Groundwater Quality in Relation to Drinking Water Health Standards and Geochemical Characteristics for 54 Domestic Wells in Clinton County, Pennsylvania, 2017

Major ions

Trace metals

Nutrients

Radio-chemicals

VOCs

Dissolved gases

Bacteria

Physical properties

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U.S. Department of the Interior
U.S. Geological Survey

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By John W. Clune and Charles A. Cravotta III

Prepared in cooperation with the Clinton County Commissioners

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Acknowledgments

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
gallon (gal)	3.785	liter (L)
Flow rate		
gallon per minute (gal/min)	0.06309	liter per second (L/s)
Pressure		
inch of mercury at 60 °F (in Hg)	3.377	kilopascal (kPa)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)

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

Despite the reliance on groundwater by approximately 2.4 million rural Pennsylvania residents, publicly available data to characterize the quality of private well water are limited. As part of a regional effort to characterize groundwater in rural areas of Pennsylvania, samples from 54 domestic wells in Clinton County were collected and analyzed in 2017. The samples were evaluated for a wide range of constituents and compared to drinking-water health standards and geochemical characteristics. The sampled wells were completed to depths ranging from 46 to 500 feet in bedrock that was of predominantly sandstone, shale, or carbonate lithology. Results of this study show that the sampled groundwater quality in Clinton County generally met most drinking-water standards that apply to public water supplies. However, a percentage of samples exceeded drinking-water maximum contaminant levels (MCLs) for total coliform bacteria (57.4 percent), *Escherichia coli* (*E. coli*) (25.9 percent), nitrate (1.9 percent), and arsenic (1.9 percent); and secondary maximum contaminant levels (SMCLs) for pH (31.5 percent), manganese (29.6 percent), iron (13 percent), total dissolved solids (7.4 percent), aluminum (1.9 percent), and chloride (1.9 percent). Sodium concentrations exceeded the U.S. Environmental Protection Agency drinking-water advisory recommendation in 16.7 percent of the samples. Radon-222 activities exceeded the proposed drinking-water standard of 300 picocuries per liter (pCi/L) in 59.3 percent of the samples. The only volatile organic compounds (VOCs) detected were acetone and methyl ethyl ketone in two separate samples; neither constituent exceeded drinking-water standards.

Higher median nitrate concentrations were found in the carbonate (3.26 milligrams per liter [mg/L]) versus shale (less than 0.04 mg/L) and sandstone (0.27 mg/L) aquifer subsets. Most of the elevated nitrate concentrations were associated with *E. coli* detections in the carbonate aquifers, where transmissive bedrock can facilitate groundwater contamination by human activities at the land surface.

The median pH of groundwater from the sandstone aquifers (6.53) was less than those for the shale aquifers (7.31) and carbonate aquifers (7.43). 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 outside this range. Many samples from the shale or sandstone aquifers, particularly those with pH less than 6.5, were identified as having serious potential corrosivity based on the combination of the calcite saturation index and the chloride to sulfate mass ratio; however, none of the samples from the carbonate aquifers was identified as seriously corrosive.

Groundwater from 3.7 percent of the wells had concentrations of methane greater than the Pennsylvania action level of 7 mg/L, and 48 of the 54 wells (88.9 percent) had detectable concentrations of methane greater than the 0.0002 mg/L detection limit. Greater methane concentrations were found more frequently in groundwater sampled from the shale aquifers than the carbonate or sandstone aquifers in the study area. Most of the samples containing elevated methane (greater than 0.2 mg/L) were located outside the area of the Appalachian Plateaus. 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 and were correlated with concentrations of iron, manganese, ammonia, sodium, lithium, barium, fluoride, and boron. The stable carbon and hydrogen isotopic compositions of methane in two of four samples analyzed for isotopes were consistent with compositions reported for mud-gas logging samples from gas-bearing geologic units (thermogenic gas) in the Appalachian Plateaus region, whereas two others were consistent with methane of microbial origin or a mixture of microbial and thermogenic gas.

Forty-two percent of samples had chloride concentrations greater than 20 mg/L with variable bromide concentrations. Corresponding chloride/bromide ratios are consistent with low-bromide sources such as road-deicing salt and septic effluent or animal waste, or, in a few cases, high-bromide brine. Brines characterized by relatively high bromide are naturally present in deeper parts of the regional groundwater system and, in some cases, may be mobilized by gas 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. One of the four groundwater samples with methane concentrations greater than 4 mg/L had chloride and bromide concentrations and a chloride/bromide ratio that indicates mixing with a salinity source such as road-deicing salt, whereas the chloride and bromide concentrations and ratios for the other three high-methane samples indicate mixing with a small amount of brine (0.03 percent or less). In two other eastern Pennsylvania county studies where gas drilling is absent, groundwater with comparable chloride/bromide ratios, bromide, and chloride concentrations plus other element associations have been reported. Additional sampling and analysis, such as isotopic analysis of the dissolved gas, fracture analysis, and more detailed evaluation of surrounding land uses, may be warranted to better understand the origin of the methane and brine constituents in groundwater at specific locations.

Introduction

Pennsylvania has the second highest number of residential wells of any state in the Nation with approximately 2.4 million residents that depend on groundwater for their domestic water supply. 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). In Clinton County, approximately 20 percent of the residents use groundwater from private domestic-supply wells as their primary drinking source (Pennsylvania Bureau of Topographic and Geologic Survey, written commun., 2017).

The U.S. Environmental Protection Agency (EPA) has established human-health water-quality standards classified as maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs), and action levels for some constituents in drinking water (U.S. Environmental Protection Agency, 2012a). MCLs generally are set because elevated concentrations of these constituents may cause adverse health effects. SMCLs generally are set for aesthetic reasons; elevated concentrations of these constituents may impart an undesirable taste or odor to water. These MCLs and SMCLs may be used as a guideline for private well owners but are only enforced for public drinking-water supplies.

Groundwater from more than one in five private domestic-supply wells in the Nation potentially exceeds a human-health water-quality standard and yet, the potential health risks associated with domestic groundwater supplies are understudied in comparison to the research and testing of public water supplies (DeSimone, 2009). Unlike public water-supply systems, managing domestic-supply wells in Pennsylvania is solely the responsibility of the homeowner. Drinking water health concerns can be associated with naturally occurring chemicals derived from the surrounding bedrock and possibly combined with anthropogenic (manmade

or human derived) inputs from sewage, agricultural activities, and chemical waste spills or disposal. Acute gastrointestinal illnesses have been attributed to parasitic, viral, and bacterial pathogens in rural private well water from human and animal waste (Raina and others, 1999; Murphy and others, 2016). Metals such as copper and lead can be present in the soil and rock or leached from plumbing components by corrosive groundwater (Belitz and others, 2016). Long-term exposure to excess copper can cause liver and kidney damage, and children exposed to lead can have delayed mental and physical development (Brown and Margolis, 2012; U.S. Environmental Protection Agency, 2012a).

The presence of naturally occurring iron and manganese in drinking water can be a nuisance owing to unpleasant taste, odor, and color, and the associated staining and clogging of household plumbing fixtures (Penn State Extension, 2017). Long-term exposure to arsenic, which is another potentially naturally occurring contaminant in groundwater (Chapman and others, 2013), has been linked to skin and internal cancers (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).

The quality of well water used for domestic supply is influenced by the regional and local setting, including the topography, geology, and land use, plus well-construction features and household plumbing. Wells drilled in the bedrock of northern Pennsylvania are typically cased from the surface down to competent bedrock without grouting and consist of an open hole that intersects water-bearing zones in the rocks (aquifer), whereas those constructed in unconsolidated sand/gravel may utilize open-ended casing or be screened in the water-bearing zone. Metallic components in the plumbing and well may corrode in acidic or saline water, adding metals to the drinking water (Swistock and others, 1993; Nguyen and others, 2010; Belitz and others, 2016). In addition, improper well construction (in other words, no grouting and [or] sanitary well cap) can facilitate the introduction of potential contaminants such as bacteria from the surface into private groundwater wells and local aquifers (Zimmerman and others, 2001; Simpson, 2004; Swistock and Sharpe, 2005; Giddings, 2014). Despite legislative attempts, Pennsylvania is one of 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).

Groundwater acquires solutes (dissolved chemicals) through natural and anthropogenic (manmade or human derived) sources 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). Groundwater that supplies most domestic wells completed in shallow fractured-bedrock aquifers is derived principally from local recharge and will be influenced by land use and geology near the well. Sampling of private wells in Pennsylvania show bedrock geology and well construction have a substantial influence on water quality, and common contaminants often include fecal-indicator bacteria, low pH, arsenic, lead, nitrate, and radon (Swistock and others, 1993, 2009). Prior regional groundwater assessments in the Clinton County area show comparatively moderate dissolved solids and hardness, with the most troublesome constituents being naturally occurring iron and manganese derived from the interactions between groundwater and the minerals that compose the bedrock aquifers (Taylor and others, 1983).

Since 2005, research done in response to unconventional natural gas development in areas of Pennsylvania underlain by the Marcellus Shale has furthered the understanding of local groundwater in Clinton County and surrounding counties (U.S. Environmental Protection Agency, 2012b; Vidic and others, 2013; Soeder, 2017). Groundwater sampling from a subset of private domestic-supply wells before and after Marcellus gas well drilling did not demonstrate major influences from recent drilling and gas development activities, but did show that 40 percent of the samples failed at least one common drinking-water health standard such as total coliform bacteria (Boyer and others, 2012). Additional evaluation of extensive groundwater datasets from the natural gas industry show common exceedances of drinking-water health standards for sodium, manganese, iron, lithium, turbidity, low pH, arsenic, lead, and barium that are often related to the geological formation, water type, and topographic position of the wells (Siegel and others, 2015).

Groundwater quality can be affected locally by contamination from animal waste, septic effluent, or road salt plus naturally occurring sources of chemicals in the bedrock that add to the dissolved solids or salinity (Hem, 1985; Reilly and others, 2015). Freshwater with relatively low concentrations of dissolved solids (less than 1,000 mg/L) that is used for drinking water is typically found at relatively shallow depths (commonly less than 500 feet [ft]), where recharging rainwater has flushed naturally occurring salts from the aquifer (Feth and others, 1965; Poth, 1962). At greater depths, below the zone of active groundwater circulation, brackish to saline water with relatively high dissolved solids may be encountered where bedrock retains some connate water (evaporated seawater trapped in the sediments when deposited) (Lohman, 1939; Feth and others, 1965; Stanton and others, 2017). In some areas of Pennsylvania, such brines may migrate upward along fractures in the rocks, thereby adding salinity to shallow aquifers, especially in valley settings (Warner and others, 2012; Llewellyn, 2014). For example, Salt Spring, a naturally occurring saline spring in Susquehanna County, exhibits water-quality characteristics that result from the mixing of upwelling brine with freshwater (Llewellyn, 2014). The development of natural gas and coal-bed methane could create additional pathways to facilitate the upward migration of brines.

Although, the potential for stray hydrocarbon gas such as methane to enter aquifers from natural gas development is a concern (Veil and others, 2004; Osborn and others, 2011; Jackson and others, 2013; Heilweil and others, 2015; Llewellyn and others, 2015), numerous studies have reported on naturally occurring sources of methane. Thermogenic- (geologic) and biogenic- (microbial) derived methane in groundwater can be common, including samples from private domestic-supply 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; Botner and others, 2018), especially in valleys and near faults (Wen and others, 2018). Various techniques used by these studies can aid in distinguishing among different sources of naturally occurring gas or stray gas associated with natural gas, coal-bed methane, or other resource development.

The U.S. Geological Survey (USGS) has conducted a series of county groundwater studies since 2007 to provide publicly available data that characterize the quality of groundwater in rural areas of Pennsylvania. Studies in Pike County and Sullivan County indicated that samples with elevated pH and methane often 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 reported similar results and included bacteria analyses that indicated exceedances of the drinking-water health standards (Senior and others, 2017; Gross and Cravotta, 2017; Clune and Cravotta, 2019).

Purpose and Scope

The purpose of this report is to evaluate the groundwater quality of private domestic-supply wells in Clinton County, Pennsylvania, in relation to (1) drinking-water standards and (2) geochemical characteristics. To meet these objectives, groundwater samples from 54 domestic wells throughout the county were collected from May through September of 2017. The samples were analyzed for physical and chemical properties, including major ions, nutrients, fecal-indicator bacteria, trace elements, 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. The measured concentrations of selected constituents were compared to the EPA drinking-water standards (MCL, SMCL, and screening values) that apply to public-water supplies. The relations among observed groundwater-quality characteristics, geology, topographic setting, land use, and other environmental variables associated with sampled wells are evaluated to explain the variability in the current (2017) quality of the groundwater. This study was conducted by the USGS in cooperation with the Clinton County Commissioners.

Description of Study Area

Clinton County occupies approximately 897 square miles of north-central Pennsylvania (fig. 1*A*). The northern three-fourths of Clinton County lies in the Appalachian Plateaus physiographic province, and the remaining southern area is in the Ridge and Valley physiographic province (fig. 1*A*). The geology of the Appalachian Plateaus is characterized as gently folded, nearly flat-lying sedimentary bedrock that is overlain locally in valleys by unconsolidated alluvium (sediments generally less than 20-ft thick deposited along streams). The bedrock of the Appalachian Plateaus within Clinton County is composed primarily of interlayered shale, siltstone, and sandstone lithologies of Devonian (419 to 359 years ago) to Pennsylvanian (323 to 299 million years ago) age. These siliciclastic sedimentary rocks are composed primarily of cemented grains of silicate and aluminosilicate minerals, including quartz, feldspar, chlorite, muscovite, and illite, plus minor carbonate, sulfate, sulfide, and oxide minerals that occur as clasts, fracture filling, and cements. The Allegheny Front is a steep sloping, transitional section of the Appalachian Plateaus that leads to the Ridge and Valley province. Generally, the geology of the Ridge and Valley province is strongly folded, with major valleys trending northeast-southwest along the axes of eroded anticlines (arching folded rocks). The bedrock of the Ridge and Valley within Clinton County is composed of carbonate, shale, siltstone, and sandstone lithologies of Cambrian to Devonian age. Carbonate rocks are mainly composed of limestone and dolomite, with minor sulfate, sulfide, and silicate minerals (Hem, 1985). Dissolution by slightly acidic groundwater creates openings (voids) in carbonate rocks where water and contaminants can rapidly enter and spread through the aquifer.

Although mineralogy is expected to vary locally, the sulfide, sulfate, and carbonate minerals in siliciclastic and carbonate bedrock are prone to relatively rapid weathering (oxidation and dissolution) in near-surface environments. Mineral weathering affects the pH, hardness, alkalinity, sulfate, and associated solute concentrations in groundwater. Likewise, cation-exchange and sorption processes between the water and clay minerals such as chlorite, muscovite, and illite, are widely recognized to affect groundwater quality (Hem, 1985; Appelo and Postma, 2005). Cation-exchange and sorption processes involve reactions between the mineral surfaces and the positively charged cations or negatively charged anions in water. For example, cation exchange by sodium-bearing minerals can produce high-pH, sodium-enriched, so-called softened groundwater (Senior and others, 2017; Gross and Cravotta, 2017). The same process occurs in a typical water softener treatment system in which hard water flows through the mineral-packed tank and sodium is displaced from the mineral surfaces in exchange for calcium and magnesium (hardness) from the water.

Land use in Clinton County is predominantly forested (87.3 percent), which includes state forest, state game lands, and private forest land (fig. 1*B*) (Multi-Resolution Land Characteristics Consortium, 2014). Agricultural land use, which consists mainly of pasture/hay (4.0 percent) and cropland (3.0 percent), is concentrated in the southern section of the county, in valleys that are underlain by carbonate bedrock. Wetland and water resources compose 0.4 percent and 0.8 percent of the landscape, respectively. The remaining land area is developed/residential land (4.3 percent) with a largely rural population of 39,238 recorded in 2010 (U.S. Census Bureau, 2011). Some of the most densely populated areas in the county include the city of Lock Haven, with nearly 10,000 residents, and the boroughs of Mill Hall, Avis, Flemington, and Renovo, with 1,000–2,000 residents each (U.S. Census Bureau, 2011).

As of summer 2017, Clinton County was 16th among all counties in Pennsylvania for the number of horizontal unconventional gas wells drilled (n=85; Pennsylvania Department of Environmental Protection, 2018. Vertical gas wells (n=670) previously developed across most of the same areas in the Appalachian Plateaus physiographic province, and the related infrastructure (well pads, pipelines, and so forth) as well as underground gas storage pools are mostly found in the northern part of the county (fig. 1*B*). Gas development has not taken place in the Ridge and Valley province in the southern part of the county (fig. 1*B*).

Topography in Clinton County is dominated by rounded hills and valleys with altitudes ranging from 492 to 2,352 ft above sea level (U.S. Geological Survey, 2009). The main streams within the county are Sinnemahoning, Kettle, Bald Eagle and Fishing Creeks, which flow into the West Branch Susquehanna River, a part of the Chesapeake Bay drainage. The local climate provides for a wet season of increased precipitation from April to June, with a mean annual rainfall of 40.9 inches per year (PRISM Group at Oregon State University, 2015a), of which approximately 12.1–20.1 inches recharges the aquifer (Risser and others, 2008). Groundwater levels fluctuate seasonally with increased recharge in the spring (April to May), a relatively stable water table during winter (November to March), and a steady decline during the summer months (June to August) owing to increased evapo-transpiration (fig. 2). The average annual mean temperature in Clinton County is 47.9 degrees Fahrenheit (PRISM Group at Oregon State University, 2015b).

A
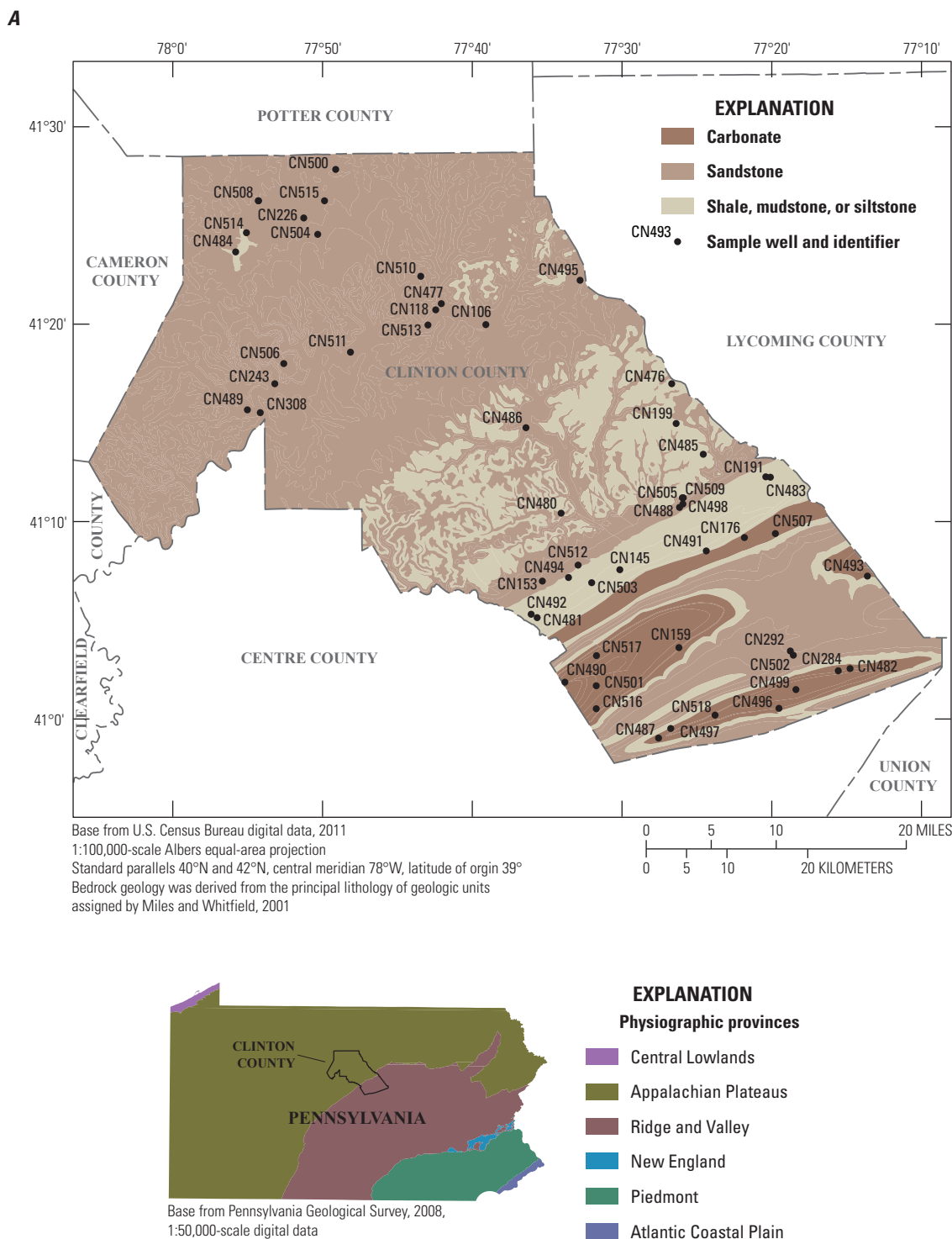
Figure 1. Predominant bedrock geology and sampling sites (*A*), and land use (*B*) in Clinton County, north-central Pennsylvania. Clinton County is located in the Appalachian Plateaus and Ridge and Valley physiographic provinces.

B

Base from U.S. Census Bureau digital data, 2011
1:100,000-scale Albers equal-area projection
Standard parallels 40°N and 42°N, central meridian 78°W, latitude of orgin 39°
Bedrock geology was derived from the principal lithology of geologic units
assigned by Miles and Whitfield, 2001

EXPLANATION

Land-use category (by percentage)—Land use
    from 2011 National Land Cover Dataset (NLCD),
    Multi-Resolution Land Characteristics
    Consortium, 2014

Water (0.8)

Wetlands (0.4)

Barren land (0.2)

Forest (87.3)

Developed (4.3)

Pasture/hay (4.0)

Cropland (3.0)

········ **Gas storage pools**

•   **Vertical gas well**

•   **Horizontal gas well**—Natural gas well locations
    from Pennsylvania Department of
    Environmental Protection, 2018

Figure 1.   —Continued

Figure 2.   Groundwater levels for the period of record (1951–2018) for U.S. Geological Survey CN 1 Clinton County observation well (411424077462201). The water table in Clinton County fluctuates seasonally with increased precipitation and recharge (wetter conditions) in the spring (April to May) and declines during the summer (June to August) due to increased evapotranspiration (drier conditions). Groundwater samples were collected across Clinton County, Pennsylvania, from May to September 2017 (shown in red).

Study Methods

A total of 54 private domestic-supply wells in Clinton County (fig. 1A), including 27 completed in sandstone aquifers, 12 in shale aquifers, and 15 in carbonate aquifers (table 1, appendix 1, table 1.1), were selected for sampling during the summer months of 2017 (fig. 2). One sample from each well was analyzed for physical and chemical properties, including major ions, nutrients, bacteria, trace elements, 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. A list of wells sampled, descriptive information (lithologic class, topographic position index), and the USGS National Water Information System (NWIS) website URL to water-quality results evaluated in this report are provided by Clune and Cravotta (2020). Using the station identification number, the NWIS water-quality results can also be retrieved with the dataRetrieval R package (Hirsch and DeCicco, 2015; Hirsch and others, 2015a,b) or through user-defined queries using USGS web services (U.S. Geological Survey, 2018). Quality assurance data results collected during sampling are also available in the USGS data release (Clune and Cravotta, 2020).

Selection of Sampling Locations

A computerized, stratified random site-selection approach was used to design a groundwater-quality network for sampling (Scott, 1990) by creating an equal-area grid of 54 cells 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 alternate sampling locations. Available well record data within Clinton County were obtained from the Pennsylvania Groundwater Information System database (Pennsylvania Bureau of Topographic and Geologic Survey, 2014) and from local well drillers. Potential wells for sampling were selected from these data based on the criteria that the well was (1) used for domestic or stock purposes, (2) had an associated well drillers record, (3) was drilled after 1970, (4) was not hand dug, 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 to obtain permission to sample and to schedule a plumbing review to verify that an untreated sample representative of the aquifer could be collected. Private domestic-supply wells meeting the criteria were prioritized for sampling. When no private wells in a grid cell met the sampling criteria, more than one well was sampled in the adjacent grid cell. Groundwater could not be sampled in some uninhabited settings such as remote forests, areas with no electricity, and ridges or steep slopes without private domestic-supply wells.

Collection and Analysis of Samples

Groundwater samples were collected following protocols outlined in the USGS National Field Manual (U.S. Geological Survey, variously dated) using Teflon tubing attached to a sampling point (outside spigot, pressure tank, and so forth) prior to any water treatment. Wells were purged using the existing pump until field properties (pH, specific conductance, water temperature, turbidity, and dissolved oxygen) stabilized. The stabilized field readings were recorded, and samples were then collected.

The samples for laboratory measurement of total dissolved solids (TDS), major ions, trace metals, and nutrient concentrations were filtered onsite through a disposable filter with a 0.45-micrometer pore size and analyzed by the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado. Samples for major ions were preserved with nitric acid and analyzed by inductively coupled plasma atomic emission spectrometry, ion chromatography, or automated colorimetry (EPA Method 524). Nutrient analyses were performed by automated colorimetry with persulfate digestion when required (Fishman, 1993; Patton and Kryskalla, 2011). The concentration of TDS was measured by evaporating a given volume of water and weighing the solid residue on evaporation (ROE) or by summing the measured concentrations of the major ions in a filtered sample (TDScalc).

Radiological samples for alpha/beta particles were preserved with nitric acid and analyzed at ALS Laboratories in Fort Collins, Colorado, by gas flow proportional counting (EPA Method 900.0). A subset of samples that had gross alpha measurements greater than 5 picocuries per liter (pCi/L) were analyzed for radium-226 and -228 by radon emanation, chemical separation, and gas flow proportional counting (EPA Method 903.1 and 904.0). Alpha particles are counted at 72 hours and 30 days from sampling because some alpha-particle emitters, such as radium-224 (half-life of 3.6 days), would not be present in the 30-day count. Radon-222 samples were obtained through an inline septum with a gas-tight syringe to avoid atmospheric contact and analyzed at the NWQL by liquid scintillation (ASTM Method D 5072-16).

Methane sampling used an impermeable collection bag, and samples were analyzed at Isotech Laboratories in 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). Four samples containing a sufficient concentration of methane were further analyzed for stable carbon isotopes ^{12}C and ^{13}C and the stable hydrogen isotopes ^{1}H and ^{2}H (deuterium). The $^{13}C/^{12}C$ and $^{2}H/^{1}H$ 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 ($\delta^{13}C$ CH_4) is reported in units of per mil (‰) or parts per thousand with respect to the Vienna Peedee belemnite standard. The hydrogen isotope ratio value in methane (δD CH_4) is reported in units of per mil with respect to the Vienna Standard Mean Ocean Water standard.

Table 1.   Descriptions of bedrock geologic map units and associated number of groundwater samples (n) and generalized lithology classification (LITHG) used for the study of Clinton County groundwater, 2017.

[LITHG is the generalized lithology, which consists primarily of sandstone (SST); shale, mudstone, or siltstone (SHL); or limestone or dolomite (CAR). Geologic map symbol, unit description, and lithology information excerpted from digital dataset polygon attributes for bedrock geology of Pennsylvania (Miles and Whitfield, 2001); —, not applicable]

Map symbol	Name	Age	n	LITHG	LITH1	LITH2	LITH3
Pa	Allegheny Formation	Pennsylvanian	1	SST	Sandstone	Shale	Limestone; clay; coal
Pp	Pottsville Formation	Pennsylvanian	2	SST	Sandstone	Conglomerate	Shale; siltstone; claystone; limestone; coal
Mmc	Mauch Chunk Formation	Mississippian	3	SHL	Shale	Siltstone	Sandstone; conglomerate; limestone
Mb	Burgoon Sandstone	Mississippian	3	SST	Sandstone	Conglomerate	Shale; coal
MDhm	Huntley Mountain Formation	Mississippian and Devonian	6	SST	Sandstone	Siltstone	Shale
Dck	Catskill Formation	Devonian	13	SST	Sandstone	Siltstone	Shale; conglomerate; mudstone
Dlh	Lock Haven Formation	Devonian	5	SHL	Mudstone	Siltstone	Sandstone; conglomerate
Dbh	Brallier and Harrell Formations, undivided	Devonian	3	SHL	Siltstone	Shale	Black shale
Dh	Hamilton Group	Devonian	0	SHL	Shale	Siltstone	Black shale; argillaceous limestone; sandstone; limestone; bentonite
Doo	Onondaga and Old Port Formations, undivided	Devonian	1	SHL	Calcareous shale	Sandstone	Limestone; argillaceous limestone; chert; shale; siliceous siltstone; bentonite
DSkm	Keyser Formation through Mifflintown Formation, undivided	Devonian and Silurian	2	CAR	Limestone	Shale	Siltstone; sandstone; mudstone; dolomite
Sc	Clinton Group	Silurian	0	SHL	Shale	Limestone	Sandstone; ferruginous sandstone
St	Tuscarora Formation	Silurian	0	SST	Quartzite	Quartzitic sandstone	Shale; siltstone; conglomerate
Oj	Juniata Formation	Ordovician	1	SST	Sandstone	Siltstone	Shale
Obe	Bald Eagle Formation	Ordovician	1	SST	Sandstone	Siltstone	Shale; conglomerate
Or	Reedsville Formation	Ordovician	0	SHL	Shale	Siltstone	Sandstone; black shale
Ocn	Coburn Formation through Nealmont Formation, undivided	Ordovician	6	CAR	Limestone	Calcareous shale	Shaly limestone; metabentonite
Obl	Benner Formation through Loysburg Formation, undivided	Ordovician	2	CAR	Limestone	Dolomitic limestone	Argillaceous, dolomitic limestone; high-calcium limestone; dolomite; metabentonite
Obv	Valentine Member of Benner Formation	Ordovician	0	CAR	High-calcium limestone	—	—
Obf	Bellefonte Formation	Ordovician	4	CAR	Dolomite	Sandstone	—
Oa	Axemann Formation	Ordovician	1	CAR	Limestone	—	—
On	Nittany Formation	Ordovician	0	CAR	Dolomite	Chert	—
Osl	Stonehenge/ Larke Formation	Ordovician	0	CAR	Limestone	Dolomite	—
Cg	Gatesburg Formation	Cambrian	0	CAR	Dolomite	Limestone	Sandstone; chert

VOCs, dissolved hydrocarbon gases (except methane), and glycol samples were analyzed by Seewald Laboratories, Inc., in Williamsport, Pennsylvania. These samples were collected onsite using a stainless-steel manifold fitting to fill vials with minimal turbulence. VOC samples were preserved with hydrochloric acid and analyzed by purge and trap gas chromatography/mass spectrometry (EPA Method 524.2). Dissolved gas samples for ethane and propane were determined by analyzing a portion of the headspace with a gas chromatograph equipped with a flame ionization detector (PA DEP Method 3686). Based upon the equilibrium gas concentration, a liquid sample concentration of these gases was calculated. Samples for glycols and alcohols were evaluated using the direct injection method, which uses a gas chromatograph equipped with a flame ionization detector that is chromatographically optimized for the separation and determination of the compounds of interest (EPA Method 8015 D). After flame-sterilizing the sampling point, the bacteria sample was collected and analyzed by the laboratory using the Colilert color method in which samples were tallied to give counts of total coliform and *Escherichia coli* (*E. c*oli) using Standard Method 9223, which is produced by the American Public Health Association, the American Water Works Association, and the Water Environment Federation.

Graphical and Statistical Analyses

Various graphical and statistical techniques were used in this report to compare water-quality data among different sites, 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. Techniques included bivariate scatter plots, mass ratios of chloride to bromide (Cl/Br), trilinear diagrams, nonparametric statistical approaches, correlation coefficients (Spearman's rho), and aqueous speciation computations.

The boxplots in the appendix compare samples by bedrock lithology (fig. 4.1), pH (fig. 4.2), specific conductance (fig. 4.3), redox (fig. 4.4), and topographic position index (fig. 4.5). Censored values were plotted at the value of the detection limit. The boxplots show a notched interval around the median that can be used by a reader to judge the significance of potential differences, except for constituents with censored data at the 25th percentile or for notched intervals less than zero (McGill and others, 1978; Velleman and Hoaglin, 1981; Helsel and Hirsch, 2002). The notches were computed using the median, 25th, and 75th percentiles (quartiles). For some constituents, the median and (or) 25th percentile is the detection limit (censored value). Substituting a value less than the detection limit for censored values affects the display of results in boxplots and other graphics. If the notched intervals around the medians for sample subsets do not overlap, the medians are statistically different at the 95-percent confidence interval. For this report, only discernable differences are interpreted as significant. Because the

graphical resolution is not high quality, inference of statistical significance where adjacent groups have similar appearance (for example, overlapping) could warrant further statistical analysis. The redox classifications used in the boxplots were classified as oxic, anoxic, or mixed, based on a modified version of the criteria and thresholds concentration from McMahon and Chapelle (2008) (table 2). The mixed category, which applies to relatively few samples, could result from physical mixing of water from multiple sources entering the well or the introduction of air during pumping. In some samples classified as mixed redox, iron or manganese may exceed the specified thresholds as a result of low pH or oxic or anoxic water; the redox classification scheme does not consider pH. 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. For simplification, two generalized TPI units were considered whereby ridge, upper slope, and steep slope were combined as the ridge category; gentle slope, lower slope, and valley were classified as the valley category.

Quality Control and Quality Assurance

For quality control (QC), filtered and unfiltered replicate samples were collected from wells CN 476 and CN 495, and field blanks were processed onsite for wells CN 482 and CN 507. All of these samples were submitted to the previously mentioned laboratories for analysis. These results demonstrate that, for most constituents, field equipment or sampling methodology did not contaminate the sample and the overall precision of analyses was good (Clune and Cravotta, 2020).

The results of the equipment blank indicate that sampling or laboratory methods generally did not affect constituent concentrations, except for the possible introduction of low levels of ammonia (0.098 microgram per liter [µg/L]) and zinc (0.67 µg/L). Low levels of the same constituents were also detected in a field blank that contained 0.01 µg/L of ammonia and 2.92 µg/L of zinc. These detections are orders of magnitude less than the lowest environmental sample results and any bias is assumed to be insignificant.

Results from two sets of replicate samples indicate combined sampling and analytical precision (reproducibility) was within 15 percent and (or) concentrations were less than two times the minimum reporting level, but still within 20 percent difference for most constituents. The relative percent difference (RPD) between the first (R_1) and second (R_2) replicate was calculated using the following equation, $RPD=(|R_1-R_2|/((R_1+R_2)/2))*100$. For the replicate sample collected from well CN 476, fluoride values were 0.010 and 0.012 mg/L with a difference of 0.002 mg/L (18 percent), beryllium values were 0.010 and 0.0192 µg/L with a difference of 0.0092 µg/L (63 percent), and methane had values

of 0.005 and 0.003 mg/L with a difference of 0.002 mg/L (50 percent). For the replicate sample collected from well CN 495, bromide values were 0.010 and 0.0186 mg/L with a difference of 0.0086 mg/L (60 percent), and ammonia had low detected values of 0.010 and 0.0158 mg/L with a difference of 0.0058 mg/L (45 percent).
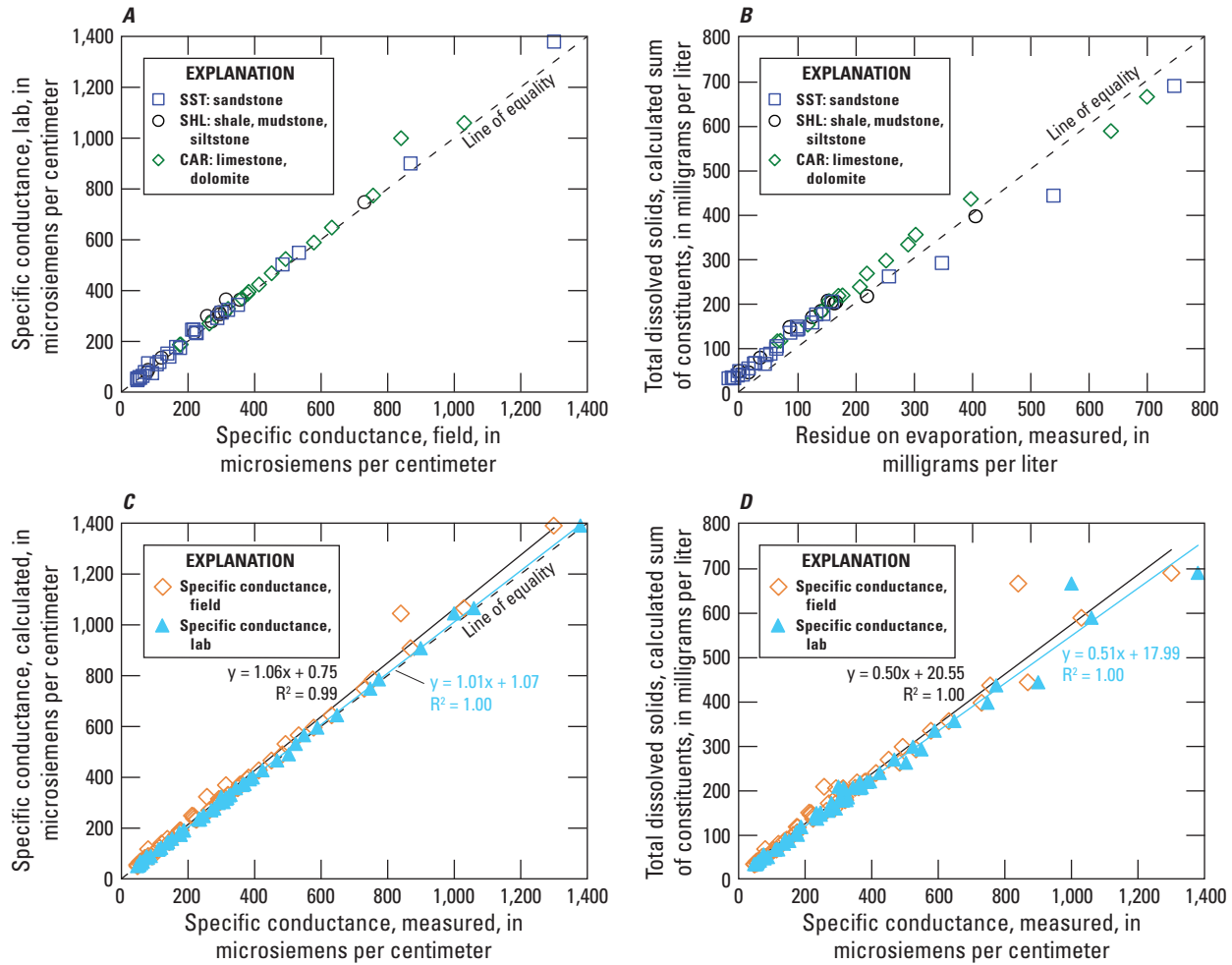
For quality assurance (QA) of the inorganic chemical analyses, intrasample characteristics were evaluated using standard procedures described by Hem (1985) and Fishman and Friedman (1989). Evaluations of accuracy and precision included comparison of field- and laboratory-measured values for pH and specific conductance for each sample. Additional QA/QC 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 specific conductance, and comparisons of

total dissolved solids (TDS) computed as the sum of major ion concentrations (TDScalc) to the measured TDS determined from residue on evaporation (ROE) at 180 degrees Celsius (°C). The measured and computed TDS were in close agreement (fig. 3), with a few exceptions. For exceptional cases, the computed TDS was less than the measured value, which could result from water retention in the evaporated sample (for example, $CaSO_4 \cdot 2H_2O$) instead of complete dehydration, as computed. Lastly, the measured specific conductance was compared to the computed specific conductance, which was estimated as the sum of ionic conductivities after accounting for aqueous speciation (McCleskey and others, 2012). The values of specific conductance measured in the field and laboratory were consistent with one another and with the computed values of specific conductance and TDS on the basis of measured solute concentrations (fig. 3).

Table 2. Criteria and threshold concentrations for identifying redox processes in groundwater (after McMahon and Chapelle, 2008).

[O_2, dissolved oxygen; NO_3^-, dissolved nitrate; $MnO_2(s)$, manganese oxide with manganese in 4^+ oxidation state; $Fe(OH)_3(s)$, iron hydroxide with iron in 3^+ oxidation state; Fe^{2+}, ferrous iron; Fe^{3+}, ferric iron; SO_4^{2-}, dissolved sulfate; HS^-, hydrogen sulfide; $CO_2(g)$, carbon dioxide gas; $CH_4(g)$, methane gas; e^-, electron; H^+, hydrogen ion; H_2O, water; mg/L, milligrams per liter; —, not applicable; <, less than; ≤, less than or equal to; >, greater than; ≥, greater than or equal to]

Redox process	Electron acceptor (reduction) half-reaction	Criteria for inferring process from water-quality data				
		Dissolved oxygen (mg/L)	Nitrate as N (mg/L)	Manganese (mg/L)	Iron (mg/L)	Sulfate (mg/L)
Oxic						
Oxic	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	>0.5	—	<0.05	<0.1	—
Anoxic						
Suboxic	Low O_2	≤0.5	<0.5	<0.05	<0.1	—
Nitrate reduction	$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2(g) + 6H_2O$; $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$	≤0.5	≥0.5	<0.05	<0.1	—
Mn^{IV} reduction	$MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	≤0.5	<0.5	≥0.05	<0.1	—
Fe^{III}/SO_4^{2-} reduction	$Fe(OH)_3(s) + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$; $SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	≤0.5	<0.5	—	≥0.1	≥0.5
Methanogenesis	$CO_2(g) + 8H^+ + 8e^- \rightarrow CH_4(g) + 2H_2O$	≤0.5	<0.5	—	≥0.1	<0.5
Mixed						
Mixed	Multiple criteria	>0.5	—	≥0.05	≥0.1	—

Figure 3.   Comparison of field, laboratory, and (or) computed values of specific conductance (SC) and total dissolved solids (TDS) for 54 groundwater samples from Clinton County, Pa., 2017. *A*, Field and laboratory measured SC; *B*, measured TDS (as residue on evaporation at 180 °C, 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, which are listed in table 1.

Groundwater Quality and Comparison to Drinking Water Health Standards

Analytical results for the 54 groundwater samples collected in Clinton County are summarized in the following sections and compared to EPA drinking-water standards and health advisories (table 3). Overall, the groundwater quality met most drinking-water standards that apply to public water supplies. However, a percentage of samples exceeded the MCLs for total coliform, *E. coli* bacteria, nitrate, and arsenic, as well as SMCLs for pH, manganese, iron, total dissolved solids, aluminum, and chloride. Radon-222 activities exceeded the proposed drinking-water standard of 300 pCi/L in a majority of the samples. The only two VOCs detected did not exceed drinking-water health standards.

Physical and Chemical Properties

Physical and chemical properties discussed in this section include temperature, pH, specific conductance, dissolved oxygen, and turbidity. Most of these properties are unstable and are determined in the field at the time a water sample is collected.

The temperature of the groundwater samples ranged from 8.6 to 16.7 °C, with a median of 12.7 °C. These temperatures generally were less than the daytime air temperatures during sampling, which reflects the generally cool conditions during seasonal recharge to the groundwater environment. Dissolved gases and carbonate minerals can dissolve to a greater extent in cooler water than in warmer water (Hem, 1985).

Dissolved oxygen (DO) concentrations ranged from 0.14 to 9.69 mg/L; the median concentration was 4.11 mg/L (table 3). Generally, most of the groundwater had DO concentrations that were substantially less than saturation at the sample temperature, indicating the waters had been out of contact with the atmosphere. 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, manganese, 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, which can occur naturally in soil or aquifer materials or can be introduced from industrial, agricultural, or domestic wastes. Of the 54 well samples in this study, 25.9 percent were classified as anoxic, 63.0 percent as oxic, and 11.1 percent as mixed, based on generalized criteria of McMahon and Chapelle (2008) (table 2) considering a DO threshold of 0.5 mg/L (fig. 4.4).

The pH is a measure of acidity and is related to the potential corrosivity of the water and its potential to leach metals, such as lead and copper, from the rock and plumbing materials. Generally, pH values of 6.5 to 7.5 are considered near neutral, values less than 6.5 are considered acidic, and values greater than 7.5 are considered basic or alkaline

(fig. 4*A*, 4.1). The field pH of water samples collected in Clinton County ranged from 4.55 to 8.70; the median pH was 7.16. The pH of 17 of the 54 samples (31.5 percent) was outside the EPA SMCL range of 6.5–8.5 (U.S. Environmental Protection Agency, 2012a). Sixteen samples had a pH less than 6.5, and one sample had a pH greater than 8.5 (table 3; fig. 4*A*). Generally, the pH varied widely within and among the three bedrock aquifers sampled, with the lowest pH values from the sandstone and shale aquifers and the highest pH values from the carbonate aquifers. The median pH of groundwater from the sandstone aquifers (6.53) was less than median pH values for the shale aquifers (7.31) and carbonate aquifers (7.43); however, the medians for the shale and carbonate aquifers were not significantly different (fig. 4.1). Generally, near-neutral samples (pH 6.5 to 7.5) had greater hardness and alkalinity concentrations than other samples with pH outside this range (fig. 4.2). 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 TDS, specific conductance, sodium, fluoride, boron, and uranium (fig. 4.2).

Specific conductance (SC) is a gross measure of the ability of dissolved chemical ions in water to conduct an electrical current and is expressed in units of microsiemens per centimeter (µS/cm). The higher the value for specific conductance, the higher the concentrations of total dissolved solids and associated ions in the water. The field-measured SC for the 54 groundwater samples ranged from 46.5 to 1,300 µS/cm at 25 °C, and the laboratory-measured SC ranged from 47.3 to 1,380 µS/cm at 25 °C (table 3; fig. 3*B*). The median laboratory SC values for the sandstone, shale, and carbonate aquifers were 174, 304, and 424 µS/cm, respectively (fig. 4.1). Values were similar for the field and laboratory-measured SC (fig. 3*A*). Because the laboratory-measured SC avoids potential issues with air bubbles that form on the electrode surfaces when the sample is first drawn from the subsurface, the laboratory SC is used for interpretation. The SC median values were lowest in the more weather resistant sandstone and highest in carbonate settings that are prone to dissolution by slightly acidic water (fig. 4.1).

Turbidity is a measure of suspended solids that block the transmission of light through the water sample. Turbidity measured on unfiltered water and is expressed in nephelometric turbidity ratio units (NTRU), which quantify the degree to which light is scattered by solid particles suspended in the water. The higher the NTRU, the more turbid the water. Turbidity concentrations ranged from 0.23 to 228 NTRU; the median concentration was 4.66 NTRU (table 3).

Samples with high turbidity were generally expected to have total concentrations of constituents that include contributions from suspended particles in addition to the dissolved constituents. This report emphasizes the interpretation of dissolved concentrations (in filtered samples) as representative of ambient aquifer conditions.

Table 3. Minimum, median, and maximum values of selected characteristics and constituents in groundwater samples collected in 54 domestic wells in Clinton County, Pa., May–September 2017. Available U.S. Environmental Protection Agency maximum contaminant levels, action levels, and secondary maximum contaminant levels for analyzed constituents are also listed (U.S. Environmental Protection Agency, 2012a).

[n, number of results; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; —, not applicable, action level, or SMCL established; °C, degrees Celsius; mg/L, milligrams per liter; μS/cm, microsiemens per centimeter; mV, millivolts; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; μg/L, micrograms per liter; <, less than; 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 (^{230}Th); 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 ^{230}Th; δ, delta; per mil, parts per thousand. In Graph column, green bar indicates no exceedance of standards, orange indicates an SMCL exceedance, and red indicates an MCL exceedance]

Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
Well characteristics											
Well depth (feet)	54	46	190	500	—	—	—	—	—	—	—
Physical properties											
Water temperature (°C)	54	8.60	12.7	16.7	54	100	—	—	—	—	—
Dissolved oxygen (mg/L)	54	0.14	4.11	9.69	54	100	—	—	—	—	—
Specific conductance, field (μS/cm)	54	46.5	268	1,300	54	100	—	—	—	—	—
pH, field (standard units)	54	4.55	7.16	8.70	54	100	17	31.5	[bar]	—	6.5–8.5
Redox potential (mV)	54	−193	152	334	54	100	—	—	—	—	—
Turbidity (Nephelometric Turbidity Ratio Units)	54	0.23	4.66	228	54	100	—	—	—	—	—
Laboratory analysis											
Specific conductance, lab (μS/cm)	54	47.3	286	1,380	72	100	—	—	—	—	—
pH, lab (standard units)	54	6.10	7.70	8.57	72	100	4	7.4	[bar]	—	6.5–8.5
Alkalinity, lab (mg/L $CaCO_3$)	54	7.08	84.4	287	72	100	—	—	—	—	—
Total dissolved solids (mg/L)	54	26.2	170	793	72	100	4	7.4	[bar]	—	500
Suspended solids (mg/L)	54	15.0	15.0	488	20	37.0	—	—	—	—	—
Hardness, total (mg/L $CaCO_3$)	46	17.6	96.5	516	46	100	—	—	—	—	—
Major ions											
Calcium (mg/L)	54	3.17	26.3	196	54	100	—	—	—	—	—
Magnesium (mg/L)	54	1.03	5.93	41.8	54	100	—	—	—	—	—
Sodium (mg/L)	54	0.33	7.90	109	54	100	9	16.7	[bar]	—	[1]30–60
Potassium (mg/L)	54	0.44	1.27	3.46	54	100	—	—	—	—	—
Chloride (mg/L)	54	0.37	4.40	355	54	100	1	1.9	[bar]	—	250

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Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
Fluoride (mg/L)	54	0.01	0.05	0.45	54	100	0	0		4	2
Sulfate (mg/L)	54	1.18	10.9	75.8	54	100	0	0		—	250
Silica (mg/L as SiO_2)	54	4.72	8.28	24.7	54	100	—	—	—	—	—
Trace elements											
Aluminum (µg/L)	54	<3.00	<3.00	233	6	11.1	1	1.9		—	50
Antimony (µg/L)	54	<0.03	<0.03	0.19	17	35.5	0	0		6	—
Arsenic (µg/L)	54	<0.05	0.14	11.2	41	75.9	1	1.9		10	—
Barium (µg/L)	54	15.1	56.7	1,840	54	100	0	0		2,000	—
Beryllium (µg/L)	54	<0.01	<0.01	0.07	11	20.4	0	0		4	—
Boron (µg/L)	54	<5.00	10.2	195	39	72.2	—	—	—	—	—
Bromide (mg/L)	54	<0.01	0.01	2.80	37	68.5	—	—	—	—	—
Cadmium (µg/L)	54	<0.03	<0.03	0.09	2	3.7	0	0		5	—
Chromium (µg/L)	54	<0.50	<0.50	0.51	1	1.9	0	0		100	—
Cobalt (µg/L)	54	<0.03	0.03	7.64	32	59.3	—	—	—	—	—
Copper (µg/L)	54	<0.20	3.28	132	43	79.6	0	0		—	1,000
Iron (µg/L)	54	<5.00	14.6	10,130	32	59.3	7	13		—	300
Lead (µg/L)	54	<0.02	0.11	5.25	40	74	0	0		15	—

Table 3. Minimum, median, and maximum values of selected characteristics and constituents in groundwater samples collected in 54 domestic wells in Clinton County, Pa., May–September 2017. Available U.S. Environmental Protection Agency maximum contaminant levels, action levels, and secondary maximum contaminant levels for analyzed constituents are also listed (U.S. Environmental Protection Agency, 2012a).—Continued

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Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
Lithium (μg/L)	54	0.27	10.2	72.1	54	100	—	—	—	—	—
Manganese (μg/L)	54	<0.40	3.47	1,840	40	74.1	16	29.6		—	50
Molybdenum (μg/L)	54	<0.05	0.16	5.74	39	72.2	—	—	—	—	—
Nickel (μg/L)	54	<0.20	0.23	8.16	28	51.9	—	—	—	—	—
Selenium (μg/L)	54	<0.05	0.06	1.52	28	51.9	0	0		50	—
Silver (μg/L)	54	<1.00	<1.00	3	0	0	0	0		—	100
Strontium (μg/L)	54	5.71	201	2,910	54	100	—	—	—	—	—
Zinc (μg/L)	54	<2.00	4.79	268	40	74.1	0	0		—	5,000
Nutrients											
Kjeldahl nitrogen, total (mg/L as Nitrogen)	54	<0.84	<0.84	5.37	14	25.9	—	—	—	—	—
Ammonia (mg/L as Nitrogen)	54	<0.01	<0.01	0.43	19	35.2	—	—	—	—	—
Nitrite (mg/L as Nitrogen)	54	<0.001	<0.001	0.007	9	16.7	0	0		1	—
Nitrate + Nitrite (mg/L as Nitrogen)	54	<0.04	0.36	49.3	37	68.5	1	1.9		10	—
Orthophosphate (mg/L as Phosphorus)	54	<0.004	0.01	0.27	38	70.4	—	—	—	—	—
Bacteria											
Total coliform (MPN/100 mL)	54	<1	8.5	8,660	31	57.4	31	57.4		0	—
Escherichia coli (MPN/100 mL)	54	<1	<1	140	14	25.9	14	25.9		0	—
Radiochemicals											
Gross alpha radioactivity, 30-d (pCi/L)	54	−2.16	0.63	8.7	23	42.6	0	0.0		15	—

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Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
Gross alpha radioactivity, 72-hr (pCi/L)	54	−0.48	1.4	8.1	44	81.5	0	0.0		15	—
Gross beta radioactivity, 30-d (pCi/L)	54	−6.49	1.69	6.52	39	72.2	1	1.9		4	—
Gross beta radioactivity, 72-hr (pCi/L)	54	−0.25	2.54	6.9	45	83.3	11	20.4		4	—
Radon-222 (pCi/L)	54	9.9	541	3,250	54	100	32	59.3		[2]300	—
Uranium (μg/L)	54	<0.01	0.08	10.4	36	66.7	0	0.0		30	—
Radium-226 (pCi/L)	4	0.15	0.21	0.42	4	100	0	0.0		5	—
Radium-228 (pCi/L)	4	0.46	0.51	0.57	4	100	0	0.0		5	—
Glycols, alcohols and oil/grease											
Ethanol (mg/L)	54	<5.00	<5.00	<5.00	0	0	—	—	—	—	—
Ethylene glycol (mg/L)	54	<5.00	<5.00	<5.00	0	0	0	0.0		14	—
Isobutyl alcohol (mg/L)	54	<5.00	<5.00	<5.00	0	0	—	—	—	—	—
Isopropyl alcohol (mg/L)	54	<5.00	<5.00	<5.00	0	0	—	—	—	—	—
Methanol (mg/L)	54	<5.00	<5.00	<5.00	0	0	—	—	—	—	—
n-Butanol (mg/L)	54	<5.00	<5.00	<5.00	0	0	—	—	—	—	—
n-Propanol (1-Propanol) (mg/L)	54	<5.00	<5.00	<5.00	0	0	—	—	—	—	—
Propylene glycol (mg/L)	54	<5.00	<5.00	<5.00	0	0	—	—	—	—	—
Volatile organic compounds[3]											
Acetone (μg/L)	54	<1.00	<1.00	45.9	1	1.39	—	—	—	—	—
Methyl ethyl ketone (μg/L)	54	<1.00	<1.00	48.3	1	1.39	—	—	—	—	—

Table 3. Minimum, median, and maximum values of selected characteristics and constituents in groundwater samples collected in 54 domestic wells in Clinton County, Pa., May–September 2017. Available U.S. Environmental Protection Agency maximum contaminant levels, action levels, and secondary maximum contaminant levels for analyzed constituents are also listed (U.S. Environmental Protection Agency, 2012a).—Continued

[n, number of results; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; —, not applicable, action level, or SMCL established; °C, degrees Celsius; mg/L, milligrams per liter; μS/cm, microsiemens per centimeter; mV, millivolts; $CaCO_3$, calcium carbonate; SiO_2, silicon dioxide; μg/L, micrograms per liter; <, less than; 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 (^{230}Th); 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 ^{230}Th; δ, delta; per mil, parts per thousand. In Graph column, green bar indicates no exceedance of standards, orange indicates an SMCL exceedance, and red indicates an MCL exceedance]

Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
Dissolved gases											
Methane (mg/L)	54	<0.0002	0.0009	29	48	88.9	2	3.7		>7	—
Ethane (mg/L)	54	<0.0002	0.0002	0.50	9	16.7	—	—	—	—	—
Propane (mg/L)	54	<0.0002	0.0002	0.002	2	3.7	—	—	—	—	—
$\delta^{13}C$ (per mil in CH_4)	4	–63.7	–44.9	–32.4	4	100	—	—	—	—	—
δ^2H (per mil in CH_4)	4	–190	–162	–104	6	100	—	—	—	—	—

[1]U.S. Environmental Protection Agency drinking water advisory recommendation (U.S. Environmental Protection Agency, 2003).

[2]Proposed U.S. Environmental Protection Agency MCL for states without an enhanced indoor air program.

[3]Volatile organic compounds (VOCs) with detections are shown. A full listing of all VOCs sampled but not detected are shown in appendix 2.

A. pH

B. Specific conductance

C. Hardness

D. Chloride

Base from U.S. Census Bureau digital data, 2011
1:100,000-scale Albers equal-area projection
Standard parallels 40°N and 42°N, central meridian 78°W, latitude of orgin 39°
Bedrock geology was derived from the principal lithology of geologic units
assigned by Miles and Whitfield, 2001

EXPLANATION

- Carbonate
- Sandstone
- Shale, mudstone, or siltstone

pH, in standard units
- ≤6.50
- >6.50 to 7.50
- >7.50 to 8.00
- >8.00

Specific conductance, in microsiemens per centimeter
- ≤200
- >200 to 300
- >330 to 600
- >600 to 1,380

Hardness, in milligrams per liter as calcium carbonate
- ≤60
- >60 to 120
- >120 to 8.00
- >8.00

Chloride, in milligrams per liter
- ≤10.0
- >10.0 to 20.0
- >20.0 to 40.0
- >40.0 to 100
- >100 to 355

Figure 4. Spatial distribution of *A*, pH values; *B*, specific conductance; *C*, hardness; *D*, chloride; *E*, bromide; *F*, methane; *G*, nitrate; *H*, total coliform in 54 wells sampled and bedrock geology in Clinton County, Pa. ≤, less than or equal to; >, greater than.

E. **Bromide**

F. **Methane**

G. **Nitrate**

H. **Total coliform**

Base from U.S. Census Bureau digital data, 2011
1:100,000-scale Albers equal-area projection
Standard parallels 40°N and 42°N, central meridian 78°W, latitude of orgin 39°
Bedrock geology was derived from the principal lithology of geologic units
assigned by Miles and Whitfield, 2001

EXPLANATION

Carbonate

Sandstone

Shale, mudstone, or siltstone

Bromide, in milligrams per liter	Methane, in milligrams per liter	Nitrate plus nitrite, in milligrams per liter as nitrogen	Total coliform, in most probable number per 100 milliliters
≤0.01	≤0.001	≤0.04	≤1
>0.01 to 0.02	>0.001 to 0.2	>0.04 to 2	>1 to 10
>0.02 to 0.10	>0.2 to 4	>2 to 5	>10 to 100
>0.10 to 1.00	>4 to 12	>5 to 10	>100 to 1,000
>1.00 to 2.80	>12 to 29	>10	>1,000 to 8,660

Figure 4.   —Continued

Major Ions

Major ions are frequently 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 that remain in the aquifer matrix or that could be mobilized from deep sources. The concentrations of major ions, TDS, salinity, and SC of groundwater are positively correlated, and generally expected to increase with progressive evaporation or dissolution of minerals (Hem, 1985). The concentrations of trace elements in solution may increase with TDS or SC, not only because of the release of trace constituents along 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, vanadium, molybdenum, arsenic, selenium, radium, uranium, lithium, and bromide) typically are present at concentrations less than 1 mg/L (Hem, 1985). Although biological (biochemical) processes can affect the concentrations of nutrients and trace constituents in groundwater directly or indirectly because of changes to pH and redox, such processes generally have minor effects on major ion concentrations.

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.

The measured TDS concentrations ranged from 26.2 to 793 mg/L; the median concentration was 170 mg/L (table 3). The TDScalc was comparable in value to the measured TDS and ranged from 33 to 688 mg/L. Out of 54 samples, 4 samples (7.4 percent) had TDS that exceeded 500 mg/L, which is the EPA SMCL for TDS in drinking water. Two of these four samples from the sandstone aquifers (wells CN 477 and CN 488) had elevated concentrations of sodium and chloride. The other two samples, from the carbonate aquifer (wells CN 482 and CN 284), had elevated concentrations of calcium, sodium, alkalinity, sulfate, chloride, and nitrate that may result from the dissolution of calcite and gypsum, plus the addition of salinity and nutrients possibly from an anthropogenic source. Elevated salinity resulting from sodium and chloride concentrations could be caused by (1) connate water in the formations and a zone of restricted groundwater flow that limits flushing by fresh recharge; (2) mixing of saline and freshwater; or (3) by the introduction of salt from near-surface contaminant sources such as road-deicing compounds, water softener additives, effluent from septic systems, or animal waste (Mullaney and others, 2009).

Dissolved sodium concentrations ranged from 0.33 to 109 mg/L. Median sodium concentrations for the sandstone, shale, and carbonate aquifers were 3.5, 15.2, and 8.0 mg/L, respectively (fig. 4.1). For individuals on a very low sodium diet (500 mg/day), the EPA recommends that drinking-water sodium not exceed 20 mg/L. In order to avoid adverse effects on taste, the EPA recommends that sodium concentrations in drinking water not exceed 30 to 60 mg/L, a threshold for taste-sensitive segments of the population (U.S. Environmental Protection Agency, 2003). Results in Clinton County show that 16.7 percent of the groundwater samples have sodium concentrations greater than the 30-mg/L guideline, including two samples that exceed the upper threshold of 60 mg/L. Dissolved concentrations of chloride ranged from 0.37 to 355 mg/L (table 3). Median chloride concentrations were 3.2, 6.8, and 11.9 mg/L for the sandstone, shale, and carbonate aquifers, respectively (fig. 4.1). Out of the 54 samples, only 1 sample (1.9 percent), from well CN 477, exceeded the EPA SMCL of 250 mg/L for chloride in drinking water (table 3). This particular sample, from the sandstone aquifer, also had the maximum values of TDScalc (688 mg/L), SC (1,380 mg/L), sodium (109 mg/L), and bromide (2.80 mg/L), plus an elevated concentration of methane (4.6 mg/L).

Hardness and Corrosivity

The alkalinity of a solution indicates its capacity to neutralize acid and commonly results from dissolved carbonate and bicarbonate ions (Hem, 1985). Alkalinity generally increases with the pH of a water sample. Alkalinity ranged from 7.08 to 287 mg/L as calcium carbonate ($CaCO_3$). Median alkalinity concentrations for the sandstone, shale, and carbonate aquifers were 46.7, 98.0, and 180 mg/L as $CaCO_3$, respectively (fig. 4.1).

The hardness of the 54 well-water samples ranged from 17.6 to 516 mg/L as $CaCO_3$. Median hardness concentrations for the sandstone, shale, and carbonate aquifers were 70.1, 84.8, and 195 mg/L as $CaCO_3$, respectively (fig. 4.1). There are no health-related standards established specifically for hardness in drinking water. 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 is influenced by the dissolution of calcium- and magnesium-bearing minerals such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), which are associated with limestone and calcareous shale and sandstone. Hard water decreases the lathering of soap and increases the potential for accumulation of mineral deposits in plumbing and cooking utensils. Using a common hardness classification (Durfor and Becker, 1964), the measured

values indicate that 17 (31.5 percent) of the 54 water samples are soft (less than 60 mg/L as $CaCO_3$), 13 samples (24.1 percent) are moderately hard (61–120 mg/L as $CaCO_3$), 10 samples (18.5 percent) are hard (121–180 mg/L as $CaCO_3$), and 14 samples (25.9 percent) are classified as very hard (greater than 180 mg/L as $CaCO_3$) (figs. 4*C*, 5). All but one of the samples from the carbonate aquifer are classified as hard waters, whereas approximately half the samples from the sandstone and shale aquifers are considered hard (fig. 5). Samples with near-neutral and alkaline pH values (greater than 6.5) generally had the greatest hardness (fig. 4.2). A few of the near-neutral and higher-pH waters with low hardness had elevated sodium, which may result from natural water-softening processes that remove calcium and magnesium in exchange for sodium.

Water resources engineers commonly consider hardness, alkalinity, and related measures to identify the potential for encrustation or corrosion of pipes and plumbing (Snoeyink and Jenkins, 1981). One such indicator, the Langelier Index (LI), calculates the difference between the measured pH and the pH at equilibrium with calcium carbonate ($CaCO_3$), which 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 the LI or SI_{CAL} is negative, then the water is undersaturated with $CaCO_3$ and will tend to be corrosive and capable of dissolving metals, such as lead and copper, from the plumbing and distribution system. An LI or SI_{CAL} close to zero is considered ideal because the water will neither be strongly corrosive nor scale forming. For the 54 groundwater samples, SI_{CAL} ranged from –5.3 to 0.2 (fig. 5). Of the 54 samples, 31 (57.4 percent) had SI_{CAL} values that were less than −0.5, indicating potentially strongly corrosive characteristics; the remaining samples are considered neither strongly corrosive nor scale forming. Evaluation of the chloride to sulfate mass ratio (CSMR) indicated that a large percentage of the samples with SICAL less than –2.0 had serious potential corrosivity on the basis of criteria presented by Nguyen and others (2010) (fig. 5). Many samples from the shale or sandstone aquifers, particularly those with pH less than 6.5, were identified as having serious potential corrosivity based on the combination of the SI_{CAL} and CSMR; however, none of the samples from the carbonate aquifers was identified as seriously corrosive (fig. 5).
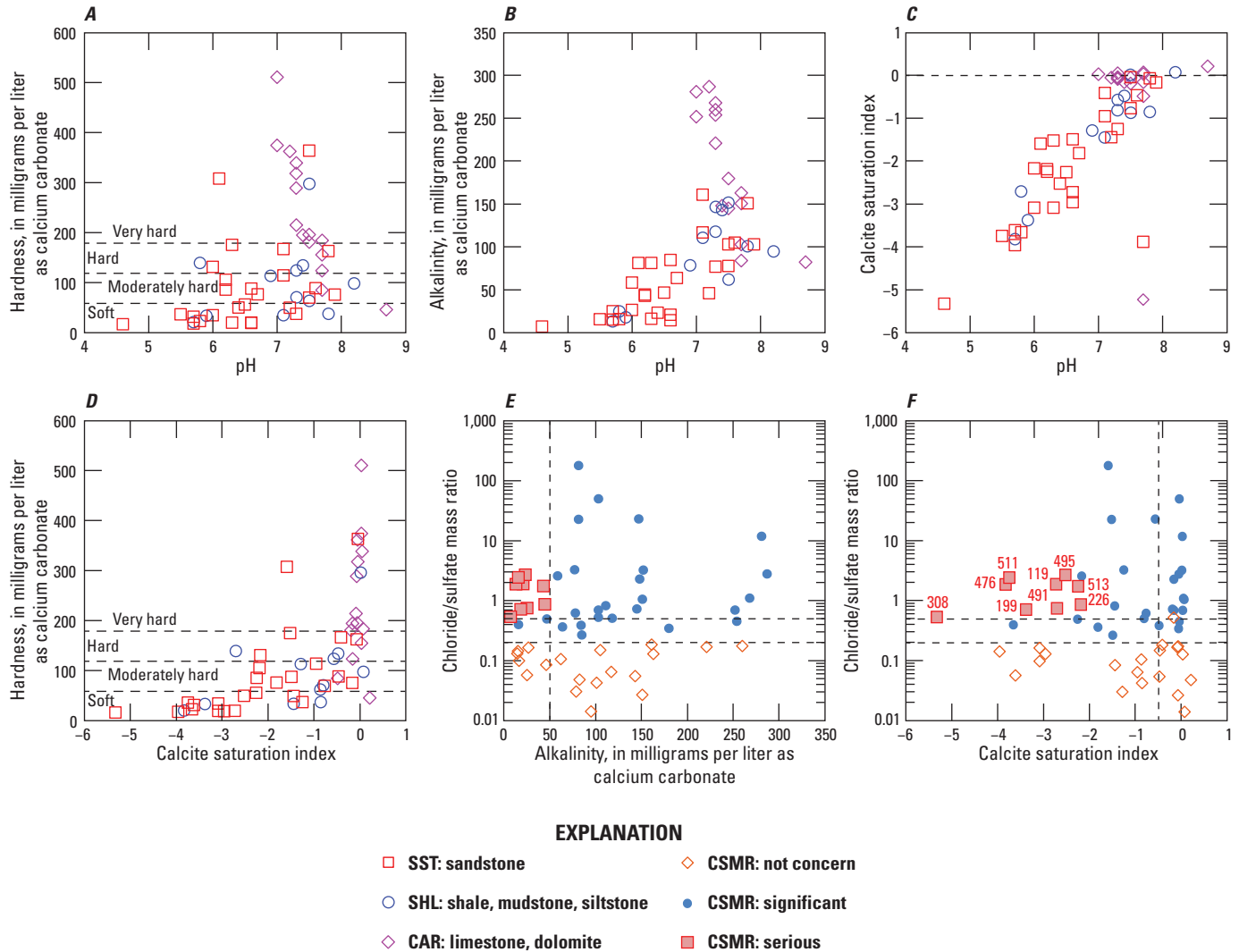
Figure 5. Hardness, alkalinity, pH, and associated measures of corrosivity of 54 groundwater samples, Clinton County, Pa., 2017. Calcite saturation index (SI_{CAL}; log(IAP/K_T)), computed with PHREEQC (Parkhurst and Appelo, 2013) using the WATEQ4F database (Ball and Nordstrom, 1991). *A–D* show symbols for primary bedrock lithology from table 1: SST, sandstone; SHL, shale, mudstone, siltstone; CAR, limestone, dolomite. *E* and *F* show symbols for corrosivity indicated by chloride to sulfate mass ratio (CSMR; Cl/SO$_4$) in relation to alkalinity and SI_{CAL}. IAP, ion activation product; Kt, solubility constant.

Nutrients

Nutrients include nitrogen and phosphorous species. Nitrogen in groundwater occurs principally as nitrate (NO_3), with subordinate nitrite (NO_2) and ammonia (NH_3), whereas phosphorus is present mainly as orthophosphate (PO_4) (table 3). Background concentrations of nutrients 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. Elevated nutrient concentrations generally indicate anthropogenic sources, which may include fertilizers, storm runoff, animal wastes, and effluent from septic systems. Excessive nitrate in drinking water causes a health risk, especially in infants, because it

disrupts oxygen transfer in the blood (U.S. Environmental Protection Agency, 2012a). Infants below the age of 6 months who drink water containing nitrate in excess of the EPA MCL (10 mg/L) could become seriously ill, and develop symptoms including shortness of breath and blue-baby syndrome. Because concentrations of nitrite are typically low in oxygenated waters, nitrate plus nitrite concentrations essentially represent nitrate concentrations. The concentration of nitrate plus nitrite in samples ranged from less than 0.04 to 49.3 mg/L as N; the median concentration was 0.36 mg/L as N (table 3). The median nitrate concentrations for the carbonate, shale, and sandstone aquifers were 3.26 mg/L, less than 0.04 mg/L, and 0.27 mg/L, respectively (fig. 4*G*). One sample from the carbonate aquifer (well CN 482) had a nitrate concentration of 49.3 mg/L that far exceeded the EPA MCL of 10 mg/L for

nitrate as N; the same sample contained only 0.01 mg/L of orthophosphate. The concentration of orthophosphate for all 54 samples ranged from less than 0.004 to 0.27 mg/L. The median concentrations for the carbonate, shale, and sandstone aquifers were 0.01, 0.009, and 0.006 mg/L, respectively.

Bacteria

All samples were analyzed for total coliform and *E. coli* bacteria. Coliform bacteria are ubiquitous in the environment and are not typically pathogenic. However, if total coliform bacteria are detected in well water it can indicate that a potential disease-causing bacteria may also have a pathway into the contributing groundwater. Some coliform bacteria, specifically strains of *E. coli* such as O157:H7, can cause severe illness. 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).

Total coliform bacteria were detected in 31 of the 54 groundwater samples (57.4 percent) (table 3). Total coliform concentrations ranged from less than 1 colony (reported as most probable number [MPN] per 100 mL) to more than 8,660 MPN/100 mL. Of the 31 samples that had total coliform bacteria, 14 samples had detectable *E. coli*, with concentrations ranging from less than 1 to greater than 140 MPN/100 mL. Most samples with detected total coliform or *E. coli* bacteria were from wells in the carbonate aquifer, where land use activities such as intensive agriculture (for example, manure application) and transmissive bedrock have been shown to contribute to such groundwater contamination (fig. 4*H*; Zimmerman and others, 2001; DeSimone, 2009).

Metals and Trace Elements

Metals and other trace elements typically are present in concentrations less than 1 mg/L in natural waters (Hem, 1985). Most metals and trace elements in groundwater are leached from soil or dissolved from underlying bedrock in minute quantities by groundwater; some are present in precipitation. Summary statistics for metals and trace elements in filtered samples are listed in table 3.

The EPA has established MCLs and SMCLs for various metals and trace elements in drinking water (table 3). One sample (1.9 percent) exceeded the EPA MCLs for arsenic and aluminum, 7 samples (13 percent) exceeded the SMCL for iron and 16 samples (29.6 percent) exceeded the SMCL for manganese. None of the samples exceeded the EPA MCL or SMCL for antimony, barium, beryllium, cadmium, chromium, copper, lead, selenium, silver, or zinc (table 3). In order to characterize the groundwater quality that is most representative of the aquifer, samples were collected after the well was purged and concentrations of some metals may be higher if samples were taken without flushing the system.

Arsenic concentrations ranged from less than 0.05 to 11.2 µg/L, with a median concentration of 0.14 µg/L (table 3). Arsenic concentrations were locally elevated and were not consistently related to pH (fig. 6). One sample from the sandstone aquifers, well CN 153 with pH of 7.6, had an arsenic concentration that exceeded the EPA MCL of 10 µg/L. Arsenate ($As^VO_4^{3-}$) and arsenite ($As^{III}O_3^{3-}$), 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 pH conditions (Dzombak and Morel, 1990; Smedley and Kinniburgh, 2002). Furthermore, under strongly acidic or reducing conditions, oxide minerals may become unstable and dissolve, releasing arsenic to solution. More detailed explanation of the effects of pH on sorption processes and the possible relations between redox state and arsenic concentration are presented in the section "Relation of Groundwater Quality to Geochemical Characteristics" of this report.

Although the highest concentrations of boron (195 µg/L), bromide (2.80 mg/L), and sodium (109 mg/L) were found in samples with pH greater than 7.5 (fig. 6), most high pH samples from the sandstone, shale, or carbonate aquifers did not have elevated concentrations of these constituents. In contrast, the highest concentrations of lead (5.25 µg/L), copper (132 µg/L), zinc (268 µg/L), and other trace metals were found in samples from the sandstone and shale aquifers that had pH less than 6.0 (fig. 6). Generally, lower concentrations of trace metals with higher 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. The increased concentrations of sodium could result from cation-exchange reactions. These reactions are explained in more detail in the section "Relation of Groundwater Quality to Geochemical Characteristics."

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 5.00 to 10,130 µg/L, with a median of 14.6 µg/L. Seven of these samples (13 percent) from the sandstone and shale aquifers exceeded the EPA SMCL of 300 µg/L for iron; none of the samples from the carbonate aquifer exceeded the MCL. Concentrations of dissolved manganese in water ranged from less than 0.40 to 1,840 µg/L; the median concentration was 3.47 µg/L. Water samples from 16 of the 54 sampled wells (29.6 percent) exceeded the EPA SMCL of 50 µg/L for manganese; none of the samples from the carbonate aquifer exceeded the SMCL.

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 Clinton County, as previously described, could acquire metals from lead or copper pipes if they are present in the household water system. Depending on water

treatment, the corrosive characteristics may or may not be mitigated. Sampling at the tap is advisable to evaluate the actual concentrations of constituents in household drinking water and to evaluate the potential effects of water treatment. As previously mentioned, levels for metals such as lead and copper observed for this study of groundwater after thorough purging of the well and distribution system could be much lower than those for samples collected before the plumbing system is flushed.
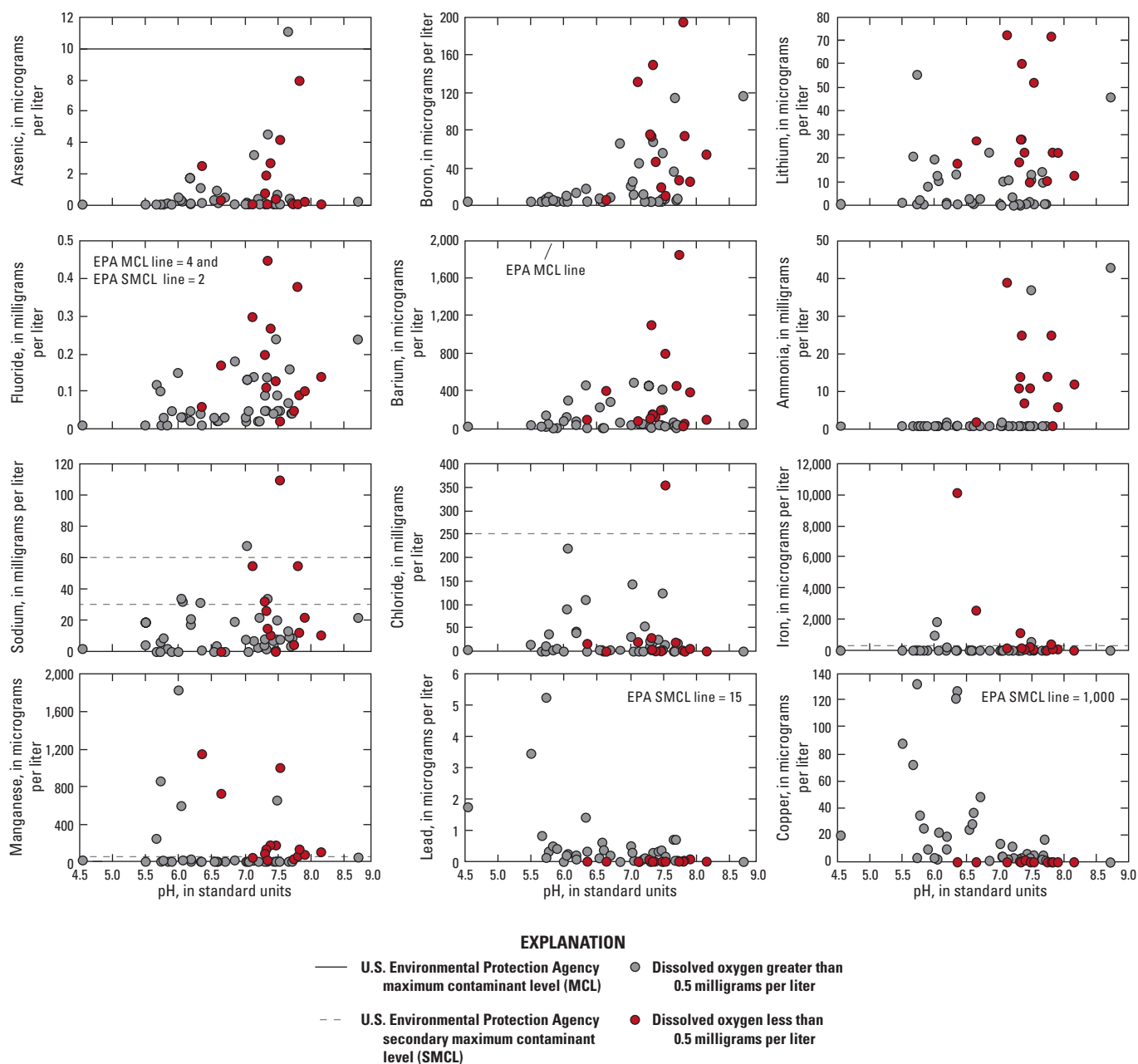
Figure 6.   Relation between pH and selected constituents for 54 groundwater samples in Clinton County, Pa. >, greater than; <, less than. Detection limits for constituents can be referenced in table 3.

Radionuclides

Radionuclides naturally present in rocks and soils may be dissolved or leached into groundwater. Analyses for radio-activity and radionuclides include gross alpha radioactivity, gross beta radioactivity, and dissolved radon-222 (radon gas). Uranium, a radioactive element, also was analyzed in the dissolved form. 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). Summary statistics for radioac-tive constituents in groundwater samples from Clinton County as well as the established or proposed EPA MCLs for some of these constituents are given in table 3.

Radon-222 was detected in all samples and frequently exceeded its proposed MCL of 300 pCi/L (table 3). The activities of radon-222 ranged from 9.9 to 3,250 pCi/L, with a median activity of 541 pCi/L (table 3). The median radon-222 activity was 1,040, 84.1, and 481 pCi/L for the sandstone, shale, and carbonate aquifers, respectively (fig. 4.1). The EPA does not regulate radon-222 in drinking water. However, 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 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 samples from 32 of the 54 wells sampled (59.3 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 median radon-222 activity for oxic samples (692 pCi/L) was substantially greater than that for anoxic samples (83.1 pCi/L) (fig. 4.4).

The gross alpha-particle radioactivity (72-hour count) in water from the 54 sampled wells ranged from –0.48 to 8.1 pCi/L; the median activity level was 1.4 pCi/L (table 3). The gross alpha-particle activity range in the 30-day count was similar to or slightly greater than the activity in the 72-hour count. No water sample exceeded the EPA MCL of 15 pCi/L for gross alpha-particle activity (table 3).

The gross-beta particle radioactivity (72-hour count) ranged from –0.25 to 6.9 pCi/L; median activity was 2.54 pCi/L. Gross beta-particle activity in the 30-day count was similar to or slightly greater than the activity in the 72-hour count in about half of the samples (table 3).

The concentration of uranium ranged from less than 0.01 to 10.4 µg/L. The median concentration was 0.08 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 54 wells sampled, was analyzed for radium-226 and radium-228. Concentrations (activities) of radium-226 ranged from 0.15 to 0.42 pCi/L in water samples, and activities of radium-228 ranged from 0.46 to 0.57 pCi/L from the four wells. None of the samples exceeded the EPA MCL of 5 pCi/L for combined radium-226 and radium-228. The highest activities of radium-226 and radium-228 were measured for the same sample from well CN 477. This sample also had the second highest radon-222 level of the 54 samples reported herein.

Dissolved Methane and Other Naturally Occurring Hydrocarbon Gases

Methane was detected in almost 90 percent of water samples and two samples had concentrations greater than the 7-mg/L action level (table 3). Water sampled from the 54 wells had concentrations of dissolved methane ranging from less than 0.0002 to 29 mg/L, in addition to lower to nondetectable concentrations of other, more complex hydrocarbon gases including ethane, ethylene glycol, propane, propylene glycol, isobutane, and N-butanol (in order of increasing number of hydrocarbon chains) (table 3). None of the samples had detect-able concentrations of the dissolved hydrocarbons isopentane, N-pentane, and hexane.

Many samples with detectible concentrations of methane were collected outside of the Appalachian Plateaus region, which has been developed for natural gas extraction. Elevated methane concentrations (greater than 0.2 mg/L) and associated water-quality characteristics were commonly associated with groundwater sampled from the shale aquifers (median 0.16 mg/L), and occasionally from carbonate (median less than 0.0004 mg/L) or sandstone (median 0.0009 mg/L) aquifers in the study area (fig. 4F). The two samples that exceeded the Pennsylvania action level of 7 mg/L for dissolved methane (Commonwealth of Pennsylvania, 2014) were both from shale aquifers. Additionally, one sample from the sandstone aquifer and another from the carbonate aquifer 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 (5–15 percent methane in air containing at least 10 percent oxygen). Elevated concentra-tions of methane generally were found in suboxic groundwater (dissolved oxygen less than 0.5 mg/L) (fig. 6) 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 in, but not limited to, those well-water samples with elevated methane.

Manmade Organic Compounds

All samples were analyzed for selected manmade organic compounds, including VOCs, glycols and alcohols, and oil and grease (appendix 2). Only two of these compounds were detected; both were VOCs at concentrations less than the MCLs, in two separate samples.

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 and leaks 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).

The EPA has established primary drinking-water MCLs for 25 of the 68 VOCs analyzed for this study (U.S. Environmental Protection Agency, 2012a). The labora- tory reporting level for the VOCs analyzed was 0.5 µg/L, which is lower than the established MCLs for all but two compounds—1,2-dibromo-3-chloropropane (DBCP) and 1,2-dibromoethane (EDB) (appendix 2). MCLs have not been established by EPA for VOCs where data are insufficient to evaluate human-health effects.

Of the 68 VOCs analyzed in the 54 groundwater samples, only two compounds were detected above the reporting level: acetone (45.9 µg/L) in well CN 484 and methyl ethyl ketone (48.3 µg/L) in well CN 498, but concentrations of the detected VOCs did not exceed an established EPA drinking-water standard. Although not necessarily a health risk, the detection of these manmade compounds in groundwater indicates a possible low level of 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 54 wells (table 3). Because the reporting levels of the analytical methods are high for these organic compounds, lower concentrations may be present but not detected in the sampled groundwater. However, at the time of this study, a more sensitive approved method with lower reporting levels was not available.

Relation of Groundwater Quality to Geochemical Characteristics

Dissolved constituents in groundwater may be derived from atmospheric, geologic, biologic, and anthropogenic sources as the water 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, the extent and sequence of contact between water and the source, the aqueous solubility and interactions among the dissolved elements, plus geochemical conditions such as pH and oxidation-reduction (redox) state that affect element form, mobility, and transport in the aqueous environment.

Relations Between Groundwater Quality, Geology, and Topographic Setting

Most wells constructed for domestic use in Pennsylvania are completed within the local freshwater-flow system, which typically extends downward from the surface to depths of 500 ft or greater, depending on local geology and topography. Brackish or saline groundwater with TDS greater than 1,000 mg/L generally is not used for domestic supplies in the northeastern United States but may be encountered below the freshwater zone (Lohman, 1939; Feth and others, 1965). In general, the groundwater in the shallow freshwater system is relatively young (elapsed time since recharge) compared to the older, underlying brackish groundwater (Stanton and others, 2017). In the study area and other areas with substantial topographic relief, depth from the land surface to brackish groundwater water generally is greater beneath uplands compared to valley settings.

The wells sampled for this study were completed to depths ranging from 46 to 500 ft, with half of the wells less than 180 ft deep. Wells in the sandstone aquifers had a median depth of 167 ft (range from 55 to 500 ft), which was less than the median well depth of 260 ft for the carbonate aquifers (range from 140 to 400 ft) (fig. 4.1). The range of well depths for the shale aquifers (46 to 430 ft) overlapped those of the sandstone and carbonate aquifers. Several wells with depths ranging from 80 to 430 ft exhibited characteristics of brine- influenced waters with SC and TDS dominated by sodium and chloride, plus elevated concentrations of bromide and methane. With one exception, these potentially brine-influenced ground- waters were sampled from the sandstone and shale aquifers, as explained in more detail below.

The well depths and associated water-quality character- istics for the Clinton County groundwater samples, classified by three primary aquifer lithologies, are illustrated by boxplots (fig. 4.1). The sandstone aquifers had lower median values for pH, SC, TDS, hardness, alkalinity, calcium, magnesium, strontium, sulfate, and nitrate, and higher median values for barium and lithium compared to those for the carbonate aquifers. However, groundwater in both sandstone and carbonate was typically oxic (DO>0.5 mg/L). The shale aquifers, which were more frequently anoxic (DO<0.5 mg/L), generally had overlapping ranges and intermediate median values for these constituents and various trace elements compared to the sandstone and carbonate aquifers, but had greater median concentrations of methane and lower median concentrations of uranium and radon-222 than the other lithologies. Furthermore, although median values were not statistically different among the three aquifers, groundwater samples from the shale aquifers had a greater frequency of elevated concentrations of sulfate, sodium, fluoride, boron, and lithium than groundwater samples from the other two aquifers.

Different aquifer lithologies, which exhibited differences in water quality, generally were associated with different topo- graphic settings as indicated by the topographic position index

(TPI). Elsewhere in northeastern Pennsylvania with relatively uniform bedrock, the TPI has been used to explain observed variations in water quality in valley settings that are oriented along deep fractures (Llewellyn, 2014). In Clinton County, the TPI may be related to both lithologic and structural variations. Specifically, most of the wells sampled from carbonate aquifers are situated on lower slopes and valley settings, whereas those in sandstone are situated in ridge and upper slope settings, and those in shale are situated in mostly steep slope settings. Thus, consistent with variations by lithologic class, the groundwater samples from wells on lower slopes and valley settings had higher pH values and greater concentrations of dissolved solids, chloride, and bromide than samples from higher topographic positions, but did not have higher methane concentrations (fig. 4.5). In Clinton County, the highest methane values were associated with groundwater samples collected from shale aquifers along steep slopes (fig. 4.5), which mainly occurs along the Allegheny Front leading from the Deep Valleys section of the Appalachian Plateaus province to the Ridge and Valley province. Gas drilling has taken place in the Appalachian Plateaus west of the Allegheny Front, but not within the Allegheny Front or Ridge and Valley areas of Clinton County (fig. 1).

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). Groundwater from sandstone and shale aquifers in the Ridge and Valley province was similar in quality to that from the Appalachian Plateaus and may be representative of less evolved, upgradient groundwater compared to more mineralized groundwater of the carbonate aquifers. Most wells in the carbonate aquifers within the Ridge and Valley province are located in the lower slopes and valleys settings, which are bounded by steep slopes and ridges held up by shale and sandstone.

Relations Among pH, Specific Conductance, and Dissolved Chemical Concentrations

Correlations among pH, SC, dissolved chemical concentrations, and environmental variables could indicate sources of water-quality constituents or potential geochemical controls on element mobility. For example, the pH for the 54 groundwater samples had a positive relation with SC and other measures of ionic strength, including TDS, whereas the pH and SC had a negative relation with the concentration of DO (figs. 7, 4.2, and 4.3). With increased pH, the concentrations of several major and trace constituents generally increased, including alkalinity, sodium (Na), strontium (Sr), boron (B), fluoride (F), and uranium (U) (figs. 6 and 7). Despite positive relationships between SC and the concentrations of chloride (Cl) and bromide (Br), those constituents had an inverse relation

with pH for the near-neutral to higher pH samples (fig. 7). Concentrations of potassium (K) showed a relation with SC but not with pH (fig. 7; appendix 3, online only).

Boxplots showing the constituent values for four different pH class intervals reveal the above patterns and exhibit differences among medians (appendix 4; fig. 4.2). The near-neutral ($6.5<pH\leq7.5$) and alkaline pH classes ($7.5<pH\leq8.7$) had higher median values for SC, TDS, hardness, calcium (Ca), magnesium (Mg), sodium (Na), alkalinity, sulfate (SO_4), F, B, Sr, molybdenum (Mo), U, and methane than the acidic ($4.5<pH\leq5.5$ and $5.5<pH\leq6.5$) pH classes. In contrast, the acidic pH classes had greater medians for dissolved oxygen, copper (Cu), lead (Pb), zinc (Zn), nickel (Ni), and radon (Rn)-222 compared to the near-neutral and alkaline pH classes.

The relation between the pH or SC with concentrations of TDS, alkalinity, Ca, Mg, and hardness is complex owing to the mixing of water types and processes such as cation exchange; correlations change from positive to negative at about pH 7.5 (fig. 7). For pH values less than 7.5, the SC and associated concentrations of TDS, SO_4, alkalinity, hardness, Ca, Mg, and other cations, including Sr, Na, and lithium (Li), generally increased with pH. However, for pH values greater than 7.5, the concentrations of hardness, Ca, Mg, barium (Ba), and chloride (Cl) decreased with increased pH, whereas SC and concentrations of TDS, SO_4, alkalinity, Na, Li, and Sr continued to increase or were unchanged. Such patterns in pH, SC, and constituent concentrations are consistent with the dissolution of calcite ($CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$) over the range of pH, combined with cation exchange at pH greater than 7.5. Through cation-exchange reactions, Ca, Mg, and Ba ions displace Na ions from exchange sites on clay minerals ($0.5Ca^{2+} + NaX = 0.5CaX_2 + Na^+$) (Appelo and Postma, 2005), which results in the removal of hardness. Water softening that removes Ca and Mg can lead to undersaturation with respect to the carbonate minerals, which promotes additional calcite or dolomite dissolution with consequent increases in pH and alkalinity along the groundwater flow path (Senior and Cravotta, 2017).

Boxplots that show constituent values for four different SC class intervals (fig. 4.3) indicate variations that may or may not be related to major lithology (fig. 4.1) or pH (fig. 4.2). The three highest SC classes ($200<SC\leq330$, $330<SC\leq600$, and $600<SC\leq1,400$) had statistically equivalent median pH values of 7.33, 7.32, and 7.21, respectively, and comparable median values for SO_4 and Na; however, the lowest SC class ($46<SC\leq200$) had a statistically lower median pH of 6.44 and lower median values for SO_4 and Na. Despite similar pH among most of the SC classes, median concentrations of alkalinity, hardness, Ca, Mg, Sr, K, Cl, and nitrate (NO_3) increased with SC, whereas F, B, and Li concentrations decreased. Concentrations of DO, NH_3, Fe, Mn, Pb, and arsenic (As) did not vary consistently with SC. Constituents that did not vary with SC and (or) pH may be controlled by other factors, such as redox state.

The constituent values for anoxic, mixed, and oxic redox class intervals are illustrated as boxplots (fig. 4.4). Although the SC, 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, F, B, Li, Ba, Fe, Mn, As, and methane, and lower median values for DO, NO_3, Cu, Pb, U, and Rn-222 than the oxic samples. The mixed redox class exhibited a wide range of values, with some constituent concentrations intermediate or comparable to those for the anoxic and oxic classes, as expected for physical mixing of such different waters. However, the mixed class also had lower median pH and greater Fe, Mn, and SO_4 concentrations than expected for simple mixing of water represented by the oxic and anoxic classes. The coincidence of acidic pH and elevated Fe, Mn, and SO_4 concentrations is consistent with the oxidation of sulfide minerals, such as pyrite, and suggests that the mixed class includes samples of various origins.

## Ionic Contributions to Conductivity and Total Dissolved Solids

Despite positive correlations between SC, TDS, and major ion concentrations, the majority of various ionic contributions to the SC and TDS varied widely (figs. 8 and 9). Calcium and bicarbonate ions were the predominant sources of ionic conductivity in most samples, especially those from carbonate aquifers. Magnesium, sodium, chloride, and sulfate were subordinate but relatively important in many samples from shale and sandstone aquifers. Contributions by nitrate were locally important, particularly for some carbonate aquifer samples.

Variations in the major ion species contributions to the SC for the averaged samples from carbonate, shale, and sandstone aquifers, plus three selected groundwater samples from each aquifer are illustrated in figure 9. To provide context, the samples illustrated in figure 9 are identified among all 54 samples in figure 8. The ions Ca^{+2}, HCO_3^-, Mg^{+2}, Na^+, SO_4^{-2}, and Cl^- are the predominant sources of ionic conductivity for the averages of the different aquifer samples and most other samples that have low to moderate SC values (fig. 9A–F), with minor contributions from nitrate, potassium, hydrogen, and hydroxyl ions. Samples with elevated SC values generally have increased contributions from sodium, bicarbonate, chloride, and sulfate ions (fig. 9G–L).

Most samples from the sandstone and shale aquifers had lower SC values but more varied compositions than those from the carbonate aquifers, as indicated by the average compositions for the three major lithologic classes (fig. 9A–C). Samples from wells CN 509 (fig. 9D) and CN 199 (fig. 9E) are representative of minimally evolved groundwaters with a relatively low SC ($\leq$78 µS/cm) and pH ($\leq$5.9) values. The low SC and pH of these samples are consistent with the evaporation of dilute, acidic rainwater plus minor dissolution of various minerals and salts. These samples from the siliciclastic aquifers, which are characteristic of recharge, would be classified as mixed hydrochemical types, which contain less than 50 percent of any single cation or anion (fig. 10).

More hydrochemically complex (evolved) samples that are comparable in ionic strength and pH for average compositions of groundwaters from the sandstone and shale aquifers, wells CN 512 (SC of 246 µS/cm and pH of 7.1; fig. 9G) and CN 191 (SC of 300 µS/cm and pH of 6.9; fig. 9H), also have mixed compositions, but with higher proportions of bicarbonate (CN 512) or sulfate and sodium (CN 191) acquired from water-rock interactions compared to the low ionic-strength recharge. Additional samples from the sandstone and shale aquifers highlight less common, but locally important characteristics attributed to (1) the introduction of salt or brine, which results in a sodium-calcium/chloride water type indicated by well CN 477 (fig. 9J) with a high SC of 1,380 µS/cm and pH of 7.5; or (2) cation exchange, which results in a sodium/bicarbonate-sulfate water type indicated by well CN 481 (fig. 9K) with moderate SC of 315 µS/cm and high pH of 7.8.

The carbonate groundwaters generally are distinguished from typical sandstone or shale groundwaters by higher SC values with predominant ionic contributions by calcium and bicarbonate (fig. 9C, F, I, L). For example, the sample from well CN 176 (fig. 9F) with a relatively low SC of 187 µS/cm and pH of 7.7 and the sample from well CN 493 (fig. 9I) with higher, more typical, SC of 468 µS/cm and pH of 7.3 are calcium/bicarbonate hydrochemical types that evolved mainly by dissolution of carbonate minerals. The sample from well CN 482 with SC of 1,000 µS/cm and pH of 7.0 (fig. 9L) also evolved through interaction with carbonate minerals, but has a possible anthropogenic source of added nitrate, which contributes to its high SC; this sample is classified as a calcium/bicarbonate-nitrate type. The compositions and potential evolution of important hydrochemical types are discussed in the following section.
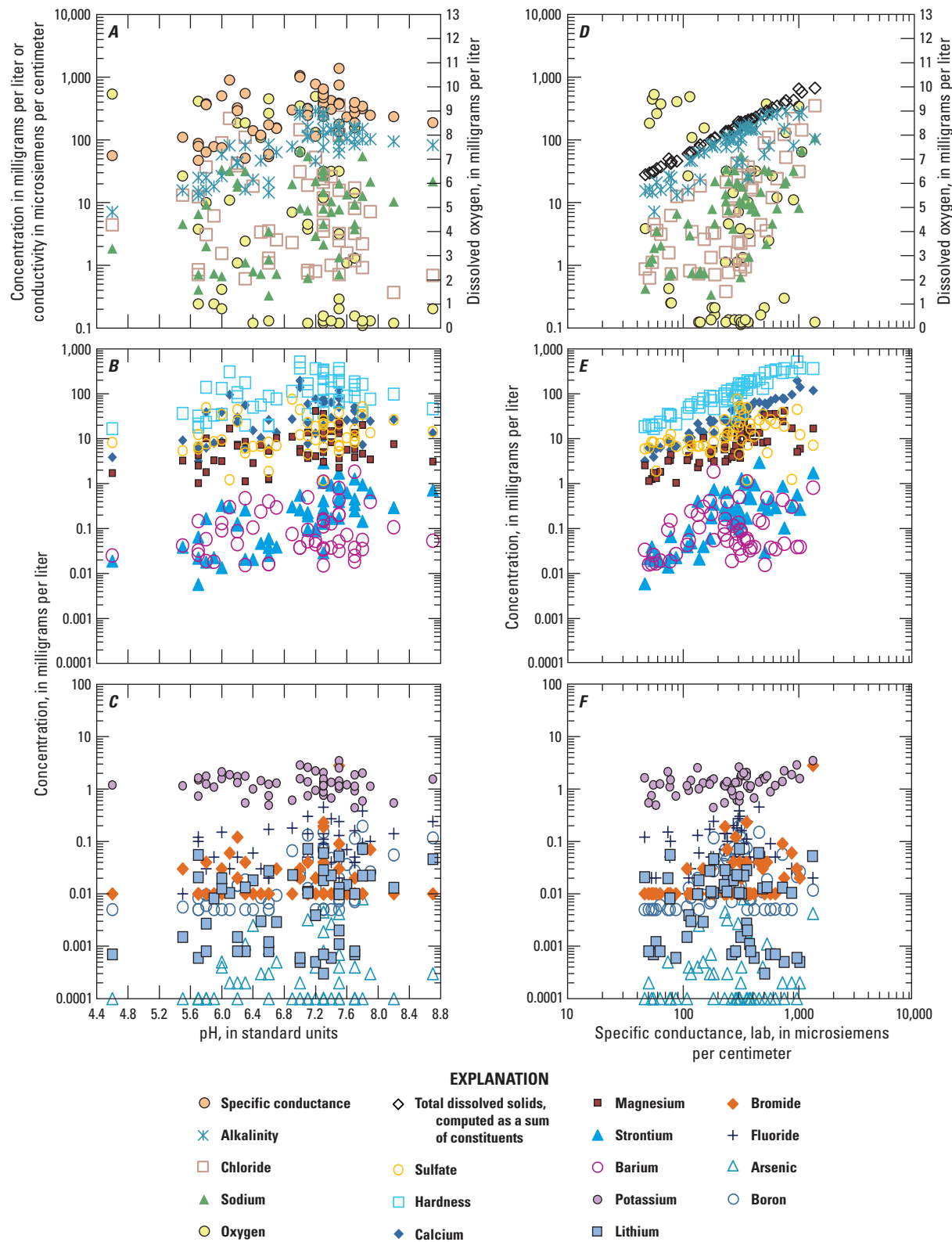
Figure 7. Concentrations of selected constituents in groundwater from Clinton County, Pa., 2017, compared to (*A–C*) pH and (*D–F*) specific conductance. SO4, sulfate; Hrd, hardness; Ca, calcium; Mg, magnesium, Sr, strontium, Ba, barium; TDS, total dissolved solids (computed as sum of constituents); ALK, alkalinity; Cl, chloride; Na, sodium; O2, oxygen; K, potassium; Li, lithium; Br, bromide; F, fluoride; As, arsenic; and B, boron. The detection limits for Br and As were 0.01 and 0.0001 mg/L, respectively; symbols plotted at those values were below detection. Detection limits for constituents can be referenced in table 3.
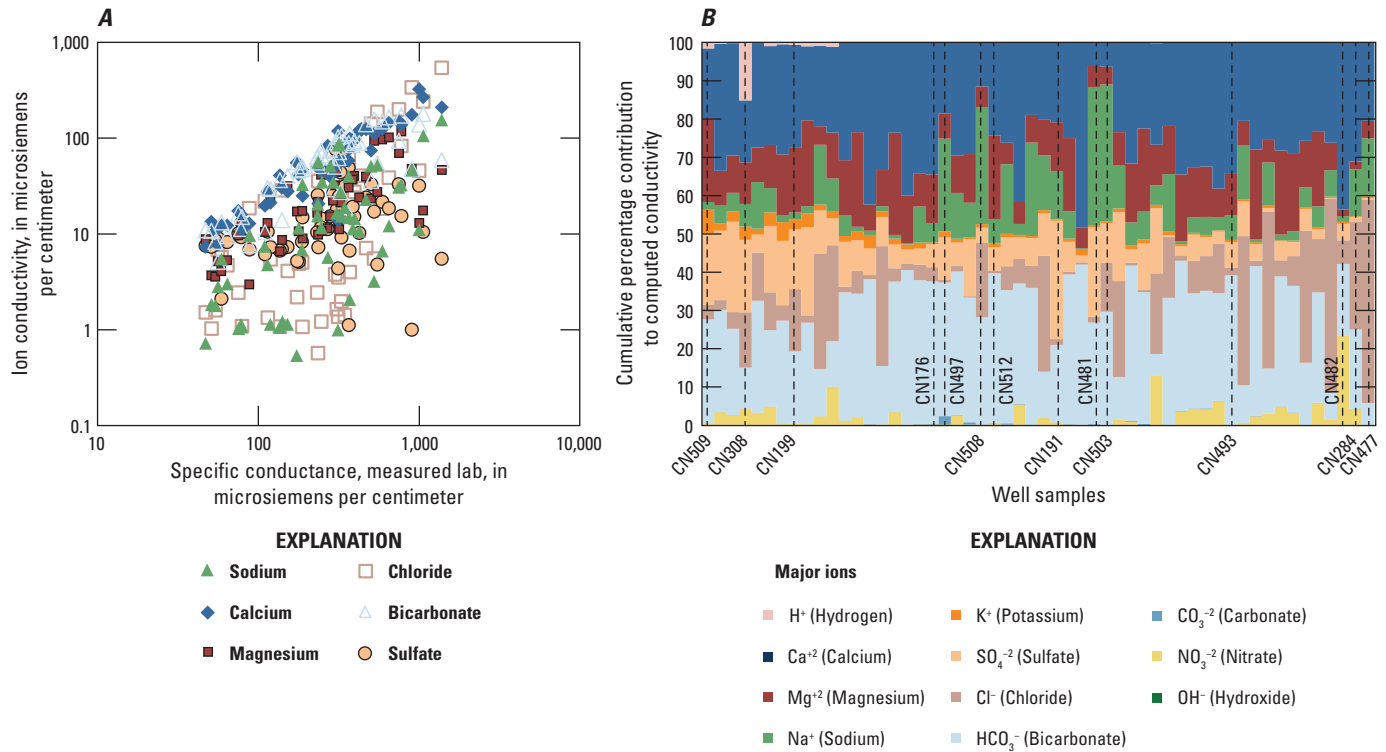
Figure 8. Major ion contributions to specific conductance (SC) for 54 groundwater samples from Clinton County, Pa., 2017. *A*, Comparison of estimated ionic conductivity contributions by sodium, calcium, magnesium, chloride, bicarbonate, and sulfate to measured SC for all 54 samples; and *B*, relative contributions by major ion species to computed SC and selected groundwater samples of representative water types, expressed in percent, in order of increasing SC. Individual ion conductivities estimated from dissolved constituent concentrations as the transport number (the relative contribution of a given ion to the overall conductivity, using the methods of McCleskey and others [2012]) after aqueous speciation calculations with PHREEQC (Parkhurst and Appelo, 2013). Samples identified in this figure are explored in more depth in figure 9.
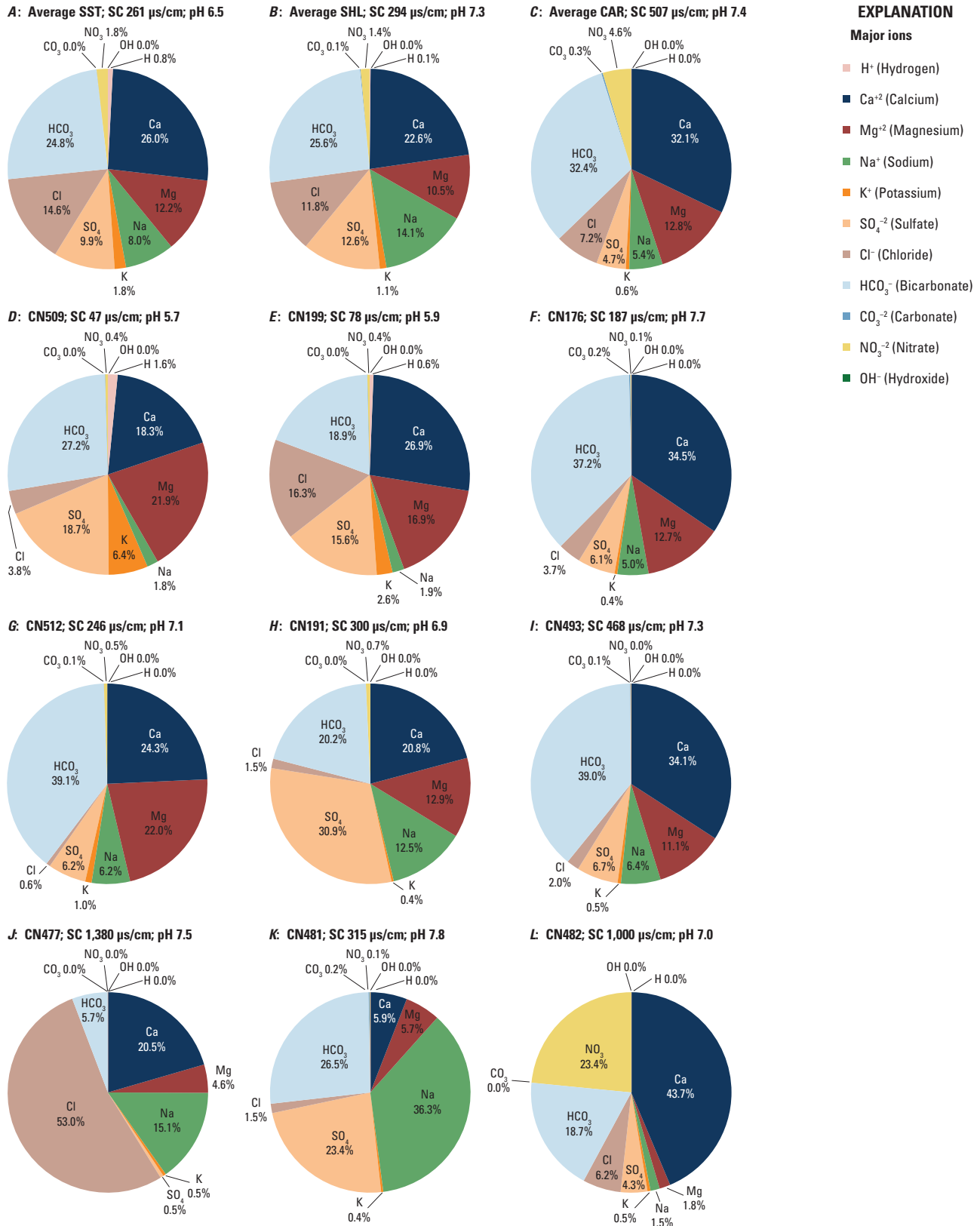
Figure 9. Ionic contributions to specific conductance computed for selected groundwater samples from Clinton County, Pa., 2017. Individual ionic conductivities estimated from dissolved constituent concentrations as the transport number (the relative contribution of a given ion to the overall conductivity, using the methods of McCleskey and others [2012]) after aqueous speciation calculations with PHREEQC (Parkhurst and Appelo, 2013). µS/cm, microsiemens per centimeter.

Major Ion Compositions Indicated by Trilinear Diagrams

Trilinear diagrams and the corresponding diamond-shaped Piper diagram indicate the percentage contributions (proportions) 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 that show ionic conductivity contributions to the SC (fig. 9), 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 somewhat different ionic proportions). The corresponding water type is identified on the basis of the predominant (greater than 50 percent) cation(s) and anion(s) shown on the trilinear diagrams (fig. 10A). For the Clinton County groundwater samples, calcium/bicarbonate hydro-chemical types were predominant for the carbonate aquifers, whereas calcium/bicarbonate and mixed water types (no dominant type) were predominant for the shale and sandstone groundwaters (fig. 10B).

In order to explain the possible origins of the observed water types, representative samples are identified on the trilinear diagram by lithology, pH, and SC classes (fig. 10). Well-water samples CN 176 (carbonate aquifer) and CN 509 (sandstone aquifer) have near-neutral pH with relatively low SC compared to other samples from the same aquifer types. These two samples and other groundwater samples plotting in the same left-corner region of the trilinear diagram are classified as calcium/bicarbonate or calcium-magnesium/bicarbonate types, which can be produced by the dissolution of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) by rainwater (recharge) or groundwater. Because continued dissolution of these minerals increases the SC and pH of the groundwater but does not substantially change its ionic composition (as percent contributions, or ratios), carbonate groundwater samples with higher SC and pH values tend to plot in the same region of the diagram (fig. 10C,D). Moving along the lower left boundary toward the lower corner of the Piper diagram, samples from well CN 497 (carbonate), CN 508 (sandstone), CN 481 (shale), and CN 503 (shale) exhibit an increased proportion of sodium and may be classified as mixed calcium-magnesium-sodium/bicarbonate or sodium-calcium-magnesium/bicarbonate-sulfate types (fig. 10A,B). Such water types are likely to form by the dissolution of calcite and (or) dolomite combined with varying degrees of cation exchange. In contrast, samples plotting in the upper third (toward the upper corner) of the diagram, such as samples from well CN 191 (shale) and CN 491 (shale), indicate an increased proportion of sulfate or chloride, 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 and could indicate effects from physical mixing of waters from different sources in a well. Finally, samples plotting near the right corner or along the upper right boundary of the Piper diagram indicate chloride as the predominant anion. The predominance of chloride implies a substantial contribution of salt (NaCl, $CaCl_2$) from road-deicing compounds, sewage or animal waste, or possibly brine of geological origin. The effect of mixing fresh groundwater with brine or road-deicing salt is shown on similar diagrams presented by Gross and Cravotta (2017) and Senior and others (2017). The sample from well CN 477 has chloride as the dominant anion and is classified as a calcium-sodium/chloride type, which is unlike any other sample collected for the study. Additional constituents, such as bromide, may be helpful to identify potential sources of salinity in this and other groundwater samples.

Sodium, Chloride, and Bromide in Groundwater

The concentrations of sodium, chloride, and bromide for the 54 groundwater samples collected for this study ranged widely (table 3) and were positively correlated with one another and with SC (appendix 3). In north-central and northeastern Pennsylvania, chloride concentrations greater than about 10 mg/L in shallow groundwater are considered elevated compared to typical values for regional aquifers from previous studies (for example, Taylor and others, 1983). The elevated chloride concentrations may be associated with elevated concentrations of sodium and, in some cases, nitrate and sulfate, which could indicate influence from human or animal waste. Elevated concentrations of chloride also may be associated with relatively higher concentrations of bromide, which may be useful to determine the potential influence from residual brine of geologic origin.

Concentrations of chloride compared to those of sodium, bromide, and chloride/bromide mass ratios are plotted with reference curves that indicate potential relations resulting from mixing of groundwater with different sources of chloride (fig. 11). These curves represent compositions resulting from mixing of different proportions of dilute groundwater with increasing proportions of (1) relatively pure sodium chloride (NaCl) salt 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 oil and gas well brines (such as those from wells that produce gas from the Marcellus Shale).

Although concentrations of sodium and chloride for the groundwater samples from Clinton County are positively correlated, many samples from all three aquifer lithologies have greater amounts of sodium than may be explained by contributions from human or animal sources of salts (NaCl) or brines. The excess sodium (greater than 1:1 [Na]:[Cl] molar ratio) (fig. 11A,B) 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, which release sodium to solution, generally result in increased pH of the groundwater, and also 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.
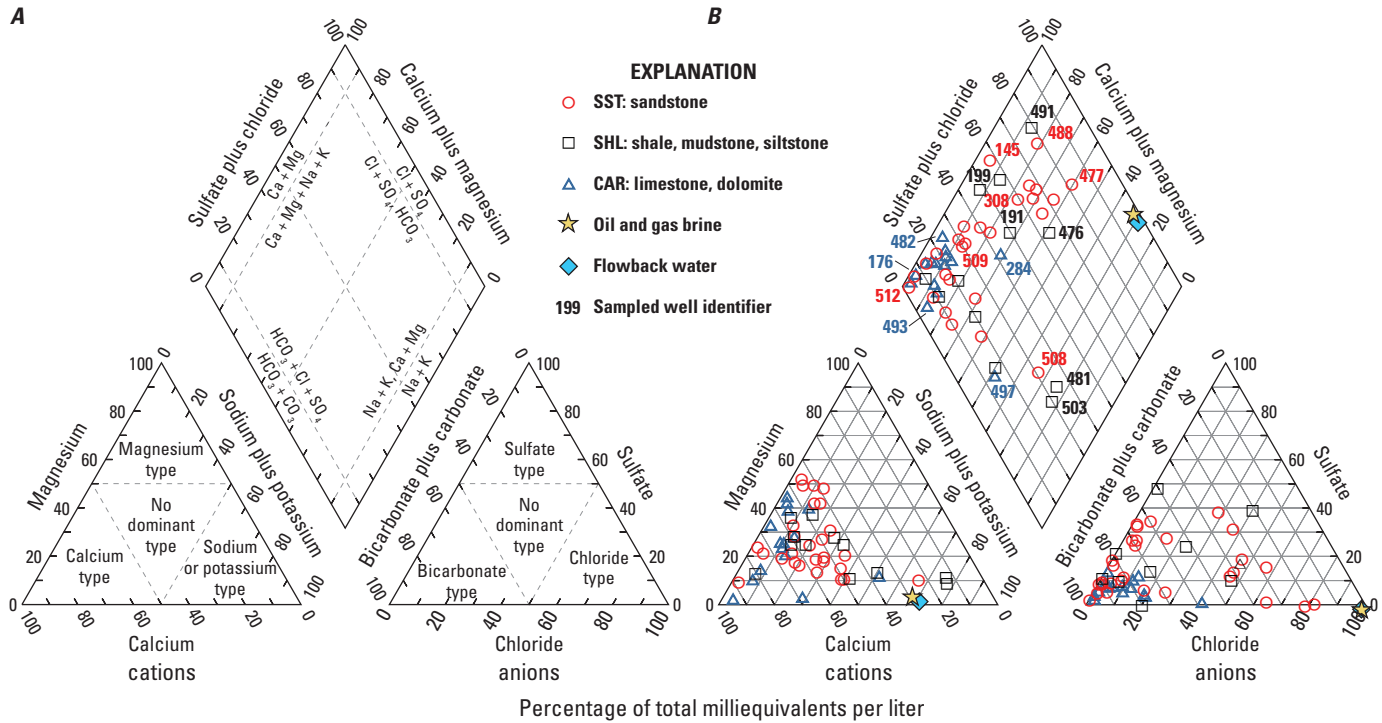
Figure 10.   Piper diagrams showing (*A*) predominant water types or hydrochemical facies (modified from Back, 1966), and (*B–D*) data for 54 groundwater samples from Clinton County, Pa., 2017, by (*B*) lithology, (*C*) pH, and (*D*) specific conductance (SC). The median composition of brine from oil and gas wells in western Pennsylvania (Dresel and Rose, 2010) and flowback water from Marcellus Shale gas wells (Hayes, 2009) are included for comparison. SST, sandstone; SHL, shale, mudstone, siltstone; CAR, limestone, dolomite; <, less than; ≤, less than or equal to.

Percentage of total milliequivalents per liter

EXPLANATION

pH, in standard units

- ● 4.5 < pH ≤5.5
- ○ 5.5 < pH ≤6.5
- ○ 6.5 < pH ≤7.5
- ○ 7.5 < pH ≤8.7
- ☆ Oil and gas well brine
- ◆ Flowback water
- **512** Sampled well identifier

EXPLANATION

Specific conductance, in microsiemens per centimeter

- · 40< SC <200
- ○ 200< SC <330
- ○ 330< SC <600
- □ 600< SC <1,000
- ◇ 1,000< SC <1,400
- ☆ Oil and gas well brine
- ◆ Flowback water
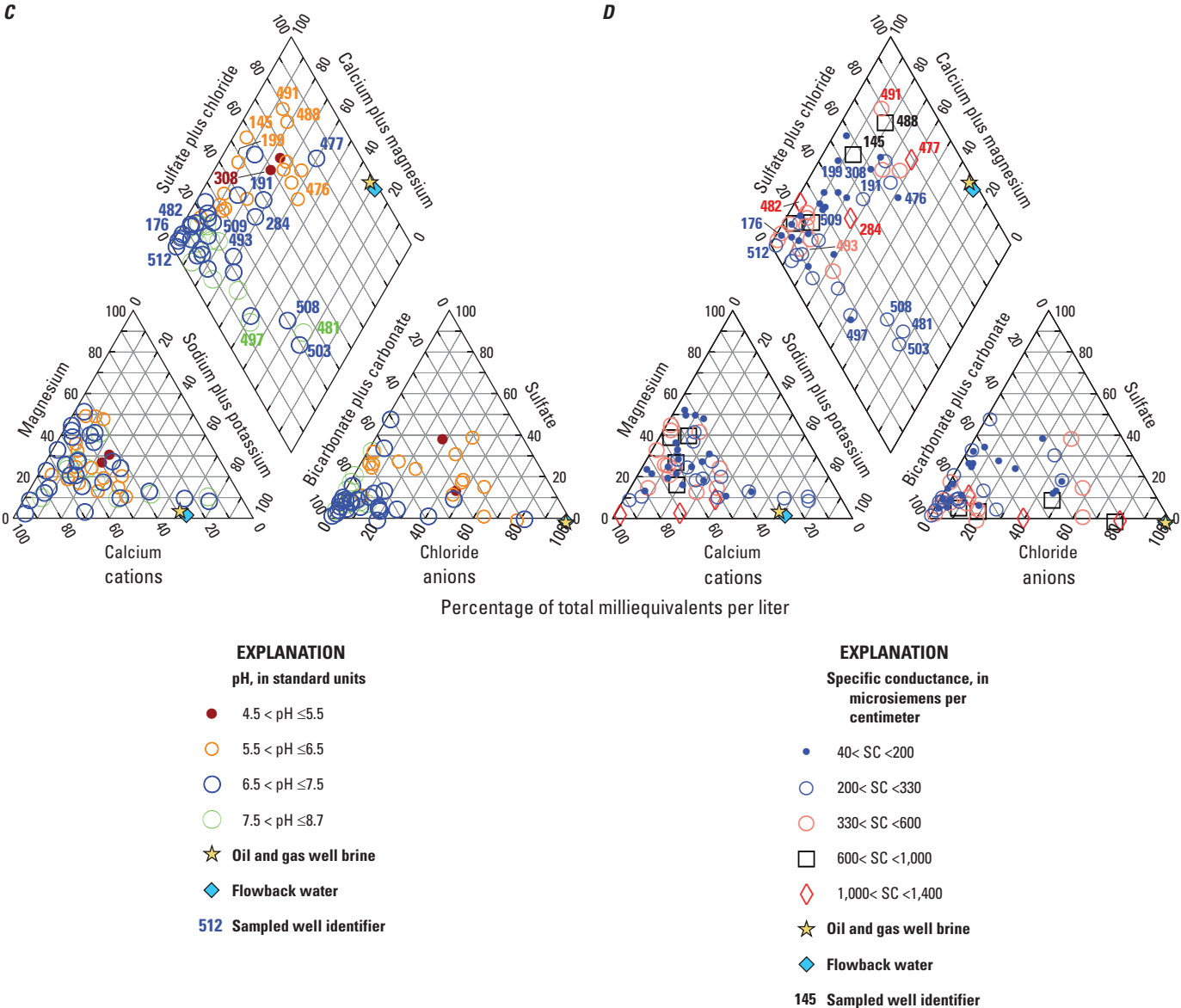- **145** Sampled well identifier

Figure 10. —Continued

Bromide, like chloride, is a soluble anion that exhibits conservative transport properties and can be used as a tracer, if present at detectable concentrations. Some sources of chloride introduced by human activities into the environment, such as salt (NaCl) used for road deicing or present in septic effluent, typically have low amounts of bromide and relatively high chloride/bromide mass ratios, whereas higher bromide amounts are often associated with brines from deeper aquifers. 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. 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.

Most of the bromide concentrations in groundwater from the three aquifer lithologies in Clinton County were at or near the detection limit of 0.01 mg/L (figs. 11*C,D* and 4.1). Several of the samples with this low concentration of bromide, including wells CN 483, CN 497, CN 514, CN 481, and CN 191 had a relatively high concentration of methane, greater than or equal to 0.2 mg/L, and plotted on the mixing curve for road-deicing salt (fig. 11*D*). Most samples with bromide concentrations greater than 0.02 mg/L had a greater proportion of bromide compared to chloride for a road-deicing salt or other salt source. The majority of Clinton County well-water samples, including samples from wells CN 488 (sandstone) and CN 284 (carbonate) with the second and third highest chloride concentrations (220 and 145 mg/L, respectively), have relatively low associated bromide concentrations (0.06 and 0.02 mg/L, respectively) and chloride/bromide ratios that plot on or near the mixing curve for deicing salt, which may indicate a salinity source from road runoff, septic effluent, or animal waste (fig. 11*C–F*). Many samples with concentrations of chloride greater than 10 mg/L and bromide greater than 0.02 mg/L, such as those from wells CN 145 (shale), CN 491 (sandstone), and CN 482 (carbonate), had compositions between the road-deicing salt and brine mixing curves. Several samples, including those from wells CN 477 (sandstone), CN 484 (shale), and CN 508 (sandstone), had compositions plotting on the brine mixing curve (fig. 11*C–F*), which suggests a possible small contribution of chloride from a brine-like source (0.3 percent or less). Salt Spring, a naturally occurring saline spring in Susquehanna County, also plots along the brine mixing curve.

The chloride/bromide relations for the Clinton County well-water samples collected for this study generally are similar to those reported for recent USGS studies in counties within the Delaware (moratorium on natural gas drilling) and Susquehanna (natural gas drilling permitted) River Basins (Sloto, 2013; Senior, 2014; Senior and Cravotta, 2017; Senior and others, 2017; Gross and Cravotta, 2017; Clune and Cravotta, 2019). The regional, localized occurrence of groundwater throughout

northeastern and north-central 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. However, in rare cases, such as well CN 477, the presence of methane, ethane, and brine constituents could indicate connectivity with a deep fracture or localized influence from gas drilling. Additional sampling and analysis, such as isotopic analysis of the dissolved gas, fracture analysis and more detailed evaluation of surrounding land uses may be warranted to understand the origin of the sampled composition at this well and others with elevated methane and brine constituents.

Isotopic Composition, Origin, and Spatial Distribution of Methane

Four samples (wells CN 191, CN 493, CN 503, CN 514) with detectable concentrations of methane (0.28–11 mg/L) were analyzed for the stable isotopic composition of methane and the associated concentrations of higher-chain hydrocarbon gases (fig. 12). Although samples from wells CN 477 and CN 484 also had relatively high concentrations of methane (4.6 and 29 mg/L, respectively) and were intended for isotopic analysis, those samples were discarded at the laboratory before isotopic analysis could be completed. Ethane (C_2H_6) was detected at concentrations ranging from 0.008 to 0.02 mg/L in three of the four samples analyzed for isotopes and was also detected in five other methane-bearing samples at concentrations ranging from 0.0004 to 0.6 mg/L (wells CN 511, CN 497, CN 481, CN 477, and CN 484, in order of increasing concentration). Microbial gas contains methane, but generally does not contain ethane and other higher chain hydrocarbons (Baldassare and others, 2014). Samples from wells CN 481 and CN 484 also contained detectible concentrations of propane (C_3H_8); however, none of the samples had detectible concentrations of butane (C_4H_{10}).

Methane in the four groundwater samples analyzed for isotopes had $\delta^{13}C_{CH4}$ values ranging from –63.7 to –32.4 per mil and δD_{CH4} values ranging from –190 to –104 per mil (table 3; fig. 12). The isotopic values for the sample from well CN 493 are consistent with the isotopic compositions reported by Baldassare and others (2014) for mud-gas logging samples from the Hamilton Group and the Marcellus Formation, and for methane gas sampled from the Marcellus Formation in nearby counties (fig. 12). However, the methane in the other three groundwater samples has lower (lighter) $\delta^{13}C_{CH4}$ values than those reported by Reese and others (2014) for Marcellus Shale methane gas samples. One sample (well CN 503), with a methane concentration of 0.28 mg/L, had an isotopic composition, $\delta^{13}C_{CH4}$ of –63.7 and δD_{CH4} of –180 per mil, as well as a molar ratio of methane to ethane and higher-chain hydrocarbons (C1/C2+) that is consistent with methane of microbial origin. The $\delta^{13}C_{CH4}$ value and C1/C2+ ratio for well CN 493 was comparable to that identified with thermogenic gas (fig. 12*B*), whereas the C1/C2+ ratios for the other two samples, wells CN 191 and CN 514, were intermediate between

values identified by Reese and others (2014) for microbial or thermogenic methane (fig. 12B). These characteristics could indicate a mixed thermogenic and microbial source (carbon-dioxide reduction process) of methane and could imply that methane of microbial origin has been oxidized (becoming isotopically heavier).
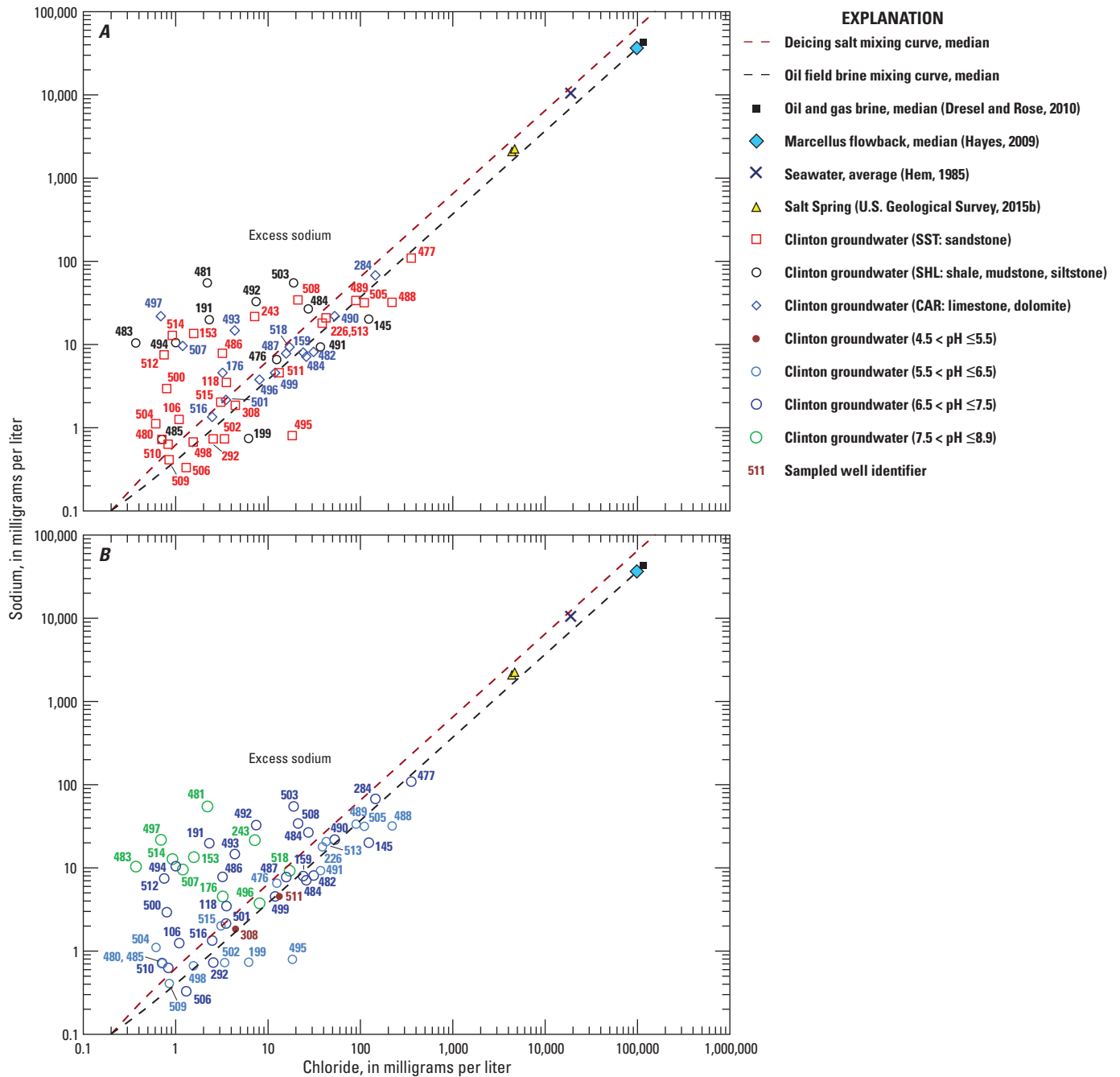
Figure 11. Chloride concentrations compared to (A,B) sodium concentrations, (C,D) bromide concentrations, and (E,F) chloride/bromide mass ratios for groundwater from Clinton County, Pa., 2017. Median values for Salt Spring (Llewellyn, 2014), flowback waters from Marcellus Shale gas wells (Hayes, 2009), and oil and gas well brines from western Pennsylvania (Dresel and Rose, 2010) are included for comparison. Mixing curves were computed for initial freshwater with chloride levels of 0.5–0.6 milligrams per liter (mg/L) and bromide levels of 0.025–0.035 mg/L mixed with road deicing salt that has a composition of $NaCl_{0.99996}Br_{0.00004}$ (dashed red line, after Llewellyn [2014]) or with a median composition of oil and gas well brine (dashed black line, after Dresel and Rose [2010]). Selected (numbered) samples have methane concentrations greater than 0.2 mg/L, alkaline pH, or other chemical characteristics that illustrate the variable compositions of the samples from Clinton County. <, less than; ≤, less than or equal to; ≥, greater than or equal to.
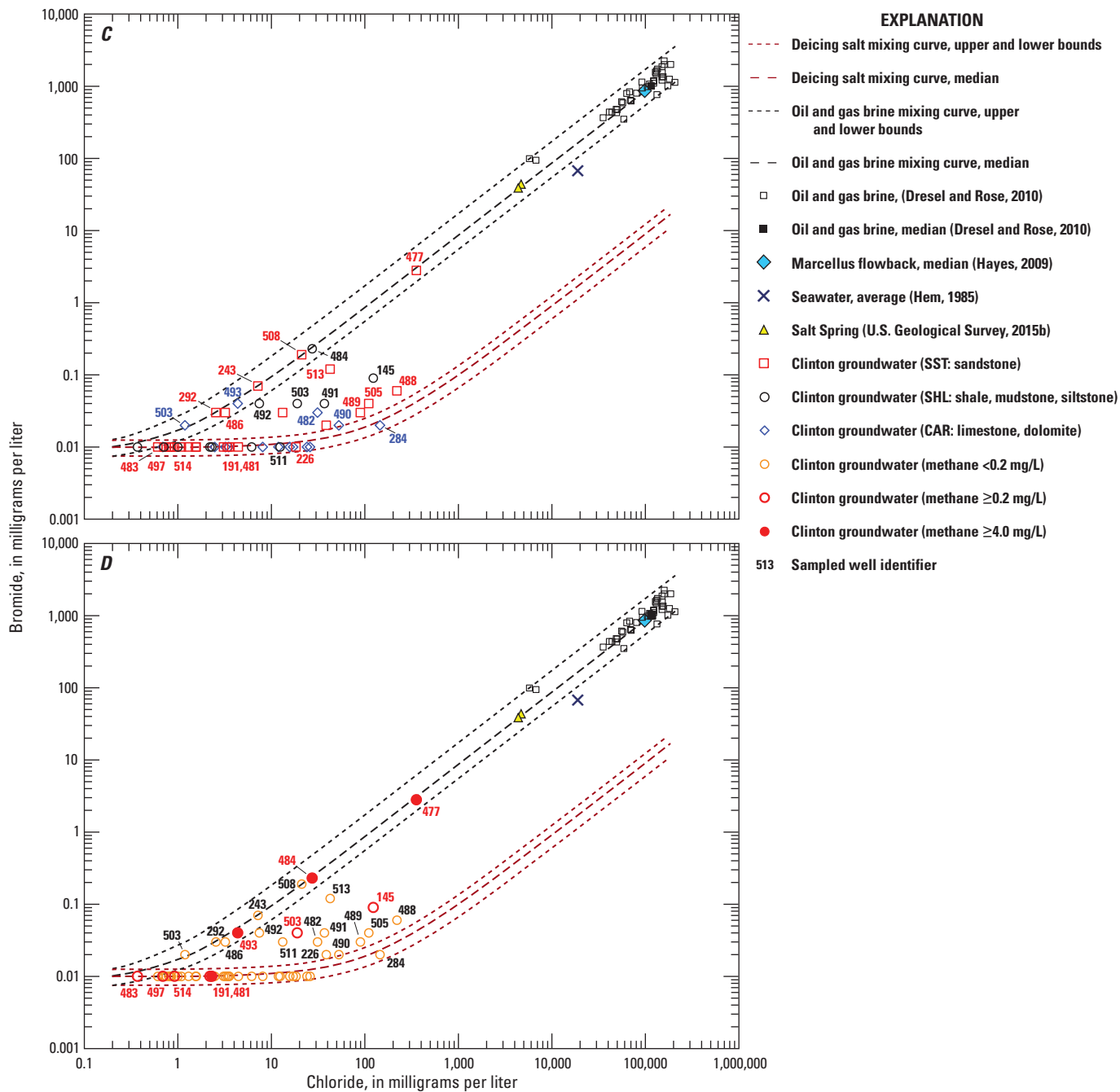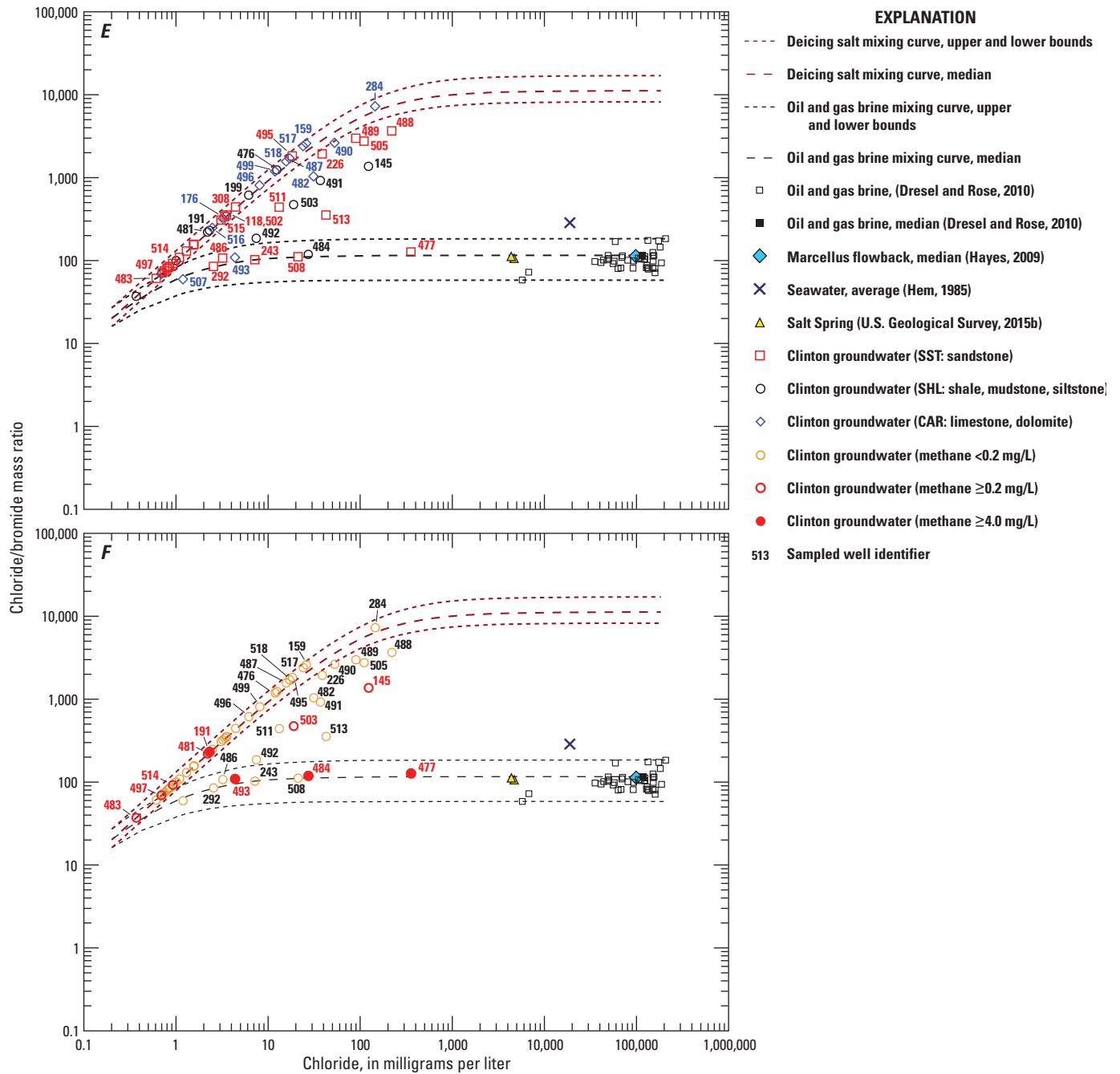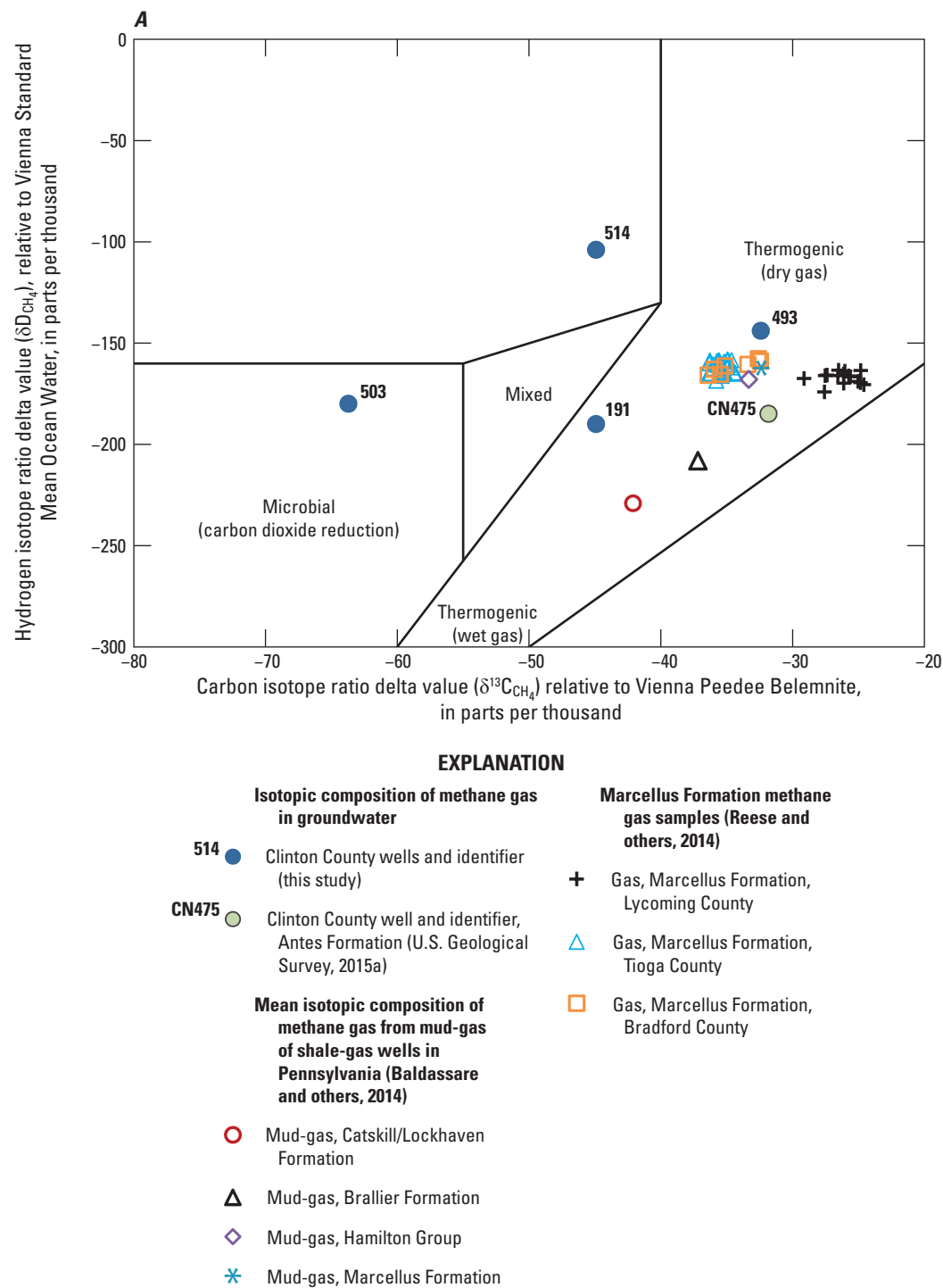
Figure 11.   —Continued

Figure 11. —Continued

Figure 12.   *A*, Isotopic composition of methane in groundwater samples collected from five wells in Clinton 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. Boundaries for microbial and thermogenic gas types and compositional shift related to gas maturation/oxidation, shown by arrow, from Reese and others (2014, fig. 30, p. 38). Marcellus Shale methane gas data for Clinton County from Reese and others (2014, table 7) and mud-gas logging data by geologic formation from Baldassare and others (2014, table 1).
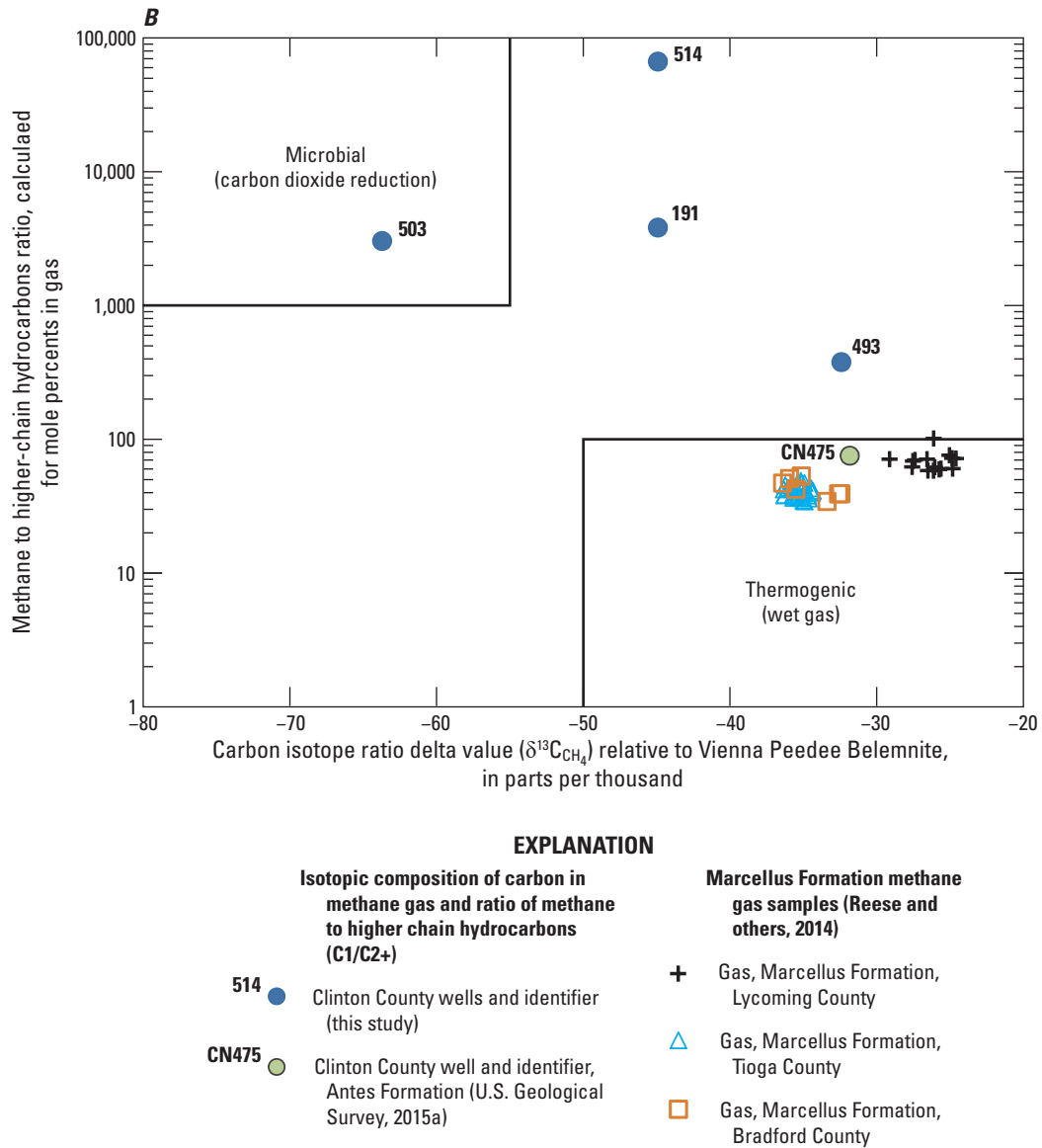
Figure 12.   —Continued

Summary and Conclusions

In Clinton County, one in five residents use groundwater from private domestic-supply wells as their primary drinking source. The groundwater used for domestic water supply in Clinton County and sampled for this study is obtained primarily from shallow bedrock to depths as great as 500 ft. Historical land use has been predominantly forested, agricultural, and residential, with conventional gas drilling at numerous locations, and, more recently, unconventional oil/gas development associated with the Marcellus Shale has also been distributed throughout the various land uses in the county.

To assess the quality of groundwater used for drinking-water supplies in Clinton County, samples were collected from 54 domestic wells from May through September 2017 and analyzed for a wide range of constituents that could be evaluated in relation to drinking-water health standards, geology, land use, and other environmental factors. Groundwater 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 the isotopic composition of methane.

Results of the 2017 study showed that groundwater quality met most drinking-water standards that apply to public water supplies, with exceptions of prevalent radon-222 and bacterial occurrences. Radon-222 activities exceeded the proposed drinking-water standard of 300 picocuries per liter (pCi/L) in 59.3 percent of the samples. Additionally, various samples exceeded primary maximum contaminant levels for total coliform bacteria (57.4 percent), *Escherichia coli* (25.9 percent), nitrate (1.9 percent), and arsenic (1.9 percent); and secondary maximum contaminant levels for pH (31.5 percent), manganese (29.6 percent), iron (13 percent), total dissolved solids (7.4 percent), aluminum (1.9 percent), and chloride (1.9 percent). Sodium concentrations exceeded the EPA drinking-water advisory recommendation in 16.7 percent of the samples. Samples from the carbonate aquifer frequently had elevated levels of coliform bacteria and nitrate concentrations. One of these samples, which had a nitrate concentration of 49.3 mg/L as N, exceeded the drinking-water standard. None of the volatile organic compounds analyzed exceeded water-quality criteria.

The pH of the groundwater ranged from 4.55 to 8.70. Near-neutral samples (pH 6.5 to 7.5) had greater hardness and alkalinity concentrations than other samples with pH outside of this range. Generally, samples that had high pH had elevated TDS, chloride, sodium, fluoride, boron, and uranium concentrations, whereas the lower pH samples had greater potential for elevated concentrations of dissolved metals, including beryllium, copper, lead, nickel, and zinc.

Methane and associated constituents that occur in high concentrations in naturally occurring brine present at depth below the aquifers sampled and in produced waters from gas and oil wells were identified in some samples. Groundwater from most of the wells sampled had detectable methane concentrations that ranged from 0.0002 to 29 mg/L. Samples from two wells had concentrations of methane greater than the Pennsylvania action level of 7 mg/L. Low levels of ethane (as much as 0.6 mg/L) were present in 10 samples with the highest methane concentrations; microbial gas contains methane, but generally does not contain ethane and other higher-chain hydrocarbons. The isotopic composition of methane in one of four groundwater samples that were analyzed for isotopes was consistent with the compositions reported for mud-gas logging samples from nearby geologic units and a thermogenic source of the methane, whereas the compositions for the other samples suggest the methane may be of microbial origin or a mixture of thermogenic and microbial gas. Two of 10 groundwater samples with some of the highest methane concentrations had concentrations of chloride and bromide with corresponding chloride/bromide ratios that indicated mixing of dilute groundwater with a small amount of brine (0.3 percent or less) similar in composition to those reported for gas and oil well brines in Pennsylvania. In two eastern Pennsylvania counties where gas drilling is absent, groundwater with comparable chloride/bromide ratios and chloride concentrations have been reported. The majority of Clinton County well-water samples, including the samples with the second and third highest chloride concentrations, have chloride/bromide ratios that indicate a mixture of dilute groundwater with small amounts of predominantly anthropogenic sources of chloride, such as road-deicing salt or septic effluent.

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Appendix 1   Compilation of data not available in the National Water Information System.

Table 1.1.   Compilation of data not available in the National Water Information System, including station name, station identification number, lithologic class, and topographic position index for domestic wells sampled by the U.S. Geological Survey in Clinton County, Pennsylvania, May–September 2017 (Clune and Cravotta, 2020).

Station name	Station identifica-tion number	Lithologic class	Topographic position index	Station name	Station identifica-tion number	Lithologic class	Topographic position index
CN106	411959077390701	Sandstone	Valley	CN492	410519077360401	Mudstone	Lower slope
CN118	412044077422701	Sandstone	Gentle slope	CN493	410715077133701	Limestone	Gentle slope
CN145	410734077301001	Siltstone	Valley	CN494	410710077333301	Mudstone	Upper slope
CN153	410659077352001	Sandstone	Valley	CN495	412214077324801	Sandstone	Upper slope
CN159	410337077261301	Limestone	Lower slope	CN496	410033077193101	Limestone	Gentle slope
CN176	410912077215101	Limestone	Gentle slope	CN497	405932077264501	Limestone	Steep slope
CN191	411215077200701	Mudstone	Valley	CN498	411112077255501	Sandstone	Upper slope
CN199	411458077262401	Shale	Ridges	CN499	410130077182301	Dolomite	Upper slope
CN226	412523077511601	Sandstone	Gentle slope	CN500	412751077490801	Sandstone	Upper slope
CN243	411659077531201	Sandstone	Lower slope	CN501	410141077314301	Limestone	Upper slope
CN284	410227077153501	Limestone	Gentle slope	CN502	410315077183401	Sandstone	Gentle slope
CN292	410327077184701	Sandstone	Gentle slope	CN503	410654077320201	Siltstone	Valley
CN308	411531077541001	Sandstone	Valley	CN504	412434077501901	Sandstone	Lower slope
CN476	411659077264001	Shale	Valley	CN505	411044077260901	Sandstone	Valley
CN477	412103077420401	Sandstone	Valley	CN506	411800077524201	Sandstone	Upper slope
CN480	411026077340401	Sandstone	Upper slope	CN507	410924077194601	Limestone	Gentle slope
CN481	410509077354101	Siltstone	Steep slope	CN508	412615077541701	Sandstone	Valley
CN482	410234077144601	Limestone	Lower slope	CN509	411112077255801	Sandstone	Upper slope
CN483	411216077202401	Mudstone	Valley	CN510	412226077432601	Sandstone	Ridges
CN484	412340077554801	Mudstone	Lower slope	CN511	411835077480701	Sandstone	Lower slope
CN485	411325077243401	Shale	Valley	CN512	410748077325601	Sandstone	Lower slope
CN486	411446077362501	Sandstone	Valley	CN513	411958077425801	Sandstone	Lower slope
CN487	405902077273301	Limestone	Valley	CN514	412438077550601	Sandstone	Steep slope
CN488	411054077255601	Sandstone	Gentle slope	CN515	412615077495301	Sandstone	Upper slope
CN489	411540077550001	Sandstone	Valley	CN516	410032077314401	Dolomite	Gentle slope
CN490	410153077334801	Dolomite	Steep slope	CN517	410313077314201	Dolomite	Lower slope
CN491	410831077242301	Calcareous shale	Lower slope	CN518	410012077234801	Limestone	Upper slope

Appendix 2   Selected volatile organic compounds sampled in groundwater from 54 domestic wells in Clinton County, Pennsylvania.

Table 2.1. Minimum, median, and maximum values of selected volatile organic compounds in groundwater samples collected from 54 domestic wells in Clinton County, Pennsylvania, May–September 2017. Available U.S. Environmental Protection Agency maximum contaminant levels, action levels, and secondary maximum contaminant levels for analyzed constituents (U.S. Environmental Protection Agency, 2012).

[n, number of results; EPA, U.S. Environmental Protection Agency; MCL, Maximum Contaminant Level; SMCL, Secondary Maximum Contaminant Level; µg/L, micrograms per liter; <, less than; —, no MCL, Action Level, or SMCL established. In Graph column, green bar indicates no exceedance of standards]

Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
1,1,1,2-Tetrachloroethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,1,1-Trichloroethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	 	200	—
1,1,2,2-Tetrachloroethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,1,2-Trichloroethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	 	5	—
1,1-Dichloroethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,1-Dichloroethene (1,1-Dichloroethylene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	 	7	—
1,1-Dichloropropene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,2,3-Trichlorobenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,2,3-Trichloropropane (1,2,3-TCP) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,2,4-Trichlorobenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	 	70	—
1,2,4-Trimethylbenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,2-Dichlorobenzene (o-Dichlorobenzene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	 	600	—
1,2-Dichloroethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	 	5	—
1,2-Dichloropropane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	 	5	—
1,3,5-Trimethylbenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,3-Dichlorobenzene (m-Dichlorobenzene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,3-Dichloropropane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
1,4-Dichlorobenzene (p-Dichlorobenzene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	 	75	—
2,2-Dichloropropane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
2-Butanone (Methyl ethyl ketone, MEK) (µg/L)	54	<1.0	<1.0	<1.0	0	0.00	—	—	—	—	—
2-Chloroethyl vinyl ether (µg/L)	54	<1.0	<1.0	<1.0	0	0.00	—	—	—	—	—

Table 2.1. Minimum, median, and maximum values of selected volatile organic compounds in groundwater samples collected from 54 domestic wells in Clinton County, Pennsylvania, May–September 2017. Available U.S. Environmental Protection Agency maximum contaminant levels, action levels, and secondary maximum contaminant levels for analyzed constituents (U.S. Environmental Protection Agency, 2012).—Continued

[n, number of results; EPA, U.S. Environmental Protection Agency; MCL, Maximum Contaminant Level; SMCL, Secondary Maximum Contaminant Level; µg/L, micrograms per liter; <, less than; —, no MCL, Action Level, or SMCL established. In Graph column, green bar indicates no exceedance of standards]

Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
2-Chlorotoluene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
4-Chlorotoluene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Acetone (µg/L)	54	<1.0	<1.0	45.9	1	1.39	—	—	—	—	—
Benzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0		5	—
Bromobenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Bromochloromethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Bromomethane (Methyl bromide) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Carbon disulfide (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Chlorobenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0		100	—
CHBrCl2, wu, µg/L	54	<0.5	<0.5	<0.5	0	0.00	0	0		—	80
Chloroethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Chloromethane, wu, µg/L	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
cis-1,2-dichloroethene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0		70	—
cis-1,3-dichloropropene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Dibromochloromethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0		80	—
Dibromomethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Ethylbenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0		700	—
Hexachlorobutadiene (1,3-Hexachlorobutadiene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Iodomethane (Methyl iodide) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Isopropylbenzene (Cumene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
m-Xylene plus p-xylene (µg/L)	54	<1.0	<1.0	<1.0	0	0.00	0	0		10,000	—
Methyl chloride (Chloromethane) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—

Table 2.1. Minimum, median, and maximum values of selected volatile organic compounds in groundwater samples collected from 54 domestic wells in Clinton County, Pennsylvania, May–September 2017. Available U.S. Environmental Protection Agency maximum contaminant levels, action levels, and secondary maximum contaminant levels for analyzed constituents (U.S. Environmental Protection Agency, 2012).—Continued

[n, number of results; EPA, U.S. Environmental Protection Agency; MCL, Maximum Contaminant Level; SMCL, Secondary Maximum Contaminant Level; µg/L, micrograms per liter; <, less than; —, no MCL, Action Level, or SMCL established. In Graph column, green bar indicates no exceedance of standards]

Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
Methyl ethyl ketone (µg/L)	54	<0.5	<0.5	48.3	1	1.39	--	--	--	--	--
Methyl *tert*-butyl ether (MTBE) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Naphthalene (µg/L)	54	0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
n-Butylbenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
n-Butyl methyl ketone (µg/L)	54	<1.0	<1.0	<1.0	0	0.00	—	—	—	—	—
n-Propylbenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
o-Xylene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	� bar	10,000	—
p-Isopropyltoluene (4-Isopropyltoluene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
sec-Butylbenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Styrene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	green bar	100	—
tert-Butylbenzene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Tetrachloroethene (Perchloroethylene, PCE) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	green bar	5	—
Tetrachloromethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Toluene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	green bar	1,000	—
trans-1,2-Dichloroethene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	green bar	100	—
trans-1,3-Dichloropropene (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—
Tribromomethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	green bar	60	—
Trichloroethene (TCE, Trichloroethylene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	green bar	5	—
Trichloromethane (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0	green bar	80	—
Trihalomethanes (THMs), summation (µg/L)	54	<2.0	<2.0	<3.43	0	0.00	—	—	—	—	—
Vinyl acetate (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	—	—	—	—	—

Table 2.1. Minimum, median, and maximum values of selected volatile organic compounds in groundwater samples collected from 54 domestic wells in Clinton County, Pennsylvania, May–September 2017. Available U.S. Environmental Protection Agency maximum contaminant levels, action levels, and secondary maximum contaminant levels for analyzed constituents (U.S. Environmental Protection Agency, 2012).—Continued

[n, number of results; EPA, U.S. Environmental Protection Agency; MCL, Maximum Contaminant Level; SMCL, Secondary Maximum Contaminant Level; µg/L, micrograms per liter; <, less than; —, no MCL, Action Level, or SMCL established. In Graph column, green bar indicates no exceedance of standards]

Constituent (units)	n	Minimum	Median	Maximum	Results above the reporting level		Results exceeding standard			EPA MCL	EPA SMCL
					Number	Percent	Number	Percent	Graph		
Vinyl chloride (Chloroethene) (µg/L)	54	<0.5	<0.5	<0.5	0	0.00	0	0		2	—
Xylene (µg/L)	54	<1.5	<1.5	<1.5	0	0.00	—	—	—	—	—

Reference

U.S. Environmental Protection Agency, 2012, 2012 edition of the drinking water standards and health advisories: U.S. Environmental Protection Agency, EPA 822-S-12-001, accessed October 2019 at https://rais.ornl.gov/documents/2012_drinking_water.pdf

Appendix 4   Boxplots of distributions for selected characteristics and constituents in groundwater samples collected from 54 domestic wells in Clinton County, Pennsylvania.

Distributions of continuous variables were compared among different sample classifications using notched boxplots (McGill and others, 1978; 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 lower hinge and upper hinge for that group; otherwise, the median is displayed at the reporting limit. The lower hinge is the median of all observations less than or equal to the sample median, and the upper hinge is the median of all observations equal to or greater than the overall sample median (Helsel and Hirsh, 2002). The boxplots show a notched interval around the median that can be used by a reader to judge the significance of potential differences (except for constituents with censored data at the 25th percentile or for notched intervals less than zero). If the notched intervals around the medians for sample subsets do not overlap, the medians are statistically different at the 95-percent confidence interval.
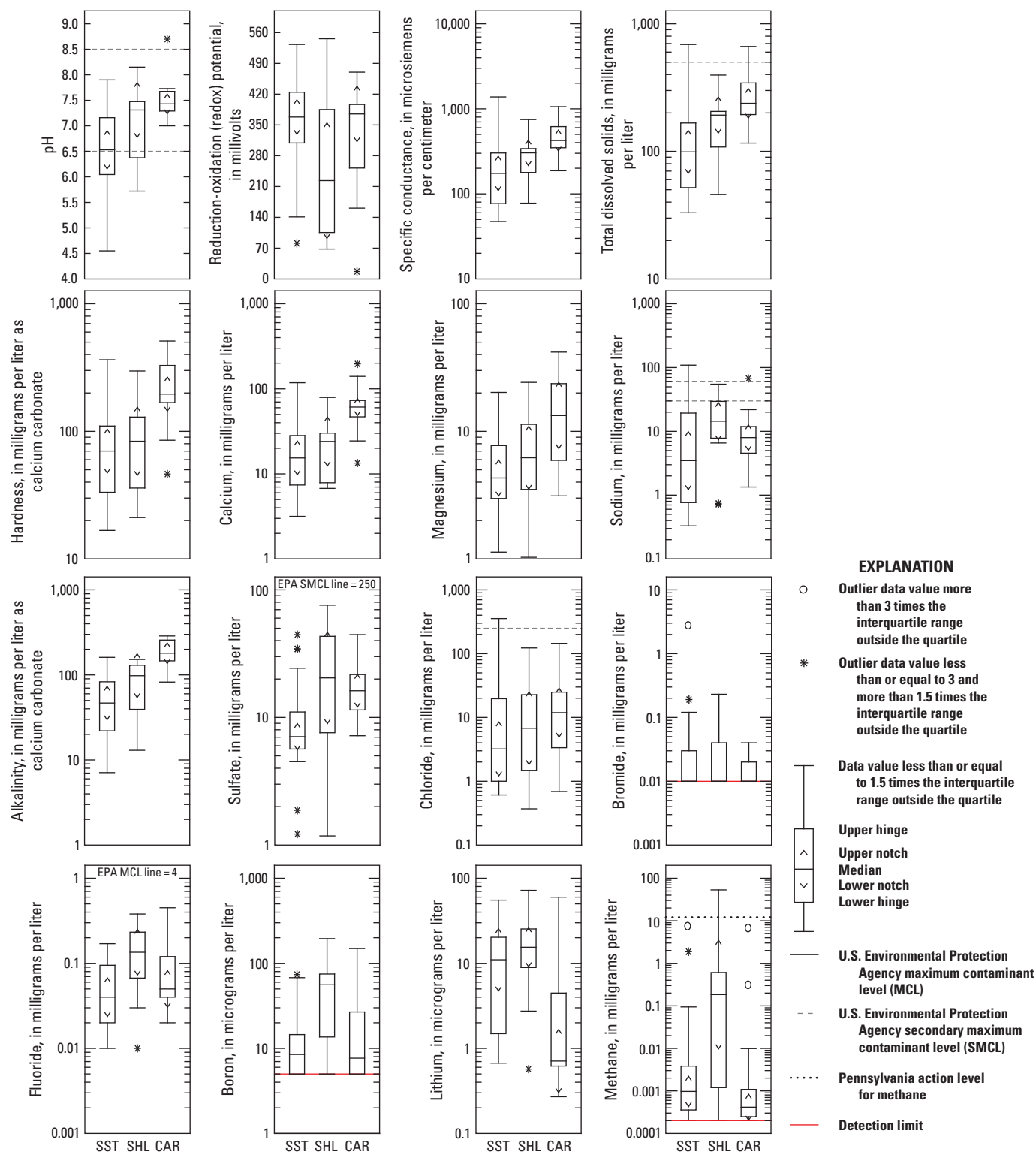
Figure 4.1. Boxplots showing the composition of 54 groundwater samples from Clinton County, Pa., 2017, classified on the basis of primary bedrock lithology. SST, sandstone (n=27); SHL, shale, mudstone, siltstone (n=12); CAR, limestone, dolomite (n=15); n, number of samples. The computations of the median and interquartile range include censored values set to the indicated detection limit noted by the red line symbol.
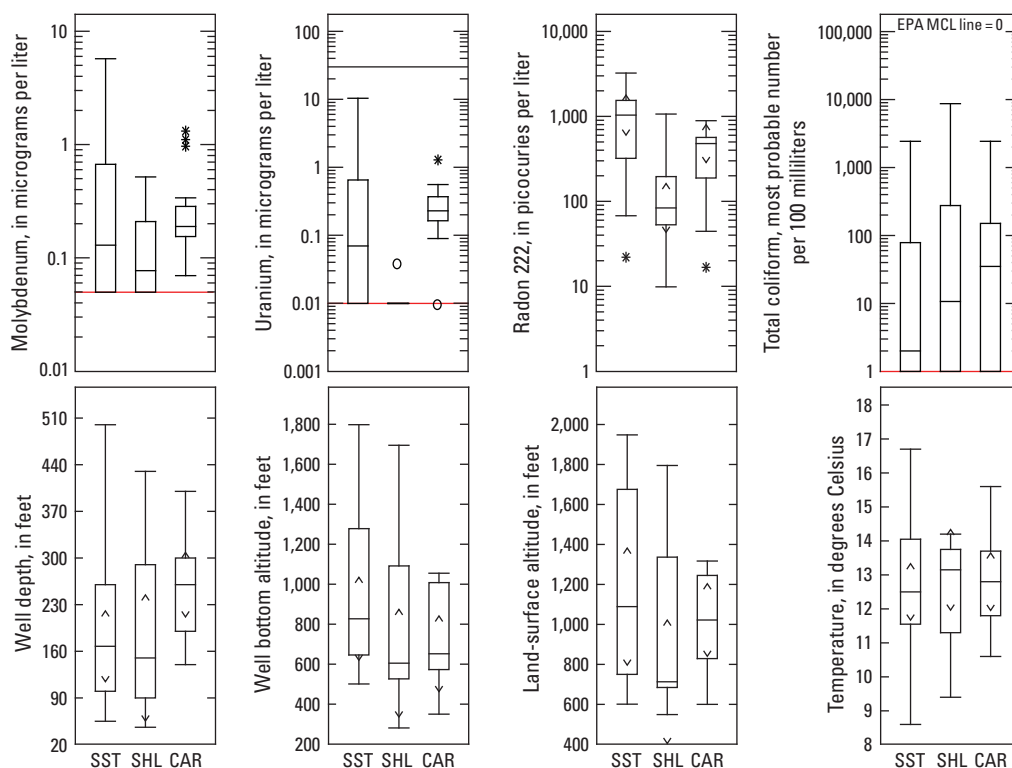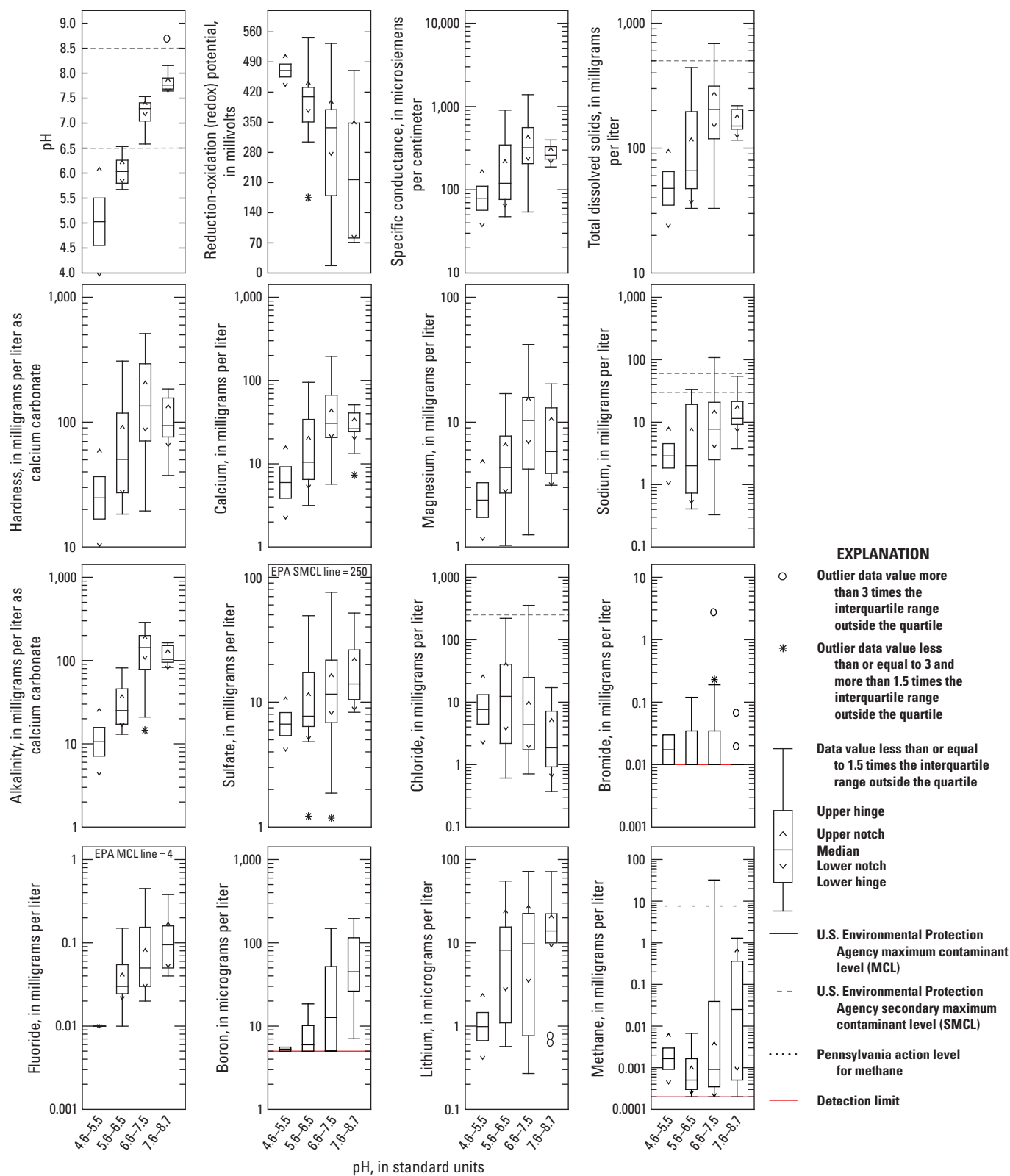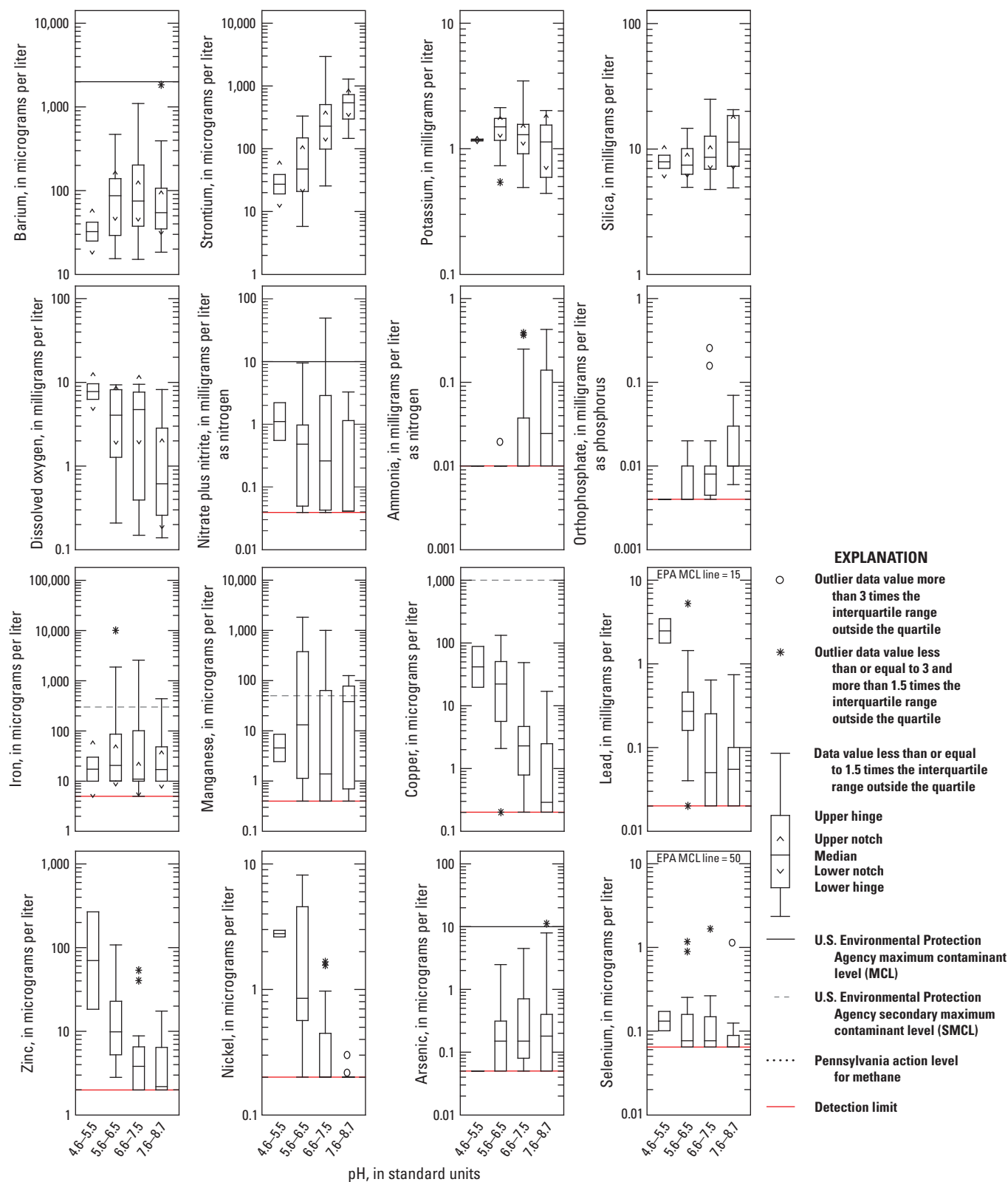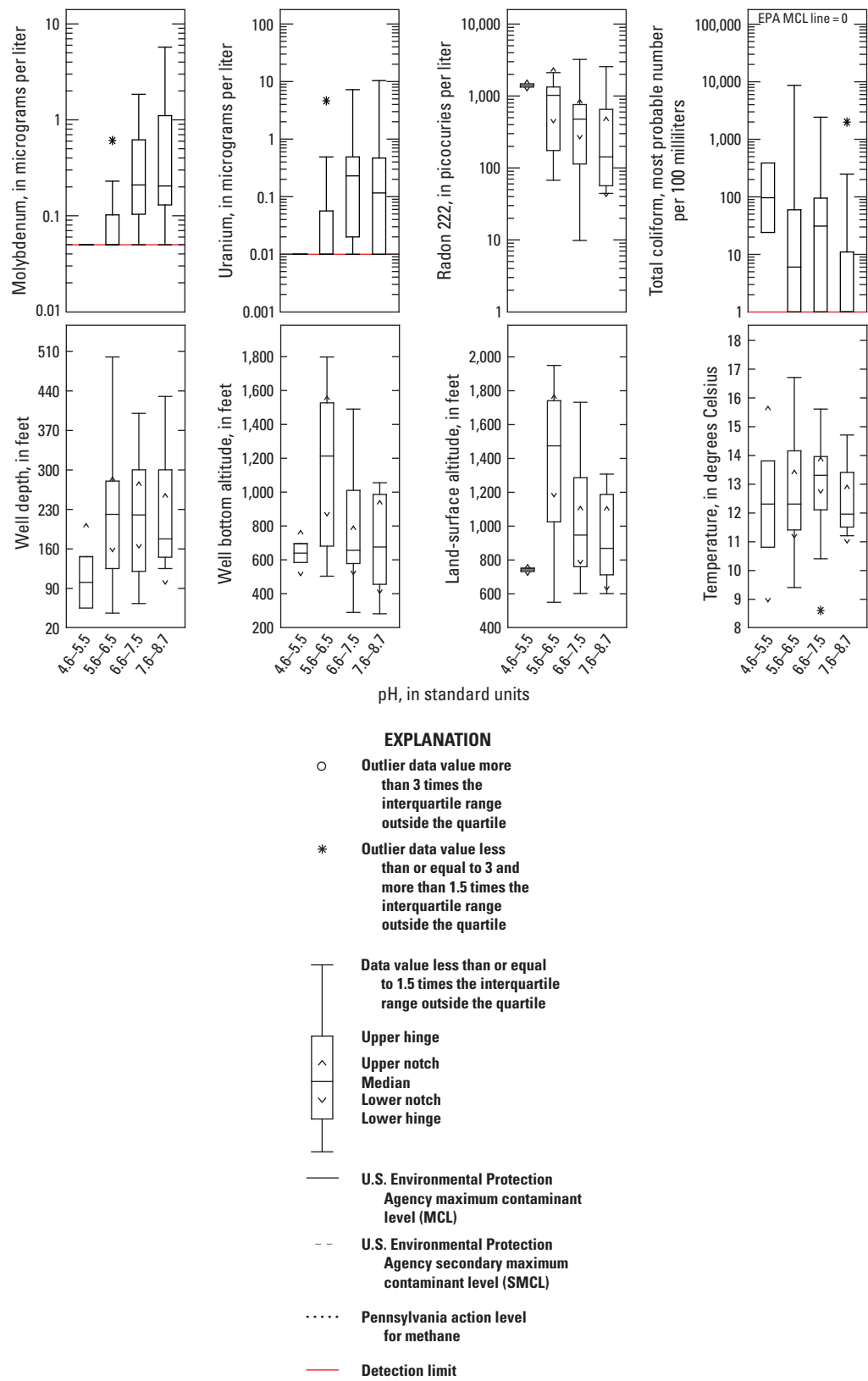
Figure 4.1.   —Continued

Figure 4.1. —Continued

Figure 4.2.   Boxplots showing the composition of 54 groundwater samples from Clinton County, Pa., 2017, classified by pH class interval. The pH range is indicated on the x-axis by the upper pH for interval (4.5<pH≤5.5, n=2; 5.5<pH≤6.5, n=15; 6.5<pH≤7.5, n=27; 7.5<pH≤8.7, n=10). <, less than; ≤, less than or equal; n, number of samples. The computations of the median and interquartile range include censored values set to the indicated detection limit noted by the red line symbol.
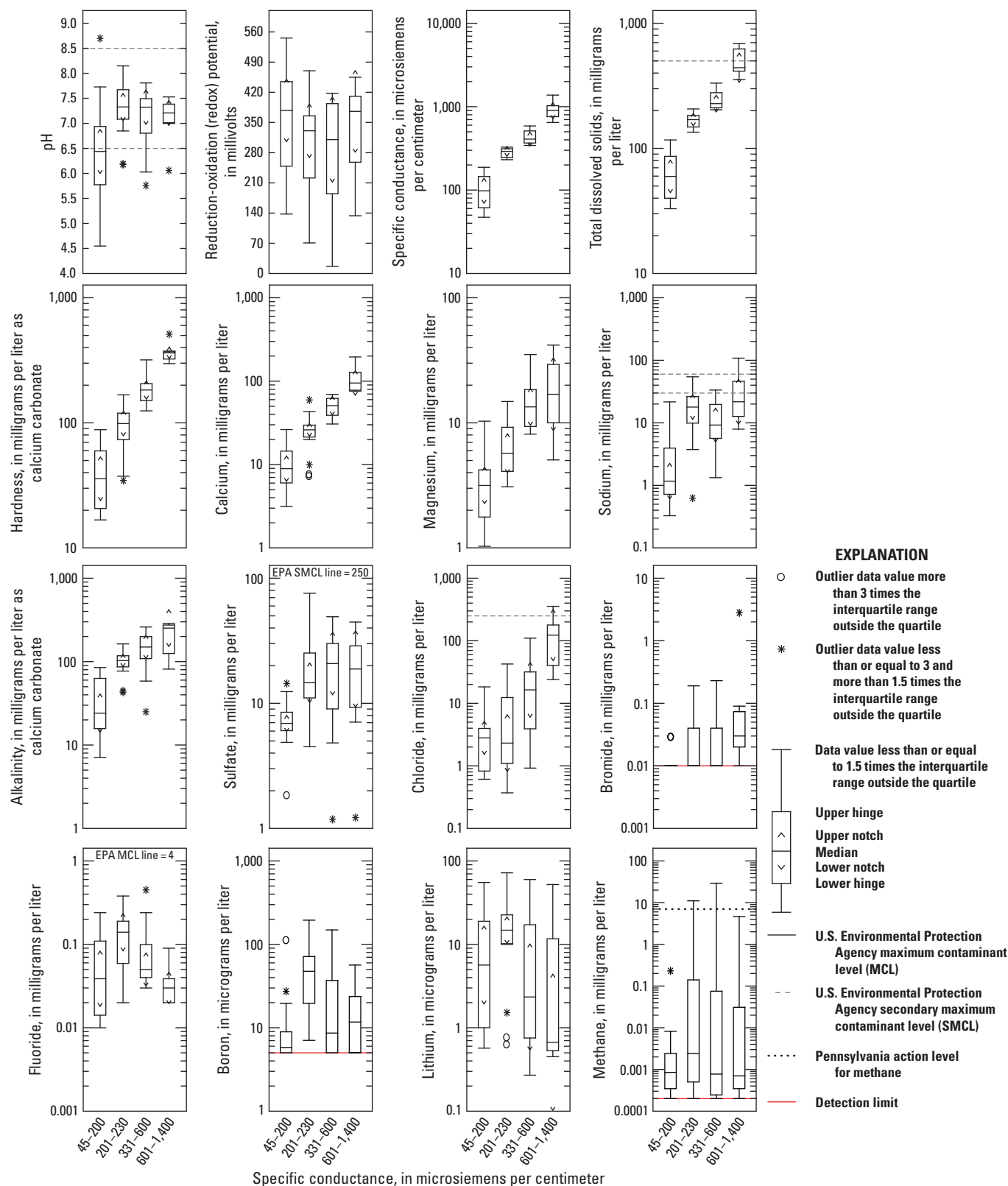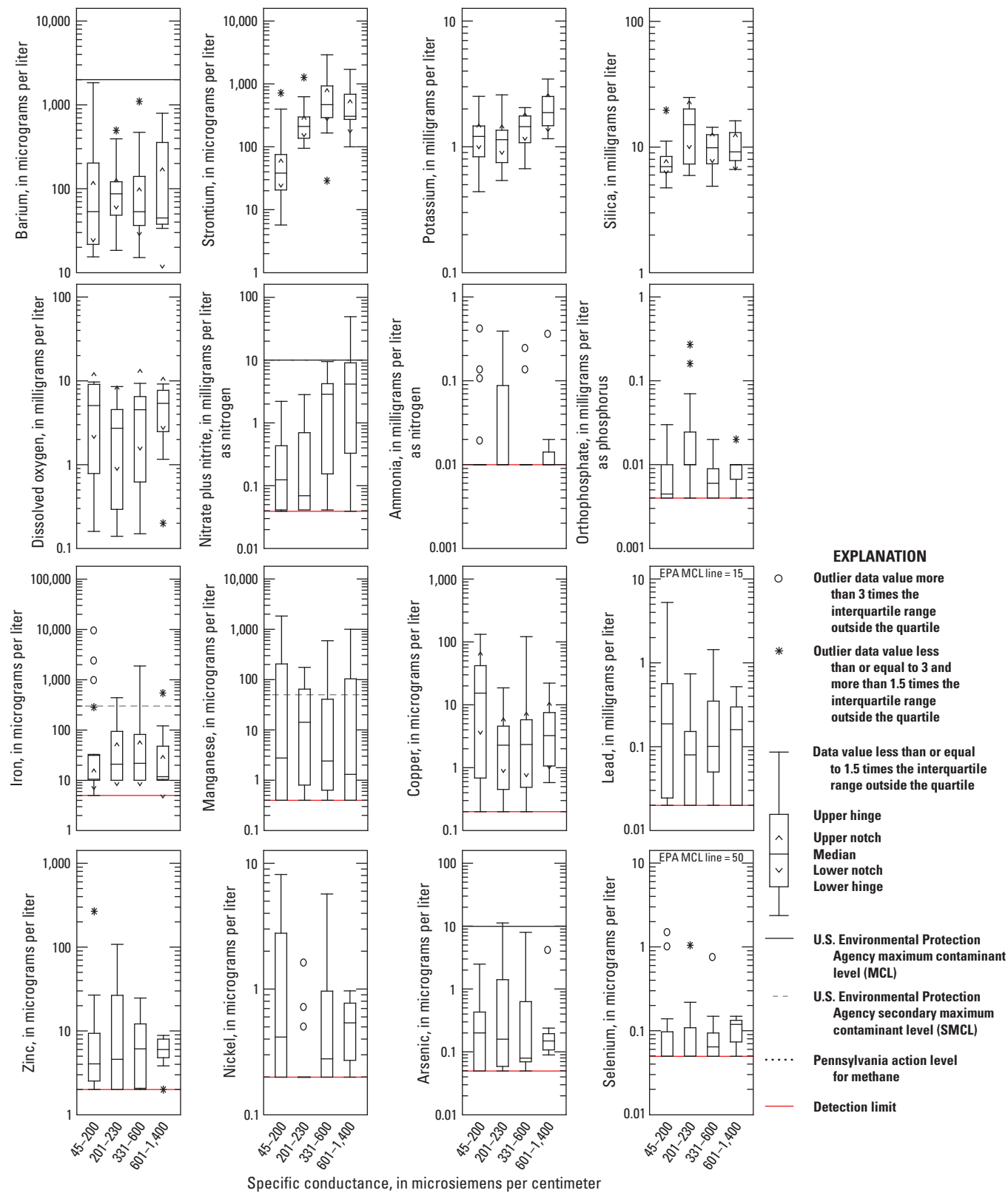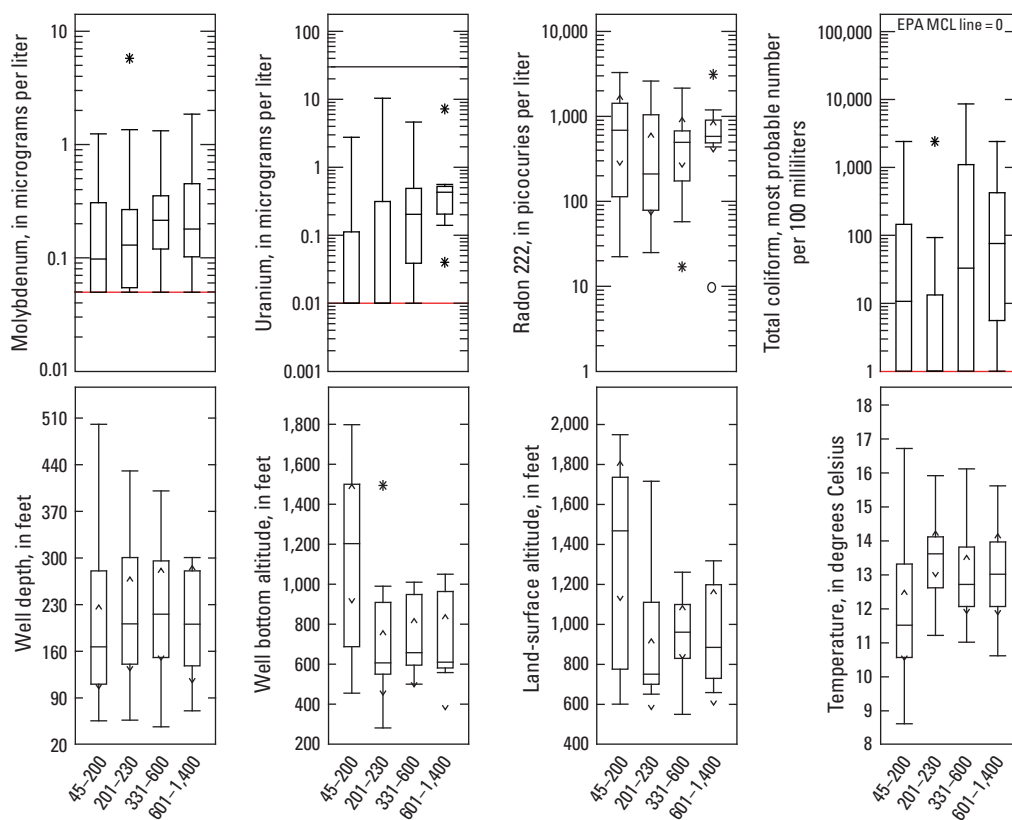
Figure 4.2.   —Continued

EXPLANATION

○	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
——	U.S. Environmental Protection Agency maximum contaminant level (MCL)
– –	U.S. Environmental Protection Agency secondary maximum contaminant level (SMCL)
·····	Pennsylvania action level for methane
——	Detection limit

Figure 4.2.   —Continued

Figure 4.3. Boxplots showing the composition of 54 groundwater samples from Clinton County, Pa., 2017, classified by specific conductance (SC) class interval. The SC range is indicated on the x-axis by the upper SC value for the interval (45<SC≤200 uS/cm, n=20; 200<SC≤330 uS/cm, n=15; 330<SC≤600 uS/cm, n=12; 600<SC≤1,400 uS/cm, n=7). <, less than; ≤, less than or equal; n, number of samples; uS/cm, microsiemens per centimeter. The computations of the median and interquartile range include censored values set to the indicated detection limit noted by the red line symbol.
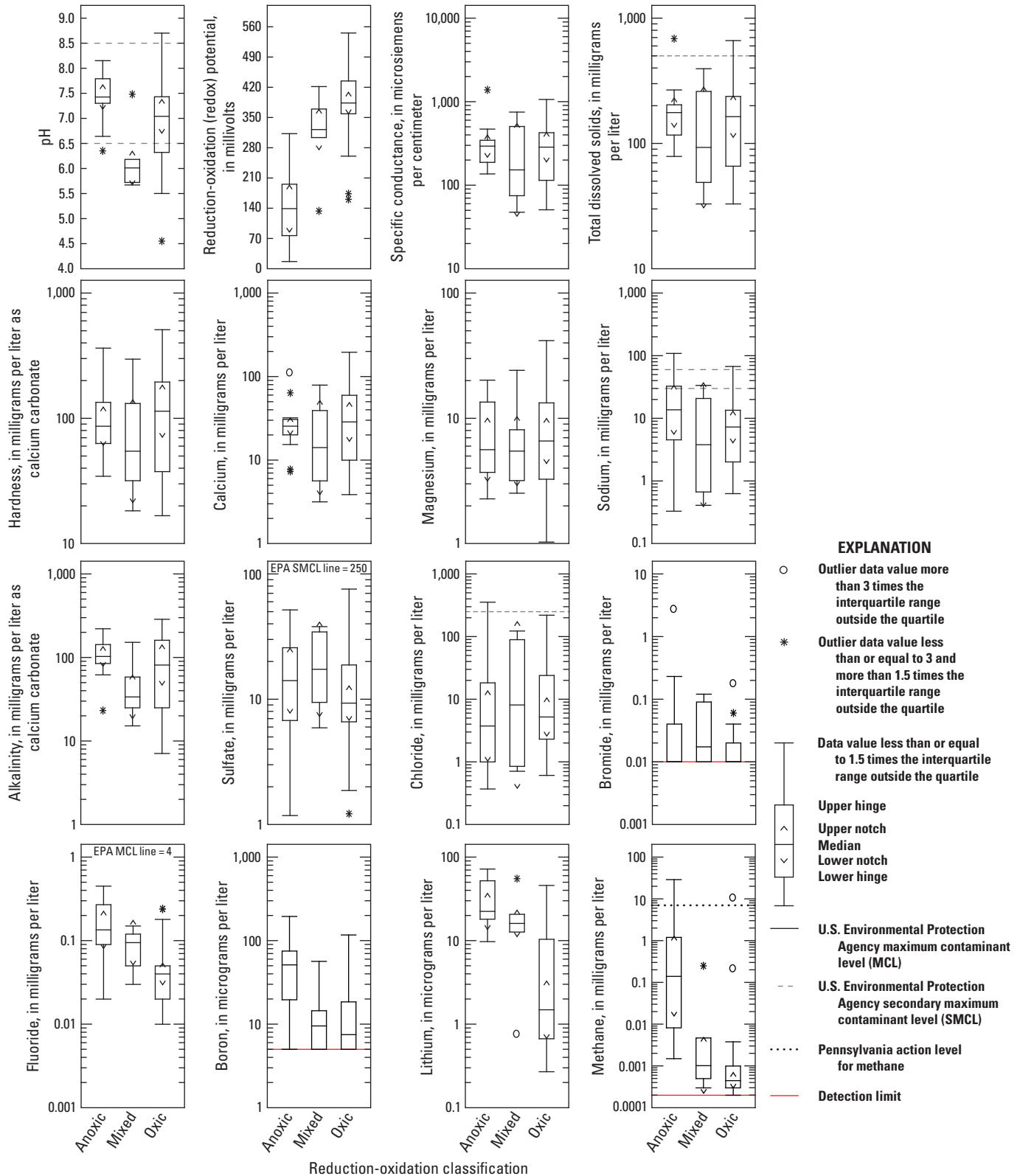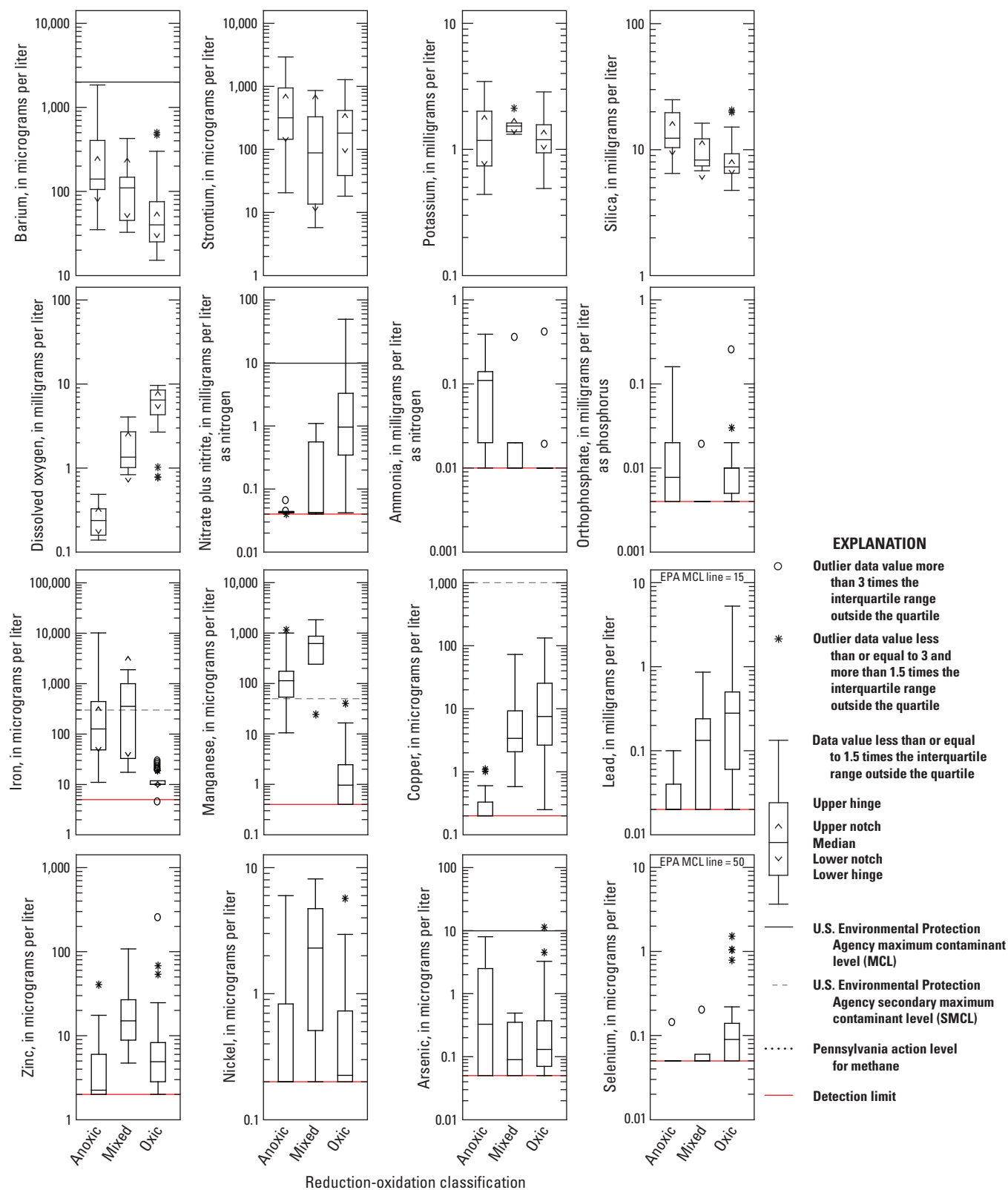
EXPLANATION

○   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

───   U.S. Environmental Protection Agency maximum contaminant level (MCL)

- - -   U.S. Environmental Protection Agency secondary maximum contaminant level (SMCL)

·····   Pennsylvania action level for methane

───   Detection limit

Specific conductance, in microsiemens per centimeter

Figure 4.3.   —Continued

Figure 4.3. —Continued

Figure 4.4.   Boxplots showing the composition of 54 groundwater samples from Clinton County, Pa., 2017, classified as anoxic (ANOX; n=14), mixed (MIXD; n=6), and oxic (OXIC; n=34) on the basis of dissolved oxygen concentration and other water-quality criteria of McMahon and Chapelle (2008). n, number of samples. The computations of the median and interquartile range include censored values set to the indicated detection limit noted by the red line symbol.
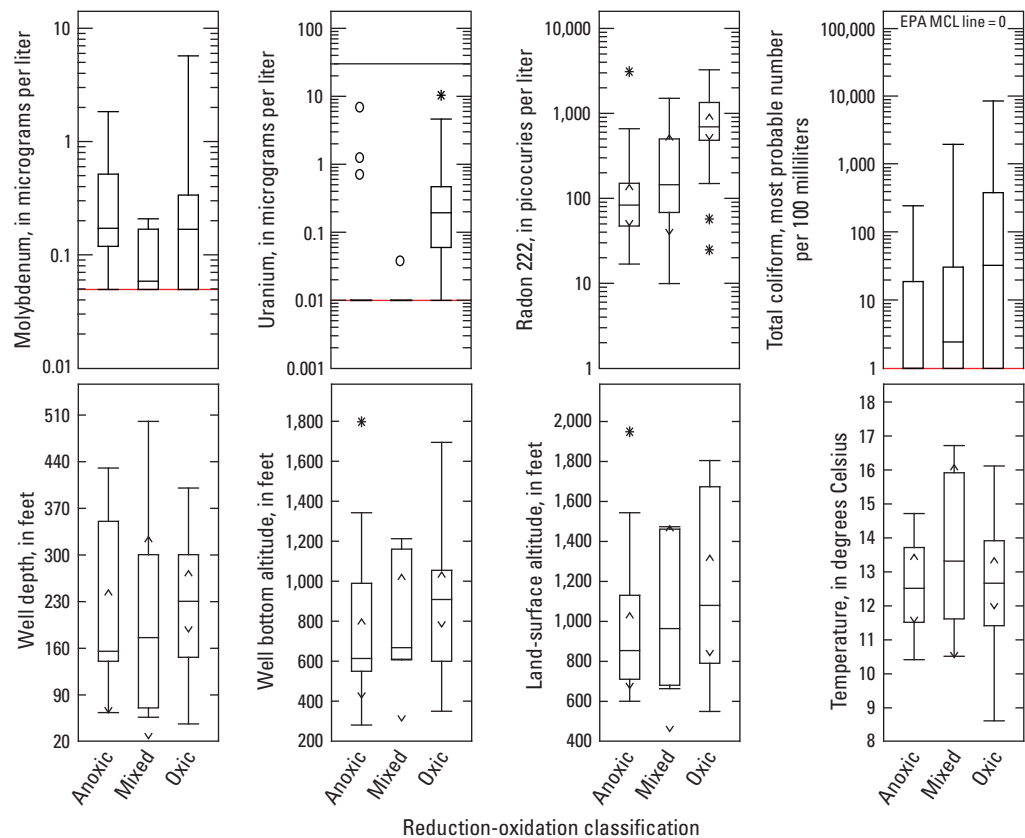
Figure 4.4.   —Continued

EXPLANATION

○ 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

— U.S. Environmental Protection Agency maximum contaminant level (MCL)

- - U.S. Environmental Protection Agency secondary maximum contaminant level (SMCL)

····· Pennsylvania action level for methane

— Detection limit

Figure 4.4. —Continued
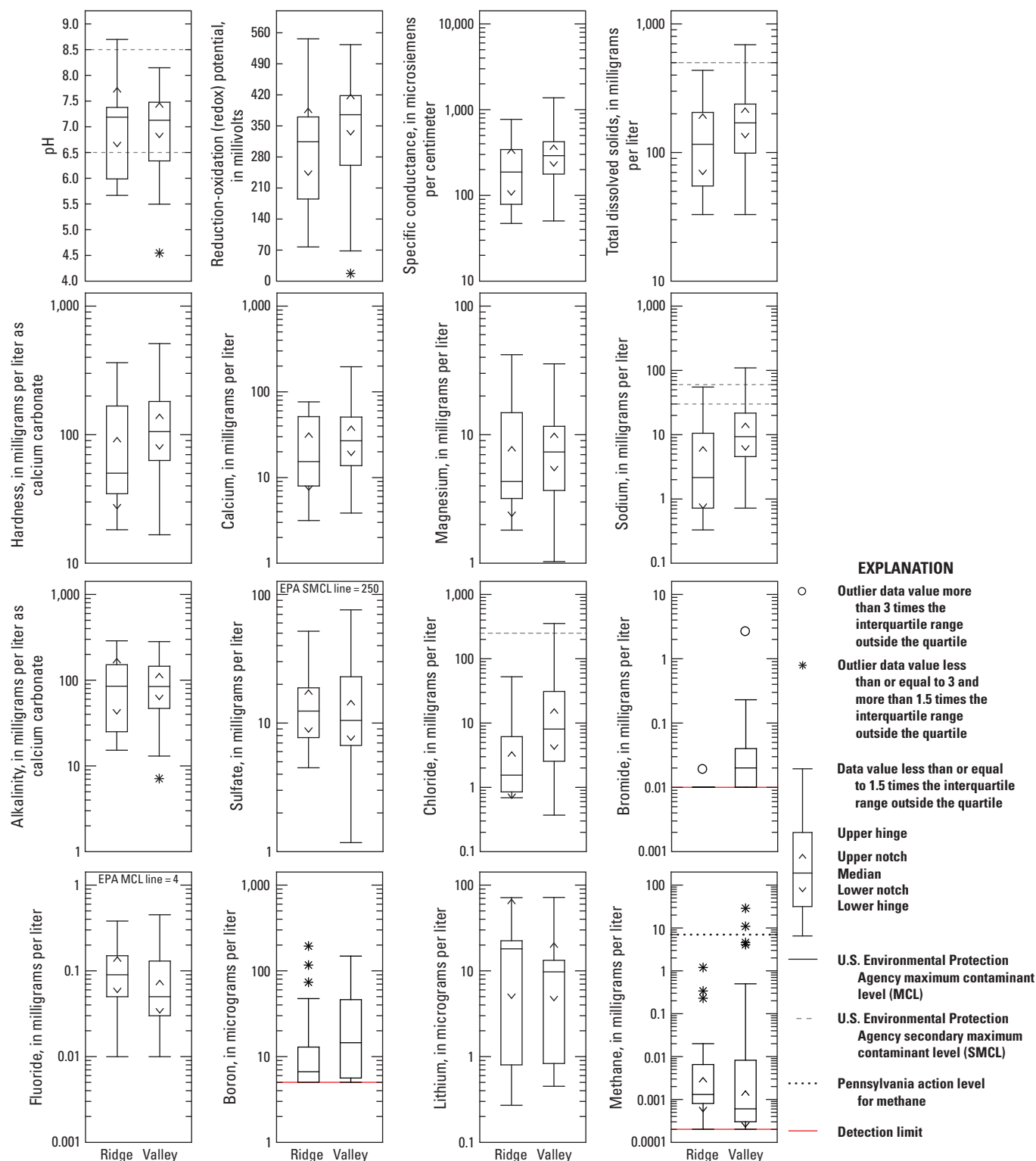
Figure 4.5. Boxplots showing the composition of 54 groundwater samples from Clinton County, Pa., 2017, classified on the basis of topographic position index (TPI). The TPI classes are ridge (RIDGE; n=2), upper slope (UPSLOPE; n=11), steep slope (STSLOPE; n =4), gentle slope (GNSLOPE; n=11), lower slope (LOSLOPE; n=11), and valley (VALLEY; n=15). n, number of samples. For simplification, two generalized TPI units were considered whereby ridge, upper slope, and steep slope were combined as the ridge category; gentle slope, lower slope, and valley were classified as the valley category. The computations of the median and interquartile range include censored values set to the indicated detection limit noted by the red line symbol.
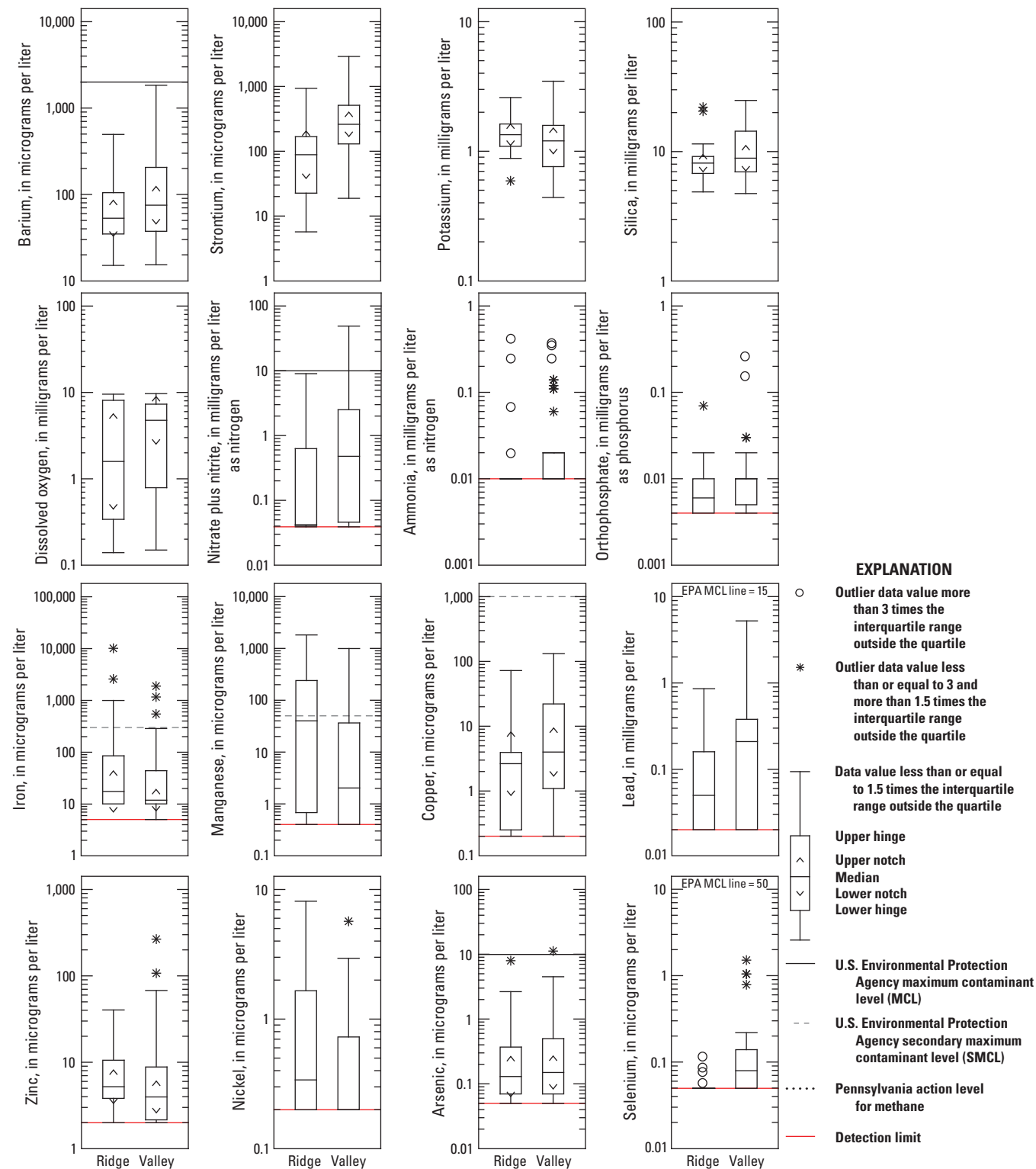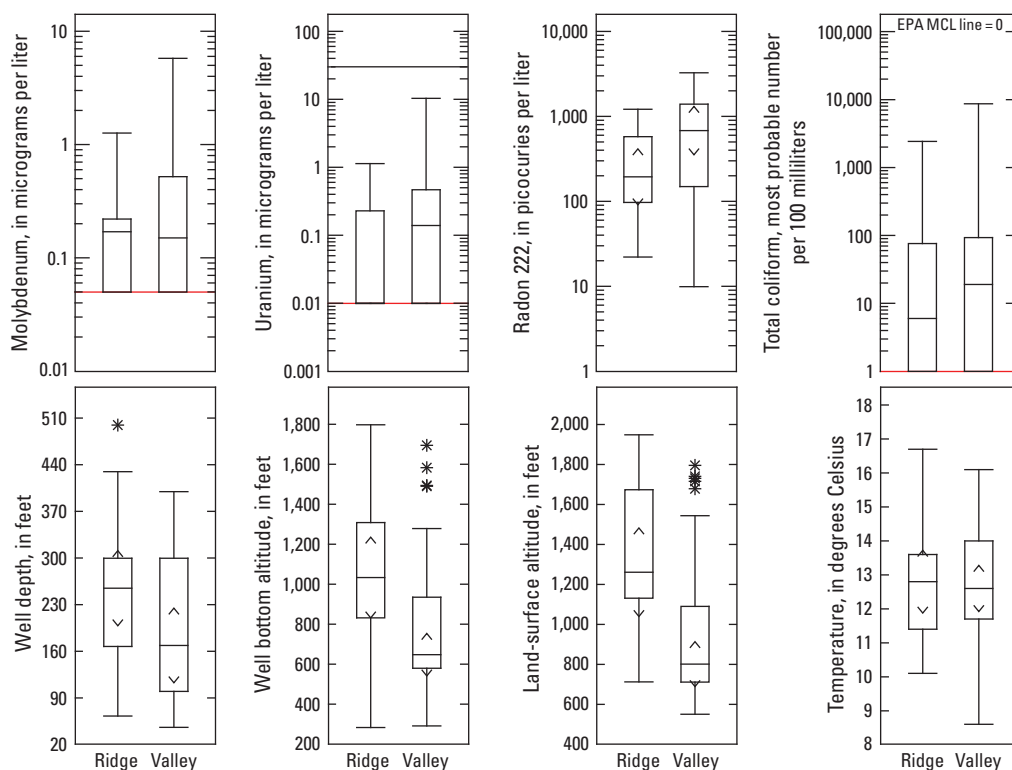
Figure 4.5.   —Continued

EXPLANATION

○   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

          U.S. Environmental Protection
              Agency maximum contaminant
              level (MCL)

– –   U.S. Environmental Protection
              Agency secondary maximum
              contaminant level (SMCL)

· · · · ·   Pennsylvania action level
                  for methane

          Detection limit

Figure 4.5.   —Continued

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