

Delaware's 2014 305(b) Groundwater-Quality Assessment Based on Public-Well Data: Results of Sampling, 2012-13

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Groundwater-Quality Highlights

Groundwater quality in Delaware was assessed based on raw-water data collected during 2012-13 from public water-supply (PWS) wells. The water-quality database consisted of over 40,000 analyses. Five aquifer types were recognized for reporting purposes: (1) unconfined, (2) confined, (3) semiconfined, (4) fractured-rock, and (5) karst. Unconfined, confined, and semi-confined aquifers occur in the mid-Atlantic Coastal Plain Physiographic Province, which comprises most (~96%) of Delaware's land-surface area. Fractured-rock and karst aquifers occur in the Piedmont Physiographic Province in the remaining northernmost portion of the state. There are 1,187 active PWS wells and more than three quarters (77%) of these wells produce from Coastal-Plain aquifers; 5% produce from Piedmont aquifers; and aquifer designations for the remaining 18% are either not known or not yet established. Well depths range from 22 to 957 ft below land surface (bls) with a median well depth of 140 ft bls. Highlights from the groundwater-quality assessment follow*:

- Based on nitrate data, almost half of the wells evaluated are susceptible to human influence. Nitrate concentrations exceeded 0.4 mg/L, a threshold indicative of human impacts, in 42.8% of the samples.
- The unconfined and karst aquifers are the most susceptible to human influence. These aquifers had the highest median nitrate concentrations (4.20 and 2.50 mg/L, respectively) and the largest fractions of concentrations exceeding 0.4 mg/L (87.3 and 100%, respectively).
- Nitrate concentrations exceeded the drinking-water standard in <5% of all samples.

 Concentrations exceeded the Primary Maximum Contaminant Level (PMCL) of 10 mg/L for drinking water in 4.3% of the samples. Areally, PMCL exceedences were primarily limited to Sussex County with the exception of one exceedance in southern Kent County.
- Overall, nitrate concentrations decrease with depth. Trends in nitrate concentrations with respect to sample depth indicate that the vertical extent of human influence was primarily limited to depths of ~400 ft below land surface and shallower. At depths greater than 400 ft, nitrate was rarely detected above the quantitation limit. The deepest nitrate detections were associated with Piedmont wells, which have very long open intervals that may allow contaminants to enter at shallower depths. Nitrate detections in Coastal-Plain wells were primarily limited to depths of 220 ft and shallower.
- Organic compounds were frequently undetectable. Organic compounds were not detected in 94.4% of the analyses. More than three-quarters (76.4%) of the detections were found at concentrations less than 1 µg/L. Tetrachloroethylene (PCE), a solvent, was the most-frequently detected organic compound.
- Organic compounds rarely exceeded drinking-water standards. Specifically, organic compounds exceeded PMCLs in 0.3% of the analyses. The following analytes were found above the PMCL: tetrachloroethylene (PCE) and methyl tert-butyl ether (MTBE).
- Some organic compounds have depth trends similar to nitrate. Specifically, concentrations of MTBE, PCE, and trichloroethylene (TCE) with respect to sample depth indicate that the vertical extent of human impact in the Coastal-Plain aquifers is limited to depths of ~215 ft bls. Organic compounds were detected at greater depths in Piedmont aquifers, the wells in which have very long open intervals that may allow contaminants to enter at shallower depths.
- Trace elements were frequently undetectable. Trace elements were not detected in 66% of the analyses. More than half (58%) of the detections were found at concentrations less than 0.1 mg/L and almost all detections (98%) were found at concentrations less than 1 mg/L. Barium, nickel, and chromium were the top three most-frequently detected trace elements.

- Arsenic detections were primarily limited to confined wells in glauconitic aquifers. Arsenic
 was one of the top five most frequently detected trace elements. Detections of arsenic were primarily
 limited to confined wells that produce from the Rancocas, Mt. Laurel, or Piney Point aquifers, which
 are associated with glauconitic geologic formations.
- Radionuclide data were very limited in this assessment. Available radionuclide data were limited
 to the following parameters: uranium-238, radium-226, radium-228, and gross alpha particle activity.
 The PMCL for uranium (0.03 mg/L) was never exceeded. Four radium-226 and radium-228
 combined results exceeded the 5 pCi/L PMCL.

Other groundwater-quality findings:

- Overall, groundwater is predominantly soft or moderately hard. Specifically, most of the results (96.4%) met either of these criteria. There were no hardness data for karst wells; based on previous assessments, this aquifer type routinely had the most elevated hardness values.
- Groundwater was acidic in almost half of the overall samples. Specifically, pH values were less than the lower limit of the Secondary Maximum Contaminant Level (SMCL) range (6.5-8.5 standard pH units) in 45.9% of the samples. Unconfined and semi-confined wells had the largest fractions of pH values below the SMCL range (85.7 and 66.7%, respectively); in contrast, confined and fractured-rock wells had pH values that were predominantly within the SMCL range (85.9 and 100%, respectively). There were no pH data for karst wells; based on previous assessments, this aquifer type had the highest median pH and the largest fraction of samples within the SMCL range.
- Iron was elevated in almost one third of the samples. Iron exceeded the SMCL (0.3 mg/L) in 29.7% of the samples. Elevated iron was detected at virtually all depths. Confined, semi-confined, and fractured-rock wells, however, had the largest fractions of iron concentrations above the SMCL (32.2, 43.8, and 66.7%, respectively).
- Groundwater is generally dilute overall based on total dissolved solids (TDS) data. Specifically, the median TDS concentration was 170 mg/L. Overall, TDS concentrations exceeded the 500 mg/L SMCL in a small fraction (2.1%) of the samples. There were no TDS data for karst wells; based on previous assessments, this aguifer type typically had the highest median TDS concentration.
- Chloride concentrations rarely exceeded the drinking-water standard. Chloride concentrations exceeded the SMCL (250 mg/L) in less than 1% of the samples. The most elevated chloride concentrations were associated with unconfined (516 mg/L) and confined (355 mg/L) well samples. Based on limited data, fractured-rock and karst wells had the highest median chloride concentrations (55.9 and 40.3 mg/L, respectively).
- Sodium concentrations were above the health advisory level in about one quarter of the samples. Sodium concentrations exceeded the Health Advisory (HA) of 20 mg/L in 26% of the samples. Sodium concentrations above the HA were found at virtually all depths. Confined wells had the largest fraction of sodium concentrations above the HA (38.3%).

^{*}Note: Because only raw or apparently raw groundwater-quality data were evaluated, the results may not be representative of finished or treated water delivered to consumers. Therefore, an exceedance of a drinking-water standard does not necessarily indicate that a public water-supply system is not in compliance

Introduction

Per Section 106(e) of the Federal Water Pollution Control Act (FWPCA; as amended through P.L. 107-303, November 27, 2002), more commonly known as the Clean Water Act, States are required to collect, compile, and analyze water-quality data and report results to the U.S. Environmental Protection (U.S. EPA) on a biennial basis. Because reporting requirements are outlined in Section 305(b) of the FWPCA, these reports are commonly referred to as "305(b) reports." Although the FWPCA focuses primarily on the quality of navigable [surface] waters, Section 106(e) states that groundwater quality must be reported "...to the extent practicable." Guidelines to this end have consequently been developed (U.S. EPA, 1997).

Inter-Departmental policy for Delaware has improved the Department of Natural Resources and Environmental Control's (DNREC's) ability to assess statewide groundwater quality (DNREC, 2007). The referenced policy requires that all groundwater samples collected in Delaware be identified by well permit number or "DNREC ID." The DNREC ID is the only statewide numbering system unique to well permits issued in Delaware and, therefore, the primary means to obtain well-construction information (DNREC, 2007). Well-construction information, in conjunction with geographic data and hydrogeologic mapping, allows for determinations of aquifer or aquifer type, basic data that are critical to any groundwater-quality investigation.

Efforts by the Department of Health and Social Services (DHSS) have been underway to identify water-quality data for public wells by DNREC ID. Electronic water-quality data are stored in the DHSS's Safe Drinking Water Information System (SDWIS). DNREC's Source Water Assessment and Protection Program (SWAPP) maintains a database (hereafter the "SWAPP database") that contains DNREC IDs, well-construction details, geographic coordinates, and hydrogeologic data for public water-supply wells in Delaware. This 305(b) groundwater-quality assessment is based on information stored in SDWIS and the SWAPP database. Methodologies for data acquisition and analysis are similar to those employed in DNREC's 2008, 2010, and 2012 305(b) groundwater-quality assessments (Kasper, 2008, 2010; Kasper and Strohmeier, 2012).

Purpose and scope

This report serves as "Part IV: Groundwater Assessment" of Delaware's overall 2014 305(b) report (DNREC, 2014). The primary purpose of this report is to summarize and report raw or apparently raw groundwater-quality data collected from public water-supply wells in Delaware during calendar years 2012 and 2013. Per U.S. EPA (1997) guidance, data are evaluated with respect to hydrogeologic setting and water-quality criteria where possible. The scope of this report is limited to available data obtained from two sources: the DHSS's SDWIS and the DNREC's SWAPP database.

Acknowledgements

Philippe Maitre of the DHSS is gratefully acknowledged for developing SDWIS queries to generate raw (or apparently raw) groundwater-quality data for public water-supply wells. Douglas Rambo of the DNREC assisted with the acquisition of up-to-date SWAPP data. Funding for this project is from a U.S. EPA grant pursuant to Section 106 of the Clean Water Act.

General hydrogeology

Delaware covers ~2,010 mi² and is comprised of two Physiographic Provinces: the Piedmont and the Atlantic Coastal Plain. The Piedmont covers ~82 mi² in northern Delaware (Figure 1) and is comprised of meta-sedimentary, meta-igneous, and igneous rocks (Plank et al., 2000). Areally, metamorphic rocks (mostly gneiss) are dominant based on 1-36,000-scale mapping of bedrock geology in Delaware's Piedmont (Schenck et al., 2000). Bedrock ages range from Precambrian to Silurian, although diabase dikes of Mesozoic age have been identified (Plank et al., 2000; Schenck et al., 2000).

Two main hydrogeologic units have been recognized in Delaware's Piedmont (after Werkheiser, 1995): non-carbonate and carbonate aquifers. Werkheiser (1995) used the term "non-carbonate aquifer" to describe the hydrologic unit occurring predominantly in fractured gneiss. For the purpose of this reporting, however, "fractured-rock aquifer" is used so as to avoid confusion with other non-carbonate aquifers occurring in Coastal-Plain sediments (Table 1). This aquifer-type designation is generally consistent with the SWAPP database. The Cockeysville aquifer, which occurs in the Cockeysville Marble, is the only carbonate aquifer in Delaware. Although the outcrop of the Cockeysville Marble is relatively small (~2.2 mi²), the Cockeysville aquifer is a major source of public and domestic water supply in northern Delaware (Talley, 1995; Werkheiser, 1995). In this report the term "karst aquifer" is used in lieu of carbonate or Cockeysville aquifer (Table 1). This aquifer-type designation is consistent with the SWAPP database.

The remaining 1,928 mi² (96%) of Delaware's land-surface area is underlain by Mid-Atlantic Coastal Plain sediments that onlap crystalline basement rocks (i.e., bedrock). These seaward-dipping and -thickening sediments range in age from Triassic to Holocene (Table 1). Depositional environments vary, but most sediments were laid down in marine, estuarine, and fluvial environments. Overall, 13 major and several minor aquifers are recognized in the Coastal Plain of Delaware (Table 1). Minor, unnamed aquifers occur mostly in Miocene-age sediments (Table 1) and hence the name "minor-Miocene aquifers" has been used to designate these hydrologic units.

For the purpose of this reporting, Coastal-Plain aquifers are subdivided into three main aquifer types: unconfined, semi-confined, and confined. These aquifer-type designations are consistent with the SWAPP database. The unconfined aquifer, also called the Columbia aquifer, occurs predominantly in Pleistocene- to Pliocene-age sediments that comprise Delaware's surficial geologic framework (Table 1). (The term "unconfined aquifer" is used in this report in lieu of "Columbia aquifer" because, as indicated in Table 1, the Columbia aquifer may be confined in some locations.) In areas where confined aquifers subcrop, however, the unconfined aquifer can be in direct hydraulic connection with older geologic units. The semi-confined and confined aquifers predominantly occur in sediments of Miocene age or older. In general, Miocene aquifers (Table 1) are tapped for potable water supply in Kent County and Sussex County; Eocene and Paleocene aquifers (Table 1) are tapped in southern New Castle County and Kent County; and Cretaceous aquifers (Table 1) are tapped in New Castle County.

Table 1. Hydrostratigraphic units in Delaware. [Modified after the Delaware Geological Survey, http://www.dgs.udel.edu/delaware-geology/hydrologic-stratigraphic-chart, accessed September 30, 2014.]

AGE	GEOLOGIC UNITS	HYDROLOGIC UNITS		
Holocene	various informal deposits	Unassigned		
	Delaware Bay Group			
	Nanticoke River Group	Columbia aquifer		
Pleistocene	Assawoman Bay Group			
	unassigned	Confining beds / minor, poor aquifer		
	Columbia Fm.	Columbia aquifor		
Pliocene	Beaverdam Fm.	Columbia aquifer		
	Bethany Fm.	Pocomoke aquifer and confining beds		
	Cat Hill Fm.	Manokin aquifer and confining beds		
	St. Marys Fm.	Confining beds / minor, poor aquifer		
	Choptank Fm.	unnamed aquifers and confining beds		
	Спортанк Епт.	Milford aquifer		
Miocene		Confining beds		
MIOCEITE		Frederica aquifer		
		Confining beds		
	Calvert Fm.	Federalsburg aquifer		
		Confining beds		
		Cheswold aquifer		
		Confining beds		
Oligocene	glauconitic unit	unassigned		
	glauconitic unit	3		
_	Piney Point Fm.	Piney Point aquifer and confining beds		
Eocene	Shark River Fm.	Confining beds		
	Deal Fm.	Comming Seas		
	Manasquan Fm.	Rancocas aquifer and confining beds		
Paleocene	Vincentown Fm.	rtaineedae aquiier and eeriiining ee ae		
	Hornerstown Fm.	Confining beds		
	Navesink Fm.			
	Mount Laurel Fm.	Mount Laurel aquifer		
	Marshalltown Fm.	Confining beds		
Cretaceous	Englishtown Fm.	Englishtown aquifer		
	Merchantville Fm.	Confining beds		
	Magothy Fm.	Magothy aquifer		
	Potomac Fm.	Potomac aquifer system and confining		
	Post-rift unconformity	beds		
Triassic and	rocks (of Jurassic age)			
Jurassic	and rift-basin rocks	unassigned		
	(inferred)			
Paleozoic to	,	Fractured-rock aquifer		
Precambrian	Various Fms. (bedrock)	Cockeysville (karst) aquifer		

Methods of investigation

Groundwater quality in Delaware was assessed based on pre-existing information stored in two separate databases: the DHSS's SDWIS and the DNREC's SWAPP database. DHSS staff developed queries to extract SDWIS records of raw or apparently raw groundwater-quality data collected from public water-supply systems during the reporting period (January 1, 2012 thru September 30, 2013). Data resulting from these queries (40,515 analyses) were provided to DNREC in a October 29, 2013 Microsoft Office Access 2007 ("Access") database. Records obtained from the SWAPP database were current as of October 28, 2013. The records included well details such as DNREC ID, depth, geographic coordinates, geologic formation, aquifer, and aquifer type.

Access was used to link and extract data from SDWIS and the SWAPP database. For wells with more than one analysis of a given analyte, results were averaged. Analytes not detected above laboratory quantitation limits ("nondetects") were treated as zeros in all calculations. Results were evaluated with respect to Primary Maximum Contaminant Levels (PMCLs), Secondary Maximum Contaminant Levels (SMCLs), and Health Advisories (HAs) for public water-supply systems (DHSS, 2005; U.S. EPA, 2012). Hardness data were evaluated with respect to the scale of Love (1962). Because only raw or apparently raw groundwater-quality data were evaluated, the results may not be representative of finished or treated water delivered to consumers. Therefore, an exceedance of a drinking-water standard does not necessarily indicate that a public water-supply system is not in compliance (see also Ferrari, 2001, p. 5).

Where possible, data were evaluated with respect to aquifer type (i.e., unconfined, confined, semi-confined, fractured-rock, or karst). Data were, however, generally insufficient in quantity for meaningful analyses of groundwater quality in specific aquifers (Table 1). Some data also were evaluated with respect to sample depth, which was taken to be the bottom of a well's screened interval. Evaluation of trends (e.g., concentration vs. depth) in this assessment are qualitative and not statistically derived. Environmental Systems Research Institute's (ESRI's) ArcMap, a geographic information system (GIS), was used for the spatial analysis of groundwater data. Tabulated statistics (e.g., Table 2) are the result Microsoft Office Excel 2007 ("Excel") calculations. Golden Software, Inc.'s Grapher version 5.01 ("Grapher") was used to construct percentile diagrams. Outliers shown on percentile diagrams (e.g., Figure 4) are computed by Grapher using the following equations:

QL –
$$1.5 \times IQR$$
 or QU – $1.5 \times IQR$

Where:

IQR is the interquartile range (i.e., the difference between the 75th and 25th percentiles) QL is the lower quartile or 25th percentile (i.e, the bottom of the box in Figure 4) QU is the upper quartile or 75th percentile (i.e., the top of the box in Figure 4)

Differences between tabulated statistics (e.g., Table 2) and corresponding percentile diagrams (e.g., Figure 4) are the result of differences in the computational methods of Excel and Grapher.

Public wells

As of October 28, 2013, there were 1,187 active public water-supply wells in the SWAPP database. Of the active wells, 1,143 (96%) have geographic coordinates and are plotted in Figure 1A. With reference to Figure 1A, there are 238 wells (21%) in New Castle County, 306 wells (27%) in Kent County, and 599 wells (52%) in Sussex County. (Percentages in this report may not total 100% due to rounding.)

Aquifer type is known for 978 (82%) of the 1,187 active wells (Figure 2). Wells where aquifer type is known and geographic coordinates are available are plotted in Figures 1B thru 1F. Out of all active wells, Coastal-Plain wells account for 919 (77%) and Piedmont wells account for 59 (5%) (Figure 2). The large percentage of Coastal-Plain wells relative to Piedmont wells is due to both land-area differences and the fact that public-water supply in the Piedmont and New Castle County is largely from surface-water resources (Wheeler, 2003). Aquifer type for the remaining 209 active wells is either unknown (due to a lack of well-construction data) or not yet assigned (Figure 2).

Coastal-Plain wells include wells screened in unconfined, semi-confined, or confined aquifers (Figures 1B thru 1D and Figure 2). Out of the 1,187 active wells, unconfined wells account for 424 (36%), confined wells account for 443 (37%), and semi-confined wells account for 52 (4%) (Figure 2). A large majority of the unconfined wells with geographic coordinates (345 of 424 or 81%) are located in Sussex County; the remaining unconfined wells include 47 (11%) in Kent County and 32 (8%) in New Castle County (Figure 1B). Confined wells are more evenly distributed throughout the Coastal Plain of Delaware, with most of these wells situated in Kent County (Figure 1C). Specifically, out of 441 confined wells with geographic coordinates, 183 (41%) are located in Kent County, 129 (29%) are located in New Castle County, and 129 (29%) are located in Sussex County. All 52 semi-confined wells have geographic coordinates (Figure 1D); 26 (50%) are located in Kent County, 19 (37%) are located in Sussex County, and 7 (13%) are located in New Castle County.

Piedmont wells include fractured-rock and karst wells and are limited to only the northernmost portion of the State (Figures 1E and 1F and Figure 2). Out of the 1,187 active wells, fractured-rock wells account for 49 (4%) and karst wells account for 10 (1%) (Figure 2). All 49 fractured-rock and 10 karst wells (Figure 2) have geographic coordinates and are plotted in Figures 1E and 1F, respectively. Karst wells coincide with the Cockeysville Marble outcrop in northern New Castle County (Figure 1F).

Well depths, taken as the bottom of the well screen, are known for 1,081 (91%) of 1,187 active wells (Figure 3). Overall, well depths range from 22 to 957 ft below land surface (bls) and are skewed (Figure 3). The median well depth is 140 ft bls and the 25th and 75th percentiles are 88 and 242 ft bls, respectively. Well depths are not known for 106 (9%) of the active wells (Figure 3).

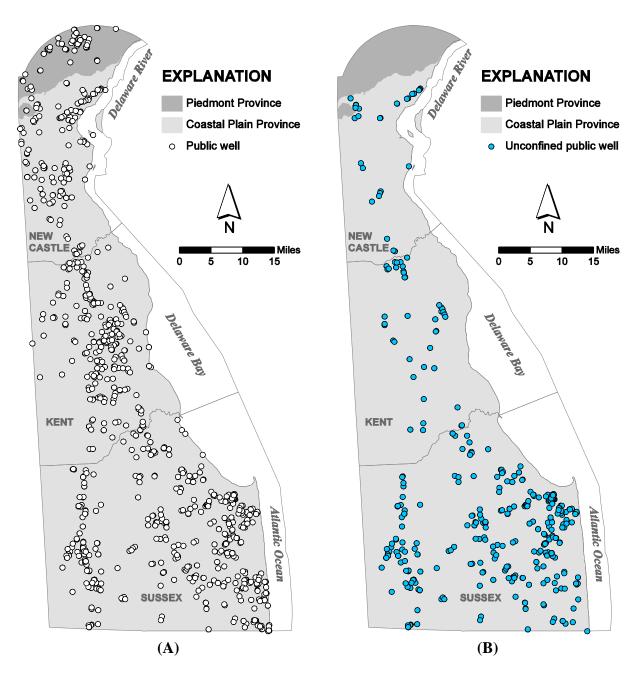


Figure 1. Maps of active public water-supply wells in Delaware - (A) all wells and (B) unconfined wells.

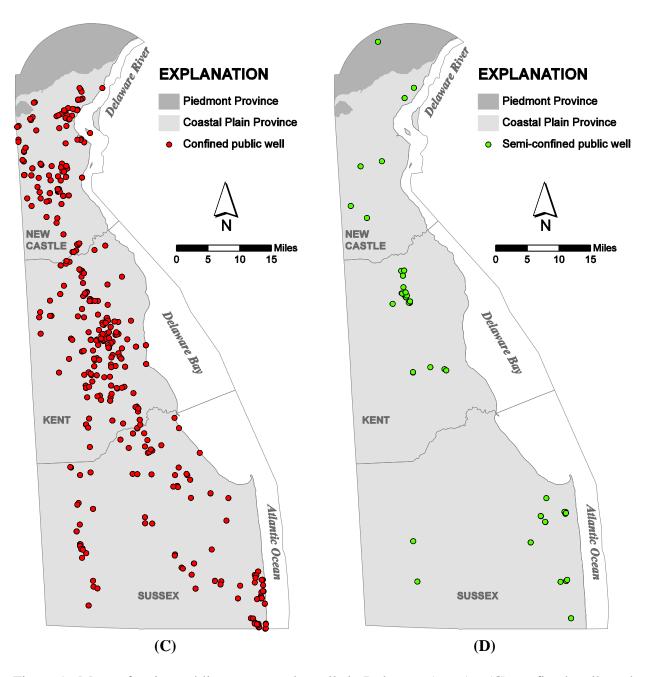


Figure 1. Maps of active public water-supply wells in Delaware (cont.) – (C) confined wells and (D) semi-confined wells.

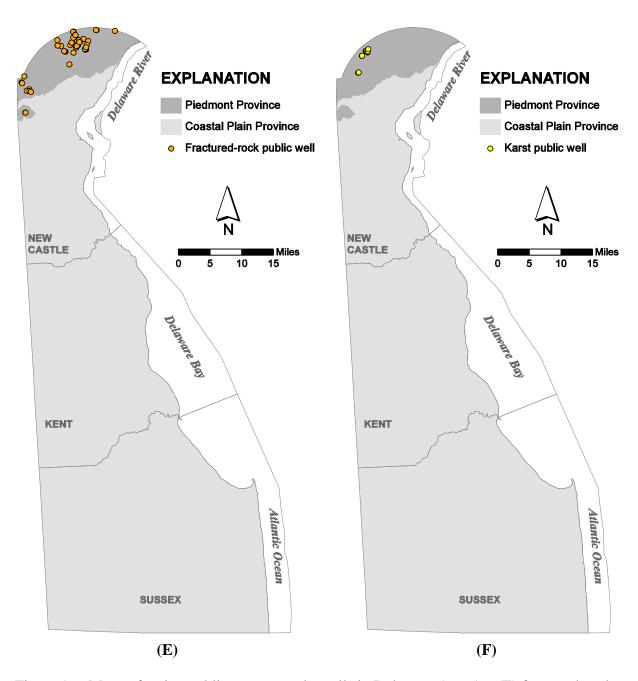


Figure 1. Maps of active public water-supply wells in Delaware (cont.) – (E) fractured-rock wells and (F) karst wells.

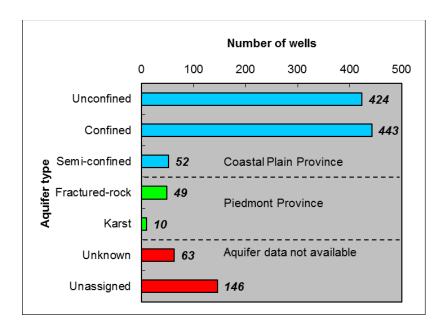


Figure 2. Histogram of active public water-supply wells by aquifer type.

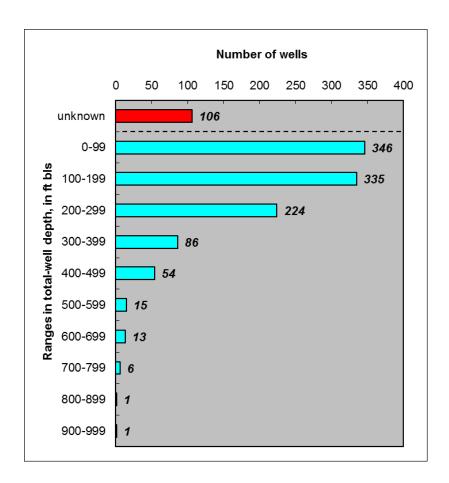


Figure 3. Histogram of active public water-supply wells by ranges in total-well depth.

Results and discussion

Results are grouped into four main categories: general chemistry, organic compounds, trace elements, and radionuclides.

General chemistry

For this assessment, general groundwater chemistry includes parameters routinely measured in public water-supply systems: Nitrate as nitrogen, total dissolved solids, chloride, sodium, iron, hardness as CaCO₃, and pH. Nitrate as nitrogen is the only parameter in this category with a PMCL (10 mg/L; U.S. EPA, 2012). Other parameters in this category include those that generally affect the aesthetic qualities of the water supply, such as taste, odor, color, corrosiveness, etc. Most of these parameters have SMCLs.

Nitrate as nitrogen

Overall, 1,193 nitrate as nitrogen ("nitrate") analyses are in the SDWIS query provided to DNREC. Of these, 348 (29%) could be linked by DNREC ID. Duplicate analyses for individual wells were averaged resulting in 278 nitrate analyses where aguifer type is known (Table 2). This number translates to ~28% of the total number of wells (978) where aguifer type is known (Figure 2). Overall, nitrate concentrations ranged from nondetectable (ND) to 21.6 mg/L with a median of ND (Table 2 and Figure 4). Nitrate was not detected above the laboratory quantitation limit in 158 (56.8%) of the 278 analyses (Table 2). Concentrations in 119 (42.8%) of the samples exceeded 0.4 mg/L (Table 2), a threshold used to distinguish between natural and human-impacted groundwater (Hamilton et al., 1993). Nitrate concentrations exceeded the PMCL (10 mg/L) in 12 (4.3%) of the 278 samples (Table 2). All but one of the PMCL exceedences occurred in Sussex County; the remaining exceedance occurred in southern Kent County (Figure 5). Overall, nitrate concentrations decrease with depth and, below depths of ~160 ft bls, concentrations never exceeded the PMCL (Figure 6). With the exception of two samples, nitrate concentrations exceeded 0.4 mg/L to depths of ~400 ft bls, however, and this may be an indication of the vertical extent of human influence on groundwater quality. The deepest nitrate detections were associated with Piedmont wells, which have very long open intervals that may allow contaminants to enter at shallower depths. Nitrate detections in Coastal-Plain wells were primarily limited to depths of 220 ft and shallower.

Unconfined wells account for 102 (36.7%) of the 278 individual samples linked by DNREC ID (Table 2). This number translates to ~24% of the total number of active unconfined wells (424) statewide (Figure 2). Nitrate was not detected above the laboratory quantitation limit in 12 (11.8%) of the 102 samples. Concentrations in 89 (87.3%) of the 102 samples exceeded 0.4 mg/L suggesting that groundwater quality in the unconfined aquifer is largely affected by human activities. Nitrate concentrations below 0.4 mg/L may reflect natural groundwater quality or geochemical conditions that do not favor nitrification. For example, the cluster of concentrations below 0.4 mg/L in southeastern Sussex County coincides with an area where shallow groundwater is largely anoxic (Figure 5a; Kasper and Strohmeier, 2007). The most elevated nitrate concentration (21.6 mg/L) was detected in an unconfined well (Table 2 and Figure 4). Out of the five aquifer types, unconfined wells had the highest median nitrate concentration (4.20 mg/L) and the second-lowest percentage of nondetects (Table 2 and Figure 4). The median nitrate concentration is in agreement with the median concentration (4.884 mg/L) from a USGS study of 30 randomly-selected unconfined public water-supply wells in

Delaware (Reyes, 2010). Moreover, the median nitrate concentration from this study is slightly lower than the median concentrations for shallow (5.4 mg/L) and intermediate (5.5 mg/L) depths in the unconfined aguifer on the Delmarva Peninsula (Denver et al., 2004). A watershed-scale study in Sussex County, Delaware, reported a higher median nitrate concentration (6.4 mg/L) for the unconfined aquifer (Kasper and Strohmeier, 2007). Land use in that watershed is and has been largely agricultural. For this assessment, nitrate exceeded the PMCL in 9 (8.8%) of the 102 unconfined aguifer samples (Table 2), all of which occurred in Sussex County (Figure 5a). This percentage of PMCL exceedences is higher than the percentage reported by Reyes (2010), who found two out of 30 public wells with nitrate above the PMCL. In contrast, other studies of shallow groundwater quality at the State scale (Pellerito et al., 2008) and watershed scale (Kasper and Strohmeier, 2007) reported higher percentages of PMCL exceedences (18 and 32%, respectively). There is no apparent trend in nitrate concentrations with depth in the unconfined aquifer (Figure 6). The most elevated concentration (21.6 mg/L) was detected at a depth of 80 ft bls. The deepest unconfined PMCL exceedance (11 mg/L) occurred at a depth of 148 ft bls and the shallowest PMCL exceedance (17.7 mg/L) occurred at a depth of 55 ft bls. At depths shallower than 55 ft bls, nitrate concentrations were <5 mg/L based on data for four unconfined wells.

Confined wells account for 152 (54.7%) of the 278 individual samples linked by DNREC ID (Table 2). This number translates to ~34% of the total number of active confined wells (443) statewide (Figure 2). Nitrate was not detected above the laboratory quantitation limit in 139 (91.4%) of the 152 samples. However, concentrations in 13 (8.6%) of the 152 wells exceeded 0.4 mg/L suggesting that the groundwater quality in a considerable fraction of confined aquifer wells may be susceptible to human activities (Table 2). Of these, almost half (6) are confined Potomac aquifer wells located in the northernmost portion of the Coastal Plain in New Castle County (Figure 5b). Nitrate exceeded the PMCL in one confined well sample (Table 2; Figure 5b). Nitrate concentrations generally decrease with depth in confined aquifers, consistent with the overall trend (Figure 6).

Semi-confined wells account for 16 (5.8%) of the 278 individual samples linked by DNREC ID (Table 2). This number translates to ~31% of the total number of active semi-confined wells (52) statewide (Figure 2). Nitrate was not detected above the laboratory quantitation limit in 6 (37.5%) of the 16 samples. Limited data suggest that semi-confined wells have an intermediate susceptibility to human impacts relative to confined and unconfined wells (Table 2). Specifically, nitrate concentrations in a large fraction of the semi-confined well samples (62.5%) exceeded 0.4 mg/L, indicating human influence on groundwater quality. Nitrate exceeded the PMCL in two semi-confined well samples (Table 2; Figure 5b).

Fractured-rock wells account for 3 (~1.1%) of the 278 individual samples linked by DNREC ID (Table 2). This number translates to ~6% of the total number of fractured-rock wells (49) statewide (Figure 2). Although data are extremely limited, nitrate concentrations in 2 of the 3 fractured-rock wells exceeded 0.4 mg/L. None of the nitrate concentrations in fractured-rock wells exceeded the PMCL. The deepest nitrate detections were associated with fractured-rock wells (Figure 6); however, the open intervals of these types of wells often intersect hundreds of feet of rock and, therefore, the nitrate may be entering these wells at shallower depths.

Karst wells account for 5 (1.8%) of the 278 individual samples linked by DNREC ID (Table 2). This number translates to 50% of the total number of karst wells (10) statewide (Figure 2). Nitrate was detected in 100% of the samples and concentrations always exceeded 0.4 mg/L. Karst wells also had the second-highest median nitrate concentration (2.5 mg/L; Table 2),

but none of the concentrations exceeded the PMCL. There is no discernible trend in nitrate versus depth for karst wells based on available data; however, some of the deepest nitrate detections are associated with karst wells (Figure 6). Note that, like fractured-rock wells, karst wells also typically have very long open intervals and nitrate may enter these wells at shallower depths.

Table 2. Statistical summary of nitrate data by aquifer type. [mg/L, milligrams per liter; ND, not detected above laboratory quantitation limit; PMCL, primary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

				Semi-	Fractured-	
	All	Unconfined	Confined	Confined	Rock	Karst
Statistics	Wells	Wells	Wells	Wells	Wells	Wells
Number of wells/samples (#)	278	102	152	16	3	5
Percent of total (%)	100	36.7	54.7	5.8	1.1	1.8
 Maximum (mg/L)	21.60	21.60	19.00	14.40	4.30	4.90
75th percentile (mg/L)	3.90	6.70	ND	3.60	2.70	4.30
50th percentile (mg/L)	ND	4.20	ND	1.60	1.10	2.50
25th percentile (mg/L)	ND	1.53	ND	ND	0.55	2.20
Minimum (mg/L)	ND	ND	ND	ND	ND	1.90
Number not detected (#ND)	158	12	139	6	1	0
Percent not detected (%ND)	56.8	11.8	91.4	37.5	33.3	0.0
	119	89	13	10	2	5
Percent > 0.4 mg/L (%)	42.8	87.3	8.6	62.5	66.7	100.0
	12	9	1	2	0	0
Percent > 10 mg/L PMCL (%)	4.3	8.8	0.7	12.5	0.0	0.0

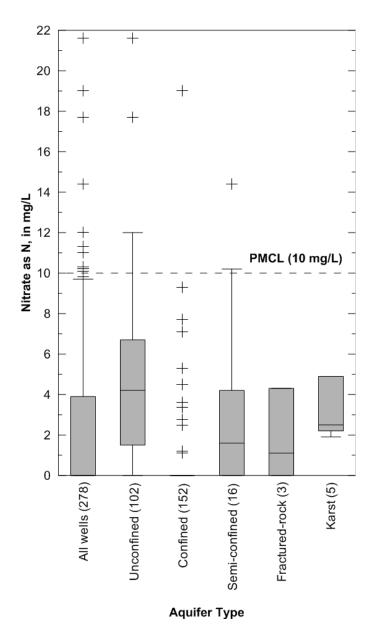


Figure 4. Percentile diagrams of nitrate data by aquifer type. [mg/L, milligrams per liter; crosses, outliers; (#), number of samples per aquifer type; PMCL, primary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

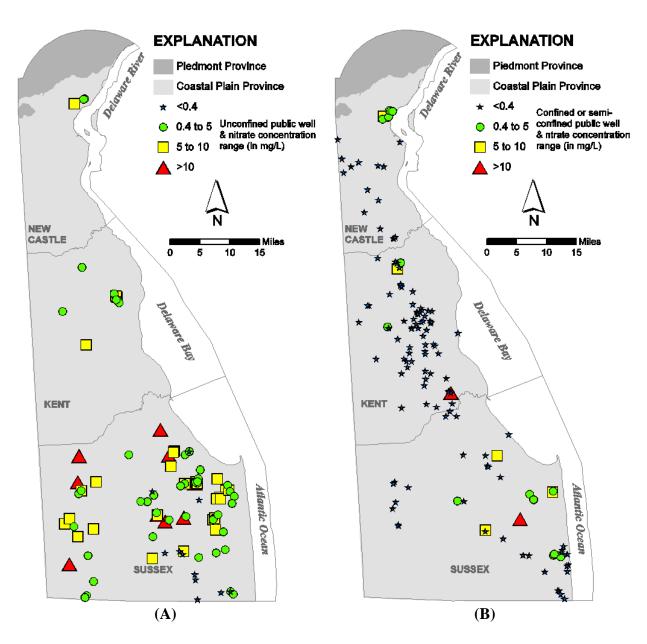


Figure 5. Maps showing nitrate concentration ranges in (A) unconfined and (B) confined and semi-confined public water-supply wells.

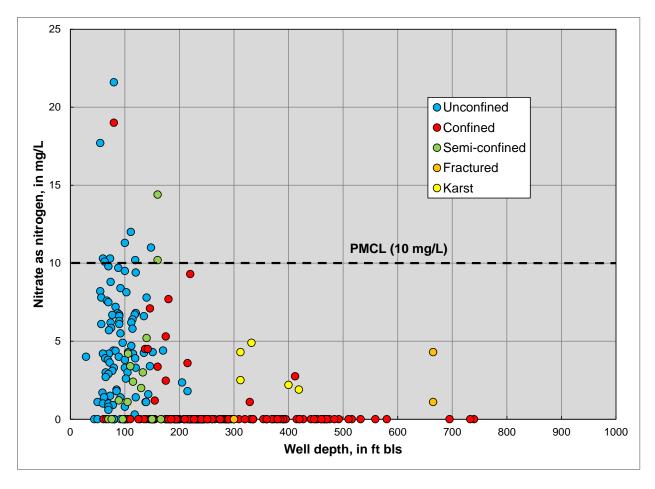


Figure 6. Scatter plot of nitrate versus well depth. [mg/L, milligrams per liter; ft bls, feet below land surface; PMCL, primary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

Total dissolved solids

Overall, 316 total dissolved solids (TDS) analyses are in the SDWIS query provided to DNREC. Of these, 257 (81%) could be linked by DNREC ID. Duplicate analyses for individual wells were averaged resulting in 191 TDS analyses where aquifer type is known (Table 3). This number translates to ~20% of the total number of wells (978) where aquifer type is known (Figure 2). Overall, TDS concentrations ranged from 36 to 928 mg/L with a median value of 170 mg/L (Table 3 and Figure 7). TDS concentrations exceeded the SMCL (500 mg/L) in 4 (2.1%) of the 191 analyses (Table 3).

There were no TDS data for karst wells for this assessment; however, this aquifer type had the highest median TDS concentration based on previous assessments (Kasper, 2010; Kasper and Strohmeier, 2012). In addition, with only three samples there were limited data for fractured-rock wells; one of the samples had TDS in excess of the SMCL (500 mg/L; Table 3). Based on previous 305(b) assessments, TDS data for karst and fractured-rock wells were in sharp contrast, a finding that is consistent with Werkheiser (1995). Elevated TDS in karst wells has been attributed to the dissolution of carbonate rocks (Werkheiser, 1995). Based on 69 samples, unconfined wells had the lowest median TDS concentration (128 mg/L; Table 3 and Figure 7), a

value that agrees in general with the median value of 116 mg/L reported by Ferrari (2001) and Reyes (2010). One unconfined TDS concentration exceeded the SMCL. Median TDS concentrations for confined and semi-confined wells were higher than concentrations for unconfined wells (Table 3), likely due to longer groundwater contact time with formation sediments. TDS concentrations in confined wells exceeded the SMCL in 2 (1.8%) of the 112 analyses (Table 3). TDS concentrations generally increase with depth; however, there are several wells that deviate from the general trend and some of these wells are screened in the confined, Potomac aquifer (Figure 8).

Table 3. Statistical summary of total dissolved solids (TDS) data by aquifer type. [mg/L, milligrams per liter; ---, no data; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

				Semi-	Fractured-	
	All	Unconfined	Confined	Confined	Rock	Karst
Statistics	Wells	Wells	Wells	Wells	Wells	Wells
				_	•	
Number of wells/samples (#)	191	69	112	7	3	0
Percent of total (%)	100	36.1	58.6	3.7	1.6	0.0
_						
Maximum (mg/L)	928	918	928	216	838	
75th percentile (mg/L)	236	166	256	180	558	
50th percentile (mg/L)	170	128	205	134	278	
25th percentile (mg/L)	116	96	156	125	196	
Minimum (mg/L)	36	36	36	114	114	
Number not detected (#ND)	0	0	0	0	0	
	-	· ·	-	•	•	
Percent not detected (%ND)	0.0	0.0	0.0	0.0	0.0	
Number > 500 mg/L SMCL (#)	4	1	2	0	1	
Percent > 500 mg/L SMCL (%)	2.1	1.4	1.8	0.0	33.3	,

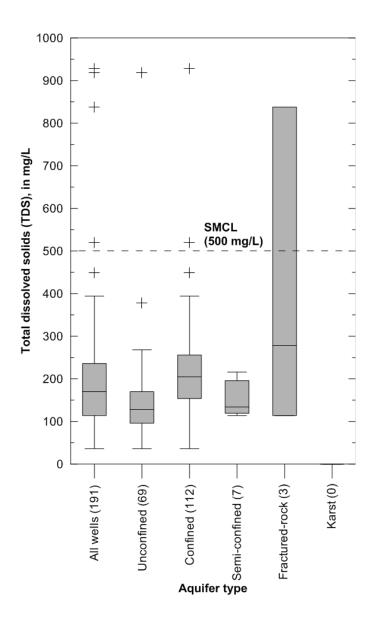


Figure 7. Percentile diagrams of total dissolved solids (TDS) data by aquifer type. [mg/L, milligrams per liter; crosses, outliers; (#), number of samples; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

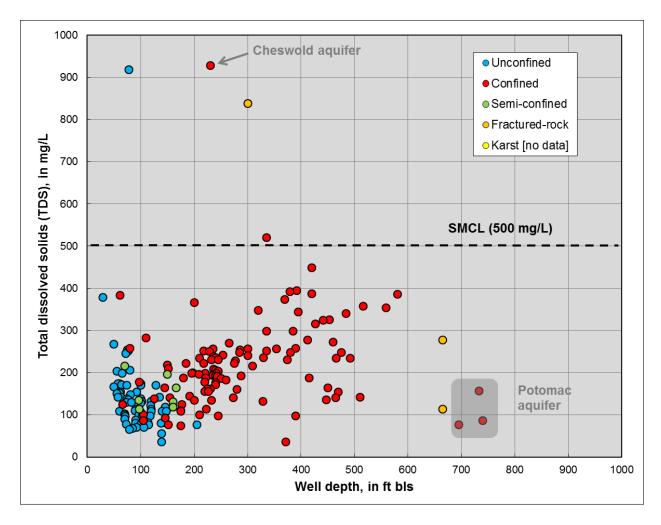


Figure 8. Scatter plot of total dissolved solids (TDS) versus well depth. [mg/L, milligrams per liter; ft bls, feet below land surface; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

Chloride

Overall, 1,163 chloride analyses are in the SDWIS query provided to DNREC. Of these, 367 (32%) could be linked by DNREC ID. Duplicate analyses for individual wells were averaged resulting in 276 chloride analyses where aquifer type is known (Table 4). This number translates to ~28% of the total number of wells (978) where aquifer type is known (Figure 2). Overall, chloride concentrations ranged from 1.1 to 516 mg/L with a median value of 11.1 mg/L (Table 4 and Figure 9). Chloride concentrations exceeded the SMCL (250 mg/L) in 2 (0.7%) of the 276 analyses (Table 4).

Although fractured-rock wells had the highest median chloride concentration (55.9 mg/L), data are extremely limited (Table 4 and Figure 9). Karst wells had the second-highest median chloride concentration (40.3 mg/L; Table 4 and Figure 9). The most elevated chloride concentration, however, was associated with an unconfined well. Unconfined wells had the third-highest median chloride concentration (15.4 mg/L). These results may be indicative of impacts from human activities occurring at or near the land surface (e.g., road salting). The

median value for the unconfined aquifer is in general agreement with Ferrari's (2001) median of 18.3 mg/L and Reyes' (2010) median of 18.6 mg/L. Semi-confined and confined wells had the lowest median chloride concentrations (12.8 and 3.4 mg/L, respectively). Although difficult to discern in Figure 10, there is a slight decreasing trend in chloride concentrations with depth; below depths of ~420 ft bls concentrations are typically <20 mg/L.

Table 4. Statistical summary of chloride data by aquifer type. [mg/L, milligrams per liter; ND, not detected above laboratory quantitation limit; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

Statistics	All Wells	Unconfined Wells	Confined Wells	Semi- Confined Wells	Fractured- Rock Wells	Karst Wells
Number of wells/samples (#)	276	100	152	16	3	5
Percent of total (%)	100	36.2	55.1	5.8	1.1	1.8
— Maximum (mg/L)	516.0	516.0	355.0	27.0	218.0	50.1
75th percentile (mg/L)	17.4	19.9	11.7	18.0	137.0	46.7
50th percentile (mg/L)	11.1	15.4	3.4	12.8	55.9	40.3
25th percentile (mg/L)	3.1	12.1	2.2	9.9	29.8	33.6
Minimum (mg/L)	1.1	5.0	1.1	5.2	3.6	17.3
Number not detected (#ND)	0	0	0	0	0	0
Percent not detected (%ND)	0.0	0.0	0.0	0.0	0.0	0.0
	2	1	1	0	0	0
Percent > 250 mg/L SMCL (%)	0.7	1.0	0.7	0.0	0.0	0.0

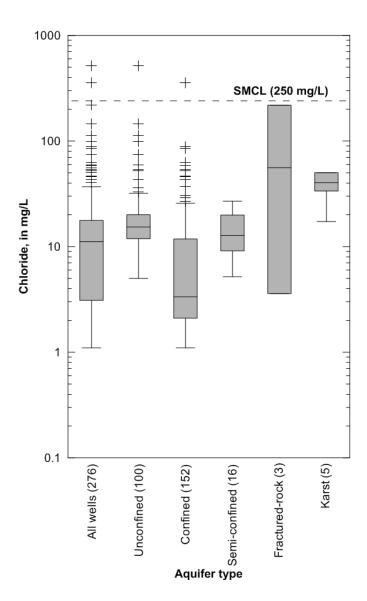


Figure 9. Percentile diagrams of chloride data by aquifer type. [mg/L, milligrams per liter; crosses, outliers; (#), number of samples; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

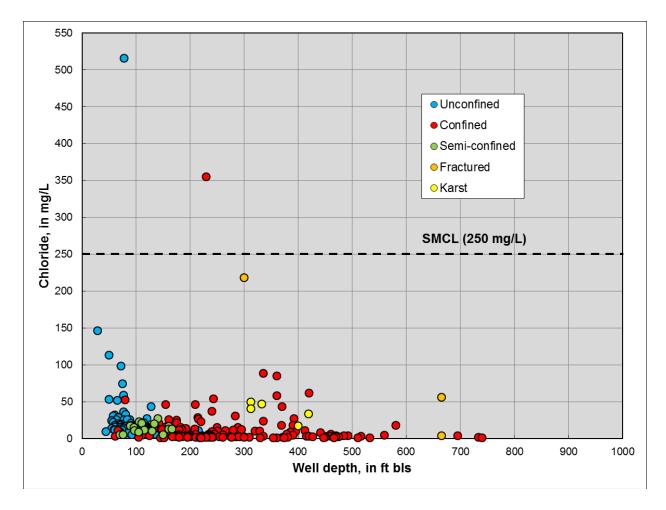


Figure 10. Scatter plot of chloride versus well depth. [mg/L, milligrams per liter; ft bls, feet below land surface; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

Sodium

Overall, 794 sodium analyses are in the SDWIS query provided to DNREC. Of these, 342 (43%) could be linked by DNREC ID. Duplicate analyses for individual wells were averaged resulting in 273 sodium analyses where aquifer type is known (Table 5). This number translates to ~28% of the total number of wells (978) where aquifer type is known (Figure 2). Overall, sodium concentrations ranged from 2.3 to 345 mg/L with a median value of 11.1 mg/L (Table 5 and Figure 11). Sodium concentrations exceeded the HA (20 mg/L) in 71 (26%) of the 273 samples (Table 5).

Median sodium concentrations were comparable amongst the various aquifer types (Table 5 and Figure 11). The median concentration for the unconfined aquifer (10.9 mg/L) was lower than Ferrari's (2001) median of 11.7 mg/L and Reyes' (2010) median of 14.2 mg/L. Unconfined wells also had a substantial fraction of concentrations above the HA (12%; Table 5 and Figure 11). Sodium is a component of the human diet and poultry manure and, therefore, its presence in shallow aquifers can reflect impacts from wastewater disposal and agricultural practices (Denver, 1989). Confined wells had the highest median sodium concentration (11.6

mg/L) and the largest fraction of concentrations above the HA (38.3%; Table 5 and Figure 11). In some instances, elevated sodium concentrations can be detected in glauconitic aquifers (e.g., the Piney Point aquifer) due to ion-exchange processes (Spoljaric, 1986). Relative to other Coastal-Plain aquifer types, semi-confined wells had the lowest median sodium concentration (10.1 mg/L) and the smallest fraction of concentrations above the HA (6.3%; Table 5 and Figure 11). Karst wells had the second-highest median sodium concentration (11.3 mg/L), but none of the concentrations exceeded the HA (Table 5 and Figure 11). Data for fractured-rock wells were limited (n=3), but one concentration exceeded the HA. Overall, sodium concentrations exceeded the HA at virtually all depths (Figure 12).

Table 5. Statistical summary of sodium data by aquifer type. [mg/L, milligrams per liter; ND, not detected above laboratory quantitation limit; HA, health advisory for public water-supply systems (U.S. EPA, 2012).]

Statistics	All Wells	Unconfined Wells	Confined Wells	Semi- Confined Wells	Fractured- Rock Wells	Karst Wells
Number of wells/samples (#)	273	100	149	16	3	5
Percent of total (%)	100	36.6	54.6	5.9	1.1	1.8
— Maximum (mg/L)	345.0	345.0	146.0	56.0	54.0	15.0
75th percentile (mg/L)	22.3	13.8	44.8	14.5	32.0	12.8
50th percentile (mg/L)	11.1	10.9	11.6	10.1	9.9	11.3
25th percentile (mg/L)	7.9	8.6	7.4	5.6	7.7	6.7
Minimum (mg/L)	2.3	4.6	2.3	4.5	5.5	4.9
Number not detected (#ND)	0	0	0	0	0	0
Percent not detected (%ND)	0.0	0.0	0.0	0.0	0.0	0.0
- Number > 20 mg/L HA (#)	71	12	57	1	1	0
Percent > 20 mg/L HA (%)	26.0	12.0	38.3	6.3	33.3	0.0

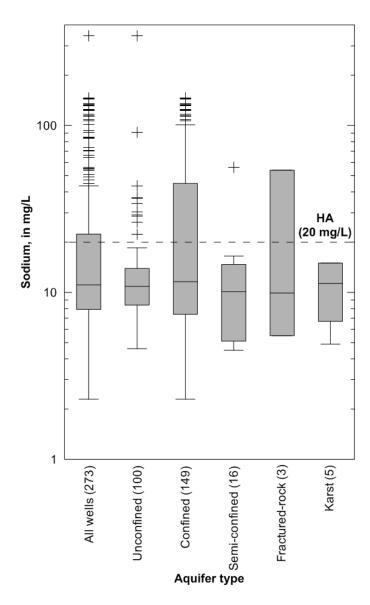


Figure 11. Percentile diagrams of sodium data by aquifer type. [mg/L, milligrams per liter; crosses, outliers; (#), number of samples; HA, health advisory for public water-supply systems (U.S. EPA, 2012).]

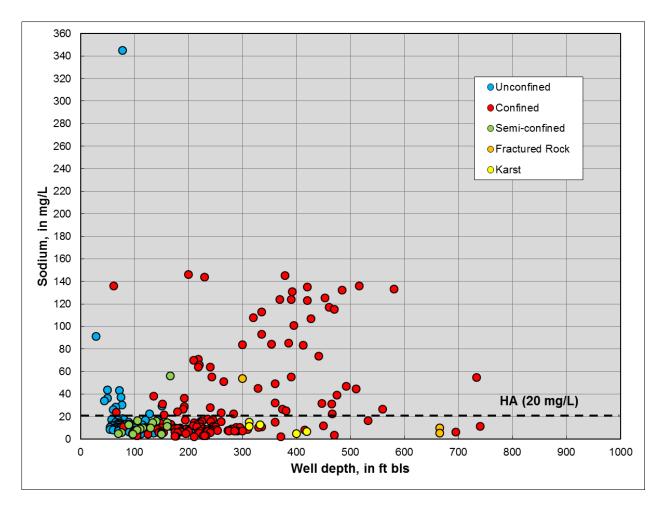


Figure 12. Scatter plot of sodium versus well depth. [mg/L, milligrams per liter; ft bls, feet below land surface; HA, health advisory for public water-supply systems (U.S. EPA, 2012.]

Iron

Overall, 822 iron analyses are in the SDWIS query provided to DNREC. Of these, 368 (45%) could be linked by DNREC ID. Duplicate analyses for individual wells were averaged resulting in 273 iron analyses where aquifer type is known (Table 6). This number translates to ~28% of the total number of wells (978) where aquifer type is known (Figure 2). Overall, iron concentrations ranged from ND to 34.4 mg/L with a median value of ND mg/L (Table 6 and Figure 13). Iron was not detected above the laboratory quantitation limit in 146 (53.5%) of the 273 analyses. Iron concentrations exceeded the SMCL (0.3 mg/L) in 81 (29.7%) of the 273 samples (Table 6).

Iron data for fractured-rock wells were limited (n=3), but two of the concentrations exceeded the SMCL; in contrast, iron was ND in all karst well samples (Table 6 and Figure 13). Relative to other Coastal-Plain aquifer types, semi-confined wells had the highest median iron concentration (0.24 mg/L), the smallest fraction of ND concentrations (37.5%), and the largest fraction of concentrations above the SMCL (43.8%; Table 6 and Figure 13). For Coastal Plain aquifers, confined wells had the second-largest fraction of concentrations above the SMCL. The most elevated iron concentration (34.4 mg/L) was associated with a unconfined well; however,

unconfined wells had the largest fraction of ND concentrations (58%) and the smallest fraction of concentrations above the SMCL (24%; Table 6 and Figure 13). The fraction of unconfined iron concentrations above the SMCL was greater than those reported by Ferrari (2001; 17%) and Reyes (2010; 13%). Overall, iron exceeded the SMCL at virtually all depths (Figure 14).

Table 6. Statistical summary of iron data by aquifer type. [mg/L, milligrams per liter; ND, not detected above laboratory quantitation limit; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

Statistics	All Wells	Unconfined Wells	Confined Wells	Semi- Confined Wells	Fractured- Rock Wells	Karst Wells
Number of wells/samples (#)	273	100	149	16	3	5
Percent of total (%)	100	36.6	54.6	5.9	1.1	1.8
— Maximum (mg/L)	34.40	34.40	20.30	29.20	21.80	ND
75th percentile (mg/L)	0.97	0.28	1.33	23.20	17.25	ND
50th percentile (mg/L)	ND	ND	ND	0.24	12.70	ND
25th percentile (mg/L)	ND	ND	ND	ND	6.35	ND
Minimum (mg/L)	ND	ND	ND	ND	ND	ND
Number not detected (#ND)	146	58	76	6	1	5
Percent not detected (%ND)	53.5	58.0	51.0	37.5	33.3	100.0
	81	24	48	7	2	0
Number > 0.3 mg/L SMCL (#)				•	_	
Percent > 0.3 mg/L SMCL (%)	29.7	24.0	32.2	43.8	66.7	0.0

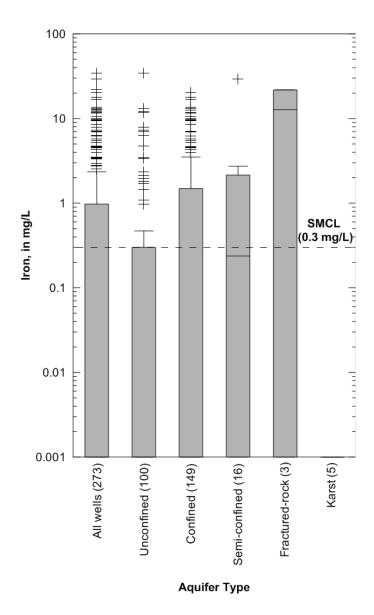


Figure 13. Percentile diagrams of iron data by aquifer type. [mg/L, milligrams per liter; crosses, outliers; (#), number of samples; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012); nondetects assigned values of 0.001 mg/L to allow display on semi-logarithmic plot.]

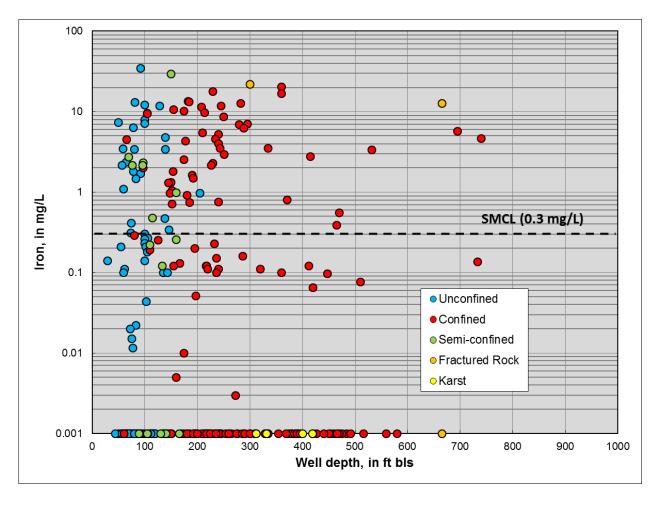


Figure 14. Scatter plot of iron versus well depth. [mg/L, milligrams per liter; ft bls, feet below land surface; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012); nondetects assigned values of 0.001 mg/L to allow display on semi-logarithmic plot.]

Hardness as CaCO₃

Overall, 302 hardness as CaCO₃ ("hardness") analyses are in the SDWIS query provided to DNREC. Of these, 246 (81%) could be linked by DNREC ID. Duplicate analyses for individual wells were averaged resulting in 192 hardness analyses where aquifer type is known (Table 7). This number translates to ~20% of the total number of wells (978) where aquifer type is known (Figure 2). Overall, hardness concentrations ranged from ND to 179 mg/L with a median value of 28.2 mg/L (Table 7 and Figure 15). Hardness was not detected above the laboratory quantitation limit in 9 (4.7%) of the 192 analyses. With respect to the hardness scale of Love (1962), most of the analyses (185 or 96.4%) were classified as soft or moderately hard; the remaining 3.6% of the analyses were classified as hard (Table 7). None of the results were classified as very hard.

There were no hardness data for karst wells for this assessment; however, based on previous assessments, this aquifer type had the highest median hardness concentration and the largest fraction of concentrations classified as very hard (Kasper, 2010; Kasper and Strohmeier,

2012). Previous hardness results for karst wells were in general agreement with Werkheiser (1995), who reported that more than 75% of karst well samples could be classified as very hard. Hardness data for karst and fractured-rock wells are typically in sharp contrast (Werkheiser, 1995). Hardness data for fractured-rock wells were limited (n=3); however, the most elevated hardness result (179 mg/L) was associated with a fractured-rock well (Table 7). Most of the confined well samples were classified as soft (67.3%), with smaller fractions classified as moderately hard (27.4%) or hard (5.3%). Most of the semi-confined well samples were classified as soft (57.1%), with the remaining 42.9% classified as moderately hard (Table 7 and Figure 15). Unconfined wells had the lowest median hardness concentration (15.9 mg/L) and the largest fraction of results classified as soft (92.8%); a small fraction of the unconfined samples (7.2%) were classified as moderately hard (Table 7 and Figure 15). Groundwater classified as hard occurred at depths ranging from ~200 to 500 ft bls; at depths shallower than ~200 ft bls, groundwater was always classified as either soft or moderately hard (Figure 16). The three deepest confined well samples were classified as soft and associated with the Potomac aquifer system (Figure 16).

Table 7. Statistical summary of hardness data by aquifer type. [mg/L, milligrams per liter; ND, not detected; ---, no data; hardness scale after Love (1962).]

				Semi-	Fractured-	
	All	Unconfined	Confined	Confined	Rock	Karst
Statistics	Wells	Wells	Wells	Wells	Wells	Wells
Number of wells/samples (#)	192	69	113	7	3	0
Percent of total (%)	100	35.9	58.9	3.6	1.6	0.0
— Maximum (mg/L)	179.0	112.0	146.0	81.0	179.0	
75th percentile (mg/L)	59.3	25.8	67.4	70.8	108.7	
50th percentile (mg/L)	28.2	15.9	40.1	55.6	38.3	
25th percentile (mg/L)	14.6	9.3	21.5	30.1	30.1	
Minimum (mg/L)	ND	ND	ND	ND	21.8	
Number not detected (#ND)	9	6	2	1	0	
Percent not detected (%ND)	4.7	8.7	1.8	14.3	0.0	
 Soft; 0-60 mg/L (#)	146	64	76	4	2	
Soft; 0-60 mg/L (%)	76.0	92.8	67.3	57.1	66.7	
 Mod. hard; 61-120 mg/L (#)	39	5	31	3	0	
Mod. hard; 61-120 mg/L (%)	20.3	7.2	27.4	42.9	0.0	
 Hard; 121-180 mg/L (#)	7	0	6	0	1	
Hard; 121-180 mg/L (%)	3.6	0.0	5.3	0.0	33.3	,
	0	0	0	0	0	
Very hard; >180 mg/L (%)	0.0	0.0	0.0	0.0	0.0	

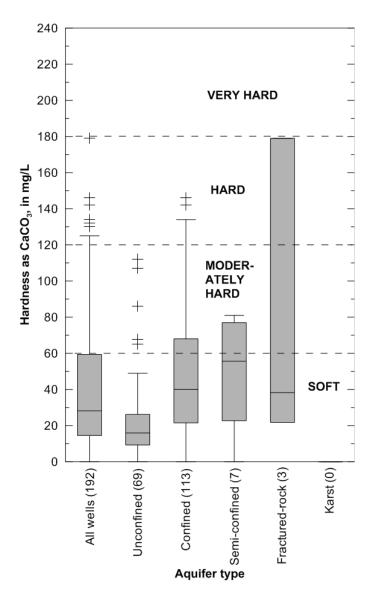


Figure 15. Percentile diagrams of hardness data by aquifer type. [mg/L, milligrams per liter; crosses, outliers; (#), number of samples; hardness scale after Love (1962).]

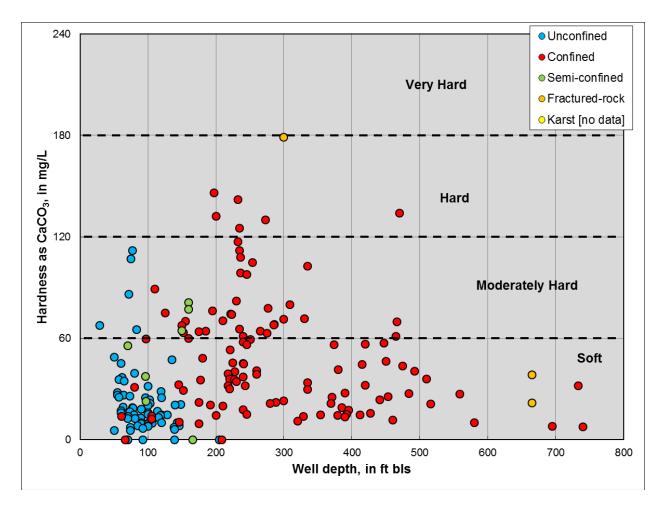


Figure 16. Scatter plot of hardness versus well depth. [mg/L, milligrams per liter; ft bls, feet below land surface; hardness scale after Love (1962).]

pH

Overall, 714 pH analyses are in the SDWIS query provided to DNREC. Of these, 231 (32.4%) could be linked by DNREC ID. Duplicate analyses for individual wells were averaged resulting in 181 pH analyses where aquifer type is known (Table 8). This number translates to ~19% of the total number of wells (978) where aquifer type is known (Figure 2). Overall, pH ranged from 4.6 to 8.7 standard units (S.U.) with a median value of 6.6 S.U. (Table 8 and Figure 17). Values of pH were below the lower limit of the SMCL range (6.5 to 8.5 S.U.) in 83 (45.9%) of the 181 samples; values were within the SMCL range in 96 (53%) of the 181 samples (Table 8). Only two pH values exceeded the upper limit of the SMCL range.

Confined wells had the highest median pH value (7.8 S.U.) and the second largest fraction of samples within the SMCL range (85.9%; Table 8). Although there were no pH data for karst wells for this assessment, based on previous assessments, this aquifer type had the highest median pH concentration and the largest fraction of values within the SMCL range (Kasper, 2010; Kasper and Strohmeier, 2012). Calcium carbonate in the karst aquifer (due to marble) and some confined and semi-confined aquifers (due to shell material) buffers the pH of groundwater that flows through these aquifers. Unconfined and semi-confined wells had

comparable median pH values (5.7 and 5.8, respectively); however, unconfined wells had the largest fraction of values below 6.5 S.U. and outside the SMCL range (85.7%; Table 8 and Figure 17). With only three results, pH data for fractured-rock wells were limited; the median pH was 6.6 S.U. with 100% of the results within the SMCL range (Table 8 and Figure 17). Overall, pH values below 6.5 S.U. occurred at nearly all depths, but were most prevalent at depths of ~250 ft bls and shallower (Figure 18).

Table 8. Statistical summary of pH data by aquifer type. [S.U., standard units; ---, no data; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

	All	Unconfined	Confined	Semi- Confined	Fractured- Rock	Karst
Statistics	Wells	Wells	Wells	Wells	Wells	Wells
Number of wells/samples (#)	181	77	92	9	3	0
Percent of total (%)	100.0	42.5	50.8	5.0	1.7	0.0
 Maximum (S.U.)	8.7	8.5	8.7	7.5	6.9	
75th percentile (S.U.)	7.8	6.1	8.1	7.3	6.8	
50th percentile (S.U.)	6.6	5.7	7.8	5.8	6.6	
25th percentile (S.U.)	5.7	5.5	6.9	5.7	6.6	
Minimum (S.U.)	4.6	4.6	4.8	5.2	6.5	
pH <6.5 SMCL (#)	83	66	11	6	0	
pH <6.5 SMCL (%)	45.9	85.7	12.0	66.7	0.0	
pH 6.5 to 8.5 (#)	96	11	79	3	3	
pH 6.5 to 8.5 (%)	53.0	14.3	85.9	33.3	100.0	
pH >8.5 SMCL (#)	2	0	2	0	0	
pH >8.5 SMCL (%)	1.1	0.0	2.2	0.0	0.0	

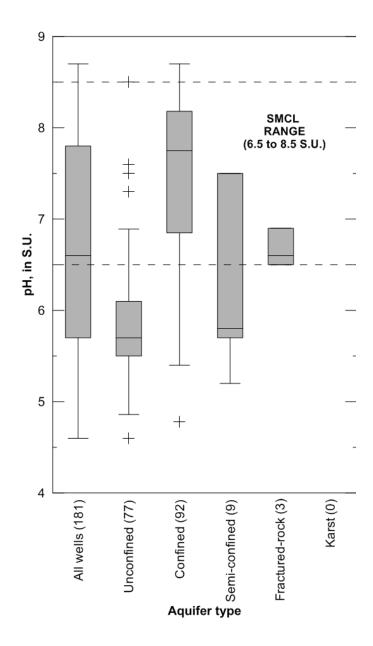


Figure 17. Percentile diagrams of pH data by aquifer type. [S.U., standard units; crosses, outliers; (#), number of samples; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

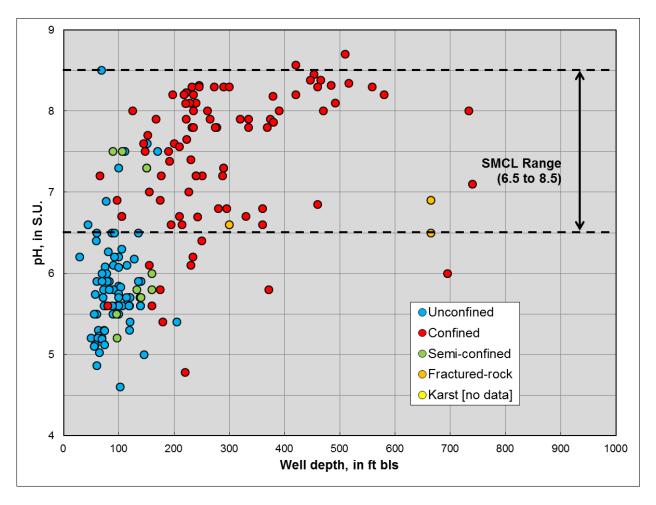


Figure 18. Scatter plot of pH versus well depth. [S.U., standard units; ft bls, feet below land surface; SMCL, secondary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

Organic compounds

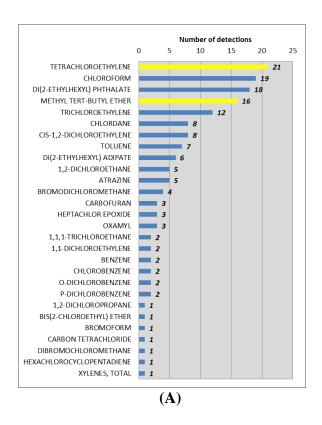
Because organic compounds (OCs) include a broad list of volatiles, semi-volatiles, and pesticides, they are treated in this report as a group of analytes rather than individual analytes. Overall, 26,478 OC analyses are in the SDWIS query provided to DNREC. Of these, 4,306 (16.3%) could be linked by DNREC ID. Duplicate analyses for individual wells were averaged resulting in 2,816 OC analyses. OCs were not detected in 2,659 (94.4%) of the 2,816 analyses. Out of the 57 organic compounds analyzed, 28 (49%) were detected (Figure 19).

Of the 157 OC detections, more than three-quarters (120 or 76.4%) were found at concentrations less than 1 μ g/L. Tetrachloroethylene (PCE), a solvent, was the most-frequently detected OC (Figure 19). Chloroform, a disinfection byproduct, was the second most-frequently detected OC. Di (2-ethylhexyl)-phthalate (DEHP), a plasticizer and common laboratory contaminant, was the third most-frequently detected OC. Methyl tert-butyl ether (MTBE), a gasoline oxygenate, was the fourth most-frequently detected OC. Trichloroethylene (TCE), a solvent, was the fifth most-frequently detected OC. These findings are generally consistent with

studies by Ferrari (2001) and Reyes (2010) involving water-quality data for 30 unconfined public water-supply wells in Delaware, as well as previous 305(b) groundwater-quality assessments (Kasper, 2008, 2010; Kasper and Strohmeier, 2012).

PMCLs were exceeded in 9 (0.3%) of the 2,816 analyses. The following analytes were found above the PMCL: PCE (7 exceedences) and MTBE (2 exceedences). Aquifer type was established for 8 of the 9 samples with PMCL exceedences. Of these, three were associated with confined wells, two were associated with unconfined wells, and three were associated with karst wells. All of the confined wells are completed in the Potomac aquifer system, an extremely heterogeneous fluvial system used most extensively for water supply in the northern, most populated portion of Delaware (McKenna et al., 2004). These findings, although limited, further illustrate the susceptibility of the unconfined aquifer, karst aquifer, and Potomac aquifer system to contamination.

MTBE, TCE, and PCE are within the top ten most frequently detected OCs (Figure 19), consistent with the findings of Ferrari (2001), Reyes (2010), and previous 305(b) groundwater-quality assessments (Kasper, 2008, 2010; Kasper and Strohmeier, 2012). Well depths were established for 73 MTBE, 74 TCE, and 73 PCE analyses, and scatter plots of these parameters versus well depth are shown in Figure 20. For unconfined, semi-confined, and confined wells, MTBE, TCE, and PCE detections were limited to depths of 215 ft bls, consistent with Kasper (2008, 2010) and Kasper and Strohmeier (2012). For fractured-rock and karst wells, these OCs were detected at greater depths (Figure 20); however, wells in these aquifer types typically have very long open intervals and, therefore, these contaminants may enter the wells at shallower depths. Overall, these findings are consistent with trends of nitrate versus well depth (Figure 5), and appear to provide another indication of the vertical extent of human impact on groundwater quality in Delaware.



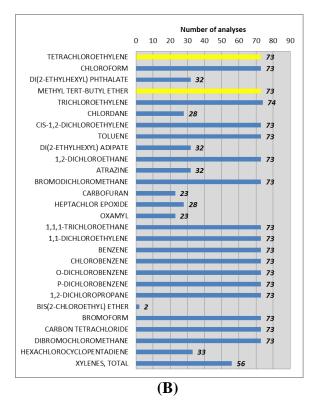


Figure 19. Frequency distributions of organic compound (A) detections and (B) analyses. [Bars highlighted yellow indicate one or more concentration above the PMCL or primary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

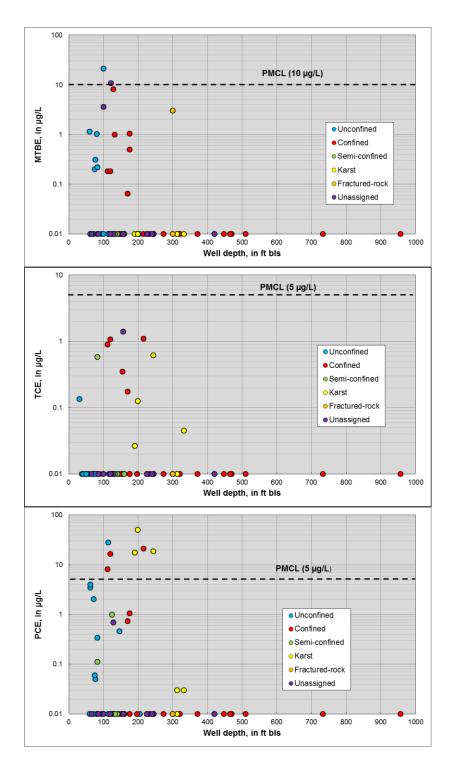


Figure 20. Scatter plots of methyl tert-butyl ether (MTBE), trichloroethylene (TCE), and tetrachloroethylene (PCE) versus well depth. [μ g/L, micrograms per liter; ft bls, feet below land surface; PMCL, primary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012); nondetectable concentrations (zeros) assigned values of 0.01 μ g/L to allow display on semi-logarithmic plots.]

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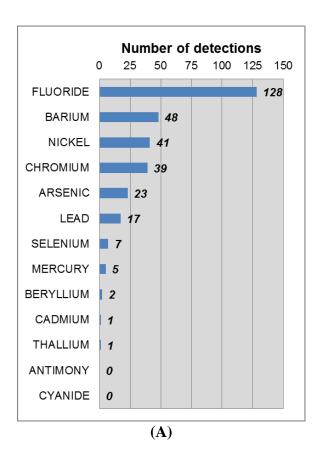
Trace elements

For this assessment, trace elements are limited to the following analytes with PMCLs (DHSS, 2005; U.S. EPA, 2012): antimony (0.006 mg/L), arsenic (0.010 mg/L), barium (2 mg/L), beryllium (0.004 mg/L), cadmium (0.005 mg/L), chromium (0.1 mg/L), cyanide (0.2 mg/L), fluoride (2 mg/L), lead (0.015 mg/L*), mercury (0.002 mg/L), nickel (0.1 mg/L), selenium (0.05 mg/L), and thallium (0.002 mg/L). (*Action level for Treatment Technique (TT; U.S. EPA, 2012).) Overall, 1,061 trace-element analyses are in the SDWIS query provided to DNREC. Duplicate analyses for individual wells were averaged resulting in 914 trace-element analyses. Trace elements were not detected in 602 (66%) of the 914 analyses.

Detectable trace-element concentrations were less than 0.1 mg/L in 180 (58%) of the 312 detections and less than 1 mg/L in 305 (98%) of the 312 detections. Barium, nickel, and chromium were the three most-frequently detected trace elements (Figure 21). (Although fluoride had the largest number of detections (128), it also had the largest number of analyses (330) and it was detected in a relatively smaller fraction (39%) of analyses (Figure 21).) Barium was detected in 48 (92.3%) of the 52 analyses, nickel was detected in 41 (78.8%) of 52 analyses, and chromium was detected in 39 (75.0%) of 52 analyses (Figure 21). Arsenic and lead were within the top five most-frequently detected trace elements (again ignoring fluoride detections); arsenic was detected in 23 (42.6%) of 54 analyses and lead was detected in 17 (53.1%) of 32 analyses (Figure 21). PMCLs or action levels were not exceeded in any of the 914 analyses.

The fate, transport, and remediation of arsenic in Delaware soil have been evaluated (DNREC, 2005; Sparks et al., 2007). Published data on arsenic in Delaware's groundwater are generally lacking, however, and limited to the surficial aquifer system (see, for e.g., Denver et al., 2004). Sources of arsenic in groundwater on the Delmarva Peninsula include, but are not limited to, poultry manure applied to agricultural fields, pesticides and fertilizers, abandoned tanneries, lumber treated with chromium copper arsenate, and glauconitic sediments deposited in marine environments (Denver et al., 2004; DNREC, 2005). A recent study of arsenic in groundwater in the Coastal-Plain aquifers of Maryland (Drummond and Bolton, 2010) found that arsenic concentrations in excess of the PMCL were primarily limited to the Piney Point and Aquia aquifers. (Note that the Aquia aquifer of Maryland is analogous to the Rancocas aquifer of Delaware; see Table 1.) Arsenic in these aquifers is apparently due to naturally-occurring sources, which may include calcareous shell material and cement, glauconite grains, phosphate pellets, goethite pellets, and iron oxyhydroxide coatings on mineral grains (Drummond and Bolton, 2010).

In this assessment, as previously noted, arsenic was detected in 23 (42.6%) of 54 analyses (Figure 21). Overall, concentrations ranged from nondetectable to 0.0093 mg/L, which is slightly below the PMCL (0.010 mg/L). Aquifer type was established for 46 (85%) of the 54 arsenic analyses. Of these 46 analyses, 15 were associated with unconfined wells, 2 were associated with a semi-confined wells, 28 were associated with confined wells, and one was associated with a fractured-rock well; no data were associated with karst wells. Although arsenic concentrations never exceeded the PMCL, the most-elevated detections were associated with confined wells with depths ranging from ~250 to 500 ft bls (Figure 22). All of these confined wells produce from either the Rancocas, Mt. Laurel, or Piney Point aquifers, which are associated with glauconitic geologic formations (Ramsey, 2005, 2007). These findings are consistent with Drummond and Bolton (2010). Arsenic was detected at very low concentrations in six of the 15 unconfined well samples as well as the single fractured-rock well sample. Arsenic was ND in the two semi-confined well samples.



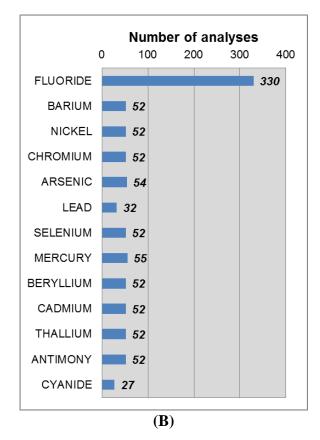


Figure 21. Frequency distributions of trace element (A) detections and (B) analyses. [Bars highlighted yellow indicate one or more concentration above the PMCL or primary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

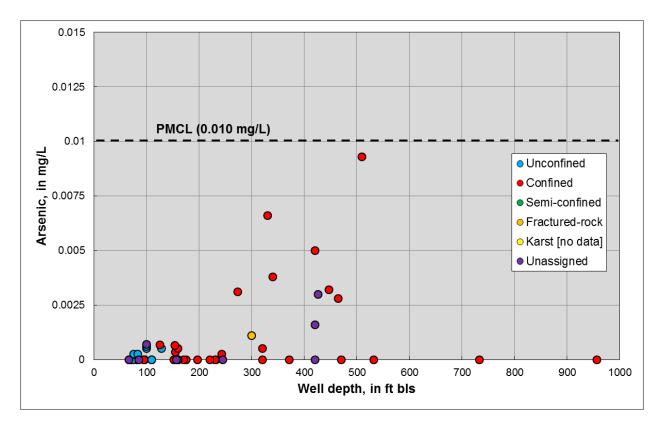


Figure 22. Scatter plot of arsenic versus well depth. [mg/L, milligrams per liter; ft bls, feet below land surface; PMCL, primary maximum contaminant level for public water-supply systems (DHSS, 2005; U.S. EPA, 2012).]

Radionuclides

Radionuclides include the following parameters and their associated PMCLs (DHSS, 2005; U.S. EPA, 2012): beta particle and photon activity (4 millirems per year (mrem/yr)); gross alpha particle activity (15 picocuries per liter (pCi/L)); radium-226 and radium-228 combined (5 pCi/L); and uranium (0.03 mg/L). For radon, there is a proposed PMCL of 300 pCi/L as well as a proposed alternative MCL or AMCL of 4,000 pCi/L (U.S. EPA, 2012). The higher AMCL would apply to multi-media mitigation (MMM) programs that also address radon in indoor air; the lower PMCL would apply if a MMM program is not in place (U.S. EPA, 1999).

For this 305(b) groundwater assessment, radionuclide data are limited to the following parameters: uranium-238, radium-226, radium-228, and gross alpha particle activity. Overall, 333 radionuclide analyses are in the SDWIS query provided to DNREC. Duplicate analyses for individual wells were averaged resulting in 75 radionuclide analyses, which are summarized as follows: uranium-238 (30 analyses), radium-226 (20 analyses), radium-228 (20 analyses), and gross alpha particle activity (5 analyses). Uranium-238 was ND in all of the analyses. Individually, none of the radium-226 or radium-228 activities exceeded the 5 pCi/L PMCL; however, 5 of the 20 radium-226 and radium-228 combined results exceeded the PMCL. Gross alpha particle activity was below the 15 pCi/L PMCL in each of the five analyses.

For more information on radionuclides in Delaware groundwater, the reader is referred to Bachman and Ferrari (1995) and Ferrari (2001). Studies in the Coastal-Plain regions of

Maryland (Bolton, 2000) and New Jersey (Szabo and dePaul, 1998; Szabo et al., 2004; dePaul and Szabo, 2007) also have been conducted.

Summary and conclusions

The Department of Natural Resources and Environmental Control (DNREC) assessed groundwater quality in Delaware based on data collected during 2012-13 from public watersupply wells. The results of this assessment serve as "Part IV: Groundwater Assessment" of Delaware's overall 2014 305(b) report (DNREC, 2014). Water-quality data were obtained from the Department of Health and Social Services (DHSS) Safe Drinking Water Information System (SDWIS). SDWIS queries developed by DHSS staff provide data (40,515 analyses) indicative of raw or apparently raw groundwater quality. Water-quality data were linked with the DNREC's Source Water Assessment and Protection Program (SWAPP) database, which contains public-well records such as DNREC ID, depth, geographic coordinates, geologic formation, aquifer, and aquifer type. Per U.S. EPA (1997) guidance, data were evaluated with respect to hydrogeologic setting where possible and drinking-water standards or criteria where applicable (DHSS, 2005; U.S. EPA, 2012; Love, 1962).

Five aquifer types were recognized in this assessment: unconfined, confined, semiconfined, fractured-rock, and karst aquifers. Unconfined, confined, and semi-confined aquifers occur in the mid-Atlantic Coastal Plain Physiographic Province, which comprises most (~96%) of Delaware's land-surface area. Fractured-rock and karst aquifers occur in the Piedmont Physiographic Province in the northernmost portion of the state. As of October 28, 2013, there were 1,187 active public water-supply wells in Delaware and aquifer type has been established for 978 (82%) of these wells. Most of the wells (77%) produce from Coastal-Plain aquifers while a much smaller percentage of the wells (5%) produce from Piedmont aquifers. General statistics on aquifer type for the 1,187 active wells follow: unconfined wells (424 or 36%), confined wells (443 or 37%), semi-confined wells (52 or 4%), fractured-rock wells (49 or 4%), and karst wells (10 or 1%). Aquifer type is not known or has not yet been established for the remaining 209 or 18% of the wells. (Percentages may not total 100% due to rounding.) Well depths range from 22 to 957 ft below land surface (bls) with a median well depth of 140 ft bls.

Overall, groundwater is predominantly soft or moderately hard based on the hardness scale of Love (1962). Specifically, most of the results (96.4%) meet either of these criteria. With respect to aquifer type, fractions of hardness results classified as soft or moderately hard are summarized as follows: unconfined wells (100%), confined wells (94.7%), semi-confined wells (100%), and fractured-rock wells (66.7%). Although there were no hardness data for karst wells for this assessment, based on previous assessments, this aguifer type had the highest median hardness concentration and the largest fraction of concentrations classified as very hard (Kasper, 2010; Kasper and Strohmeier, 2012). Groundwater is partially acidic overall, with pH values less than the lower limit of the Secondary Maximum Contaminant Level (SMCL) range (6.5 to 8.5 S.U.) in 45.9% of the samples; pH values were within the SMCL range in 53% of the samples. Unconfined and semi-confined wells had the largest fractions of pH values below the SMCL range (85.7 and 66.7%, respectively); in contrast, confined and fractured-rock wells had pH values that were predominantly within the SMCL range (85.9 and 100%, respectively). There were no pH data for karst wells for this assessment; however, based on previous assessments, this aquifer type had the highest median pH concentration and the largest fraction of values within the SMCL range (Kasper, 2010; Kasper and Strohmeier, 2012). Overall, iron exceeded the 0.3 mg/L SMCL in a considerable fraction of the samples (29.7%) and was found

above the SMCL at virtually all depths. Confined, semi-confined, and fractured-rock wells, however, had the largest fractions of concentrations greater than the SMCL (32.2, 43.8 and 66.7%, respectively). Groundwater is generally dilute overall with a median total dissolved solids (TDS) concentration of 170 mg/L. TDS concentrations exceeded the 500 mg/L SMCL in a small fraction (2.1%) of the samples. Although there were no TDS data for karst wells for this assessment, based on previous assessments, this aquifer type had the highest median TDS concentration (Kasper, 2010; Kasper and Strohmeier, 2012). TDS concentrations generally increase with depth, with some exceptions. Chloride concentrations exceeded the SMCL (250 mg/L) in a small fraction (0.7%) of the samples. The most elevated chloride concentrations were associated with unconfined (516 mg/L) and confined (355 mg/L) well samples. Although data were limited, fractured-rock and karst wells had the highest median chloride concentrations (55.9 and 40.3 mg/L, respectively). Sodium concentrations exceeded the 20 mg/L Health Advisory or HA in a considerable fraction of the samples (26%) and at virtually all depths. Confined wells had the highest median sodium concentration (11.6 mg/L) and the largest fraction of concentrations above the HA (38.3%).

Nitrate data were used as a proxy of the extent of human influence on groundwater quality. Overall, nitrate concentrations exceeded the Primary Maximum Contaminant Level (PMCL; 10 mg/L) in 4.3% of the analyses. A large fraction of the wells (42.8%) had nitrate concentrations greater than 0.4 mg/L, a threshold indicative of anthropogenic impacts (Hamilton et al., 1993). Of the aquifer types evaluated, the unconfined and karst aquifers appear to be the most susceptible to human impacts. These aquifers had the highest median nitrate concentrations (4.20 and 2.50 mg/L, respectively) and the largest fractions of concentrations greater than 0.4 mg/L (87.3 and 100%, respectively). The unconfined aquifer also had the most elevated nitrate concentration (21.60 mg/L) and the second largest fraction of concentrations above the 10 mg/L Primary Maximum Contaminant Level or PMCL (8.8%). Nitrate concentrations in the karst aguifer never exceeded the PMCL, however. The semi-confined aguifer had an intermediate median nitrate concentration (1.60 mg/L) with 62.5% of the concentrations greater than 0.4 mg/L; in addition, 2 (12.5%) of the semi-confined samples exceed the PMCL. With only three samples, the fractured-rock aquifer is not well represented in this assessment; the median nitrate concentration was 1.10 mg/L with two-thirds of the concentrations greater than 0.4 mg/L. Confined aquifers had the lowest median nitrate concentration (nondetectable) and the smallest fraction of concentrations greater than 0.4 mg/L (8.6%). Confined aguifers also had the largest fraction of nondetectable nitrate concentrations (91.4%). Regardless of aquifer type, the vertical extent of human influence was primarily limited to depths ~400 ft below land surface (bls) and shallower; at greater depths nitrate was rarely detected above the quantitation limit. Nitrate detections at depths greater than 400 ft bls were associated with fractured-rock wells with extremely long open intervals, which may allow nitrate to enter the wells at shallower depths. Areally, PMCL exceedences were primarily limited to Sussex County with the exception of one exceedance in southern Kent County.

Organic compounds (OCs) were not frequently detected and, when detected, rarely exceeded PMCLs. Specifically, OCs were not detected in 2,659 (94.4%) of 2,816 analyses. Of the 157 OC detections, more than three-quarters (120 or 76.4%) were found at concentrations less than 1 μ g/L. Chloroform, a disinfection byproduct, was one of the most-frequently detected OCs. PMCLs were exceeded in a very small fraction (9 or 0.3%) of the 2,816 analyses. The following analytes were found above the PMCL: tetrachloroethylene (PCE; 7 exceedences) and methyl tert-butyl ether (MTBE; 2 exceedences). PMCL exceedences that could be linked by

aquifer type were associated with confined wells in the Potomac aquifer system, unconfined wells, and karst wells. MTBE, PCE, and trichloroethylene (TCE) were among the top-ten most-frequently detected OCs. For unconfined, semi-confined, and confined wells, concentrations of MTBE, TCE, and PCE with respect to sample depth indicate that the vertical extent of human impact is limited to depths of 215 ft bls and shallower; at greater depths these contaminants were not detected. For fractured-rock and karst wells, these OCs were detected at greater depths; however, wells in these aquifer types typically have very long open intervals and, therefore, these contaminants may enter the wells at shallower depths. As previously noted, similar trends in nitrate with respect to sample depth were identified. Many of the OC results are in agreement with Ferrari (2001), Reyes (2010), and previous 305(b) groundwater-quality assessments (Kasper, 2008, 2010; Kasper and Strohmeier, 2012).

Similar to OCs, trace elements were not frequently detected. Specifically, trace elements were not detected in 602 (66%) of 914 analyses. Of the 312 trace-element detections, 180 (58%) were found at concentrations less than 0.1 mg/L and 305 (98%) were found at concentrations less than 1 mg/L. Barium, nickel, and chromium were the top three most-frequently detected trace elements. PMCLs or action levels were not exceeded in any of the 914 analyses. Arsenic was one of the top five most frequently detected trace elements. The most elevated arsenic detections were primarily limited to confined wells with depths ranging from ~250 to 500 ft bls. All of these confined wells produce from either the Rancocas, Mt. Laurel, or Piney Point aquifers, which are associated with glauconitic geologic formations (Ramsey, 2005, 2007). This finding is consistent with Drummond and Bolton (2010) and previous 305(b) groundwater-quality assessments (Kasper, 2008, 2010; Kasper and Strohmeier, 2012).

Radionuclide data were very limited in this assessment and available data were limited to the following parameters: uranium-238, radium-226, radium-228, and gross alpha particle activity. Uranium-238 was ND in all of the analyses (n = 30). Five of the 20 radium-226 and radium-228 combined results exceeded the 5 pCi/L PMCL. Gross alpha particle activity was below the 15 pCi/L PMCL in each of the five analyses.

This 305(b) groundwater-quality assessment is DNREC's fourth attempt to report raw or apparently raw groundwater data with respect to hydrogeologic setting on a statewide basis. The results of this assessment represent a subset of the total number of active public water-supply wells in Delaware and, therefore, should be viewed in that context. Provided that water-quality data in SDWIS continue to be identified by DNREC ID, future 305(b) groundwater-quality assessments should provide a more complete picture of groundwater quality in Delaware.

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