45 wells were available for resampling during fall 2019 (table 1). An additional well was added to bring the total number of wells sampled to 46. Groundwater samples from these wells were collected between October and December 2019. Samples were analyzed for field parameters, nutrients, major ions, alkalinity, stable isotopes of hydrogen and oxygen in water, and of nitrogen and oxygen isotopes in nitrate.

Network Design

The shallow aquifer well network is comprised of wells previously used to monitor pesticides (Blaier and Baxter, 2000) and water quality within the surficial aquifer (Debrewer and others, 2007; Koterba and others, 1990; Shedlock and others, 1993). The original 48 wells were selected due to their shallow screened depth (11ft-34ft), proximity to agricultural areas, and their likely high oxygen content (Fleming and others, 2017). Much of the previously reported and documented spatial variability in nitrate concentrations on the Delmarva Peninsula included results from networks with wells in both oxic and anoxic groundwater (Debrewer and others, 2007). This study sample collection was designed to represent shallow, oxic groundwater conditions in the Delaware Coastal Plain. In 2019, samples were collected between October and December for a direct comparison to the sampling time frame in 2014. Wells with higher oxygen content were sought for this network as low dissolved oxygen leads to the removal of nitrogen from water through microbial activity. The original 48 wells sampled in 2014 (Fleming and others, 2017) were revisited in 2019 to assess for resampling following USGS protocols (USGS, variously dated). An initial reconnaissance of available wells from the 2014 sampling event was completed and three wells were determined to be unusable for sampling; one well was found dry (Pf41-02), one was destroyed (Fa45-07), and one well owner could not be reached for permission (Oc21-03). A well identified as Ib32-08 was added to the group of wells to sample (table 1). A total of 46 groundwater wells were sampled for this study.

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Groundwater sample collection and analysis

Groundwater 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) and same sampling protocol outlined in Fleming and others (2017). All groundwater samples were collected using Teflon tubing and a 0.45-micrometer capsule filter inside a clean sampling chamber. Filtered water samples for major inorganics analysis were preserved using nitric acid to a pH below 2. All samples were analyzed for field parameters, nutrients, major ions, and stable isotopes of hydrogen, oxygen, and the nitrogen-15 and oxygen-18 isotopes of the nitrate fraction in water.

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), and samples for stable isotopes were analyzed at the Reston Stable Isotope Laboratory using methods described in Coplen and others (2012) and Revesz and others (2012). Sampling results from this study will be available for comparison to sampling results from past and future studies, data collected during this study is available through the Water Quality Portal (Water Quality Portal, 2021).

Quality Control

Equipment blanks, field blanks, and sequential replicate samples were collected following protocols described in Koterba and others (1995) to estimate potential contamination bias and measurement variability from water-quality data-collection processes. An equipment blank was collected prior to the commencement of sampling. Four field blanks and five replicates were collected during field activities at selected wells.

Field blanks were collected to ensure that sample collections and processing did not result in contamination. No nutrients or major ions were detected in the field blanks.

Replicate samples measure the combined precision of sampling and laboratory analysis procedures. Replicate samples demonstrated consistent chemistry with their paired environmental sample. A relative percent difference (RPD) of 20 percent between environmental and replicate results was used as an indication of variability from sampling procedures for this study. In the 2019 sampling event the only instances of greater than 20% RPD occurred near the reporting limit of analytic instrumentation.

During this study an issue was discovered in quality assurance at the NWQL for a single dissolved orthophosphate (OP) result for one site. An error in the calibration procedure of the analytical instrument led to a result which the NWQL suggested was biased low, meaning the actual OP concentration was likely higher. The affected site, Nf52-02, had an OP concentration of 0.051 mg/L. Due to the quality assurance review, this result was not included in the statistics in table 2. While the 2019 OP concentration from well Nf52-02 was withheld from the statistics table, it’s concentration of 0.051 mg/L is nearly identical as the well’s 2014 concentration of 0.05 mg/L.

Data Analysis

A nonparametric matched pair test, the Wilcoxon Rank Sum (WRS) test (Helsel and others, 2020), was applied to compare nutrient or major ion concentrations between 2014 and 2019 for wells which had been resampled. Resampled wells in 2019 were also grouped based on previously assigned geochemical classification described in Fleming and others (2017) for agricultural, mixed and urban type water. Stable isotopes of water sampled in 2019 were examined and compared against modeled isotope data (Bowen, 2024) to estimate the source of sampled water. Nitrogen isotope ratios from sampled nitrate were evaluated to identify sources of nitrate in groundwater, including inputs from synthetic fertilizers, manure, septic discharge, or natural processes (Böhlke, 2002).

Spatial analysis

Spatial analysis was used to relate observed water quality to potential influences at the land surface. Agronomic survey and census data related to the acreage of various crops and years of production were provided by the US Department of Agriculture (USDA) (USDA-NASS, 2024). In a spatial analysis, the preceding crop grown over the summer of 2019 as described by the USDA NASS’s cropland data layer was extracted from the area within 500 m from each well location. The proportion of the dominant crop was then related to the nitrate concentration observed within the well through a correlation test. Spatial datasets of estimated enrichment ratios of stable isotopes within precipitation were used to estimate approximate season of groundwater recharge (Bowen, 2024)

Comparison of Water Quality in Shallow Groundwater, 2014 and 2019

Fleming and others (2017) identified and described three major geochemical types of groundwater during the 2014 study. The same grouping applied to the 2014 sampling of wells was utilized for the 45 resampled wells in 2019 and allowed for a paired comparison between years (Fleming and others, 2017). For reference, Group 1 (Agricultural) is a calcium-magnesium-nitrate water type, which was previously identified as an agricultural signature in the Delmarva Peninsula (Denver, 1989; Hamilton and others, 1993; Böhlke, 2002), Group 3 (Urban) is a sodium-potassium-chloride water type, and Group 2 (Mixed) is a mixture of Agricultural and Urban groups (Fleming and others, 2017). While all wells were selected for their locations in predominantly agricultural settings, the Urban Group generally had the highest percentage of urban land use and road density (Fleming and others, 2017).

Field parameters

Samples had a median specific conductance of 220 microsiemens per centimeter (µS/cm) and ranged from 80 µS/cm to 667 µS/cm in 2019 (table 2). The Urban Group had higher specific conductance concentrations than the Mixed group (WRS $p<0.05$) and the Agricultural Group (WRS $p=0.09$). The median specific conductance of all samples in 2019 were slightly lower than 2014 but the difference was not statistically significant. The differences within groups between the 2014 and 2019 sampling events were not statistically significant.

In 2019 samples had a median pH of 5.2 and ranged from 4.4 to 6.7 (table 2). The Urban Group had a higher median pH of 5.6 than the Mixed Group with a median of 4.85 (WRS $p<0.05$) and the median 5.05 of Agricultural Group (WRS $p=0.07$). There was no statistically significant difference between median concentrations in 2014 and 2019 or, within groups between 2014 and 2019.

Dissolved oxygen values for the 2019 sampling event ranged from 1.7mg/L to 9.6 mg/L and had a median concentration of 5.3 mg/L (table 2). While there were slight differences between groups, the differences were not statistically significant (WRS $p>0.05$). While the 2019 sampling event had lower median than the 6.3 mg/L found in 2014, this difference was also not significantly different (WRS $p=0.2$).

Table 2. Summary statistics for water quality results from the 2014 and 2019 sampling of shallow wells within the Delaware surficial aquifer network.

Constituent (units)	Year	Total samples			Agricultural Group			Mixed Group			Urban Group		
		Min	Median	Max	Min	Median	Max	Min	Median	Max	Min	Median	Max
Specific conductance (uS/cm @25C)	2014	100	230	1510	119	209	681	100	197	619	118	403.5	1510
	2019	80	220	667	140	242	520	80	159	512	86	307	667
pH (std units)	2014	4.3	5.15	6.7	4.5	5.15	6	4.3	4.8	5.3	4.5	5.7	6.7
	2019	4.4	5.2	6.7	4.5	5.05	5.9	4.4	4.85	5.6	4.6	5.6	6.7
Oxygen (mg/L)	2014	0.3	6.5	10.2	1.2	7.75	9.9	1	6.8	10.2	2.7	5.5	9.1
	2019	1.7	5.3	9.6	1.8	6.05	9.3	2	6.65	9.6	1.7	5.2	8.7
Total Dissolved Solids (mg/L)	2014	52	145	791	75	145	409	52	112	340	65	227	791
	2019	51	125.5	347	82	142	329	51	95	272	59	162	347
Inorganic nitrogen (nitrate and nitrite) (mg/L as N)	2014	0.34	4.955	41.5	3	10.15	41.5	2.21	5.55	10.2	0.34	1.56	6.83
	2019	0.45	5.09	30.7	4	10.7	30.7	2.5	4.95	16.7	0.45	1.745	6.47
Orthophosphate (mg/L as P)	2014	<0.004	<0.004	0.057	<0.004	0.0065	0.057	<0.004	<0.004	0.01	<0.004	<0.004	0.05
	2019	<0.004	<0.004	0.043	<0.004	<0.004	0.043	<0.004	<0.004	0.007	<0.004	<0.004	0.021
Bromide (mg/L)	2014	<0.03	<0.03	0.108	<0.03	0.03	0.073	<0.03	<0.03	0.108	<0.03	0.037	0.066
	2019	<0.01	0.0225	0.063	<0.01	0.026	0.063	<0.01	0.022	0.032	<0.01	0.019	0.06
Calcium (mg/L)	2014	1.21	11.3	59.5	9.16	18.4	56.9	5.06	7.5	20.2	1.21	11.1	59.5
	2019	0.837	11.75	45	10.5	17.3	45	4.04	6.18	18.6	0.837	7.63	33.6
Chloride (mg/L)	2014	5.66	27.15	430	5.66	14.65	54.6	9.35	29.6	137	12.8	89.7	430
	2019	1.95	17.75	137	6.8	14.5	50.3	5.41	16.5	127	1.95	54.6	137
Magnesium (mg/L)	2014	0.826	5.425	32.9	3.39	9.01	23.5	0.826	3.63	12.3	1.67	4.17	32.9
	2019	0.748	4.405	17.9	2.99	10	17.9	0.748	3.51	9.01	1.27	3.38	13.6
Manganese (mg/L)	2014	<0.2	13.95	451	0.44	17.45	451	6.97	24.9	130	<0.2	4.78	31.3
	2019	<0.2	9.27	269	0.56	18.1	269	4.52	29.6	118	<0.2	3.19	17
Potassium (mg/L)	2014	<0.3	2.59	11	1.11	2.585	8.06	1.26	2.77	7.39	<0.3	2.5	11
	2019	0.36	2.45	9.14	1.42	3.14	9.14	1.18	2.27	7.48	0.36	2.11	7.65
Silica (mg/L)	2014	2.85	8.07	22	5.17	11.5	20.9	5.68	9.52	22	2.85	6.76	13.7
	2019	2.58	9.33	23.1	5.39	13	20.5	4.88	10.7	23.1	2.58	6.8	14.8
Sodium (mg/L)	2014	2.67	14.05	223	2.67	5.98	18.7	6.55	14.2	72.9	8.85	40.2	223
	2019	3.6	10.95	102	3.6	7.62	25.9	5.17	11.1	60.8	5.71	34.6	102
Sulfate (mg/L)	2014	3.5	19.4	99.3	3.93	27.3	99.3	5.73	10.7	36.6	3.5	21	65.7
	2019	3.33	16.85	73.6	4.78	27	73.6	5.04	11.2	38	3.33	13.9	30.4

Nitrate

In 2019, as in 2014, nitrate was the dominant form of nitrogen found within the shallow aquifer network of the Delaware Coastal plain. Samples from the entire network had a median nitrate concentration of 5.09 mg/L in 2019, with a range from 0.45 mg/L to 30.7 mg/L. When the wells were split into their geochemical groups and compared, water sampled from the Agricultural Group had a median nitrate concentration of 10.7 mg/L, higher than the 4.95 mg/L median concentration from the Mixed Group (WRS $p<0.05$) and the Urban Group (1.75 mg/L, WRS $p<0.0001$); the difference between the Mixed and Urban Groups was also statistically significant (WRS $p<0.05$) (table 2, fig. 4). The difference between groups in 2019 was similar to the 2014 sampling, where nitrate concentrations between groups were significantly different from one another (WRS $p < 0.05$). There were no significant changes within groups between 2014 and 2019 (fig. 4). The median nitrate concentration of all samples in 2019, was slightly higher than the median concentration observed in 2014, but not statistically significant (table 2, WRS $p=0.56$). Eleven samples collected in 2019 had nitrate concentrations above 10 mg/L, the U.S. Environmental Protection Agency (EPA) primary drinking water quality threshold (Environmental Protection Agency, 2024a). All but 2 of the 11 samples from the Agricultural Group were higher than the threshold.

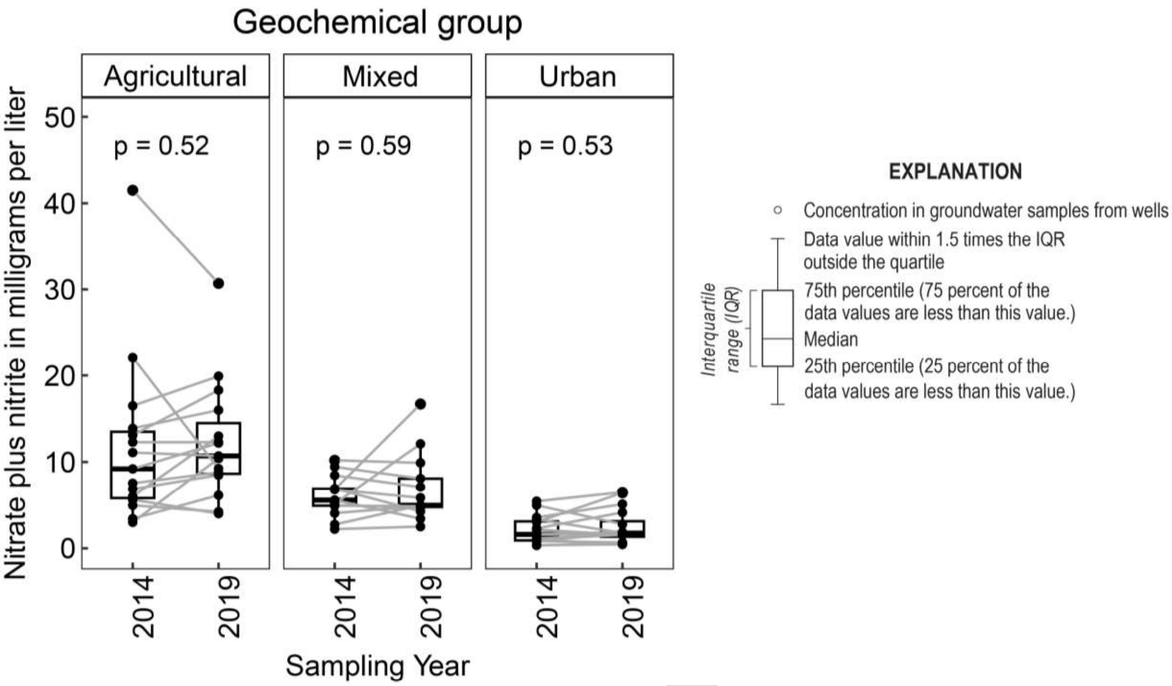

Figure 4 Boxplots of nitrate plus nitrite as nitrogen from the 2014 and 2019 sampling events of the Delaware shallow aquifer network. Resampled wells are connected by a line to show changes in individual concentrations. Panels represent the geochemical groups identified by Fleming and others (2017), and p values from a Wilcoxon Rank Sum test are displayed for a comparison within groups between 2014 and 2019.

Relationships between specific conductance, nitrate, and chloride

In 2014, specific conductance was positively correlated with concentrations of chloride in the Urban Group and both chloride and nitrate in the Agricultural Group (Fleming and others, 2017). Data from 2019 showed the same relationship between chloride and specific conductance in the Urban Group of wells, where a linear regression indicated that specific conductance described a high degree of variability in chloride concentrations (r^2=0.87). Wells within the urban group maintained a significantly higher median concentration of chloride than wells in the other groups (WRS < 0.05). Correlations between specific conductance and nitrate among groups varied from weak (r^2=0.041) in the Urban Group to moderate (r^2=0.68) in the Agricultural Group. When data from 2014 and 2019 were combined and the linear regression was repeated, the relationships within groups remained consistent (fig. 5). A multivariate regression using both specific conductance and magnesium as explanatory variables increased the r^2 value to 0.82 within the Agricultural group (table 3). The power of specific conductance and magnesium to predict nitrate concentrations decreased in the Mixed and Urban groups (table 3), which have lower magnesium concentrations than the Agricultural group of wells (WRS p<0.01, table 2).

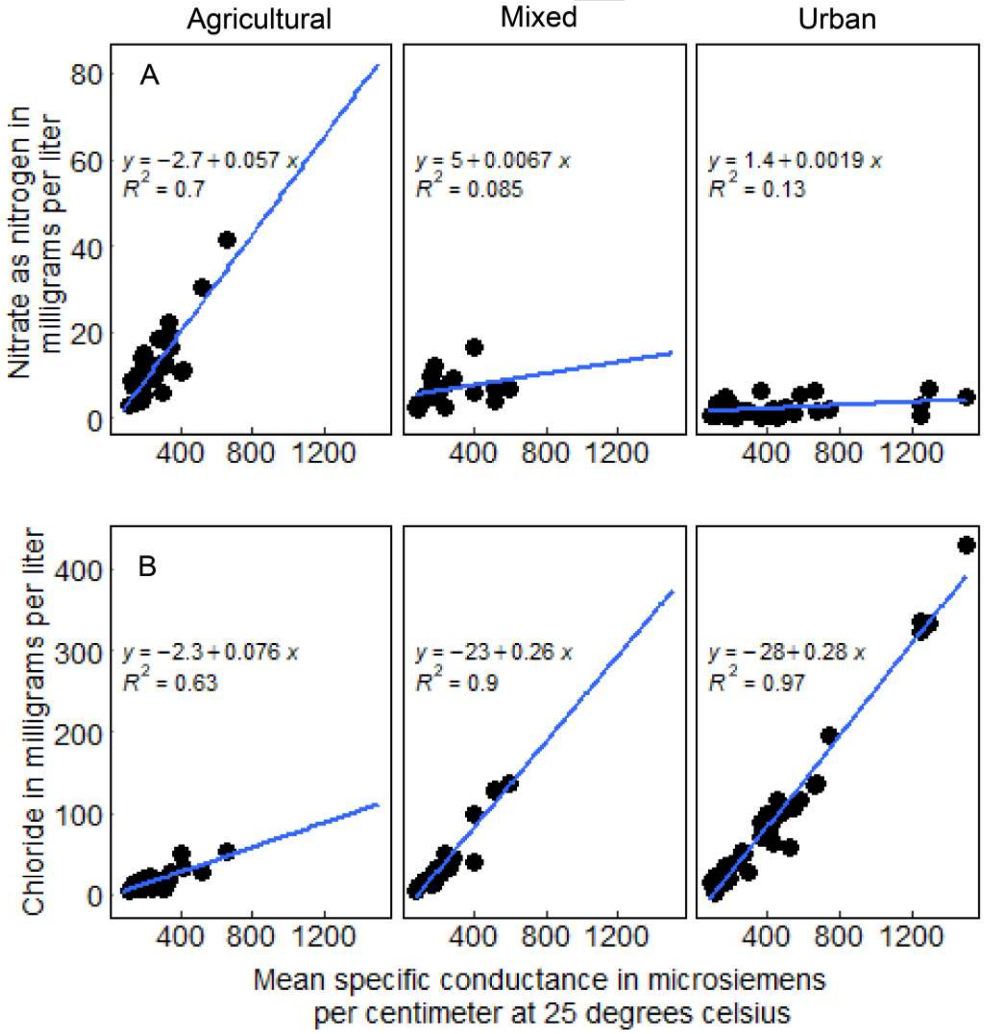

Figure 5 Bivariate plots with regression line demonstrating the relationship between specific conductance with (A) nitrate and (B) chloride concentrations in each geochemical well group for data collected in 2014 and 2019.

Table 3. Estimated coefficients for a regression predicting nitrate concentrations using magnesium and specific conductance in microsiemens per centimeter at 25 degrees C. Geochemical groups were identified by Fleming and others (2017).

Geochemical group	Intercept	Specific Conductance	Magnesium	r-square
Agricultural	-2.315	0.100	-1.079	0.80
Mixed	3.933	-0.003	0.736	0.252
Urban	1.553	0.002	-0.050	0.148

Orthophosphate

Groundwater concentrations of orthophosphate (OP) were generally low; with 18 of the 46 samples above the detection limit of 0.004 mg/L (table 2). A majority of OP detections occurred in the Agricultural and Urban groups where almost half of the samples collected had a detection of OP. Orthophosphate concentrations within groundwater are generally low as OP is easily bound to ionic exchange sites on soil and sediment (Sharpley and others, 2013). Soils which have received repeated phosphorus applications may experience a saturation of available binding sites and orthophosphate may be released to subsurface transport and groundwater (Kleinman and others, 2007). While OP concentrations measured in the 2019 sampling were generally low, there were 3 samples above the recommended regional criteria for total phosphorus of 0.031mg/L (EPA, 2000). Three of these sites also had OP concentrations above 0.031mg/L in the 2014 sampling effort. Orthophosphate concentrations at or above eco-region-specific criteria are likely the result of sediment which are near or above saturation of adsorbed phosphorus (Domagalski and Johnson, 2011). As a comparison the Choptank River at Greenboro, MD surface-water gaging station (Site ID = 01491000), which has a majority of its watershed in Delaware, had a median OP concentration of 0.0.041 mg/L and a mean of 0.048mg/L for all environmental samples collected from 2014 to 2019 (U.S. Geological Survey, 2024).

Chloride, sodium and chloride:bromide ratios

Chloride observed in 2019 had a median concentration of 17.75 mg/L, which was less than the 2014 median of 27.15 mg/L but not significantly different (WRS $p = 0.2$, table 2). Wells within the Agricultural Group had a similar chloride concentration in both sampling years while the Mixed and Urban groups had lower concentrations in 2019 compared with 2014 (table 2). Unlike in 2014, in 2019 there were no samples which exceeded the chloride EPA Secondary Drinking Water Standard of 250 mg/L (Environmental Protection Agency, 2024b). In both 2014 and 2019 samples with high sodium also had higher chloride concentrations (fig. 6A). Wells from the Mixed and Urban Groups had consistently higher concentrations of sodium and chloride regardless of spatial position (WRS<0.05, fig. 6A), this relationship suggests that proximity to urban land use and roadways is a stronger indicator of sodium and chloride concentrations than latitude.

Previous studies have used the mass ratio of chloride to bromide as an indicator of chloride source (Mullaney and others, 2009). The ratio of chloride to bromide generally found in The Agricultural wells (fig. 6B) are similar to agricultural areas surveyed by Mullaney and others (2009) which received both animal manure as well as potash fertilizer (potassium chloride), while values from the Urban Group (fig. 6B) of 2019 were indicative of land which received deicing treatments (Mullaney and others, 2009). In areas with dilute groundwater, ratios of chloride to bromide are relatively low (below 1000) and increase as anthropogenic sources of chloride are added (Mullaney and others). The increase in chloride to bromide ratio occurs as anthropogenic sources of chloride such as deicing agents and water softeners have high concentrations of chloride and little bromide.

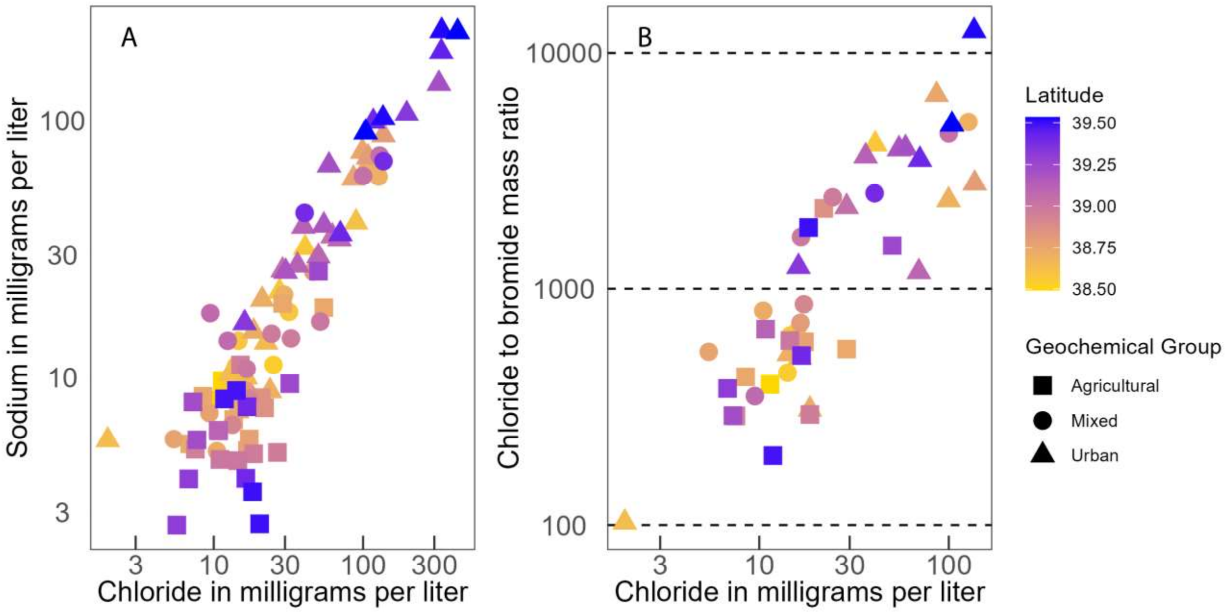

Figure 6 Bivariate plots of A, sodium and chloride in 2014 and 2019 and B, chloride to bromide mass ratios in 2019 versus chloride concentrations with geochemical groups following the classification of Fleming and others (2017).

Silica

Silica in groundwater comes from the dissolution of silicate minerals which dominate soil and aquifer sediments and has previously been related to estimated groundwater age (Denver and others, 2018). In 2014, 18 samples from the shallow network were analyzed for estimated groundwater age using sulfur hexafluoride (SF_6). Figure 7A shows the relationship between silica concentrations and estimated groundwater age and show a wide range of silica concentrations indicated similar groundwater age and a weak relationship driven by an outlying data point. The high variation in silica to groundwater age is likely because of the variation in aquifer properties within the shallow well network compared to that of an individual field (Denver and others, 2018). In addition, a Wilcoxon Rank Sum test found significant differences between the Urban and Mixed wells, and Urban and Agricultural wells in both 2014 (fig. 7B) and 2019 (fig. 7C). The differences observed between these groups suggest that while silica maybe a reliable surrogate for age on a local-scale, there is insufficient evidence to estimate groundwater age from silica on a state-wide basis. The differences between hydrogeochemical groups suggests that land use may also influence silica concentrations. Despite the weak relationship between silica concentrations and relative groundwater age calculated from SF_6 concentrations, the relative ages (fig. 7A) of samples collected from this network suggest that all water sampled was modern in nature.

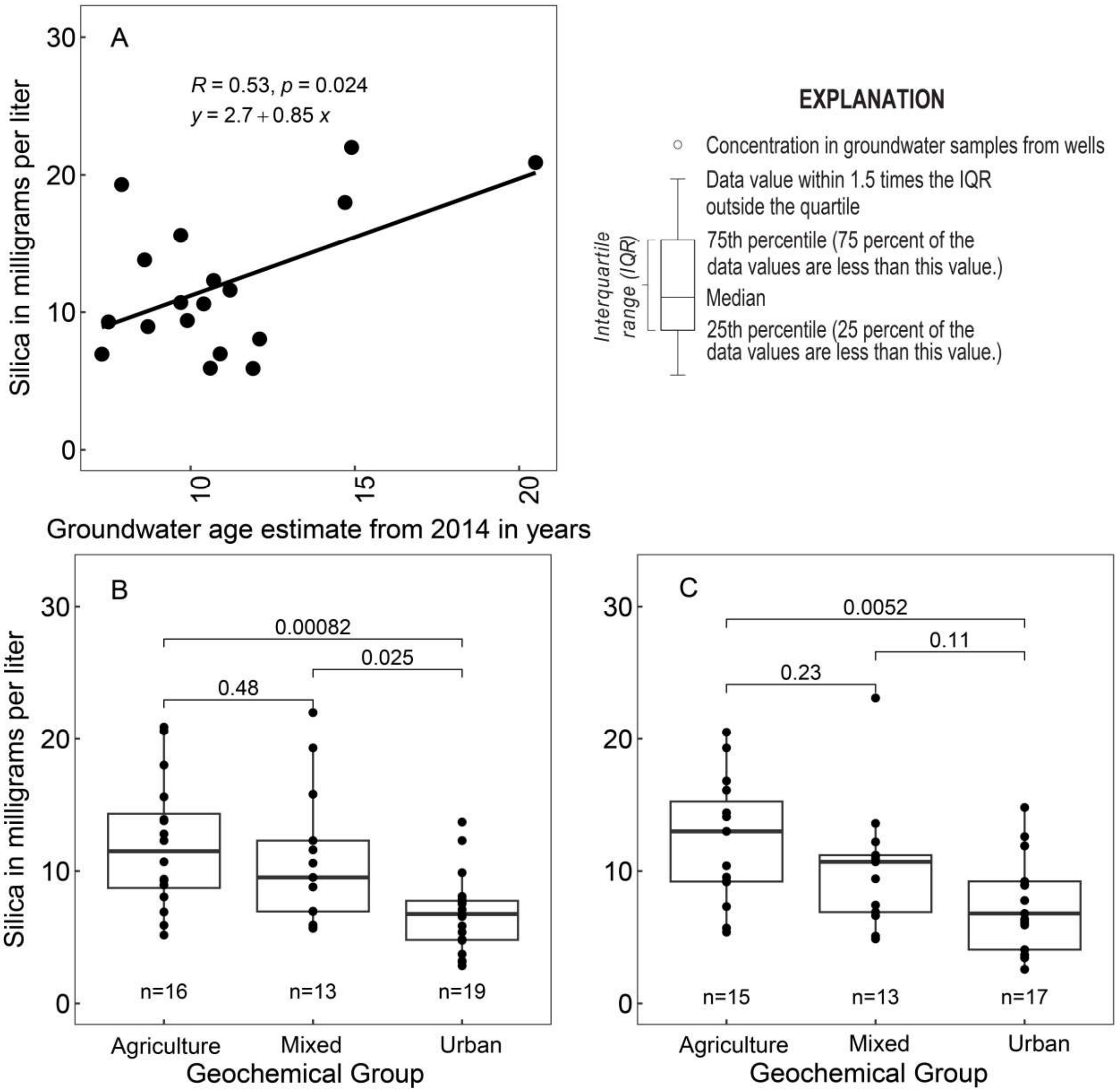

Figure 7 Silica concentrations with estimated groundwater ages from 2014 (A), and silica concentrations versus geochemical group for 2014 (B) and 2019 (C). Horizontal lines above individual boxplots indicate the comparison between groups with a p-value shown above the comparison line from the Wilcoxon Rank Sum test, 2019 (B) and, (C).

Isotopes

Stable isotopes of water

The isotopes δ^2H and $\delta^{18}O$ are naturally occurring variations of hydrogen and oxygen and are found in low concentrations within water molecules. These molecules are heavier than their counterparts δ^1H and $\delta^{16}O$ because they contain additional neutrons within the nucleus. The relative enrichment of water with δ^2H and $\delta^{18}O$ isotopes is determined by physical processes such as evaporation and precipitation. The ratios of isotope occurrence in water are known as "enrichment ratios" and they can indicate the source and possibly timing of groundwater recharge from precipitation. Previous studies on stable isotopes indicate that recharge may occur year-round in Delaware (Stahl and others, 2020) which is supported by recharge estimates by Sanford and Pope (2012).

Stable isotope samples analyzed from the shallow aquifer network were compared against monthly isotope data modeled from the Isomaps Program (fig. 8; Bowen, 2024). Water sampled during 2019 fell within the range of previously sampled groundwater on the Delmarva Peninsula. One well, Ph34-15 stood out from the other samples due to its low enrichment of both δ^2H and $\delta^{18}O$compared to the rest of the network (figure 8). This well is close to the Delaware inland bays (fig. 1) and it is possible that the water is influenced by the inland bays, as oceanic sources of water are generally less enriched than water from continental land masses (Stahl and others, 2020). When compared with the Water Isotope Program data, the Delaware shallow isotopes were in the middle of the range of values estimated by the Isomaps data suggesting that the water sampled was from mixed time periods and or sources. This would be expected as water samples from a well with a three-ft screened interval, such as those in this network, which represent a composite of water from several recharge events that occurred over a longer time frame than a single recharge event.

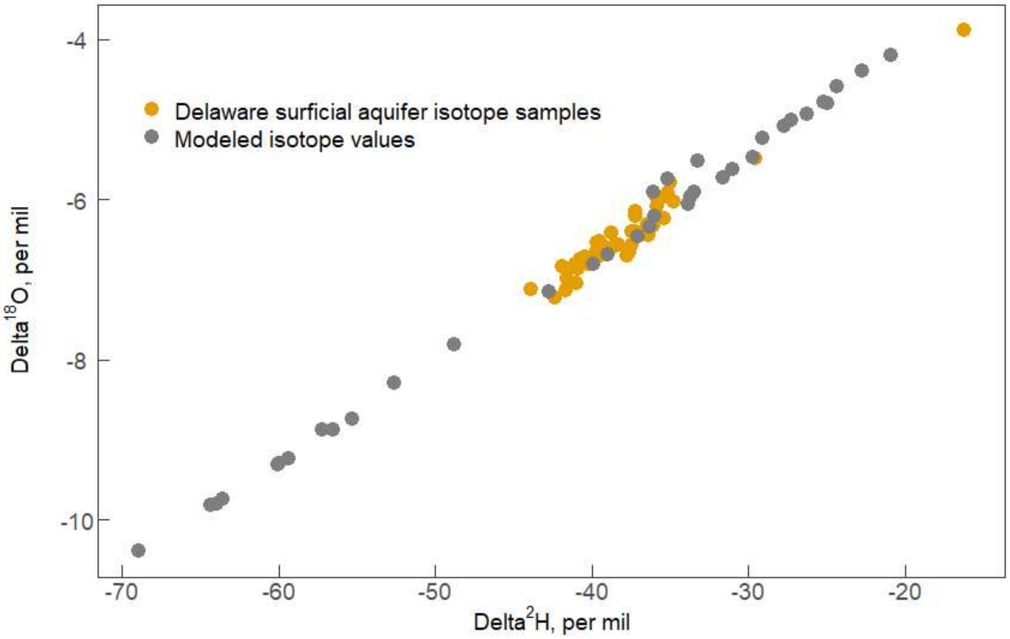

Figure 8 δ18O values and δ2H values from the 2019 Shallow agricultural network and, modeled isotope values.

Nitrate Isotopes

Nitrate isotopes $\delta^{15}N$ and $\delta^{18}O$, are naturally occurring isotopes of nitrogen and oxygen, and their abundance is determined by the sources of nitrogen and biological transformations such as denitrification (Böhlke and Denver, 1995). Sources of nitrogen added to the landscape and in the atmosphere provide the basis for $\delta^{15}N$ concentrations in water. Synthetic nitrogen fertilizers (such as urea or ammonium sulphate) are created from atmospheric N^2 gas and generally range from -3‰ (per mil) $\delta^{15}N$ to +7‰ $\delta^{15}N$ (Michalski and others, 2015). A survey of 270 different synthetic fertilizers sold in the United States in 2015 indicated that 80% of fertilizers had -3‰ $\delta^{15}N$ to +3‰ $\delta^{15}N$ (Michalski and others, 2015). Once in the soil profile, nitrification processes alter the commercial fertilizer such that the commonly found range of isotopes are -5‰ δ^{15}N to +5‰ δ^{15}N (Zhang and others 2018). Other sources of nitrogen which come through biological pathways such as manure or septic systems typically have higher δ^{15}N (Kendal and others, 2009). Previous literature indicates that manure and septic systems have a range of 10‰ δ^{15}N to 20‰ δ^{15}N (Kendal and others, 2009; Böhlke and Denver, 1995). Denitrification can produce nitrate values between 10‰ and 30‰ δ^{15}N and similarly raise δ^{18}O isotopes fractions compared to the groundwater pool of nitrate (Kendal and others, 2008).

The nitrogen isotopes measured in nitrate from water samples in 2019 indicate the main source of nitrogen measured in the shallow aquifer network appears to be a mixture of synthetic fertilizer and manure.in all groups (fig. 9, table 4). There was no significant difference between groups when comparing nitrate isotopes. Partial denitrification was evident in some of the water samples due to their greater enrichment of both nitrate isotopes (fig. 9). Greater enrichment of nitrate isotopes can occur as microbes preferentially metabolize isotopes with less mass (Kendal and others, 2008). Water from well Gc14-04 had the highest δ^{15}N and δ^{18}O values; this well is located near wetlands and had a relatively low dissolved oxygen value of 1.8 mg/L in 2019 compared to the rest of the network. Despite the relatively low oxygen content and the enriched isotopic signature, the sample from Gc14-04 in 2019 contained 6.1mg/L nitrate.

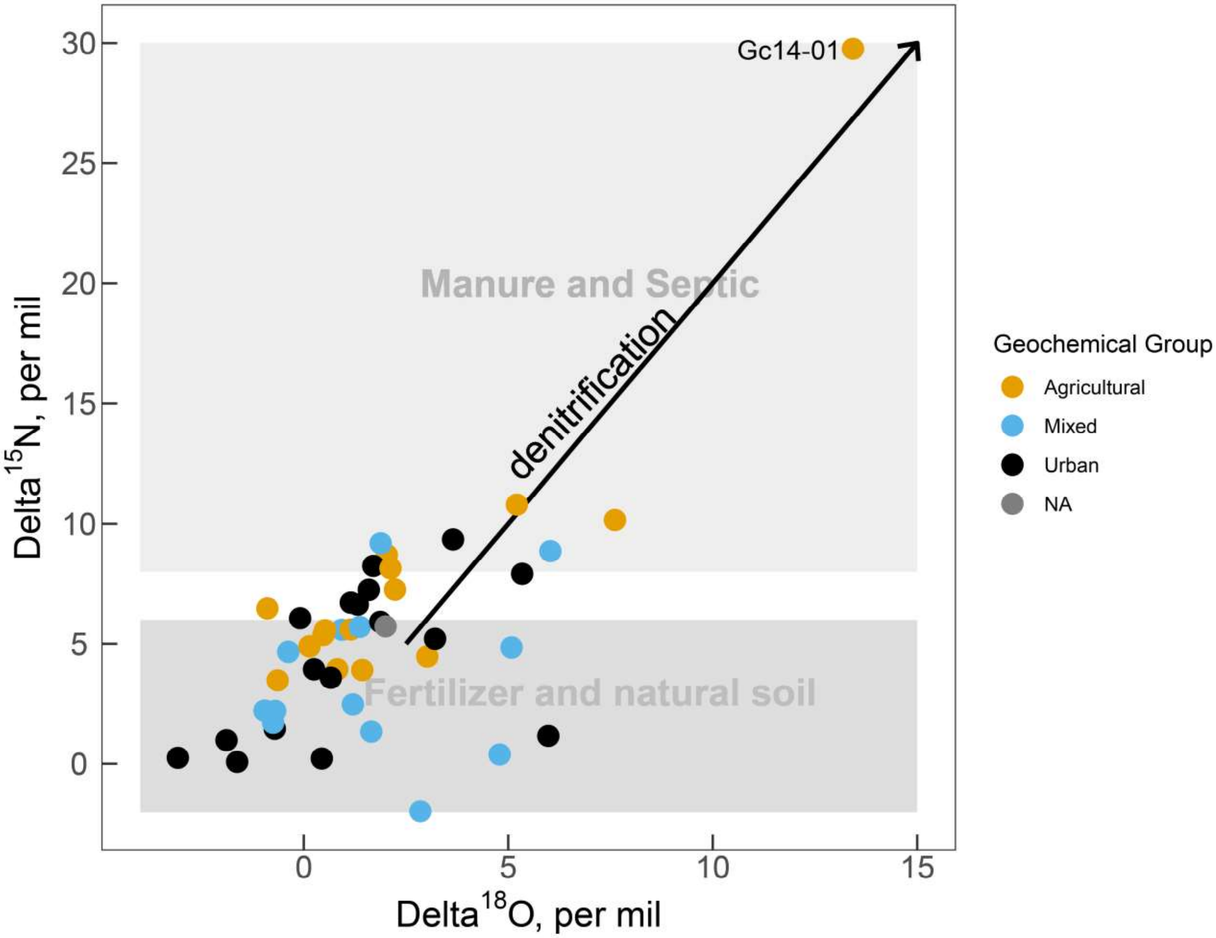

Figure 9 Delta N15 and delta O18 isotope values are shown for nitrate in samples from the 2019 Delaware Shallow Aquifer network sampling effort. A line denoting the range of isotopic values associated with partial denitrification is shown.

Table 4. Summary Statistics for stable isotopes of water and the nitrogen and oxygen isotopes of nitrate in the surficial aquifer of the coastal plain, 2019.

Constituent (units)	Year	Total samples				Geochemical Group 1				Geochemical Group 2				Geochemical Group 3			
		No. samples	Min	Median	Max	No. samples	Min	Median	Max	No. samples	Min	Median	Max	No. samples	Min	Median	Max
Nitrate $\delta^{15}N$ and $\delta^{18}O$ Isotopes																	
Delta ^{15}N	2019	46	-1.97	5.29	29.76	15	3.49	5.6	29.76	13	-1.97	2.48	9.19	17	0.08	5.21	9.35
Delta ^{18}O	2019	46	-3.08	1.345	13.43	15	-0.89	1.43	13.43	13	-0.96	1.37	6.03	17	-3.08	1.15	5.98
Stable $\delta^{2}H$ and $\delta^{18}O$ isotopes of water																	
Delta ^{2}H	2019	46	-43.9	-38.475	-16.24	15	-42.36	-39.39	-29.58	13	-43.9	-36.36	-35.02	17	-41.58	-38.28	-16.24
Delta ^{18}O	2019	46	-7.23	-6.56	-3.89	15	-7.23	-6.6	-5.49	13	-7.12	-6.44	-5.78	17	-6.98	-6.56	-3.89

Factors influencing groundwater chemistry

This well network was designed to sample shallow groundwater across the State of Delaware to better understand spatial and temporal variation in groundwater chemistry through repeated sampling over time. Changes in groundwater chemistry driven by leaching of nutrientsin excess of crop uptake applied to the land surface should be observed relatively soon after application in the shallow well network where groundwater age is relatively young. (fig. 7). However, results from the second sampling of the network in 2019 suggests that there was little change in nutrients and most other major ions indicating significant change was occurring.

Ages of groundwater (fig. 7A) are generally estimated groundwater age around 10 years. Assuming that the wells which weren’t analyzed for age-dating characteristics had similar ages due to their depth and placement in the aquifer the sampling of this network included groundwater which recharged to the aquifer from approximately 2004-2014 for the first round of sampling and 2009-2019 for the second (fig. 10). The range of corn yields over each 10-year timespan indicates that there were factors influencing nutrient utilization of crops which varied inter-annually. In 2014 for example, the water sampled reflected years where Delaware corn yields varied from 99 bushels per acre in 2007 to 200 bushels per acre in 2014. This variation in yield is likely related to variable growing conditions and not drastic changes in farming practices in the State. This inter-annual variation in crop production may have implications for water quality on shorter time scales, as previous research has shown considerable variation in groundwater chemistry within the growing seasons (Denver and others, 2018).

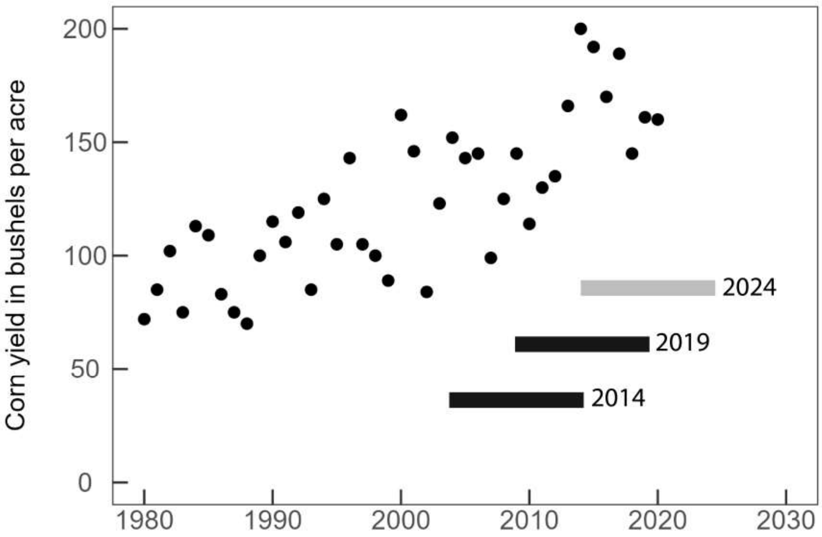

Figure 10 Corn yields in Delaware and approximate time of recharge of groundwater for the shallow well network for wells sampled in 2014 and 2019 with an example of potential recharge times if the network was resampled in 2024. Groundwater ages reflect an approximate age of 10 years as described by sulfur hexafluoride age-dating techniques from Fleming and others 2017.

Shallow groundwater chemistry may vary over short timeframes, as well as space, due to land management activities and recharge events which can concentrate or dilute water chemistry. Variations in groundwater nitrate on a seasonal basis were shown by Denver and others (2018) who demonstrated near Bucks Branch in Delaware that nitrate-nitrogen concentrations were the highest in both soil and very shallow groundwater during the main growing season. The increased nitrate concentrations in soil and groundwater at Bucks Branch were related to nutrient application timing and precipitation events (Denver and others, 2018). The higher concentrations near the water-table surface decreased later in the growing season as more recharge reached the aquifer. One of the monitoring wells included in this study, Ng45-02, had daily nitrate and conductivity values collected from 2014-2020 through the USGS (fig. 11) also shows short-term changes in water quality. These samples were collected by an automatic sampler that samples water from a very short interval in the aquifer that would correspond to a short timeframe of recharge. In figure 11, greater depth to groundwater indicates a relatively dry period, while wetter conditions lead to higher groundwater levels. Daily data from Ng45-02 showed that a single recharge event may either increase ionic concentrations or dilute them (fig. 11). Increases in groundwater level frequently corresponded to increases in specific conductance (fig. 11). Due to the strong relationship ($r^2 = 0.92$) between specific conductance and nitrate at this site (fig. 12), we may infer that nitrate concentrations were also variable. Discrete samples of nitrate at Ng45-02 showed an increase in maximum observed concentrations from 13.1mg/L in 2014 to 18.3mg/L in 2019. This increase was likely caused by a change in cropping practices from hay production to a corn and soybean rotation in 2014. It illustrates how nitrate concentrations can change in groundwater in a relatively short timeframe when agricultural practices change significantly. While samples collected in 2014 and 2019 targeted the same timeframe (October-December), there were differing antecedent moisture conditions leading into the sampling event.

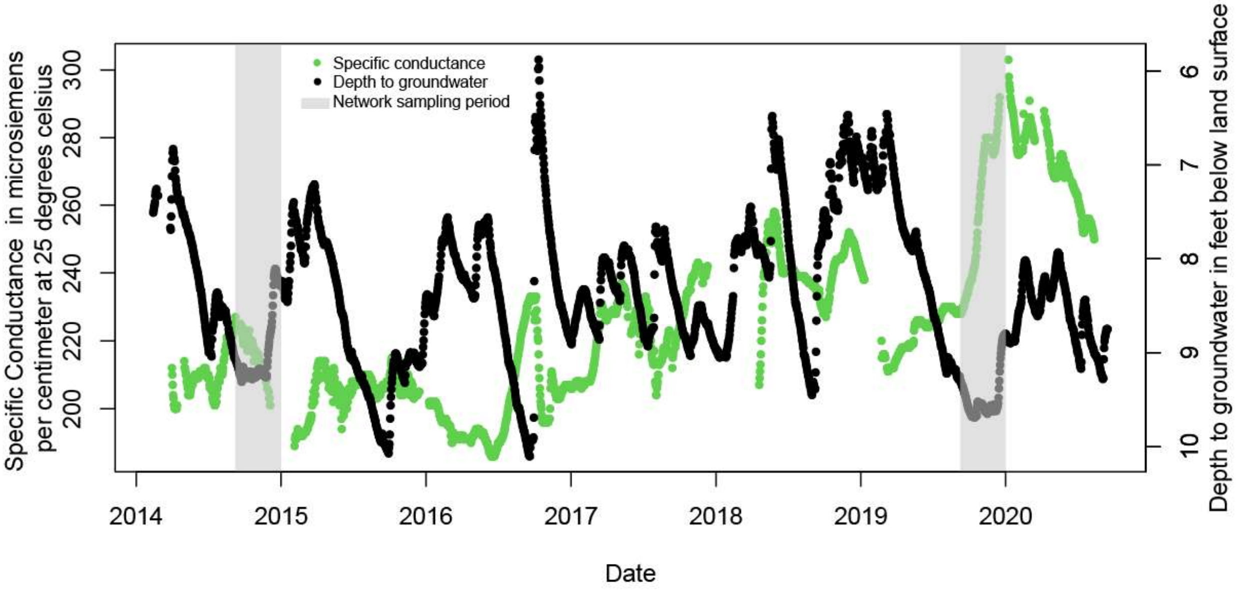

Figure 11 Specific conductance and depth to groundwater versus time from monitoring well Ng45-02 near Milton, Delaware.

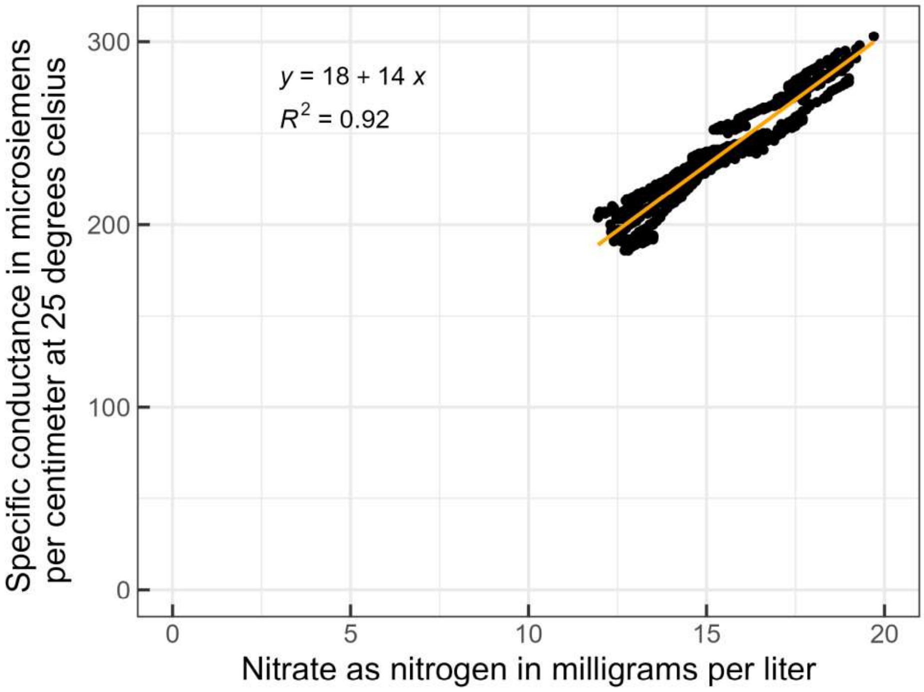

Figure 12 Daily values of specific conductance and nitrate nitrogen from 2016 to 2020 in monitoring well Ng45-02, near Milton, Delaware.

The Palmer Drought Severity Index (PDSI) reflects the relative availability of moisture at a given point in time (Palmer, 1965). Positive PDSI values indicate wetter-than-average conditions while negative PDSI values indicated drier-than-average conditions. During the sampling events for 2014 and 2019, Delaware started the calendar year with relatively wet conditions (fig. 11, fig. 13) which dried out over the summer growing season. This pattern of greater dryness towards the end of the growing season is consistent with daily groundwater elevations reported from Ng45-02 (fig. 11). In 2019, the calendar year started relatively wet compared to 2014 (fig. 12). By late spring in 2014 and 2019, PDSI values were decreasing in the State of Delaware (fig. 12). Thus, during and after periods of typical nitrogen applications, the state experienced similar hydrologic conditions.

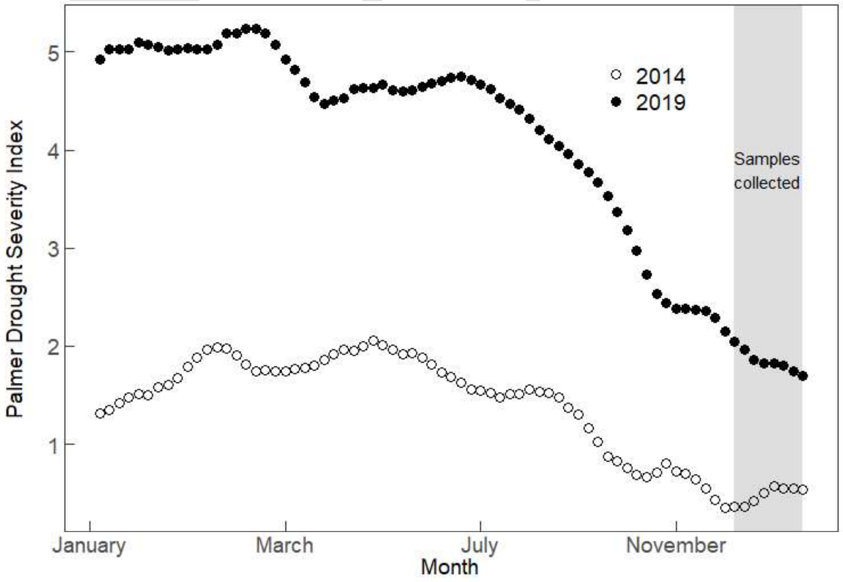

Figure 13 Weekly Palmer Drought Severity Index values for the state of Delaware in 2014 and 2019, a shaded box describes the time period of water quality sampling.

While groundwater chemistry maybe variable, the wells within the shallow aquifer network maintained relatively consistent concentrations of nitrate, magnesium and chloride which were defining characteristics of the geochemical groups in 2014 and 2019. Wells which had high nitrate and phosphorus in 2014 also had high nitrogen and phosphorus in 2019; the same was true for chloride concentrations. The sampling method of the shallow aquifer network was designed for a relatively short timeframe to control for changes in antecedent moisture conditions (fig. 11). This relatively short sampling window provided a synoptic of water quality across the state. Despite variation in groundwater chemistry between sampling events appearing limited, repeated sampling of groundwater networks allows for the detection of a trend despite variable weather signals (Lindsey and others, 2023). Thus, continued sampling of the shallow aquifer network should indicate changes in long term shallow groundwater chemistry.

Summary and conclusions

The U.S. Geological Survey, in cooperation with the Delaware Department of Agriculture, re-sampled a network of wells designed to monitor shallow groundwater quality in the surficial aquifer of the Delaware Coastal plain in 2019. The shallow aquifer network of wells was selected from existing networks to assess changes in Delaware's shallow water quality in areas with oxic water that was influenced by agricultural land use. This network was first sampled in 2014 and results from this sampling event were used to classify the water into three main groups which reflected agricultural type water, water with high urban land cover, and a mix of the previous groups' chemistry. This network was re-sampled in 2019 to compare groundwater quality between 2014 and 2019. Of the original 48 wells, 45 were resampled and an additional well was added.

In a comparison of the 2014 and 2019 sampling events, there were few statistically significant changes in water quality constituents across the time period at the network level or between groups. Land use factors continue to be a driving influence on groundwater quality. The Agricultural well group continued to have the highest concentration of nitrate-nitrogen. There were no statistically significant differences in nitrate concentrations between 2014 and 2019. The Urban well group had the highest chloride values; the Urban and Mixed Groups showed decreases in chloride while the Agricultural Group showed no change. Unlike the 2014 sampling, which showed higher chloride concentrations at more northern latitudes, the values from 2019 appeared mixed spatially and may have been affected by antecedent moisture conditions (Lindsey and others, 2023). Nitrate concentrations were similar in 2014 and 2019 at the network level and within groups. The isotopic signatures of nitrate-nitrogen indicate that there were a mix of contributing sources and there was no difference observed between groups. Silica concentrations compared to groundwater age dates estimated from sulfur hexafluoride indicated that there was a relationship between silica and age; however, this relationship was weak and silica concentrations varied between groups of wells. One well, with daily water quality results between the two sampling periods, showed how groundwater can vary on a sub-seasonal basis. This well also indicated that change can be detected in groundwater over a five-year time period if changed in nutrient input and land management practices result in significant changes in nutrient leaching to groundwater,

The network, targets groundwater conditions where Nitrogen as Nitrate is present (oxic) and where changes may be observed in reasonable time frames (young groundwater). Between the two sampling events (2014 and 2019), relatively few changes in groundwater quality were observed. The overall concentration of nitrate did not change at the network level and the distribution of geochemical properties remained consistent within well groups. While changes in groundwater water quality may take years or decades to respond to changes on the landscape, tracking landscape conservation practices and accounting for hydrologic variability can improve our understanding of the effectiveness of agricultural conservation practices on shallow groundwater quality. The lack of difference between groundwater nutrient chemistry between 2014 and 2019 presents a challenge to understanding how changes to land management practices have affected the aquifer. However, studies on the impact of conservation practices on regional water quality indicate varying and limited effectiveness (Ator and others, 2020; Fox and others, 2021; Sekellick and others, 2023). Continued sampling of the relatively “young” water within the shallow aquifer network should indicate long-term changes in water quality.

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