Maryland Department of Natural Resources
Resource Assessment Service
MARYLAND GEOLOGICAL SURVEY
Richard A. Ortt, Jr., Director

REPORT OF INVESTIGATIONS NO. 85

WELLWATER QUALITY IN THE APPALACHIAN PLATEAU PHYSIOGRAPHIC PROVINCE OF MARYLAND

by

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Prepared in cooperation with the
Maryland Department of the Environment

DNR Publication No. 12 –4142017-654

2018

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ACRONYMS AND ABBREVIATIONS USED IN THIS REPORT

commun.	Communication
CBE	Charge Balance Error
DNR	Department of Natural Resources
DHMH	Maryland Department of Health and Mental Hygiene
GAPA	Gross alpha particle activity
GBPA	Gross beta particle activity
GCHD	Garrett County Health Department
GPS	Global Positioning System
HA	Health Advisory
MCL	Maximum Contaminant Level
MGS	Maryland Geological Survey
MDE	Maryland Department of the Environment
MDE-BOM	Maryland Department of the Environment, Bureau of Mines
NHD	National Hydrography Dataset
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
RL	Reporting Level
SMCL	Secondary Maximum Contaminant Level
TDS	Total dissolved solids
TOC	Total organic carbon
USEPA	United States Environmental Protection Agency
USDA	United States Department of Agriculture
USGS	United States Geological Survey

µg/L	micrograms per liter
mg/L	milligrams per liter
mL	milliliter
meq/L	milliequivalents per liter
pCi/L	picocuries per liter
pt-co	platinum-cobalt units
ft	feet
ft bls	feet below land surface
µS/cm	microsiemens per centimeter at 25 degrees Celsius
<	less than
>	greater than

KEY RESULTS

Wellwater quality data from the Appalachian Plateau Physiographic Province of Maryland (Garrett County and western Allegany County) were compiled from local, state, and federal agencies. Concentrations of major ions, nutrients, trace elements, radioactivity, and indicators (pH, total dissolved solids, specific conductance, dissolved oxygen) were evaluated from 2,314 wells with respect to drinking water standards, geologic units, land use, topographic position, and other factors.

- Wellwater samples in the study area tended to have a near-neutral pH (median: 7.1), and were moderately hard (median: 70 mg/L as $CaCO_3$), reduced (dissolved oxygen <1 mg/L), and low in dissolved solids (median: 132 mg/L).
- Twenty-two percent of wells exceeded the Drinking Water Advisory for sodium of 20 mg/L (for individuals on a 500 mg/day restricted sodium diet).
- Manganese exceeded the 0.3 mg/L Lifetime Health Advisory in 15 percent of wells.
- Arsenic concentrations exceeded the Maximum Contaminant Level (MCL) of 0.010 mg/L in approximately 7 percent of wells sampled. Approximately 22 percent of samples collected in the Hampshire Formation exceeded the MCL.
- Fifty-seven percent of wells exceeded the Secondary Maximum Contaminant Level (SMCL) – established for taste, odor, or other aesthetic considerations – for iron (0.3 mg/L); the highest percentage of iron exceedances was observed in the Allegheny Formation (88 percent of wells); the lowest was in the Hampshire Formation (37 percent).
- Fifty-four percent of wells exceeded the manganese SMCL of 0.05 mg/L. The highest percentage of manganese exceedances were observed in the Allegheny Formation (96 percent of wells) and the lowest was in the Hampshire Formation (52 percent).
- Chloride concentrations exceeded the SMCL of 250 mg/L in about 2 percent of wells. Most of the high chloride concentrations are associated with road salt and possibly other surface-based anthropogenic chloride sources. A small subset of wells having chloride concentrations greater than 50 mg/L had a different chemical composition than other high-chloride wells in the study area, and more closely resembles the impact of shallow brackish water rather than road salt.
- Gross alpha-particle activity (an indicator of radioactivity in water) was low (only one in 61 wells tested exceeded the MCL of 15 pCi/L). The median radon concentration was 230 pCi/L.
- There were no clear differences in wellwater quality between wells in different land use categories, or between wells in different topographic settings. There were also no clear relations between wellwater quality and well depth, casing depth, or age of wells.
- Dissolved solids, hardness, pH, iron, and manganese tended to be higher and dissolved oxygen and nitrate tend to be lower in Appalachian Plateau wellwater compared to wellwater in the crystalline-rock regions in Baltimore, Cecil, and Howard Counties.

INTRODUCTION

The Appalachian Plateau Physiographic Province of western Maryland includes all of Garrett County and western Allegany County. Wellwater quality data have been collected in this region by many local, state, and federal agencies, including the Garrett and Allegany Health Departments, the Maryland Department of the Environment (MDE), the Maryland Geological Survey (MGS), and the U.S. Geological Survey (USGS). Water samples have been collected for various purposes and analyzed for differing chemical constituents. However, to date there has been no attempt to compile the available data into one source. MGS previously compiled available data in Garrett County from the Garrett County Health Department (GCHD), MDE, USGS, and MGS and evaluated data with respect to arsenic, chloride, manganese, and radon (Bolton and others, 2014). This report, which expands on that work, will provide a reference for future sampling efforts and identify problems with wellwater quality in the Appalachian Plateau.

PURPOSE AND SCOPE

The purpose of this report is to present and summarize wellwater quality data from drinking-water wells in the Appalachian Plateau Physiographic Province of Maryland. Data discussed in this report include major ions and field measurements (pH, specific conductance, dissolved oxygen), trace elements, and radionuclides. The report discusses how data from each source were acquired, edited, mapped, and how data from the separate databases were compared and combined. Constituent concentrations are discussed and evaluated with respect to the U.S. Environmental Protection Agency's (USEPA) Primary and Secondary Drinking Water Standards. Major ion concentrations are evaluated with respect to geologic unit and other factors. General geochemical environments are identified. The data are discussed with respect to site characteristics (land use, topographic position, and well construction). Wellwater quality in the Appalachian Plateau is compared to studies of the Maryland Piedmont.

LOCATION OF THE STUDY AREA

The study area is the Appalachian Plateau Physiographic Province of Maryland, which consists of all of Garrett County and the area of Allegany County located west of Dans Mountain (fig. 1). Land use in the Appalachian Plateau was approximately 77 percent forested, 15 percent agricultural, 6 percent residential/commercial, and 2 percent water (Homer and others, 2015). Elevation in the area ranges from 3,360 feet (ft) above sea level at Backbone Mountain (the highest point in Maryland) in Garrett County to about 730 feet on the Potomac River in Allegany County.

Water supply in the region is provided by a combination of community water systems (which utilize both surface water and groundwater sources) and individual water supplies consisting of private water wells and springs. Towns with community water systems in the study area include Accident, Barton, Bloomington, Crellin, Deer Park, Friendsville, Gorman, Grantsville, Kitzmiller, Lonaconing, Midland, Mountain Lake Park, Oakland, Frostburg, Westernport, McHenry, and Thayerville (Maryland Department of the Environment, 2016). Outside of these areas, water is supplied by private wells and springs.

GEOLOGIC SETTING

The Appalachian Plateau Physiographic Province of Maryland is underlain by sedimentary rocks of Permian, Pennsylvanian, Mississippian, and Devonian age (tab. 1) that consist of alternating layers of sandstone, siltstone, shale, conglomerate, limestone, and coal (Brezinski and Conkwright, 2013). These rocks are gently folded in a series of northeast-southwest-trending anticlines and synclines (fig. 2). Several economically viable coal seams have been mined in the Pennsylvanian-age rocks found in the synclines, while the Accident Dome and Deer Park anticlines have produced natural gas from the (Devonian) Needmore/Oriskany/Helderberg section (Schwarz, 1996). The Accident natural gas field has been used as a natural-gas storage field for more than 40 years (Schwarz, 1996). The Marcellus Shale, which is located several hundred feet above the Oriskany sand, is believed to be the source of natural gas in the Accident anticline (Brezinski, 2012). The Marcellus Shale occurs in the subsurface of the Appalachian Plateau, and outcrops further east in Maryland. It is Devonian in age, and includes very dark gray to black shale, interbedded with limestone and siltstone (Brezinski and Conkwright, 2013).

ACKNOWLEDGMENTS

This project was funded by the Maryland Department of Natural Resources and Maryland Department of the Environment. Rodney Glotfelty, Stephen J. Sherrard, and Craig Umbel (Garrett County Health Department) and Brian Dicken (Allegany County Health Department) provided County water quality data for this project, and provided comments on the manuscript. John Grace, Nancy Reilman, and John Smith (Maryland Department of the Environment, Water Supply Program) provided guidance and data from the community water systems. Al Hooker (Maryland Department of the Environment, Bureau of Mines Division) provided data from wells sampled near mines. Charles Walker, Anna Baker, and other staff from the U.S. Geological Survey Maryland-Delaware-DC Water Science Center provided assistance with the water quality data management. Colleague reviews by Brandon Fleming (U.S. Geological Survey), Simeon Suter (Pennsylvania Department of Conservation and Natural Resources, Bureau of Topographic and Geologic Survey), and Emelia Furlong (Maryland Department of the Environment) provided many helpful comments on the manuscript.

DATA SOURCES

Water quality data were compiled from the GCHD PatTrac database, wellwater radon data collected by GCHD, the USGS National Water Information System (NWIS), the MDE Public Water Supply Program, the ACHD, the MDE Bureau of Mines (MDE-BOM), and data collected by MGS for methane and other water quality studies. The data used for this study includes inorganic constituents, nutrients and radionuclides. Although some databases also included pesticides and other organic constituents, these data were not included in this study. 6,281 analyses were collected for 84 different water quality constituents; not all samples were analyzed for all constituents, and some wells were sampled multiple times. Sample dates range from 1946 to 2016, with 93 percent of samples collected after January 1, 2000. A total of 2,314 wells having permit numbers and chemical analyses were used in this study. The data set for this study only includes samples where the individual well permit number and locational data were available; results from unidentified wells were not included. Well construction and other data were obtained from MDE's Access well database (referred to hereafter as the MDE source table), a comprehensive Access file that contains information from well permit applications and well completion reports.

GARRETT COUNTY HEALTH DEPARTMENT

Water quality data from GCHD were retrieved from the client-management software PatTrac. The data, which were originally compiled for a previous report evaluating groundwater quality data in Garrett County, includes samples collected between August, 1995 and April, 2013 (Bolton and others, 2014). Samples were collected by GCHD and were analyzed by the Maryland Department of Health and Mental Hygiene (DHMH) laboratory. The PatTrac database includes alkalinity, arsenic, chloride, conductivity, fluoride, hardness, iron, lead, manganese, nitrate, nitrite, pH, turbidity, and total solids. Many wells were sampled multiple times, often before and after installation of a water treatment system, to assess the effectiveness of treatment. Well locations were determined or refined by several methods, including Global Positioning

Systems (GPS) locations provided by the drillers, geocoded addresses determined by the Garrett County 911 address database (which indicates the location of the dwelling structure on a property, which was used as a surrogate for well location), and location of property centroids (for properties smaller than 10 acres). Accuracy of many well locations was also improved by GCHD staff locating the wells using Google Earth[1] satellite imagery.

A second data set containing wellwater radon concentrations was also included in this evaluation. The GCHD collected radon samples from 252 wells between 1994 and 1998. In most cases, two radon samples were collected at each site. The radon values in this study represent the average of the samples for each well.

ALLEGANY COUNTY HEALTH DEPARTMENT

The ACHD provided two spreadsheets, one containing water chemistry information and another containing well information. Only wells included in both sheets were used. Wellwater chemistry data included alkalinity, arsenic, calcium, chloride, color, conductivity, fluoride, hardness, iron, nitrate-plus-nitrite, pH, sodium, sulfate, dissolved solids, and turbidity, although not all samples were tested for all constituents. Many wells were sampled multiple times, before and after treatment, to assess the effectiveness of treatment. Wells were checked against the location information in MDE's source table. Based on the location in the MDE source table, wells far to the east of the Appalachian Plateau section of Allegany County were removed. The remaining wells were then plotted with the source table coordinates, and compared to tax map and parcel information included in the ACHD well information spreadsheet and in the MDE source table, sketch maps on permits and well completion reports, and information in Maryland Department of Planning's Digital Parcel Mapping Files and Parcel Viewer and Maryland Department of Assessments and Taxation SDAT website. Where the locational information provided was satisfactory, the well locations were plotted at the centroid of each property. Wells that could not be located or that were located outside of the Appalachian Plateau Physiographic Province were not used. For parcels larger than ten acres, the well location was assumed to be adjacent to the structure on the property, as determined from Google Earth.

U.S. GEOLOGICAL SURVEY

Data were retrieved from the USGS NWIS for wells in Garrett County for an earlier report (Bolton and others, 2014) on September 22, 2013, and included a wide range of inorganic constituents and radionuclides. More recent data from Garrett County were retrieved on June 27, 2016, and data from western Allegany County were retrieved on June 21, 2016. Data from 111 wells were retrieved from the USGS dataset. Forty-eight of these wells were sampled by MGS personnel between 2008 and 2015 as part of an ongoing statewide groundwater monitoring program that began in 1987 (Bolton, 1996); these data are referred to as "USGS-MGS data." The rest of the wells, collected by USGS personnel, were collected between 1946 and 2016, and are referred to as "USGS historic data". Additionally, water quality data from test wells drilled as a pre-Marcellus Shale development baseline study are included (Drummond and others, in preparation). All these samples were analyzed for major ions, nutrients, trace elements, radon, gross alpha-particle and gross beta-particle activity, and field parameters (including pH, conductivity, dissolved oxygen). Water quality analysis for all USGS samples was performed by the U.S. Geological Survey National Water Quality Laboratory (NWQL) or its subcontracted laboratories. These wells comprise most of the major ion, trace element, and radionuclide data discussed in this report. Most of these samples are from private drinking water wells, although several are from monitoring wells. Wellwater samples collected by MGS were purged either from a spigot providing untreated water or a pump discharge line

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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.

until measurements of temperature, specific conductivity, pH, and dissolved oxygen were stable over three consecutive five-minute readings. (In rare cases, readings did not stabilize.) Samples were usually collected from a pressure tank spigot. Radon samples were collected using a syringe such that the sample did not come in contact with the atmosphere. Major ions, nutrients, trace elements, and gross alpha- and beta-particle activity were analyzed on 0.45-micron-filtered samples. Samples were shipped by overnight courier to NWQL and subcontracted laboratories on the same day they were collected.

The USGS historic data were collected for different projects with varying objectives. Samples collected prior to 2000 are identified as "presumed satisfactory" by the USGS (M. Pajerowski, U.S. Geological Survey, written commun., 2016). USGS data entered into the NWIS database after 2000 have been reviewed and are considered satisfactory.

The USGS NWIS contains the latitude and longitude of each well in the system. Coordinates are generally listed either to the nearest second or tenth of a second, depending on the method used to determine location. The locations given were converted to Maryland State Plane NAD83 coordinates using Corpscon6, and rounded to the nearest meter. Several monitoring wells used to monitor the effects of mining activity on groundwater quality were not used in the final database.

MARYLAND DEPARTMENT OF THE ENVIRONMENT

Water Supply Program

Data for public water supply wells were compiled mostly from paper files located at MDE's offices. Much of the water quality data in the files were related to systems that could comprise several wells and springs, and could therefore not be linked to specific wells or could not be assumed to be untreated ("raw") water. Other samples were identified as being untreated and could be linked to individual wells, mostly when a new well was being tested for suitability for use. These samples were tested for a range of inorganic constituents.

The locational information for wells in MDE's files varied, and included aerial imagery, topographic maps, maps on permits and completion reports, and descriptions of locations relative to other wells. The locational information in the files was supplemented by locational information in the MDE source table.

Bureau of Mines

Data from MDE-BOM were compiled from paper files kept in the Frostburg office, including a mining application and monitoring reports of individual wells in the Casselman Basin, a study of water supply and water quality, investigations of private wells in the Georges Creek Basin, and a mining application and investigations of private wells in the Upper Potomac River Basin. Data included acidity, alkalinity, aluminum, calcium, color, conductivity, hardness, iron, magnesium, manganese, pH, sulfate, total dissolved solids (TDS), total suspended solids, and zinc.

The locational information for wells in MDE-BOM files were derived from various sources (shapefile, maps from MDE studies, etc.), and included a shapefile of several wells created by an engineering company (likely with GPS), aerial imagery, topographic maps, plat maps, and maps on well permit applications and completion reports. Wells lacking locational data were not used.

MARLYAND GEOLOGICAL SURVEY METHANE STUDY

MGS collected water samples from 87 wells in 2012 – 2014 for a study of dissolved methane in untreated wellwater in the Appalachian Plateau Physiographic Province of Maryland. The samples were analyzed for ethane, ethene, isobutane, methane, n-butane, and propane, and field measurements (alkalinity, chloride, conductivity, dissolved oxygen, hardness, and pH). Only the field measurements are discussed in this report; the results of the methane data are discussed in Bolton and others (2016).

METHODS OF DATA ANALYSIS

Data from each source were compiled in separate Microsoft Excel files. Sites whose permit numbers could not be determined were removed. Microsoft Access was used to link wells by permit number to well characteristics stored in the MDE source table.

Well locations were determined using a variety of methods, depending on the information available, and plotted in ArcGIS using the Maryland State Plane Coordinate System, NAD83, meters. The Physiographic map of Maryland (Reger and Cleaves, 2008) was used to identify samples located within the Appalachian Plateau (Garrett County and western Allegany County). The geologic map of Garrett, Allegany, and western Washington Counties in Maryland (Brezinski and Conkwright, 2013) was used to correlate geologic units to individual wells. Fields were added to indicate the bedrock unit on which each well was mapped and the distance from the well to the nearest boundary between bedrock units. Wells that could not be located or fell outside the Appalachian Plateau Physiographic Province (as defined by Reger and Cleaves [2008]) were removed.

Data from all sources were combined into one file. The units, sample conditions, and analytical methods varied across the different databases, and in some cases were not known and thus, were assumed. Units were converted where necessary to allow for comparison across the data set. The data were organized so that each unique well had only one value for each constituent analyzed; this process is discussed below. If both field-filtered and unfiltered water were analyzed for one constituent for a sample, the unfiltered value was used, as it was assumed to be more representative of what would be consumed by a well owner. If a qualifier was listed in the original database indicating either no detection or below the reporting limit, the qualifier was removed and the constituent concentration was listed as being below the reporting limit of the data set.

Several wells and individual samples overlap between the different databases. These wells were compared for locational consistency across the different databases. Where a well had multiple locations, one location was selected based on proximity to a permanent structure and parcel shape, and all samples were assigned to that location.

One value for each constituent was selected for each site. If wells had multiple samples tested for a given constituent, the highest value was generally used (the median value was used for pH). This increased the likelihood that the value represents untreated water where the treatment method is not known, as treated water tends to have lower concentrations of constituents. Additionally, it will allow future samples to be compared to the highest previously known water quality value of each well. A total of 2,314 wells were included in the final database (fig. 3). Because samples were collected over a 70-year period, the data as a whole cannot be considered as a “snapshot” of wellwater quality at a specific time.

The finalized dataset has some suspect data of which only two samples were removed from the final database: a pH value of 0.4 and a dissolved oxygen concentration of 16 mg/L – this measurement was subsequently reviewed by the USGS and discarded from the dataset. Clerical and transcription errors are likely in such a large dataset, however, the data are still valuable as they can be evaluated together to look at the entire Appalachian Plateau of Maryland. Charge balance errors (CBE) were calculated for samples with major constituents, typically samples collected by the USGS, where CBE was low (samples less than 5 or 10 percent), increasing confidence that the data are of good quality.

To determine potential associations among chemical constituents and between constituents and other factors, a Spearman’s Rank Order Correlation was performed between major ions, TDS, pH, DO, and arsenic for all data. The Spearman Rank Order Correlation is a nonparametric test that does not require data points to be normally distributed with a constant variance or linearly related. The Spearman Rank Order Correlation coefficient does not assign variables as independent or dependent but rather the strength of association is measured between variables. Correlations were identified as significant with a p-value less than 0.05 and a correlation coefficient greater than the critical value of the Spearman’s Ranked Correlation Coefficient, dependent upon the number of sample pairs (Zar, 1984). Positive correlation coefficients indicate that the variables are increasing together, and negative correlation coefficients indicate that one variable increases as the other variable decreases.

WELLWATER QUALITY

This section presents an overview of individual constituents (including major ions, trace elements, nitrogen species, and radionuclides) and water quality indicators (TDS, total solids, pH, dissolved oxygen, hardness, and specific conductance) reported in wells from the Appalachian Plateau of Maryland. Individual water quality constituents are summarized in Appendix A and were reported from 11 geologic units throughout the Appalachian Plateau (tab. 1). Median values were calculated for constituents with more than ten samples.

WATER QUALITY IN RELATION TO DRINKING WATER STANDARDS AND HEALTH ADVISORIES

The USEPA has established drinking-water standards for many chemical constituents (U. S. Environmental Protection Agency 2012; 2016). Maximum Contaminant Levels (MCLs) are health-related standards for contaminants that may have an adverse effect on human health. They are enforceable standards for public water-supply systems but may not be enforceable for private water wells. Testing is required for new wells for some contaminants known to be present in an area, such as arsenic in Garrett County. A Lifetime Health Advisory (HA) is the concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects over a lifetime of exposure. Secondary Maximum Contaminant Levels (SMCLs) are standards that are established for aesthetic reasons (such as taste or odor) rather than for health-related reasons. Information on the health effects of regulated water quality constituents can be found on the USEPA website.

Overall, detections of chemical constituents above health-related standards were fairly uncommon. MCLs or HAs were exceeded in some wells for arsenic, barium, fluoride, lead, nitrate (in this report, “nitrate” refers to nitrate-plus-nitrite), sodium, sulfate, manganese, strontium, gross alpha-particle activity, and radium-226 plus radium-228 (tab. 2). Exceedances for barium, fluoride, lead, strontium, gross alpha-particle activity, and radium-226 plus radium-228 were observed in only one or two wells. Arsenic exceeded the MCL of 10 micrograms per liter (µg/L) in approximately 7 percent of wells tested; most samples were from wells completed either in the Hampshire Formation (more than half the exceedances) or the Foreknobs Formation; these are discussed later in this report. Arsenic is associated with skin damage, circulatory system problems, and other medical issues (U.S. Environmental Protection Agency, 2016; World Health Organization, 2010; 2016). Mortality risk increases for bladder, kidney, lung, liver, and colon cancers when exposed to arsenic in drinking water (Chen and others, 1985). The mortality risk for ingesting water with arsenic concentrations greater than 50 ppb has been estimated as high as 1 in 100 (National Research Council, 2001). Three out of 1,904 wells exceeded the 10 mg/L MCL for nitrate. Elevated concentrations of nitrate in water may cause serious illness in infants younger than six months, with symptoms including shortness of breath and blue-baby syndrome (U.S. Environmental Protection Agency, 2012). One well exceeded the 2 mg/L MCL for barium, which is associated with high blood pressure. One well exceeded the 4 mg/L MCL for fluoride, which is associated with mottled teeth in children and bone disease. Two wells exceeded the MCL for lead, which is associated with physical and developmental issues in children and kidney problems and high blood pressure in adults. One well exceeded the MCL for both radium-226-plus-radium-228 and gross alpha-particle activity (an indicator of radium-226 and other alpha-emitting isotopes). Radium is a known human carcinogen and is associated with bone sarcomas, head cancer, and deterioration of skeletal tissue (Agency for Toxic Substances and Disease Registry, 1990). About 22 percent of wells exceeded the 20 mg/L Drinking Water Advisory for sodium (a non-enforceable level recommended for individuals on a 500 milligrams-per-day restricted sodium diet [U.S.

Environmental Protection Agency, 2012]). About 15 percent of wells exceeded the manganese Drinking Water Advisory of 0.3 mg/L. Ten of 282 wells exceeded the 500 mg/L Drinking Water Advisory level for sulfate.

Many wells exceeded one or more SMCLs (tab. 3). Iron and manganese exceeded their SMCLs (0.3 and 0.05 mg/L, respectively) in 57 and 54 percent of wells, respectively. The highest percentage of iron exceedances were observed in the Allegheny Formation (88 percent of wells); the lowest was in the Hampshire Formation (37 percent). The highest percentage of manganese exceedances were observed in the Allegheny Formation (96 percent of wells) and the lowest was in the Hampshire Formation (52 percent). These metals, which are common naturally occurring components of groundwater throughout the state, can be present in both dissolved and colloidal form, although the widespread reducing conditions in the Appalachian Plateau are conducive to dissolved iron and manganese. Iron-bearing minerals in the region include pyrite and iron oxides and oxyhydroxides that often coat mineral surfaces. pH (a measure of how acidic or basic the water is) was outside the SMCL range of 6.5 to 8.5 in about 25 percent of samples tested, with most of these having pH less than 6.5 (slightly acidic). SMCL exceedances for color may be indicative of colloidal-size particles present in groundwater and possible mineral precipitation in the samples after sample collection. Chloride exceeded the SMCL of 250 mg/L in about 2.5 percent of wells tested. While salt beds and naturally occurring brines have been encountered in western Maryland and elsewhere in the Appalachian Plateau (Foster, 1980; Nutter and others, 1980; Dresel and Rose, 2010), most of the elevated chloride concentrations are more likely associated with human activities such as application of deicing salts to roads and back-flushing of water softening treatment systems.

WATER CHEMISTRY

Generally, the samples had near-neutral pH (median pH: 7.1), were moderately hard (median hardness 70 mg/L as $CaCO_3$), displayed reducing conditions (median dissolved oxygen: less than 1 mg/L), with fairly low TDS (median TDS 132 mg/L). Saturation indices were calculated for 101 water samples using the geochemical computer program - graphical user interface, PHREEQCI Version 3.0 (Parkhurst and Appelo, 2013). The saturation index (SI) is a measure of how close a mineral water is to equilibrium. When the SI for a particular mineral is negative, the water is undersaturated (dissolved) with respect to that mineral; when the SI is positive, the water is supersaturated (precipitated). Nine samples were supersaturated with respect to calcite and two samples were supersaturated with respect to dolomite. No samples were supersaturated with respect to gypsum. Calcite was supersaturated in all wells identified as brackish and this is likely caused by the “salting out” effect. Salt compounds (found in brackish waters) dissociate in aqueous solutions, where some of the water molecules are attracted to dissociated salt ions, thus forcing other ions to precipitate out. As salt is added to a solution (water becomes more brackish), the solubility of minerals decreases and precipitate out, and thus calcite is supersaturated in the brackish water (Appelo and Postma, 2010).

Water chemistry data were classified using a Piper diagram, which is a tri-linear diagram that is a graphical representation of water chemistry (fig. 4). Samples tended to be calcium-bicarbonate or calcium-magnesium-bicarbonate water types (figs. 4, 5). Sodium was the dominant cation in most samples for wells having more than 50 percent milliequivalent concentrations of chloride. Representative water samples from different geological formations are also displayed as Stiff diagrams, which show major ion analyses as polygons whose shapes are defined by the milliequivalent concentrations of ions (fig. 5). Several wells in the Devonian-age aquifers displayed sodium-chloride dominated water, specifically within the Accident Anticline. These wells will be discussed later in this report.

Total Dissolved Solids and Specific Conductance

TDS for all samples ranged from less than 10 to 2,560 mg/L (median: 132 mg/L) (fig. 6). TDS was measured using residue on evaporation where the water sample was dried at 180°C. Specific conductance is the ability of water to conduct an electrical current, and is measured in microsiemens per centimeter at 25 degrees Celsius (µS/cm). TDS is highly correlated with specific conductance (R^2=0.8926) (fig. 7). Because of this strong relation, specific conductance can be used as a quick and easy surrogate in the field for TDS. Specific conductance values ranged from 21 to 4,800 µS/cm for all samples (median: 197 µS/cm). The Conemaugh Group had the highest median TDS (211 mg/L) and highest median specific conductance (308 µS/cm). The Conemaugh Group is composed of mostly shale, sandstone, and limestone, which are more easily weathered because of their high solubility, likely resulting in higher TDS and specific conductance. Samples from the Pottsville Formation had the lowest specific conductance and TDS of all formations. The Pottsville Formation is very resistant to erosion, and forms the crests of Backbone, Big Savage, and other mountains in the Appalachian Plateau (Amsden, 1954).

pH

pH is a measure of the acidity or alkalinity of water; waters with a pH less than 7 are acidic, and those with a pH greater than 7 are alkaline (basic). pH values in the region ranged from 3.5 to 10 (median: 7.1). pH was less than 6.5 in 228 samples and greater than 8.5 in 35 samples (fig. 8). Wells in the Foreknobs Formation and the Mauch Chunk Formation both had the highest median pH values of 7.5. This more basic pH is likely due to the carbonate minerals as well as the absence of pyrite. Carbonate minerals tend to dominate acid-base reactions due to the fast dissolution kinetics of carbonates, which can buffer pH. Both the Pottsville (median pH: 6.5) and Allegheny Formations (median pH: 6.1) contain pyrite (R. Kavage Adams, Maryland Geological Survey, oral commun., 2017) which can lower pH as a result of sulfide oxidation (Langmuir, 1997). While the Appalachian Plateau wellwater is generally reduced, it is possible for zones of oxidation to occur, especially within sandstones or unconfined aquifers. Localized oxidized zones may facilitate pyrite oxidation in formations, thus acidifying wellwater.

Dissolved oxygen

Dissolved oxygen concentrations ranged from 0.1 to 9.8 mg/L (median: <1 mg/L) in wellwater samples from the Appalachian Plateau. Based on dissolved oxygen measurements, groundwater in the Appalachian Plateau is generally reduced (<1 mg/L), where 59 of the 114 samples were below the reporting limit of 1 mg/L. Dissolved oxygen is derived from atmospheric oxygen and is consumed by the decomposition of organic material and by the oxidation of oxidation/reduction (redox)-reactive minerals such as pyrite.

Color

Color in the Appalachian Plateau wellwater ranged from less than 1 to 130 color units (median: 5 color units). Color in wellwater may indicate colloidal-size particles present in groundwater and potentially mineral precipitates in samples after sample collection. Color in water can be derived from several potential sources, including leached organic material, oxidation of iron and manganese and fine-grained particulate matter. Color in a water sample is measured by comparing the sample to dilutions of various standards, composed of cobalt chloride and potassium chloroplatinate solutions, and color is reported in platinum-cobalt units (pt-co).

Total organic carbon

Total organic carbon (TOC) was analyzed in 34 samples; only three samples had concentrations greater than the reporting limit of 0.7 mg/L. TOC can be used as an indicator of groundwater chemistry as well as to detect organic spills and to help ensure that no organic contamination is present.

Major ions

Cations

Major cations in Appalachian Plateau groundwater include calcium, magnesium, sodium, potassium, iron, and manganese. (Ammonium [NH_4^+] is discussed in the section on nitrate.) Cation concentrations in groundwater are governed by aquifer minerals, redox conditions, travel time, position in the groundwater flow system, and other factors. General water chemistry can be identified on the Piper and Stiff diagrams (figs. 4,5), where aquifers are grouped by geologic age. Generally, the Pennsylvanian-age aquifers had high calcium concentrations, with a broad range of sodium, potassium, magnesium, iron, and manganese concentrations. The Mississippian-age aquifers generally had higher calcium concentrations, moderate to high sodium and potassium concentrations, and a low to moderate amount of magnesium, iron, and manganese. The Devonian-age aquifers had lower calcium concentrations in conjunction with higher sodium and potassium concentrations, with a moderate amount of magnesium, iron, and manganese.

The Conemaugh Group (Pennsylvanian) had the highest median magnesium (10.4 mg/L) and calcium (47.9 mg/L). The Conemaugh Group had the lowest median sodium (3.3 mg/L), where sodium concentrations (fig. 6) in all samples ranged from 0.3 to 846 mg/L (median: 5.1 mg/L). Elevated sodium may be derived from various sources including deicing salts applied to roads, connate seawater (remnant seawater that has not been flushed from the sediments) that has been vertically mobilized by historic gas wells and various test borings (Feth and others, 1965; Wilmoth, 1972), and backwash from water softening brines. The (Devonian) Hampshire Formation had the highest median sodium (12 mg/L) which may be due to large outcrop areas and thus more input for deicing salts. Potassium concentrations did not vary greatly between geologic units. Both sodium and potassium concentrations, typically dissolved from most rocks and minerals, can increase from contact with ancient brines and longer residence time.

Water hardness refers to the amount of dissolved calcium and magnesium in water (tab. 4). Hard water requires more soap to create a lather, produces soap scum and hard water deposits, and is generally not corrosive to plumbing systems. Water samples in the Appalachian Plateau (fig. 9) were moderately hard (median: 70 mg/L), with the hardest water observed in the Conemaugh Group (median: 131 mg/L as $CaCO_3$) and the softest water observed in the Allegheny Formation (median: 28 mg/L). Because the Conemaugh Group includes carbonate units, the wellwater contains calcium and magnesium, thus facilitating formation of hard water (Amsden, 1954). The Allegheny Formation is composed of shale, siltstone, claystone, sandstone, and coal, where water likely contains lower concentrations of calcium and magnesium, thus producing softer water.

Iron concentrations (fig. 10) ranged from less than 0.004 to 312 mg/L in all samples (median: 0.44 mg/L). Manganese concentrations (fig. 11) ranged from less than 0.01 to 22.78 mg/L in all samples (median: 0.07 mg/L). Iron and manganese were positively correlated (Spearman's rank order correlation; $P<0.05$) (Appendix B). The Allegheny Formation had the highest median iron (5.2 mg/L) and the highest median manganese (0.3 mg/L). The Hampshire and Mauch Chunk Formations had the lowest median iron (0.2 mg/L for both) and manganese (0.025 mg/L for both). Elevated iron within the Allegheny Formation may be derived from coal-bearing units, pyrite-bearing shales, or clay ironstone, observed as concretions (Singewald, 1909). Elevated iron and manganese concentrations may be derived from a slightly acidic pH, which may facilitate the dissolution of oxide minerals, and low dissolved oxygen content, which may facilitate the reduction of iron. Elevated manganese concentrations are likely derived from siderite concretions found within the Allegheny Formation and released as a result of reducing groundwater conditions (Maryland Geological Survey, 1902).

Anions

Major anions in Appalachian Plateau groundwater include alkalinity (bicarbonate), chloride, sulfate, and nitrate, which are derived from both natural and anthropogenic sources. General water chemistry can be identified from the Piper and Stiff diagrams, where aquifers are divided by geologic age (figs. 4, 5). Pennsylvanian-age aquifers had variable water chemistry, with no clear trend for anions. Mississippian-age aquifers had very little chloride, high alkalinity, and low sulfate and nitrate concentrations. Generally, Devonian-age aquifers had the highest concentrations of chloride, high alkalinity and low concentrations of sulfate and nitrate. The elevated chloride concentrations could be due to more roads located on Devonian outcrops or the large percentage of outcrop size. The generalized geologic map with Stiff diagrams (fig. 5) illustrates these water chemistry observations.

Alkalinity concentrations ranged from 0 to 482 mg/L (median: 83 mg/L). Alkalinity is the capacity of an aqueous solution to neutralize acid. At the pH range encountered in the study area, virtually all alkalinity is attributed to dissolved bicarbonate (HCO_3^-) (Hem, 1985), which is the dominant anion in most of the wells (fig. 4). Bicarbonate is derived from reactions of atmospheric and biogenic carbon dioxide with water and carbonate minerals. Bicarbonate values are calculated from total alkalinity values determined from titration. The Conemaugh Group had the highest and the Allegheny Formation had the lowest median alkalinity (135 mg/L and 41 mg/L, respectively). Both the Allegheny Formation and Conemaugh Group contain various amounts of limestone, however, the Conemaugh Group has more prevalent limestone intervals as well as calcareous redbeds (R. Kavage Adams, Maryland Geological Survey, written commun., 2017).

Sulfate concentrations ranged from 0.08 to 1,905 mg/L (median: 15.7 mg/L) (fig. 6). Naturally occurring sulfate can be mobilized by the dissolution of sulfur-containing minerals such as pyrite, barite, anhydrite, and gypsum. Anthropogenic sulfate is a major dissolved constituent in coal ash leachate (Chugh and others, 1996). The Greenbrier Formation had the lowest median sulfate (8.1 mg/L). The Conemaugh Group had the highest median sulfate (19.5 mg/L), likely due to the presence of coal seams (Brezinski, 2016).

Chloride concentrations ranged from 0.1 to 4,300 mg/L (median: 10 mg/L). Chloride concentrations exceeded the SMCL of 250 mg/L in 47 of 1,885 wells. Chloride in groundwater can be derived from both human and natural sources. Sources of chloride related to human activity include road deicing salts, agricultural amendments, water softener backwash, and septic effluent. Naturally-occurring sources in the region include diluted brines and evaporate minerals. Most of the wells exceeding the SMCL of 250 mg/L chloride are near Interstate 68 or state-maintained roads (fig. 12), suggesting impacts from deicing salts. For wells having 10 mg/L (the overall median value) or less chloride, the median distance was approximately 235 ft, compared with a median distance of about 338 ft for wells with more than 10 mg/L chloride (fig. 13). County-maintained roads are treated predominantly with crushed limestone and fly ash, with lesser amounts of deicing salts (P. Harvey, Garrett County Department of Public Works, oral commun., 2017).

Chloride:bromide mass ratios can be used to help identify potential sources of chloride to groundwater. Chloride and bromide are relatively unreactive in groundwater, are not easily sorbed by geological materials, and are not involved in oxidation-reduction reactions, and therefore can be useful as indicators of chloride sources to groundwater (Andreasen and Fleck, 1997; Davis and others, 1998; Mullaney and others, 2009). Connate saline waters typically have chloride:bromide ratios between 200 and 400; waters impacted by halite dissolution (road salts and other surface activities) typically have ratios greater than 1,000, although variations in these ranges may occur (Davis and others, 1998). In western Pennsylvania, chloride:bromide ratios in brines generally range from 100 to 300 (Poth, 1962); saline springs and basin brines in Illinois are generally between 300 and 500 (Panno and others, 2005).

Twenty samples from 18 wells had both chloride and bromide analyses above their respective reporting limits. When chloride:bromide ratios are plotted against chloride concentrations, two patterns can be seen for wells with more than about 20 mg/L chloride (fig. 14). In one group of wells, chloride:bromide ratios increased with increasing chloride concentrations, and were consistent with the chloride:bromide ratio measured in a sample dissolved road salt from a State Highway Administration salt storage facility in Garrett County. Most of these wells were located near state roads or Interstate 68, and the suspected chloride source is road deicing salts, although backflushing of ion-exchange-type water softeners with saltwater brine may also be a source. A second group of wells (hereafter referred to as the shallow brackish-water wells) had chloride:bromide ratios between 100 and 200, and the ratio did not increase with chloride concentrations. Chloride concentrations in most of these wells exceeded 100 mg/L. The chloride:bromide ratios are consistent with oilfield brines (although brines are much more concentrated). These wells also have higher ionic proportions of sodium and lower proportions of calcium than other high-chloride wells in the area (fig. 15). Most of these shallow brackish-water wells, which range in depth from 80 to 780 ft below land surface, are located approximately 2 miles northeast of the town of Accident, and are located along roads that are not typically treated with road salt. This occurrence of salty groundwater in the area northeast of Accident was identified in the 1970s (E. Dougherty, Maryland Department of the Environment, written commun., 2002). Although the chloride:bromide ratios in the wells are similar to that of landfill leachate, this is not believed to be the source, as there are no landfills in the area where the shallow brackish water is found.

Brines are present in deep sedimentary aquifers of the Appalachian Plateau, and have chloride concentrations of several tens of thousands of milligrams per liter (Poth, 1962; Slaughter, 1962). Brackish groundwater may result from shallow fresh water mixing with deeper saline water or from dissolution of Paleozoic evaporate deposits and mixed with the shallow freshwater aquifers. The Texas Eastern Transmission No. 2 Bowman-Seibert well, located in the Accident Dome in northern Garrett County, encountered salt beds at a depth of 8,396 to 8,959 ft below land surface (bls) in Garrett County (Nutter and others, 1980). Brackish groundwater has been observed in the Hampshire Formation (Catskill Formation) and Appalachian Plateau since the 1930’s (Piper, 1933; Feth and others, 1965) at depths ranging from 500 to 1,000 ft bls. The fresh water/brackish water interface is often within several hundred feet of the land surface in the Appalachian Plateau; the presence of salt springs in Pennsylvania attests to the near-surface circulation of brine (Trapp and Horn, 1997). Depth to the base of fresh groundwater was found to vary greatly in West Virginia (Foster, 1980). Fluctuations in the elevation of the interface can result from complicated geological and hydrological conditions, including continuity of the confining units, historical recharge patterns, thermal regime, fracture density, landscape evolution, and brine density (Trapp and Horn, 1997; Lahm and others, 1998; Yager and others, 2017). Fractures and/or faults may have provided pathways for fluid transport from deeper to shallower portions of the flow system. Brezinski (2015) mapped several faults in the vicinity of the shallow brackish-water wells that extend from depth to the surface.

Another possible source of brackish water is brine from the deeper geologic units that may have migrated upward along improperly cased or abandoned gas wells in vicinity of these wells. Natural gas was discovered in the Accident Dome area in 1953, and 19 gas production wells were eventually drilled (Schwarz, 1996). Since 1962, the Accident Gas field has been used as a natural gas storage facility. However, there are few known gas wells in the immediate vicinity of the shallow brackish-water wells; furthermore, many water wells in the area near the affected wells do not have elevated chloride concentrations (Nutter and others, 1980; E. Dougherty, Maryland Department of the Environment, written commun., 2002). Additional investigation is needed to explain the localized presence of shallow brackish water in Garrett County.

The principal nitrogen species in wellwater are nitrate (NO_3^-) and ammonium (NH_4^+). Nitrogen is highly mobile in aquatic systems. Sources of nitrogen to groundwater include fertilizers, organic waste, leakage from septic systems and sewage, and decomposition of naturally occurring organic material. Nitrogen compounds are also present in the atmosphere, partially due to the burning of fossil fuels, and may enter groundwater through the infiltration of precipitation (Hem, 1985; U.S. Environmental Protection Agency, 2016). In this report, “nitrate” includes values reported as nitrate-plus-nitrite, since nitrite concentrations were negligible relative to nitrate in samples that were analyzed for both.

Nitrate concentrations are relatively low in the Appalachian Plateau wellwater. Ninety percent of wells had less than 1 mg/L nitrate; almost one-quarter of samples were less than reporting levels (fig. 6). Nitrate concentrations ranged from less than 0.01 to 38 mg/L as N (median: 0.2 mg/L). Ammonium, the dominant nitrogen species under reducing conditions, was analyzed in 54 samples; concentrations ranged from less than 0.01 to 1.68 mg/L (median: 0.06 mg/L) (fig. 6). Only three of 1,904 wells (0.2 percent of all samples) exceeded the MCL of 10 mg/L, compared with about 33 percent of wells on the Delmarva Peninsula (Delaware, Maryland, and Virginia) (Hamilton and others, 1993). The Delmarva Peninsula has a larger percentage of agricultural land (48 percent of land area compared with 15 percent in the Appalachian

Plateau) and more intense use of applied nitrogen on the Delmarva Peninsula (DeBrewer and others, 2007; Ator and Denver, 2015). Wells also tend to be shallower on the Delmarva Peninsula and draw water from the unconfined surficial aquifer, which is very susceptible to contamination. It may also reflect a prevalence of anoxic conditions in the Appalachian Plateau groundwater, which would favor ammonium as the stable nitrogen phase. Nitrate and ammonium tend to be mutually exclusive in wellwater: nitrate concentrations above about 0.5 mg/L tend to have little or no detectable ammonium present, and nitrate is rarely detected in samples having more than 0.1 mg/L ammonium (fig. 16a). Samples with detectable ammonium have little or no dissolved oxygen present, and oxic waters rarely have ammonium present (fig. 16b). Samples with both detectable ammonium and dissolved oxygen may indicate a mixture of oxygen-rich and oxygen-poor waters, which is plausible given that most of the wells in the Appalachian Plateau have long open intervals and could be drawing water from different parts of the aquifer.

Trace Elements

Trace constituents are defined as elements that are typically found in concentrations of less than 1 mg/L in natural waters (Hem, 1985). They may occur naturally as a result of mineral dissolution; they may also be derived from a variety of anthropogenic sources, including wastewater from industries, refineries, mines, drilling, agricultural runoff and pesticide use, corrosion of pipes, septic systems, sewage, water treatment, and the burning of coal and gasoline (Hem, 1985; U.S. Environmental Protection Agency, 2016).

Concentrations of trace element in the Appalachian Plateau generally were low (relative to drinking-water standards), with the exception of arsenic. Samples from 1,434 wells were tested for arsenic, 824 of which had concentrations below reporting levels (fig. 17). Concentrations ranged from less than the reporting level to 8 mg/L. Several wells with reported arsenic concentrations greater than 1 mg/L may represent sampling or recording errors. Twenty-two percent of wells in the Hampshire Formation and 9 percent of wells in the Foreknobs Formation exceeded the MCL of 0.010 mg/L arsenic. Only two percent of wells in all other geologic formations exceeded the MCL (figs. 17, 18). Overall, arsenic concentrations exceeded the MCL in more than 7 percent of samples. Elevated arsenic concentrations have also been observed in groundwater in the Hampshire Formation of northwest Virginia and in the Catskill Formation (equivalent to the Hampshire Formation) in Somerset County, Pennsylvania (which borders on northern Garrett County) (McElroy, 2000; VanDerwerker, 2016).

Naturally-occurring arsenic has been identified in different geological environments in Maryland, (Drummond and Bolton, 2010), elsewhere in the United States (Maine, New Hampshire, the upper Midwest, Nevada, Arizona, southern California, and Texas) (Ryker, 2003), and around the world (Bangladesh, India, China, Vietnam, Taiwan, Thailand, and Nepal) (Smedley, 2003). Arsenic has several oxidation states and can exist in inorganic or organic forms. Potential sources of arsenic within the Appalachian Plateau include arsenopyrite, metal hydroxides, oxyhydroxides, and clay minerals within shales, such as illite and smectite. Arsenopyrite (FeAsS) is the most abundant arsenic-bearing mineral and generally exists in anaerobic environments along with other minerals such as sulfides, oxides, phosphates, carbonates, and silicates (Smedley and Kinniburgh, 2002). Arsenic can be released from aquifer solids into groundwater in several ways, including oxidation-reduction reactions (including reductive dissolution of iron oxides and oxidation of pyrite), desorption from mineral surfaces, and competition of ions for adsorption sites (Woolson, 1977; Violante and Pigma, 2002). In some cases, relations between arsenic concentrations and those of other chemical constituents (e.g., pH, sulfate, iron, manganese) can be indicative of an arsenic source or a particular mobilization mechanism. However, no obvious relations or associations between constituents were observed in this dataset. Determining the sources and mobilization mechanisms of groundwater arsenic in the Maryland Appalachian Plateau was beyond the scope of this project, and would require a comprehensive approach involving detailed geochemical and hydrogeologic methods.

Radionuclides

Radionuclides and radionuclide indicators that have been analyzed in the study area include radium-226 (Ra-226), radium-228 (Ra-228), gross alpha-particle activity (GAPA), gross beta-particle activity (GBPA), and radon-222 (Rn-222). GAPA and GBPA indicate the presence of alpha-particle-emitting radionuclides (such as Ra-226 and Ra-224) and beta-particle-emitting radionuclides (such as Ra-228), but do not measure concentrations of individual isotopes. GAPA and GBPA analyses are usually performed as a preliminary test for the presence of radionuclides: if elevated levels are detected, then follow-up testing is performed specifically for Ra-226 and Ra-228, which are known human carcinogens (Cancer Group A) (U.S. Environmental Protection Agency, 2012). Private water wells are not regularly tested for radionuclides in the Maryland Appalachian Plateau. Most GAPA and GBPA samples were obtained from the USGS dataset, with each water sample being analyzed twice: once within approximately three days after sample collection ("short-term" GAPA and GBPA) and again at about 30 days after sample collection ("long-term" GAPA and GBPA). If a sample showed a large decrease in GAPA or GBPA over this time period, this may indicate the presence of short-lived alpha- or beta-emitting isotopes.

GAPA was analyzed in samples from 61 wells. Short-term GAPA ranged from less than 1 to 12 pCi/L (n=48); 20 samples were less than 1 pCi/L. Long-term GAPA (including samples with unknown lag time between sample collection and analysis) ranged from less than 1 to 20 pCi/L (n=61); 54 samples were less than 3 pCi/L (Appendix A). Only one well exceeded the 15 pCi/L MCL for GAPA; this was one of the wells with elevated chloride and a chloride:bromide ratio that suggests a brackish-water source (discussed earlier). Because brines are known to contain naturally occurring radioactive materials (Fisher, 1998; Rowan and others, 2011), this is consistent with a non-anthropogenic source of GAPA. Another well had 15 pCi/L long-term GAPA, with a corresponding short-term GAPA of 12 pCi/L. Short-term GAPA and long-term GAPA showed little variation and thus the results were combined in Appendix A, while retaining the highest concentration of the two analyses.

Fifty-four wells were tested for GBPA. Short-term GBPA ranged from less than 1 to 11.4 pCi/L (n=48); at least seven samples were less than 1 pCi/L. Long-term GBPA (including those with unknown lag time between sample collection and analysis) ranged from less than 1 to 11.4 pCi/L (n=54); 46 samples were less than 4 pCi/L. Short-term GBPA and long-term GBPA showed little variation and thus the results were also combined in Appendix A, while retaining the highest concentration of the two analyses.

Ra-226 and Ra-228 were each measured in four wells. Ra-226 ranged from 0.61 to 4.9 pCi/L; Ra-228 ranged from 0.41 to 3.1 pCi/L. Ra-226 plus Ra-228 exceeded the MCL of 5 pCi/L in only one well. Significantly, GAPA in this well was 9 pCi/L, which is less than the 15 pCi/L MCL for GAPA that triggers further regulatory testing specifically for Ra-226 and Ra-228. This suggests that short-term GAPA may be insufficient as a screening tool for radium-226-plus-radium-228. This well also had chloride:bromide ratio suggesting a shallow brackish-water source, and is located approximately 1,500 ft from the well that exceeded 15 pCi/L.

Radon-222 was measured in 292 wells, most of which were sampled in the 1990's by the GCHD. Radon concentrations ranged from less than 20 to 32,800 pCi/L (median: 230 pCi/L). Samples from the Mauch Chunk and the Hampshire Formations had the highest median concentrations (1,190 and 980 pCi/L, respectively); the Allegheny Formation has the lowest median concentration (55 pCi/L). Median radon concentrations from all other formations were less than 500 pCi/L. No final MCL has been established for radon in drinking water; however, the U.S. Environmental Protection Agency (1999) had previously proposed a two-tiered approach. For states that develop a multimedia mitigation plan in place for reducing radon in air, the proposed MCL for public water systems was 4,000 pCi/L. If no multimedia mitigation plan is established, the proposed MCL was 300 pCi/L (U.S. Environmental Protection Agency, 1999). Four wells in this study (1.3 percent) exceeded 4,000 pCi/L; 135 wells (46 percent) exceeded 300 pCi/L.

FACTORS RELATED TO WELLWATER QUALITY

Land Use

Land use in the Appalachian Plateau was determined by the United States Department of Agriculture (USDA) Geospatial Data Gateway and obtained as a raster file for the state of Maryland (Homer and others, 2015). Land use classifications were condensed from 15 classifications to three generalized categories (tab. 5). The original land use classification "open water" was removed as wells identified with this classification are not located within open water and this is likely due to the 30 x 30-meter grid spacing of the land use layer. Wells identified in the "open water" category were not included in box-and-whisker plots for each of the three generalized categories. Based on the Homer and others (2015) data layer, land use coverage in the Appalachian Plateau was approximately 77 percent forested, 15 percent agricultural, 6 percent residential/commercial, and 2 percent open water. Of the wells evaluated in this report, 63 percent were in forested areas, 17 percent were in agricultural areas, and 19 percent were in residential/commercial areas (fig. 19).

Overall, there were no clear differences between water quality constituents in different land use categories. Median chloride concentrations appeared slightly higher in commercial/residential areas than other land use categories (fig. 20). There was little difference in nitrate concentrations between land use categories. These observations are not considered conclusive because of the potential land use changes over the time span represented by the data.

Topographic position

Wells were classified as being in either valley or upland topographic positions, based on whether they were located within 1,000 ft of a major National Hydrography Dataset (NHD) flowline (valley setting) or more than 1,000 ft from such a flowline (upland setting). Using this methodology, 1,117 wells were determined to be in valley settings; 1,197 wells were in upland settings. Major ions, TDS, pH, DO, and arsenic were visually examined for variations between the upland and valley topographic settings using box-and-whisker plots for each setting, where selected constituents of interest were included in this report (fig. 21). There were no major differences in any of the constituents concentrations between upland and valley wells.

Well characteristics

Spearman's rank-order correlations were calculated between chemical constituents (major ions, arsenic, TDS, pH, dissolved oxygen) and well characteristics (well age, casing depth, total well depth). Several constituents were selected for a more focused review (App. B). Positive correlations ($p<0.05$) were identified between well casing depth and calcium, and total depth and arsenic. Slight negative correlations of interest were identified between well age, and sulfate and well age and sodium, and well age and potassium. Correlation coefficients are relatively small (0.215 to -0.290), and the correlations are not considered definitive. The lack of strong correlations suggest that at the scale of this study, well characteristics do not affect water quality. However, at a local level, well construction may mitigate specific issues. For example, if high-chloride groundwater is encountered at shallow depths while drilling a well, a second well can be drilled to a deeper depth, and the shallow high-chloride zone cased and grouted such that only deeper, fresher water is pumped (L. Brenneman, Brenneman Well Drilling Inc., oral commun., 2017). Due to the limitations of the data set, these observations are not considered conclusive.

WELLWATER QUALITY IN THE APPALACHIAN PLATEAU IN RELATION TO THE PIEDMONT AND COASTAL PLAIN PHYSIOGRAPHIC PROVINCES OF MARYLAND

There are distinct differences in wellwater quality between the Appalachian Plateau and other areas of the state. Dissolved solids, hardness, pH, iron, and manganese tend to be higher and dissolved oxygen and nitrate tend to be lower in Appalachian Plateau wellwater compared to wellwater in the crystalline-rock regions in Baltimore, Cecil, and Howard Counties (tab. 6) (Otton and others, 1988; Dine and others, 1995; Bolton, 1998). The differences in dissolved solids, hardness, and pH may be explained in part by general lack of carbonate minerals in those counties in the Piedmont. The Piedmont counties in this comparison are underlain by dense crystalline rock that is resistant to chemical weathering (with the exception of areas in the Piedmont that are underlain by marble), whereas bedrock in the Appalachian Plateau includes carbonate formations as well as formations that have carbonate minerals as cementing agents (Amsden, 1954). Iron and manganese concentrations tend to be higher in Appalachian Plateau wellwater, likely due to more prevalent reducing conditions. Groundwater circulation is shallower in crystalline-rock terrain, and groundwater occurs under water-table conditions; both of these characteristics favor oxidizing conditions and hence lower iron and manganese concentrations.

Nitrate concentrations in Appalachian Plateau wellwater are low in comparison to both the crystalline-rock aquifers of the Piedmont and the unconsolidated sand and gravel aquifers of the Delmarva Peninsula in Maryland. Less than one percent of all samples in the Appalachian Plateau exceeded the nitrate MCL of 10 mg/L, compared with about 33 percent of wells on the Delmarva Peninsula (Delaware, Maryland, and Virginia) (Hamilton and others, 1993). While much of this may be related to more agricultural land on the Delmarva Peninsula (48 percent of land area compared with 15 percent in the Appalachian Plateau) and different types of agricultural practices, it also relates to hydrogeologic conditions of the aquifers. Many of the Coastal Plain wells are completed in the (unconfined) surficial aquifer. Although these aquifers are geologically distinct from crystalline-rock aquifers of the Piedmont, groundwater tends to be oxygen-rich in both areas due to shallow circulation and rapid recharge from precipitation, thus facilitating nitrate as the dominant nitrogen form.

SUMMARY AND CONCLUSIONS

Wellwater quality data from the Appalachian Plateau Physiographic Province of Maryland (Garrett County and western Allegany County) were compiled from local, state, and federal agencies. Concentrations of major ions, nutrients, trace elements, radioactivity, and indicators (pH, total dissolved solids, specific conductance, dissolved oxygen) were evaluated from 2,314 wells with respect to drinking water standards, geologic formations, land use, topographic position, and other factors. Well locations were obtained, established, or refined by several methods, including GPS locations included with water quality reports, well permit applications and completion reports, geocoded addresses, 911 location database (Garrett County only), location of property centroids (for properties smaller than 10 acres), and agency staff knowledge of sites. For wells with multiple samples, the highest value of each constituent was used in the assessment, so that the dataset represents the maximum concentrations. Samples spanned the time period from 1946 to 2016, with 93 percent of samples having been collected since January 1, 2000.

Overall, wellwater in the study area generally had a near-neutral pH (median: 7.1), was moderately hard (median: 70 mg/L as $CaCO_3$), low in dissolved oxygen (median: <1 mg/L), and low in total dissolved solids (median: 132 mg/L). Samples tended to have calcium-bicarbonate or calcium-magnesium-bicarbonate water types. Overall, the concentrations of chemical constituents were below health-related standards, with the exception of arsenic. Arsenic concentrations exceeded the U.S. Environmental Protection Agency's Maximum Contaminant Level (MCL) of 0.010 milligrams per liter in about 7 percent of all wells. Approximately 22 percent of wells completed in the Hampshire Formation and 9 percent of wells in the Foreknobs Formation exceeded the arsenic MCL. Drinking Water Standards for other health-related criteria were exceeded in only one or two wells for barium, fluoride, lead, strontium, gross alpha-particle activity, and radium-226-plus-radium-228. Twenty-two percent of wells exceeded the Drinking Water Advisory for sodium of 20 mg/L (for individuals on a 500 mg/day restricted sodium diet). Manganese exceeded the 0.3 mg/L Lifetime Health Advisory in fifteen percent of wells. The median nitrate concentration was 0.2 mg/L; only three of 1,804 wells having nitrate analyses exceeded the MCL of 10 mg/L as N. This low rate of exceedance relative to other areas of Maryland is likely due to smaller amounts of agriculture, deeper wells, and anoxic conditions (dissolved oxygen <1 mg/L) in the Appalachian Plateau.

Fifty-seven percent of wells exceeded the Secondary Maximum Contaminant Level (established for taste, odor, or other aesthetic considerations) for iron (0.3 mg/L). The highest percentage of iron exceedances were observed in the Allegheny Formation (88 percent of wells); the lowest was in the Hampshire Formation (37 percent). Fifty-four percent of wells exceeded the manganese SMCL of 0.05 mg/L. The highest percentage of manganese exceedances were observed in the Allegheny Formation (96 percent of wells) and the lowest was in the Hampshire Formation (52 percent).

Chloride concentrations exceeded the SMCL of 250 milligrams per liter in about 2 percent of wells. Most of these high chloride concentrations are associated with road salt and possibly other surface-based anthropogenic chloride sources. A small subset of wells having chloride concentrations greater than 50 mg/L has a different chemical composition than other high-chloride wells in the area, and more closely resembles shallow brackish water than road salt impacts. Gross alpha-particle activity (an indicator of radioactivity in water) was low (only one in 61 wells tested exceeded the MCL of 15 pCi/L). The median radon concentration was 230 pCi/L. Dissolved solids, hardness, pH, iron, and manganese tended to be higher and dissolved oxygen and nitrate tended to be lower in Appalachian Plateau wellwater compared to wellwater in the crystalline-rock regions in Baltimore, Cecil, and Howard Counties. There were no clear differences in wellwater quality between wells in different land use categories, or between wells in different topographic settings (valleys vs. upland). There were also no clear relations between wellwater quality and well depth, casing depth, or age of wells.

Several areas of investigation would help improve our understanding of wellwater quality and hydrochemical processes. These include:

- Analyze future residential water sample for bromide as well as chloride. Chloride:bromide ratios would help identify areas in Garrett County where brackish water may exist at relatively shallow depths.
- Develop subsurface contour maps showing the tops of the major geologic units in the Appalachian Plateau. These could be used to determine whether wells have open intervals that span more than one geologic unit, and could help refine the current understanding of water quality in individual aquifers.
- Test selected wells for specific forms of arsenic (As^{3+}, As^{5+}, inorganic versus organic forms). Different forms have different degrees of toxicity.
- Investigate the geological sources of arsenic as well as arsenic mobilization processes.

Lack of information on sample collection and analytical procedures limits the interpretation of data. Documentation of the PatTrac database and other county databases would be highly encouraged to ensure data quality and produce the most meaningful data. Similar organization of databases among counties would allow for more thorough analysis and interpretation for water quality assessments.

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Appendix A. Summary of water quality data for wells in the Appalachian Plateau Physiographic Province of Maryland with respect to geologic unit.

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

Geologic unit	*Dominant water type*	**Alkalinity (mg/L)**		**Aluminum (mg/L)**		**Ammonium (mg/L)**	
		Range (n)	**Median**	**Range (n)**	**Median**	**Range (n)**	**Median**
Monongahela Group	--	144-214 (4)	--	0.2 (1)	--	--	--
Conemaugh Group	Calcium bicarbonate and sodium bicarbonate	<0.1- 454 (411)	135	<0.0022-1 (60)	0.04	<0.01-1.68 (19)	0.24
Allegheny Formation	Calcium-sodium bicarbonate	<1-169 (103)	41	<0.003-0.49 (8)	--	0.04-0.16 (5)	--
Pottsville Formation	variable	<0.1-281 (136)	61	<0.003-0.0048 (4)	--	<0.01-0.08 (4)	--
Mauch Chunk Formation	Calcium bicarbonate	4-391 (96)	80	<0.003-0.274 (3)	--	<0.02 (2)	--
Greenbrier Formation	Calcium bicarbonate	1-162 (59)	78	<0.1 (4)	--	<0.01-0.08 (4)	--
Purslane Formation	Calcium bicarbonate	1-370 (99)	77	<0.08 (5)	--	0.015-0.064 (3)	--
Rockwell Formation	variable	4-299 (78)	77	<0.0034-0.025 (3)	--	0.026--0.07 (2)	--
Hampshire Formation	variable	4-235 (280)	68	<0.0022-0.068 (12)	0.002	<0.01-0.311 (11)	0.082
Foreknobs Formation	Calcium-magnesium bicarbonate	0-482 (246)	80	<0.003-0.0277 (4)	--	<0.01-0.179 (4)	--
Harrell-Brallier-Sherr Formations	--	59 (1)	--	--	--	--	--
All	Calcium bicarbonate	0-482 (1,513)	83	<0.0022-1 (104)	0.01	<0.01-1.68 (54)	0.06

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Antimony (mg/L)		Arsenic (mg/L)		Barium (mg/L)	
Geologic unit	**Range (n)**	**Median**	**Range (n)**	**Median**	**Range (n)**	**Median**
Monongahela Group	--	--	--	--	--	--
Conemaugh Group	<0.006 (20)	<0.000027	<0.0001-0.03 (286)	<0.002	0.00814-1.9 (25)	0.15
Allegheny Formation	<0.01 (5)	--	<0.00004-0.01 (97)	<0.002	0.0506-0.275 (6)	--
Pottsville Formation	<.000027-0.000046 (4)	--	<0.0001-4 (153)	<0.002	0.0196-0.142 (4)	--
Mauch Chunk Formation	<0.000027-0.00025 (2)	--	0.00038-0.65 (96)	<0.002	0.0156-0.0785 (2)	--
Greenbrier Formation	<0.002 (5)	--	<0.0001-3.5 (56)	<0.002	0.0407-1.65 (5)	--
Purslane Formation	<0.002 (7)	--	0.0013-0.02 (113)	<0.002	0.014-0.128 (7)	--
Rockwell Formation	<0.000054 (2)	--	0.00009-0.07 (98)	0.002	0.0504-0.1 (3)	--
Hampshire Formation	<0.005 (16)	0.00009	<0.0001-0.2 (289)	0.005	<0.0028-3.65 (17)	0.164
Foreknobs Formation	<0.000027-0.000327 (4)	--	<0.002-8 (245)	0.002	0.146-0.704 (4)	--
Harrell-Brallier-Sherr Formations	--	--	<0.002 (1)	--	--	--
All	all <0.01 (65)	0.000029	<0.00004-8 (1,434)	<0.002	<0.0028-3.65 (73)	0.12

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

Geologic unit	Beryllium (mg/L)		Boron (mg/L)		Bromide (mg/L)	
	Range (n)	Median	Range (n)	Median	Range (n)	Median
Monongahela Group	--	--	--	--	--	--
Conemaugh Group	<0.002 (24)	<0.00002	<0.01-0.105 (22)	0.021	<0.01-0.066 (16)	0.03
Allegheny Formation	<0.000006-0.0008 (6)	--	<0.005-0.1 (5)	--	<0.03-0.089 (4)	--
Pottsville Formation	<0.00002-0.000198 (4)	--	<0.005-0.04 (4)	--	<0.03 (4)	--
Mauch Chunk Formation	<0.00002-0.000019 (2)	--	0.009-0.013 (2)	--	<0.03-0.037 (2)	--
Greenbrier Formation	<0.002 (6)	--	<0.005-0.043 (3)	--	<0.03-0.102 (3)	--
Purslane Formation	<0.001 (7)	--	0.011-0.037 (3)	--	<0.02-0.045 (3)	--
Rockwell Formation	<0.00002-0.000037 (2)	--	0.005-0.224 (2)	--	0.014-0.03 (4)	--
Hampshire Formation	<0.001 (16)	<0.00002	<0.005-0.488 (12)	0.0905	<0.02-10.1 (12)	0.219
Foreknobs Formation	<0.00002 (4)	--	0.009-0.378 (4)	--	<0.03-2.62 (4)	--
Harrell-Brallier-Sherr Formations	--	--	--	--	--	--
All	all <0.002 (71)	<0.00002	<0.005-0.488 (57)	0.021	<0.01-10.1 (52)	0.03

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

Geologic unit	Cadmium (mg/L) Range (n)	Cadmium (mg/L) Median	Calcium (mg/L) Range (n)	Calcium (mg/L) Median	Chloride (mg/L) Range (n)	Chloride (mg/L) Median
Monongahela Group	--	--	--	--	0.25-11 (3)	--
Conemaugh Group	<0.005 (25)	<0.00003	1-384 (51)	47.9	0.1-4,300 (460)	10
Allegheny Formation	<0.005 (6)	--	0.1-104 (11)	8.4	0.25-228 (127)	9
Pottsville Formation	<0.000053 (4)	--	1.1-33.7 (6)	--	0.3-300 (178)	9
Mauch Chunk Formation	<0.00003 (2)	--	9.6-22 (6)	--	<0.1-910 (125)	10
Greenbrier Formation	<0.004 (5)	--	5-108 (9)	--	0.701-825 (75)	10
Purslane Formation	<0.002 (7)	--	8.4-70.1 (11)	22	0.1-375 (134)	10
Rockwell Formation	<0.005 (3)	--	0.647-22 (6)	--	0.36- 1,190 (106)	12
Hampshire Formation	<0.005 (17)	0.000025	2.96 -39.6 (23)	12.2	<1-1,460 (353)	11
Foreknobs Formation	<0.00003 (4)	--	6.6-29 (11)	13.3	0.25-2,060 (322)	10
Harrell-Brallier-Sherr Formations	--	--	--	--	16-79 (2)	--
All	all <0.005 (73)	0.00003	0.1-384 (134)	20.7	<0.1-4,300 (1,885)	10

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Chromium (mg/L)		Cobalt (mg/L)		Color (pt/co)	
Geologic unit	**Range (n)**	**Median**	**Range (n)**	**Median**	**Range (n)**	**Median**
Monongahela Group	--	--	--	--	2-5 (2)	--
Conemaugh Group	<0.01 (25)	<0.0003	<0.00005-0.00651 (22)	0.000082	<1-130 (113)	5
Allegheny Formation	<0.01 (6)	--	<0.000023-0.00748 (5)	--	<1-20 (15)	5
Pottsville Formation	<0.0003 (4)	--	0.000071-0.0132 (4)	--	<1-15 (6)	--
Mauch Chunk Formation	<0.0003-0.00036 (2)	--	0.000056-0.00308 (2)	--	<1-20 (8)	--
Greenbrier Formation	<0.008 (5)	--	<0.00005-0.0155 (3)	--	<1-15 (8)	--
Purslane Formation	<0.002-0.0049 (7)	--	<0.00005-0.005 (4)	--	5-35 (7)	--
Rockwell Formation	<0.01 (3)	--	<0.00005-0.00173 (2)	--	3-10 (5)	--
Hampshire Formation	<0.01 (17)	<0.0003	<0.00002-0.000674 (12)	<0.00005	<1-30 (20)	
Foreknobs Formation	<0.0003-0.00044 (4)	--	<0.00005-0.000073 (4)	--	<1-30 (15)	5
Harrell-Brallier-Sherr Formations	--	--	--	--	--	--
All	all <0.01 (73)	0.0003	<0.00002-0.0155 (58)	0.000068	<1-130 (199)	5

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

Geologic unit	Copper (mg/L)		Dissolved Oxygen (mg/L)		Fluoride (mg/L)	
	Range (n)	Median	Range (n)	Median	Range (n)	Median
Monongahela Group	--	--	--	--	--	--
Conemaugh Group	<0.0008-0.05 (27)	0.001	0.2-7.9 (37)	<1	<0.1-1.6 (42)	0.1
Allegheny Formation	0.0008-0.05 (6)	--	0.2-7 (5)	--	<0.1-0.58 (9)	--
Pottsville Formation	0.0008-0.0261 (4)	--	<1-4.7 (7)	--	<0.1-15 (7)	--
Mauch Chunk Formation	0.0024-0.0203 (2)	--	<1-8.6 (6)	--	<0.08-0.14 (7)	--
Greenbrier Formation	<0.0008-0.0259 (5)	--	<1-9.1 (7)	--	<0.1-0.2 (9)	--
Purslane Formation	<0.001-0.0068 (7)	--	<1-7.3 (7)	--	<0.1-0.22 (11)	0.1
Rockwell Formation	<0.001-0.05 (3)	--	<1 (3)	--	<0.1-0.28 (5)	--
Hampshire Formation	<0.0008-0.0542 (16)	0.0017	0.1-9.8 (34)	1.5	<0.04-1.23 (23)	0.08
Foreknobs Formation	0.00052-0.017 (4)	--	<2 (8)	--	0.09-0.51 (11)	0.1
Harrell-Brallier-Sherr Formations	--	--	--	--	--	--
All	<0.0008-0.0542 (74)	0.00115	<1-9.8 (114)	<1	<0.04-15 (124)	0.1

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Gross alpha-particle activity (pCi/L) (combined short-term and long-term analyses)		Gross beta-particle activity (pCi/L) (combined short-term and long-term analyses)		Hardness[1] (mg/L as $CaCO_3$)	
Geologic unit	Range (n)	Median	Range (n)	Median	Range (n)	Median*
Monongahela Group	--	--	--	--	132-212 (3)	--
Conemaugh Group	<0.1--3.1 (18)	<1.4	<0.3 – 6.4 (18)	1.8	0.2-1,620 (360)	131 (hard)
Allegheny Formation	<0.1–1 (4)	--	<1—2.3 (4)	--	<1-268 (97)	28 (soft)
Pottsville Formation	<0.1—1.6 (4)	--	<1.3—4.1 (4)	--	<2-182 (134)	33 (soft)
Mauch Chunk Formation	<0.12—1.3 (2)	--	<0.3—0.7 (2)	--	2-206 (93)	70 (mod. hard)
Greenbrier Formation	<0.1—15 (6)	--	<1—8.5 (4)	--	4-560 (56)	80 (mod. hard)
Purslane Formation	<1.65—3.3 (6)	--	<2.19—3 (4)	--	<2-230 (93)	68 (mod. hard)
Rockwell Formation	<0.1-0.7 (3)	--	1.3 (2)	--	<2-910 (74)	96 (mod. hard)
Hampshire Formation	<0.1—20 (14)	0.75	0.8—11.4 (12)	<2.25	<2-360 (269)	56 (soft)
Foreknobs Formation	<0.1—1.5 (4)	--	<1.2—5.8 (4)	--	<2-1,100 (247)	62 (mod. hard)
Harrell-Brallier-Sherr Formations	--	--	--	--	50 (1)	--
All	<0.1—20 (61)	0.45	<0.3—11.4 (54)	1.8	<1-1620 (1,427)	70 (mod. hard)

[1] Hardness medians include data that were below the reporting level (either 1 or 2 mg/L), where these data were used in the calculation as the reporting level, i.e. <1 mg/L was used as 1 mg/L.

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

Geologic unit	Iron (mg/L)		Lead (mg/L)		Lithium (mg/L)	
	Range (n)	Median	Range (n)	Median	Range (n)	Median
Monongahela Group	0.4-300 (3)	--	--	--	--	--
Conemaugh Group	<0.03-56.1 (451)	0.6	<.000025-0.01 (26)	0.0000875	0.00134-0.027 (23)	0.00525
Allegheny Formation	0.0088-38 (120)	5.2	<0.000025-0.01 (6)	0.000048	0.0063-0.016 (5)	--
Pottsville Formation	<0.05-65.4 (169)	1.1	<0.00004-0.00104 (4)	--	0.00423-0.0148 (4)	--
Mauch Chunk Formation	<0.05-10.8 (112)	0.2	<0.005 (3)	--	0.00069-0.00136 (2)	--
Greenbrier Formation	<0.021-114 (64)	0.4	0.000057-0.002 (6)	--	0.00282-0.0583 (3)	--
Purslane Formation	<0.06-56.1 (123)	0.6	<0.00004-0.017 (9)	--	0.0156-0.0247 (3)	--
Rockwell Formation	<0.05-60.9 (105)	0.3	<0.00004-0.06 (5)	--	0.0118-0.101 (2)	--
Hampshire Formation	<0.004-17.7 (308)	0.2	<0.00004-0.015 (22)	0.000424	<0.0088-1.08 (12)	0.0158
Foreknobs Formation	<0.05-312 (277)	0.4	0.00004-0.006 (7)	--	0.01-0.425 (4)	--
Harrell-Brallier-Sherr Formations	1.06 (1)	--	--	--	--	--
All	<0.004-312 (1,733)	0.44	<0.000025-0.06 (88)	0.000148	<0.0088-1.08 (58)	0.00973

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Magnesium (mg/L)		**Manganese (mg/L)**		**Mercury (mg/L)**	
Geologic unit	**Range (n)**	**Median**	**Range (n)**	**Median**	**Range (n)**	**Median**
Monongahela Group	--	--	0.05-0.42 (3)	--	--	--
Conemaugh Group	0.2-80.7 (50)	10.4	0.003-22.78 (445)	0.07	<0.000752 (9)	--
Allegheny Formation	0.1-5.4 (10)	2.5	<0.01-10.7 (119)	0.3	<0.0005 (2)	--
Pottsville Formation	0.5-6.8 (6)	--	0.0129-5.59 (169)	0.13	--	--
Mauch Chunk Formation	0.7-5.2 (6)	--	0.00038-0.84 (113)	0.025	--	--
Greenbrier Formation	1.7-53.1 (8)	--	0.00056-21.6 (65)	0.05	<0.0006 (3)	--
Purslane Formation	2.7-8.87 (7)	--	<0.005-7.11 (123)	0.15	<0.0005 (5)	--
Rockwell Formation	0.182-9.8 (6)	--	0.00846-20.01 (105)	0.11	<0.0005 (1)	--
Hampshire Formation	0.499-8.98 (19)	4.7	<0.01-2.56 (309)	0.025	0.000043-0.000511 (9)	--
Foreknobs Formation	1.38-12 (11)	6.3	0.005-1.57 (275)	0.05	--	--
Harrell-Brallier-Sherr Formations	--	--	0.13 (1)	--	--	--
All	0.1-80.7 (123)	5.5	<0.005-22.78 (1,727)	0.07	all <0.000752 (29)	<0.0002

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

Geologic unit	Molybdenum (mg/L)		Nickel (mg/L)		Nitrate (mg/L)[1]	
	Range (n)	Median	Range (n)	Median	Range (n)	Median
Monongahela Group	--	--	--	--	<0.1-0.3 (3)	0.1
Conemaugh Group	0.00004-0.004 (22)	0.000335	<0.02 (23)	0.00065	<0.2-12 (464)	0.1
Allegheny Formation	<0.001 (5)	--	<0.0002-0.05 (6)	--	<0.04-4.9 (135)	0.1
Pottsville Formation	<0.00005-0.00388 (4)	--	0.0002-0.0113 (4)	--	<0.04-1.4 (179)	0.1
Mauch Chunk Formation	0.000292-0.000829 (2)	--	0.00028-0.00077 (2)	--	<0.01-2.4 (125)	0.3
Greenbrier Formation	<0.00005-0.000308 (3)	--	<0.0002-0.0364 (5)	--	<0.04-2.9 (79)	0.3
Purslane Formation	0.000105-0.000268 (3)	--	<0.0002-0.0126 (7)	--	<0.04-3.3 (143)	0.2
Rockwell Formation	0.000027-0.000265 (2)	--	<0.0002-0.05 (3)	--	<0.04-4.2 (101)	0.2
Hampshire Formation	<0.00056-0.00887 (12)	0.002295	<0.0002-0.0091 (16)	0.00053	<0.04-7.7 (342)	0.3
Foreknobs Formation	0.00023-0.000778 (4)	--	<0.0002-0.00051 (4)	--	<0.04-38 (331)	0.2
Harrell-Brallier-Sherr Formations	--	--	--	--	<0.1-0.1 (2)	--
All	<0.00005-0.00887 (57)	0.000349	<0.0002-0.05 (70)	0.000695	<0.01-38 (1,904)	0.2

[1] includes nitrate-plus-nitrite

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Nitrite (mg/L)		Orthophosphate (mg/L)		pH	
Geologic unit	**Range (n)**	**Median**	**Range (n)**	**Median**	**Range (n)**	**Median**
Monongahela Group	--	--	--	--	6.5-7.83 (3)	--
Conemaugh Group	<0.001-0.15 (28)	<0.01	<0.004-0.077 (19)	0.005	3.6-8.9 (306)	7.2
Allegheny Formation	<0.1 (8)	--	<0.004-0.058 (5)	--	3.5-8.9 (73)	6.1
Pottsville Formation	<0.1 (7)	--	<0.004-0.02 (4)	--	3.5-9.5 (88)	6.5
Mauch Chunk Formation	<0.1 (4)	--	0.011-0.012 (2)	--	5.5-9.7 (56)	7.5
Greenbrier Formation	<0.02 (8)	<0.01	<0.024-0.06 (4)	--	3.98-8.4 (39)	7.2
Purslane Formation	<0.2 (13)	<0.1	0.006-0.045 (3)	--	3.5-10 (83)	7.0
Rockwell Formation	<0.001-0.003 (6)	--	0.006 -0.048 (2)	--	5.1-9.4 (50)	7.1
Hampshire Formation	<0.001-0.039 (28)	<0.01	0.008-0.071 (11)	0.02	5-10 (200)	7.2
Foreknobs Formation	<0.1 (8)	<0.1	0.005-0.135 (4)	--	3.79-9.5 (157)	7.5
Harrell-Brallier-Sherr Formations	--	--	--	--	6.9 (1)	--
All	all <0.2 (110)	<0.1	<0.004-0.135 (54)	0.014	3.5-10 (1,056)	7.1

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Phosphate (mg/L)		Phosphorus (mg/L)		Potassium (mg/L)	
Geologic unit	**Range (n)**	**Median**	**Range (n)**	**Median**	**Range (n)**	**Median**
Monongahela Group	--	--	--	--	--	--
Conemaugh Group	<0.01-0.03 (20)	0.01	0.01-0.07 (14)	0.01	0.3-4.6 (39)	1.4
Allegheny Formation	0.01-0.05 (4)	0.04	<0.02-0.05 (4)	0.04	0.2-1.8 (10)	1.1
Pottsville Formation	<0.01 (2)	<0.01	<0.02 (4)	<0.02	0.43-1.3 (6)	--
Mauch Chunk Formation	0.01-0.04 (4)	0.02	<0.02 (1)	--	0.64-1.1 (6)	--
Greenbrier Formation	<0.01-0.07 (5)	0.02	<0.02 (2)	0.02	0.53-4.6 (7)	--
Purslane Formation	<0.01-0.06 (6)	0.04	0.03 (1)	--	0.7-2.0 (7)	--
Rockwell Formation	<0.01-0.11 (4)	0.01	0.03 (1)	--	0.9-1.9 (6)	--
Hampshire Formation	<0.01-0.11 (13)	0.02	<0.02-0.07 (4)	0.03	0.85-5.83 (18)	1.5
Foreknobs Formation	<0.01-0.07 (7)	0.01	<0.02-0.12 (3)	0.03	0.6-2.4 (11)	1.1
Harrell-Brallier-Sherr Formations	--	--	--	--	--	--
All	<0.01-0.11 (65)	0.02	<0.02-0.12 (34)	0.01	0.2-5.83 (110)	1.2

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Radium-226 (pCi/L)		Radium-228 (pCi/L)		Radon (pCi/L)	
Geologic unit	Range (n)	Median	Range (n)	Median	Range (n)	Median
Monongahela Group	--	--	--	--	--	--
Conemaugh Group	--	--	--	--	14-1,390 (76)	110
Allegheny Formation	--	--	--	--	<80—515 (17)	55
Pottsville Formation	--	--	--	--	35--2,885 (25)	445
Mauch Chunk Formation	--	--	--	--	85—2,285 (16)	1,190
Greenbrier Formation	1.36 (1)	--	1.35 (1)	--	25—1,300 (13)	470
Purslane Formation	--	--	--	--	30—785 (22)	137.5
Rockwell Formation	--	--	--	--	50—495 (16)	337.5
Hampshire Formation	2.5-4.9 (2)	--	2.35-3.1 (2)	--	30—32,800 (61)	980
Foreknobs Formation	0.61 (1)	--	0.41 (1)	--	20—1,305 (46)	130
Harrell-Brallier-Sherr Formations	--	--	--	--	--	--
All	0.61-4.9 (4)	--	0.41-3.1 (4)	--	14—32,800 (292)	230

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Selenium (mg/L)		**Silver (mg/L)**		**Silica (mg/L)**	
Geologic unit	**Range (n)**	**Median**	**Range (n)**	**Median**	**Range (n)**	**Median**
Monongahela Group	--	--	--	--	--	--
Conemaugh Group	<0.01 (25)	<0.00005	<0.005 (21)	<0.00002	0.1-10.8 (38)	6.905
Allegheny Formation	<0.01 (6)	--	<0.005 (5)	--	5.4-28 (9)	--
Pottsville Formation	<0.00005-0.0001 (4)	--	<0.00002 (4)	--	4-13.4 (6)	--
Mauch Chunk Formation	0.00009-0.00038 (2)	--	<0.00002 (2)	--	5.8-11 (6)	--
Greenbrier Formation	<0.002 (5)	--	<0.00002 (3)	--	6.2-15.4 (7)	--
Purslane Formation	<0.025 (7)	--	<0.004 (5)	--	6.2-17 (7)	--
Rockwell Formation	<0.01 (3)	--	<0.005 (3)	--	7-15.4 (5)	--
Hampshire Formation	<0.01 (17)	0.00035	<0.005 (13)	<0.00002	6.93-15 (18)	9.065
Foreknobs Formation	<0.00005-0.00007 (4)	--	<0.00002 (4)	--	7.6-23 (11)	15
Harrell-Brallier-Sherr Formations	--	--	--	--	--	--
All	<0.00005-0.0125 (73)	0.00006	all <0.005 (60)	0.00002	0.1-28 (107)	7.7

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Sodium (mg/L)		Specific Conductance (µS/cm)		Strontium (mg/L)	
Geologic unit	**Range (n)**	**Median**	**Range (n)**	**Median**	**Range (n)**	**Median**
Monongahela Group	--	--	914 (1)	--	--	--
Conemaugh Group	0.3-160 (41)	3.3	25-2,510 (215)	308	0.0228-1.07 (19)	0.264
Allegheny Formation	0.42-77.2 (11)	5.8	30-1,000 (50)	132	0.0163-0.278 (4)	--
Pottsville Formation	0.4-10.3 (6)	--	21-341 (62)	98	0.00619-2.18 (4)	--
Mauch Chunk Formation	1.6-3.74 (6)	--	34-775 (39)	179	0.0244-0.15 (2)	--
Greenbrier Formation	0.64-149 (9)	--	30-2,650 (35)	189	0.0432-0.329 (3)	--
Purslane Formation	0.6-15.4 (10)	5.2	31-901 (50)	183	0.0371-0.45 (3)	--
Rockwell Formation	1-86.2 (6)	--	84-2,900 (33)	201	0.014-0.0234 (2)	--
Hampshire Formation	1.3-846 (23)	12	47-4,800 (158)	169	<0.008-5.61 (12)	0.4695
Foreknobs Formation	2.5-299 (11)	6.8	44-2,660 (123)	182	0.0695-1.49 (4)	--
Harrell-Brallier-Sherr Formations	--	--	154 (1)	--	--	--
All	0.3-846 (123)	5.1	21-4,800 (767)	197	<0.008-5.61 (53)	0.263

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Sulfide (mg/L)		Sulfate (mg/L)		Thallium (mg/L)	
Geologic unit	Range (n)	Median	Range (n)	Median	Range (n)	Median
Monongahela Group	--	--	16.1-325 (4)	--	--	--
Conemaugh Group	<1 (2)	--	0.08-1,905 (170)	19.5	<0.002 (20)	<0.00003
Allegheny Formation	--	--	1-630 (21)	14	<0.005 (5)	--
Pottsville Formation	--	--	3.6-19.1 (7)	--	<0.00003 (4)	--
Mauch Chunk Formation	--	--	4.2-31.8 (8)	--	<0.00003 (2)	--
Greenbrier Formation	<0.03 (2)	--	0.97-22.2 (11)	8.1	<0.002 (5)	--
Purslane Formation	<1 (4)	--	<2-18.6 (10)	12.9	<0.001 (7)	--
Rockwell Formation	--	--	7.6-25 (6)	--	<0.00003 (2)	--
Hampshire Formation	<2 (4)	--	0.11-50 (27)	11.9	<0.002 (15)	<0.00004
Foreknobs Formation	--	--	1.1-41 (18)	8.3	<0.002 (4)	--
Harrell-Brallier-Sherr Formations	--	--	--	--	--	--
All	all <2 (12)	<1	<2-1,905 (282)	15.7	all <0.005 (64)	<0.00003

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

Geologic unit	Total Dissolved Solids (mg/L)		Total Organic Carbon (mg/L)		Uranium (mg/L)	
	Range (n)	Median	Range (n)	Median	Range (n)	Median
Monongahela Group	74-654 (4)	--	--	--	--	--
Conemaugh Group	25-2,242 (246)	211	<0.7-1.6 (14)	<0.7	<0.000004-0.001 (19)	0.000029
Allegheny Formation	14-726 (50)	100	<0.7 (4)	--	<0.000014 (4)	--
Pottsville Formation	4- 276 (59)	82	<0.7-0.8 (4)	--	<0.000014-0.000136 (4)	--
Mauch Chunk Formation	4-468 (36)	111	<0.7 (1)	--	0.000119-0.000506 (2)	--
Greenbrier Formation	30-2,092 (32)	110	<0.7 (2)	--	<0.000006-0.000603 (3)	--
Purslane Formation	2-644 (48)	119	<0.7 (1)	--	<0.000014-0.000025 (3)	--
Rockwell Formation	54-490 (30)	130	<0.7 (1)	--	<0.000008-0.000019 (2)	--
Hampshire Formation	<10-2,560 (146)	112	<0.7 (4)	--	<0.000006-0.0107 (12)	0.000186
Foreknobs Formation	22-2,546 (120)	118	<0.7 (3)	--	<0.000014-0.000194 (4)	--
Harrell-Brallier-Sherr Formations	90 (1)	--	--	--	--	--
All	<10-2,560 (772)	132	<0.7-1.6 (34)	<0.7	<0.000004-0.0107 (53)	0.000025

Appendix A. Continued

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; n, number of samples; pt/co, platinum cobalt scale; pCi/L, picocuries per liter; -- represents no or too few samples collected for selected geologic units (geologic units with less than 10 samples did not have a median calculated). Median values were rounded to maximum number of significant figures for each constituent.]

	Vanadium (mg/L)		Zinc (mg/L)	
Geologic unit	Range (n)	Median	Range (n)	Median
Monongahela Group	--	--	--	--
Conemaugh Group	<0.00008-0.001 (21)	<0.00016	<0.0014-0.58 (30)	0.0061
Allegheny Formation	<0.0001-0.001 (5)	--	<0.0014-0.13 (6)	--
Pottsville Formation	<0.0001-0.00016 (4)	--	0.0073-0.0326 (4)	--
Mauch Chunk Formation	0.00014-0.00099 (2)	--	0.084-0.098 (2)	--
Greenbrier Formation	<0.0001-0.00067 (3)	--	<0.002-0.0497 (5)	--
Purslane Formation	<0.0001-0.00012 (3)	--	<0.005-0.04 (7)	--
Rockwell Formation	≤0.00016 (2)	--	<0.002-0.1 (3)	--
Hampshire Formation	<0.00008-0.0019 (11)	0.00021	<0.002-0.607 (15)	0.004
Foreknobs Formation	<0.0001-0.0044 (4)	--	<0.002-0.225 (4)	--
Harrell-Brallier-Sherr Formations	--	--	--	--
All	<0.00008-0.0044 (55)	0.00008	<0.0014-0.607 (76)	0.00575

Appendix B. Abbreviated Maryland Appalachian Plateau Spearman's Rank Order Correlation.

Cell Contents:
Correlation Coefficient
P-Value
Number of Samples

The pair(s) of variables with positive correlation coefficients and p-values below 0.050 tend to increase together. For the pairs with negative correlation coefficients and p-values below 0.050, one variable tends to decrease while the other increases. For pairs with p-values greater than 0.050, there is no significant relationship between the two variables. A significant correlation was determined for variable pairs with p-values less than 0.050 and the critical correlation as noted by Zar (1984). Shaded/bolded cells indicate significant correlations.

Constituents	Well Age	Casing Depth	Total Depth	Arsenic	Calcium	Iron	Manganese	Sulfate	Sodium
pH	-0.0620 0.0513 990	0.107 7.89E-04 982	0.153 1.35E-06 987	**0.280** **2.10E-14** **726**	0.0694 0.438 127	**-0.260** **1.332E-15** **917**	**-0.341** **2E-07** **913**	**-0.198** **0.00232** **235**	**0.507** **8.48E-09** **116**
Well Age		**-0.393** **2E-07** **2194**	**-0.314** **2E-07** **2207**	-0.0723 0.00756 1365	-0.138 0.126 123	-0.144 3.73E-09 1654	-0.102 3.59E-05 1648	**-0.217** **3.8E-04** **266**	**-0.290** **0.00201** **112**
Casing Depth			**0.341** **2E-07** **2189**	0.0353 0.194 1352	**0.207** **0.0231** **121**	0.101 3.9E-05 1639	0.0109 0.659 1633	0.0799 0.197 263	0.00853 0.929 110
Total Depth				**0.183** **1.249E-11** **1362**	0.0128 0.888 122	-0.0117 0.636 1651	-0.0875 3.85E-04 1645	0.0673 0.275 265	0.0452 0.637 111
Arsenic					0.0331 0.779 74	-0.0830 0.00178 1415	-0.115 1.38E-05 1418	0.119 0.291 81	0.203 0.0852 73
Calcium						**0.215** **0.0133** **132**	**0.209** **0.0167** **131**	**0.523** **6.627E-11** **131**	-0.0709 0.437 122
Iron							**0.636** **2E-07** **1723**	**0.237** **9.37E-05** **269**	-0.150 0.0994 121
Manganese								0.158 0.0102 265	-0.145 0.113 121
Sulfate									0.116 0.204 122

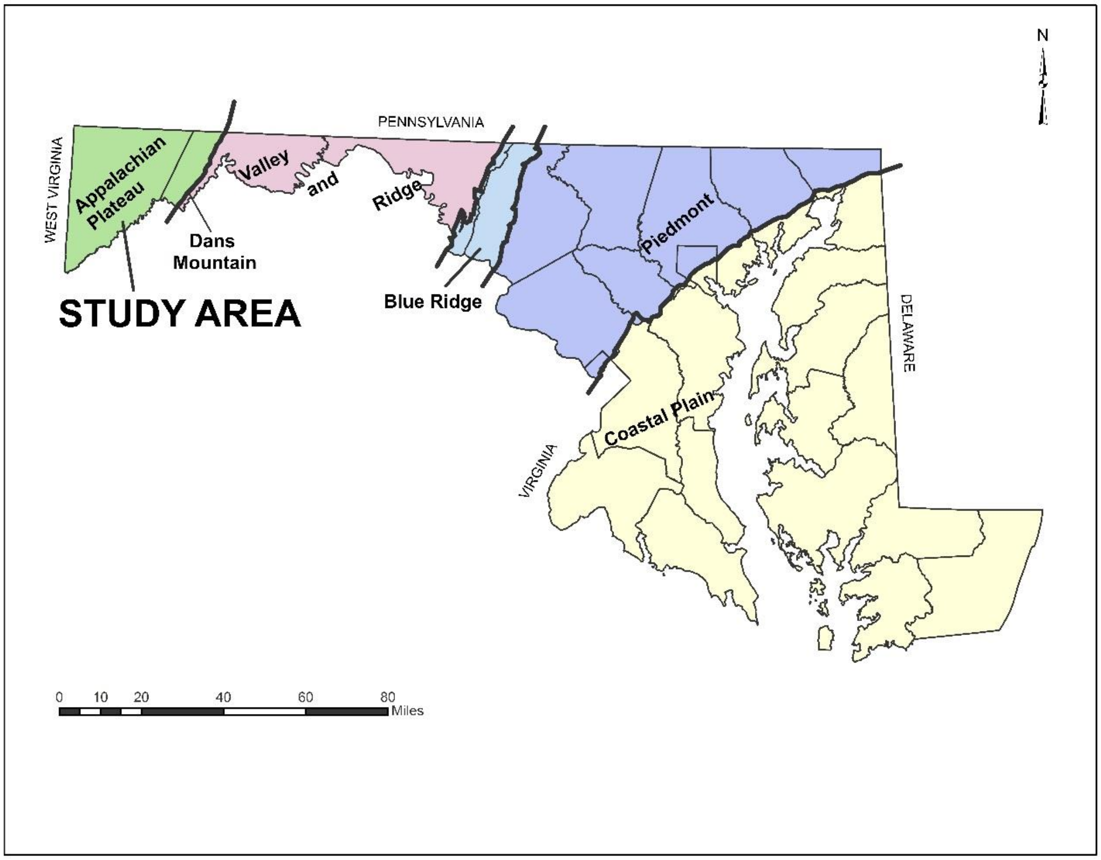


Figure 1. Location of the study area.

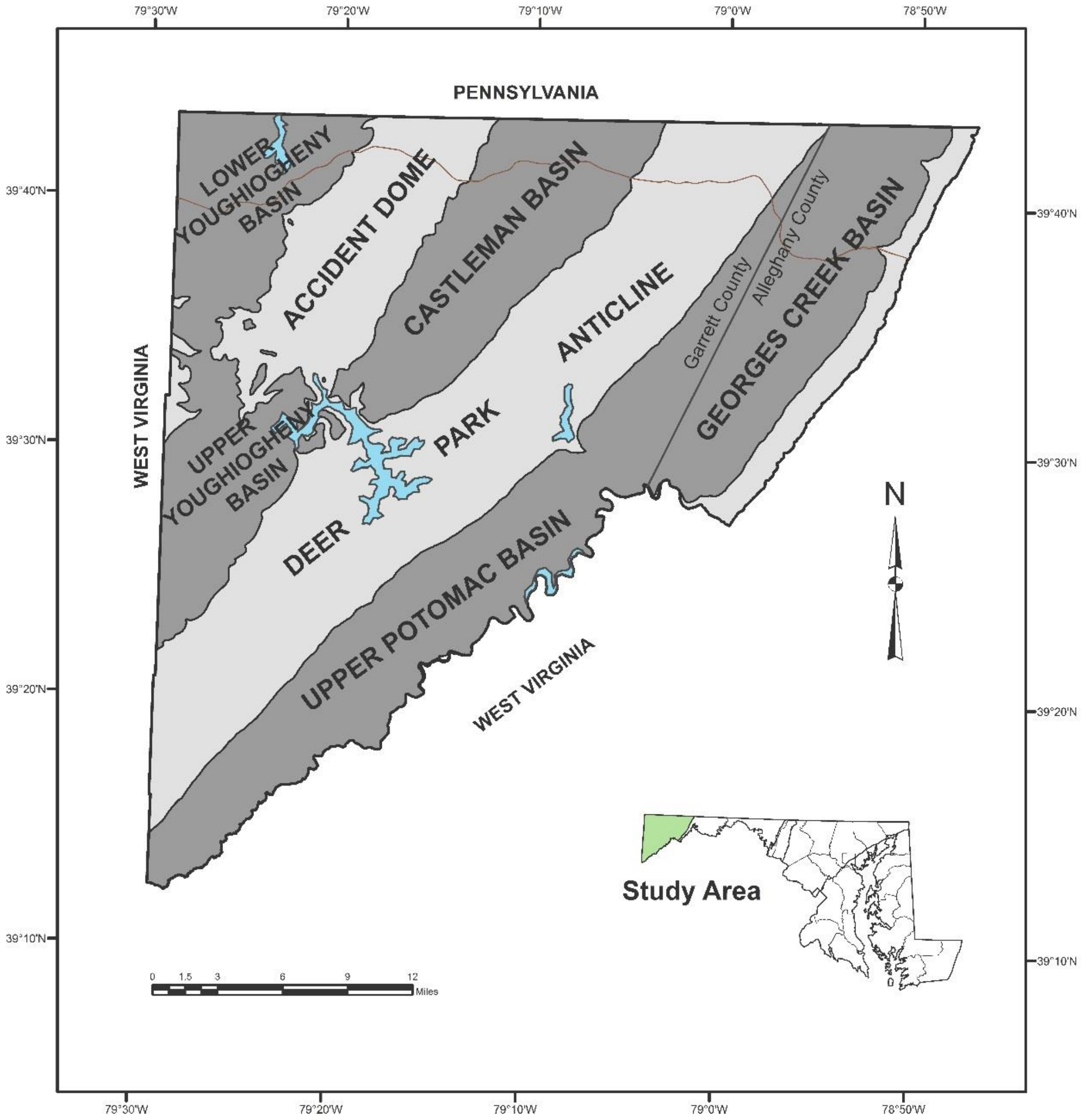


Figure 2. Geologic structure of the Appalachian Plateau Physiographic Province of Maryland. Synclines are shown in dark gray, and anticlines are in light gray. Modified from Overbeck (1954).

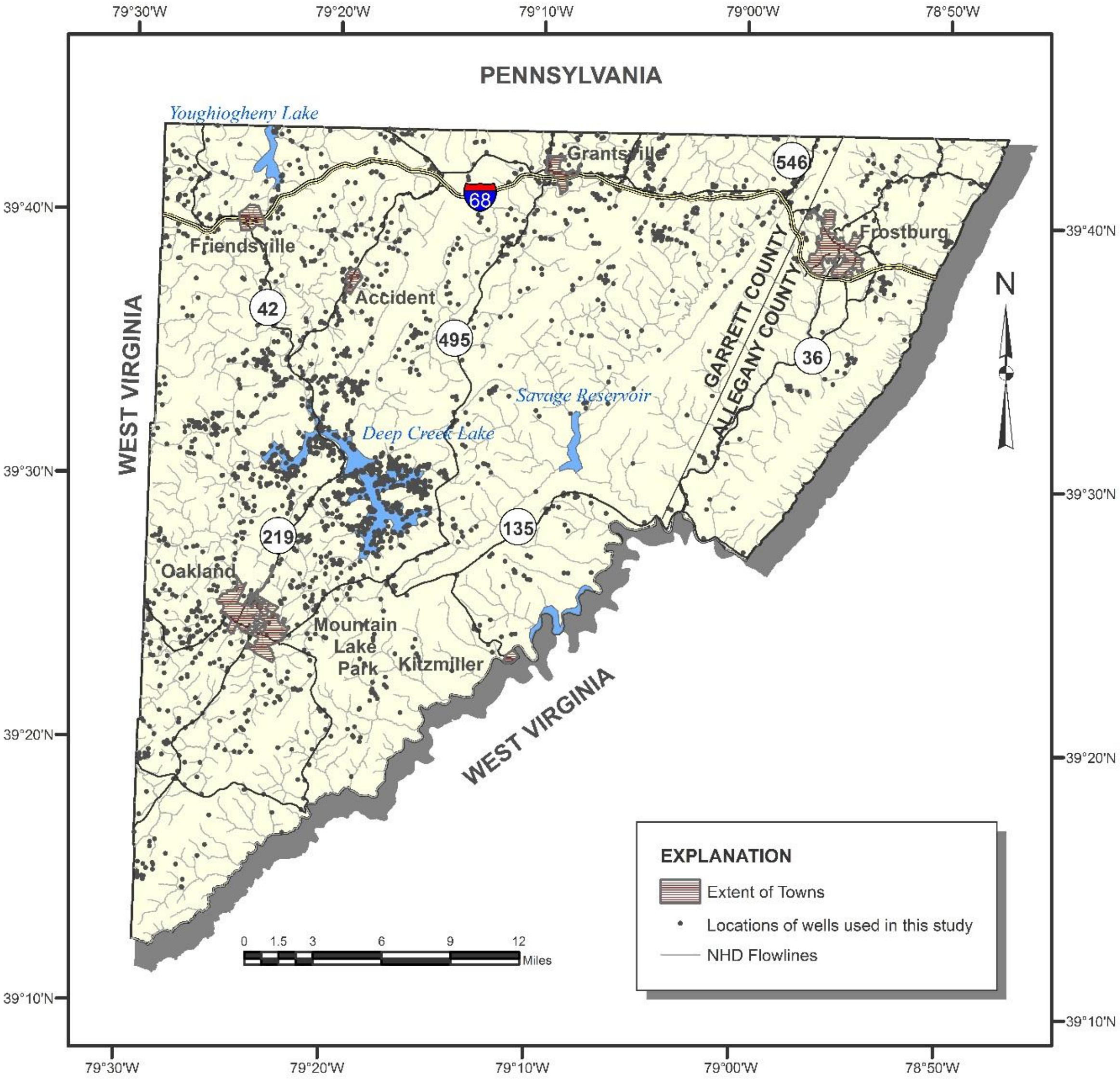


Figure 3. Locations of wells included in this report.

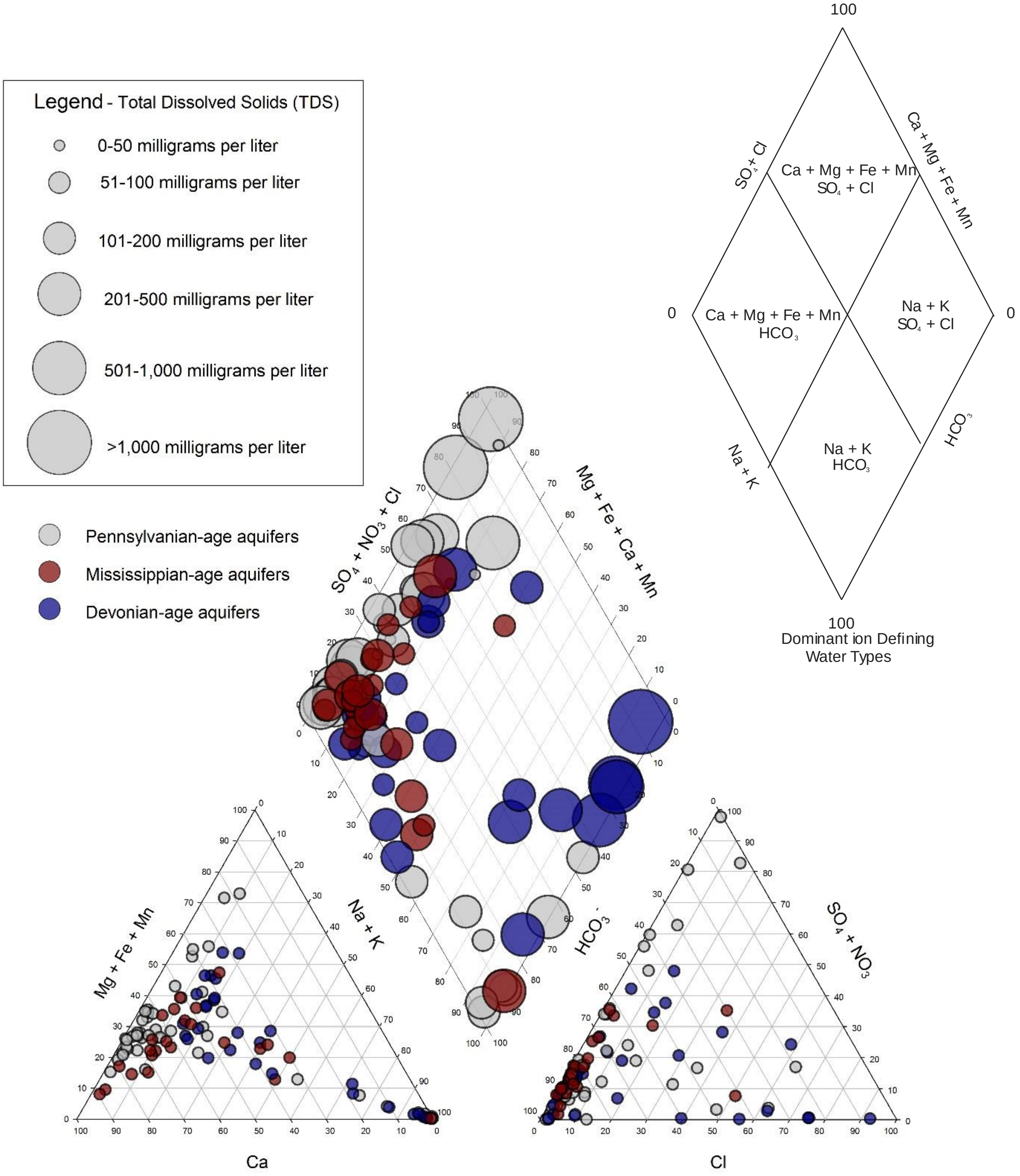
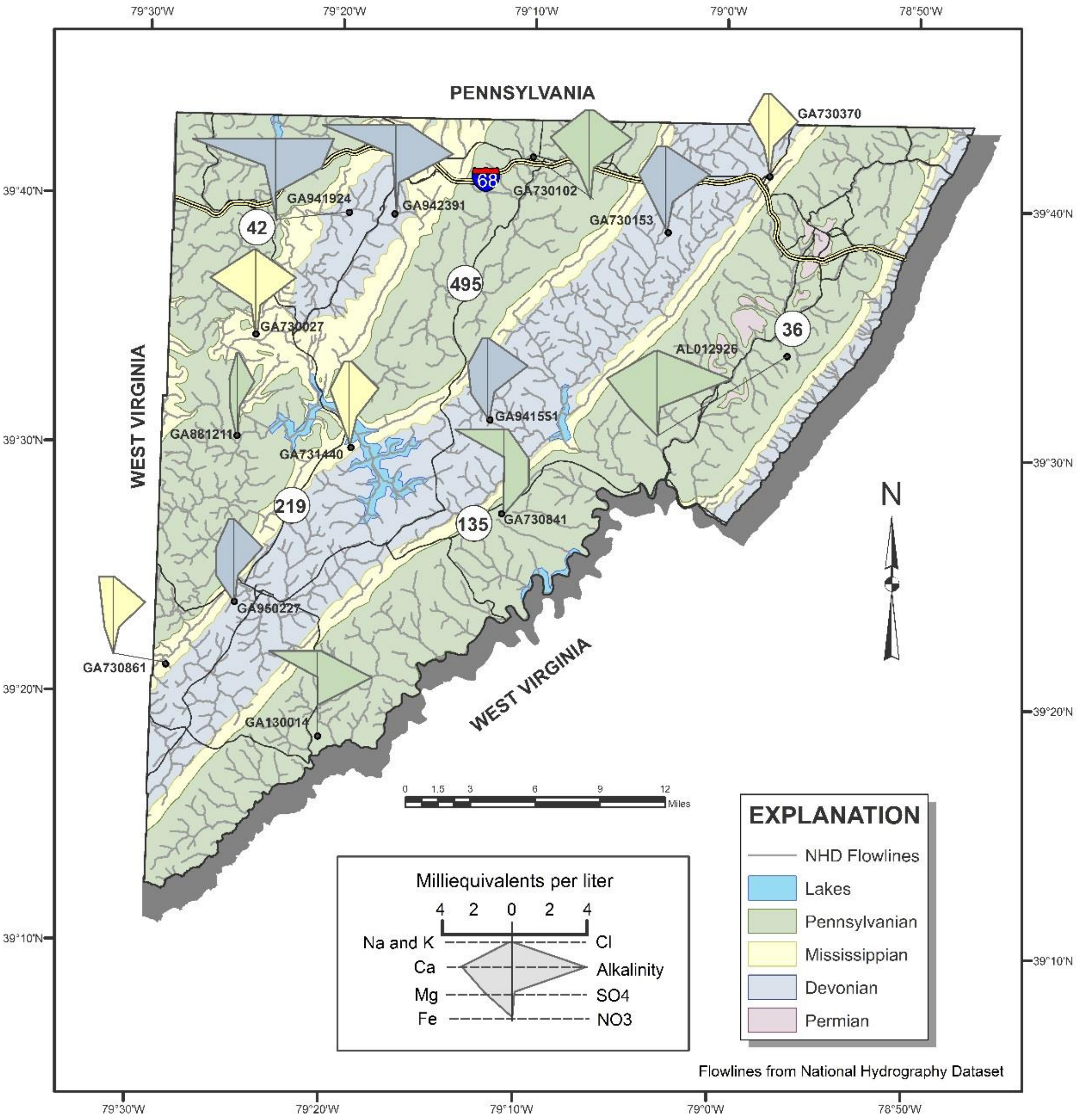


Figure 4. Piper diagram showing milliequivalent percentages of major ions and total dissolved solids of samples evaluated in this report.



Flowlines from National Hydrography Dataset

Figure 5. Generalized geologic map of the Appalachian Plateau with Stiff diagrams. Well permit numbers are identified for each well.

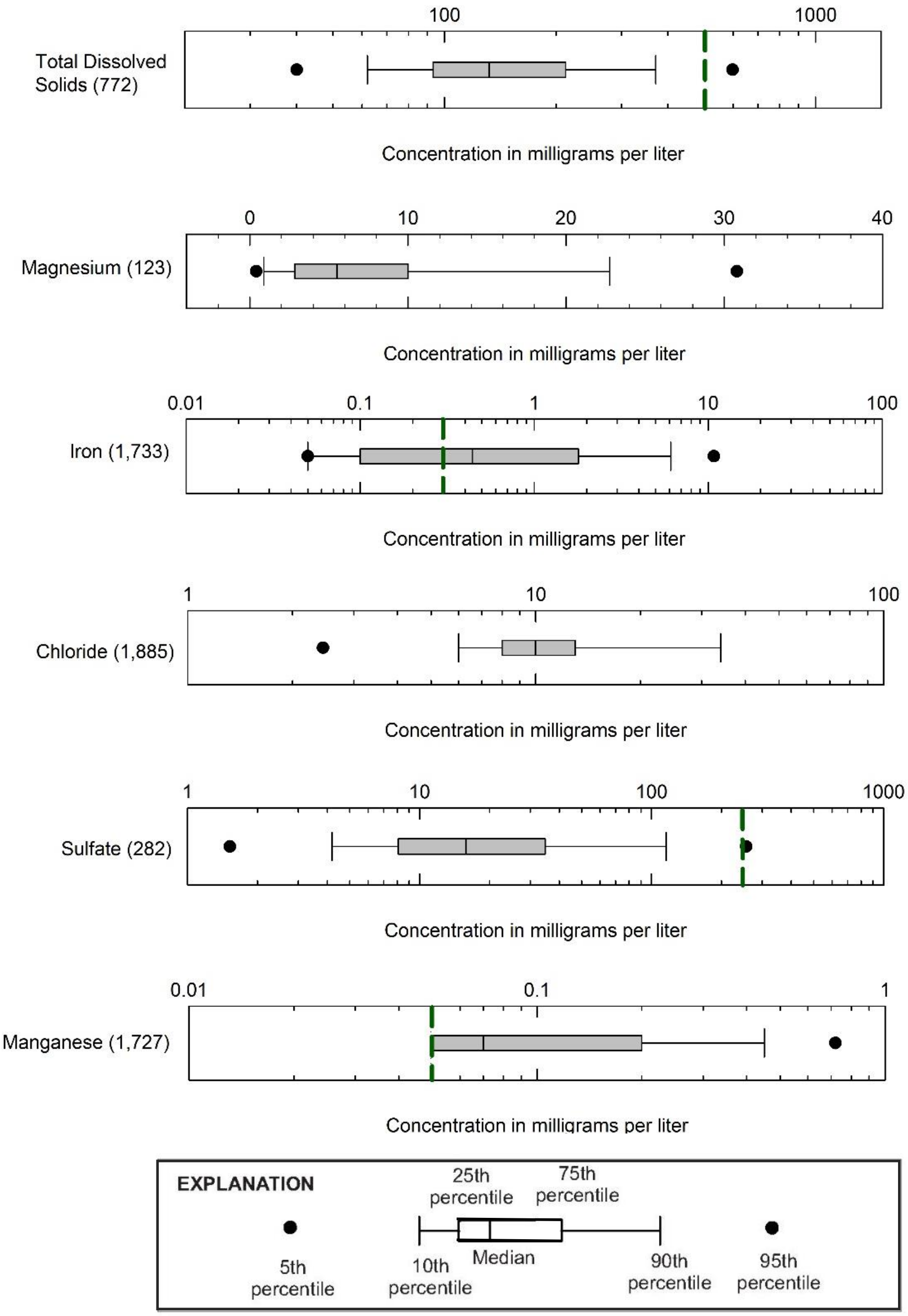


Figure 6. **Box-and-whisker plots of selected inorganic constituents. Constituents below their respective reporting limit were plotted as one-half the reporting limit. Respective MCLs are shown as red dashed line, SMCLs are shown as a green dashed line, and most common RLs are shown as dotted line.**

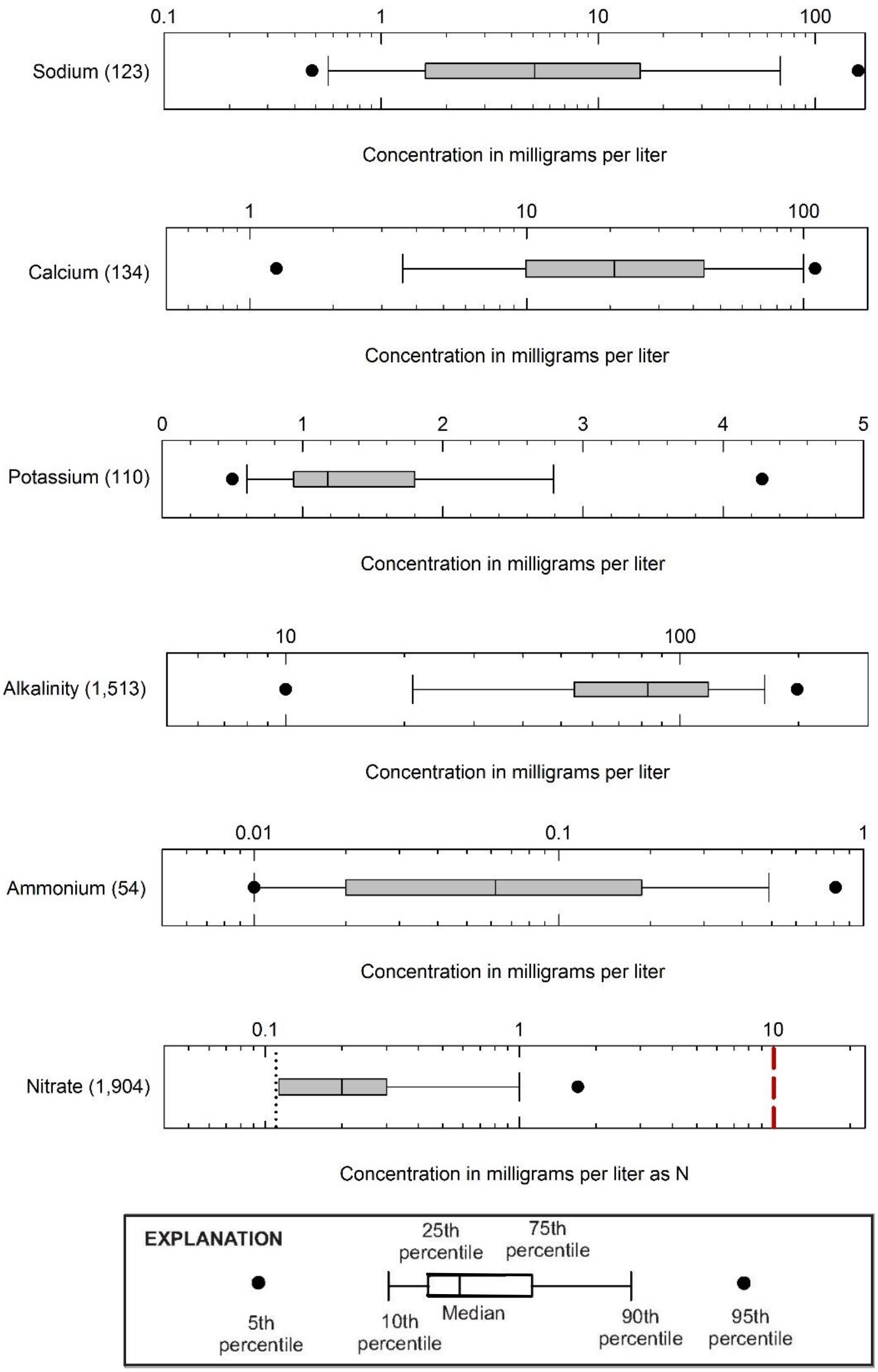


Figure 6, continued. Box-and-whisker plots of selected inorganic constituents. Constituents below their respective reporting limit were plotted as one-half the reporting limit. Respective MCLs are shown as red dashed line, SMCLs are shown as a green dashed line, and most common RLs are shown as dotted line. Sample size is shown in parentheses.

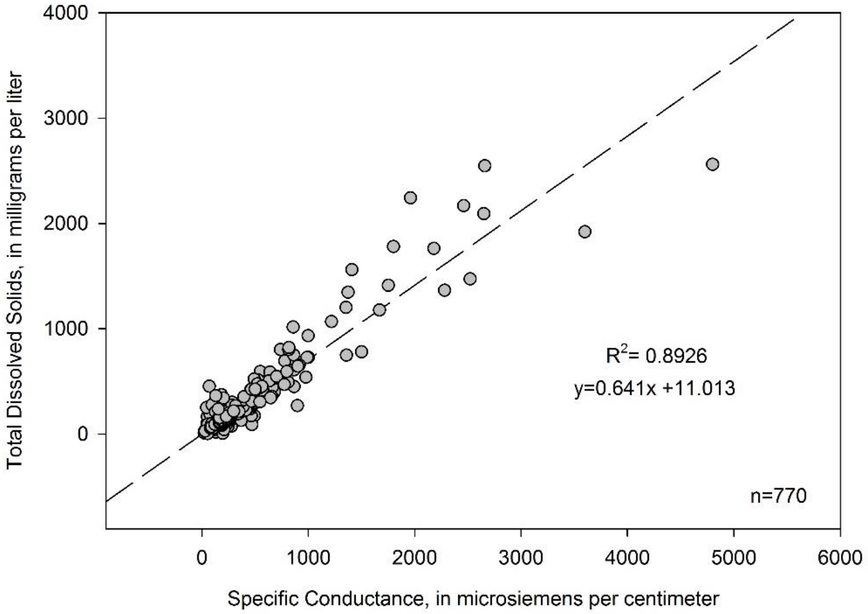


Figure 7. Relation between specific conductance and total dissolved solids (TDS). One TDS sample was reported as below the reporting level of 5 mg/L (plotted as 2.5 mg/L). Two samples were identified as outliers and were not plotted on this figure.

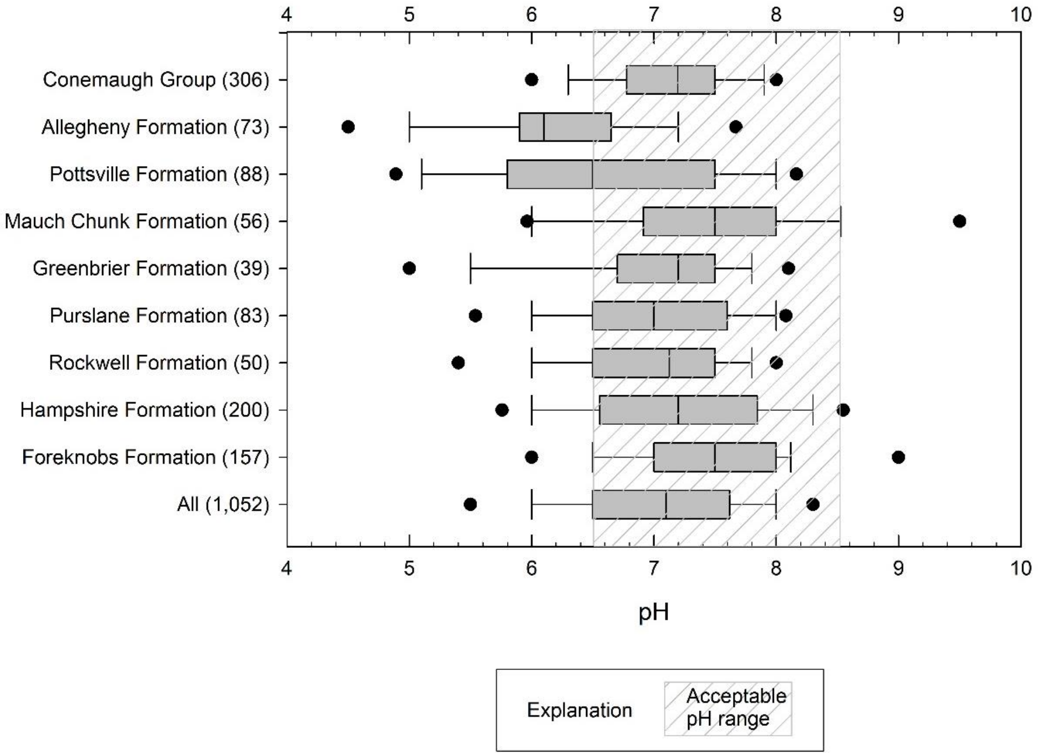


Figure 8. Box-and-whisker plots of pH with respect to geologic unit. Harrell-Brallier-Sherr Formations and Monongahela Group not shown due to small sample size. See figure 6 for explanation of box-and-whisker plots. Sample size is shown in parentheses.

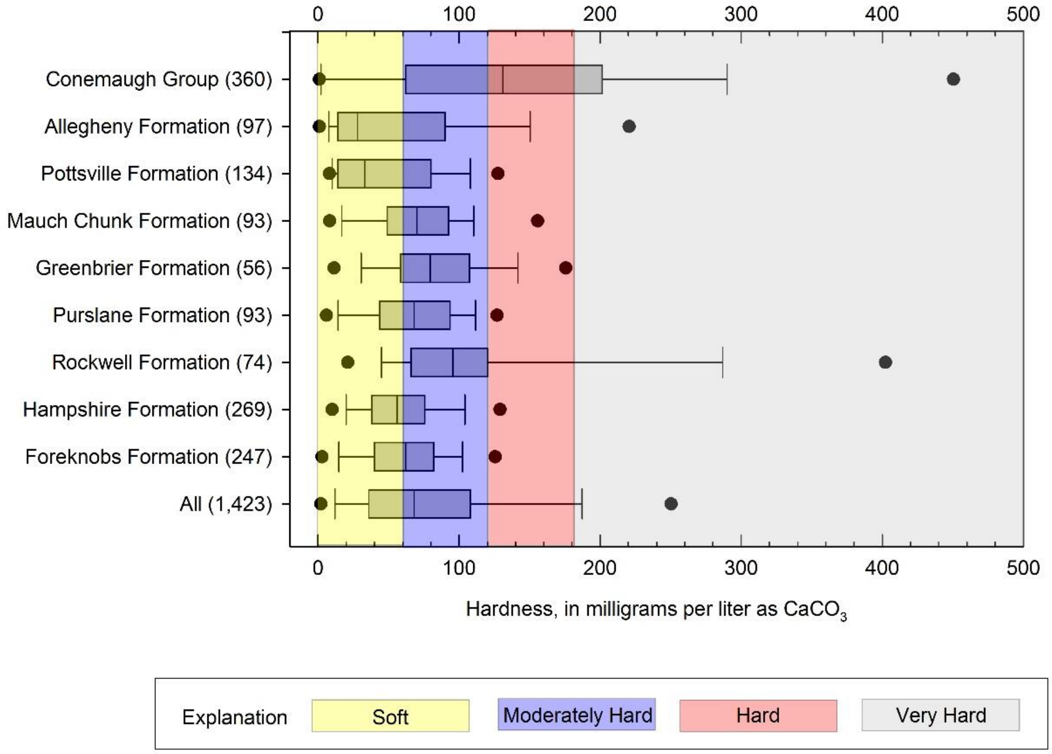


Figure 9. Box-and-whisker plots of hardness with respect to geologic unit. Harrell-Brallier-Sherr Formations and Monongahela Group not shown due to small sample size. See figure 6 for explanation of box-and-whisker plots. Sample size is shown in parentheses.

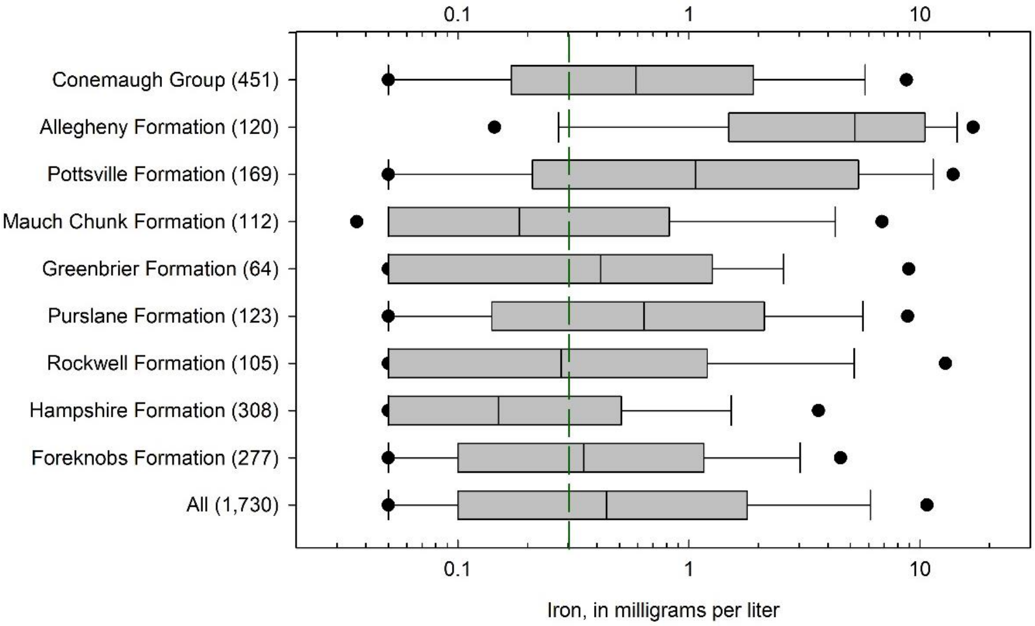


Figure 10. Box-and-whisker plots of iron with respect to geologic unit. Harrell-Brallier-Sherr Formations and Monongahela Group not shown due to small sample size. Green dashed line represents SMCL of 0.3 mg/L. See figure 6 for explanation of box-and-whisker plots.

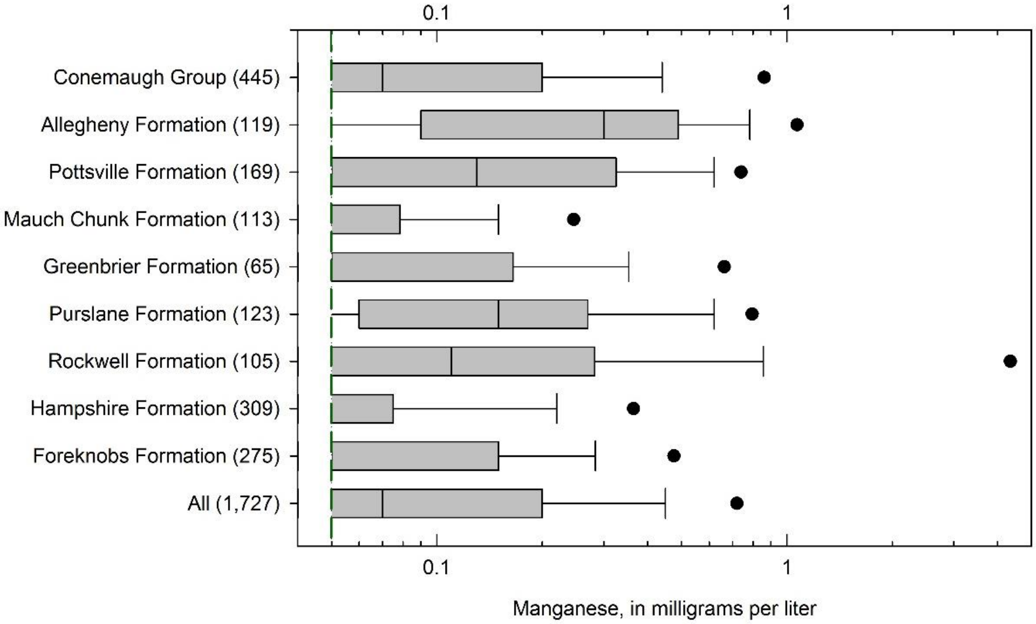


Figure 11. Box-and-whisker plots of manganese with respect to geologic unit. Harrell-Brallier-Sherr Formations and Monongahela Group not shown due to small sample size. Green dashed line represents SMCL of 0.05 mg/L. See figure 6 for explanation of box-and-whisker plots.

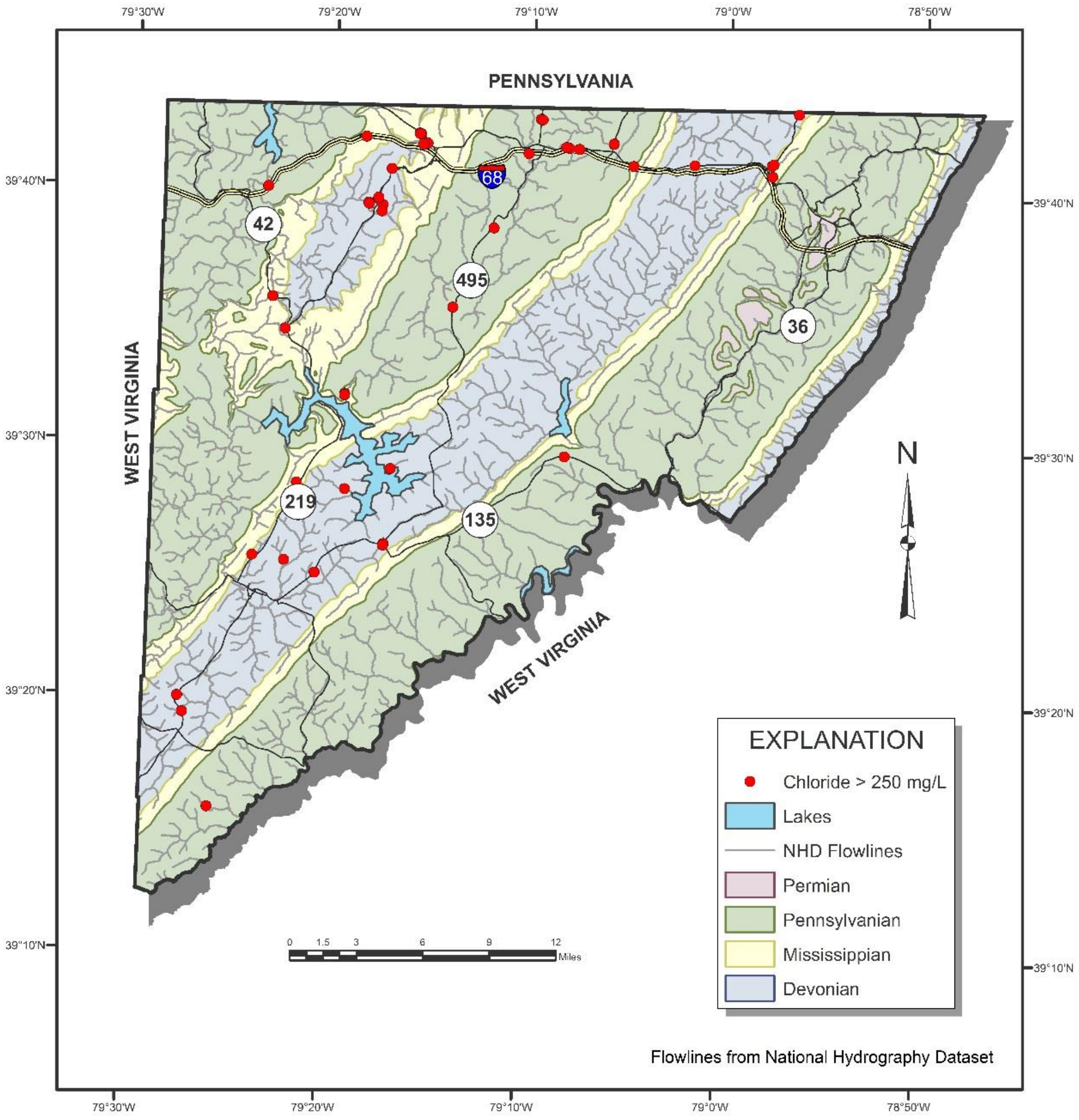


Figure 12. Locations of wells with chloride concentrations greater than 250 mg/L.

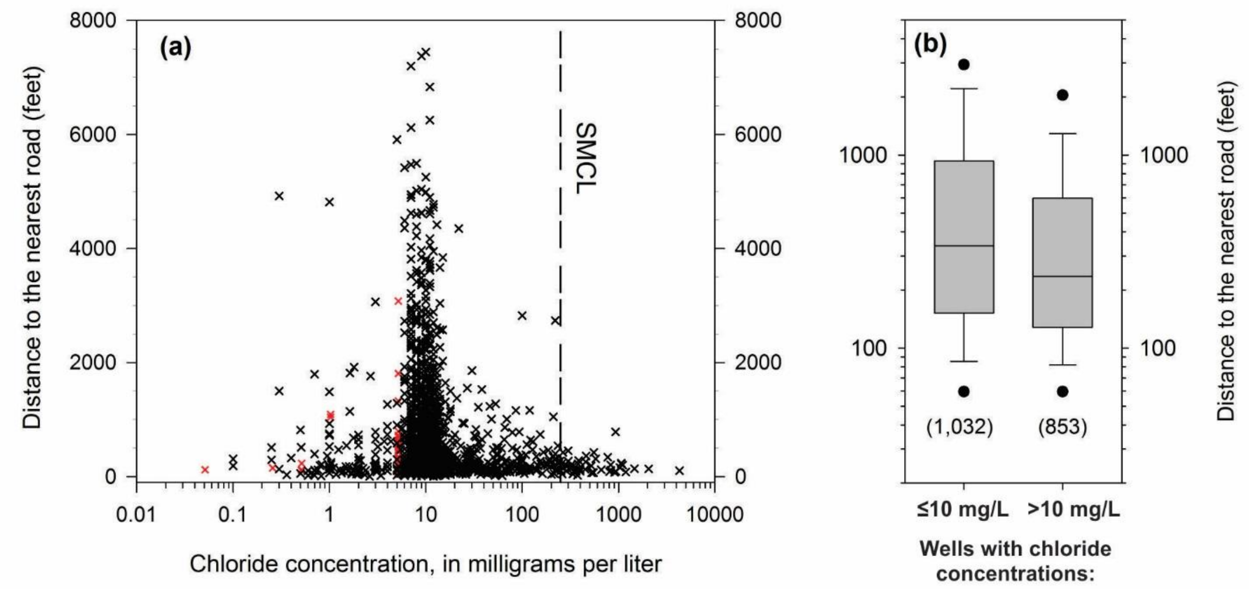


Figure 13. Wellwater chloride concentrations in relation to distance to nearest road. (a) Scatterplot of chloride concentrations with respect to distance to the nearest road; (b) Box-and-whisker plot of range of chloride concentrations with respect to the nearest road. Number of samples is in parentheses. Chloride concentrations below reporting limits are plotted as one-half the reporting limit, and are shown in red. See Figure 6 for explanation of box-and-whisker plots. Sample size is shown in parentheses.

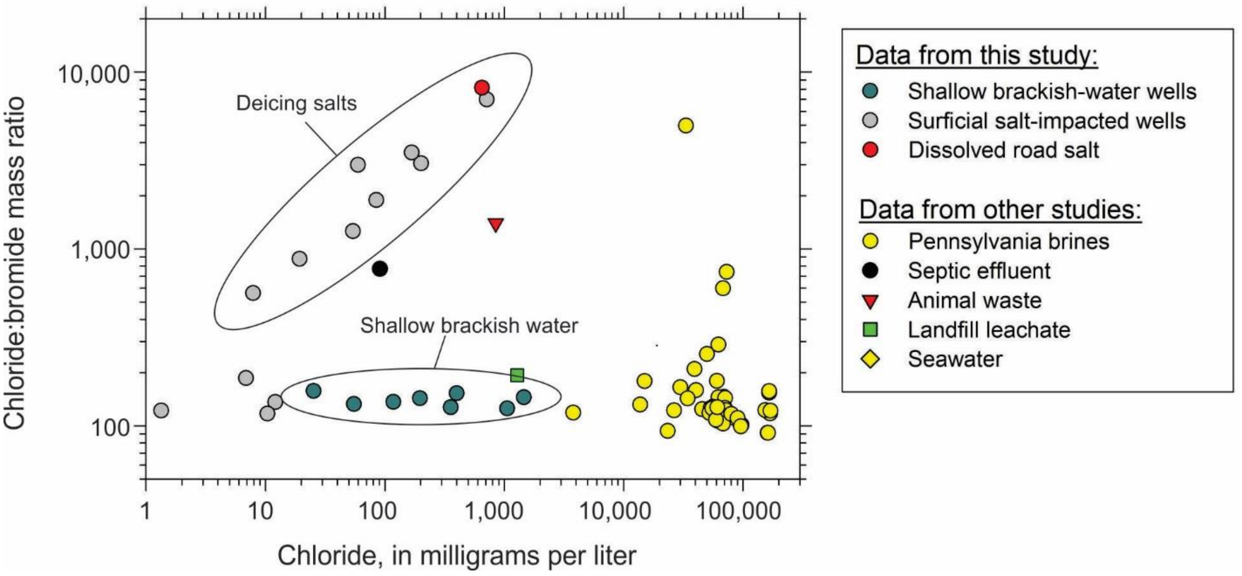


Figure 14. Relation between chloride/bromide ratios and chloride concentrations. Sources of data: Pennsylvania brines, Poth (1962); septic effluent, animal waste, and landfill leachate, Panno and others (2005); seawater, Hem (1985). Data from septic effluent, animal waste, and landfill leachate represent median values from Panno and others (2005).

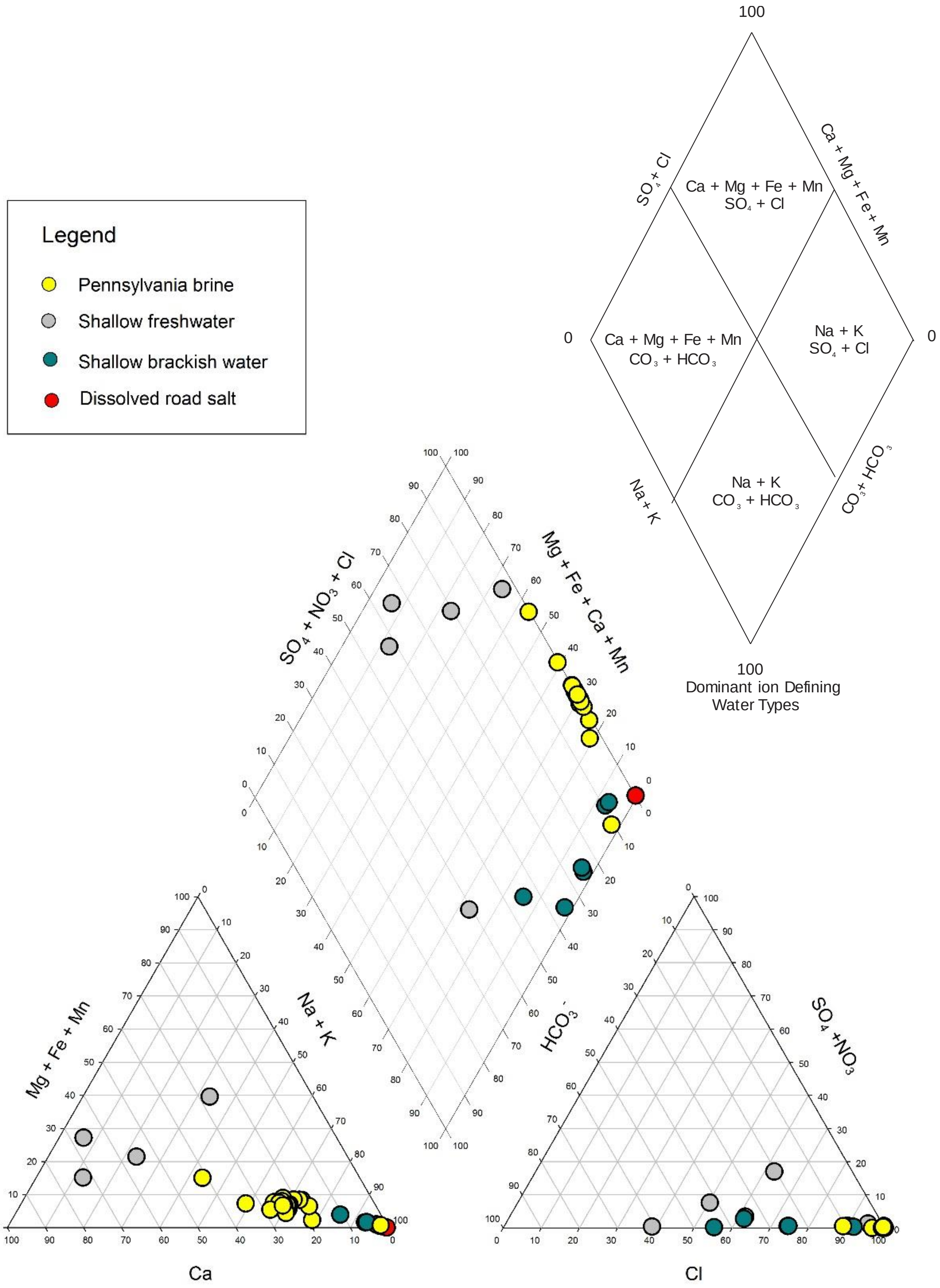


Figure 15. **Piper diagram showing milliequivalent percentages of major ions for different groups of wells with chloride greater than 50 mg/L. Source for Pennsylvania brine data: Poth (1962).**

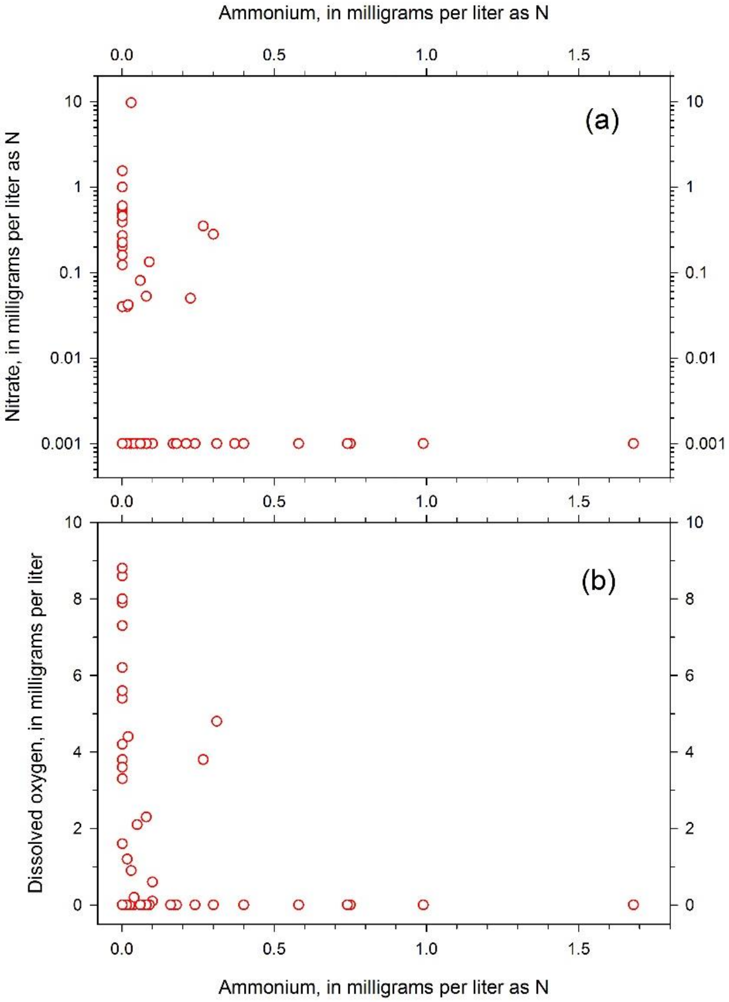


Figure 16. Relation of ammonium to (a) nitrate; and (b) dissolved oxygen for wells in the Maryland Appalachian Plateau.

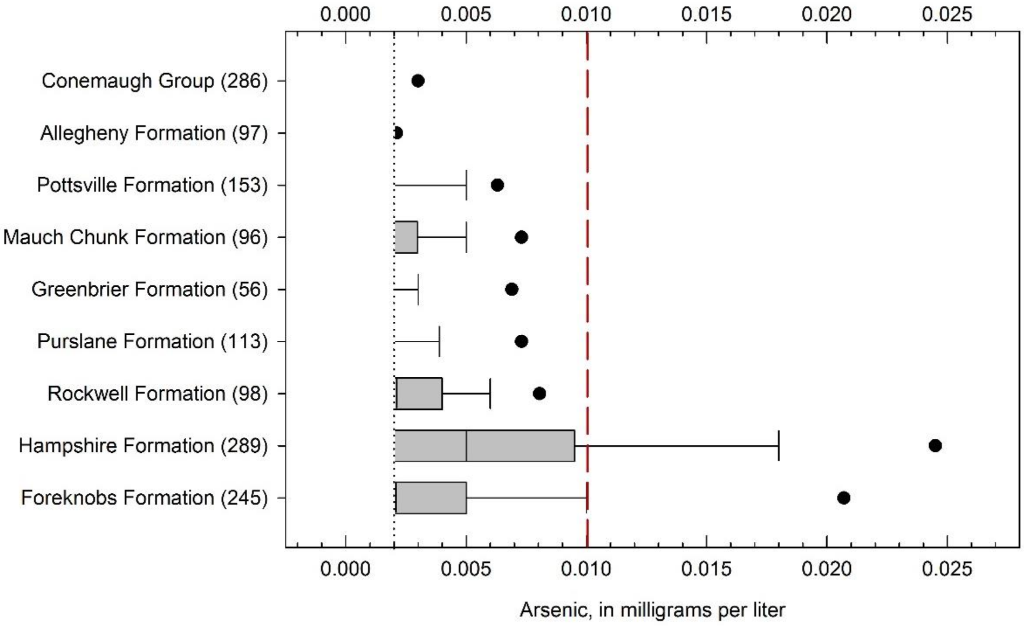


Figure 17. Box-and-whisker plots of arsenic concentrations with respect to geologic unit. MCL (0.01 mg/L) is shown as a red dashed line and reporting level (0.002 mg/L) is shown as a dotted line. See figure 6 for explanation of box-and-whisker plots. Sample size is shown in parentheses.

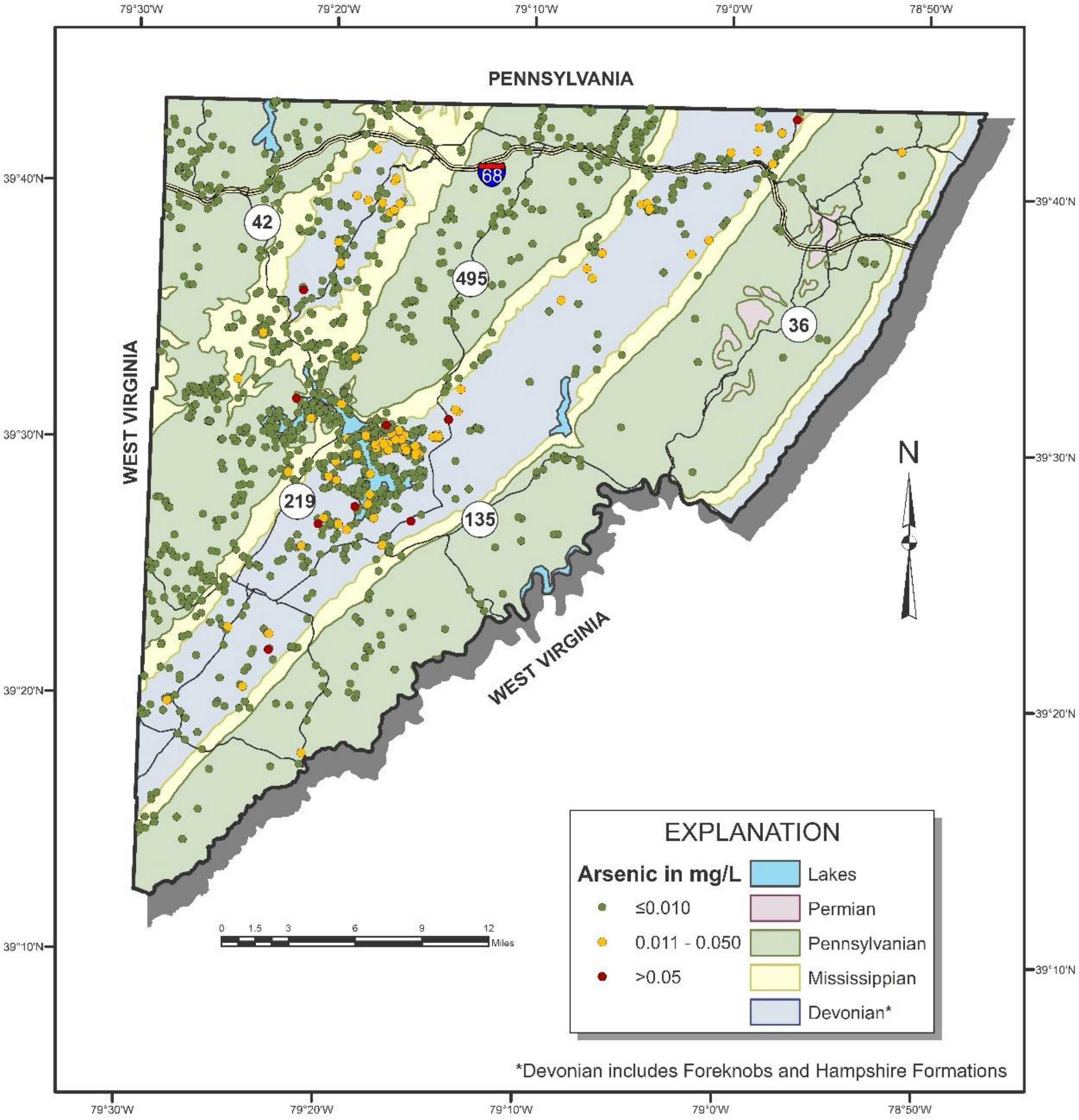


Figure 18. Distribution of arsenic concentrations in aquifers in the Maryland Appalachian Plateau.

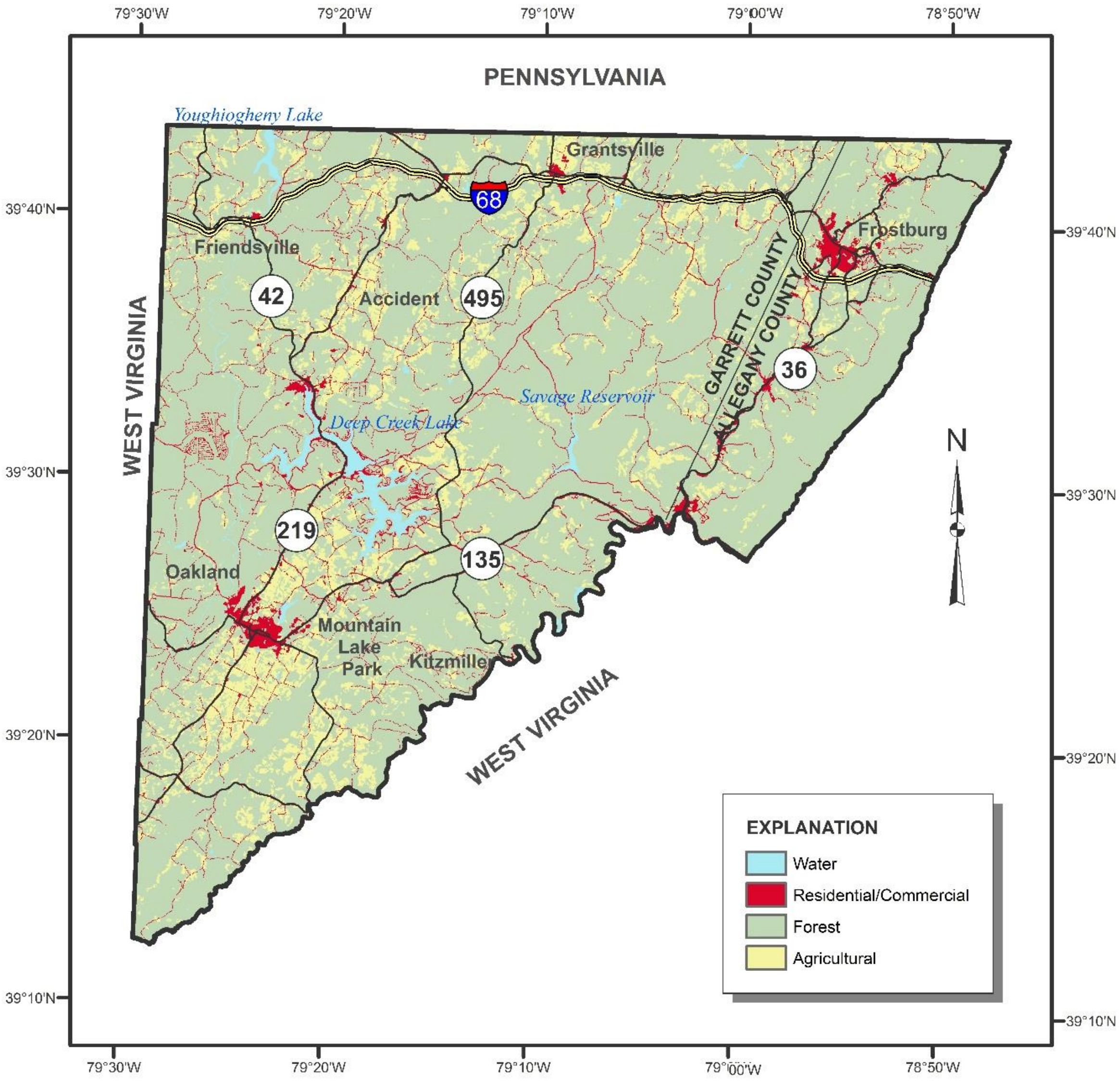


Figure 19. Generalized land use in the Appalachian Plateau. Data from Homer and others (2015).

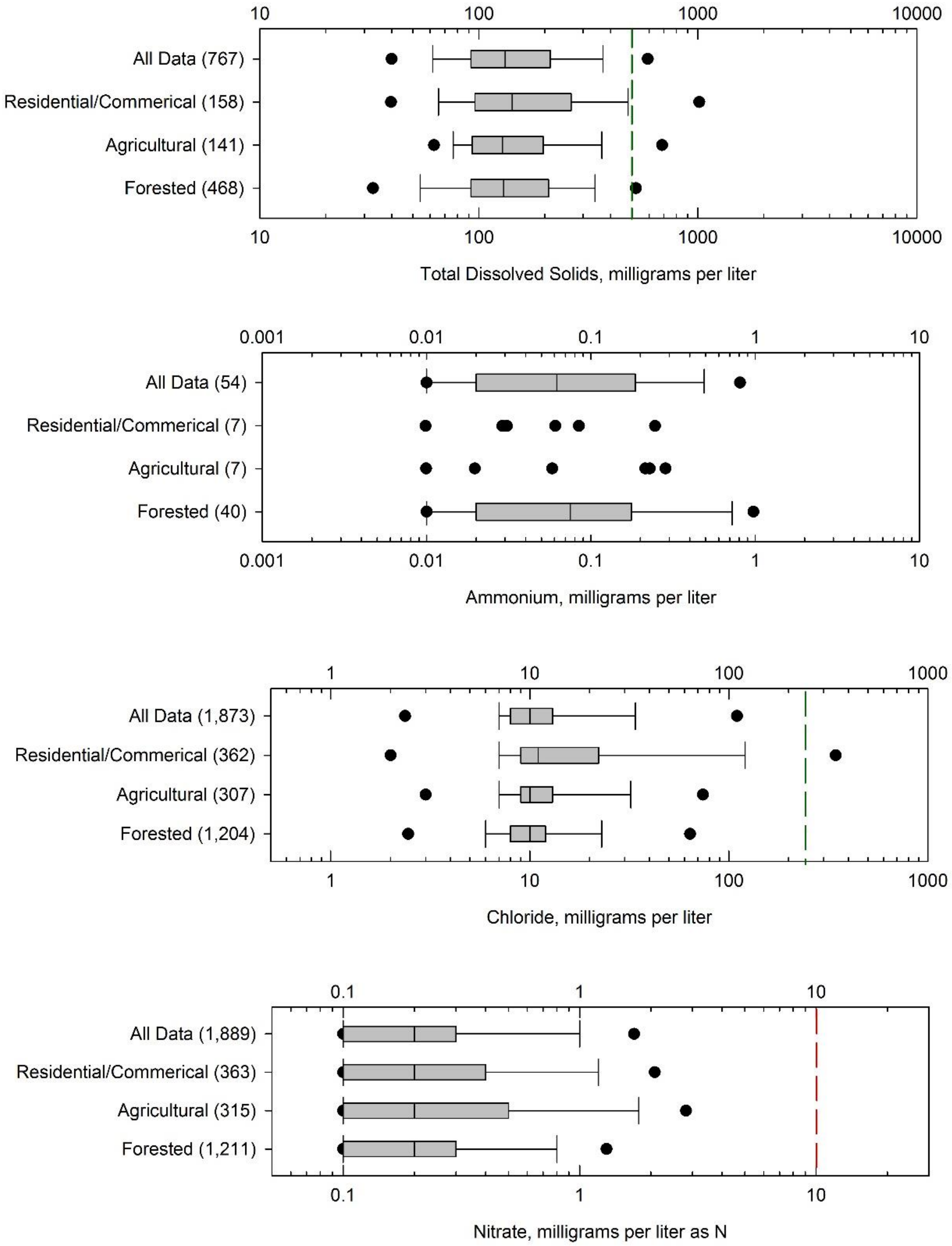


Figure 20. Box-and-whisker plots for selected inorganic constituents with respect to land use. Wells identified as "open water" were not included in these plots. Respective MCLs are shown as red dashed line, SMCLs are shown as a green dashed line, and most common Reporting levels are shown as dotted line. See figure 6 for explanation of box-and-whisker plots. Sample size is shown in parentheses.

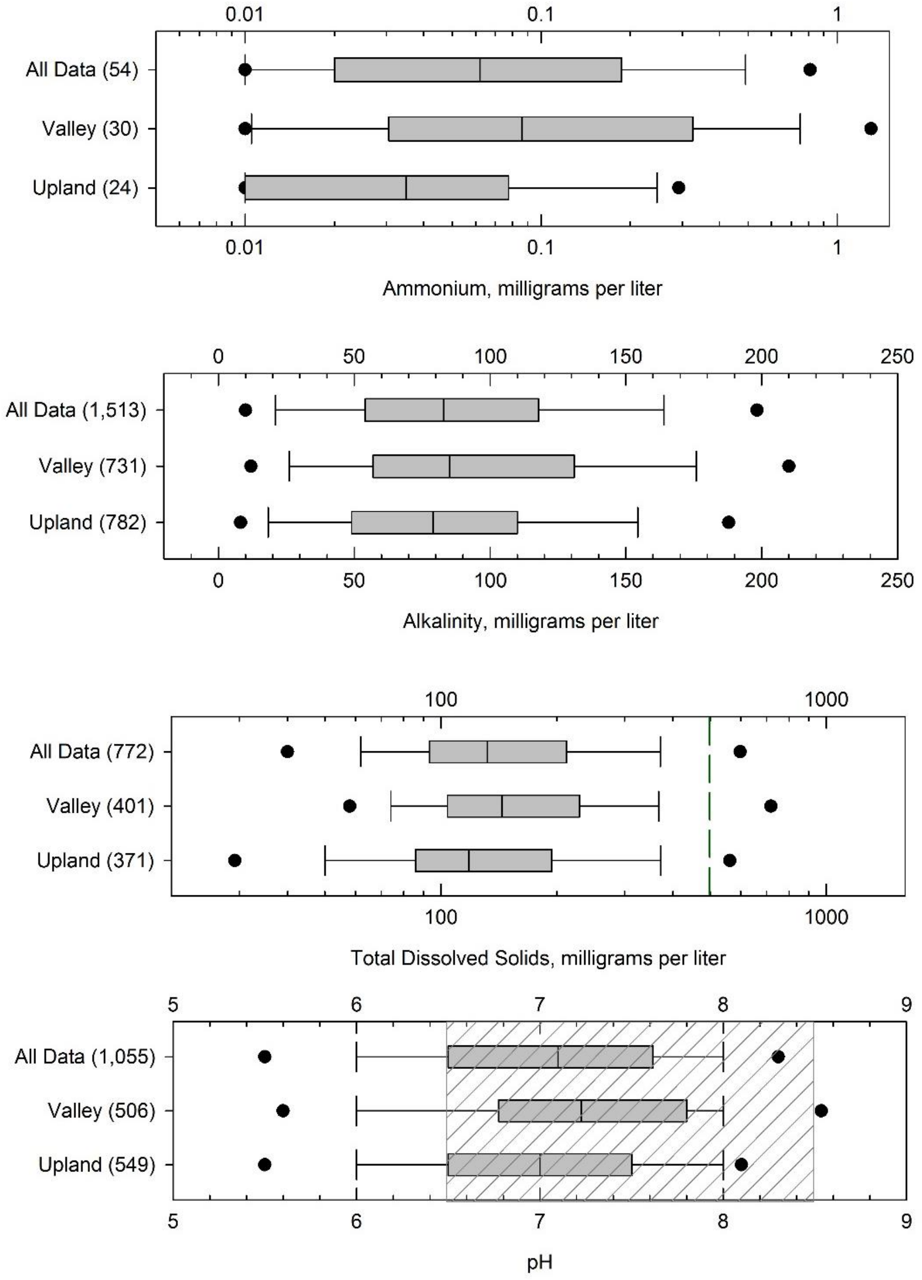


Figure 21. Box-and-whisker plots for selected inorganic constituents with respect to topographic position. Shaded area indicates acceptable drinking water pH. Respective MCLs are shown as red dashed line, SMCLs are shown as a green dashed line, and most common reporting levels are shown as dotted line. See figure 6 for explanation of box-and-whisker plots. Sample size is shown in parentheses.

Table 1. Description of geologic units in the Maryland Appalachian Plateau Physiographic Province. Adapted from Brezinski and Conkwright (2013).

Age	Name	Description
Permian?	Dunkard Formation	Interbedded, medium gray to dark gray, carbonaceous, silty shale and siltstone; light to medium gray, micaceous, medium- to coarse-grained sandstone; and thin, discontinuous nodular limestone, and thin coal beds. Thickness up to 250 feet.
Pennsylvanian	Monongahela Group	Interbedded, medium gray to dark gray, carbonaceous, silty shale and siltstone; light to medium gray, micaceous, medium- to coarse-grained sandstone, and thin, discontinuous, nodular limestone, and coal beds. Thickness 225-250 feet.
	Conemaugh Group (Undivided)	Interbedded, light gray, micaceous sandstone and gray silty shale and thin, dark gray, marine shales in the lower half of the group, and greenish-gray and reddish brown to variegated mudstone, shale, claystone, and nodular nonmarine limestone in its upper part. Thickness 800-900 feet.
	Allegheny Formation	Interbedded, medium to dark gray shale and siltstone, tan to light gray sandstone, claystone, and mineable coal beds. Thickness 200-250 feet.
	Pottsville Formation	Dominantly light gray to tan, medium- to coarse-grained sandstone and conglomerate with subordinate amounts of dark gray shale, siltstone, and coal. Thickness 180-200 feet.
Mississippian	Mauch Chunk Formation	Interbedded, reddish brown shale; variegated, root-mottled mudstone and siltstone, and reddish brown to greenish gray lenticular sandstone. Thickness 300-600 feet.
	Greenbrier Formation	Light gray cross-bedded, sandy limestone to calcareous sandstone at the base (Loyalhanna Member); overlain by interbedded, reddish, fossiliferous mudstone, and tan to reddish brown, fine-grained sandstone, and reddish brown siltstone and variegated shale (Savage Dam Member); succeeded by thin- to medium bedded, light to medium gray, argillaceous, fossiliferous limestone at the top (Wymps Gap Member). Thickness 150-200 feet.
	Purslane Formation	Light gray, tan, and reddish brown, coarse-grained to conglomeratic, thickbedded to cross-bedded sandstone and thin beds of gray shale, and coaly shale. Thickness 150-more than 300 feet.
Devonian	Rockwell Formation	Interbedded, gray, silty shale, light gray to tan sandstone, and coaly and reddish shale. In Allegany and Washington counties a reddish brown to gray, polymictic diamictite marks the base of the formation. Thickness less than 100-more than 400 feet.
	Hampshire Formation	Interbedded, reddish brown to brownish red, locally greenish gray sandstone, reddish brown siltstone, shale, and rooted claystone. Thickness approximately 2,000-more than 3,000 feet.
	Foreknobs Formation	Interbedded, olive-gray medium- to coarse-grained, cross-bedded sandstone; greenish gray to dusky red, fossiliferous shale and siltstone. Thick (>30 feet) sandstone intervals occur both near the base and near the top of the formation. Thickness 1,200-more than 1,500 feet.
	Harrell-Brallier-Sherr Formations (Undivided)	The Harrell Shale is a dark gray, fissile, calcareous, thinly laminated, shale that weathers to thin yellowish gray shale chips. The base of the Harrell is marked by the black, very fissile Burket Shale Member. The Harrell grades eastward into the Brallier Formation. Thickness up to 150 feet. The Brallier Formation is a succession of thinly interbedded, gray to olive-gray shale and siltstone and thin, fine-grained sandstone. Thickness 2,000-2,500 feet. The Sherr Formation is interbedded, reddish- -brown to grayish brown shale; thin, gray siltstone; and fine-grained, bioturbated and fossiliferous sandstone. Thickness approximately 1,000 feet in Garrett County; becomes indistinct in eastern Allegany and western Washington counties.

Table 2. Summary of water quality data from wells in the Maryland Appalachian Plateau Physiographic Province with respect to Primary Maximum Contaminant Levels (MCLs) and Health Advisories (HAs). Sources: U.S. Environmental Protection Agency (2012, 2016).

[mg/L, milligrams per liter; pCi/L, picocuries per liter; N, nitrogen]

MAXIMUM CONTAMINANT LEVELS:

Contaminant	MCL	Number of sites tested	Percentage of sites exceeding MCL	Number of sites exceeding MCL
Antimony	0.006 mg/L	65	0	0
Arsenic	0.01 mg/L	1,434	7	101
Barium	2 mg/L	73	1.4	1
Beryllium	0.004 mg/L	71	0	0
Cadmium	0.005 mg/L	73	0	0
Chromium	0.1 mg/L	73	0	0
Copper	1.3 mg/L	74	0	0
Fluoride	4.0 mg/L	124	<1	1
Lead	0.015 mg/L	88	2.3	2
Mercury (inorganic)	0.002 mg/L	29	0	0
Nitrate	10 mg/L as N	1,904	<1	3
Nitrite	1 mg/L as N	110	0	0
Selenium	0.05 mg/L	73	0	0
Sodium	20 mg/L*	123	22	27
Sulfate	500 mg/L*	282	3.5	10
Thallium	0.002 mg/L	64	0	0
Uranium	0.03 mg/L	53	0	0
Gross alpha-particle activity	15 pCi/L	61	1.7	1
Gross beta-particle activity	4 millirems per year	54	--	--
Radium-226 plus Radium-228	5 pCi/L	4	25	1

* Drinking Water Advisory (DWA)

Table 2, continued.

HEALTH ADVISORIES AND DRINKING WATER ADVISORIES:				
Contaminant	**Lifetime Health Advisory (mg/L)**	**Number of sites tested**	**Percentage of sites exceeding HA or DWA**	**Number of sites exceeding HA or DWA**
Ammonia	30	24	0	0
Boron	6	57	0	0
Manganese	0.3	1,727	15	267
Mercury	0.002	29	0	0
Molybdenum	0.04	57	0	0
Nickel	0.1	70	0	0
Silver	0.1	60	0	0
Sodium	20[1,2]	123	22	27
Strontium	4	53	2	1
Sulfate	500[2]	282	3.5	10
Zinc	2	76	0	0

[1] For sodium-restricted diet
[2] Drinking Water Advisory

Table 3. Summary of water quality data from wells in the Maryland Appalachian Plateau Physiographic Province with respect to Secondary Maximum Contaminant Levels (SMCLs) and Action Levels (ALs).

[mg/L, milligrams per liter; p-c, platinum-cobalt]

Contaminant	SMCL or AL	Number of sites tested	Percentage of samples exceeding SMCL or AL	Number of sites exceeding SMCL or AL
Aluminum	0.05 to 0.2 mg/L	104	28	24>0.05 mg/L 5>0.2 mg/L
Chloride	250 mg/L	1,885	2.5	47
Color	15 p-c units	199	11	22
Copper	1.0 mg/L	74	0	0
Fluoride	2.0 mg/L	124	0.8	1
Iron	0.3 mg/L	1,733	57	994
Manganese	0.05 mg/L	1,727	54	939
pH	6.5-8.5	1,055	25	35 >8.5 228 <6.5
Silver	0.1 mg/L	60	0	0
Sodium	60 mg/L[1] 20 mg/L[2]	123	12 22	15 27
Sulfate	250 mg/L	282	5	14
Total Dissolved Solids (TDS)	500 mg/L	772	6.6	51
Zinc	5 mg/L	76	0	0

[1] Drinking Water Advisory

[2] For individuals on a 500 mg/day restricted-sodium diet

Table 4. Classification of water hardness.

[Source: Durfor and Becker, 1964 (p. 24)]

Hardness range		
Milligrams per liter as $CaCO_3$	**Grains per gallon**	**Description**
0-60	0-3.51	Soft
61-120	3.57-7.02	Moderately Hard
121-180	7.08-10.52	Hard
>180	>10.52	Very Hard

Table 5. Summary of land use categories in the Maryland Appalachian Plateau Physiographic Province.

[Open water did not have a MGS generalized land use description as wells located within this classification, are not actually within open water.]

USDA Land Use Descriptions	MGS Generalized Land Use Descriptions
Open Water	--
Developed, Open Space	Residential/Commercial
Developed, Low Intensity	
Developed, Medium Intensity	
Developed, High Intensity	
Barren Land	Forested
Deciduous Forest	
Evergreen Forest	
Mixed Forest	
Shrub/Scrub	
Herbaceous	
Woody Wetlands	
Emergent Herbaceous Wetlands	
Hay/Pasture	Agricultural
Cultivated Crops	

Table 6. Comparison of selected wellwater quality constituents in the Appalachian Plateau and Piedmont Physiographic Provinces of Maryland.

[Sources: Howard County, Dine and others (1995); Cecil County, Otton and others (1988); Baltimore County, Bolton (1998). Top number is median value; number in parentheses are the range of values].

Constituent	Appalachian Plateau (this report)	Piedmont		
		Howard County	Baltimore County	Cecil County
Dissolved solids (mg/L)	132 (<10—2,560)	--	104 (18—718)	111 (41—1,170)
Hardness (mg/L as $CaCO_3$)	70 (0.2—1,620)	--	57 (9—480)	52 (14—410)
Dissolved oxygen (mg/L)	<1 (0.1—9.8)	7.4 (0—14.6)	7.4 (<1—9.8)	--
pH	7.1 (3.5—10)	5.9 (4.7—8.5)	6.0 (5.1—8.0)	6.0 (5.4—8.1)
Iron (mg/L)	0.44 (<0.004—312)	0.010 (<0.003—18)	0.100[1] (<0.010—380)	0.011 (<0.003—1.9)
Manganese (mg/L)	0.07 (<0.01—22.78)	<0.001—2.4 (0.011)	<0.010[1] (<0.010—0.290)	0.010 (<0.001—0.3)
Nitrate plus nitrite (mg/L as N)	0.2 (<0.01—38)	2.1 (<0.10—13)	2.9 (<0.05—35)	2.2 (<0.1—21)
Chloride (mg/L)	10 (<0.1—4,300)	5.7 (0.8—250)	8.6 (1.2—280)	6.9 (1.2—590)

[1] Unfiltered

Larry Hogan
Governor

Boyd K. Rutherford
Lt. Governor
Secretary

Mark J. Belton
Secretary

Joanne Throwe
Deputy

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.

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DNR Publication Number: 12 –4142017-654

2018