Groundwater Quality in Relation to Drinking Water Health Standards and Hydrogeologic and Geochemical Characteristics for 47 Domestic Wells in Potter County, Pennsylvania, 2017
Groundwater Quality in Relation to Drinking Water Health Standards and Hydrogeologic and Geochemical Characteristics for 47 Domestic Wells in Potter County, Pennsylvania, 2017

By Daniel G. Galeone, Charles A. Cravotta III, and Dennis W. Risser

Prepared in cooperation with the County of Potter

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Conversion Factors

U.S. customary units to International System of Units

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

°F = (1.8 × °C) + 32.

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

°C = (°F – 32) / 1.8.
Datum

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

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

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

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Activities for radioactive constituents in water are given in picocuries per liter (pCi/L).
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Abstract

As part of a regional effort to characterize groundwater in rural areas of Pennsylvania, water samples from 47 domestic wells in Potter County were collected from May through September 2017. The sampled wells had depths ranging from 33 to 600 feet in sandstone, shale, or siltstone aquifers. Groundwater samples were analyzed for physicochemical properties that could be evaluated in relation to drinking-water health standards, geology, land use, and other environmental factors. Laboratory analyses included concentrations of major ions, nutrients, bacteria, trace elements, volatile organic compounds (VOCs), ethylene and propylene glycol, alcohols, gross-alpha/beta-particle activity, uranium, radon-222, and dissolved gases. A subset of samples was analyzed for radium isotopes (radium-226 and -228) and for the isotopic composition of methane.

Results of this 2017 study show that groundwater quality generally met most drinking-water standards that apply to public water supplies. However, a percentage of samples exceeded maximum contaminant levels (MCLs) for total coliform bacteria (69.6 percent), Escherichia coli (30.4 percent), arsenic, and barium; and secondary maximum contaminant levels (SMCLs) for field pH, manganese, sodium, iron, total dissolved solids, aluminum, and chloride. All of the analyzed VOCs were below limits of detection and associated drinking water criteria. Radon-222 activities exceeded the proposed drinking-water standard of 300 picocuries per liter in 80.9 percent of the samples.

The field pH of the groundwater ranged from 4.6 to 9.0. Generally, the lower pH samples had greater potential for elevated concentrations of dissolved metals, including beryllium, copper, lead, nickel, and zinc, whereas the higher pH samples had greater potential for elevated concentrations of total dissolved solids, sodium, fluoride, boron, and uranium. Near-neutral samples (pH 6.5 to 7.5) had greater hardness and alkalinity concentrations than other samples with pH values outside this range. Calcium/bicarbonate waters were the predominant hydrochemical type for the sampled aquifers, with mixed water types for many samples, including variable contributions from calcium, magnesium, and sodium combined with bicarbonate, sulfate, chloride, and nitrate.

Water from 45 wells had concentrations of methane greater than the 0.0002 milligrams per liter (mg/L) detection limit. One sample had the maximum value of 11 mg/L, which exceeds the Pennsylvania action level of 7 mg/L. Additionally, three other samples had concentrations of methane greater than 4 mg/L. Outgassing of such levels of methane from the water to air within a confined space can result in a potential hazard. The elevated concentrations of methane generally were associated with suboxic groundwater (dissolved oxygen less than 0.5 mg/L) that had near-neutral to alkaline pH with relatively elevated concentrations of iron, manganese, ammonia, lithium, fluoride, and boron. Other constituents, including barium, sodium, chloride, and bromide, commonly were elevated, but not limited to, those well-water samples with elevated methane. Low levels of ethane (as much as 1.2 mg/L) were present in eight samples with the highest methane concentrations. Five samples were analyzed for methane isotopes. The isotopic and hydrocarbon compositions in these five samples suggest the methane may be of microbial origin or a mixture of thermogenic and microbial gas, but differed from the compositions reported for mud-gas logging samples collected during drilling of gas wells.

The concentrations of sodium (median 8.2 mg/L), chloride (median 7.64 mg/L), and bromide (median 0.02 mg/L) for the 47 groundwater samples collected for this study ranged widely and were positively correlated with one another and with specific conductance and associated measures of ionic strength. Sixty percent of the Potter County well-water samples had chloride concentrations less than 10 mg/L. Samples with higher chloride concentrations had variable bromide concentrations and corresponding chloride/bromide ratios that are consistent with sources such as road-deicing salt and septic effluent (low bromide) or brine (high bromide). Brines are naturally present in deeper parts of the regional groundwater system and, in some cases, may be mobilized by gas drilling. It is also possible that valley
wells were drilled close to or into the brine-freshwater interface, so brine signatures do not necessarily indicate contamination due to drilling. The chloride, bromide, and other constituents in road-deicing salt or brine solutions tend to be diluted by mixing with fresh groundwater in shallow aquifers used for water supply. Although 1 of 8 groundwater samples with the highest methane concentrations (greater than 0.2 mg/L) had concentrations of chloride and bromide with corresponding chloroform/bromide ratios that indicated mixing with road-deicing salt, the other 7 of 8 samples with elevated methane had concentrations of chloride and bromide with corresponding chloride/bromide ratios that indicated mixing with a small amount of brine (0.02 percent or less) similar in composition to those reported for gas and oil well brines in Pennsylvania. In several eastern Pennsylvania counties where gas drilling is absent, groundwater with comparable chloride/bromide ratios and chloride concentrations have been reported. Approximately 50 percent of Potter County well-water samples, including two samples with the fourth (72.9 mg/L) and fifth (47.0 mg/L) highest chloride concentrations, have chloride/bromide ratios that indicate predominantly anthropogenic sources of chloride, such as road-deicing salt or septic effluent.

Introduction

Pennsylvania has approximately 2.4 million residents that depend on groundwater for their domestic water supply and has the second highest number of domestic wells of any State in the Nation. Despite the widespread reliance on groundwater in rural areas of the State, publicly available data to characterize the quality of private well water are sparse (Low and Chichester, 2006; Giddings, 2014; Johnson and Belitz, 2017). Homeowners are not required to test the chemical or bacteriologic quality of their well water. In Potter County, approximately 68 percent of the homes use privately owned wells for their drinking-water supply (Bryan Swistock, Penn State Extension, written commun., 2019).

Water from more than 1 in 5 domestic wells in the Nation potentially exceeds at least one human-health water-quality standard and yet, the potential health risks associated with domestic groundwater supplies are often understudied in comparison to the research and testing of public water supplies (DeSimone, 2009). Unlike public water-supply systems, the management of domestic, privately owned, wells in Pennsylvania is solely the responsibility of the homeowner. Acute gastrointestinal illnesses have been attributed to parasitic, viral, and bacterial pathogens in rural private well water (Raina and others, 1999; Murphy and others, 2016). Metals such as lead may either be present in the aquifer or leached from plumbing components by corrosive groundwater, causing impaired mental and physical development (Brown and Margolis, 2012; Belitz and others, 2016). The presence of naturally occurring iron and manganese in drinking water can be a nuisance owing to unpleasant taste, odor, and color, and often require maintenance to avoid staining and clogging of household plumbing fixtures (Penn State Extension, 2017). Manganese has been shown to cause neurological issues in infants and small children (Ljung and Vahter, 2007). Exposure to arsenic, which is another potentially naturally occurring contaminant in groundwater (Chapman and others, 2013), has been linked to skin and internal cancers (U.S. Environmental Protection Agency, 2000; National Research Council, 1999). Various naturally occurring radioactive elements and manmade volatile organic compounds (VOCs) that may be present in drinking water can be carcinogenic, mutagenic, or teratogenic (Otton, 1992; National Research Council, 1998; Hopke and others, 2000). Elevated levels of dissolved methane and associated hydrocarbon gases can pose an explosive safety risk if wells or water tanks are not properly vented and the gas is ignited (Swistock and Sharpe, 2006).

Groundwater acquires solutes through natural and anthropogenic loading of constituents in the recharge area from precipitation, weathering reactions of minerals in the soil and aquifer materials, and constituents applied by human activities at or near the land surface (Hem, 1985; Appelo and Postma, 2005). The quality of well water used for domestic supply is influenced by the regional and local setting, including the topography, geology, and land use, and by well-construction features and household plumbing. Metallic components in the well and plumbing may corrode, adding metals to drinking water (Swistock and others, 1993; Nguyen and others, 2010; Belitz and others, 2016). In addition, improper well construction (in other words, insufficient grout leading to casing leakage, and (or) the absence of or a faulty sanitary well cap) can facilitate the introduction of potential contaminants from the surface into drinking-water supply wells and aquifers. Increased methane gas production associated with brine injection may affect nearby drinking-water supply wells (Swistock and others, 2001; Simpson, 2004; Swistock and Sharpe, 2005; Giddings, 2014). Elevated methane concentrations may also indicate casing leakage, and (or) the absence of or a faulty sanitary well cap can facilitate the introduction of potential contaminants from the surface into drinking-water supply wells and aquifers. Increased methane gas production associated with brine injection may affect nearby drinking-water supply wells (Swistock and others, 2001; Simpson, 2004; Swistock and Sharpe, 2005; Giddings, 2014). Despite legislative attempts, Pennsylvania is one of only two States without statewide water-well construction standards intended to protect groundwater from surface-derived contaminants (Swistock, 2012; Wagner, 2012; LaRegina, 2013; Giddings, 2014; Pennsylvania General Assembly, 2015a,b, 2016). Pennsylvania does require each well driller to be permitted with the State, and the driller must provide a Water Well Completion Report (describing where, when, and how the well was constructed) to the State and the homeowner (Pennsylvania Department of Conservation and Natural Resources, 2018).

Most of the publicly available laboratory test results for groundwater-quality samples in Potter County were collected more than 20 years ago (Lohman, 1939; Taylor and others, 1983; Williams and others, 1998) and do not include the broad suite of the current analytes of concern, such as total and fecal coliform bacteria, barium, strontium, chloride, bromide, hydrocarbon gases, trace metals, radon-222, and other radiochemicals. Without current data for associated groundwater-quality constituents, it is not possible to evaluate the sources of constituents or future potential groundwater-quality changes. Future changes in groundwater quality can...
be the result of natural variability or of human activities, including coal mining, oil and gas exploration, agricultural practices, onsite septic systems, or land development.

The current study of the quality of groundwater in Potter County was conducted by the U.S. Geological Survey (USGS) in cooperation with the County of Potter. At the local level, the results will serve the needs of resource managers through a comparison of the quality of private well water with drinking-water health standards and an evaluation of potential natural and anthropogenic (manmade) influences on local groundwater quality. More broadly, the results and interpretations of the data described in this report further inform the national, statewide, and regional understanding of groundwater used for potable water supply.

Previous Investigations

Analyses of water samples collected from domestic wells in northeastern Pennsylvania as part of earlier studies indicate that bedrock geology and well construction have an important influence on groundwater quality, and contaminants commonly include arsenic, lead, nitrate, and radon (Swistok and others, 1993; 2009). In a regional assessment of groundwater quality in the formerly glaciated valleys in the northern third of Potter County, Williams and others (1998) found a wide range in hardness and total dissolved solids (TDS) in the water. Analyses of samples collected from 43 wells as part of that assessment showed hardness values ranging from 12–242 milligrams per liter (mg/L) as calcium carbonate (CaCO₃), and TDS ranging from 54–1,260 mg/L. Water that has a hardness value less than 60 mg/L CaCO₃ is considered soft; water ranging from 61–120 mg/L CaCO₃ is considered moderately hard; water ranging from 121–180 mg/L CaCO₃ is considered hard; and water with a CaCO₃ concentration greater than 180 mg/L is considered very hard (U.S. Geological Survey, 2019a).

A study of groundwater pollution in northeastern Pennsylvania (focused on Bradford, Lycoming, Sullivan, and Tioga Counties) found that groundwater is affected locally by contamination from the infiltration of animal waste, septic effluent, or seasonally applied road salt (Reilly and others, 2015). In addition, the many gas wells and associated underground natural gas storage reservoirs in this area, and the potential for the “escape” of methane and its potential for contamination of groundwater as a consequence of natural gas development, is a concern (Osborn and others, 2011; Jackson and others, 2013; Heilweil and others, 2015; and Lewellyn and others, 2015). Given this concern, however, it must be noted that naturally occurring thermogenic methane (produced by geologic processes) and biogenic-derived methane (produced by living organisms) is commonly found in groundwater from domestic wells outside of areas developed for natural gas (Molofsky and others, 2011, 2013; Heisig and Scott, 2013; Senior and others, 2017; Senior and Cravotta, 2017; and Botner and others, 2018), especially in valleys and near faults (Wen and others, 2018).

The USGS has conducted a series of county-wide groundwater studies since 2007 in order to provide publicly available data to better characterize the quality of groundwater in rural areas of Pennsylvania. Studies in Pike County and Sullivan County indicated few exceedances of the drinking water health standards, and samples that had elevated levels of pH and concentrations of methane commonly also showed higher concentrations of sodium, lithium, boron, fluoride, and bromide (Senior, 2009, 2014; Sloto, 2013; Senior and Cravotta, 2017). Studies in Wayne County, Lycoming County, and Bradford County presented similar results but also included analyses of water samples for total coliform bacteria that indicated exceedances of the drinking water health standards; these studies also employed geochemical modeling techniques that offered further insight into the effect that water–rock reactions, topographic position, and pH have on the regional groundwater chemistry (Senior and others, 2017; Gross and Cravotta, 2017; Clune and Cravotta, 2019). Naturally occurring radioactivity is described in detail in previous reports on groundwater quality in Wayne, Pike, and Lycoming Counties in Pennsylvania (Senior and others, 2017; Senior and Cravotta, 2017; and Gross and Cravotta, 2017, respectively).

Purpose and Scope

This report (1) compares the quality of water in domestic wells in Potter County, Pennsylvania, to drinking-water standards, and (2) evaluates natural and anthropogenic influences on groundwater quality in the county. To meet these objectives, water samples were collected from 47 domestic wells throughout Potter County from May through September of 2017. The samples were analyzed for physical and chemical properties, including major ions, nutrients, bacteria, trace elements, volatile organic compounds (VOCs), ethylene and propylene glycol, alcohols, gross-alpha/beta-particle activity, uranium (U), radon-222, and dissolved gases (see appendix 1 for complete listing of analytical constituents). A subset of samples was analyzed for radium isotopes (radium-226 and radium-228) and for the isotopic composition of methane. The groundwater-quality data, summary statistics, and geochemical computations presented here document the current (2017) chemical characteristics of groundwater from domestic wells in Potter County.

Description of Study Area

Potter County occupies 1,082 square miles in north-central Pennsylvania, where it is bordered by Alleghany and Steuben Counties, in New York, and Tioga, Lycoming, Clinton, Cameron, and McKean Counties in Pennsylvania, clockwise from north (fig. 1A). The northern part of Potter County lies in the Glaciated High Plateau section of the Appalachian Plateau physiographic province, and the southern area is in the Deep Valleys section (fig. 1C). The geology of the Appalachian Plateau is generally characterized as gently
folded clastic sedimentary bedrock that is overlain locally by unconsolidated glacial deposits and alluvium (less than 20 feet thick). The Appalachian Plateau province within Potter County “is underlain by nearly flat-lying sedimentary bedrock and unconsolidated deposits of glacial and postglacial origin. The bedrock consists primarily of shale, siltstone, and sandstone of Devonian to Pennsylvanian age” (Williams and others, 1998) (fig. 1B; table 1). Fractures and solution enlargement of bedding planes and fractures can increase porosity in water-bearing zones that provide groundwater to wells. The groundwater is obtained primarily from wells completed in shallow bedrock or unconsolidated alluvial deposits that overlie the bedrock. Wells drilled in bedrock typically are cased from the land surface into competent rock and grouted to limit the potential for contamination from the surface. Below the bottom of the casing, this type of well consists of an open hole through the water-bearing bedrock zones, whereas wells drilled and completed in unconsolidated deposits may obtain water through an open-ended casing or are screened within the water-bearing zones of the unconsolidated material.

The primary lithologies of the bedrock in Potter County—shale, siltstone, and sandstone—contain silicate and aluminosilicate minerals, including quartz, feldspar, chlorite, muscovite, and illite, plus minor carbonate, sulfate, sulfide, and oxide minerals that are present as clasts, fracture filling, and cements (Hem, 1985). Although mineralogy is expected to vary locally, the carbonate, sulfate, and sulfide minerals in the bedrock are prone to weathering in near-surface environments where they will affect pH, hardness, alkalinity, sulfate, and associated solutes that contribute to the dissolved solids concentrations of the water flowing through the rock. Likewise, chlorite, muscovite, illite, and other clay minerals readily accommodate ionic substitutions and are widely recognized to be involved in cation-exchange and sorption processes that further influence the pH, hardness, and associated concentrations of the solutes (Hem, 1985; Appelo and Postma, 2005). The land cover in Potter County is predominantly forested (approximately 78 percent), consisting of both State and privately owned lands (U.S. Geological Survey, 2014). Shrub and herbaceous vegetation compose about 6.8 percent of the landscape. Agricultural land covers about 12.5 percent of county, with the primary use for hay and pasture (10.9 percent of county), followed by cultivated cropland (1.6 percent). Of the remaining land area, about 2 percent is developed and 1 percent remains as water or wetland (fig. 1D). Conventional and unconventional gas wells have been developed across most of the same areas in the Appalachian Plateau physiographic province, and the related infrastructure (well pads, pipelines, and access roads) plus underground gas storage reservoirs are found in northern and southern parts of the county (figs. 1C and 1D). On the basis of data for 2018 from the Pennsylvania Department of Environmental Protection (PADEP), there are 1,185 active conventional gas wells and 85 active unconventional gas wells in Potter County; in addition, there are 904 and 37 inactive wells that are conventional and unconventional, respectively (fig. 1D). The inactive wells are abandoned or plugged. Potter County is largely rural, with a population of 17,457 recorded in 2010 (U.S. Census Bureau, 2011). Some of the most densely populated areas in the county include the boroughs of Coudersport, Galeton, and Shinglehouse, with 1,000 to 2,000 residents per town (U.S. Census Bureau, 2011).

Topography in Potter County consists mostly of land of low to moderate relief with rounded hills and valleys having altitudes ranging from 990 feet (ft) to 2,560 ft (U.S. Geological Survey, 2009). Streams in Potter County drain to three major river basins: the Genesee River Basin, which drains to the north; the West Branch Susquehanna River Basin, which drains to the south and east; and the Allegheny River Basin, which drains to the south and west. The local climate provides some seasonal variation in precipitation, with an average monthly precipitation of 4.2 inches from April through September and 3.2 inches from October through March (Pennsylvania State Climatologist, 2019). Mean annual precipitation is 42 inches (PRISM Group at Oregon State University, 2012a), of which approximately 16–18 inches becomes groundwater recharge (Reese and Risser, 2010). Groundwater levels fluctuate seasonally with a steady decline from April to August (fig. 2) owing to increased evapotranspiration. The overall mean air temperature for Potter County is 7.0 degrees Celsius (°C), with average minimum and maximum temperatures of 1.3 °C and 12.8 °C, respectively (PRISM Group at Oregon State University, 2012b, c, d).
Figure 1. Maps of A, bedrock geology, B, lithology, C, physiographic sections in the Appalachian Plateau physiographic province, underground gas storage areas, and sampling locations, and D, land use and gas wells in Potter County, north-central Pennsylvania.
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Table 1. Descriptions of bedrock geologic map units for Potter County, percent of Potter County, Pa., underlain by geologic unit, associated number of groundwater samples collected for each geologic unit, and well depth and casing depth summary statistics by geologic unit, for the Potter County groundwater study, 2017. Information excerpted from digital data set polygon attributes for bedrock geology of Pennsylvania (Miles and Whitfield, 2001).

[NA, Not applicable]

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<td>99</td>
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<tr>
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<td>Mudstone</td>
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<tr>
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<td>Sandstone</td>
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<td>160</td>
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Study Methods

A total of 47 domestic wells in Potter County (fig. 1C) were selected for sampling during 2017. Samples from all wells were analyzed for physical and chemical properties, including major ions, nutrients, bacteria, trace elements, VOCs, ethylene and propylene glycol, alcohols, gross-alpha/beta-particle activity, U, radon-222, and dissolved gases. A subset of samples was analyzed for radium isotopes (radium-226 and radium-228) and for the isotopic composition of methane. A list of the wells sampled, descriptive information, and quality-assurance/quality control data are provided in Galeone (2019). Water-quality results are provided in the USGS National Water Information System (NWIS) database (U.S. Geological Survey, 2019b).

The measured concentrations of analyzed constituents in the water samples were compared to U.S. Environmental Protection Agency (EPA) (2018) drinking-water standards that apply to public water supplies. The relations among observed chemical, biological, and radiological characteristics of the water samples, geology, topographic setting, land use, and other environmental variables associated with sampled wells are evaluated to explain the variability in the quality of the groundwater.

Selection of Sampling Locations

A computerized, stratified random site-selection approach was used to design a groundwater-quality sampling network (Scott, 1990) by creating an equal-area grid of cells (Belitz and others, 2010), with a randomly placed population of potential sites across the county. The program arbitrarily specified one site from each cell as a primary sampling point and three additional sites as alternative sampling locations. The best available well data within Potter County were obtained from the Pennsylvania Groundwater Information System database (Pennsylvania Bureau of Topographic and Geologic Survey, 2014) and from well records provided by Potter County (Will Hunt, Potter County Planning Commission, written commun., 2017). Potential wells for sampling were selected from these data based on the criteria that the well was (1) used for domestic supply or livestock purposes, (2) had an associated well drillers record, (3) was drilled after 1970, (4) was not a dug well, and (5) the top of the casing was above land surface. Wells located within 1 mile of one of the computer-generated random sampling points were identified, and well owners were contacted for permission to collect samples. Plumbing fixtures and any issues that could affect the collection of a representative water sample were discussed over the phone. Domestic wells meeting the criteria were prioritized for sampling. The random distribution of well sampling sites was limited by lack of wells in some grid cells that fell within undeveloped forested land.
All of the wells were completed in bedrock and most of the selected wells were completed in Devonian-age bedrock, either the Catskill Formation (sample size (n) = 36) or the Huntley Mountain Formation (n = 7), in which sandstone is the dominant lithology. One well completed in the Pennsylvanian-age Pottsville Formation, which is classified as sandstone, was also selected for sampling. The remaining three wells sampled were completed in “shale” (siltstone and mudstone) aquifers of the Devonian-age Chadakoin and Lock Haven Formations (table 1).

Collection and Analysis of Samples

Sampling sites included 47 wells throughout Potter County (fig. 1C) that were drilled with an open-hole interval in bedrock. Water samples were collected from the wells from May through September 2017, following protocols outlined in the USGS National Field Manual (U.S. Geological Survey, variously dated). The samples were collected using Teflon tubing attached to a sampling point (either an outside spigot, pressure tank, or hydrant on the well casing) prior to any water treatment. Wells were purged until field parameters (pH, Eh, specific conductance (SC), water temperature, turbidity, and dissolved oxygen) stabilized and the final readings were recorded. Samples were then collected for laboratory analysis.

Samples for measurement of TDS (residue on evaporation), and dissolved forms of major ions, trace metals, and nutrients were filtered onsite through a disposable capsule filter with a 0.45-micrometer pore size and analyzed by the USGS National Water Quality Laboratory in Denver, Colorado. Samples for determination of concentrations of major ions were preserved with nitric acid and analyzed at the laboratory by inductively coupled plasma atomic emission spectrometry, ion chromatography, or automated colorimetry. Nutrient analyses were performed by automated colorimetry with persulfate digestion when required (Fishman, 1993; Patton and Kryskalla, 2011).

Radiological samples for alpha/beta particle determinations were preserved with nitric acid and analyzed at ALS Laboratories in Fort Collins, Colorado, by gas flow proportional counting (EPA Method 900.0) (U.S. Environmental Protection Agency, 1980a). Differences between gross alpha and gross beta radioactivity measured soon after sample collection (within 72 hours) and after 30 days indicate whether short-lived radionuclides (such as radium-224, half-life of 3.6 days) are present in the sample. A subset of samples in which gross alpha (72-hour count) was greater than 4 picocuries per liter (pCi/L) was analyzed further for radium-226 (EPA Method 903.1) (U.S. Environmental Protection Agency, 1980b) and radium-228 (EPA Method 904) (U.S. Environmental Protection Agency, 1980c) by radon emanation, chemical separation, and gas flow proportional counting. Radon-222 samples were obtained through an inline septum with a gas-tight syringe to avoid atmospheric contact and analyzed at the laboratory by liquid scintillation (ASTM Method D 5072-16) (ASTM, 2016). The samples were also analyzed for their concentration of dissolved uranium.

Samples for analyses of dissolved gases were collected in an impermeable bag, and were analyzed at Isotech Laboratories, Champaign, Illinois, by gas compositional analysis to determine the concentration of fixed gases and light hydrocarbon gases dissolved in the sample (Dai and others, 2012). Five samples containing a sufficient concentration of methane were further analyzed for stable carbon (C) isotopes (13C and 12C and the stable hydrogen (H) isotopes H and D (deuterium). The 13C/12C and 2H/H ratios were determined by an isotope ratio mass spectrometric analysis that compared the sample to a reference standard. The carbon isotope ratio value in methane (CH4) (δ13CCH4) is reported in terms of per mil (‰) notation with respect to the Vienna Peedee belemnite standard. The hydrogen isotope ratio value in methane (δDCH4) is reported in terms of per mil notation with respect to the Vienna Standard Mean Ocean Water standard.

The remaining unfiltered samples were analyzed by Seewald Laboratories, Inc., in Williamsport, Pennsylvania. Samples for analyses of VOCs, dissolved hydrocarbon gases, and glycol were collected onsite using a stainless-steel manifold fitting to fill vials with minimal turbulence. Samples for analysis of VOC were preserved in vials with hydrochloric acid and analyzed by purge and trap gas chromatography/mass spectrometry (EPA Method 524.2) (U.S. Environmental Protection Agency, 1992). The concentrations of dissolved ethane and propane in the collection vials were determined by analyzing a portion of the headspace in the vials with a gas chromatograph equipped with a flame ionization detector (PADEP Method 3686) (Pennsylvania Department of Environmental Protection, 2012). Based upon the equilibrium gas concentration, a liquid sample concentration of these gases is calculated. Samples for glycols and alcohols were evaluated using the direct injection method, in which a gas chromatograph equipped with a flame ionization detector is chromatographically optimized for the separation and determination of the compounds of interest (EPA Method 8015 D) (U.S. Environmental Protection Agency, 2013). Oil and grease samples were preserved with hydrochloric acid and analyzed in the laboratory using hexane to determine the petroleum hydrocarbon fraction (EPA Method 1664 B) (U.S. Environmental Protection Agency, 2010). After sterilizing and flaming the sampling point in the field, the bacteria sample was collected and later analyzed in the laboratory using the Colilert color method, in which samples were enumerated to give counts of total coliform and Escherichia coli (E. Coli) (Standard Method 9223) (Standard Methods for the Examination of Water and Wastewater, 2017).

Graphical and Statistical Analyses

Various graphical and statistical techniques were used to compare water-quality data among sampling sites (wells), to distinguish natural and anthropogenic sources of dissolved
constituents, and to identify possible factors affecting the occurrence or transport of solutes in the aquifers in the study area. These techniques included the construction of bivariate scatter plots, boxplots, and trilinear (Piper) diagrams; calculation of mass ratios of chloride to bromide (Cl/Br) and correlation coefficients (Spearman’s rho); and aqueous speciation computations.

The boxplots considered physiographic province/section (appendix fig. 2.1), pH (fig. 2.2), SC (fig. 2.3), oxidation-reduction potential (redox) (fig. 2.4), and topographic position index (fig. 2.5) to classify the data. The boxplots show a notch interval around the median (Velleman and Hoaglin, 1981; Helsel and Hirsch, 2002). The redox classifications used in the boxplots were based on concentration thresholds of McMahon and Chapelle (2008) but were simplified to consider only three major classes (dissolved oxygen (DO); iron (Fe); manganese (Mn)):

1. “anoxic” (DO ≤0.5 mg/L, Mn ≥50 μg/L, and Fe ≥100 μg/L);
2. “mixed” (DO >0.5 mg/L and either Mn ≥50 μg/L or Fe ≥100 μg/L); or
3. “oxic” (DO >0.5 mg/L, Mn <50 μg/L, and Fe <100 μg/L).

The topographic position index (TPI) used in the boxplots was computed on the basis of a 25-meter digital elevation model (U.S. Geological Survey, 2009) using criteria reported by Llewellyn (2014) to indicate six potential TPI classes: (1) ridge, (2) upper slope, (3) steep slope, (4) gentle slope, (5) lower slope, or (6) valley.

Piper diagrams indicate the percentage contributions of the major cations and anions, in equivalents (molar concentration multiplied by ionic charge), relative to the total equivalents for cations and anions in a sample. Although similar in concept to the pie graphs showing ionic conductivity contributions to the laboratory-measured SC (SCL), the factors used to compute the equivalents do not consider ion size and mobility, which are incorporated with the transport numbers for ionic conductivity (giving different ionic proportions). The hydrochemical type of the water (sample) is identified on the basis of the predominant (greater than 50 percent) cation(s) and anion(s) shown on the trilinear plots and various mixed types on the diamond-shaped plot.

Quality Control and Quality Assurance

For quality control, filtered and unfiltered replicate samples were collected from wells PO 110 and PO 302 (PO - Potter County abbreviation and well number assigned by USGS), and field blanks were processed onsite for wells PO 326 and PO 335. A field blank is a blank solution used to determine potential contamination that can occur through all stages of sample collection, processing, preservation, transportation, and handling (Francy and others, 1998). An equipment blank test was conducted in the laboratory in late April 2017 prior to any field sampling. An equipment blank is similar to a field blank except it is used to determine potential contamination from the equipment cleaning process. An equipment blank is processed in the relatively controlled environment of an office or laboratory (Francy and others, 1998). All these samples were submitted to the laboratories for analysis. The results indicate that, for most constituents, neither the field equipment nor the sampling procedure contaminated the samples. The results of the equipment blank test indicate that sampling equipment may introduce low levels of two constituents into the samples—concentrations of as much as about 0.098 milligrams per liter (mg/L) for dissolved ammonia plus organic nitrogen and 0.67 micrograms per liter (μg/L) for zinc. Only zinc and boron were detected in the two field blanks. Zinc was detected in both field blanks at concentrations of 2.36 and 0.55 μg/L, and boron was detected at 66 μg/L in one field blank (Galeone, 2019).

The results of the analyses of two sets of replicate samples indicate combined sampling and analytical precision (reproducibility) was within 5 percent and (or) concentrations were less than two times the minimum reporting level for most constituents. No VOCs or alcohols were detected in the routine/replicate sample pairs. Relative percent differences (RPD) greater than 5 percent were evident for concentrations of dissolved fluoride (6.76 percent) and dissolved iron (13.14 percent) for samples from well PO 302. Samples from well PO 110 showed RPDs exceeding 5 percent for acid neutralizing capacity (26.24 percent), total aluminum (15.95 percent), dissolved copper (10.47 percent), and dissolved lead (11.71 percent). No bacteria colonies were identified in either sample collected from well PO 302. Samples from well PO 110 had a RPD of 6.67 percent for total coliform and no E. coli colonies in the regular sample, but two colonies were identified in the replicate sample. Radiological results, specifically gross alpha and beta radioactivity counts, showed large variation for the replicate samples. Gross alpha 72-hour and 30-day counts (as pCi/L) showed RPDs of 9.02 percent and 92.61 percent, respectively, for samples from well PO 302 and 58.52 percent and 261.54 percent, respectively, for samples from well PO 302. Samples from well PO 100 showed RPDs exceeding 5 percent for total coliform and no E. coli colonies in the regular sample, but two colonies were identified in the replicate sample. Radioactivity results, specifically gross alpha and beta radioactivity counts, showed large variation for the replicate samples. Gross alpha 72-hour and 30-day counts (as pCi/L) showed RPDs of 9.02 percent and 92.61 percent, respectively, for samples from well PO 302 and 58.52 percent and 261.54 percent, respectively, for samples from well PO 100. Gross beta 72-hour and 30-day counts showed RPDs of 4.38 percent and 79.14 percent for well PO 302, respectively, and 117.24 percent and 114.67 percent for well PO 100. The RPDs for radon-222 for replicate samples from wells PO 110 and PO 302 were 4.28 percent and 4.38 percent, respectively, and 117.24 percent and 114.67 percent for well PO 302 and 58.52 percent and 261.54 percent, respectively, for samples from well PO 302. Samples from well PO 100 showed RPDs exceeding 5 percent for total coliform and no E. coli colonies in the regular sample, but two colonies were identified in the replicate sample. Radiological results, specifically gross alpha and beta radioactivity counts, showed large variation for the replicate samples. Gross alpha 72-hour and 30-day counts (as pCi/L) showed RPDs of 9.02 percent and 92.61 percent, respectively, for samples from well PO 302 and 58.52 percent and 261.54 percent, respectively, for samples from well PO 100. Gross beta 72-hour and 30-day counts showed RPDs of 4.38 percent and 79.14 percent for well PO 302, respectively, and 117.24 percent and 114.67 percent for well PO 100, respectively. The RPDs for radon-222 for replicate samples from wells PO 110 and PO 302 were 4.28 percent and 8.64 percent, respectively. Analyses for radium-226 and radium-228 in the well PO 302 samples showed RPDs of 6.25 percent and 40.91 percent, respectively (Galeone, 2019).

For quality assurance of the inorganic chemical analyses, intrasample characteristics were evaluated using standard procedures described by Hem (1985) and Fishman and Friedman (1989). Evaluations of accuracy and precision included comparison of field- and laboratory-measured values for pH and SC for each sample. Additional quality assurance/quality control checks involved comparisons of the computed cation and anion equivalents concentrations and
the corresponding ionic charge balance, comparisons of the ratios of cation or anion equivalents to SC, and comparisons of TDS computed as the sum of major ion concentrations to the measured residue on evaporation (ROE) at 180 °C. The measured ROE and the computed TDS as the sum of constituent concentrations were in close agreement (fig. 3). Lastly, the measured SC was compared to the computed SC, which was estimated as the sum of ionic conductivities after accounting for aqueous speciation (McCleskey and others, 2012). The values of SC measured in the field and laboratory were consistent with one another and with the computed values of SC and TDS based on measured solute concentrations (fig. 3).

Figure 3. Graphs showing comparison of field, laboratory, and (or) computed values of specific conductance (SC), total dissolved solids (TDS), or residue on evaporation at 180 degrees Celsius (ROE) for 47 groundwater samples from Potter County, Pa., 2017: A, field and laboratory measured SC; B, measured TDS (as ROE) and calculated TDS as the sum of dissolved constituent concentrations; C, field or laboratory measured SC and calculated SC on the basis of ionic conductivities; and D, field or laboratory measured SC and calculated TDS on the basis of dissolved constituent concentrations. A and B show symbols by primary bedrock lithology: “SST” sandstone and “SHL” shale, mudstone, siltstone.
Groundwater Quality and Comparison to Drinking Water Health Standards

Analytical results for the water samples collected from 47 wells in Potter County are summarized in the following sections and compared to EPA drinking-water standards and health advisories (U.S. Environmental Protection Agency, 2018). The EPA has established maximum contaminant levels (MCLs), and secondary maximum contaminant levels (SMCLs) for some constituents in drinking water (table 2). MCLs generally are set because elevated concentrations of these constituents have been shown to cause adverse effects on human health. SMCLs generally are set for aesthetic reasons; elevated concentrations of these constituents may impart an undesirable taste or odor to water. MCLs and SMCLs may be used as a guideline for private well owners but are only regulated for public drinking-water supplies in Pennsylvania.

Physical and Chemical Properties

The physical and chemical properties discussed in this section include temperature, pH, SC, dissolved oxygen, and turbidity. These properties are measured in the field when a water sample is collected.

The temperature of the groundwater samples ranged from 9.0 to 17.8 °C, with a median of 11.6 °C (table 2). These temperatures generally were less than the daytime air temperatures during sampling, but higher than the overall mean annual air temperature for Potter County (7.0 °C) (PRISM Group at Oregon State University, 2012b).

Dissolved oxygen (DO) concentrations ranged from 0.2 to 11.1 mg/L; the median concentration was 2.4 mg/L (table 2). Generally, the concentrations of DO in most of the samples were substantially less than saturation at the sample temperature, indicating the waters had been out of contact with the atmosphere. Low DO concentrations are associated with higher pH values; the 19 water samples with a DO concentration of less than 2 mg/L had a median pH of 7.5 compared to a median pH of 6.5 for the 28 samples with DO concentrations greater than 2 mg/L. Low DO concentrations are related to chemical or biochemical reactions that consume oxygen and may be associated with chemically reducing conditions that promote the release of iron (Fe), manganese (Mn), and associated metals from rock and other solids in contact with water along its flow path. The chemical reactions that consume oxygen generally involve organic carbon that can be naturally occurring in soil or aquifer materials, or can be introduced from industrial, agricultural, or domestic wastes. Of the 47 well samples in this study, 23.4 percent were classified as “anoxic” (DO <0.5 mg/L), 68.1 percent as “oxic” (DO >0.5 mg/L), and 8.5 percent as “mixed” (DO >0.5 mg/L with Mn ≥50 µg/L or Fe ≥100 µg/L), based on criteria of McMahon and Chapelle (2008) (appendix 2). Of the 11 samples classified as anoxic, 5 had chemical characteristics consistent with MnIV and FeIII reducing conditions as defined by McMahon and Chapelle (2008) (DO <0.5 mg/L, nitrate (NO3) <0.5 mg/L, Mn ≥50 µg/L, Fe ≥100 µg/L, and SO4 >0.5 mg/L), but none were identified with more strongly reducing conditions necessary for methanogenesis (DO <0.5 mg/L, NO3 <0.5 mg/L, Mn ≥50 µg/L, Fe ≥100 µg/L, and sulfate (SO4) <0.5 mg/L). The sample from well PO 323 met most of the criteria for methanogenesis except that the SO4 concentration of 0.67 mg/L exceeded the 0.5-mg/L threshold for methanogenesis. Nevertheless, the sample had a greater methane concentration than that in all but two other samples, 4.2 mg/L, and was methanogenic.

The pH is a measure of acidity and is an indicator of the potential corrosivity of the water and its potential to leach metals, such as lead and copper, from the rock into which the well is drilled, and from pipes and plumbing. Generally, waters with pH values of 6.5 to 7.5 are considered near neutral, those with pH values less than 6.5 are considered acidic, and waters with pH values greater than 7.5 are considered basic or alkaline. The field pH of water samples collected in Potter County ranged from 4.6 to 9.0 (fig. 4.4); the median pH was 7.1. The pH of 16 of the 47 samples (34.0 percent) was outside the EPA SMCL range of 6.5–8.5 (U.S. Environmental Protection Agency, 2018). Fourteen samples had a pH less than 6.5, and two samples had a pH greater than 8.5 (table 2). The median pH of water from the sandstone aquifers (6.53) was comparable to that for the shale aquifers (7.31). Generally, samples with pH values from 7.5 to 8.5 had greater hardness and alkalinity concentrations than other samples with pH values outside this range (fig. 2.2). Samples with pH below 6.5 had greater potential for elevated concentrations of dissolved metals, including copper, lead, nickel, and zinc, whereas higher pH samples had greater potential for elevated concentrations of TDS, SC, sodium, fluoride, boron, and uranium (fig. 2.2, Appendix 3).

Specific conductance (SC) is an indicator of the ability of dissolved chemical ions in water to conduct an electrical current and is expressed in units of microsiemens per centimeter at 25 degrees Celsius (µS/cm). The higher the value for SC, the higher the concentrations of TDS and associated ions in the water. The field-measured SC for the 47 groundwater samples ranged from 27 to 1,210 µS/cm, and the SCL ranged from 31 to 1,230 µS/cm (table 2). The median SC values were 162 and 172 µS/cm for the field and laboratory measurements, respectively (table 2). Because the laboratory-measured SC avoids potential issues with air bubbles forming on the electrode surfaces when the sample is first drawn from the subsurface, the laboratory SC is used for interpretations.

Turbidity is a measure of suspended solids that block the transmission of light through water. Turbidity is expressed in nephelometric turbidity units (NTU), which quantify the degree to which light is scattered by the suspended particles. The higher the NTU value, the more turbid the water. Turbidity concentrations ranged from 0.4 to 92 NTU; the median concentration was 4.3 NTU (table 2). In general, samples with high turbidity have total concentrations of constituents that include contributions from suspended particles, in addition to the dissolved component.
Table 2. Minimum, median, and maximum values of selected characteristics and constituents in groundwater samples collected in 47 domestic wells in Potter County, Pa., May–September 2017. Available U.S. Environmental Protection Agency Maximum Contaminant Levels, and Secondary Maximum Contaminant Levels for analyzed constituents (2018 Edition of the Drinking Water Standards and Health Advisories [EPA 822-F-18-001])

[n, number of results; EPA, U.S. Environmental Protection Agency; MCL, Maximum Contaminant Level; SMCL, Secondary Maximum Contaminant Level; —, no MCL or SMCL established; °C, degrees Celsius; mg/L, milligrams per liter; μS/cm, microsiemens per centimeter; mV, millivolts; CaCO₃, calcium carbonate; SiO₂, silicon dioxide; μg/L, micrograms per liter; <, less than; N, nitrogen; MPN/100 mL, most probable number per 100 milliliters; >, greater than; pCi/L, picocuries per liter; 72-hr, sample analyzed for gross alpha concentration at approximately 72 hours after sample collection as referenced to a detector calibrated using thorium-230 (230Th); 30-d, sample used for the 72-hour gross alpha analysis is counted a second time approximately 30 days after the initial count as referenced to a detector calibrated using 230Th; δ, delta; mil, million. In Graph column, green bar indicates no exceedence of standards, orange indicates an SMCL exceedance, and red indicates an MCL exceedance]

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<td>Fluoride, dissolved (mg/L)</td>
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<td>47</td>
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<td>Sulfate, dissolved (mg/L)</td>
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<td>Antimony, dissolved (µg/L)</td>
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<td>&lt;0.03</td>
<td>0.46</td>
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<td>Arsenic, dissolved (µg/L)</td>
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<td>&lt;0.05</td>
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<td>Barium, dissolved (µg/L)</td>
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<td>8.85</td>
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<td>Boron, dissolved (µg/L)</td>
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<td>Bromide, dissolved (mg/L)</td>
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<td>&lt;0.01</td>
<td>0.02</td>
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<td>Cobalt, dissolved (µg/L)</td>
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<td>Iron, dissolved (µg/L)</td>
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<td>Lead, dissolved (µg/L)</td>
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<td>41</td>
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<td>Lithium, dissolved (µg/L)</td>
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<td>0.47</td>
<td>8.22</td>
<td>86.3</td>
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<td>Manganese, dissolved (µg/L)</td>
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<td>691</td>
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<td>Molybdenum, dissolved (µg/L)</td>
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<td>Nickel, dissolved (µg/L)</td>
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<td>&lt;0.2</td>
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<td>8.9</td>
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<td>Selenium, dissolved (µg/L)</td>
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<td>&lt;0.05</td>
<td>&lt;0.05</td>
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<td>44.7</td>
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<tr>
<td>Silver, dissolved (µg/L)</td>
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<td>&lt;1</td>
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<td>Strontium, dissolved (µg/L)</td>
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<td>9.27</td>
<td>78.3</td>
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<td>Zinc, dissolved (µg/L)</td>
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<td>1,220</td>
<td>39</td>
<td>83.0</td>
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### Table 2


[n, number of results; EPA, U.S. Environmental Protection Agency; MCL, Maximum Contaminant Level; SMCL, Secondary Maximum Contaminant Level; —, no MCL or SMCL established; °C, degrees Celsius; mg/L, milligrams per liter; μS/cm, microsiemens per centimeter; mV, millivolts; CaCO₃, calcium carbonate; SiO₂, silicon dioxide; μg/L, micrograms per liter; <, less than; N, nitrogen; MPN/100 mL, most probable number per 100 milliliters; >, greater than; pCi/L, picocuries per liter; 72-hr, sample analyzed for gross alpha concentration at approximately 72 hours after sample collection as referenced to a detector calibrated using thorium-230 (230Th); 30-d, sample used for the 72-hour gross alpha analysis is counted a second time approximately 30 days after the initial count as referenced to a detector calibrated using 230Th; δ, delta; mil, million. In Graph column, green bar indicates no exceedence of standards, orange indicates an SMCL exceedance, and red indicates an MCL exceedance]

<table>
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<th>Constituent (units)</th>
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<th>Minimum</th>
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<th>Maximum</th>
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<td></td>
<td></td>
<td>Number</td>
<td>Percent</td>
<td>Number</td>
<td>Percent</td>
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<td>Nutrients</td>
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<td>Kjeldahl N, total (mg/L as N)</td>
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<td>&lt;0.84</td>
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<td>10 21</td>
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<td>Ammonia, dissolved (mg/L as N)</td>
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<td>&lt;0.01</td>
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<td>Nitrite, dissolved (mg/L as N)</td>
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<td>&lt;0.001</td>
<td></td>
<td>0.007</td>
<td>7 15</td>
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<td>Nitrate + Nitrite, dissolved (mg/L as N)</td>
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<td>&lt;0.04</td>
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<td>5.14</td>
<td>36 76.6</td>
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<td>Orthophosphate, dissolved (mg/L as phosphorus)</td>
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<td>&lt;0.004</td>
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<td>0.060</td>
<td>43 91</td>
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<td>Bacteria</td>
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<td>Total coliform (MPN/100 mL)</td>
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<td>&gt;2,420</td>
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<td>Escherichia Coli (MPN/100 mL)</td>
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<td>&lt;1</td>
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<td>14 30.4</td>
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<td>Gross alpha radioactivity, dissolved, 30-d (pCi/L)</td>
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<td>−0.85</td>
<td>0.76</td>
<td>7.90</td>
<td>21 44.7</td>
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<td>−0.09</td>
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<td>9.50</td>
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<td>Gross beta radioactivity, dissolved, 30-d (pCi/L)</td>
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<td>−0.26</td>
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<td>6.16</td>
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<td>Gross beta radioactivity, dissolved, 72-hr (pCi/L)</td>
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<td>Radium-226, dissolved (pCi/L)</td>
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<td>1.67</td>
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<td>Radium-228, dissolved (pCi/L)</td>
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<td>0.68</td>
<td>0.97</td>
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<td>Glycols, alcohols, and petroleum hydrocarbons</td>
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<tr>
<td>Ethanol, total (mg/L)</td>
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<td>Ethylene glycol, total (mg/L)</td>
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<td>14</td>
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<td>Isobutyl alcohol, total (mg/L)</td>
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<td>Isopropyl alcohol, total (mg/L)</td>
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<td>n-Butanol, total (mg/L)</td>
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<th>Maximum</th>
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<td>Percent</td>
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<td>n-Propanol (1-Propanol), total (mg/L)</td>
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<tr>
<td>Propylene glycol, total (mg/L)</td>
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<tr>
<td>Total petroleum hydrocarbons (mg/L)</td>
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<td>&lt;6</td>
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<td>0</td>
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<td>Benzene, total (µg/L)</td>
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<td>&lt;0.5</td>
<td>0.63</td>
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<td>&lt;0.5</td>
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<td>Trihalomethanes, total (µg/L)</td>
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<td>Toluene, total (µg/L)</td>
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<td>&lt;0.5</td>
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<td>4.26</td>
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<td>Methane, dissolved (mg/L)</td>
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<td>&lt;0.0018</td>
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<td>45</td>
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<td>Ethane, dissolved (mg/L)</td>
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<td>&lt;0.0002</td>
<td>1.2</td>
<td>8</td>
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<td>Propane, dissolved (mg/L)</td>
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<td>&lt;0.0002</td>
<td>&lt;0.0002</td>
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<tr>
<td>δ13C(CH4) (per mil in methane)</td>
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<td>−61.18</td>
<td>−53.68</td>
<td>−52.26</td>
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<td>100</td>
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<tr>
<td>δD(CH4) (per mil in methane)</td>
<td>5</td>
<td>−216.8</td>
<td>−196.8</td>
<td>−167.4</td>
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<td>100</td>
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<td>—</td>
</tr>
</tbody>
</table>

1Number of samples exceeding the higher standard listed.
2MCL for gross beta is 4 millirems per year, which is not directly comparable to results expressed in pCi/L. Screening levels between 15 and 50 pCi/L have been proposed by EPA.
3MCL is for radium-226 and radium-228 combined.
4Proposed EPA MCL for states without an enhanced indoor air program.
5Volatile organic compounds (VOCs) with detections are shown. A full listing of all VOCs sampled are shown in Appendix 4.
6Action level from Pennsylvania Oil and Gas Well regulations based on explosion hazard (Commonwealth of Pennsylvania, 2014).
Groundwater Quality and Comparison to Drinking Water Health Standards

A. pH

B. Specific conductance

C. Chloride

D. Hardness

Figure 4. Maps showing spatial distribution of A, pH (field); B, specific conductance (laboratory); C, dissolved chloride; D, hardness; E, dissolved nitrate; F, dissolved arsenic; G, total coliform; and H, dissolved methane in samples collected from 47 wells in 2017 in Potter County, Pa. Wells are plotted on a geologic map of the county.
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**Major Ions**

The major ions in water are derived from the dissolution of common minerals, including carbonates, silicates, oxides, sulfates, and sulfides, and can be influenced by ion-exchange, redox processes, and mixing of freshwater with residual brines in the aquifer matrix or mobilized from deep sources. The concentrations of major ions, TDS, salinity, and SC of groundwater are directly related, and generally expected to increase with progressive dissolution of minerals (Hem, 1985). The concentrations of trace elements in solution also may increase with TDS or SC, not only because of the release of trace constituents with the major ions dissolved from minerals, but because of the potential for displacement of adsorbed or exchangeable trace ions from mineral surfaces by the major ions (Chapman and others, 2013).

Major cations (positively charged ions such as calcium, magnesium, sodium, and potassium), major anions (negatively charged ions such as sulfate, chloride, fluoride, and bicarbonate), and nonionic solutes (uncharged solutes such as silica) typically are present in natural waters at concentrations greater than 1 mg/L, whereas dissolved trace constituents (such as iron, manganese, zinc, lead, copper, nickel, molybdenum, arsenic, selenium, uranium, lithium, and bromide) typically are present at concentrations less than 1 mg/L (Hem, 1985). Background concentrations of nutrients (such as nitrogen and phosphorus compounds) from natural sources typically are less than 1 mg/L (Dubrovsky and others, 2010) but vary because of biological processes that involve the production or metabolism of organic carbon compounds that contain nitrogen and phosphorus. Although biological (biochemical) processes can affect the concentrations of nutrients and trace constituents in groundwater directly or indirectly (through pH and redox changes), such processes generally have minor effects on major ion concentrations.

Analyses for major ions were conducted on filtered and unfiltered samples to represent both dissolved concentrations and total concentrations in the samples. Major anions, in order of decreasing median dissolved concentration, were bicarbonate (alkalinity), sulfate, chloride, nitrate, fluoride, and bromide; major cations were calcium, sodium, magnesium, and potassium. These cations and anions, plus uncharged silica, are the primary contributors to TDS and SC. For the major ions in drinking water, the EPA has established an MCL value only for nitrate and fluoride. Because concentrations of nitrate are so low, the combined concentrations of nitrate and nitrite are in essence the concentrations of nitrate. Nitrate concentrations ranged from less than 0.04 to 5.14 mg/L as nitrogen; none of the samples exceeded the MCL of 10 mg/L as nitrogen (table 2). Fluoride concentrations ranged from 0.01 to 0.38 mg/L; none exceeded the EPA MCL (4 mg/L) or SMCL (2 mg/L).

The concentration of TDS can be measured by evaporating a given volume of water and weighing the ROE or by summing the measured concentrations of the major ions (TDS) in a filtered sample. The measured ROE concentrations ranged from less than 20 to 814 mg/L; the median concentration was 108 mg/L (table 2). The computed TDS was comparable in value to the ROE and ranged from 22 to 585 mg/L, with a median of 106 mg/L. Out of 47 samples, one sample had a computed TDS and measured ROE that exceeded 500 mg/L, which is the EPA SMCL for TDS in drinking water. This sample (from well PO 326) had elevated concentrations of sodium (105 mg/L) and chloride (277 mg/L), and these two concentrations were the highest detected for chloride and sodium for all 47 samples.

Elevated concentrations of sodium and chloride could be caused by mixing of freshwater with saline connate water in the formations through which a well is drilled or by the introduction of mineral salts from near-surface contaminant sources such as road deicing compounds, water softener additives, effluent from septic systems, or animal waste (Mullaney and others, 2009; Corsi and others, 2015; New Hampshire Department of Environmental Sciences, 2010); thus, high concentrations of sodium and chloride may be related to land use as well as the geologic formation. Dissolved concentrations of sodium ranged from 0.5 to 105 mg/L; the median concentration was 8.2 mg/L (table 2). The EPA has issued a taste threshold for sodium in public water supplies that recommends reducing sodium concentrations to between 30 and 60 mg/L (U.S. Environmental Protection Agency, 2003). Dissolved sodium concentrations exceeded 30 mg/L in 10 samples. Dissolved concentrations of chloride ranged from 0.30 to 277 mg/L; the median concentration was 7.64 mg/L. Out of the 47 samples, only the sample from well PO 326 exceeded the EPA SMCL of 250 mg/L for chloride in drinking water (table 2). This sample, from a well completed in the Catskill Formation sandstone aquifer, also had the maximum values for measured TDS (814 mg/L), SCL (1,230 mg/L) (fig. 4B), dissolved sodium (105 mg/L), dissolved bromide (2.76 mg/L), and dissolved methane (11 mg/L) (Galeone, 2019) for all well samples collected in Potter county in 2017.

The alkalinity of a solution indicates its capacity to neutralize acid and commonly results from dissolved carbonate and bicarbonate ions (Hem, 1985). Alkalinity (the sample for analysis is filtered through a 0.45-micron filter), also referred to as the acid neutralizing capacity for unfiltered samples, generally increases with the pH of a water sample (fig. 5). Alkalinity ranged from 4 to 216 mg/L as CaCO\(_3\); the median concentration was 57.1 mg/L (table 2).

The hardness of the 47 well-water samples ranged from 6 to 310 mg/L as CaCO\(_3\) (fig. 4D) with a median value of 51 mg/L as CaCO\(_3\) (table 2). Hardness is directly related to the concentrations of calcium and magnesium (computed as the sum of calcium, in mg/L, multiplied by a factor of 2.5 plus magnesium, in mg/L, multiplied by a factor of 4.1) and generally is comparable to the alkalinity. The alkalinity and associated hardness of groundwater are a consequence of the dissolution of calcium- and magnesium-bearing minerals, such as calcite (CaCO\(_3\)) and dolomite (CaMg(CO\(_3\))\(_2\)), which are associated with limestone, dolomite, and other calcareous...
Drinking Water Health Standards and Hydrogeologic and Geochemical Characteristics for 47 Domestic Wells in Potter County, Pa.

Sedimentary rocks, including calcareous shale and sandstone. Hard water decreases lathering properties with soap and poses an increased potential for accumulation of mineral deposits in plumbing and cooking utensils (Hem, 1985). Using a common hardness classification (Durfur and Becker, 1964), the measured values indicate that 28 (60 percent) of the 47 water samples are soft (less than 60 mg/L as CaCO$_3$), 15 samples (32 percent) are moderately hard (61 to 120 mg/L as CaCO$_3$), 3 samples (6 percent) are hard (121 to 180 mg/L as CaCO$_3$), and 1 sample (2 percent) is classified as very hard (greater than 180 mg/L as CaCO$_3$) (figs. 5 and 6D). Samples with near-neutral to slightly alkaline pH values (7.0 to 8.0) generally had the greatest hardness. A few of the near-neutral and higher-pH waters with low hardness had elevated concentrations of dissolved sodium, which may result from natural water-softerning processes that remove calcium and magnesium in exchange for sodium. There are no health-related standards established specifically for hardness in drinking water.

Hard water has a greater potential than soft water to form scale or encrustations on plumbing and fixtures. Water resources engineers commonly identify the potential for encrustation or corrosion on the basis of the Langelier Index (LI) (Langelier, 1936), which provides an indication for the potential for lead and copper to enter water supplies from pipes and plumbing (Snoeyink and Jenkins, 1981). The LI, which is the difference between the measured pH and the pH at equilibrium with CaCO$_3$, is equal in value to the calcite saturation index (SI$_{CAL}$). If the LI or SI$_{CAL}$ is positive, the pH is greater than that at equilibrium with CaCO$_3$, and the water will tend to deposit CaCO$_3$ coatings or scale that can insulate pipes, boilers, and other components of a system from contact with water; however, if those values are negative, the water is undersaturated with CaCO$_3$ and will tend to be corrosive in the distribution system. An optimum condition is desired whereby the LI or SI$_{CAL}$ is close to zero, so that the water will neither be strongly corrosive nor scale forming. For the 47 groundwater samples, SI$_{CAL}$ ranged from −5.1 to 0.1 (fig. 5). Of the 47 samples, 35 (74 percent) had SI$_{CAL}$ values that were less than −0.5, indicating potentially high corrosive characteristics; the remaining samples would be considered neither strongly corrosive nor scale forming. Classification based on the chloride to sulfate mass ratio (CSMR) indicated a large percentage of the samples with SI$_{CAL}$ less than −2.0 had high potential corrosivity on the basis of criteria of Nguyen and others (2010) (fig. 5).

**Figure 5.** Graphs showing hardness, alkalinity, pH, and associated measures of corrosivity of water samples collected from 47 wells in Potter County, Pa., from May to September 2017. Plots A to D show symbols for primary bedrock lithology. Plots E and F show symbols for corrosivity indicated by chloride (Cl) to sulfate (SO$_4$) mass ratio and associated alkalinity. (CSMR, chloride to sulfate mass ratio)
Metals and Trace Elements

Metals and other trace elements in natural waters typically are present at concentrations less than 1 mg/L. When present in groundwater at such low concentrations, most of these elements are leached from soil or dissolved from underlying bedrock, though some may enter the aquifer by infiltration of precipitation. In addition, some metals and other trace constituents in water originate from anthropogenic sources (Hem, 1985). The EPA has established MCLs and SMCLs for various metals and trace elements in drinking water (U.S. Environmental Protection Agency, 2018; table 2). In analyses for concentrations of dissolved trace elements, 2 samples (4.3 percent) exceeded the EPA MCL for arsenic, 1 sample exceeded the EPA MCL for barium, 11 samples (23 percent) exceeded the SMCL for dissolved manganese, 5 samples (10.6 percent) exceeded the SMCL for dissolved iron, and 1 sample exceeded the SMCL for dissolved aluminum (2.1 percent). Concentrations of dissolved barium ranged from 8.85 to 3,390 μg/L (median = 68.3 μg/L) with one value exceeding the MCL of 2,000 mg/L, and those for dissolved aluminum ranged from less than 3 to 287 μg/L (median = <3; SMCL = 50–200 μg/L). None of the samples exceeded the EPA MCL or SMCL for antimony, beryllium, cadmium, chromium, copper, lead, molybdenum, selenium, silver, or zinc (table 2).

Concentrations of dissolved arsenic ranged from less than 0.05 to 36.8 μg/L, with a median concentration of 0.41 μg/L (table 2). Samples from wells PO 302 and PO 309 had arsenic concentrations of 36.8 and 13.1 μg/L, respectively, which exceed the EPA MCL of 10 μg/L. Dissolved arsenic occurs at elevated concentrations only locally (fig. 4F), and the analyses showed increased concentrations of dissolved arsenic in a sample with increased pH to 8.5, and then a decrease in dissolved arsenic with pH greater than 8.5 (fig. 2.2). Possible health effects associated with long-term ingestion of drinking water with arsenic in excess of the MCL include skin damage, circulatory system problems, and increased cancer risk (Ayotte and others, 1999). Arsenate (As(V)O₄³⁻) and arsenite (As(III)O₃³⁻), which are the predominant forms of arsenic in groundwater, tend to adsorb to a variety of aquifer materials, including iron oxides, aluminum oxides, and clay minerals, at mildly acidic to neutral pH, but not at alkaline (high pH) conditions (Dzombak and Morel, 1990; Smedley and Kinniburgh, 2002). Furthermore, under either strongly acidic or strongly reducing conditions, oxide minerals may become unstable and dissolve, releasing arsenic to solution. More detailed explanation of the effects of pH on adsorption processes and the possible relations between redox state and arsenic concentration are presented in a later section of this report.

The highest concentration of dissolved boron (246 μg/L) was detected in a sample having pH (7.59) greater than 7.5 (Galeone, 2019). In contrast, the highest concentrations of dissolved lead (2.16 μg/L), copper (66.8 μg/L), zinc (1,220 μg/L), and other trace metals were detected in samples that had pH less than 7.0 (fig. 6). Generally, relatively lower concentrations of trace metals with relatively higher values of pH may be explained by their strong adsorption at alkaline pH by iron and manganese oxides, whereas the increased concentrations of trace anions, such as arsenic or boron (present as borate), may result from their desorption at alkaline pH, which is explained in more detail further on.

Elevated concentrations of iron and manganese in water may impart a bitter taste and stain laundry and plumbing fixtures with a yellowish or brownish-orange color. Concentrations of dissolved iron ranged from less than 10 to 3,430 μg/L with a median of less than 10 μg/L; the EPA SMCL of 300 μg/L for iron was exceeded in five samples (10.6 percent). Concentrations of dissolved manganese in the samples ranged from less than 0.4 to 691 μg/L and the median concentration was 2.7 μg/L; the EPA SMCL of 50 μg/L for manganese was exceeded in samples from 11 (23 percent) of the 47 wells (table 2).

Although none of the groundwater samples had concentrations of lead or copper in excess of the respective MCL and SMCL values of 15 and 1,000 μg/L, widely occurring corrosive water in Potter County (74 percent of the well samples had SI values that were less than −0.5, indicating potentially strongly corrosive characteristics) could acquire metals from lead, brass, or copper pipes in the household water system. Long-term exposure to excess copper in drinking water can cause liver damage (National Institutes of Health, 2019), whereas lead can cause neurological problems, especially in young children (Agency for Toxic Substances and Disease Registry, 2017). Depending on water
treatment, the corrosive characteristics of a water source may or may not be mitigated. The concentration of any contaminant or chemical constituent, such as lead or copper, detected in a sample of a domestic water supply source can be affected by the location of the sample collection point relative to any water treatment system installed in the water line. Sampling at the tap would be needed to evaluate the actual concentrations of constituents in household drinking water and to evaluate the potential effects of water treatment. Lead and copper concentrations detected after thorough purging of the well and distribution system could be much lower than those for samples collected before the plumbing is flushed. Also, in some instances, much of the distribution system was bypassed by collecting water at the pressure tank.

Figure 6. Graphs showing concentrations of selected constituents in water samples collected from 47 wells in Potter County, Pa., from May to September 2017. Plots A–D relate pH to selected constituents, and plots E–H relate specific conductance (laboratory) to selected constituents.
Figure 6. Graphs showing concentrations of selected constituents in water samples collected from 47 wells in Potter County, Pa., from May to September 2017. Plots A–D relate pH to selected constituents, and plots E–H relate specific conductance (laboratory) to selected constituents.—Continued
**Bacteria**

All samples were analyzed for total coliform and *E. coli* bacteria to determine the associated human-health risk of potentially pathogenic (disease-causing) waterborne microorganisms. Coliform bacteria are ubiquitous in the environment and are not always pathogenic. They are found in digestive tracts of animals and in animal waste but are also found in plant material and soils. Fecal coliforms are the group of total coliforms present in the gut and feces of warm-blooded animals. *E. Coli* is the major species in the fecal coliform group that typically does not grow in the environment and is generally considered the best indicator of fecal pollution and possible pathogens (New York State Department of Health, 2004). Some strains of *E. coli*, such as O157:H7, can cause severe illness, and the presence of *E. coli* indicates general fecal contamination. Possible sources of fecal coliform bacteria contamination include municipal wastewater discharges, seepage from domestic septic systems, combined sewer overflows, runoff or seepage from livestock-producing areas, and wildlife populations (Rasmussen and Ziegler, 2003). Any detection of *E. coli* in public drinking-water supplies is considered cause for concern and a violation of health standards (U.S. Environmental Protection Agency, 2001); EPA criteria can be used to provide a reference point for domestic wells. The MCLs for total coliform and *E. Coli* in a water sample are exceeded with any counts greater than zero (U.S. Environmental Protection Agency, 2018). Total coliform bacteria were detected in 32 of the 46 groundwater samples collected in this study (70 percent) (table 2). Total coliform concentrations ranged from less than 1 colony (reported as most probable number [MPN] per 100 milliliters [mL]) to greater than 2,420 MPN/100mL (fig. 4G). Of the 32 samples that contained total coliform bacteria, 14 samples had detectable *E. coli*, thus exceeding the MCL, with concentrations ranging from 1 to 125 MPN/100mL.

**Organic Compounds**

All samples were analyzed for selected manufactured volatile organic compounds (VOCs), glycols and alcohols, and oil and grease (appendix 1). Of these organic compounds, only four were present in detectable concentrations. At least one VOC was detected in samples from only 3 of the 47 wells, and more than one VOC was detected only in the sample from well PO 325.

VOCs include a wide range of natural and synthetic carbon-based compounds that have high vapor pressure and relatively low solubility in water. VOCs are used in industrial, commercial, and domestic applications and can enter the groundwater as liquid through spills, leaks, vapor transport, or by atmospheric deposition. VOCs typically found in groundwater include industrial solvents, fuel hydrocarbons and oxidizers, fumigants, organic synthesis compounds, refrigerants, and disinfection byproducts (trihalomethanes) (Carter and others, 2010). VOCs are the most commonly found contaminant associated with industrial and commercial sites, dumps, landfills, hazardous waste facilities, and military bases (Zogorski and others, 2006) and are widespread where such human activities occur in developed countries. Historically, many waste chemicals were disposed of indiscriminately, and the widespread use of VOCs has resulted in a considerable mass of material released to the environment. VOCs are released locally from many sources, including leaking storage tanks, direct application of pesticides containing the compounds (Barbash and Resek, 1996), septic systems, and leaking sewer systems. VOCs also are released to the atmosphere through engine exhausts, aerosol sprays, leakage of refrigerants, and application of fumigants and pesticides. Trihalomethanes are commonly associated with chlorinated water and chlorinated cleaning products (Zogorski and others, 2006).

The EPA has established primary drinking-water MCLs for 25 of the 68 VOCs analyzed for this study (U.S. Environmental Protection Agency, 2018). The laboratory reporting level for most of the VOCs analyzed was 0.5 µg/L, which is lower than the established MCLs (table 2). Thus, if VOCs are present in groundwater at concentrations less than the reporting level of 0.5 µg/L, those concentrations would not exceed an established EPA MCL.

Of the 68 VOCs for which samples were analyzed, only three compounds were detected at concentrations above the reporting level—benzene (0.63 µg/L), toluene (1.65 and 1.18 µg/L), and trichloroethane (4.72 µg/L) (table 2). The concentration of trihalomethanes by summation is also reported in table 2 for well PO 325, but this is virtually a repeat of the trichloroethane concentration found in that sample. Benzene and toluene were detected in well PO 307, toluene was also detected in well PO 308, and trichloroethane was detected in well PO 325. None of the detected VOCs exceeded EPA drinking-water standards. Although the measured VOC concentrations do not pose any known or established health risk, the detection of these manufactured compounds in groundwater indicates groundwater contamination by human activities.

Concentrations of glycols, alcohols, and total petroleum hydrocarbons were less than the 5-mg/L reporting levels in samples from all 47 wells (table 2). Because the reporting levels of the analytical methods are high for organic compounds (for example, the reporting level for benzene was 0.5 µg/L), lower concentrations may be present in the sampled groundwater. At the time of this study, however, a more sensitive approved method with lower reporting levels was not available.
Radionuclides

Radionuclides naturally present in rocks and soils may be dissolved or leached into groundwater. Analyses for radioactivity and radionuclides include those for gross alpha radioactivity, gross beta radioactivity, dissolved radon-222 (radon gas), and dissolved uranium.

The activities of radon-222 in water from the 47 sampled wells ranged from 0 to 3,140 pCi/L with a median activity of 934 pCi/L (table 2). The EPA does not regulate radon-222 in drinking water, but under the framework specified by the 1999 Notice for the Proposed Radon in Drinking Water Rule (Federal Register, 1999), the EPA proposed an alternative maximum contaminant level (AMCL) of 4,000 pCi/L for radon-222 for community water-supply systems that use groundwater for all or some of the supply in states with an enhanced indoor air radon program. For states without an enhanced indoor air program, the EPA proposed an MCL of 300 pCi/L for radon-222. Water from 38 of the 47 wells sampled (81 percent) exceeded the proposed EPA MCL of 300 pCi/L, but no samples exceeded the proposed EPA AMCL of 4,000 pCi/L for radon-222.

The gross alpha-particle radioactivity (72-hour count) in water from the 47 sampled wells ranged from nondetect (values that are less than the sample-specific critical level (SSCL)) to 9.50 pCi/L. Values below the SSCL ranged from −0.09 to 0.69 pCi/L. The SSCL is the smallest measured concentration that is statistically different from the concentration of the instrument background or analytical blank, and it serves as the detection threshold for deciding whether the radionuclide is present in a sample. Analysis of a radiological sample produces a gross signal response that is related to the quantity of the radionuclide present. Negative results are possible owing to the randomness of the measurement process; however, a negative value does not imply that there is negative radioactivity (McCurdy and others, 2008). The median activity level for gross alpha-particle radioactivity (72-hour count) in the samples analyzed was 1.09 pCi/L (table 2). The activity in 18 samples was less than the SSCL. Comparison of gross alpha-particle activity between the 72-hour and 30-day counts for samples with at least one detection above the SSCL showed small changes in activity—increasing in 12 samples and decreasing in 23 samples. None of the water samples exceeded the EPA MCL of 15 pCi/L for gross alpha-particle activity in either the 72-hour or 30-day counts (table 2).

The gross-beta particle radioactivity (72-hour count) ranged from nondetect to 5.44 pCi/L; median activity was 1.75 pCi/L (table 2). Values below SSCL ranged from −0.17 to 1.50. Comparison of gross beta-particle activity between the 72-hour and 30-day counts for samples with at least one detection above the SSCL showed small changes in activity—increasing in 17 samples and decreasing in 22 samples.

The concentration of dissolved uranium ranged from less than 0.01 to 3.14 µg/L. The median concentration was 0.10 µg/L. No water samples exceeded the EPA MCL of 30 µg/L for uranium.

A subset of four samples, which had the highest gross-alpha and gross-beta activities of the 47 wells sampled, was analyzed for radium-226 and radium-228. Concentrations (activities) of radium-226 in these samples ranged from 0.9 to 1.67 pCi/L, and activities of radium-228 ranged from 0.68 to 1.55 pCi/L in samples from the four wells. None of the samples exceeded the EPA MCL of 5 pCi/L for combined radium-226 and radium-228.

Dissolved Methane and Other Naturally Occurring Hydrocarbon Gases

Samples collected from the 47 wells in Potter County had concentrations of dissolved methane ranging from less than 0.0002 to 11 mg/L (table 2). Ethane was detected in eight samples and propane in two samples, both at concentrations greater than 0.0002 mg/L (table 2). One sample also contained N-butane, propene, isopentane, and N-pentane (on the basis of mole percentage of hydrocarbon gases reported by the analytical laboratory). This sample had concentrations of methane, ethane, and propane of 4.6, 1.2, and 0.49 mg/L, respectively (Galeone, 2019).

Methane was detected at concentrations of 0.0002 mg/L or greater in samples from 45 (96 percent) of the 47 wells sampled (table 2). The sample that contained the highest detected concentration of methane, 11 mg/L, was the only sample in which the level of methane exceeded the Pennsylvania action level for methane of greater than 7 mg/L (Commonwealth of Pennsylvania, 2014). Three other samples had methane concentrations ranging from 4.2 to 5.0 mg/L. Outgassing of such elevated levels of methane from the water to air within a confined space can result in a potential explosion hazard (which is posed by a 5- to 15-percent methane content in air containing at least 10 percent oxygen) (Water Research Center, 2011). Elevated concentrations of methane (defined as greater than 4 mg/L for this study) generally were found in suboxic groundwater (dissolved oxygen less than 0.5 mg/L) (fig. 2.4) that had near-neutral to alkaline pH and relatively elevated concentrations of dissolved iron, manganese, ammonia, lithium, fluoride, and boron. Other constituents with elevated levels, including barium, sodium, chloride, and bromide, were present, but were not limited to, those water samples containing elevated levels of methane. For one sample (from well PO 307), the methane concentration was 4.6 mg/L, pH was slightly alkaline (7.59), and concentrations of manganese, ammonia, lithium, fluoride, and boron were well above median values; however, DO was 6.7 mg/L (Galeone, 2019).
Relation of Groundwater Quality to Hydrogeologic and Geochemical Characteristics

Dissolved constituents in groundwater are derived from atmospheric, geologic, biologic, and anthropogenic sources as the aqueous solution interacts with various materials along transport pathways. Solute concentrations can range widely depending on the presence of constituent elements in the rock and other sources. More specifically, those concentrations are affected by (a) the extent and sequence of contact between the water and the source, (b) the aqueous solubility and interactions among the dissolved elements, and (c) geochemical conditions such as pH and oxidation-reduction (redox) state that affect element form, mobility, and transport in the aqueous environment.

Brackish water is defined as water that has a TDS content greater than freshwater but less than seawater. Water is typically considered to be brackish if it contains TDS between 1,000 and 10,000 mg/L (U.S. Geological Survey, 2013). Groundwater with TDS greater than 1,000 mg/L is rarely used for domestic supplies in the northeastern United States but may be encountered below the freshwater zone (Lohman, 1939; Feth and others, 1965). A USGS study compiled depths to brackish groundwater in the Eastern Midcontinent Region, which extends from New Jersey west to eastern Kansas, north to Michigan’s Upper Peninsula and south to central Alabama. The median depths to brackish water for wells in aquifers of Mississippian, Pennsylvanian, and Silurian-Devonian aged aquifers within the region were 300, 200, and 334 ft, respectively (Stanton and others, 2017). In general, the groundwater in the shallow freshwater system is relatively young (elapsed time since recharge) compared to the older, underlying brackish groundwater. In this study area and in other areas with substantial topographic relief, depth from the land surface to brackish groundwater generally is greater beneath uplands than beneath valley settings.

Relations Between Groundwater Chemistry, Well Construction, Geology, and Topographic Setting

Most wells constructed for domestic use in Pennsylvania are completed within the local freshwater-flow system. The wells sampled in Potter County for this study were completed to depths ranging from 33 to 600 ft. The samples from wells ranging in depth from 33 to 420 ft (89 percent of sampled wells) exhibited characteristics of “brine-influenced” waters, with SC and TDS dominated by sodium and chloride, plus elevated concentrations of bromide and methane. The elevated bromide concentrations in addition to high sodium and chloride concentrations are typical of “brine-influenced” water rather than water affected by anthropogenic sources such as road deicing materials. With one exception, these potentially brine-influenced groundwaters were sampled from the non-glaciated Deep Valleys section of the study area (fig. 1C), as explained in more detail below. Most of the wells sampled in the Deep Valleys section of Potter County, and all eight wells sampled in the Glaciated Plateau section, were completed in the sandstone aquifer of the Catskill Formation.

Differences in water quality among the sampled bedrock formations could not be statistically evaluated because of the unbalanced sample distribution. Thirty-six samples were collected from wells completed in the Catskill Formation, 7 samples from wells completed in the Huntley Mountain Formation, 2 samples from wells completed in the Chadakoin Formation, and 1 sample from both the Pottsville and Lock Haven Formations (table 1). Thus, 91 percent of the wells sampled in Potter County for this study were completed in sandstone aquifers of the Catskill and Huntley Mountain Formations. Median well depth was less for wells completed in the Catskill Formation (160 ft) than for wells completed in the Huntley Mountain Formation (412 ft). Median values for field pH, SCL, and TDS were 7.3, 216 μS/cm, and 129 mg/L, respectively, for samples collected in the Catskill Formation, and 6.7, 134 μS/cm, and 85 mg/L, respectively, for samples collected in the Huntley Mountain Formation. No methane was detected at concentrations greater than 0.01 mg/L in samples collected from the Huntley Mountain Formation; in contrast, in five samples collected from wells completed in the Catskill Formation, methane concentrations were greater than 1 mg/L.

The chemical characteristics of the Potter County groundwater samples are classified according to locations in Deep Valleys section (n = 39) or Glaciated High Plateau section (n = 8) and illustrated as boxplots (fig. 2.1). The samples collected from wells in the Deep Valleys section had significantly lower median values for pH, SCL, TDS, hardness, alkalinity, dissolved calcium, dissolved magnesium, dissolved fluoride, and dissolved silica, and higher median values for dissolved bromide and dissolved copper compared to samples from wells in the Glaciated High Plateau section. Both subsets had a wide range of redox characteristics; however, a substantially greater fraction of the samples from the Deep Valleys section was classified as oxic (72 percent) compared to samples from wells in the Glaciated section (37 percent). Given the similar bedrock in these areas, weathering of the fine-grained, calcium-enriched glacial deposits overlying bedrock in the Glaciated High Plateau section may explain the higher pH, hardness, and other differences in chemical characteristics observed in the samples from these wells, with associated effects from pH and redox characteristics on other constituents. Williams and others (1998) show that Pleistocene-age glacial deposits in northern Pennsylvania tend to be of the calcium-bicarbonate type and yield water with a median hardness of 110 mg/L CaCO₃ for confined units and 150 mg/L CaCO₃ for unconfined units.

Some chemical characteristics of groundwater, as well as a sample of that water, are related to and influenced by the depth below the land surface, and thus the depth of the well, from which the sample was collected. When water-quality
data for the Potter County wells were grouped on the basis of ranges in well depths (depths of 33–102 ft, 103–160 ft, 161–315 ft, and 316–600 ft), the highest concentrations of methane (11 mg/L) and the highest median concentration of methane (0.017 mg/L) were detected in wells in the 33–102 ft depth range. The lowest maximum methane concentration and lowest median methane concentration were detected in wells in the 316–600 ft depth range. There was also a downward trend in radon-222 concentrations in groundwater with increasing well depth. The median concentration of radon-22 in water from wells in the 33–102 ft depth range was 1,351 pCi/L. For wells at intermediate depths (103–315 ft), the median value was 900 pCi/L, whereas water from the deepest wells (depths 316–600 ft) had a median radon concentration of 557 pCi/L.

In other areas in northeastern Pennsylvania with relatively uniform bedrock type or formation, the topographic position index (TPI) has been applied to explain observed variations in groundwater quality in valley settings that are oriented along deep fractures compared to that in surrounding areas (Llewellyn, 2014). In Potter County, most samples were collected from wells in valley (n = 27) or upper slope (n = 8) settings, with four or fewer samples from wells in other topographic settings (fig. 2.5). Although observations of increasing concentrations of dissolved solids, chloride, and methane along potential groundwater flow paths (high to low topographic position) have been reported for other counties in Pennsylvania (Senior and others, 2017; Senior and Cravotta, 2017), no such spatial patterns or trends in concentrations of dissolved solids, dissolved chloride, methane, or other water-quality constituents could be definitively related to TPI for the Potter County data. Well depth and land-surface altitude were the only statistically significant parameters related to TPI classes, with decreasing median values in those parameters from the ridge and upper slopes to lower slopes and valley settings. In contrast, the median altitude at the bottom of the well (land-surface altitude minus well depth) was statistically the same among the TPI classes (fig. 2.5).

**Relations among pH, Specific Conductance, Redox Conditions, and Constituent Concentrations**

Correlations among chemical constituents, properties, and characteristics of groundwater could indicate common sources or similar geochemical controls on element mobility. For example, pH was positively correlated with SCL and other measures of ionic strength, including TDS, whereas the pH and SCL were negatively correlated with the concentration of DO (Appendix 3). With increased pH, alkalinity also increased, as did the concentrations of several major elements, and trace constituents generally increased, including alkalinity, and dissolved forms of sodium, potassium, strontium, barium, lithium, boron, fluoride, molybdenum, and methane (fig. 6, Appendix 3, fig. 2.2). Boxplots showing the constituent concentrations in the water at five different pH class intervals (pH ≤ 5.5; 5.5 ≤ pH ≤ 6.5; 6.5 ≤ pH ≤ 7.5; 7.5 ≤ pH ≤ 8.5; 8.5 ≤ pH ≤ 9.5) reveal the above patterns and exhibit significant differences among median values (fig. 2.2). Samples with pH values in the near-neutral to alkaline pH class intervals (6.5 ≤ pH ≤ 7.5, 7.5 ≤ pH ≤ 8.5, and 8.5 ≤ pH ≤ 9.5) had higher median values for SC, TDS, alkalinity, and dissolved forms of fluoride, boron, sodium, strontium, lithium, molybdenum, and arsenic than did samples in the acidic (pH ≤ 5.5 and 5.5 ≤ pH ≤ 6.5) pH class intervals. In contrast, water in the acidic pH class intervals had greater median values of DO, dissolved copper, and dissolved lead compared to water in the near-neutral to alkaline pH class intervals.

The relation between the pH and concentrations of TDS, alkalinity, dissolved calcium, dissolved magnesium, and hardness are complex, with correlations changing from positive to negative at about pH 7.5 (fig. 2.2 and fig. 5). For pH values less than 7.5, the SCL and associated concentrations of TDS, alkalinity, hardness, dissolved calcium, dissolved magnesium, dissolved strontium, and dissolved lithium, generally increased with pH based on Spearman correlation coefficients. However, for pH values greater than 7.5, based on Spearman correlation coefficients, the concentrations of dissolved calcium and magnesium decreased with increased pH. Such patterns in pH, SCL, and constituent concentrations are consistent with the dissolution of calcite (CaCO₃ → hydrogen ion (H⁺) = calcium ion (Ca²⁺) + bicarbonate ion (HCO₃⁻)) over the range of pH, combined with cation exchange at pH greater than 7.5. Through cation-exchange reactions, calcium and magnesium ions displace sodium ions (Na⁺) from exchange sites (X) on clay minerals (0.5Ca²⁺ + NaX = 0.5CaX₂ + Na⁺) (Appelo and Postma, 2005), resulting in the removal of hardness-causing mineral species. Such a water-softening process that removes calcium and magnesium can lead to undersaturation with respect to the carbonate minerals, promoting additional calcite or dolomite dissolution with consequent increases in pH and alkalinity along the groundwater flow path (Senior and Cravotta, 2017).

Boxplots showing constituent concentrations in water at four different SCL class intervals also indicate variations that may or may not be related to pH (fig. 2.3). The three highest SCL class intervals (units in μS/cm) (210 < SCL ≤ 350, 350 < SCL ≤ 500, and 500 < SCL ≤ 1,300) had statistically equivalent median pH values of 7.60, 7.12, and 7.59, respectively; however, the lowest SCL class interval (41 < SCL ≤ 100) had a statistically lower median pH of 6.25. Despite similar pH values among the higher SCL class intervals, median concentrations of alkalinity, hardness, and dissolved forms of calcium, magnesium, arsenic, strontium, barium, sodium, potassium, lithium, chloride, bromide, boron, and molybdenum in the water generally increased with SCL, whereas dissolved silica and fluoride concentrations were unchanged or decreased. The three highest SCL class intervals had comparable median values for dissolved silica and fluoride, which were greater than medians for the lowest SCL class interval. Concentrations of dissolved oxygen, nitrate, ammonia, iron, manganese, lead, and zinc did not vary consistently with SCL.
Constituents that did not vary with SCL and (or) pH may be controlled by other factors, such as redox state.

The constituent concentrations for anoxic, mixed, and oxic redox class intervals are illustrated as boxplots (fig. 2.4). Although the SCL, TDS, and most major cation and anion concentrations did not vary with redox, the medians for several constituents were significantly different between the anoxic and oxic redox classes. The anoxic samples had higher median values for pH, alkalinity, and dissolved forms of fluoride, lithium, barium, iron, manganese, and arsenic, and lower median values for dissolved nitrate, ammonia, copper, and lead than the oxic samples. Methane concentrations were similar for the anoxic and oxic redox classes.

Generally, samples with the lowest pH values had greater potential to contain elevated concentrations of dissolved metals, including beryllium, copper, lead, nickel, and zinc, whereas the higher pH samples had greater potential for elevated concentrations of total dissolved solids, sodium, fluoride, boron, and uranium. Near-neutral samples (pH 6.5 to 7.5) had greater hardness and alkalinity concentrations than the samples with pH values outside this range.

### Ionic Contributions to Conductivity and Total Dissolved Solids

Despite positive correlations between SCL, TDS, and major ion concentrations, the predominance of various ionic contributions to the SCL and TDS in the water varied widely (figs. 7 and 8). Part of the variation is due to the well setting relative to the groundwater flow path. The SCL and pH values generally increase along the flow path as groundwater reacts with aquifer minerals, acquiring solutes. Different ionic contributions are also induced by different “mixes” of land use, as well as by geochemical controls. Calcium and bicarbonate ions were the predominant contributions to conductivity in most samples, especially those with near-neutral pH and intermediate SCL. Magnesium, sodium, chloride, and sulfate ions were subordinate but relatively important contributors to conductivity in many samples, and contributions by nitrate ions were locally important. The three highest concentrations of nitrate detected (greater than 3 mg/L) were all in samples from wells in agricultural settings (fig. 1D) in the eastern half of the county (fig. 4E).

Variations in the major ion species contributions to the SCL in samples from selected wells are illustrated in figure 8. These samples were selected because each well is topographically located in a valley setting (Galeone, 2019), and the samples are fairly representative and provide good examples of ionic contributions identified in the samples collected from the 47 wells in Potter County. Calcium (Ca), bicarbonate (HCO$_3^-$), magnesium (Mg), sodium (Na), sulfate (SO$_4^{2-}$), and chloride (Cl) ions are the predominant sources of ionic conductivity for most samples having low to moderate SCL values (fig. 7B, 8A–E), with minor contributions from nitrate, potassium, hydrogen, and hydroxyl ions. Samples with elevated SCL values generally have increased contributions from sodium and chloride (fig. 7B, 8F).

Samples from wells PO 110 and PO 303 are characteristic of low pH recharge, or groundwater in an upgradient position, near the beginning of its subsurface flow path. The sample from well PO 110 (fig. 8A) is representative of minimally evolved groundwater with relatively low SCL (31 μS/cm) and pH (5.6) values. PO 110 is a shallow well (70 ft) and drilled into the Catskill Formation. The ionic composition and associated SCL and pH of this sample can be attributed to rainwater evaporation plus minor dissolution of minerals and salts. The sample from well PO 303, drilled into the Chadakoin Formation to a depth of 97 ft, also has low pH (5.7) but higher SCL (113 μS/cm) that can be attributed to added NaCl and CaCl$_2$, which will increase ionic strength without affecting pH. The higher Cl could originate from mixing of dilute freshwater with natural salinity sources or anthropogenic sources such as road-deicing salt. Both water samples are mixed hydrochemical types, containing less than 50 percent of any single cation or anion. The sample from well PO 110 may be described as Ca-Mg/NO$_3$-HCO$_3^-$ hydrochemical type, and the sample from well PO 303 as Ca-Na-Mg/Cl type (fig. 9). Samples from wells PO 110 and PO 303 are characteristic of recharge or groundwater in an upgradient position, near the beginning of its subsurface flow path. Water samples with low pH can indicate the well is in a recharge area or in a short flow path from a recharge area, thereby yielding a minimally evolved water type.

Most freshwater used for water supply in Potter County has moderate SCL, near-neutral pH, and contains bicarbonate, Ca, and Mg as major ions. For example, the sample from well PO 311, with SCL of 243 μS/cm and pH of 7.6 (fig. 8C), and that from well PO 323, with SCL of 154 μS/cm and pH of 7.1 (fig. 8D) have increased proportions of bicarbonate, Ca, and Mg compared to a well with low ionic strength recharge (PO 110) (fig. 8A). Samples from wells PO 308 and PO 326, both drilled into the Catskill Formation, exhibit less common but locally important chemical characteristics. The sample from well PO 308 is a sodium/bicarbonate hydrochemical type with moderate SCL (227 μS/cm) and high pH (9.0) (fig. 8E), with the excess sodium resulting from cation exchange. Well PO 308 is located approximately 2 miles from well PO 311, but the cation exchange process has exchanged Ca and Mg evident at PO 323 with Na at well PO 308. The sample from well PO 326 is a Na-Ca/Cl type with a high SCL (1,230 μS/cm) and near-neutral pH (7.4) (fig. 8F) that results from mixing with salt or brine. Well PO 326 is not near any major roadway where deicing salts would be used, but the well is relatively shallow (61 ft), so it is possible that road salt applications distant from the well contributed to elevated chloride concentrations. The compositions and potential evolution of important hydrochemical types are discussed further below.

The predominant sources of ionic conductivity for most samples having low to moderate SCL values are Ca, HCO$_3^-$,
Mg, Na, SO$_4^-$, and Cl ions. Samples with elevated SCL values generally have increased contributions from sodium and chloride. The added chloride could originate from mixing of dilute freshwater with natural salinity sources or anthropogenic sources.

Figure 7. Graphs showing major ion contributions to specific conductance (SC) for 47 groundwater samples from Potter County, Pa., 2017: A, comparison of estimated ionic conductivities to measured laboratory SC for all 47 samples; B, relative contributions by major ion species to computed SC, expressed in percent, in order of increasing SC. Individual ionic conductivities estimated from dissolved constituent concentrations using methods of McCleskey and others (2012) after aqueous speciation calculations with PHREEQC (Parkhurst and Appelo, 2013).
Figure 8. Pie charts showing ionic contributions to specific conductance (SC) computed for selected groundwater samples from Potter County, Pa., 2017. Individual ionic conductivities estimated from dissolved constituent concentrations using methods of McCleskey and others (2012) after aqueous speciation calculations with PHREEQC (Parkhurst and Appelo, 2013) (SCL, laboratory measured specific conductance; µS/cm, microsiemens per centimeter).
Figure 9. Piper diagrams showing A, predominant water types or hydrochemical facies (modified from Back, 1966), and B, C, and D, data for 47 groundwater samples, Potter County, Pa., 2017, plus median composition of brine from oil and gas wells in western Pennsylvania (Dresel and Rose, 2010) and flowback water from Marcellus Shale gas wells (Hayes, 2009). Symbols for Potter County groundwater samples are varied as follows: B, lithology; C, pH; and D, specific conductance.
Figure 9. Piper diagrams showing \( A \), predominant water types or hydrochemical facies (modified from Back, 1966), and \( B \), \( C \), and \( D \), data for 47 groundwater samples, Potter County, Pa., 2017, plus median composition of brine from oil and gas wells in western Pennsylvania (Dresel and Rose, 2010) and flowback water from Marcellus Shale gas wells (Hayes, 2009). Symbols for Potter County groundwater samples are varied as follows: \( B \), lithology; \( C \), pH; and \( D \), specific conductance.—Continued
Major Ion Compositions Indicated by Piper Diagrams

In order to explain possible origins of the observed hydrochemical water types, representative samples are identified on trilinear plots and the corresponding diamond-shaped plots by lithology, pH, and SCL classes (fig. 9). In the water samples collected from wells completed in either sandstone or shale aquifers in Potter County, calcium bicarbonate (Ca(HCO₃)₂) and calcium-magnesium bicarbonate (Ca-Mg/HCO₃⁻) water types predominate in samples with pH values from 6 to 8, whereas either mixed or other types of water predominate in the samples with either more acidic or more alkaline pH values (figs. 9A to 9C). Samples that had elevated values of SCL (greater than 350 μS/cm) generally had increased contributions to conductivity from Na, Cl, and (or) SO₄ (fig. 9D).

Samples from wells PO 110 (sandstone aquifer) and PO 323 (shale aquifer) have relatively low SCL compared to other samples from the same aquifer types. These two samples and other samples plotting in the left corner region of the Piper diagram are classified as Ca/HCO₃⁻ or Ca-Mg/HCO₃⁻ types, which can be produced by the dissolution of minor amounts of calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) by rainwater (recharge) or groundwater. Because dissolution of these carbonate minerals increases SC and buffers pH so that it is near neutral, but does not substantially change the hydrochemical composition, samples with pH values from 6 to 8 and a wide range of SCL (indicating a wide range of concentrations) continue to plot in the same region of the diagram (indicating similar concentration ratios) (fig. 9C and 9D).

Toward the lower corner of the diagram, sample PO 308 (sandstone) exhibits an increased proportion of Na and may be classified as Na/HCO₃⁻ type. Various other samples that plot between the left and lower corners of the Piper diagram have mixed compositions, with variable contributions from Ca, Mg, and Na. Such water types are likely to form by the dissolution of CaCO₃ and (or) CaMg(CO₃)₂ combined with varying degrees of cation exchange.

In contrast, samples plotting toward the upper corner of the diagram, such as samples from wells PO 330 (sandstone) and PO 303 (shale), indicate an increased proportion of SO₄ or Cl, whereas those plotting toward the center indicate important contributions from multiple cations and anions. The mixed water types imply that multiple sources of constituents or processes may be important.

Finally, samples plotting near the right corner or along the upper right boundary of the Piper diamond plot indicate Cl as the predominant anion. The predominance of Cl implies a substantial contribution of salt (NaCl, CaCl₂) from road-deicing compounds, sewage or animal waste, or possibly from brine of geological origin (fig. 10). The effect of mixing fresh groundwater with either brine or road-deicing salt is shown on similar diagrams presented by Gross and Cravotta (2017) and by Senior and others (2017). The Potter County sample from well PO 326, in which Cl is the dominant anion, is classified as a Ca-Na/Cl type of water. Additional constituents, such as bromide (Br), may be helpful to identify potential sources of salinity in this and other groundwater samples.

Piper diagrams indicate that Potter County groundwaters are primarily Ca/HCO₃⁻ and Ca-Mg/HCO₃⁻ hydrochemical types at near neutral pH. Mixing that modifies these hydrochemical types and some samples collected for this study had elevated concentrations of Na, SO₄, and Cl as a result of cation exchange processes and source contributions from anthropogenic salts or brine of geologic origin.

Sodium, Chloride, and Bromide in Groundwater

The concentrations of sodium (range = 0.5 to 105 mg/L; median = 8.2 mg/L), chloride (range = 0.3 to 277 mg/L; median = 7.64 mg/L), and bromide (range = less than 0.01 to 2.76 mg/L; median = 0.02 mg/L) for the 47 groundwater samples collected for this study ranged widely (table 2) and were positively correlated with one another and with laboratory-determined specific conductance (SCL) (Appendix 3). In north-central and northeastern Pennsylvania, including Potter County, concentrations of chloride greater than about 10 mg/L in shallow groundwater are considered elevated above background (Reilly and Lee, 1998). The elevated concentrations of chloride may be associated with elevated concentrations of sodium and, in some cases, with elevated concentrations of nitrate and sulfate, which could indicate influence from human or animal waste (Reilly and others, 2015). Elevated concentrations of chloride also may be associated with elevated (although two or more orders of magnitude smaller) concentrations of bromide, which may be an indicator of the potential influence of residual brine of geologic origin, as discussed below. The sodium, bromide, and chloride/bromide mass ratios compared to chloride concentrations for the Potter County well-water samples are shown in figure 10. Curves shown in figure 10 represent chemical compositions resulting from mixing of different proportions of dilute groundwater with (1) relatively pure salt (NaCl) containing only a trace of bromide (such as salt used for road deicing, in water softeners, and present in human and animal waste), or (2) bromide-rich brines associated with oil and gas wells.

Although concentrations of sodium and chloride in the groundwater samples from Potter County are positively correlated (Appendix 3), many samples have greater amounts of sodium than may be explained by contributions from human or animal sources or brines. The “excess” sodium (greater than 1:1 [Na⁺]:[Cl⁻] molar ratio) (fig. 10A) generally may be attributed to (1) cation-exchange processes described previously or (2) dissolution of associated sodium-rich clay minerals or other sodium sources that do not contain chloride. Cation-exchange processes generally result in increased pH of the groundwater and can facilitate increased alkalinity from carbonate mineral dissolution. The majority of samples with excess sodium have near-neutral or higher pH values. In contrast, many samples that had a relative deficiency of sodium compared to the NaCl mixing curve had lower pH values (fig. 10A).
Bromide, like chloride, is a soluble anion that exhibits conservative transport properties and can be used as a tracer, if present at detectable concentrations. Recent studies of groundwater quality in nearby Susquehanna County in northeastern Pennsylvania (Warner and others, 2012; Llewellyn, 2014; Siegel and others, 2015; Johnson and others, 2015) have reported groundwater from domestic wells that has concentrations of chloride and chloride/bromide ratios that indicate possible mixing with higher salinity brines containing bromide. The naturally occurring brines from undetermined depths below the freshwater aquifer are postulated to discharge in valley settings at locations such as Salt Spring in Susquehanna County. As the brines migrate to shallower depths, they mix with more dilute fresh groundwater used as water supply. In contrast to higher bromide brines, some sources of chloride introduced into the environment by human activities, such as salt (sodium chloride) used for road deicing or present in septic effluent, typically have low amounts of bromide and relatively high chloride/bromide mass ratios.

The concentrations of bromide in most of the samples of groundwater collected in Potter County for this study were at or near the detection limit of 0.01 mg/L (fig. 10B). With one exception, samples with this low concentration of bromide had concentrations of methane less than 0.2 mg/L and plotted on the mixing curve for road-deicing salt (fig. 10B). The only sample from well PO 309, which had a low concentration of bromide and plotted on the mixing curve for road-deicing salt, had a relatively high concentration of methane, greater than or equal to 0.02 mg/L (fig. 10B). Most samples with bromide concentrations greater than 0.02 mg/L including the three samples with the highest chloride concentrations (from wells PO 333, PO 302, and PO 326) and all but one sample with methane concentrations greater than 0.2 mg/L (from wells PO 323, PO 308, PO 307, PO 304, PO 333, PO 302, and PO 326) plotted on or near the brine mixing curve (fig. 10B), suggesting a possible small contribution of chloride and bromide from a brine-like source (0.02 percent or less). Also plotting along the brine mixing curve is the water of Salt Spring, a naturally occurring saline spring in Susquehanna County. Three Potter County groundwater samples having elevated chloride concentrations from 20 to 79 mg/L (from wells PO 303, PO 338, and PO 301), but with relatively low bromide and methane concentrations, plotted on the road-deicing salt mixing curve. Several samples with concentrations of chloride greater than 10 mg/L and bromide greater than 0.2 mg/L, such as those from wells PO 330 and PO 331, had compositions between the road-deicing salt and brine mixing curves, suggesting salinity contributions from various sources.

Approximately 50 percent of Potter County wellwater samples have chloride/bromide ratios that indicate predominantly anthropogenic sources of chloride. The chloride, bromide, and other constituents in road-deicing salt or brine solutions tend to be diluted by mixing with fresh groundwater in shallow aquifers used for water supply. Samples with higher chloride concentrations had variable bromide concentrations and corresponding chloride/bromide ratios that are consistent with sources such as road-deicing salt and septic effluent (low bromide) or brine (high bromide). It is possible that wells in valley settings were drilled close to or into the brine-freshwater interface, so that brine signatures do not necessarily indicate contamination as a result of improper drilling practices.

The chloride/bromide ratios for groundwater samples collected for this study generally are similar to those for groundwater samples collected and reported by the USGS for Sullivan County (Sloto, 2013), Pike County (Senior, 2014; Senior and Cravotta, 2017), Wayne County (Senior and others, 2017), Lycoming County (Gross and Cravotta, 2017), and Bradford County (Clune and Cravotta, 2019). The regional, localized occurrence of groundwater throughout northeastern and northcentral Pennsylvania that has elevated chloride and chloride/bromide ratios that plot along the mixing curve for brine implies a natural origin for many of the observed chloride, bromide, methane, and associated constituents. In rare cases, however, such as in samples from wells PO 326, PO 323, and PO 307, the presence of methane, ethane, and brine constituents could indicate connectivity with a deep fracture or local influence from gas drilling. Additional study, such as isotopic analysis of the dissolved gas in concert with fracture analysis may be warranted to understand the origin of the sampled composition at these wells.

**Methane, Other Hydrocarbons, Isotopic Composition, and Source Identification**

Five samples (from wells PO 302, PO 308, PO 323, PO 326, PO 333) with detectable concentrations of methane (1.7 to 11 mg/L) were analyzed for the stable isotopic compositions of methane and associated concentrations of higher-chain hydrocarbon gases (fig. 11). Ethane (C2H6) was detected at concentrations ranging from 0.001 to 0.14 mg/L in the five samples analyzed for isotopes and as high as 1.2 mg/L in other methane-bearing samples, including samples from wells PO 307 and PO 334. In addition to methane and ethane, the sample from well PO 307 also had detectible concentrations of propane (C3H8), butane (C4H10), and pentane (C5H12); these higher-chain (C2+) hydrocarbons are generally associated with methane of thermogenic origin (Water Research Center, 2011).

The methane in the five groundwater samples analyzed for isotopes had carbon isotope ratio values for methane (δ13CH4) ranging from −61.18 to −52.26 per mil and hydrogen isotope ratio values for methane (δDCH4) ranging from −216.8 to −167.4 per mil (table 2 and fig. 11). McMahon and others (2019) report carbon isotopes for methane for five wells completed in the Catskill and Lock Haven Formations in north-central Pennsylvania. The samples from three of these wells had δ13CCH4 values ranging from −72.9 to −67.9 per mil, indicating biogenic (microbial) sources, whereas the other two wells had δ13CCH4 values of −35 and −44 per mil, indicating methane of primarily thermogenic origin but with some signature of microbial activity (McMahon and others, 2019). None of the five groundwater samples collected for this study in Potter County had isotopic compositions consistent with
the compositions reported by Baldassare and others (2014) for mud-gas logging samples from these geologic units and for methane gas sampled from the Marcellus Formation in nearby counties (fig. 11). In all cases, the methane in the Potter County groundwater samples has lower (lighter) δ13CCH4 values than those reported by Reese and others (2014) for Marcellus Shale methane gas samples. Three samples (from wells PO 323, PO 333, and PO 326) had a molar ratio of methane to ethane and higher-chain hydrocarbons (C1/C2+) that is somewhat consistent with methane of thermogenic origin, whereas the other two samples (from wells PO 302 and PO 308) had C1/C2+ ratios consistent with gas of microbial origin (carbon-dioxide reduction process) (fig. 11B). Relatively low δ13CCH4 values and C1/C2+ ratios for samples from wells PO 323, PO 333, and PO 326 could indicate a mixed thermogenic and microbial source of methane.

Figure 10. Graphs showing chloride concentrations compared to A, sodium concentrations, B, bromide concentrations; and C, chloride/bromide mass ratios for water samples collected from 47 wells in Potter County, Pa., 2017. The graphs also show median values for those concentrations and the chloride/bromide ratio for Salt Spring (Johnson and others, 2015; U.S. Geological Survey data collected in 2015), for flowback waters from Marcellus Shale gas wells (Hayes, 2009), and for oil and gas well brines from Western Pennsylvania (Dresel and Rose, 2010).
Figure 10. Graphs showing chloride concentrations compared to A, sodium concentrations, B, bromide concentrations; and C, chloride/bromide mass ratios for water samples collected from 47 wells in Potter County, Pa., 2017. The graphs also show median values for those concentrations and the chloride/bromide ratio for Salt Spring (Johnson and others, 2015; U.S. Geological Survey data collected in 2015), for flowback waters from Marcellus Shale gas wells (Hayes, 2009), and for oil and gas well brines from Western Pennsylvania (Dresel and Rose, 2010).—Continued
Relation of Groundwater Quality to Hydrogeologic and Geochemical Characteristics

Hydrogen isotope ratio delta value ($\delta^{13}$DCH$_4$), relative to Vienna Standard Mean Ocean Water, in per mil

Thermogenic (dry gas)

Thermogenic (wet gas)

Mixed

Microbial (carbon dioxide reduction)

EXPLANATION

Isotopic composition of methane gas in groundwater

326

Potter County (2017) well and identifier

Catskill/Lock Haven Formation

Antes Formation

Mean isotopic composition of methane gas from mud-gas of shale-gas wells in Pennsylvania (Baldassare and others, 2014)

Mud-gas, Catskill/Lockhaven Formation

Mud-gas, Brallier Formation

Mud-gas, Hamilton Group

Mud-gas, Marcellus Formation

Marcellus Formation methane gas samples (Reese and others, 2014)

Gas, Marcellus Formation, Lycoming County

Gas, Marcellus Formation, Tioga County

Gas, Marcellus Formation, Bradford County

Figure 11. Graphs showing: A, Isotopic composition of methane in groundwater samples collected from five wells in Potter County, Pa., 2017; and B, ratio of methane to higher chain hydrocarbons (C1/C2+) in relation to carbon isotopic composition for methane in these samples. Groundwater samples from Catskill/Lock Haven and Antes Formations were obtained with thief samplers in drill holes by the U.S. Geological Survey (unpub. data). Boundaries for microbial and thermogenic gas types and compositional shift related to gas maturation/oxidation, shown by arrow, from Reese and others (2014, figure 30, p. 38).
Figure 11. Graphs showing: A, Isotopic composition of methane in groundwater samples collected from five wells in Potter County, Pa., 2017; and B, ratio of methane to higher chain hydrocarbons (C1/C2+) in relation to carbon isotopic composition for methane in these samples.—Continued
Summary and Conclusions

Sixty-eight percent of the homes in Potter County, Pennsylvania, use groundwater from domestic wells as their primary source of drinking water. Conventional gas wells have been drilled at many sites and across the various historical land-use types in the county—predominantly forested, agricultural, and residential. More recently, unconventional oil and gas wells associated with the Marcellus Shale have been drilled. Underground natural gas storage areas also exist in Potter County.

To assess the quality of the drinking water supplies in Potter County, samples were collected from 47 domestic wells from May through September 2017 and analyzed for a wide range of constituents that could be evaluated with respect to drinking-water health standards, geology, and topographic settings of the wells, land use, and other environmental factors. The samples were analyzed for physical and chemical properties, including major ions, nutrients, bacteria, trace elements, volatile organic compounds, ethylene and propylene glycol, alcohols, gross-alpha/beta-particle activity, uranium, radon-222, and dissolved gases. A subset of samples was analyzed for radium isotopes (radium-226 and -228) and for isotopic composition of any contained methane.

Evaluation of the laboratory analytical results showed that groundwater quality met most drinking-water standards, with the exception of relatively widespread occurrence of bacterial contamination. Some samples exceeded Federal primary maximum contaminant levels for total coliform bacteria (69.6 percent), *Escherichia coli* (30.4 percent), arsenic (4.3 percent), and barium (2.1 percent); and secondary maximum contaminant levels for pH (34.0 percent), manganese (23.0 percent), sodium (21.0 percent), iron (10.6 percent), total dissolved solids (2.1 percent), aluminum (2.1 percent), and chloride (2.1 percent). Radon-222 activities exceeded the U.S. Environmental Protection Agency’s proposed drinking-water standard of 300 pCi/L in 80.9 percent of the samples. None of the volatile organic compounds analyzed exceeded associated water-quality standards.

Generally, samples that had elevated concentrations of total dissolved solids, chloride, or hardness also had high values of pH. The pH of the groundwater ranged from 4.6 (acidic) to 9.0 (alkaline). Lower pH samples had greater potential for elevated concentrations of dissolved metals, including beryllium, copper, lead, nickel, and zinc, whereas higher pH samples had greater potential for elevated concentrations of total dissolved solids, sodium, fluoride, boron, and uranium. Near-neutral samples (pH 6.5 to 7.5) had greater hardness and alkalinity concentrations than did samples with pH values outside this range. Most of the analyzed samples were a calcium/bicarbonate type; other samples were classified as mixed water types.

Methane gas and associated inorganic constituents, such as sodium, chloride, and bromide, which occur in high concentrations in naturally occurring, deep brine and are contained in water encountered during the drilling of gas and oil wells, were locally abundant. Water samples from 45 of the 47 wells (96 percent) had concentrations of methane greater than the 0.0002 milligram per liter (mg/L) detection limit. The maximum concentration of methane detected in samples collected for this study was 11 mg/L (for only a single sample), which exceeds the Pennsylvania action level for methane of 7 mg/L. Three additional samples had concentrations of methane greater than 4 mg/L. Outgassing of such levels of methane from the water to air within a confined space can result in a potential explosion hazard. Low levels of ethane (as much as 1.2 mg/L) were present in eight samples with the highest methane concentrations. None of the five water samples that were analyzed for methane isotopes had isotopic compositions consistent with the compositions reported for mud-gas logging samples collected from the same sampled geologic units in this study, and none had a thermogenic source of the methane. The isotopic and hydrocarbon compositions in these five samples suggest the methane may be of microbial origin or a mixture of thermogenic and microbial gas.

The concentrations of sodium (range = 0.5 to 105 mg/L; median = 8.2 mg/L), chloride (range = 0.3 to 277 mg/L; median = 7.64 mg/L), and bromide (range = less than 0.01 to 2.76 mg/L; median = 0.02 mg/L) for the 47 groundwater samples collected for this study ranged widely and were positively correlated with one another and with specific conductance and associated measures of ionic strength. One of eight samples with the highest methane concentrations (greater than 0.2 mg/L) had concentrations of chloride and bromide with corresponding chloride/bromide ratios that indicated mixing with road-deicing salt. The other seven samples with elevated levels of methane had concentrations of chloride and bromide with corresponding chloride/bromide ratios that indicated mixing with a small amount of brine (0.02 percent or less) similar in composition to those reported for gas and oil well brines in Pennsylvania. In several eastern Pennsylvania counties, however, where no gas drilling has occurred, groundwater with comparable chloride/bromide ratios and chloride concentrations has been reported. Many of the Potter County well-water samples, including two samples with elevated concentrations of chloride, have chloride/bromide ratios that indicate predominantly anthropogenic (human-caused) sources of chloride, such as road-deicing salts or septic system effluent.
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## Appendix 1  Potter County 2017 Well Sampling Analytical Constituent List.

Appendix 1. Potter County 2017 well sampling analytical constituent list.

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<thead>
<tr>
<th>Major Ions and Metals</th>
<th>Volatile Organic Chemicals</th>
<th>VOCs (continued)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid neutralizing capacity</td>
<td>1,1,2-Tetrachloroethane</td>
<td>Chloroethane</td>
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<td>Alkalinity</td>
<td>1,1,2-Trichloroethane</td>
<td>Chloroform (Trichloromethane)</td>
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<td>Aluminum, total and dissolved</td>
<td>1,1,2,2-Tetrachloroethane</td>
<td>Dibromochloromethane</td>
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<tr>
<td>Antimony, dissolved</td>
<td>1,1,2-Trichloroethane</td>
<td>Dibromomethane</td>
</tr>
<tr>
<td>Arsenic, total and dissolved</td>
<td>1,1-Dichloroethane</td>
<td>Dichlorodifluoromethane</td>
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<tr>
<td>Barium, total and dissolved</td>
<td>1,1-Dichloroethene</td>
<td>Ethylbenzene</td>
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<tr>
<td>Beryllium, dissolved</td>
<td>1,1-Dichlororopene</td>
<td>Hexachlorobutadiene</td>
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<td>Boron, total and dissolved</td>
<td>1,2,3-Trichlorobenzene</td>
<td>Iodomethane</td>
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<tr>
<td>Bromide, total and dissolved</td>
<td>1,2,3-Trichloropropane</td>
<td>Isopropylbenzene</td>
</tr>
<tr>
<td>Cadmium, dissolved</td>
<td>1,2,4-Trichlorobenzene</td>
<td>Methyl Bromide (Bromomethane)</td>
</tr>
<tr>
<td>Calcium, total and dissolved</td>
<td>1,2,4-Trimethylbenzene</td>
<td>Methyl Chloride (Chloromethane)</td>
</tr>
<tr>
<td>Chloride, total and dissolved</td>
<td>1,2-Dichlorobenzene</td>
<td>Methyl tert-butyl ether (MTBE)</td>
</tr>
<tr>
<td>Chromium, total and dissolved</td>
<td>1,2-Dichloroethane</td>
<td>Methylene Chloride (Dichloromethane)</td>
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<td>Cobalt, dissolved</td>
<td>1,2-Dichloroethane</td>
<td>Naphthalene</td>
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<tr>
<td>Copper, total and dissolved</td>
<td>1,3,5-Trimethylbenzene</td>
<td>Styrene</td>
</tr>
<tr>
<td>Fluoride, dissolved</td>
<td>1,3-Dichlorobenzene</td>
<td>Tetrachloroethene</td>
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<tr>
<td>Hardness, total and dissolved</td>
<td>1,3-Dichloropropane</td>
<td>Toluene</td>
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<tr>
<td>Iron, total and dissolved</td>
<td>1,4-Dichlorobenzene</td>
<td>Total Trihalomethanes</td>
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<tr>
<td>Lead, dissolved</td>
<td>2,2-Dichloropropane</td>
<td>Trichloroethene</td>
</tr>
<tr>
<td>Lithium, total and dissolved</td>
<td>2-Butanone (Methyl ethyl ketone)</td>
<td>Trichlorofluoromethane</td>
</tr>
<tr>
<td>Magnesium, total and dissolved</td>
<td>2-Chloroethyl vinyl ether</td>
<td>Vinyl Acetate</td>
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<tr>
<td>Manganese, total and dissolved</td>
<td>2-Chlorotoluene</td>
<td>Vinyl Chloride</td>
</tr>
<tr>
<td>Molybdenum, dissolved</td>
<td>2-Hexanone (n-Butyl methyl ketone)</td>
<td>Xylenes, Total</td>
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<tr>
<td>Nickel, dissolved</td>
<td>4-Chlorotoluene</td>
<td>cis-1,2-Dichloroethene</td>
</tr>
<tr>
<td>Potassium, total and dissolved</td>
<td>4-Methyl-2-Pentanone (Isobutyl methyl ketone)</td>
<td>cis-1,3-Dichloropropene</td>
</tr>
<tr>
<td>Selenium, total and dissolved</td>
<td>Acetone</td>
<td>m+p-Xylenes</td>
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<tr>
<td>Silica, dissolved</td>
<td>Benzene</td>
<td>n-Butylbenzene</td>
</tr>
<tr>
<td>Silver, dissolved</td>
<td>Bromobenzene</td>
<td>n-Propylbenzene</td>
</tr>
<tr>
<td>Sodium, total and dissolved</td>
<td>Bromochloromethane</td>
<td>o-Xylene</td>
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<tr>
<td>Strontium, total and dissolved</td>
<td>Bromodichloromethane</td>
<td>p-Isopropyltoluene (4-Isopropyltoluene)</td>
</tr>
<tr>
<td>Sulfate, total and dissolved</td>
<td>Bromoform (Tribromomethane)</td>
<td>sec-Butylbenzene</td>
</tr>
<tr>
<td>Uranium, natural, dissolved</td>
<td>Carbon Disulfide</td>
<td>tert-Butylbenzene</td>
</tr>
<tr>
<td>Vanadium, total</td>
<td>Carbon Tetrachloride (Tetrachloromethane)</td>
<td>trans-1,2-Dichloroethene</td>
</tr>
<tr>
<td>Zinc, total and dissolved</td>
<td>Chlorobenzene</td>
<td>trans-1,3-Dichloropropene</td>
</tr>
<tr>
<td>Dissolved Gases</td>
<td>Alcohols1</td>
<td>Radiochemicals</td>
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<tr>
<td>Methane</td>
<td>Ethanol</td>
<td>Radon-222</td>
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<tr>
<td>Ethane</td>
<td>Isobutyl Alcohol (2-Methyl-1-propanol)</td>
<td>Gross Alpha Count (72 hour)</td>
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<tr>
<td>Propane</td>
<td>Isopropyl Alcohol (2-Propanol)</td>
<td>Gross Alpha Count (30 day)</td>
</tr>
<tr>
<td>Nutrients</td>
<td>Methanol</td>
<td>Gross Beta Count (72 hour)</td>
</tr>
<tr>
<td>Ammonia, dissolved</td>
<td>n-Butyl alcohol (1-Butanol)</td>
<td>Gross Beta Count (30 day)</td>
</tr>
<tr>
<td>Nitrite, dissolved</td>
<td>Propyl Alcohol (1-Propanol)</td>
<td>Organic indicators, Dissolved Solids, Suspended Solids</td>
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</table>
### Appendix 1. Potter County 2017 well sampling analytical constituent list.—Continued

<table>
<thead>
<tr>
<th>Major Ions and Metals</th>
<th>Volatile Organic Chemicals¹</th>
<th>VOCs (continued)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrite + nitrate, dissolved</td>
<td>sec-Butyl Alcohol (2-Butanol)</td>
<td>Total Dissolved Solids</td>
</tr>
<tr>
<td>Total Kjeldahl Nitrogen (TKN)</td>
<td>tert-Butyl Alcohol</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>Orthophosphate, dissolved</td>
<td>Ethylene Glycol</td>
<td>Total Petroleum Hydrocarbons</td>
</tr>
<tr>
<td>Bacteria</td>
<td>Propylene Glycol</td>
<td></td>
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</tbody>
</table>

**Total Coliform Bacteria Enumeration**  
**Escherichia coli Bacteria Enumeration**

¹All constituents were analyzed in total samples
Appendix 2

Distributions of continuous variables were compared among different sample classifications using notched boxplots (Velleman and Hoaglin, 1981; Helsel and Hirsch, 2002). Where the median for a group is greater than the common reporting limit, it is displayed as a horizontal line within the box that is defined by the 25th and 75th percentiles for that group; otherwise, the median is displayed at the reporting limit. Boxplots were generated using the Tukey method (Helsel and Hirsch, 2002). Non detect values were plotted at the detection-level value.

Appendix 2.1. Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified on the basis of physiographic province and section.

Appendix 2.2. Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified by field pH class interval.

Appendix 2.3. Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified by laboratory specific conductance class interval.

Appendix 2.4. Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified as “anoxic,” “mixed,” and “oxic” on the basis of the dissolved oxygen concentration and other water-quality criteria of McMahon and Chapelle (2008).

Appendix 2.5. Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified on the basis of topographic position index (TPI) Llewellyn (2014).

References Cited


**Figure 2.1.** Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified on the basis of physiographic province and section. [SCL, specific conductance, laboratory; mg/L, milligrams per liter; CaCO₃, calcium carbonate; µg/L, micrograms per liter; SiO₂, silica dioxide; col/100ml, colonies per 100 milliliters; MSL, mean sea level; AP.DV, Appalachian Plateau, Deep Valleys; AP.GL, Appalachian Plateau, Glaciated]
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Figure 2.2. Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified by pH class interval. The pH range is indicated on the X-axis by the upper pH for interval. [SCL, specific conductance, laboratory; mg/L, milligrams per liter; CaCO₃, calcium carbonate; µg/L, micrograms per liter; SiO₂, silica dioxide; col/100ml, colonies per 100 milliliters; MSL, mean sea level]
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Figure 2.3. Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified by laboratory specific conductance (SCL) class interval. The SCL range is indicated on the X-axis by the upper SCL value for the interval.

- pH
- Eh, in millivolts
- Specific conductance, lab, in microsiemens per centimeter
- Total dissolved solids, calculated, in milligrams per liter
- Hardness, calculated, in milligrams per liter as calcium carbonate
- Alkalinity, in milligrams per liter as calcium carbonate
- Dissolved sulfate, in milligrams per liter
- Dissolved chloride, in milligrams per liter
- Dissolved bromide, in milligrams per liter
- Dissolved calcium, in milligrams per liter
- Dissolved magnesium, in milligrams per liter
- Dissolved sodium, in milligrams per liter
- Dissolved fluoride, in milligrams per liter
- Dissolved boron, in micrograms per liter
- Dissolved lithium, in micrograms per liter
- Dissolved methane, in milligrams per liter

Legend:
- Number of observations
- Outlier data value more than 3 times the interquartile range outside the quartile
- Outlier data value less than or equal to 3 and more than 1.5 times the interquartile range outside the quartile
- Data value less than or equal to 1.5 times the interquartile range outside the quartile
- Upper hinge
- Upper notch
- Median
- Lower notch
- Lower hinge
- Detection level
- Number of nondetects

Explanations:
- [mg/L, milligrams per liter; CaCO₃, calcium carbonate; µg/L, micrograms per liter; SiO₂, silica dioxide; col/100ml, colonies per 100 milliliters; MSL, mean sea level]
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Appendix 2

Figure 2.4. Boxplots showing the composition of 47 groundwater samples from Potter County, Pa., 2017, classified as “anoxic” (ANOX), “mixed” (MIXD), and “oxic” (OXIC) on the basis of the dissolved oxygen concentration and other water-quality criteria of McMahon and Chapelle (2008). [SCL, specific conductance, laboratory; mg/L, milligrams per liter; CaCO$_3$, calcium carbonate; µg/L, micrograms per liter; SiO$_2$, silica dioxide; col/100ml, colonies per 100 milliliters; MSL, mean sea level]
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<table>
<thead>
<tr>
<th>Substance</th>
<th>Unit</th>
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<tbody>
<tr>
<td>Dissolved barium</td>
<td>µg/L per liter</td>
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</tr>
<tr>
<td>Dissolved strontium</td>
<td>µg/L per liter</td>
<td>0.1 - 10</td>
</tr>
<tr>
<td>Dissolved potassium</td>
<td>mg/L per liter</td>
<td>1 - 100</td>
</tr>
<tr>
<td>Dissolved silica</td>
<td>mg/L as silicon dioxide</td>
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</tr>
<tr>
<td>Dissolved oxygen</td>
<td>mg/L per liter</td>
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</tr>
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<td>Dissolved iron</td>
<td>µg/L per liter</td>
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<td>Dissolved manganese</td>
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<td>Dissolved copper</td>
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</tr>
<tr>
<td>Dissolved lead</td>
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<td>0.01 - 0.1</td>
</tr>
<tr>
<td>Orthophosphate</td>
<td>mg/L as phosphorus</td>
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<tr>
<td>Dissolved zinc</td>
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<tr>
<td>Dissolved nickel</td>
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<tr>
<td>Dissolved arsenic</td>
<td>µg/L per liter</td>
<td>0.1 - 10</td>
</tr>
<tr>
<td>Dissolved selenium</td>
<td>µg/L per liter</td>
<td>0.01 - 0.1</td>
</tr>
</tbody>
</table>

**EXPLANATION**

- Number of observations
- Outlier data value more than 3 times the interquartile range outside the quartile
- Outlier data value less than or equal to 3 and more than 1.5 times the interquartile range outside the quartile
- Data value less than or equal to 1.5 times the interquartile range outside the quartile

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Appendix 3.

Appendix 3 is available at https://doi.org/10.3133/sir20205038.