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WATER QUALITY AND TEMPORAL VARIATIONS IN CHLORIDE CONCENTRATIONS IN GROUNDWATER IN THE MARYLAND PIEDMONT

by

Tiffany J. VanDerwerker

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Abbreviations appearing in this report

commun.	Communication
CBE	Charge Balance Error
Cl:Br	Chloride to Bromide ratio
COMAR	Maryland Code of Regulations
DO	Dissolved Oxygen
DNR	Department of Natural Resources
GAPA	Gross alpha-particle activity
GBPA	Gross beta-particle activity
MDE	Maryland Department of the Environment
MDH	Maryland Department of Health
MGS	Maryland Geological Survey
NWIS	National Water Information System
NWQL	USGS National Water Quality Laboratory
QAQC	Quality Assurance and Quality Control
RL	Reporting Level
RPD	Relative Percent Difference
TDS	Total Dissolved Solids
USGS	United States Geological Survey

mg/L	milligrams per liter
pCi/L	picocuries per liter
ft	feet
µ	micron
µg/L	microgram per liter
µS/cm	microsiemens per centimeter at 25 degrees Celsius
<	less than
>	greater than

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KEY RESULTS

From the early 1970s to the early 2000s the Maryland Geological Survey and the U.S. Geological Survey sampled many wells in the Maryland Piedmont region, testing the water samples for chloride, major ions, and other constituents. These data provide a valuable baseline against which future water-quality samples can be compared to monitor changes in groundwater chemistry. With expanded urbanization of rural areas of the Maryland Piedmont, including increased road-traffic volumes, there is an elevated risk of chloride contamination from road salt and other anthropogenic sources. The purpose of this study is to: (1) assess overall groundwater quality of the Maryland Piedmont; (2) identify sources, concentrations, and temporal variations in chloride concentrations; and (3) determine if elevated concentrations of other chemical constituents (i.e. trace metals and radionuclides) correlate with elevated chloride concentrations.

The groundwater quality of the Maryland Piedmont was evaluated by collecting samples from 25 wells and analyzing for major ions, trace metals, nutrients, radionuclides, and bromide. Wells sampled in the study are on average 177 feet deep with an average casing depth of 37 feet, and completed in 16 different geological formations, including igneous, metamorphic, and sedimentary rock types. Key results from this study are:

- Groundwater is acidic (median pH = 6.1), oxidized (median dissolved oxygen = 5.9 milligrams per liter), moderately hard (median hardness = 77.1 milligrams per liter), with a median alkalinity of 47 milligrams per liter, median total dissolved solids of 195 mg/L, and median specific conductance of 346 microsiemens per centimeter at 25°C.

- Twelve of the 25 wells sampled had low chloride concentrations (less than ~18 milligrams per liter). Using the chloride to bromide ratio, two of the 25 wells with elevated chloride concentrations (above ~18 mg/L) are likely affected by agricultural activities, 10 of the 25 wells by road-deicing salts, and one by septic effluent.

- The maximum chloride concentration analyzed was 571 milligrams per liter in well CE Bc 56, located approximately 100 feet from Interstate-95. Median chloride concentration for wells sampled was 62 milligrams per liter; average chloride concentration was 114 milligrams per liter. Chloride concentrations in five wells exceeded the U.S. Environmental Protection Agency's Secondary Maximum Contaminant Level of 250 milligrams per liter in drinking water.

- Chloride concentrations have increased by at least 25 percent in 15 of the 25 wells sampled since the initial chloride analyses.

- Groundwater chemistry data collected during this study indicates moderate correlations between chloride and strontium ($R^2 = 0.51$) and nickel ($R^2 = 0.54$). Temporal variations of strontium, lithium, barium, and nickel concentrations in wells MO Dg 34 and MO De 50 generally correspond to changes in chloride concentrations.

- Continuous specific conductance measurements were collected in a monitoring well in Layhill Local Park in Montgomery County since December 2018. Specific conductance ranged from a high of approximately 1,550 microsiemens per centimeter in the winter to less than 1,000 microsiemens per centimeter in the spring. After road-deicing salt applications have ceased for the season, conductivity decreased and stabilized.

INTRODUCTION

The use of road-deicing salts has been shown to adversely affect groundwater and potentially contribute elevated chloride concentrations to streams via baseflow in the Piedmont of Maryland (Cooper, and others, 2014; Morgan and others, 2012). Chloride concentrations have been increasing in Maryland streams for several decades, including those feeding into Liberty Reservoir (a water source for Baltimore City) (Kaushal and others, 2005; Kaushal and others, 2018).

In the Maryland Piedmont, the unconfined aquifer is the primary drinking-water source for the population not served by public-supplied surface water. These aquifers are susceptible to surface contamination because of their relatively shallow depth and often direct hydraulic connection to the surface. Baltimore County has had an increasing number of complaints regarding high-chloride groundwater (K. Koepenick, written commun., Baltimore County Department of Environmental Protection and Sustainability, 2015; Ensor, 2016). Chloride concentrations in groundwater in Baltimore County decrease with increasing distance from paved roads, suggesting road-deicing salts as the source (Bolton, 1998). Chloride is difficult and costly to remove from water, often requiring reverse osmosis filtration. High-chloride water can damage plumbing fixtures, appliances, and pipes. Since chloride is chemically conservative, it moves easily through surface and groundwater environments. Additionally, increased chloride concentrations can potentially mobilize trace metals and radionuclides in groundwater.

From the early 1970s to the early 2000s, the Maryland Geological Survey (MGS) and U.S. Geological Survey (USGS) sampled many wells in the Maryland Piedmont, testing the water samples for chloride, major ions, and other constituents. These data provide a valuable baseline against which future water-quality samples can be compared to monitor changes in groundwater chemistry. Because of land use changes in the rural areas of the Maryland Piedmont, there is an increased risk of rising chloride concentrations in this region.

PURPOSE AND SCOPE

The purpose of this study is to: (1) assess overall groundwater quality of the Maryland Piedmont; (2) identify sources, concentrations, and temporal variations in chloride concentrations; and (3) determine if elevated concentrations of other chemical constituents (i.e. trace metals and radionuclides) correlate with elevated chloride concentrations. The study was limited to samples collected and analyzed in 25 wells and evenly distributed throughout the Maryland Piedmont, and to the available chemical data stored in the USGS's National Water Information System (NWIS).

LOCATION OF STUDY AREA

The Piedmont Physiographic Province is located in central Maryland and consists of portions of Baltimore, Carroll, Cecil, Frederick, Harford, Howard, and Montgomery Counties, as well as Baltimore City (fig. 1). Land use in the Maryland Piedmont is approximately 35 percent forested, 37 percent agricultural, 27 percent residential/commercial, and 1 percent water (Homer and others, 2015). Elevation ranges from sea level to approximately 1,120 feet (ft) above sea level (Fact Sheet 1, Maryland Geological Survey, 2005).

Water supply in the region is provided by a combination of community and public systems tapping either surface or groundwater, and individual private wells. Groundwater supplies up to 20 percent of potable drinking water in Montgomery, Howard, and Baltimore Counties, 40 to 60 percent in Frederick and Harford Counties, and 61 to 80 percent in Cecil and Carroll Counties (S. Kasraei, Maryland Department of the Environment, Water Supply, written communication, 2019). Public water supply in Baltimore City is solely from surface water.

GEOLOGICAL SETTING

The Piedmont region is underlain by precambrian and early Paleozoic rocks, including gabbro, granite, gneiss, schist, marble, and limestone (Bennett and Meyer, 1952; Dingman and Meyer, 1954; Meyer, 1958). Also present are Jurassic intrusive rocks throughout the region, and Triassic sedimentary rocks of the Culpeper Basin in parts of Montgomery, Frederick, and Carroll Counties.

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METHODS

WELL SELECTION

All historical chloride data from groundwater wells was obtained from the USGS's NWIS database. Site-specific information, including well permit numbers and well-construction data, were also retrieved. Locations of wells with historical chloride data were mapped in ArcGIS to examine spatial distribution. Twenty-five of these wells were selected based on the following criteria: (1) low chloride (less than [<] 50 milligrams per liter [mg/L]) and little expected change (generally in more rural areas, away from major roads); (2) low chloride (<50 mg/L) with expected change (close proximity to major roads); and (3) high chloride (greater than [>] 50 mg/L) with expected change (close proximity to major roads) (fig. 2).

Wells with multiple samples over time were preferred over those with only one sample. A representative spatial distribution was also sought throughout the Piedmont region with at least two wells in each Piedmont county. Exact locations of the wells were determined and permissions to sample were acquired from the property owners. Well-construction information was obtained from well-completion reports, including well depth, casing depth, and casing diameter (tab. 1). The average depth of well is 177 ft deep with an average casing depth of 37 ft. The wells are completed in 16 different geological formations including igneous, metamorphic, and sedimentary rock types.

DATA COLLECTION AND ANALYSIS

Twenty-five wells were sampled for major ions, trace metals, nutrients, radionuclides, and bromide. Groundwater samples were collected and sent to the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado for analysis. However, from December 22, 2018 to January 25, 2019 the federal government was partially shutdown. This shutdown included the USGS NWQL. In order to remain on schedule for sample collection, water samples were analyzed by the MDH Lab for holding times less than seven days, and Enviro-Chem Laboratories for samples with holding times greater than seven days but less than 28 days. Adequate quality assurance and quality control (QAQC) measures were implemented to ensure all samples were of acceptable data quality (app. A).

Water treatment (neutralizers, water softeners, etc.) is common in domestic wells throughout the Piedmont and in order to collect untreated water, samples were taken from the pressure tank when site conditions allowed, or the treatment system was bypassed and samples were collected from an outside spigot. Prior to sample collection, the well was purged to remove water stored in the casing or pressure tank. Water was purged at an approximate rate of 2 to 4 gallons per minute for at least 20 minutes. Purge water flowed into a bucket, where pH, specific conductance, dissolved oxygen (DO), and temperature were monitored. Readings were taken at 5-minute intervals until the following stabilization criteria were met: pH, ±0.05 pH units; specific conductance, ±5 percent (if specific conductance was greater than 100 microsiemens per centimeter [µS/cm]) or ±5 µS/ cm (if specific conductance was less than 100 µS/ cm); and temperature, ±0.5 °C. After stabilization criteria were met, samples were collected. Unfiltered samples were collected first and were collected directly from the spigot.

For monitoring wells MO Dg 34, MO De 50, and HA Ca 23, water was purged using a submersible pump that was brought onsite by MGS. The pump was decontaminated prior to sampling using methods detailed in the National Field Manual for the Collection of Water-Quality Data (Wilde, 2004). The wells were purged to stability using the same methodology described above.

Three of the 25 wells (CE Bc 56, CL Cd 181, and HO Ab 3) were sampled quarterly (April 2019 and July 2019) for major ions and bromide. Monitoring well MO Dg 34 was monitored for continuous specific conductance using an In-Situ Aqua Troll 200[1] conductivity probe. This well was selected due to the numerous chloride samples collected over time and an observed spike in chloride concentrations in 2015. Continuous conductivity monitoring began in December 2018 and is ongoing.

Well construction records for the sampled wells were compiled (tab. 1). All wells are open-hole with 6-inch casing. Total depth for wells ranged from 23 to 360 ft below land surface (bls). Casing depth for wells ranged from 7 to 109 ft bls. Four wells had plastic casing, 20 wells had steel casing, and one well was buried and no casing material was identified on the completion report.

Using QAQC procedures (app. A), the data were generally determined to be of good quality. Data quality were examined using two metrics: charge balance errors (CBEs) and duplicate samples. CBEs can indicate overall accuracy of major ion analyses. Water is assumed to be charge neutral, where the milliequivalent sum of the cations is equal to the milliequivalent sum of the anions. Eighty-eight percent of samples had CBEs less than ±5 percent, indicating high accuracy and completeness (app. A). Wells FR Fd 92, HA Ca 23, and CE Aa 23 had CBEs greater than 5 percent, but less than 12 percent. The discrepancy in CBE may be derived from laboratory or field activities.

Two duplicate samples were collected in this study and submitted to the NWQL where the relative percent difference (RPD) for all constituents was less than 20 percent, indicating good reproducibility (tab. 2); however, short-term gross beta-particle activity (GBPA), long-term gross alpha-particle activity (GAPA), long-term GBPA and total iron had greater RPD in duplicate pairs. The National Functional Guidelines for Inorganic Superfund Methods Data Review (2017) provides a detailed methodology for qualifying data from duplicate samples, which was implemented in this study. Duplicate samples were determined to be chemically similar to the sample group and, therefore, samples analyzed by the NWQL for short-term and long-term GBPA, long-term GAPA, and total iron analyses were qualified as estimated ("J" for results greater than the quantitation limit and "UJ" for results less than the quantitation limit).

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[1] The use of company names, tradenames, or product names in the report is for identification purposes only, and does not constitute endorsement by the Maryland Geological Survey.

OVERALL GROUNDWATER QUALITY

Groundwater quality in the Maryland Piedmont based on the 25 wells sampled for this study was determined to be acidic (median pH = 6.1), oxidized (median DO = 5.9 mg/L), moderately hard (median hardness = 77.1 mg/L), with a median alkalinity of 47 mg/L, median total dissolved solids (TDS) of 195 mg/L, and median specific conductance of 346 µS/cm at 25°C (tab. 3). Water-chemistry data were classified using a Piper diagram, which is a trilinear diagram that is a graphical representation of water chemistry with the sum of certain cations and anions represented (fig. 3). Samples tended to be calcium-chloride or calcium-magnesium-bicarbonate water types. Wells sampled in the study are on average 177 ft deep with an average casing depth of 37 ft, and completed in 16 different geological formations (tab. 1).

Samples were compared to relevant primary, secondary, and proposed U.S. Environmental Protection Agency drinking water standards (U.S. Environmental Protection Agency, 2016a). Seventeen wells exceeded the secondary drinking water standard for pH (out of acceptable range 6.5-8.5); four wells exceeded the secondary drinking water standard for TDS (500 mg/L); 12 wells exceeded the health advisory for sodium (20 mg/L); five wells exceeded the secondary drinking water standard for chloride (250 mg/L); one well (filtered) and four wells (unfiltered) exceeded the secondary drinking water standard for iron (300 µg/L); two wells (filtered) and three wells (unfiltered) exceeded the secondary drinking water standard for manganese (50 µg/L); two wells exceeded the primary drinking water standard for nitrate/nitrite, as N (10 mg/L) and; two wells exceeded the proposed drinking water standard for radon (4,000 pCi/L). All samples were below the primary drinking water standard for gross alpha particle activity (GAPA) of 15 pCi/L; however, one well (MO Cc 31) had a short-term GAPA just below the limit at 14.2 pCi/L.

CHLORIDE

SOURCES

Potential sources of chloride in groundwater in the Maryland Piedmont include road-deicing salts, agriculture (fertilizers, animal waste, etc.), and septic and water-softener effluent (discharged to septic systems or released to the ground). Halite and other evaporite minerals are not present in the Maryland Piedmont, nor are there deep confined aquifers that might contain connate seawater. These wells are also far enough inland that saltwater intrusion is not a source of elevated chlorides in groundwater. The ratio of chloride to bromide (Cl:Br) was used to help distinguish the source of chlorides for samples with elevated chloride concentrations (fig. 4; tab. 4). Cl:Br ratios from 1,000 to 10,000 may indicate road salt contamination (Davis and others, 1998). However, Cl:Br ratios can be as high as 58,621 in first flushing events from winter storms (Granato, 1996). Ratios from 300 to 600 may indicate septic effluent (Davis and others, 1998). Water-softener effluent, consisting of brine used to recharge ion exchange media, may have a Cl:Br ratio similar to road-deicing salt (Panno and others, 2006), thus making it difficult to distinguish from road-deicing salt. Panno and others (2006) determined that plotting the Cl:Br ratio against nitrate provided a means to distinguish samples affected by septic effluent from those affected by road-deicing salts. Mean Cl:Br ratio for water affected by agrichemicals has been reported to be approximately 845 (Panno and others, 2006). By contrast, shallow groundwater unaffected by anthropogenic contamination have Cl:Br ratios generally less than 200 (Davis and others, 1998).

Road salt

Of the 25 wells sampled, 10 had elevated chloride likely from road-deicing salts (Cl:Br ratios from 1,579 to 15,261) (fig. 4). Chloride concentrations in these wells ranged from 61.8 to 571 mg/L. For those wells, a weak logarithmic correlation ($R^2 = 0.23$) was observed between chloride concentrations and distance to nearest paved (salted) road. Chloride concentrations generally decreased with increasing distance to the nearest paved road (fig. 5). Wells likely impacted by road-deicing salts were all within 250 ft from a paved road (tab. 4). This correlation is consistent with other studies that determined that chloride concentrations are generally higher near roads (Bolton, 1998; Pieper and others, 2018; Kelly and others, 2018). It is possible that these wells may also be impacted by septic effluent, but due to topography and site conditions, it is not likely.

Agricultural

Potassium chloride is often applied as fertilizer for crops (Zörb and others, 2014), where potassium chloride application can increase chloride concentrations in groundwater (Panno and others, 2006). However, it is possible that chloride could also be sourced from application of manure as fertilizer. Two wells had elevated chloride likely from agricultural operations. Well BA Bc 267 had a chloride concentration of 175 mg/L and a Cl:Br ratio of 875. The well (a supply well for a farmhouse) is located in a rural setting in close proximity to row crop fields and within several hundred feet of a livestock pen (Bolton, 1998). While there is a septic field on site, there was no water-softener in operation. Well Ba De 637 had a chloride concentration of 81.8 mg/L and a Cl:Br ratio of 818. The well is located downgradient from an agricultural field and upgradient (approximately 20 ft higher) from onsite septic field, where there was a water-softener system onsite.

Septic effluent

One well (CL Be 120) sampled in this study had an elevated chloride concentration of 67 mg/L that was likely from septic effluent, including water softener effluent. By plotting the Cl:Br ratio with nitrate, well CL Be 120 was separated from other samples as it had the highest nitrogen concentrations (15.1 mg/L) of all wells sampled in this study (fig. 7). Boron can also be used as an indicator for septic effluent as it is often found in laundry detergents (Katz and others, 2011). Most wells had boron below the detection limit. Well CL Be 120 had a boron concentration of 11 µg/L. Landon and others (2008) found that boron concentrations greater than 50 µg/L in shallow unconfined aquifers were associated with upgradient septic tank systems. The highest boron concentration was observed at well CL Cd 181 (41 µg/L), but this well is likely impacted from road-deicing salts and not septic effluent based on distance to cul-de-sac and topography of site. The Maryland Code of Regulations (COMAR) 26.04.04, states that groundwater wells must be sited at least 10 ft from property lines, 15 ft from a road or right-of-way, 30 ft from a building foundation, and 100 ft from identifiable sources of contamination and subsurface sewage disposal areas in unconfined aquifers (Code of Maryland Regulations, 2015). Therefore, to the extent that criteria is met in the field, any impacts to wells from septic effluent would likely originate from an upgradient neighboring property.

CONCENTRATIONS AND TEMPORAL VARIATIONS

Chloride concentrations ranged from 0.5 to 571 mg/L in the 25 wells sampled (fig. 7). The maximum chloride concentration was in well CE Bc 56, located approximately 100 ft from Interstate-95. The median chloride concentration was 62 mg/L and average chloride concentration was 114 mg/L. When compared to previously collected chloride data, 68 percent of all wells saw an increase in chloride (tab. 5). Fifteen of the 25 wells saw at least a 25-percent increase in chloride concentrations, while nine samples had a reduction in chloride concentration.

RELATION OF OTHER CHEMICAL CONSTITUENTS TO ELEVATED CHLORIDE CONCENTRATIONS

TRACE METALS

Granato and others (1995) evaluated trace metal concentrations in groundwater using wells located both upgradient and downgradient from a highway. They determined that strontium and barium were observed at higher concentrations in downgradient wells and were highest when chloride concentrations were highest, suggesting that mobilization may be caused by road salt migration. In this study, moderate correlations were observed between chloride and the alkaline earth metal, strontium, and chloride and the transition metal, nickel.

Strontium

Strontium is a naturally-occurring trace metal found in various rock types, such as limestones (Skougstad and Horr, 1963). High doses of strontium can induce decreased resorption and reduce bone density (Cabrera and others, 1999). The USEPA, after making a preliminary decision to regulate strontium, has decided to delay implementing a final drinking water standard (U.S. Environmental Protection Agency, 2016b). The current health advisory for strontium in drinking water is 1.5 mg/L (U.S. Environmental Protection Agency, 2018). Groundwater chemistry data collected during this study indicated moderate correlations between chloride and strontium (R^2 = 0.51, fig. 8A). Temporal variations of strontium concentrations in wells MO Dg 34 and MO De 50 generally corresponded to changes in chloride concentrations (figs. 9A and 10A). Generally, strontium concentrations were higher in wells likely impacted by road salt (fig. 8A).

Lithium

Lithium is a naturally-occurring trace metal found in a variety of rock types including clays, as well as in salt lakes and brine reservoirs (Mohr and others, 2012). Temporal variations of lithium concentrations in wells MO Dg 34 and MO De 50 generally corresponded to changes in chloride concentrations (figs. 9B and 10B). However, lithium and chloride showed no correlation for wells sampled in this study (R^2 = 0.06, fig. 8B).

Barium

Barium is a naturally-occurring trace metal found in granitic rocks, occurring as a trace or minor element in potassium feldspar and mica (Johnson and others, 2017). Temporal variations of barium concentrations in wells MO Dg 34 and MO De 50, generally corresponded to changes in chloride concentrations (figs. 9C and 10C). However, for wells sampled in this study, chloride and barium only showed a weak correlation (R^2 = 0.11, fig. 8C).

Nickel

Nickel is a naturally-occurring trace metal and has been observed as a contaminant derived from highway runoff (Turer and others, 2001). Increases in nickel were reported in groundwater and soil samples associated with a runoff from a major highway (Earon and others, 2012). Nickel concentrations increased in well MO Dg 34 (fig. 9D) after the construction of the Intercounty Connector (MD-200) and generally coincided with changes in chloride concentrations. An increase in nickel concentrations in conjunction with an increase in chloride concentrations was also observed in well MO De 50 (fig. 10D). Nickel and chloride showed a moderate correlation for wells sampled in this study ($R^2 = 0.54$, fig. 8D).

RADIONUCLIDES

Associations between radionuclides radium and radon have been observed with road-deicing salt in groundwater (McNaboe and others, 2017). Radionuclides are found as trace elements in many rocks and soils as part of the uranium-238 and thorium-232 decay series (Zapecza and Szabo, 1986). Decay occurs by the emission of an alpha particle or a beta particle. These decay products, quantified in groundwater as gross alpha particle-activity (GAPA) and gross beta particle-activity (GBPA), can be used to determine the presence of individual radionuclides, most commonly radium-224 and radium-226 (alpha-particle emitters), and radium-228 (beta-particle emitter) (Senior, 2014). In the 25 wells sampled in this study, GAPA (short-term and long-term) concentrations were below the maximum contaminant level of 15 pCi/L, with the exception of one well (BA Ea 90) that had a GAPA concentration of 22 pCi/L, suggesting the presence of radium-224 that has a relatively short half-life of 3.64 days. GAPA (short-term and long-term) was not correlated with elevated chloride concentrations in the 25 wells sampled. Short-term GBPA was moderately associated with chloride ($R^2 = 0.30$) (fig. 11).

Radon-222 is a colorless, odorless radioactive gas that is formed in the uranium-238 decay series. Radon concentrations in groundwater are dependent upon rock type. Crystalline rocks, such as granites and certain high-grade metamorphic rocks, generally have the highest radon concentrations, and low-grade metamorphic rocks and sedimentary deposits generally have the lowest radon concentrations (King and others, 1982; Hall and others, 1987; Loomis, 1987). Radon concentrations in the 25 wells tested in this study ranged from <20 to 13,120 pCi/L. Two wells (BA Ea 90 and HO Cd 206) exceeded the U.S. Environmental Agency proposed limit in drinking water from community water supplies of 4,000 pCi/L. There was no observed correlation between radon and elevated chloride in the wells tested in the study.

CONTINUOUS SPECIFIC CONDUCTANCE MONITORING

Conductivity can be used as a surrogate for chloride concentration in groundwater since the relation between the two is essentially linear (Hem, 1989). Continuous specific conductance measurements were made in well MO Dg 34 located in Layhill Local Park, Montgomery County, starting in December 2018 (fig. 12). The conductivity probe was tested against various ranges of conductivity standards every other month to ensure instrument drift was not occurring. Measurement error was less than three percent for every standard. Conductivity in the well ranged from a high of approximately 1,550 µS/cm in the winter to less than 1,000 µS/cm in the spring. Two rapid decreases in specific conductance can be observed in Figure 12. The late December 2018 decrease may have been caused by extensive rainfall which flushed chloride further downgradient of the well. The decrease in specific conductance in February 2019 was likely caused by sampling activities, where the well was purged dry to collect a water sample. After road-deicing salt applications have ceased for the season, specific conductance decreased and stabilized. This well is located downgradient from a storm-water management area (infiltration basin and dry detention pond). Snodgrass and others (2017) found that routing runoff contaminated with road salts to storm water ponds resulted in plumes of highly contaminated groundwater moving from ponds to streams. Chloride concentrations from samples collected between 2003 and 2011 in MO Dg 34 were relatively low (29 to 60 mg/L). However, in 2015, chloride concentrations increased to 736 mg/L, likely caused by the construction of the Intercounty Connector (MD-200) in late 2011. Chloride concentrations decreased to 273 mg/L during the last sampling event (February 2019).

QUARTERLY SAMPLING

Three wells (HO Ab 103, CE Bc 56, and CL Cd 181) were sampled quarterly in April and July of 2019 for major ions and bromide (tab. 6) in addition to the initial sampling in January 2019. Chloride concentrations and specific conductance decreased slightly in wells CE Bc 56 and CL Cd 181, likely resulting from aquifer flushing after road deicing applications have ceased. Well HO Ab 103 had consistent chloride concentrations over the two sampling events (~65 mg/L). Laboratory results from the July sampling event were not available at the time of this report and therefore no conclusions can be made regarding seasonal changes in major ion and bromide concentrations.

SUMMARY

Samples were collected from 25 wells throughout the Maryland Piedmont and analyzed for major ions, trace metals, nutrients, radionuclides, and bromide. Groundwater quality in the Maryland Piedmont was determined to be acidic (median pH = 6.1), oxidized (median dissolved oxygen = 5.9 milligrams per liter), moderately hard (median hardness = 77.1 milligrams per liter), with a median alkalinity of 47 milligrams per liter, median total dissolved solids of 195 milligrams per liter, and median specific conductance of 346 microsiemens per centimeter at 25°C. Twelve of the 25 wells had low chloride concentrations (less than 20 milligrams per liter). Using the chloride to bromide ratio, elevated chloride concentrations (above ~18 milligrams per liter) in two of the 25 wells are likely from agricultural activities, 10 of the 25 wells from road-deicing salts, and one from septic effluent. The maximum chloride concentration analyzed was 571 milligrams per liter in well CE Bc 56, located approximately 100 feet from Interstate-95. Five wells exceeded the secondary drinking water standards for chloride (250 milligrams per liter). Chloride concentrations have increased by at least 25 percent in 15 wells since initial chloride analysis. Median chloride concentration for wells sampled was 62 milligrams per liter; average chloride concentration was 114 milligrams per liter. Groundwater chemistry data collected during this study indicates moderate correlations between chloride and strontium ($R^2 = 0.51$) and nickel ($R^2 = 0.54$). Temporal variations of strontium, lithium, barium, and nickel concentrations in wells MO Dg 34 and MO De 50 generally correspond to changes in chloride concentrations. Continuous specific conductance measurements were collected in a monitoring well in Layhill Local Park in Montgomery County since December 2018. Specific conductance ranged from a high of approximately 1,550 microsiemens per centimeter in the winter to less than 1,000 microsiemens per centimeter in the spring. After road-deicing salt applications have ceased for the season, conductivity decreased and stabilized. Quarterly sampling of three wells was completed in April and July 2019 for major ions and bromide. Chloride concentrations decreased slightly in two wells and remain constant in one well over the approximate three month period.

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Appendix A. Quality Assurance and Quality Control Procedures

Laboratory Analysis

Samples were sent to the USGS NWQL in Denver, Colorado, with the exception of a few samples – see below. The NWQL develops and revises a wide variety of standard operating practices to assure consistency and comparability in results over time. The use of comprehensive internal and external QA/QC processes to monitor method and analyst performance insures that NWQL meets its commitment to publish high quality data of known and documented quality. The following wells had samples sent to the MDH lab and were analyzed for TDS, GAPA (short-term), GBPA (short term), and radon:

CE Aa 23, CE Bc 56, CE Ad, 67, HA Cd 168, HA Bc 33, HA Ab 12, BA De 637, BA Bc 267, CL Ag 6.

Additionally, in the aforementioned samples, the following constituents were analyzed by Enviro-Chem Laboratories in Sparks, Maryland: sulfate, nitrogen, ammonia, fluoride, chloride, bromide, and phosphorus. Sample containers were obtained from the MDH lab, Baltimore County Health Department, and containers from previous MGS projects. Nitric acid was obtained from USGS and was used to preserve all necessary samples sent to all labs.

Sampling Procedures

To provide the most reliable data, all water samples were collected in a similar manner. Steps for sample collection include calibration of field equipment, well purging, monitoring of field parameters, sample collection, sample treatment, sample storage, and sample transport to the laboratories.

The Thermo Scientific Orion Star (multi-meter) was calibrated for DO, pH, and specific conductance in accordance with the manufacturer's instructions. The multi-meter was calibrated using solutions supplied by a commercial laboratory supply company that generally bracketed the expected values of the well water.

After calibration of field equipment, wells were purged until field parameter stabilization indicating that fresh groundwater was being accessed. The purge hose was attached to one outlet of a Y-adaptor attached to the spigot at the base of the pressure tank. If the spigot was not accessible, another sampling point will be chosen that is as close to the pressure tank as possible. Water was purged at an approximate rate of 2 gallons per minute. Purge water flowed into a bucket, where pH, specific conductance, DO, and temperature were monitored. Readings were taken at 5 minute intervals until the following stabilization criteria was met: pH, ±0.05 pH units; specific conductance, ±5% (if specific conductance was greater than 100 μS/cm) or ±5 μS/cm (if specific conductance was less than 100 μS/cm); and temperature, ±0.5 °C. If all stabilization criteria were not met, a decision was made as to whether to proceed with sampling.

After stabilization criteria have been met, samples were collected. All workers onsite wore the appropriate personal protective equipment including disposable nitrile gloves and eye protection. Unfiltered samples were collected first and were collected directly from the spigot. Filtered samples were collected through a 0.45 μ disposable capsule filter and peristaltic pump. The filter was rinsed with deionized water first, followed by a rinse of the sample water, where samples were collected. After all samples were collected, alkalinity was titrated. Alkalinity was determined by digital titration with sulfuric acid. All field measurements were recorded in a field notebook.

Equipment Cleaning Procedures

All sample equipment was cleaned at the site while equipment was still wet. Equipment cleaned includes, hardware connected to the sampling spigot, tubing connected to pressure tank, and other equipment that comes in contact with the sample water. Unless the turbidity of a sample was elevated, the tubing was rinsed with a 10% HCl solution and followed by a rinse of deionized water. Fittings were rinsed in deionized water.

Sample Transport

MGS sent all samples to the USGS NWQL (and other labs as stated in Methods section) via FedEx and preserved as needed. All samples requiring preservation were acidified before transport and samples requiring ice for transport were packed in order to achieve temperatures below 4°C (US Environmental Protection Agency, 2015). Samples not sent to the USGS NWQL were transported and hand delivered by MGS personnel to Enviro-Chem and MDH laboratories.

Quality Assurance Objectives

Qualitative quality assurance objectives for this study include assuring representativeness and completeness of the data. The data are meant to be representative of groundwater in the Piedmont Physiographic Province of Maryland.

<u>Representativeness -</u> Wells were selected using the following criteria: (1) wells in which previous chloride concentrations were low (<50 mg/L) and change in chloride is expected to be minimal; (2) wells in which previous chloride concentrations were low and change in chloride is likely to have occurred; and (3) wells in which previous chloride concentrations were elevated (>50 mg/L).

<u>Comparability -</u> All samples were collected in a similar manner, as noted in previous sections. All samples were collected by MGS staff.

Analytical Procedures and Calibration

Samples were analyzed by the USGS (with the exception of several samples – see Methods section) in accordance to documented methodology.

Quality Assurance Samples

Quality assurance samples, consisting of blank and duplicate samples, were collected along with any environmental samples as requested by USGS. Two duplicate samples were collected. See below for a description of QA Samples:

<u>Field blank</u> – A sample of pure water poured into a sample container in the field, preserved and shipped to the laboratory with other samples. Filtered samples were filtered before collecting sample. The purpose of the field blank is to assess any contamination from field conditions that may have occurred during sampling.

<u>Duplicates</u> – Duplicate samples are field samples obtained from a single location and divided into separate containers. They are treated as unique samples (and labeled as such) throughout the remaining sample handling and analytical processes. These samples will be used to assess the precision associated with analytical procedures.

Data reduction, Validation and Reporting

Data were evaluated using the following criteria:

<u>Blanks</u> – If less than the Reporting Level (RL), then blank samples are not contaminated. If blank samples have concentrations 5 times greater than the RL, the sample has been contaminated.

<u>Duplicates</u> – The RDP between the duplicate and original sample must be ≤20%.

Calculation of RPD:

$$\text{RPD} = \frac{(C_1 - C_2) \times 100}{(C_1 + C_2)/2}$$

RPD = relative percent difference

C_1 = larger of two observed values

C_2 = smaller of two observed values

Two duplicate samples were collected in this study and submitted to the NWQL where the RPD for all constituents was less than 20 percent, indicating good reproducibility. In exception, short-term GBPA, long-term GAPA, long-term GBPA and total iron had greater RPD in duplicate pairs. The National Functional Guidelines for Inorganic Superfund Methods Data Review (2017) provides a detailed methodology for qualifying data from duplicate samples, which was implemented in this study. Duplicate samples were determined to be chemically similar to the sample group. Therefore, samples analyzed by the NWQL for short-term and long-term GBPA, long-term GAPA, and total iron results were qualified as estimated (J for samples greater than quantitation limit, UJ for samples less than the quantitation limit).

Charge Balance Calculation – Recovery for these samples should be between 95 and 105%.

The Charge balance error can be calculated using the following formula:

$$CBE = \frac{(\Sigma cations\ -\ \Sigma anions)}{(\Sigma cations + \Sigma anions)}\ x\ 100$$

The above criteria were used to evaluate data quality, but are not definitive measures of data usability.

References

U.S. Environmental Protection Agency, 2015, Federal Register 40 CFR Part 136 Clean Water Act Methods Update Rule for the Analysis of Effluent; Proposed Rule, v. 80, no. 33, p.8999-9001.

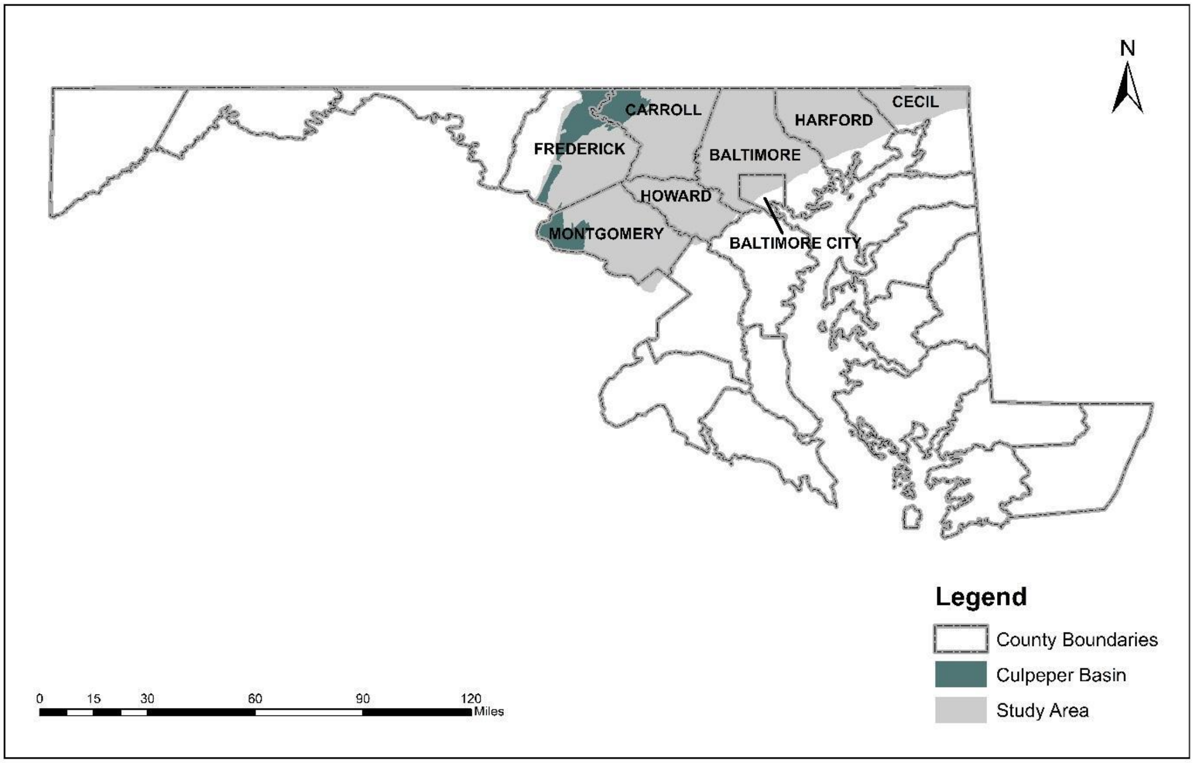

Figure 1. Location of the study area.

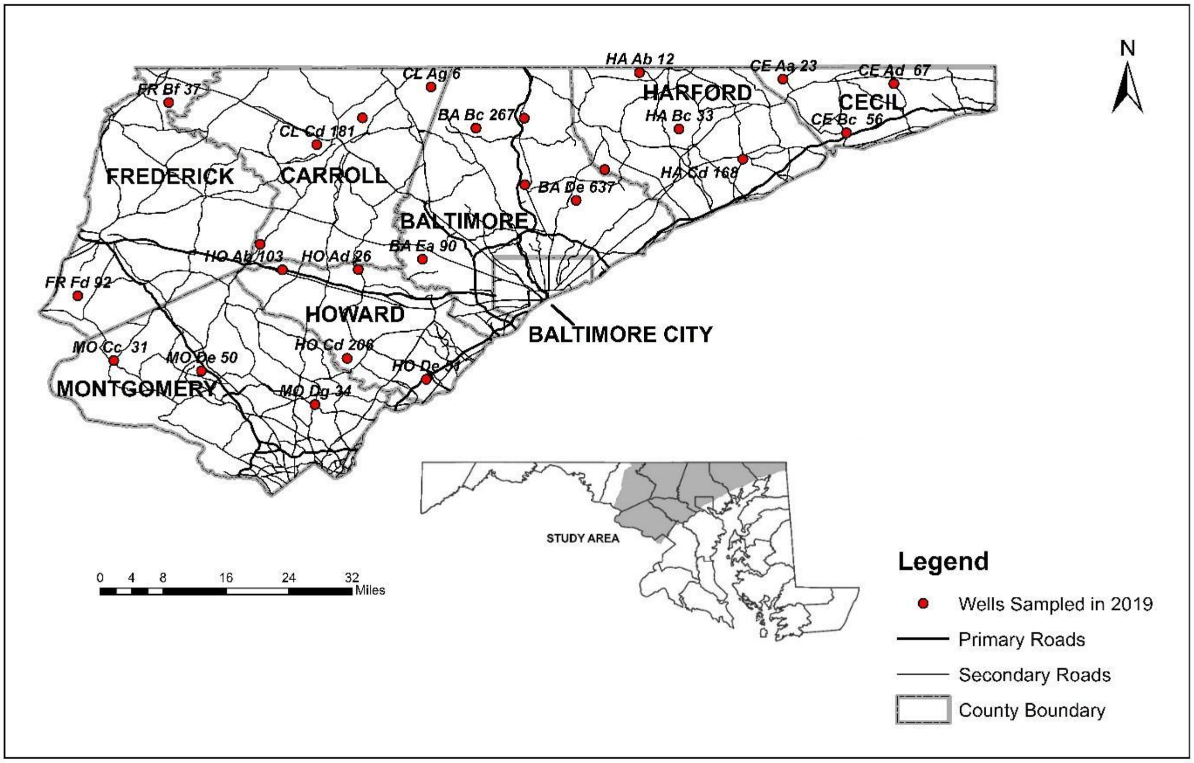

Figure 2. Locations of wells sampled in this study.

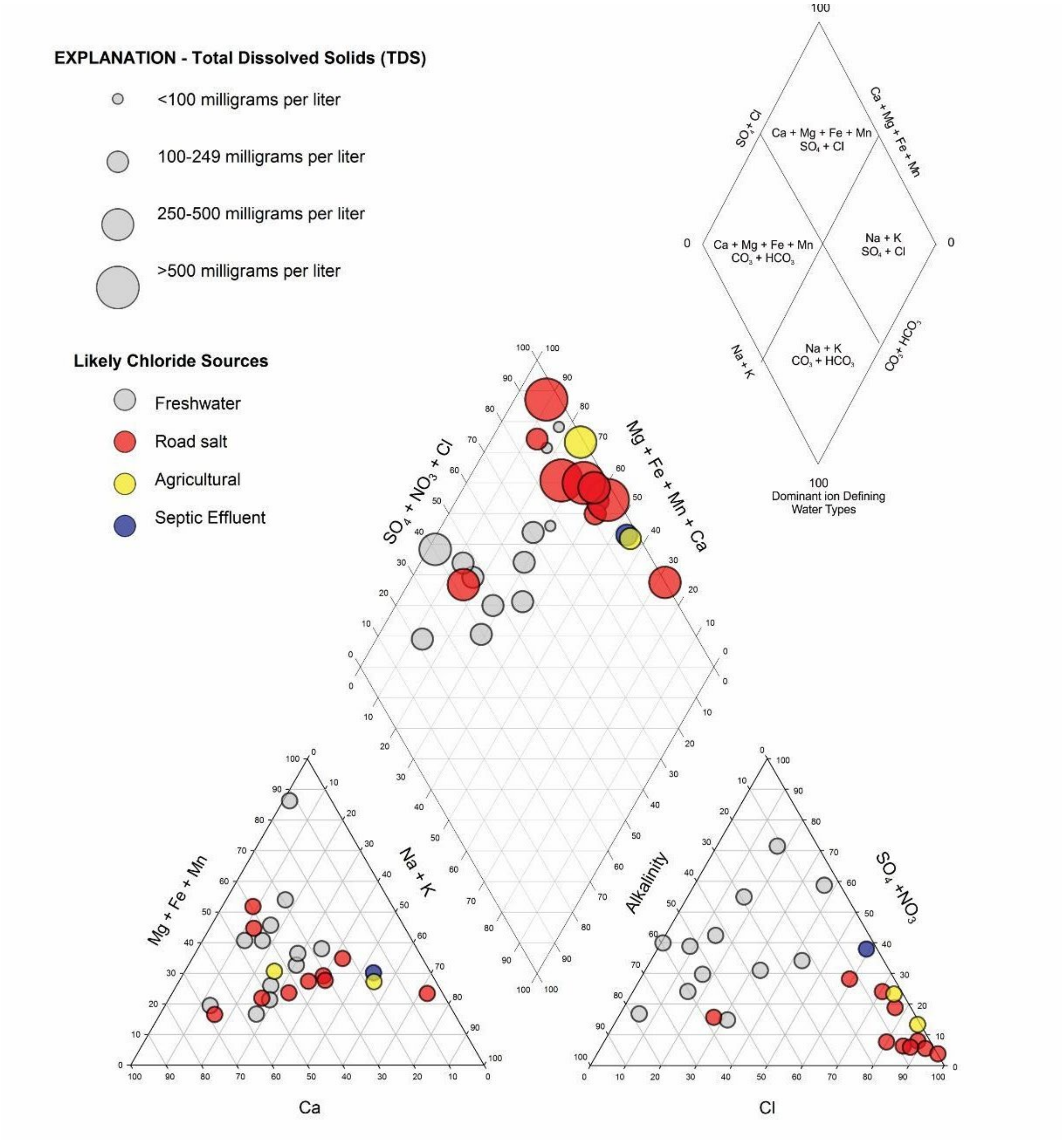

Figure 3. Piper diagram of groundwater samples in the Maryland Piedmont. Likely chloride sources are indicated by red circles for road-deicing salt, yellow circles for agricultural, blue circles for septic effluent, and grey circles for freshwater samples.

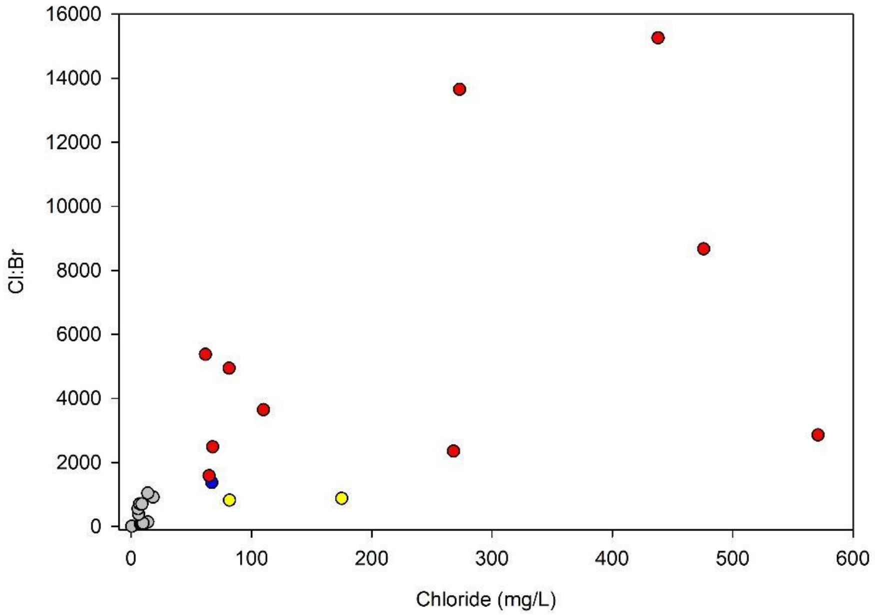

Figure 4. Relation of chloride to Cl:Br ratio. Likely chloride sources are indicated by red circles for road-deicing salt, yellow circles for agricultural, blue circles for septic effluent, and grey circles for freshwater samples.

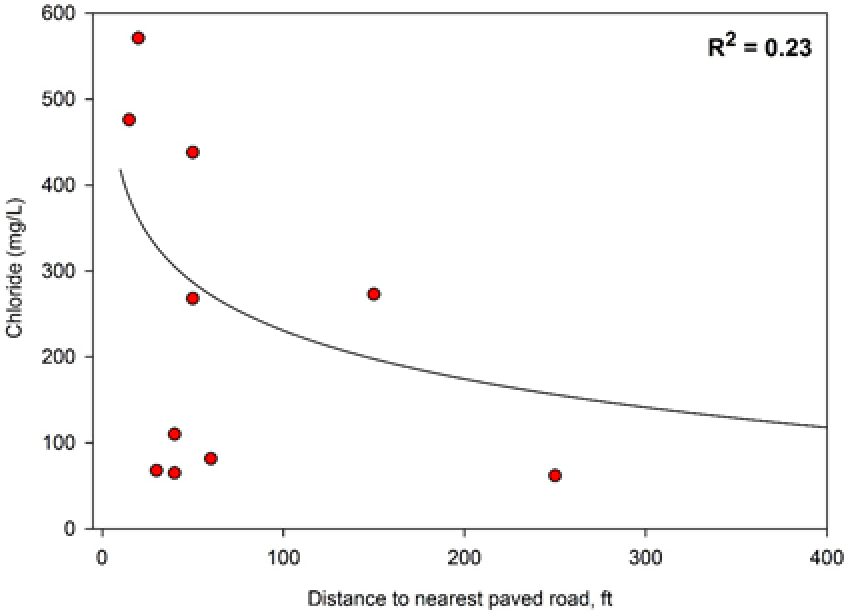

Figure 5. Relation of chloride concentration to distance to nearest paved road. The trend line is logarithmic with R^2 = 0.26.

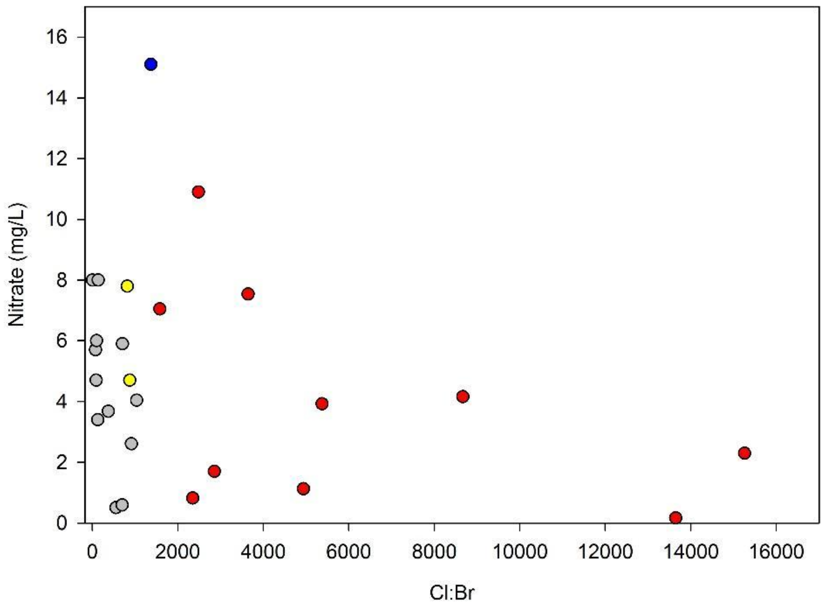

Figure 6. Relation of nitrate to Cl:Br ratio. Likely chloride sources are indicated by red circles for road-deicing salt, yellow circles for agricultural, blue circles for septic effluent, and grey circles for freshwater samples.

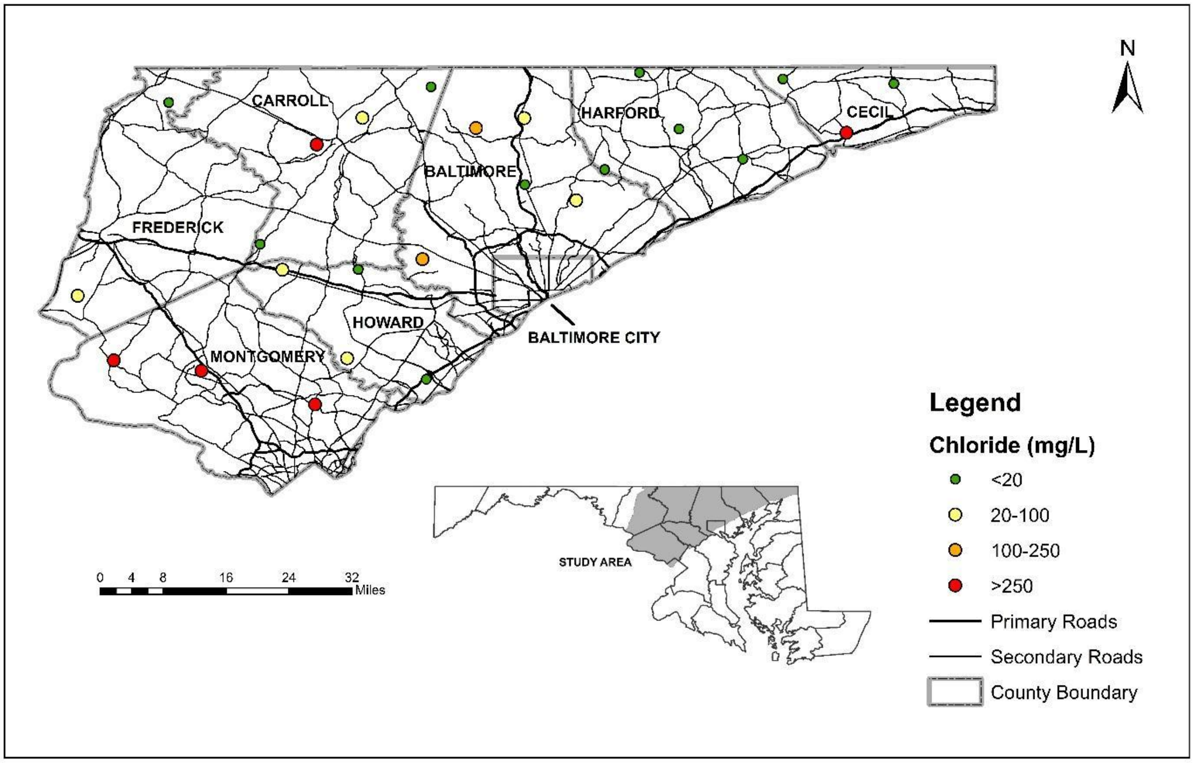

Figure 7. Chloride concentrations in wells sampled in this study.

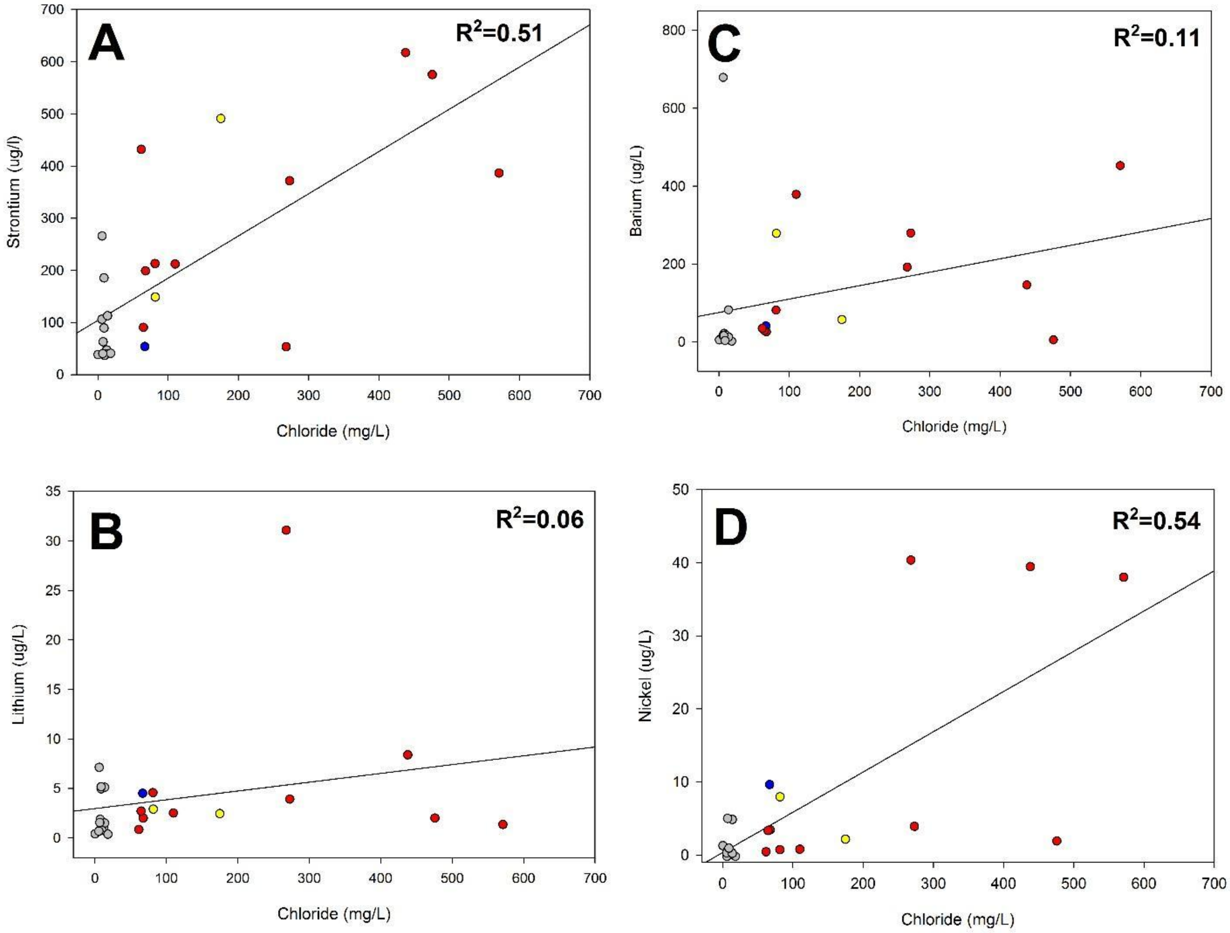

Figure 8. Relation of chloride to (A) strontium, (B) lithium, (C) barium, and (D) nickel. Likely chloride sources are indicated by red circles for road-deicing salt, yellow circles for agricultural, blue circles for septic effluent, and grey circles for freshwater samples.

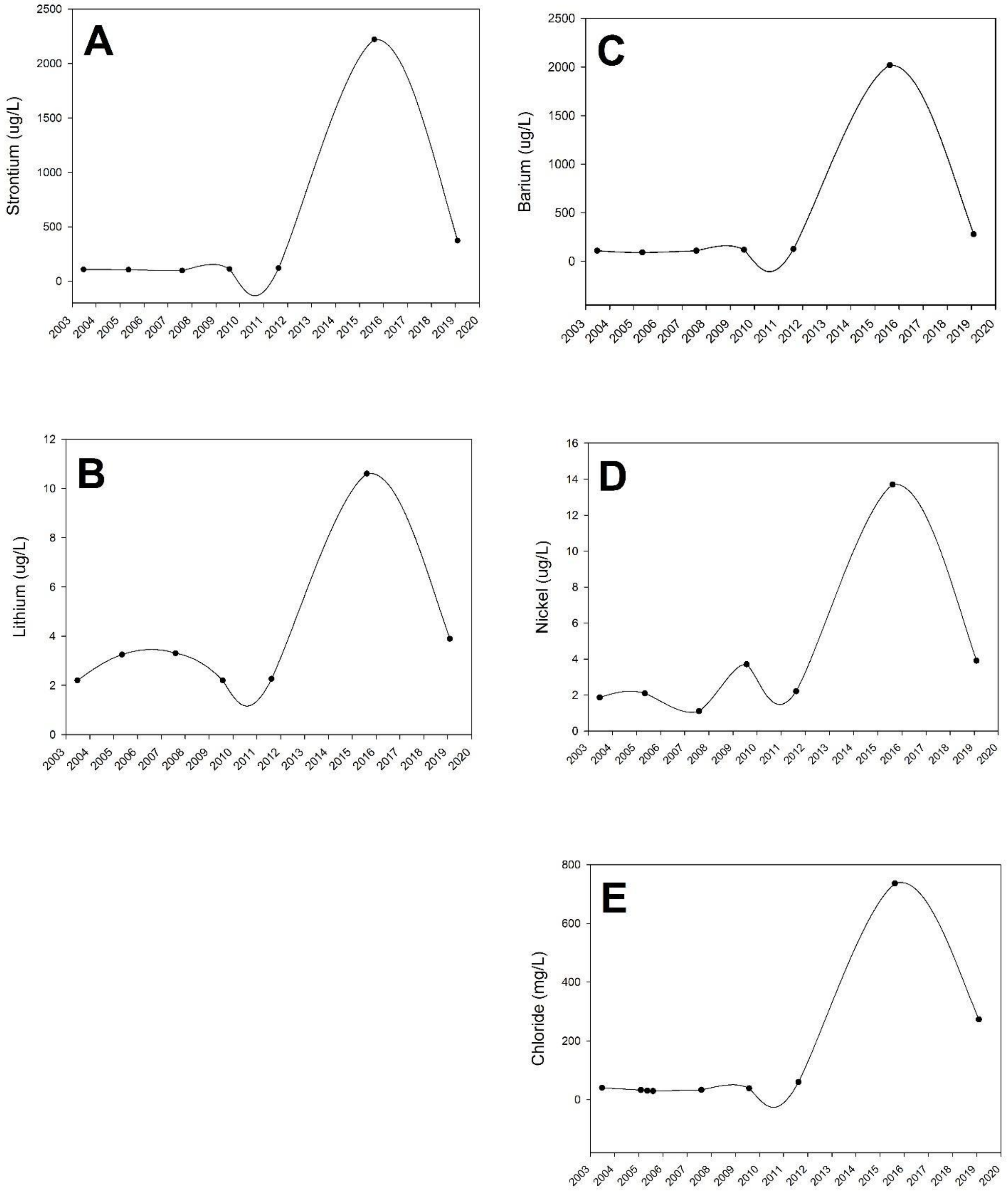

Figure 9. Concentrations of (A) strontium, (B) lithium, (C) barium, (D) nickel, and (E) chloride over time in well MO Dg 34.

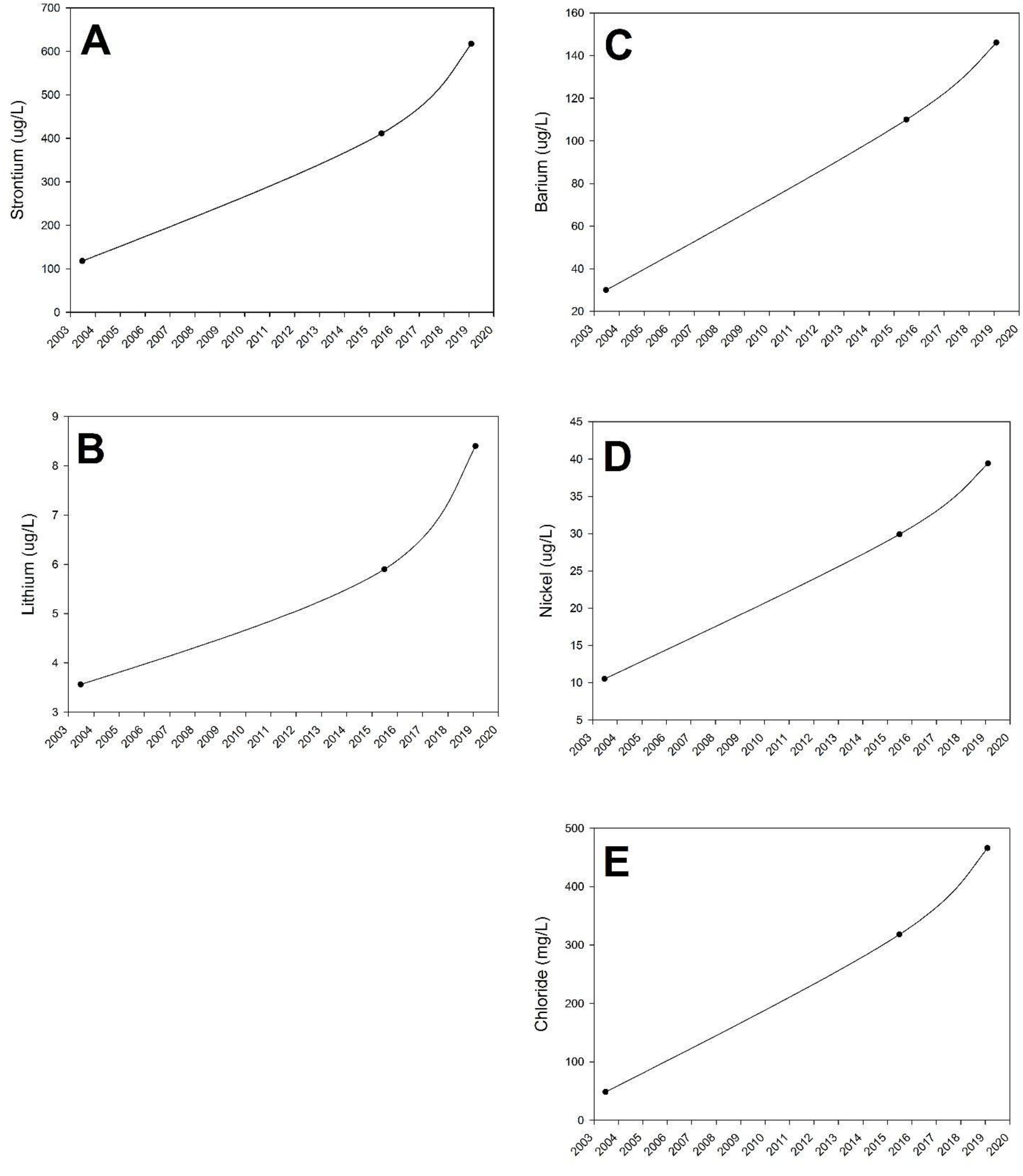

Figure 10. Concentrations of (A) strontium, (B) lithium, (C) barium, (D) nickel, and (E) chloride over time in well MO De 50.

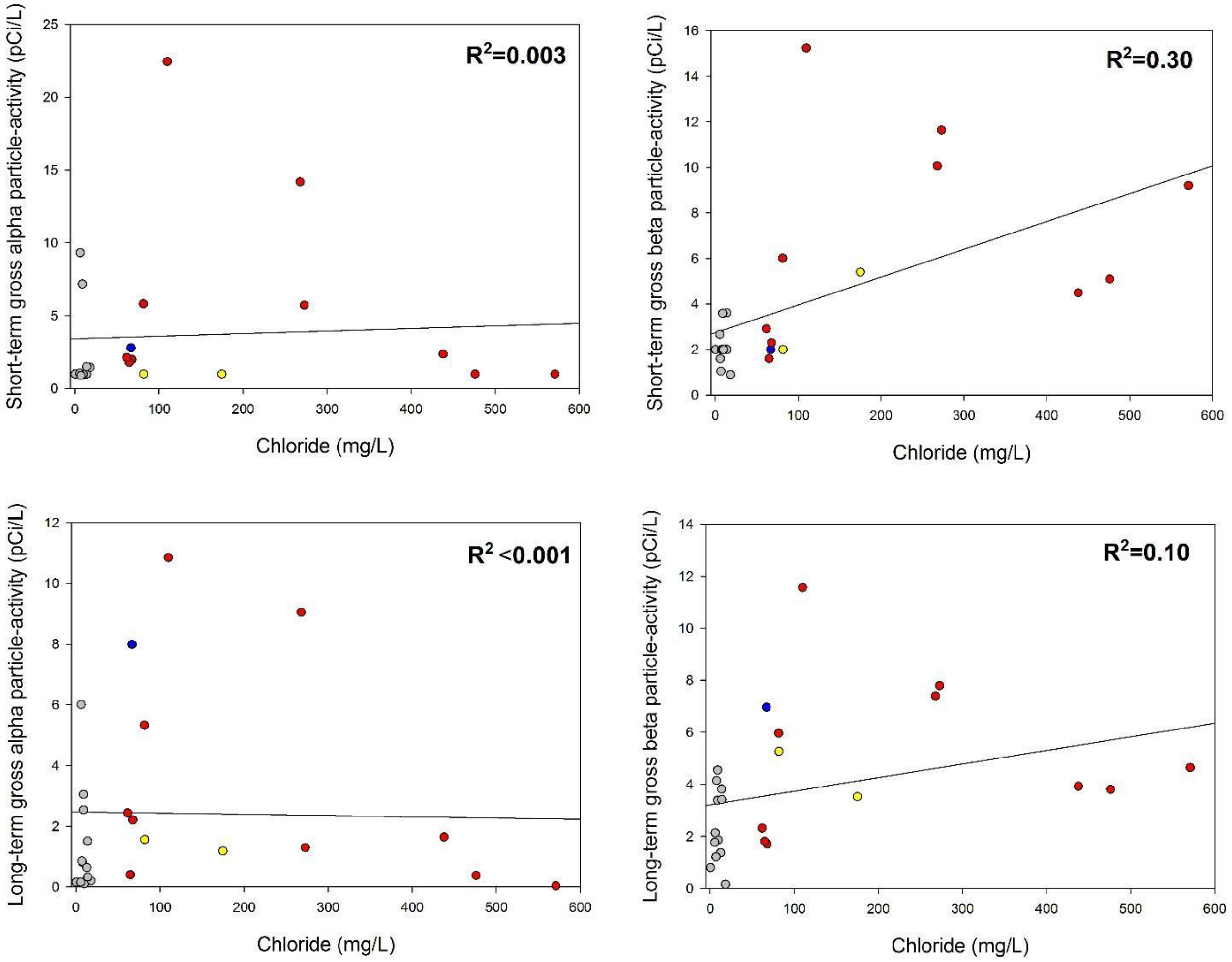

Figure 11. Relation of gross alpha and gross beta particle-activity and chloride concentrations. Likely chloride sources are indicated by red circles for road-deicing salt, yellow circles for agricultural, blue circles for septic effluent, and grey circles for freshwater samples. Results below their respective reporting level were plotted as half the reporting level.

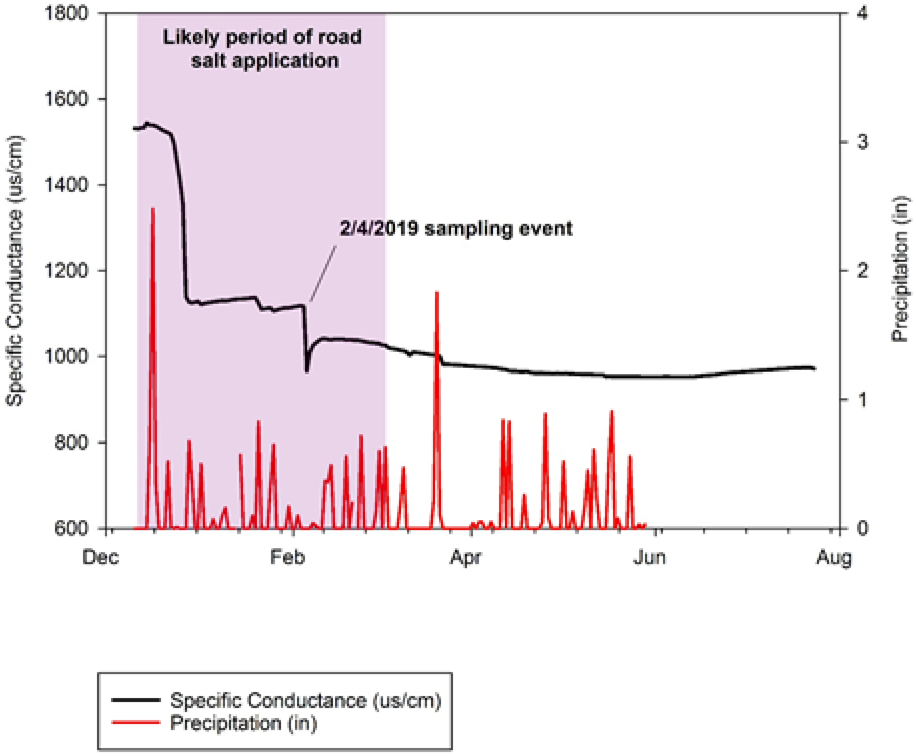

Figure 12. Continuous specific conductance measurements (black line) in well MO Dg 34, from December 2018 through July 2019. Precipitation data from National Oceanic and Atmospheric Administration (red line) from December 2018 to June 2019.

Table 1. Construction records of wells used in this study. All wells are open hole with a 6-inch casing.

[ft, feet]

Well permit	Well number	Completion year	Total depth, ft	Casing depth, ft	Geologic formation
BA-81-0773	BA Bc 267	1982	150	40	Prettyboy Schist
BA-88-0204	BA Bd 234	1992	175	60	Pleasant Grove Schist
BA-94-0644	BA Cd 241	1995	300	30	Baltimore Gneiss
BA-73-3110	BA De 637	1976	125	62	Loch Raven Schist
BA-81-1609	BA Ea 90	1989	23	7	Baltimore Gneiss
CE-68-0229	CE Aa 23	1968	70	44	Gabbro – Baltimore Complex
CE-88-0058	CE Ad 67	1988	107	82	Wissahickon Formation
CE-81-0485	CE Bc 56	1982	200	25	James Run Formation
CL-71-0247	CL Ag 6	1971	175	109	Prettyboy Schist
CL-73-9807	CL Be 120	1981	153	26	Wissahickon Formation
CL-81-2221	CL Cd 181	1985	165	52	Sams Creek Metabasalt
CL-81-0573	CL Ec 106	1983	360	30	Marburg Formation
FR-81-4865	FR Bf 37	1987	275	20	Gettysburg Shale
FR-81-1710	FR Fd 92	1984	225	22	Frederick Limestone
HA-73-6033	HA Ab 12	1980	150	26	Wissahickon Formation
HA-88-1190	HA Bc 33	1990	350	61	Loch Raven Schist
HA-73-1630	HA Ca 23	1974	200	24	Loch Raven Schist
HA-68-0549	HA Cd 168	1968	108	20	James Run Formation
HO-81-1646	HO Ab 103	1986	160	44	Prettyboy Schist
HO-81-1618	HO Ad 26	1986	345	21	Sykesville Formation
HO-73-0825	HO Cd 206	1974	205	38	Cockeysville Marble
HO-73-3792	HO De 51	1981	125	35	Mount Washington Amphibolite
MO-73-0502	MO Cc 31	1974	160	21	Ijamsville Formation
MO-94-2651	MO De 50	2002	74.13	19	Wissahickon Formation
MO-94-2645	MO Dg 34	2002	45.13	18	Kensington Quartz Diorite

Table 2. Relative Percent Difference (RPD) for duplicate groundwater samples. Samples with greater than 20% RPD are shaded in grey.

[-, indicates not calculated]

Constituent	HO Cd 206	HO Cd 206 Duplicate	RPD	BA Ea 90	BA Ea 90 Duplicate	RPD
TDS (mg/L)	195.14	162.60	18.2	284.48	284.10	0.1
Radon (pCi/L)	13120	13290	1.3	4910	5860	17.6
Short Term GAPA (pCi/L)	5.82	4.82	18.8	22.45	25.05	10.9
Short Term GBPA (pCi/L)	6.01	3.73	46.8	15.24	16.30	6.7
Long Term GAPA (pCi/L)	5.33	7.26	30.6	10.85	7.29	39.3
Long Term GBPA (pCi/L)	5.97	4.76	22.5	11.56	13.02	11.9
Bromide (mg/L)	0.02	0.02	0.0	0.03	0.03	0.7
Chloride (mg/L)	81.50	81.35	0.2	110	110	0.0
Fluoride (mg/L)	0.02	0.02	5.4	0.03	0.03	0.0
Nitrite, as N (mg/L)	<0.001	<0.001	-	<0.001	<0.001	-
Nitrate/Nitrite, as N (mg/L)	1.12	1.14	1.8	7.54	7.79	3.2
Sulfate (mg/L)	0.54	0.52	4.4	5.11	5.11	0.0
Ammonia (mg/L)	<0.01	<0.01	-	<0.01	<0.01	-
Phosphorus (mg/L)	<0.02	<0.02	-	<0.02	<0.02	-
Orthophosphate (mg/L)	0.01	0.01	3.2	0.02	0.02	2.7
Calcium (mg/L)	17.77	17.69	0.5	31.36	31.40	0.1
Magnesium (mg/L)	7.87	7.99	1.5	11.95	11.99	0.3
Potassium (mg/L)	3.10	3.17	2.1	4.71	4.64	1.5
Sodium (mg/L)	22.92	22.83	0.4	31.20	31.25	0.2
ANC (mg/L)	15.85	16.18	2.1	15.60	15.46	0.9
Aluminum (ug/L)	<3.00	<3.00	-	8.88	9.07	2.1
Barium (ug/L)	81.39	79.42	2.4	378.54	379.01	0.1
Beryllium (ug/L)	0.23	0.21	9.0	0.47	0.46	2.4
Cadmium (ug/L)	<0.03	<0.03	-	0.28	0.28	0.5
Chromium (ug/L)	<0.50	<0.50	-	<0.50	<0.50	-
Cobalt (ug/L)	<0.03	<0.03	-	0.19	0.21	10.2
Copper (ug/L)	0.97	0.96	1.0	23.87	23.99	0.5
Iron (ug/L)	<10	<10	-	41.29	41.32	0.1
Lead (ug/L)	0.14	0.14	2.8	6.09	6.07	0.4
Lithium (ug/L)	4.55	4.26	6.4	2.51	2.53	1.0
Manganese (ug/L)	2.51	2.41	4.0	103.42	104.00	0.6
Molybdenum (ug/L)	<0.05	<0.05	-	<0.05	<0.05	-
Nickel (ug/L)	0.71	0.66	7.4	0.76	0.83	8.3
Silver (ug/L)	<1.00	<1.00	-	<1.00	<1.00	-
Silica (mg/L)	13.77	13.93	1.1	22.68	22.81	0.6
Strontium (ug/L)	212.65	208.48	2.0	212.00	216.31	2.0
Thallium (ug/L)	<0.04	<0.04	-	<0.04	<0.04	-
Vanadium (ug/L)	<0.10	<0.10	-	<0.10	<0.10	-
Zinc (ug/L)	2.39	2.21	8.0	12.78	13.21	3.3
Antimony (ug/L)	<0.06	<0.06	-	<0.06	<0.06	-
Arsenic (ug/L)	<0.10	<0.10	-	<0.10	<0.10	-
Boron (ug/L)	<5.00	<5.00	-	35.09	35.13	0.1
Selenium (ug/L)	<0.05	<0.05	-	0.41	0.39	4.3
Uranium (ug/L)	0.11	0.11	1.5	0.10	0.09	4.3
Total Iron (ug/L)	39.3	12.8	101.8	172.7	123.1	33.5
Total Manganese (ug/L)	2.90	2.65	9.2	97.28	99.60	2.4

Table 3. Water quality results from wells sampled in the Maryland Piedmont.

[μs/cm, microsiemens per centimeter; mg/L milligrams per liter; constituents that exceed their respective drinking water standard (including proposed drinking water standards) are bolded and italicized; “-“ indicates that no sample was analyzed; J/UJ, results are estimated]

Well number	USGS site number	Date sampled	Water temperature (°C)	Specific conductance – Field (μs/cm at 25 °C)	Hardness (mg/L)
BA Bc 267	393633076443801	1-16-2019	10.1	744	217
BA Bd 234	393739076391801	3-6-2019	13.4	420	146
BA Cd 241	393019076391401	2-25-2019	12.3	176	65.7
BA De 637	392837076333401	1-15-2019	13.5	413	68.6
BA Ea 90	392206076503201	2-6-2019	13.7	465	128
CE Aa 23	394157076104601	1-7-2019	11.8	490	240
CE Ad 67	394127075583101	1-8-2019	12.9	179	47.5
CE Bc 56	393602076034501	1-8-2019	13.9	2149	491
CL Ag 6	394106076493501	1-16-2019	11.5	104	26.8
CL Be 120	393741076570901	1-28-2019	10.8	402	75.0
CL Cd 181	393444077021201	1-28-2019	13.7	1839	611
CL Ec 106	392345077082701	3-27-2019	12.9	155	48.2
FR Bf 37	393922077183201	1-30-2019	9.7	339	146
FR Fd 92	391806077284001	2-26-2019	13.0	763	324
HA Ab 12	394240076263501	1-14-2019	12.4	143	43.5
HA Bc 33	393627076221301	1-14-2019	12.3	194	56.5
HA Ca 23	393158076302601	2-5-2019	13.2	168	52.2
HA Cd 168	393308076151101	1-9-2019	13.8	184	68.6
HO Ab 103	392056077055901	2-12-2019	11.7	346	77.3
HO Ad 26	392058076573701	3-26-2019	12.9	192	60.1
HO Cd 206	391111076585101	2-13-2019	13.8	346	77.1
HO De 51	390852076500701	2-13-2019	14.3	181	71.3
MO Cc 31	391057077243501	2-26-2019	13.6	983	108
MO De 50	390948077145401	2-4-2019	15.0	1535	631
MO Dg 34	390606077022201	2-4-2019	17.7	1105	294

Table 3., Continued

Well number	pH - Field	Alkalinity – Field (mg/L)	Total dissolved solids (mg/L)	Dissolved oxygen – Field (mg/L)
BA Bc 267	***5.76***	14	422	9.46
BA Bd 234	***4.12***	-	214	4.58
BA Cd 241	***6.31***	54	130	7.62
BA De 637	***5.87***	10.9	204	7.93
BA Ea 90	***4.19***	-	284	2.5
CE Aa 23	7.15	129	265	2.4
CE Ad 67	***4.56***	-	114	6.74
CE Bc 56	***6.14***	501	***1176***	4.06
CL Ag 6	***6.02***	15.6	61	9.34
CL Be 120	***6.32***	15	247	6.1
CL Cd 181	7.13	138	***1068***	5.52
CL Ec 106	***5.69***	10.1	78	7.58
FR Bf 37	8.4	174	193	5.88
FR Fd 92	7.43	226	417	3.55
HA Ab 12	***6.1***	9.7	72	9.08
HA Bc 33	6.79	47	118	9.23
HA Ca 23	***4.84***	-	110	6.78
HA Cd 168	***6.23***	47.4	124	4.94
HO Ab 103	6.65	37	175	6.88
HO Ad 26	7.44	58	108	1.63
HO Cd 206	***4.84***	-	195	8.93
HO De 51	***5.54***	49	132	7.79
MO Cc 31	***5.3***	16	486	1.89
MO De 50	***4.23***	-	***789***	5.31
MO Dg 34	6.59	45	***527***	0.91

Table 3., Continued

Well number	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	Chloride (mg/L)	Cl:Br	Bromide (mg/L)
BA Bc 267	54.5	19.6	***32.4***	2.61	175	875	0.2
BA Bd 234	30.4	16.9	8.84	1.43	67.78	2482	0.027
BA Cd 241	21.3	3.02	10.0	2.27	5.79	526	0.011
BA De 637	12.5	9.02	***36.5***	3.67	81.8	818	0.1
BA Ea 90	31.4	12	***31.2***	4.71	110	3627	0.03
CE Aa 23	14.4	49.6	1.93	<0.3	0.5	5	0.1
CE Ad 67	8.70	6.23	10.3	2.46	7.7	77	0.1
CE Bc 56	87.2	66.3	***165***	3.06	***571***	2855	0.2
CL Ag 6	6.1	2.78	5.11	0.53	12.7	127	<0.1
CL Be 120	12.4	10.7	***38.6***	2.02	67	1370	0.049
CL Cd 181	181	38.2	***98***	3.24	***476***	8678	0.055
CL Ec 106	9.36	6.01	3.73	1.28	7.05	705	<0.01
FR Bf 37	47	6.7	9.58	0.51	6.26	368	0.017
FR Fd 92	108	12.7	***26.2***	2.2	61.8	5371	0.011
HA Ab 12	6.71	6.46	2.99	1.79	13.8	138	<0.1
HA Bc 33	15.5	4.31	8.06	2.36	8.9	89	<0.1
HA Ca 23	11.0	5.99	8.37	2.49	13.9	1069	0.013
HA Cd 168	14.9	7.58	6.07	0.69	9.9	99	0.1
HO Ab 103	17.4	8.20	***22.8***	1.33	64.9	1578	0.041
HO Ad 26	17.8	3.77	9.91	2.09	8.99	300	0.03
HO Cd 206	17.8	7.87	***22.9***	3.10	81.5	4939	0.017
HO De 51	16.3	7.44	4.28	0.32	18.3	915	0.02
MO Cc 31	11.5	19.2	***128***	1.31	***268***	2351	0.114
MO De 50	117	82.1	***26.1***	3.29	***438***	15271	0.029
MO Dg 34	81.7	21.7	***62.5***	7.46	***273***	13648	<0.02

Table 3., Continued

Well number	Sulfate (mg/L)	Fluoride (mg/L)	Iron (filtered - µg/L)	Iron (unfiltered – µg/L)	Manganese (filtered – µg/L)	Manganese (unfiltered – µg/L)
BA Bc 267	12.8	<0.2	10.3	161 J	19.8	21.8
BA Bd 234	1.96	0.01	<10	<10 UJ	5.66	6.3
BA Cd 241	31.2	0.04	<10	19.8 J	0.53	10.5
BA De 637	3.8	<0.2	<10	24.8 J	23.3	23.3
BA Ea 90	5.11	0.03	41.3	173 J	<0.4	***97.3***
CE Aa 23	41.6	<0.2	13.4	27.9 J	<0.4	0.3
CE Ad 67	9.9	<0.2	<10	***718 J***	6.80	9.1
CE Bc 56	15.9	<0.2	23.4	135 J	5.73	7.1
CL Ag 6	<1	<0.2	<10	69.9 J	3.20	3.1
CL Be 120	2.33	0.02	14.1	57.5 J	36.1	36.1
CL Cd 181	24.1	0.06	<10	<10 UJ	<2	<0.2
CL Ec 106	18.7	0.03	<10	34.6 J	18.5	20.2
FR Bf 37	9.87	0.05	<10	17.5 J	<0.4	0.6
FR Fd 92	26.3	0.21	<10	32.7 J	<0.4	0.6
HA Ab 12	1.2	<0.2	<10	<10 UJ	46.4	45.1
HA Bc 33	23.8	<0.2	<10	<10 UJ	0.42	0.5
HA Ca 23	2.54	0.06	29.2	217 J	4.74	5.4
HA Cd 168	<1	<0.2	<10	199 J	5.23	5.6
HO Ab 103	2.31	0.01	<10	<10 UJ	12.8	12.8
HO Ad 26	14.8	0.12	<10	<10 UJ	18.9	18.2
HO Cd 206	0.54	0.02	<10	39.2 J	2.51	2.9
HO De 51	0.53	0.01	<10	<10 UJ	<0.4	<0.2
MO Cc 31	0.41	0.061	66.6	***1400 J***	***535***	***505***
MO De 50	26.1	0.03	72.1	***1130 J***	5.92	34.5
MO Dg 34	12.1	0.03	***921***	***17100 J***	***394***	***474***

Table 3., Continued

Well number	Nitrate/Nitrite (mg/L), as N	Nitrite (mg/L)	Ammonia (mg/L)	Orthophosphate (mg/L)	Phosphorus (mg/L)
BA Bc 267	4.7	<0.2	<0.1	-	<0.05
BA Bd 234	***10.9***	<0.001	<0.01	0.075	<0.02
BA Cd 241	0.501	<0.001	<0.01	0.041	0.03
BA De 637	7.8	<0.2	<0.1	-	<0.05
BA Ea 90	7.54	<0.001	<0.01	0.017	<0.02
CE Aa 23	8	<0.2	<0.1	-	<0.05
CE Ad 67	5.7	<0.2	<0.1	-	<0.05
CE Bc 56	1.7	<0.2	<0.1	-	<0.05
CL Ag 6	3.4	<0.2	<0.1	-	<0.05
CL Be 120	***15.1***	<0.001	<0.01	0.012	<0.02
CL Cd 181	4.15	<0.001	<0.01	0.032	0.02
CL Ec 106	5.9	<0.001	<0.01	0.005	0.03
FR Bf 37	3.67	<0.001	<0.01	0.042	0.02
FR Fd 92	3.92	<0.001	<0.01	0.028	<0.02
HA Ab 12	8	<0.2	<0.1	-	<0.05
HA Bc 33	4.7	<0.2	<0.1	-	0.06
HA Ca 23	4.04	<0.001	<0.01	0.022	<0.02
HA Cd 168	6	<0.2	<0.1	-	<0.05
HO Ab 103	7.04	<0.001	<0.01	0.007	<0.02
HO Ad 26	0.592	<0.001	0.01	0.017	<0.02
HO Cd 206	1.12	<0.001	<0.01	0.012	<0.02
HO De 51	2.61	<0.001	<0.01	0.028	0.03
MO Cc 31	0.818	<0.001	0.01	<0.004	<0.02
MO De 50	2.29	<0.001	<0.01	0.029	<0.02
MO Dg 34	0.165	0.001	0.01	<0.004	<0.02

Table 3., Continued

Well number	Aluminum (µg/L)	Antimony (µg/L)	Arsenic (µg/L)	Barium (µg/L)	Beryllium (µg/L)	Boron (µg/L)
BA Bc 267	<3	0.064	<0.1	57.3	0.011	7
BA Bd 234	5	<0.06	<0.1	25.7	0.011	<5
BA Cd 241	<3	<0.06	<0.1	15.8	<0.01	<5
BA De 637	11	<0.06	<0.1	278	0.118	<5
BA Ea 90	9	<0.06	<0.1	379	0.467	35
CE Aa 23	<3	<0.06	<0.1	4.89	<0.01	<5
CE Ad 67	<3	<0.06	<0.1	22.1	<0.01	<5
CE Bc 56	<9	<0.18	<0.3	452	<0.03	<15
CL Ag 6	<3	<0.06	<0.1	5.96	<0.01	<5
CL Be 120	18	<0.06	<0.1	41	0.018	11
CL Cd 181	<15	<0.3	<0.5	4.99	<0.05	41
CL Ec 106	14	<0.06	<0.1	16.3	0.016	13
FR Bf 37	<3	<0.06	2.9	678	<0.01	15
FR Fd 92	<3	<0.06	<0.1	34.3	<0.01	9
HA Ab 12	54	<0.06	<0.1	82.1	0.089	9
HA Bc 33	<3	<0.06	<0.1	11.8	<0.01	<5
HA Ca 23	<3	<0.06	<0.1	12.5	<0.01	<5
HA Cd 168	<3	<0.06	<0.1	17.8	<0.01	<5
HO Ab 103	4.875	<0.06	<0.1	28.6	<0.01	6
HO Ad 26	<3	0.196	0.4	3.53	<0.01	11
HO Cd 206	<3	<0.06	<0.1	81.4	0.226	<5
HO De 51	<3	<0.06	<0.1	1.71	<0.01	11
MO Cc 31	75	<0.06	<0.1	192	0.119	<5
MO De 50	<6	<0.12	<0.2	146	<0.02	<15
MO Dg 34	<6	<0.12	<0.2	379	<0.02	<10

Table 3., Continued

Well number	Cadmium (μg/L)	Cobalt (μg/L)	Copper (μg/L)	Chromium (μg/L)	Lead (μg/L)
BA Bc 267	0.101	0.191	27.1	1.2	1.03
BA Bd 234	0.053	0.216	8.9	0.73	0.537
BA Cd 241	<0.03	0.037	60.6	<0.50	0.256
BA De 637	1.04	1.53	96.4	<0.50	4.45
BA Ea 90	0.278	0.190	23.9	<0.50	6.09
CE Aa 23	<0.03	0.035	15.7	12.0	2.89
CE Ad 67	<0.03	<0.03	17.6	5.2	0.151
CE Bc 56	<0.09	<0.09	21	2.2	0.364
CL Ag 6	<0.03	0.054	12.2	<0.50	0.166
CL Be 120	0.146	1.03	25	<0.50	11.4
CL Cd 181	<0.15	0.227	5.5	3.8	0.204
CL Ec 106	<0.03	0.457	8.5	<0.50	0.526
FR Bf 37	<0.03	<0.03	6.5	<0.50	0.314
FR Fd 92	<0.03	0.118	3.4	<0.50	0.323
HA Ab 12	0.053	0.107	8.8	<0.50	1.28
HA Bc 33	<0.03	0.034	10.4	<0.50	1.03
HA Ca 23	<0.03	<0.03	1.5	<0.50	0.14
HA Cd 168	<0.03	<0.03	6.9	5.7	0.158
HO Ab 103	0.039	0.151	85	<0.50	0.958
HO Ad 26	<0.03	<0.03	2.3	<0.50	0.143
HO Cd 206	<0.03	<0.03	0.97	<0.50	0.138
HO De 51	<0.03	<0.03	7.2	<0.50	0.119
MO Cc 31	0.135	12.6	215	<0.5	6.17
MO De 50	<0.06	0.113	4.6	<1.00	0.226
MO Dg 34	<0.06	0.901	<0.8	<1.00	<0.04

Table 3., Continued

Well number	Lithium (µg/L)	Molybdenum (µg/L)	Nickel (µg/L)	Selenium (µg/L)	Silica (µg/L)	Silver (µg/L)
BA Bc 267	2.43	<0.05	2.1	0.36	-	<1
BA Bd 234	2	<0.05	3.4	0.18	11.9	<1
BA Cd 241	0.67	0.137	0.28	0.59	23.2	<1
BA De 637	2.88	<0.05	7.9	0.116		<1
BA Ea 90	2.51	<0.05	0.76	0.41	22.7	<1
CE Aa 23	0.40	<0.05	1.3	<0.05	-	<1
CE Ad 67	1.86	<0.05	0.70	1.4	-	<1
CE Bc 56	1.34	<0.15	38	0.31	-	<3
CL Ag 6	0.97	<0.05	0.33	<0.05	-	<1
CL Be 120	4.49	<0.05	9.6	0.07	6.40	<1
CL Cd 181	1.99	<0.25	1.9	<0.25	18.6	<5
CL Ec 106	1.54	<0.05	5.0	0.11	4.50	<1
FR Bf 37	7.12	1.33	<0.2	0.91	19.4	<1
FR Fd 92	0.83	<0.05	0.42	0.26	8.02	<1
HA Ab 12	1.49	<0.05	4.8	0.09	-	<1
HA Bc 33	4.94	<0.05	0.47	2.0	-	<1
HA Ca 23	5.10	<0.05	0.21	0.18	23.0	<1
HA Cd 168	0.75	<0.05	0.26	<0.05	-	<1
HO Ab 103	2.69	<0.05	3.3	0.08	8.09	<1
HO Ad 26	5.14	1.2	0.91	0.23	17.5	<1
HO Cd 206	4.55	<0.05	0.71	<0.05	13.8	<1
HO De 51	0.36	<0.05	<0.2	<0.05	13.8	<1
MO Cc 31	31.1	0.07	40.3	0.05	7.78	<1
MO De 50	8.39	0.140	39.4	0.12	30.3	<2
MO Dg 34	3.90	0.252	3.9	0.19	16.5	<2

Table 3., Continued

Well number	Strontium (µg/L)	Thallium (µg/L)	Uranium (µg/L)	Vanadium (µg/L)	Zinc (µg/L)	Radon (pCi/L)
BA Bc 267	491	<0.04	<0.03	<0.1	13.6	1,516
BA Bd 234	199	<0.04	0.042	<0.1	18.7	1,543
BA Cd 241	106	<0.04	<0.03	0.19	7.6	227
BA De 637	149	0.080	<0.03	<0.1	74.2	2,233
BA Ea 90	212	<0.04	0.095	<0.1	12.8	***4,910***
CE Aa 23	38.3	<0.04	0.038	4.1	37.1	41.9
CE Ad 67	62.9	<0.04	0.138	1.3	10.7	2,453
CE Bc 56	386	<0.12	<0.09	0.73	24	126
CL Ag 6	47.4	<0.04	<0.03	<0.1	8.6	1,142
CL Be 120	53.9	<0.04	<0.03	<0.1	90.5	1,879
CL Cd 181	575	<0.2	<0.15	0.77	<10	<20
CL Ec 106	40.2	<0.04	<0.03	<0.1	15.4	2,150
FR Bf 37	266	<0.04	2.84	3.5	3.7	1,354
FR Fd 92	432	<0.04	0.190	0.2	4.9	498
HA Ab 12	39.7	<0.04	<0.03	<0.1	16.7	602
HA Bc 33	185	<0.04	0.090	0.26	14.0	2,565
HA Ca 23	113	<0.04	<0.03	<0.1	5.8	2,720
HA Cd 168	36.8	<0.04	0.031	7.3	2.4	1,009
HO Ab 103	90.6	<0.04	<0.03	<0.1	17.2	3,200
HO Ad 26	89.4	<0.04	1.89	0.38	3.4	2,290
HO Cd 206	213	<0.04	0.111	<0.1	2.4	***13,120***
HO De 51	40.8	<0.04	<0.03	1.6	8.4	235
MO Cc 31	53.3	<0.04	<0.03	<0.1	228	1,154
MO De 50	617	<0.08	<0.06	1.1	23.7	616
MO Dg 34	372	<0.08	<0.06	<0.2	19.5	99

Table 3., Continued

Well number	Gross alpha-particle activity (short term – pCi/L)	Gross alpha-particle activity (long term – pCi/L)	Gross beta-particle activity (short term – pCi/L)	Gross beta-particle activity (long term – pCi/L)
BA Bc 267	<2	1.2	5.4	3.5
BA Bd 234	2	2.2 J	2.3 J	1.7 J
BA Cd 241	1.1	<0.3 UJ	2.7 J	1.7 J
BA De 637	<2	1.6	<4	5.3
BA Ea 90	22	10.8 J	15.2 J	11.6 J
CE Aa 23	<2	<0.3	<4	0.8
CE Ad 67	<2	0.8	<4	4.1
CE Bc 56	<2	0.0	9.2	4.6
CL Ag 6	<2	0.6	<4	1.4
CL Be 120	2.8	8	<4	7
CL Cd 181	<2	0.4	5.1	3.8
CL Ec 106	<1.8	<1.7 UJ	<2.1 UJ	<2.4 UJ
FR Bf 37	9.3	6.0 J	1.6 J	2.1 J
FR Fd 92	2.1	0.2 J	2.9 J	0.7 J
HA Ab 12	<2	1.5	<4	3.8
HA Bc 33	<2	3.1	<4	3.4
HA Ca 23	1.5	0.3 J	3.6 J	3.4 J
HA Cd 168	<2	<0.2	<4	1.9
HO Ab 103	1.8	<0.8 UJ	1.6 J	1.8 J
HO Ad 26	7.2	2.5 J	3.6 J	4.5 J
HO Cd 206	5.8	5.3 J	6.0 J	6.0 J
HO De 51	0.5	<0.4 UJ	0.9 J	<0.3 UJ
MO Cc 31	14.2	9.1 J	10.1 J	7.4 J
MO De 50	2.4	1.6 J	4.5 J	3.9 J
MO Dg 34	5.7	1.3 J	11.6 J	7.8 J

Table 4. Likely sources of chloride for wells sampled in the Maryland Piedmont.

[Yellow background indicates agricultural-sourced chloride; red background indicates road-deicing salt sourced chloride; blue background indicates septic effluent/water softener backwash sourced chloride; and white background indicates freshwater]

Well number	Chloride (mg/L)	Cl:Br ratio	Nitrate, as N, (mg/L)	Boron (ug/L)	Approximate distance to road, ft	Septic field onsite?	Water-softener installed?	Near agricultural activities?
BA Bc 267	175	875	4.7	7	5000	Yes	No	Yes
BA De 637	81.8	818	7.8	<5	60	Yes	Yes	Yes
BA Bd 234	67.8	2483	10.9	<5	30	Yes	Yes	No
BA Ea 90	110	3642	7.54	35	40	Yes	No	No
CE Bc 56	571	2855	1.7	<15	20	Yes	Yes	No
CL Cd 181	476	8670	4.15	41	15	Yes	Yes	No
FR Fd 92	61.8	5374	3.92	9	250	Yes	Yes	No
HO Ab 103	64.9	1579	7.04	6	40	Yes	No	No
HO Cd 206	81.5	4939	1.12	<5	60	Yes	Yes	No
MO Cc 31	268	2349	0.818	<5	50	Yes	No	No
MO De 50	438	15261	2.29	<15	50	No	No	No
MO Dg 34	273	13650	0.165	<10	150	No	No	No
CL Be 120	67	1370	15.1	11	70	Yes	Yes	Yes
BA Cd 241	5.791	552	0.501	<5	700	Yes	No	No
CE Aa 23	0.5	5	8	<5	80	Yes	No	Yes
CE Ad 67	7.7	77	5.7	<5	120	Yes	No	No
CL Ag 6	12.7	127	3.4	<5	350	Yes	No	No
CL Ec 106	7.05	705	5.9	13	275	Yes	No	No
FR Bf 37	6.26	375	3.67	15	350	Yes	No	Yes
HA Ab 12	13.8	138	8	<5	1200	Yes	No	Yes
HA Bc 33	8.9	89	4.7	<5	300	Yes	No	No
HA Ca 23	13.9	1037	4.04	<5	1800	No	No	Yes
HA Cd 168	9.9	99	6	<5	180	Yes	Yes	No
HO Ad 26	8.99	697	0.592	11	300	Yes	No	No
HO De 51	18.3	915	2.61	<5	350	Yes	No	No

Table 5. Comparison of historical and 2019 chloride concentrations.

[mg/L, milligrams per liter]

Well number	**2019 Chloride (mg/L)**	**Historical Chloride (mg/L)** [year collected][1]	**Difference in concentration between 2019 and most recent historical (mg/L)**	**Percent difference between 2019 and most recent historical**
BA Bc 267	175	**120** [2000] **92** [1996] **91** [1995] **82** [1994]	**+55**	**+46**
BA Bd 234	67.78	**9.5** [1996]	**+59.28**	**+613**
BA Cd 241	5.79	**6.8** [1995]	**-1.01**	**-15**
BA De 637	81.8	**130** [1995]	**-48.2**	**-37**
BA Ea 90	110	**4.9** [1994]	**+105.1**	**+2,145**
CE Aa 23	0.5	**31** [1983]	**-30.5**	**-98**
CE Ad 67	7.7	**6.3** [1994]	**+1.4**	**+22**
CE Bc 56	571	**2.4** [1983]	**+568.6**	**+23,692**
CL Ag 6	12.7	**1.7** [1975]	**+11**	**+647**
CL Be 120	67	**144** [2014] **30** [1994]	**-77**	**-53**
CL Cd 181	476	**118** [2002] **87** [1996]	**+358**	**+303**
CL Ec 106	7.05	**15.6** [2002]	**-8.55**	**-55**
FR Bf 37	6.26	**5.61** [1999]	**+0.65**	**+12**
FR Fd 92	61.8	**19** [1994]	**+42.8**	**+225**
HA Ab 12	13.8	**14** [1994]	**-0.2**	**-1**
HA Bc 33	8.9	**16** [1996]	**-7.1**	**-44**
HA Ca 23	13.9	**10.6** [2001] **9.49** [1997] **8.3** [1994] **7.5** [1993] **7.7** [1992] **7.5** [1991] **9.6** [1990] **6.8** [1989] **7.3** [1988] **4.2** [1974]	**+3.3**	**+31**
HA Cd 168	9.9	**1.6** [1974]	**+8.3**	**+519**
HO Ab 103	64.9	**14** [1989]	**+50.9**	**+364**
HO Ad 26	8.99	**5.7** [1989]	**+3.29**	**+58**
HO Cd 206	81.5	**20** [1989]	**-61.5**	**+308**
HO De 51	18.3	**5.5** [1988]	**+12.8**	**+233**
MO Cc 31	268	**3.2** [1978]	**+264.8**	**+8,275**
MO De 50	438	**318** [2015] **48.3** [2003]	**+120**	**+38**
MO Dg 34	273	**736** [2015] **60** [2011] **38.5** [2009] **33.1** [2007] **29.3** [2005] **40.3** [2003]	**-463**	**-63**

[1] Some wells were sampled monthly – not all samples are listed in the table.

Table 6. Quarterly sampling results from wells HO Ab 103, CL Cd 181, and CE Bc 56.

[-, indicates sample not analyzed]

Well Number	**HO Ab 103**		**CL Cd 181**		**CE Bc 56**	
Sample Date	2/13/2019	4/30/2019	1/28/2019	4/30/2019	1/8/2019	5/1/2019
pH - Field	6.65	6.08	7.13	7.01	6.14	6.9
Alkalinity (mg/L) - Field	37	20	138	141	51	48
Specific conductance (us/cm at 25C) - Field	346	326	1839	1684	2149	2083
Dissolved oxygen (mg/L)	6.88	7.13	5.52	5.21	4.06	4.16
Chloride (mg/L)	64.9	64.6	476	404	571	568
Bromide (mg/L)	0.0411	0.0399	0.0549	0.048	0.2	0.0532
Fluoride (mg/L)	0.012	0.013	0.061	0.067	<0.2	0.022
Calcium (mg/L)	17.370	-	181.400	-	87.170	-
Magnesium (mg/L)	8.199	-	38.180	-	66.280	-
Potassium (mg/L)	1.329	-	3.236	-	3.060	-
Silica (mg/L)	8.092	7.787	18.600	18.195	-	23.281
Sodium (mg/L)	22.790	-	98.040	-	165.100	-
Iron (ug/L)	<10	<10	<10.000	<10	23.360	96.04
Manganese (ug/L)	12.797	24.320	<0.2	<0.2	5.734	5.258
Total dissolved solids (mg/L)	175	181	1068	986	1176	1076
Sulfate (mg/L)	2.315	3.588	24.099	22.627	15.9	13.739

Larry Hogan
Governor

Jeannie Haddaway-Riccio
Secretary

Boyd K. Rutherford
Lt. Governor

A message to Maryland's citizens

The Maryland Department of Natural Resources (DNR) seeks to balance the preservation and enhancement of the living and physical resources of the state with prudent extraction and utilization policies that benefit the citizens of Maryland. This publication provides information that will increase your understanding of how DNR strives to reach that goal through the earth science assessments conducted by the Maryland Geological Survey.

MARYLAND DEPARTMENT OF NATURAL RESOURCES
Resource Assessment Service
Tawes State Office Building
580 Taylor Avenue
Annapolis, Maryland 21401
Toll free in Maryland: 1-877-620-8DNR
Out of State call: 1-410-260-8021
TTY users: Call via the Maryland Relay
Internet Address: www.dnr.Maryland.gov

MARYLAND GEOLOGICAL SURVEY
2300 St. Paul Street
Baltimore, Maryland 21218
Telephone Contact Information: 410-554-5500
Internet Address: www.mgs.md.gov

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