

Prepared in cooperation with the County of Lycoming

Groundwater Quality for 75 Domestic Wells in Lycoming County, Pennsylvania, 2014



Scientific Investigations Report 2016–5143

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By Eliza L. Gross and Charles A. Cravotta III

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Conversion Factors

U.S. customary units to International System of Units

| Multiply | By | To obtain |
|---------------------------------|---------|-------------------------------------|
| Length | | |
| inch (in.) | 2.54 | centimeter (cm) |
| 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 $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$.

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as $^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8$.

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 ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Abbreviations

| | |
|-------------------------|--|
| °C | degrees Celsius |
| = | equal to |
| > | greater than |
| ≥ | greater than or equal to |
| < | less than |
| ≤ | less than or equal to |
| $\mu\text{g}/\text{L}$ | micrograms per liter |
| $\mu\text{S}/\text{cm}$ | microsiemens per centimeter |
| ‰ | parts per thousand, or per mil* |
| ALK | alkalinity |
| DO | dissolved oxygen |
| <i>E. coli</i> | <i>Escherichia coli</i> |
| EPA | U.S. Environmental Protection Agency |
| HAL | health advisory level |
| IAP | ion activity product |
| K_T | Equilibrium constant for reaction at temperature T |
| LI | Langelier Index |
| MCL | maximum contaminant level |
| mg/L | milligrams per liter |
| mmol/L | millimoles per liter |
| MPN/100mL | most probable number per 100 milliliters |
| NTRU | Nephelometric Turbidity Ratio Units |
| NWQL | National Water Quality Laboratory |
| PC | principal component |
| PCA | principal components analysis |

*The isotope ratio delta value (δ), in parts per thousand, or per mil (‰), is defined as:

$$\delta E = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \cdot 1,000$$
 where E is an element (in this report C or H) and R is the ratio of $^{13}\text{C}/^{12}\text{C}$ or $^2\text{H}/^1\text{H}$ in the sample or standard. The symbol D for deuterium is commonly used instead of ^2H .

| | |
|-------------------|-------------------------------------|
| pCi/L | picocuries per liter |
| redox | oxidation-reduction |
| ROE | residue on evaporation |
| SC | specific conductance |
| SI | Saturation Index |
| SI _{CAL} | calcite Saturation Index |
| SLI | Seewald Laboratories Incorporated |
| SMCL | secondary maximum contaminant level |
| TDS | total dissolved solids |
| THM | trihalomethane |
| TPI | topographic position index |
| USGS | U.S. Geological Survey |
| VOC | volatile organic compound |
| VPDB | Vienna Pee Dee Belemnite |
| VSMOW | Vienna Standard Mean Ocean Water |

Groundwater Quality for 75 Domestic Wells in Lycoming County, Pennsylvania, 2014

By Eliza L. Gross and Charles A. Cravotta III

Abstract

Groundwater is a major source of drinking water in Lycoming County and adjacent counties in north-central and northeastern Pennsylvania, which are largely forested and rural and are currently undergoing development for hydrocarbon gases. Water-quality data are needed for assessing the natural characteristics of the groundwater resource and the potential effects from energy and mineral extraction, timber harvesting, agriculture, sewage and septic systems, and other human influences.

This report, prepared in cooperation with Lycoming County, presents analytical data for groundwater samples from 75 domestic wells sampled throughout Lycoming County in June, July, and August 2014. The samples were collected using existing pumps and plumbing prior to any treatment and analyzed for physical and chemical characteristics, including nutrients, major ions, metals and trace elements, volatile organic compounds, gross-alpha particle and gross beta-particle activity, uranium, and dissolved gases, including methane and radon-222.

Results indicate groundwater quality generally met most drinking-water standards, but that some samples exceeded primary or secondary maximum contaminant levels (MCLs) for arsenic, iron, manganese, total dissolved solids (TDS), chloride, pH, bacteria, or radon-222. Arsenic concentrations were higher than the MCL of 10 micrograms per liter ($\mu\text{g/L}$) in 9 of the 75 (12 percent) well-water samples, with concentrations as high as 23.6 $\mu\text{g/L}$; arsenic concentrations were higher than the health advisory level (HAL) of 2 $\mu\text{g/L}$ in 23 samples (31 percent). Total iron concentrations exceeded the secondary maximum contaminant level (SMCL) of 300 $\mu\text{g/L}$ in 20 of the 75 samples. Total manganese concentrations exceeded the SMCL of 50 $\mu\text{g/L}$ in 20 samples and the HAL of 300 $\mu\text{g/L}$ in 2 of those samples. Three samples had chloride concentrations that exceeded the SMCL of 250 milligrams per liter (mg/L); two of those samples exceeded the SMCL of 500 mg/L for TDS. The pH ranged from 5.3 to 9.15 and did not meet the SMCL range of 6.5 to 8.5 in 22 samples, with 17 samples having a pH less than 6.5 and 8 samples having pH greater than 8.5. Generally, the samples that had elevated TDS, chloride, or arsenic concentrations had high pH.

Total coliform bacteria were detected in 39 of 75 samples (52 percent), with *Escherichia coli* detected in 10 of those 39 samples. Radon-222 activities ranged from non-detect to 7,420 picocuries per liter (pCi/L), with a median of 863 pCi/L , and exceeded the proposed drinking-water standard of 300 pCi/L in 50 (67 percent) of the 75 samples; radon-222 activities were higher than the alternative proposed standard of 4,000 pCi/L in 3 samples.

Water from 15 of 75 (20 percent) wells had concentrations of methane greater than the reporting level of 0.01 mg/L ; detectable methane concentrations ranged from 0.04 to 16.8 mg/L . Two samples had methane concentrations (13.1 and 16.8 mg/L) exceeding the action level of 7 mg/L . Low levels of ethane (up to 0.12 mg/L) were present in the five samples with the highest methane concentrations (near or above 1 mg/L) that were analyzed for hydrocarbon compounds and isotopic composition. The isotopic composition of methane in four of these groundwater samples, from the Catskill and Lock Haven Formations and the Hamilton Group, have sample carbon isotopic ratio delta values (carbon-13/carbon-12) ranging from -42.36 to -36.08 parts per thousand (‰) and hydrogen isotopic ratio delta values (deuterium/protium) ranging from -212.0 to -188.4 ‰, which are consistent with the isotopic compositions reported for mud-gas logging samples from these geologic units and a thermogenic source of the methane. However, the isotopic composition and ratios of methane to ethane in a fifth sample indicate the methane in that sample may be of microbial origin that subsequently underwent oxidation. The fifth sample had the highest concentration of methane, 16.8 mg/L , with a carbon isotopic ratio delta values of -50.59 ‰ and a hydrogen isotopic ratio delta values of -209.7 ‰.

The six well-water samples with the highest methane concentrations also had among the highest pH values (8.25 to 9.15) and elevated concentrations of sodium, lithium, boron, fluoride, arsenic, and bromide. Relatively elevated concentrations of some other constituents, such as barium, strontium, and chloride, commonly were present in, but not limited to, those well-water samples with elevated methane.

Three of the six groundwater samples with the highest methane concentrations had chloride/bromide ratios that indicate mixing with a small amount of brine (0.02 percent or less) similar in composition to those reported at undetermined

depth below the freshwater aquifer and for gas and oil well brines in Pennsylvania. The sample with the highest methane concentration and most other samples with low methane concentrations (less than about 1 mg/L) have chloride/bromide ratios that indicate predominantly anthropogenic sources of chloride, such as road-deicing salt, septic systems, and (or) animal waste. Brines that are naturally present may originate from deeper parts of the aquifer system, while anthropogenic sources are more likely to affect shallow groundwater because they occur on or near the land-surface.

The spatial distribution of groundwater compositions generally indicate that (1) uplands along the western border of Lycoming County usually have dilute, slightly acidic, oxygenated, calcium-bicarbonate type waters; (2) intermediate altitudes or areas of carbonate bedrock usually have water of near neutral pH, with highest amounts of hardness (calcium and magnesium); (3) stream valleys, low elevations where groundwater may be discharging, and deep wells in uplands usually have water with pH values greater than 8 and highest arsenic, sodium, lithium, bromide concentrations. Geochemical modeling indicated that for samples with elevated pH, sodium, lithium, bromide, and alkalinity, the water chemistry could have resulted by dissolution of calcite (calcium carbonate) combined with cation-exchange and mixing with a small amount of brine. Through cation-exchange reactions between water and bedrock, which are equivalent to processes in a water softener, calcium ions released by calcite dissolution are exchanged for sodium ions on clay minerals. Thus, the assessment of groundwater quality in Lycoming County indicates groundwater is generally of good quality, but various parts of Lycoming County can have groundwater with low to moderate concentrations of methane and other constituents that appear in naturally present brine and produced waters from gas and oil wells at high concentrations.

Introduction

Lycoming County, which is in north-central Pennsylvania, is mostly forested (fig. 1). Approximately 43 percent of the total population of Lycoming County relies on groundwater as a source of drinking water (Pennsylvania Department of Environmental Protection, 2013; U.S. Bureau of the Census, 2010). Publicly available data describing the chemical quality of groundwater from private domestic-supply wells in Lycoming County are needed for assessing natural characteristics of the groundwater resource and potential effects from activities such as coal and mineral mining, oil and gas extraction, timber harvesting, agriculture, sewage and on-lot septic systems, and other types of development. The Marcellus Shale, which is being developed for natural gas throughout northern and western Pennsylvania, lays thousands of feet below 85 percent of the land surface of Lycoming County (fig. 1; U.S. Geological Survey, 2002). Drilling and hydraulic fracturing of unconventional horizontal shale-gas wells, in addition to other human

activities, have the potential to contaminate the base flow of streams and freshwater aquifers that provide drinking water (fig. 1; Kargbo and others, 2010; Kerr, 2010; U.S. Environmental Protection Agency, 2014).

Although hundreds of samples have been collected by the natural-gas industry to characterize the chemistry of groundwater in private wells of Lycoming County, few results from these samples are readily available to the public. Most of the publicly available results for groundwater-quality samples were collected more than 30 years ago (Lloyd and Carswell, 1981; Taylor and others, 1983) and do not include the broad suite of the current (2016) analytes of concern, such as total and fecal coliform bacteria, barium, strontium, chloride, bromide, hydrocarbon gases, trace metals, radon-222, and other radiochemicals (Pennsylvania Department of Environmental Protection, 2012). Without current data for associated groundwater-quality constituents, it is not possible to evaluate the sources of constituents or future potential groundwater-quality changes. Future changes in groundwater quality can be the result of natural variability or of human activities, including coal mining, oil and gas exploration, agricultural practices, onsite septic systems, or land development.

Previous Investigations

In the early 1980s, two published assessments of groundwater resources in the study area focused on hydrogeology and evaluated general groundwater quality, including major ions, nutrients, iron, and manganese. Lloyd and Carswell (1981) collected samples from 462 wells and 6 springs in a region surrounding Williamsport, Pennsylvania, which encompassed a large part of Lycoming County and small parts of Clinton, Union, Northumberland, and Montour Counties (fig. 1). The study by Lloyd and Carswell (1981) reported sample concentrations exceeding U.S. Environmental Protection Agency (EPA) standards for iron, manganese, sulfate, chloride, dissolved solids, hydrogen sulfide, barium, cadmium, lead, nitrate, and zinc. The study by Taylor and others (1983) reported major ion and trace-metal concentrations for 47 samples from wells in Lycoming County. Taylor and others (1983) concluded that primarily calcareous (carbonate) and primarily noncalcareous rock units had the most major differences in natural groundwater chemistry. Their results indicated that some groundwater was affected by high concentrations of iron and manganese, hydrogen sulfide, hardness, nitrate, and (or) bacterial organisms resulting from natural sources combined with contamination by sewage, agricultural practices, acid mine drainage, petroleum products from buried storage tanks, and (or) landfill leachate.

Recent studies of potential effects of gas drilling on groundwater quality from domestic wells in Lycoming and nearby counties in north-central and northeastern Pennsylvania reported that some samples had elevated concentrations of methane, sodium, chloride, bromide, and other dissolved constituents (Warner and others, 2012; Llewellyn, 2014; Siegel

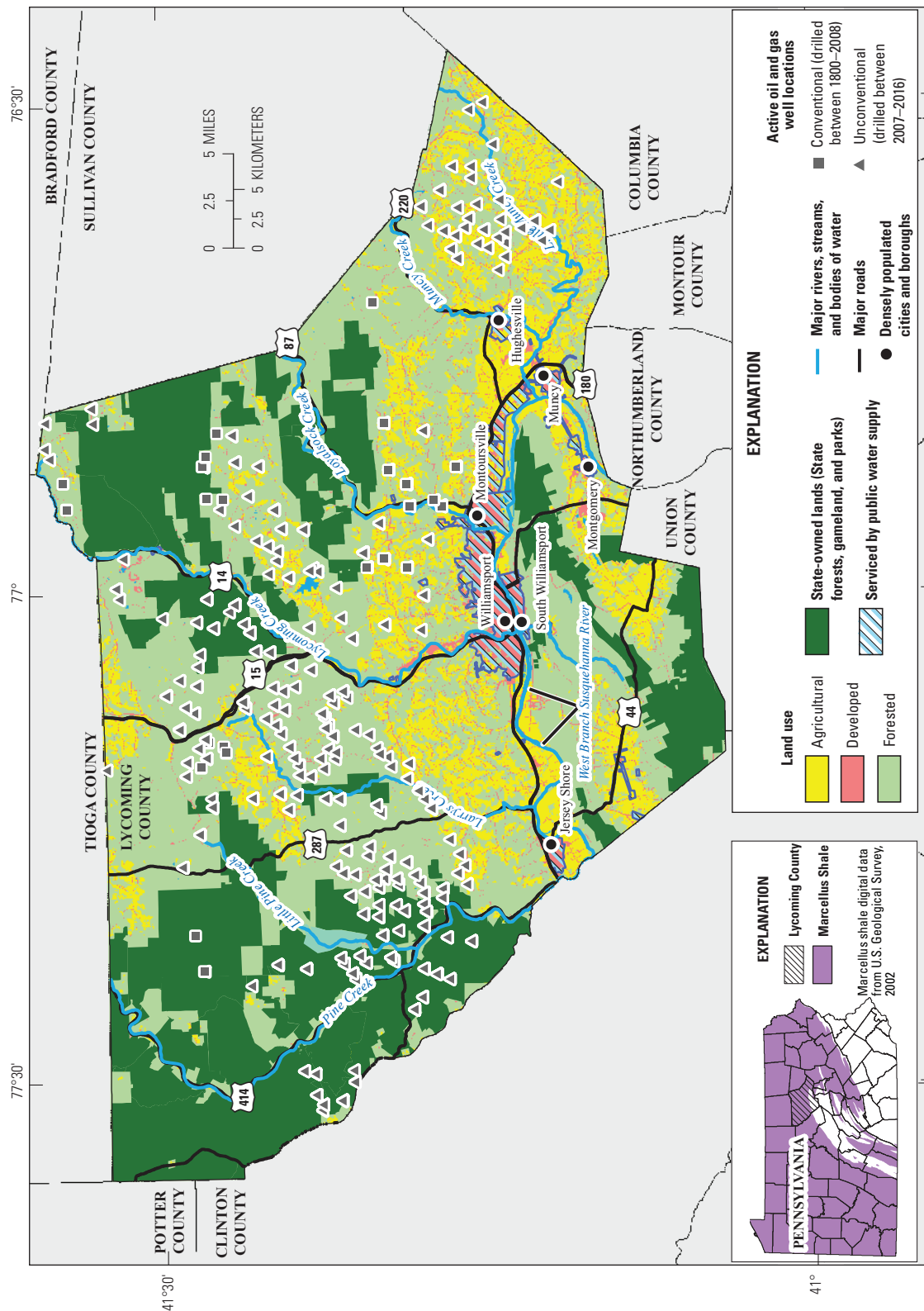


Figure 1. Land use, State-owned lands, conventional and unconventional active oil and gas well locations drilled as of June 2016, and water supply in Lycoming County, Pennsylvania.

and others, 2015; Reilly and others, 2015). Instead of contamination of shallow aquifers by flowback fluids from gas drilling and fracturing processes, these studies identified naturally present saline groundwater as the primary source of salinity in the sampled domestic wells. Such saline groundwater, which commonly contains methane, has been reported historically in Pennsylvania (Poth, 1962; Feth, 1965). Results also indicated that in addition to, or instead of, the influence of natural brines or other natural sources, some groundwater samples had been contaminated by animal waste, septic waste, or road-deicing salt (Llewellyn, 2014; Reilly and others, 2015). Thus, current water-quality data are needed for assessing natural characteristics and potential effects from mining, oil and gas extraction, forestry, agriculture, sewage or septic disposal, and other activities.

Purpose and Scope

This report, prepared in cooperation with Lycoming County, presents analytical data for groundwater samples from 75 domestic wells sampled throughout Lycoming County, Pennsylvania in June, July, and August 2014. The water samples were analyzed for nutrients, major ions, metals and trace elements, volatile organic compounds (VOCs), alcohols, gross-alpha particle and gross beta-particle activity, uranium, and dissolved gases, including methane and radon-222. A subset of 10 samples was analyzed for the radium isotopes radium-226 and radium-228. A subset of samples that had relatively elevated methane concentrations (approximately 1 mg/L and higher) was analyzed for the isotopic composition of methane and the concentrations of associated higher-chain hydrocarbons. Measured concentrations of analyzed constituents in groundwater are compared to EPA drinking-water standards. The relations among observed groundwater-quality characteristics, geology, topographic setting, land use, and other environmental variables associated with sampled wells are evaluated. The groundwater-quality data, summary statistics, and geochemical computations are presented to further the understanding of the current chemical quality of groundwater from freshwater aquifers used by private domestic-supply wells in Lycoming County and to update and fill the gap in existing groundwater-quality data.

Description of Study Area

Lycoming County occupies roughly 1,244 square miles in north-central Pennsylvania (fig. 1). Land surface elevations range from 452 feet above the North American Vertical Datum of 1988 (NAVD 88) in the south central area where the West Branch Susquehanna River flows out of Lycoming County to 2,404 feet above the NAVD 88 in the northeast part of the county (U.S. Geological Survey, 2009). Average annual temperatures in Lycoming County range from about 45 to 50 degrees Fahrenheit with the valley of the West Branch

Susquehanna River having the warmest average annual temperatures and the mountainous areas in the northeastern part of the county having the coldest average annual temperatures (PRISM Group at Oregon State University, 2006a, 2006b). Average annual precipitation varies from an average of 37 inches in the northwestern part of county to an average of 50 inches in the south central part of the county (PRISM Oregon State University, 2006c).

Population, Water Supply, and Land Use

Lycoming County is largely rural with a total population of 116,111 recorded in 2010 (U.S. Bureau of the Census, 2011). Seasonal dwellings made up an estimated 9 percent of housing units in the county in 1999 (Lycoming County Planning Commission, 2001). Some of the most densely populated areas in the county include the city of Williamsport and the boroughs of South Williamsport, Montoursville, Jersey Shore, Muncy, Hughesville, and Montgomery (fig. 1) with 2010 populations of 29,381; 6,379; 4,615; 4,361; 2,477; 2,128; and 1,579, respectively (U.S. Bureau of the Census, 2011). About 6 percent of the county consists of developed land, and these areas are also where population densities are highest (fig. 1). Developed areas with high population density commonly include public water supply service (fig. 1; Pennsylvania Department of Environmental Protection, 2013). In the less populated areas, residents use groundwater wells as their source of domestic water supply. Approximately 97 percent of Lycoming County is outside of public water supply service areas, and 43 percent of the total population within the county is assumed to be using a self-supplied water supply (Pennsylvania Department of Environmental Protection, 2013; U.S. Bureau of the Census, 2010).

Outside of the more densely populated areas in Lycoming County, agricultural lands account for about 18 percent of the land area and are typically found in the narrow valley bottoms in the northern part of the county and throughout the valley of the West Branch Susquehanna River in the southern part of the county. In addition, about 76 percent of the county is forested with approximately 42 percent of forested land consisting of State parks, forests, and gamelands in the northern half of the county (fig. 1; U.S. Geological Survey, 2014).

Forested, agricultural, and State-owned parts of the county also coincide with locations of both conventional and unconventional active oil and gas wells. Unconventional wells were not drilled in the county until more recently (after 2007) than conventional wells, which were drilled as early as the 1800's (fig. 1). Unconventional wells differ from conventional wells because they are purposely drilled into geologic shale formations where natural gas generally cannot be produced at economic flow rates or volumes without vertical or horizontal well bores being stimulated by hydraulic fracture treatments or by using multilateral well bores or other techniques to expose more of the geologic shale formation to the well bore (Pennsylvania Department of Environmental Protection, 2016).

Physiography and Geologic Setting

The northern two-thirds of Lycoming County is in the Appalachian Plateaus Physiographic Province, whereas the southern one-third of the county is in the Ridge and Valley Physiographic Province (Pennsylvania Bureau of Topographic and Geologic Survey, 1998). The northernmost parts of the county are in a glaciated area (fig. 2) known as the Glaciated Low Plateau and Glaciated High Plateau Sections of the Appalachian Plateaus Physiographic Province, which are characterized by broad to narrow, rounded to flat, elongated uplands and shallow valleys. South of this glaciated area is the Deep Valleys Section of the Appalachian Plateaus Physiographic Province, which is characterized by very deep, angular valleys with some broad to narrow uplands. South of the relatively flat-lying rocks of the Appalachian Plateaus is the Appalachian Mountain section of the Ridge and Valley Physiographic Province, which is characterized by narrow to broad valleys with steep uplands or linear ridge and mountain tops.

Lycoming County is underlain by 23 mapped geologic units (fig. 2 and table 1) ranging in age (youngest to oldest) from Pennsylvanian to Mississippian, Devonian, Silurian, to Ordovician (Pennsylvania Bureau of Topographic and Geologic Survey, 2001). Alluvium and glacial outwash and drift overlie the bedrock in major stream valleys. In some areas, the alluvium, which consists of gravel, sand, and clay that fills some valleys to depths of more than 200 feet, has been transported relatively long distances as a result of glacial processes (outwash), and in other areas, it has been weathered from the nearby rock formations (Taylor and others, 1983). For the purposes of this study, the 23 geologic units cropping out in Lycoming County were divided into four principal lithologic classes, consisting of carbonate, shale, siltstone, or sandstone lithology, based on the primary lithology reported by the Pennsylvania Bureau of Topographic and Geologic Survey (2001) and additional lithologic and water-quality descriptions from Taylor and others (1983; fig. 3 and table 1).



Example of common topographic features in the Ridge and Valley Physiographic Province of Bastress Township, Lycoming County, Pennsylvania. (Photograph provided by Brian Renninger, Bastress Township, Lycoming Conservation District)

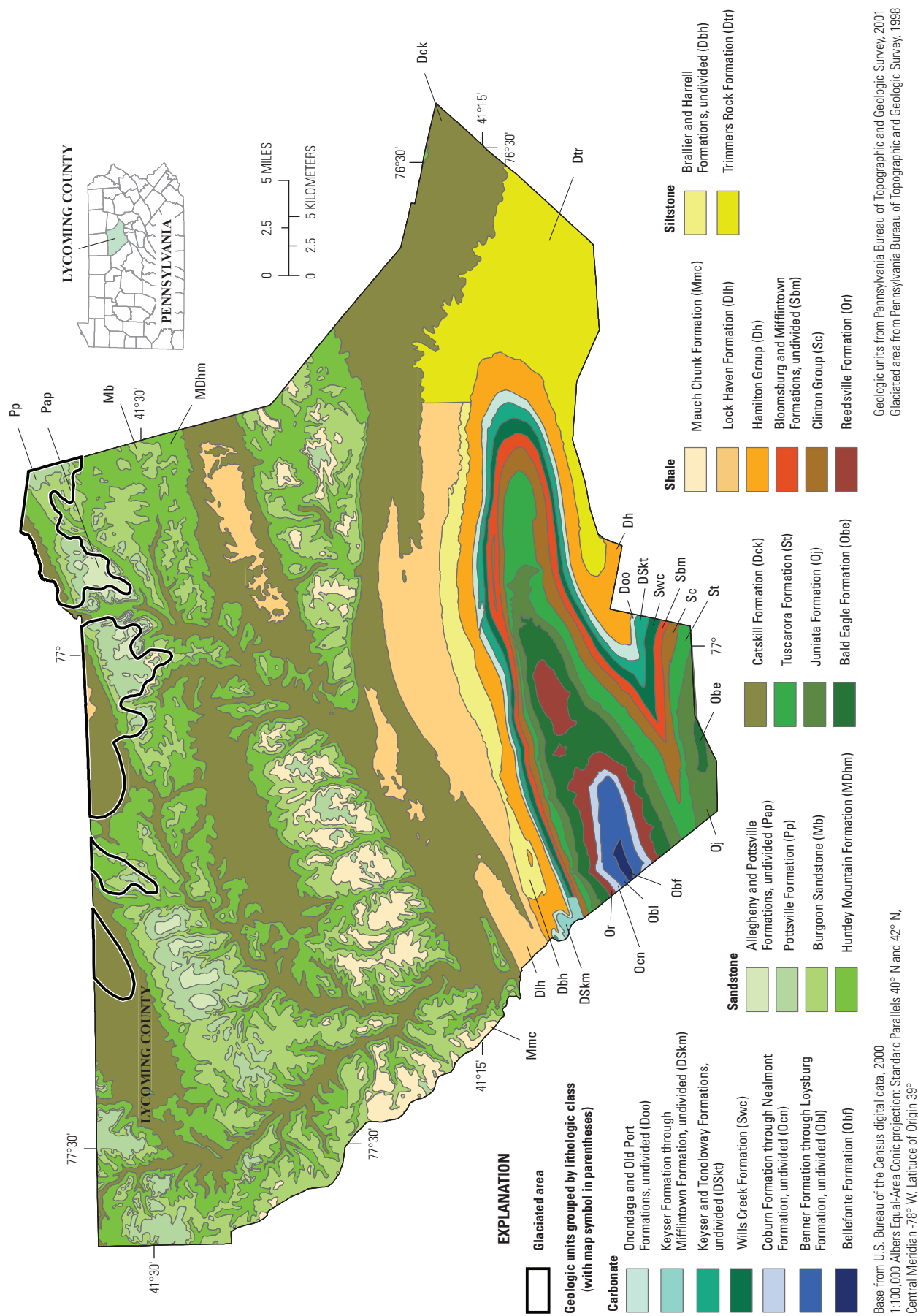


Figure 2. Geologic units (most near surface bedrock) and glaciated area in Lycoming County, Pennsylvania.

Table 1. Geologic units grouped by lithologic class based on geologic unit characteristics, including name, map symbol, age, and primary lithology from Pennsylvania Bureau of Topographic and Geologic Survey (2001) and additional lithologic and water quality descriptions from Taylor and others (1983).

| Geologic unit characteristics | | | | | | |
|-------------------------------|---|------------|----------------------------|-------------------|---|---|
| Lithologic class | Name ¹ | Map symbol | Age | Primary lithology | Additional lithologic description | Water quality |
| Carbonate | Onondaga and Old Port Formations, undivided | Doo | Devonian | Calcareous shale | Limestone | High iron and manganese; moderate hardness and dissolved solids |
| | Keyser Formation through Mifflintown Formation, undivided | DSkm | Devonian and Silurian | Limestone | Calcareous shale | Moderate hardness and dissolved solids |
| | Keyser and Tonoloway Formations, undivided | DSkt | Devonian and Silurian | Limestone | Dolomite, shale, siltstone | High iron and manganese; hardness and dissolved solids increase with depth |
| | Wills Creek Formation | Swc | Silurian | Calcareous shale | Siltstone | Very hard; moderately high dissolved solids |
| | Coburn Formation through Nealmont Formation, undivided | Ocn | Ordovician | Limestone | Shaly and fossiliferous limestone, calcareous shale | High iron and manganese; hard; moderate dissolved solids |
| | Benner Formation through Loysburg Formation, undivided | Obl | Ordovician | Limestone | Argillaceous and dolomitic limestone, dolomite | High iron and manganese; hard; moderate dissolved solids |
| | Bellefonte Formation | Obf | Ordovician | Dolomite | Limestone interbeds | Very hard; high dissolved solids |
| Sandstone | Allegheny and Pottsville Formations, undivided | Pap | Pennsylvanian | Sandstone | Coal | High iron and manganese |
| | Pottsville Formation | Pp | Pennsylvanian | Sandstone | Thin coal beds | High iron and manganese; moderate hardness |
| | Burgoon Sandstone | Mb | Mississippian | Sandstone | Shale, conglomerate, mudstone | High iron and manganese |
| | Huntley Mountain Formation | MDhm | Mississippian and Devonian | Sandstone | Thin siltstone or clay shale beds | High iron, manganese, dissolved solids |
| | Catskill Formation | Dck | Devonian | Sandstone | Siltstone, shale, conglomerate | High iron, manganese, chloride, arsenic; moderate hardness and dissolved solids |
| | Tuscarora Formation | St | Silurian | Quartzite | White quartzite | Soft to moderate hardness; low dissolved solids |
| | Juniata Formation | Oj | Ordovician | Sandstone | Siltstone | High iron; soft to moderate hardness; low dissolved solids |
| | Bald Eagle Formation | Obe | Ordovician | Sandstone | Conglomerate | Soft to moderate hardness; low dissolved solids |

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Table 1. Geologic units grouped by lithologic class based on geologic unit characteristics, including name, map symbol, age, and primary lithology from Pennsylvania Bureau of Topographic and Geologic Survey (2001) and additional lithologic and water quality descriptions from Taylor and others (1983).—Continued

| Geologic unit characteristics | | | | | | |
|-------------------------------|---|------------|---------------|-------------------|---|--|
| Lithologic class | Name ¹ | Map symbol | Age | Primary lithology | Additional lithologic description | Water quality |
| Shale | Mauch Chunk Formation | Mmc | Mississippian | Shale | Sandstone, siltstone, mudstone | Moderate dissolved solids |
| | Lock Haven Formation | Dlh | Devonian | Mudstone | Sandstone, siltstone, shale, conglomerate | High iron, manganese, and dissolved solids |
| | Hamilton Group (contains Mahantango and Marcellus Formations) | Dh | Devonian | Shale | Siltstone, limestone | High iron and manganese; moderate hardness |
| | Bloomsburg and Mifflintown Formations, undivided | Sbm | Silurian | Shale | Siltstone, claystone, sandstone and limestone interbeds | Hard; moderate dissolved solids |
| | Clinton Group | Sc | Silurian | Shale | Siltstone and sandstone interbeds | High iron and manganese; soft to moderate hardness; low dissolved solids |
| | Reedsville Formation | Or | Ordovician | Shale | Siltstone, sandstone interbeds | Hard; moderate dissolved solids; hydrogen sulfide |
| Siltstone | Brallier and Harrell Formations, undivided | Dbh | Devonian | Siltstone | Shale, sandstone | High iron and manganese; moderate dissolved solids |
| | Trimmers Rock Formation | Dtr | Devonian | Siltstone | Shale | High iron and manganese; moderate hardness; low dissolved solids |

¹Geologic unit names from Pennsylvania Bureau of Topographic and Geologic Survey (2001)

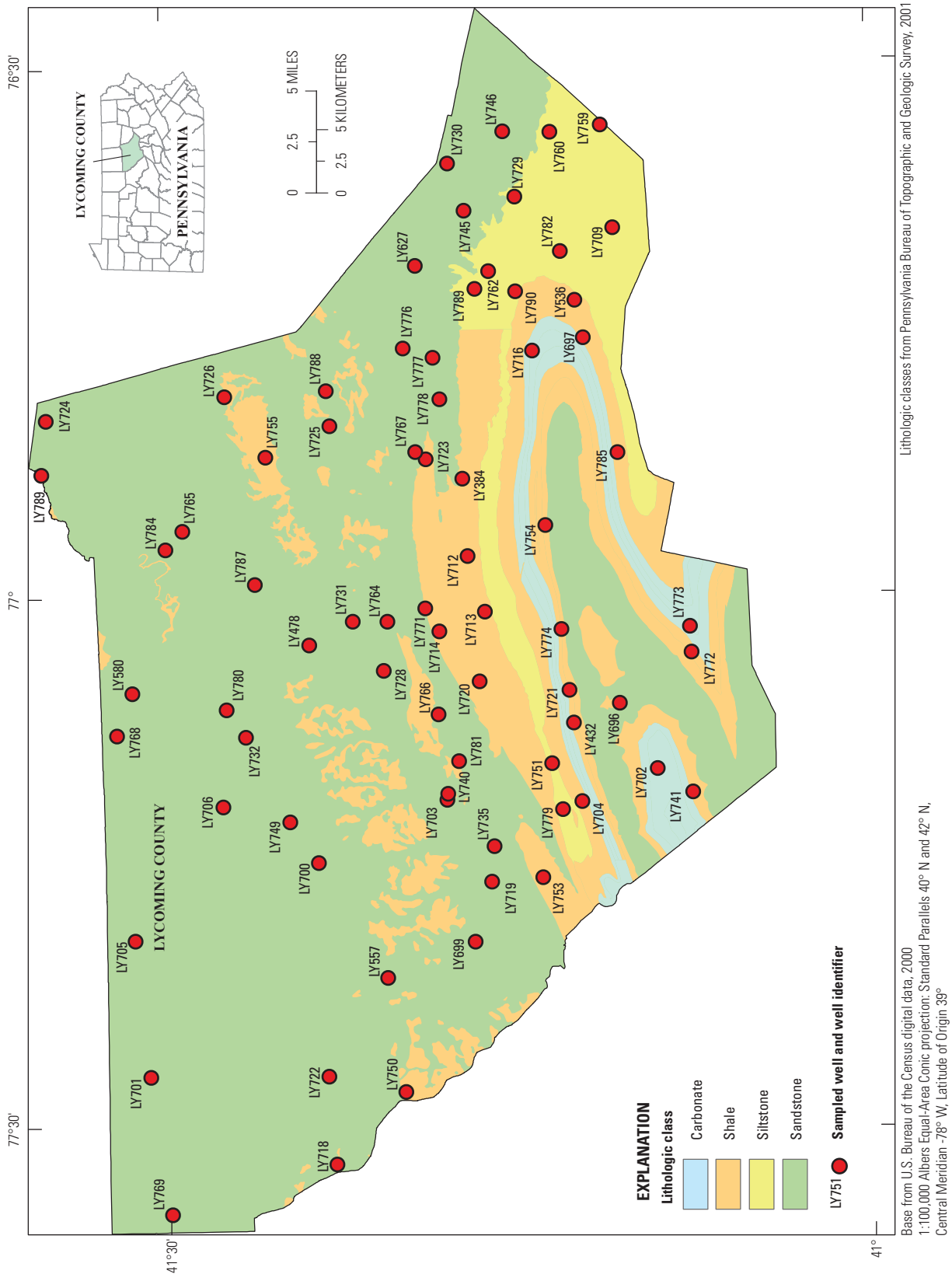


Figure 3. Spatial distribution of 75 domestic water wells sampled and lithologic classes in Lycoming County, Pennsylvania.

Study Methods

To provide current data on methane and quality of groundwater used for water supply in Lycoming County, groundwater samples were collected from 75 domestic wells during summer months in 2014 (fig. 3). One sample from each well was analyzed for nutrients, major ions, metals and trace elements, VOCs, ethylene and propylene glycol, alcohols, radioactivity, bacteria, and dissolved gases, including methane and radon-222.

Selection of Sampling Locations

Selection of wells for sampling involved several steps: (1) establishing an area of interest within the Lycoming County study area, (2) applying a stratified random selection program for site selection (Scott, 1990), (3) obtaining well location and construction record data (Pennsylvania Bureau of Topographic and Geologic Survey, 2014), (4) establishing well selection criteria, (5) identifying potential wells for sampling, (6) contacting well owners, and (7) conducting a plumbing review. The stratified random site-selection procedure permits the estimation of the probability of finding a small target. Given a grid of 75 cells, a small target is unlikely to be detected if it is present in less than 0.1 percent of the aquifer system, but is unlikely to be missed (at the 90-percent confidence interval) if it occupies more than 3 percent of the aquifer (Belitz and others, 2010). Because domestic wells in Lycoming County were being targeted for sampling, it was necessary to establish an area of interest within the relatively undeveloped parts of the county where domestic wells are the predominant source of water supply (fig. 1). State-owned lands, including State parks, forests, and gamelands, were excluded from the area of interest in order to remove widely unpopulated areas of the county from the site-selection process. In addition, those areas in Lycoming County serviced by public water suppliers were excluded from the area of interest because domestic wells in those areas would no longer be in use because those homes were assumed to be serviced by a public water supplier. Once an area of interest was defined for domestic well selection, a computerized stratified random site-selection approach was used to design a groundwater-quality network for sampling (Scott, 1990). An equal-area site-selection method was used to create an equal-area grid of cells and equally spaced population of potential sites, and the program arbitrarily specified one site from each cell as a primary sampling point and three additional sites as alternate sampling locations. Next, well record data within the defined area of interest in Lycoming County were obtained from the Pennsylvania Groundwater Information System database (Pennsylvania Bureau of Topographic and Geologic Survey, 2014), and potential wells for sampling were selected from these data based on the following criteria: the well is used for domestic or stock purposes; the well has an associated drill record or the homeowner knows well depth and construction

information; the well was drilled after 1970; the well was not hand dug; and the top of the casing is above the land surface. The latter criterion helped to eliminate shallow wells completed in alluvium or glacial outwash areas. Wells located within 1 mile of one of the computer generated random sampling points were prioritized. Homeowner contact information was obtained for those properties containing well records meeting the selection criteria, and homeowners were contacted to set up an appointment for a plumbing review. During the plumbing review, a U.S. Geological Survey (USGS) employee located the well, collected descriptive and spatial information about the well, made sure that the well met the criteria listed above, verified that a raw and untreated sample representative of the underground aquifer would be able to be collected, and obtained homeowner permission for future sample collection. Wells meeting the criteria listed above were prioritized for sampling, and not all wells that received plumbing reviews were sampled. All wells selected for sampling were private domestic wells.

Collection and Analysis of Samples

Groundwater samples from 75 wells were collected from June 9 through August 28, 2014 using established methods that attempt to characterize conditions within the aquifer (U.S. Geological Survey, variously dated). The water samples were collected using existing pumps and plumbing. Any water-treatment systems, including filtration, water softening, or bacteriological treatment were bypassed by attaching Teflon tubing to a raw-water tap at a pressure tank or outdoor faucet. If possible, a water level measurement was recorded at the well prior to pumping. Field measurements of physical and chemical properties (pH, temperature, specific conductance [SC], dissolved oxygen [DO] concentration, and turbidity) were conducted using a multiparameter probe that was immersed in gently flowing water. Wells were purged until the field measurements reached stable values and then samples were collected following USGS protocols (U.S. Geological Survey, variously dated). Alkalinity was measured the day of sampling with most measurements occurring at the hotel and several in the field.

Unfiltered subsamples without added preservatives were collected for physical properties, radioactivity, and dissolved gases. Filtered water samples, using sample-rinsed disposable 0.45-micrometer pore size cellulose capsule filters, and corresponding unfiltered samples were preserved with nitric acid for subsequent analysis of major ions, metals, and trace elements. Samples for radon-222 analysis were obtained through an inline septum with a gas-tight syringe to avoid atmospheric contact.

Unfiltered samples were stored on ice in coolers until hand delivered to Seewald Laboratories Incorporated (SLI) in Williamsport, Pa for analyses of bacteria, methane and other hydrocarbon gases, oil and grease, VOCs, ethylene and propylene glycol, alcohols, Total Kjeldahl nitrogen, and total

concentrations of major ions, metals, and trace elements. The remaining samples were shipped by overnight delivery to the following laboratories: (1) the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado, for analysis of major ions, nutrients, metals, trace elements, and radon-222; (2) TestAmerica, Inc., in Richland, Washington, for analysis of gross alpha and beta radioactivity for all wells and radium-226 and radium-228 for a subset of wells; and (3) Isotech, Inc., in Champaign, Illinois, for analysis of dissolved methane, associated higher-chain hydrocarbons, and isotopes of hydrogen and carbon in methane, explained below. Dissolved gas amounts were reported in terms of mole percent in headspace for the water sample, and also for methane and ethane as a dissolved concentration. Descriptions of analytical methods for constituents analyzed by the USGS NWQL are available through U.S. Geological Survey (variously dated). The analytical results for all of the field and laboratory measurements completed for this study are available through the USGS National Water Information System (U.S. Geological Survey, 2015). To facilitate access to these data, the official station numbers and selected descriptive information for the sampled wells are listed in the appendix table 1–1.

The concentrations of major ions typically are reported in milligrams per liter, which are approximately equivalent to parts per million. Nitrogen compounds, such as nitrate and ammonia, are reported in milligrams per liter as nitrogen, and phosphorus compounds, such as orthophosphate, are reported in milligrams per liter as phosphorus. The concentrations of trace elements and organic compounds typically are reported in micrograms per liter, which are approximately equivalent to parts per billion; a concentration value of 1,000 micrograms per liter ($\mu\text{g/L}$) is equal to 1.0 milligram per liter (mg/L). The most commonly used unit for reporting radon-222 and other radioactivity in water is picocuries per liter, explained in more detail where the data are presented.

Water samples containing a sufficient concentration of methane, generally greater than 0.9 mg/L , were further analyzed at Isotech, Inc., for the stable carbon isotopes (carbon-12 and carbon-13) and the stable hydrogen isotopes (protium and deuterium). The carbon-13/carbon-12 ratio and deuterium/protium ratios were determined by a mass spectrometric analysis that compared the sample to a reference standard. The carbon isotope ratio value in methane is reported in terms of parts per thousand (‰) with respect to the Vienna Pee Dee Belemnite (VPDB) standard. The hydrogen isotope ratio value in methane is reported in terms of ‰ with respect to the Vienna Standard Mean Ocean Water (VSMOW) standard.

Quality Assurance and Quality Control

For quality control, one equipment blank was analyzed before the sampling season began; filtered and unfiltered replicate samples were collected from wells, LY701, LY712, LY745, and LY789; a field blank was processed onsite at LY536; and a standard reference sample was processed at SLI.

Field blank samples were submitted to SLI and USGS NWQL to be analyzed for major ions, nutrients, metals and trace elements, and manmade organic compounds. Replicate samples were submitted to SLI to be analyzed for major ions and manmade organic compounds. Additional samples were collected from well LY745 to compare analytical results for manmade organic compounds between USGS NWQL and SLI. Equipment and field blanks demonstrated that the tubing, filtration apparatus, and other sample processing steps did not add contaminants to the samples, because results for all constituents were less than the minimum reporting levels. Results from replicate samples indicate that combined sampling and analytical precision (reproducibility) was within 5 percent for all major ions and most trace elements at concentrations that were greater than two times the minimum reporting level. Within two times the minimum reporting level, the concentrations were less precise but still within 20 percent. For the replicate sample collected from LY789, copper was 36.95 $\mu\text{g/L}$ greater than the environmental sample concentration (100-percent increase), and zinc was 5.743 $\mu\text{g/L}$ greater than the environmental sample concentration (272-percent increase). Samples collected from LY745 and analyzed at both USGS NWQL and SLI were comparable, with most results being less than the minimum reporting levels.

For quality assurance of the inorganic chemical analyses, intrasample characteristics were evaluated using standard procedures described by Hem (1985) and Fishman and Friedman (1989). Evaluations of accuracy and precision included comparison of field- and laboratory-measured values for pH and SC for each sample, along with a comparison of the concentrations of constituents in the unfiltered (total) and filtered (dissolved) subsamples. Generally, the field- and laboratory-measured values were consistent with one another, and the total concentrations of a constituent were greater than or equal to the dissolved concentration.

Additional quality control and quality assurance checks involved comparisons of the computed cation and anion equivalents concentrations and the corresponding ionic charge balance, comparisons of the ratios of cation or anion equivalents to SC, and comparisons of total dissolved solids (TDS) computed as the sum of major ion concentrations to the measured residue on evaporation (ROE) at 180 degrees Celsius ($^{\circ}\text{C}$). Deviations in the ionic charge balance that could be attributed to errors in the measured alkalinity were evaluated by computing the alkalinity concentration to achieve an ionic charge balance. The alkalinity is a potentially significant source of ionic imbalance because bicarbonate generally is the predominant ion in freshwater samples (Hem, 1985). Lastly, the measured SC was compared to the computed SC, which was estimated as the sum of ionic conductivities after accounting for aqueous speciation (McCleskey and others, 2012).

The values of SC measured in the field and laboratory were consistent with one another, and with the computed values of SC and TDS on the basis of measured solute concentrations (fig. 4*A* and *F*). The measured TDS concentration as ROE by two different laboratories and the computed TDS as

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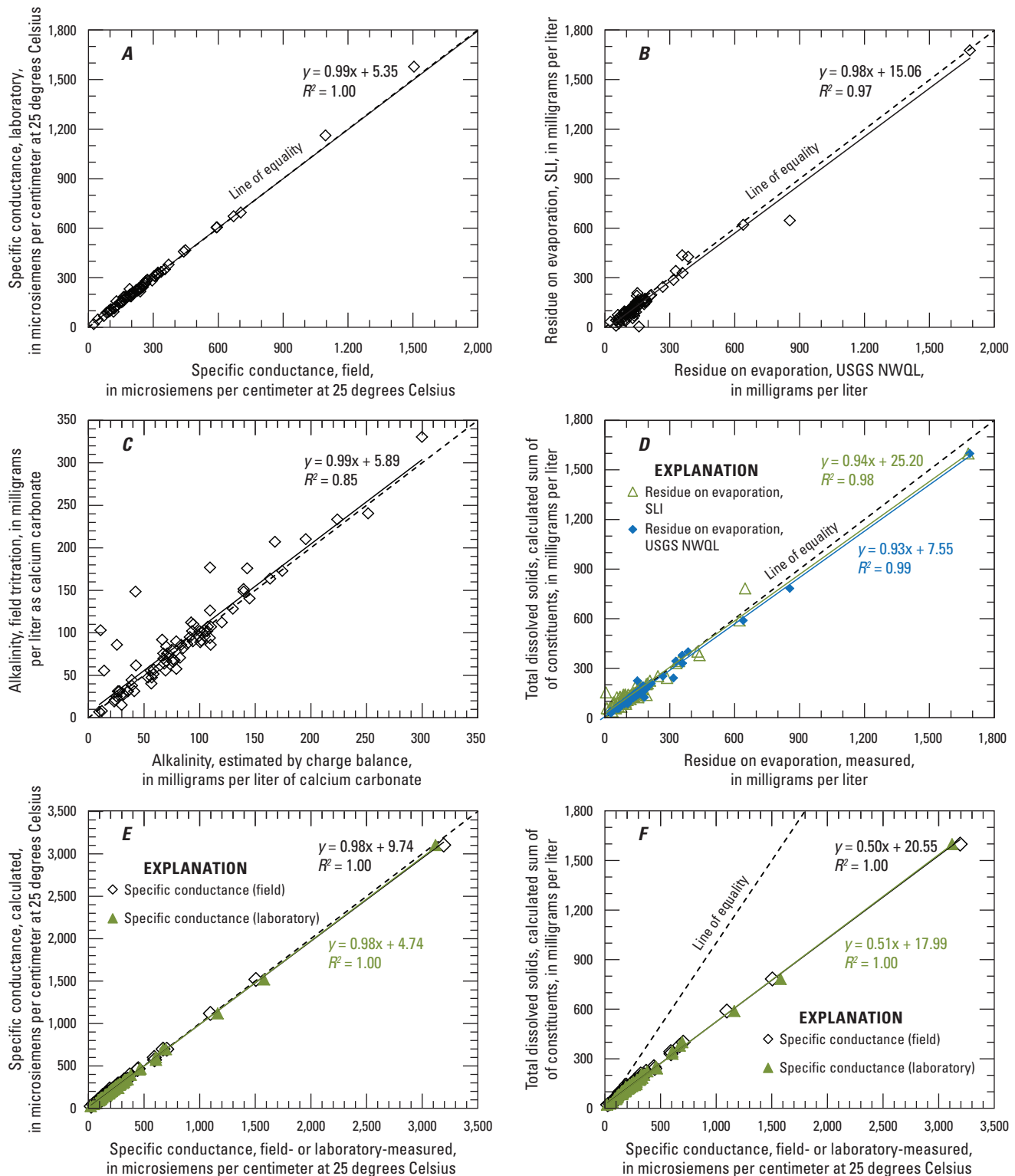


Figure 4. Comparison of field, laboratory, and (or) computed values of specific conductance (SC), total dissolved solids (TDS), or alkalinity for 75 groundwater samples from Lycoming County, Pennsylvania, 2014. *A*, field- and laboratory-measured SC; *B*, measured TDS as residue on evaporation (ROE) at 180 degrees Celsius by two different laboratories; *C*, alkalinity measured by incremental titration in the field and the computed value, estimated to achieve ionic charge balance; *D*, measured TDS (as ROE) and calculated TDS as the sum of dissolved constituent concentrations, including the estimated alkalinity; *E*, field- or laboratory-measured SC and calculated SC on the basis of ionic conductivities; and *F*, field- or laboratory-measured SC and calculated TDS on the basis of dissolved constituent concentrations. [SLI, Seewald Laboratories Incorporated; USGS, U.S. Geological Survey; NWQL, National Water Quality Laboratory]

the sum of constituent concentrations were in close agreement (figs. 4B and D). The computed TDS considered an estimated concentration of alkalinity to achieve ionic charge balance instead of the measured alkalinity value (figs. 4B and 4D). The estimated alkalinity concentration and the corresponding measured alkalinity for most samples were in close agreement (fig. 4C); however, several of the measured alkalinity values produced excessive charge imbalances and were inconsistent with other measures such as the measured SC and TDS. Therefore, the estimated alkalinity concentration was used for subsequent evaluations that considered the major ion data.

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 amount or transport of solutes in the aquifers in the study area. Bivariate scatter plots were created to illustrate potential relations among pH, selected constituent concentrations, and the saturation index values for minerals that may be sources or controls of the constituents. Additional plots of the mass ratio of chloride to bromide and the concentrations of bromide or sodium compared to the concentration of chloride were created to illustrate potential for different sources of salinity, including road-deicing salts and brines from oil and gas operations (Mullaney and others, 2009; Whittemore, 2007). Likewise, major ion data were plotted on trilinear diagrams and Piper diagrams (Appelo and Postma, 2005; Back, 1966; Hem, 1985) to illustrate the range of compositions of the samples collected for this study and possible processes such as calcite dissolution, cation-exchange, and mixing with road-deicing salt or brine that could produce the observed variations in major ions. The Piper diagrams were generated using the Geochemist's Workbench computer program (Bethke and Yeapel, 2010).

In general, nonparametric, rank-based statistical approaches were used to accommodate non-normally distributed and censored (below detection) data typical of most environmental samples (Helsel and Hirsch, 2002). Data for chemical concentrations were censored to a common level, and censored values were set to a common lowest value before ranks were computed for use in statistical tests. Relations between chemical variables were evaluated with scatter plots and correlation coefficients (Spearman's rho); distributions were compared among different sample classifications using notched boxplots (Velleman and Hoaglin, 1981; Helsel and Hirsch, 2002; P-STAT, Inc., 2008). Statistically significant correlation coefficients are presented in appendix table 2-1, and boxplots are presented in appendix 3. Where the median for a group is greater than the common reporting limit, it is displayed as a horizontal line within the box that is defined by the 25th and 75th percentiles for that group; otherwise, the median is displayed at the reporting limit. If the notched intervals

around the medians for sample subsets do not overlap, the medians are statistically different at the 95-percent confidence interval.

The boxplots in appendix 3 considered pH (fig. 3-1), SC (fig. 3-2), oxidation-reduction state (redox; fig. 3-3), and lithologic class (fig. 3-4) variables to classify and subset the data. The redox classifications used in this report were based on concentration thresholds of McMahon and Chapelle (2008) but were simplified to consider only three major classes: (1) "anoxic" (DO less than <0.5 mg/L); (2) "mixed" (DO greater than >0.5 mg/L and either manganese >50 $\mu\text{g/L}$ or iron >100 $\mu\text{g/L}$); or (3) "oxic" (DO >0.5 mg/L, manganese <50 $\mu\text{g/L}$, and iron <100 $\mu\text{g/L}$). The topographic position index (TPI) 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 classes for topographic setting: (1) ridge, (2) upper slope, (3) steep slope, (4) gentle slope, (5) lower slope, or (6) valley. No samples were collected from the steep slope TPI category. Furthermore, relations among the constituent concentrations and TPI classes were not apparent from the boxplots, and therefore, boxplots using TPI classifications are not included in the appendix.

Principal components analysis (PCA), computed with SAS 9.2 (SAS Institute, Inc., 2012), was used to evaluate multivariate correlations among the system variables (pH, SC, temperature) and dissolved constituents in the regional groundwater dataset without prior classification. The goal was to identify important hydrochemical processes or master variables that could explain element associations and distributions (Joreskog and others, 1976; Drever, 1997; Thyne and others, 2004). The Spearman-rank correlation coefficient matrix for the groundwater dataset (table 2-1) provided the standardized input for the PCA. Before computing ranks for the correlation analysis, censored values were set to a factor of 0.99 of the highest common reporting level (e.g. bromide <0.03 mg/L was changed to bromide equal to $=0.0299$ mg/L). Although bromide was included in the PCA, other constituents that were censored in more than 40 percent of the samples were excluded, including dissolved methane, organic nitrogen, and various trace elements. Only one variable was included for constituents that were considered redundant, such as field- and laboratory-measured values for pH or SC, or autocorrelated (not independent) variables, such as hardness and concentrations of calcium and magnesium. The PCA was optimized with varimax rotation to maximize the differences among the principal components; only principal components with eigenvalues greater than unity, equivalent to correlations with a probability greater than or equal to $(\geq) 0.999$, were retained (Joreskog and others, 1976; Thyne and others, 2004). Loadings for each constituent included in the PCA are equivalent to the Spearman-rank correlation coefficient between that constituent and the principal component. To aid in interpretations, the scores for each principal component in the PCA were compiled and then evaluated by correlation or graphical analysis with additional variables that had not been included

in the PCA, such as land surface elevation, well depth and bottom elevation, and the excluded trace elements. For simplification of displayed results, the loading values and Spearman-rank correlation coefficient values are multiplied by 100 and rounded. Significant correlation coefficients for the additional variables are displayed beneath the main PCA results; only correlation coefficients with probability ≥ 0.999 are considered significant.

Aqueous speciation computations were conducted with PHREEQC (Parkhurst and Appelo, 2013), a computer program designed to perform a wide variety of aqueous geochemical calculations based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, solid solutions, exchangers, and sorption surfaces. Thermodynamic data for the aqueous species and gas and mineral phases from the *wateq4f.dat* database file were included. The *wateq4f.dat* database file is derived from the WATEQ4F ion-association aqueous model (Ball and Nordstrom, 1991), which uses field measurements (e.g. temperature, pH, DO, alkalinity) and the chemical analysis of a water sample as input to calculate the distribution of aqueous species, ion activities, and mineral saturation indices that indicate the tendency of a water to dissolve or precipitate a set of minerals (Drever, 1997; Nordstrom and Munoz, 1986). In addition to data from the *wateq4f.dat* database file, cation-exchange equilibrium reactions as defined by Appelo and Postma (2005) were also included.

The molal concentrations of aqueous species were used to estimate the ionic contributions to specific conductance (McCleskey and others, 2012). The mineral saturation index (SI) values for various major and trace minerals were used to indicate the potential for mineral dissolution and precipitation. If a mineral phase is undersaturated in groundwater (SI < 0), that mineral phase (if present) has the potential to be dissolved by the groundwater. Likewise, if a mineral is supersaturated in groundwater (SI > 0), that mineral phase feasibly could precipitate, thus limiting the dissolved constituent concentrations. Geochemical modeling with PHREEQC was used to evaluate processes that could feasibly produce the observed concentrations of constituents in the groundwater samples (Parkhurst and Appelo, 2013). A series forward reaction model was developed that simulated the progressive addition of calcite, road-deicing salt, or brine to the dilute background water in order to illustrate the general trends in concentrations of major and minor ions. The chemical compositions indicated by the mass-transfer models were then plotted relative to the amount of solid reactant or brine added to the groundwater and also on Piper diagrams and scatter plots showing the changes in pH or constituent concentration with reaction progress.

Groundwater Quality and Relation to Human-Health Standards

Analytical results for the 75 groundwater samples collected in Lycoming County are provided in the following sections and compared to EPA drinking-water standards and health advisories (U.S. Environmental Protection Agency, 2012). The EPA has established maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs), and health advisory levels (HALs) for some constituents in drinking water (table 2). 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 must be followed for public drinking-water supplies. HALs established by the EPA provide information on contaminants that can cause human-health effects. Although HALs are non-enforceable, they are meant to provide technical guidance on health effects, analytical methodologies, and treatment technologies associated with drinking-water contamination.

Physical and Chemical Properties

Physical and chemical properties discussed in this section include temperature, DO, pH, alkalinity (ALK), SC, hardness, and turbidity. These properties are unstable and are determined in the field at the time a water sample is collected. ALK titrations were conducted the day of sampling to determine bicarbonate and carbonate ALK as calcium carbonate. Summary statistics for the unstable physical and chemical properties are given in table 3.

The temperature of the groundwater samples ranged from 10.2 to 17.9 °C, with a median of 13.1 °C. These temperatures generally were less than the daytime air temperatures during sampling, which reflects the generally cool groundwater environment. Dissolved gases and carbonate minerals can dissolve to a greater extent in cool water than in warm water (Hem, 1985).

DO concentrations ranged from 0.18 to 10.3 mg/L; the median concentration was 2.54 mg/L (table 3). Generally, most of the groundwater had DO concentrations that were less than saturation at the sample temperature, indicating the waters had been out of contact with the atmosphere. Low DO concentrations are associated with higher pH values; 14 of the 20 water samples with a DO concentration < 1 mg/L had a pH

Table 2. Available U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs), and health advisory levels (HALs) for analyzed constituents (U.S. Environmental Protection Agency, 2012).

[AMCL, alternative maximum contaminant level; mg/L, milligram per liter; µg/L, microgram per liter; pCi/L, picocuries per liter; --, no MCL, SMCL, or HAL established]

| Regulated constituent | Units | EPA MCL ¹ | EPA SMCL | EPA HAL |
|----------------------------------|------------------|----------------------|----------|---------|
| Physical and chemical properties | | | | |
| pH | pH units | -- | 6.5–8.5 | -- |
| Total dissolved solids | mg/L | -- | 500 | -- |
| Major ions | | | | |
| Chloride | mg/L | -- | 250 | -- |
| Fluoride | mg/L | 4 | 2 | -- |
| Sodium | mg/L | -- | -- | 20 |
| Sulfate | mg/L | -- | 250 | 500 |
| Nutrients | | | | |
| Ammonia | mg/L as nitrogen | -- | -- | 30 |
| Nitrate as N | mg/L as nitrogen | 10 | -- | -- |
| Nitrite as N | mg/L as nitrogen | 1 | -- | -- |
| Metals and trace elements | | | | |
| Aluminum | µg/L | -- | 50-200 | -- |
| Antimony | µg/L | 6 | -- | -- |
| Arsenic | µg/L | 10 | -- | 2 |
| Barium | µg/L | 2,000 | -- | -- |
| Beryllium | µg/L | 4 | -- | -- |
| Boron | µg/L | -- | -- | 7,000 |
| Cadmium | µg/L | 5 | -- | -- |
| Chromium | µg/L | 100 | -- | -- |
| Copper | µg/L | 1,300 | 1,000 | 1,000 |
| Iron | µg/L | -- | 300 | -- |
| Lead | µg/L | ² 15 | -- | -- |
| Manganese | µg/L | -- | 50 | 300 |
| Molybdenum | µg/L | -- | -- | 40 |
| Nickel | µg/L | -- | -- | 100 |
| Selenium | µg/L | 50 | -- | -- |
| Silver | µg/L | -- | 100 | -- |
| Strontium | µg/L | -- | -- | 4,000 |
| Zinc | µg/L | -- | 5,000 | 2,000 |
| Radionuclides | | | | |
| Gross alpha radioactivity | pCi/L | 15 | -- | -- |
| Radon-222 | pCi/L | 300 (proposed) | -- | -- |
| Uranium | µg/L | 30 | -- | 20 |
| Volatile organic compounds | | | | |
| 1,1,1,2-Tetrachloroethane | µg/L | -- | -- | 70 |
| 1,1,1-Trichloroethane | µg/L | 200 | -- | -- |
| 1,1,2,2-Tetrachloroethane | µg/L | -- | -- | 40 |
| 1,1,2-Trichloroethane | µg/L | 5 | -- | -- |

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Table 2. Available U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs), and health advisory levels (HALs) for analyzed constituents (U.S. Environmental Protection Agency, 2012).—Continued

[AMCL, alternative maximum contaminant level; mg/L, milligram per liter; µg/L, microgram per liter; pCi/L, picocuries per liter; --, no MCL, SMCL, or HAL established]

| Regulated constituent | Units | EPA MCL ¹ | EPA SMCL | EPA HAL |
|---|-------|----------------------|----------|---------|
| 1,1-Dichloroethene (1,1-Dichloroethylene) | µg/L | 7 | -- | -- |
| 1,2,3-Trichloropropane (1,2,3-TCP) | µg/L | -- | -- | 100 |
| 1,2,4-Trichlorobenzene | µg/L | 70 | -- | -- |
| 1,2-Dichlorobenzene (<i>o</i> -Dichlorobenzene) | µg/L | 600 | -- | -- |
| 1,2-Dichloroethane | µg/L | 5 | -- | -- |
| 1,2-Dichloropropane | µg/L | 5 | -- | -- |
| 1,3-Dichlorobenzene (<i>m</i> -Dichlorobenzene) | µg/L | -- | -- | 600 |
| 1,4-Dichlorobenzene (<i>p</i> -Dichlorobenzene) | µg/L | 75 | -- | -- |
| 2-Butanone (Methyl ethyl ketone, MEK) | µg/L | -- | -- | 4,000 |
| 2-Chlorotoluene | µg/L | -- | -- | 100 |
| 4-Chlorotoluene | µg/L | -- | -- | 100 |
| Benzene | µg/L | 5 | -- | -- |
| Bromobenzene | µg/L | -- | -- | 60 |
| Bromochloromethane | µg/L | -- | -- | 90 |
| Bromodichloromethane | µg/L | ³ 80 | -- | -- |
| Bromoform (Tribromomethane) | µg/L | ³ 80 | -- | -- |
| Bromomethane (Methyl bromide) | µg/L | -- | -- | 10 |
| Carbon Tetrachloride (Tetrachloromethane) | µg/L | 5 | -- | -- |
| Chlorobenzene | µg/L | 100 | -- | -- |
| <i>cis</i> -1,2-dichloroethene | µg/L | 70 | -- | -- |
| <i>cis</i> -1,3-dichloropropene | µg/L | -- | -- | 40 |
| Dibromochloromethane | µg/L | ³ 80 | -- | -- |
| Dibromomethane | µg/L | -- | -- | -- |
| Dichlorodifluoromethane (Freon 12) | µg/L | -- | -- | 1,000 |
| Ethylbenzene | µg/L | 700 | -- | -- |
| Hexachlorobutadiene (1,3-Hexachlorobutadiene) | µg/L | -- | -- | 10 |
| Isopropylbenzene (Cumene) | µg/L | -- | -- | 4 |
| <i>m</i> + <i>p</i> -Xylene (<i>m</i> -Xylene plus <i>p</i> -xylene) | µg/L | 10,000 | -- | -- |
| Methyl chloride (Chloromethane) | µg/L | -- | -- | 400 |
| Methylene Chloride (Dichloromethane, DCM) | µg/L | 5 | -- | -- |
| Naphthalene | µg/L | -- | -- | 100 |
| <i>o</i> -Xylene | µg/L | 10,000 | -- | -- |
| Styrene | µg/L | 100 | -- | -- |
| Tetrachloroethene (Perchloroethylene, PCE) | µg/L | 5 | -- | -- |
| Toluene | µg/L | 1,000 | -- | -- |
| <i>trans</i> -1,2-Dichloroethene | µg/L | 100 | -- | -- |
| <i>trans</i> -1,3-Dichloropropene | µg/L | -- | -- | 40 |
| Trichloroethene (TCE, Trichloroethylene) | µg/L | 5 (under review) | -- | -- |
| Trichlorofluoromethane (Freon 11) | µg/L | -- | -- | 2,000 |

Table 2. Available U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs), and health advisory levels (HALs) for analyzed constituents (U.S. Environmental Protection Agency, 2012).—Continued

[AMCL, alternative maximum contaminant level; mg/L, milligram per liter; µg/L, microgram per liter; pCi/L, picocuries per liter; --, no MCL, SMCL, or HAL established]

| Regulated constituent | Units | EPA MCL ¹ | EPA SMCL | EPA HAL |
|-------------------------------|-------|----------------------|----------|---------|
| Trichloromethane | µg/L | ³ 80 | -- | -- |
| Total trihalomethanes (TTHMs) | µg/L | ³ 80 | -- | -- |
| Vinyl Chloride (Chloroethene) | µg/L | 2 | -- | -- |
| Glycols and alcohols | | | | |
| Ethylene glycol | mg/L | 14 | -- | -- |

¹In addition to a proposed MCL, radon-222 has a proposed AMCL of 4,000 pCi/L. States that have multimedia mitigation programs to address radon-222 risks in indoor air would be required to comply with the proposed AMCL, which is higher than the proposed MCL.

²Lead in domestic water supplies is regulated by a treatment technique that requires water purveyors to control the corrosiveness of their water. If more than 10 percent of tap-water samples exceed the action level, the water purveyor must take additional steps. Domestic-supply wells are not regulated.

³1998 “Final Rule for Disinfectants and Disinfection By-products” states the total for trihalomethanes (TTHMs) is 80 µg/L.

Table 3. Minimum, median, and maximum of well characteristics, physical and chemical properties, major ions, nutrients, and bacteria determined in the laboratory for water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for dissolved concentrations in filtered samples done by U.S. Geological Survey National Water Quality Laboratory, and laboratory analysis for total concentrations in unfiltered samples done by Seewald Laboratories Incorporated.

[°C, degrees Celsius; mg/L, milligram per liter; µS/cm, microsiemen per centimeter; MPN/100mL, most probable number per 100 milliliters; <, less than; --, not applicable; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HAL, health advisory level]

| Well characteristics and physical and chemical properties | Units | Number (percent) above reporting level | Minimum | Median | Maximum | Number (percent) exceeding standard | EPA MCL | EPA SMCL | EPA HAL |
|---|-------------------------------------|--|---------|--------|---------|-------------------------------------|---------|----------|---------|
| Well characteristics | | | | | | | | | |
| Well depth | feet | 75 | 40 | 225 | 620 | -- | -- | -- | -- |
| Field properties | | | | | | | | | |
| Water temperature | °C | 75 (100) | 10.2 | 13.1 | 17.9 | -- | -- | -- | -- |
| Dissolved oxygen | mg/L | 75 (100) | 0.18 | 2.54 | 10.3 | -- | -- | -- | -- |
| Specific conductance, field | µS/cm at 25 °C | 75 (100) | 24.7 | 214 | 3,193 | -- | -- | -- | -- |
| pH, field | pH units | 75 (100) | 5.3 | 7.33 | 9.15 | 25 (33) | -- | 6.5–8.5 | -- |
| Alkalinity (dissolved) | mg/L as calcium carbonate | 75 (100) | 7.1 | 85.9 | 331 | -- | -- | -- | -- |
| Turbidity | Nephelometric Turbidity Ratio Units | 75 (100) | 0.13 | 1.12 | 180 | -- | -- | -- | -- |
| Laboratory analyses | | | | | | | | | |
| Specific conductance, laboratory | µS/cm at 25 °C | 75 (100) | 19.5 | 217 | 3,120 | -- | -- | -- | -- |
| pH, laboratory | pH units | 75 (100) | 5.79 | 7.78 | 9.3 | 25 (33) | -- | 6.5–8.5 | -- |

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Table 3. Minimum, median, and maximum of well characteristics, physical and chemical properties, major ions, nutrients, and bacteria determined in the laboratory for water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for dissolved concentrations in filtered samples done by U.S. Geological Survey National Water Quality Laboratory, and laboratory analysis for total concentrations in unfiltered samples done by Seewald Laboratories Incorporated.—Continued

[°C, degrees Celsius; mg/L, milligram per liter; µS/cm, microsiemen per centimeter; MPN/100mL, most probable number per 100 milliliters; <, less than; --, not applicable; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HAL, health advisory level]

| Well characteristics and physical and chemical properties | Units | Number (percent) above reporting level | Minimum | Median | Maximum | Number (percent) exceeding standard | EPA MCL | EPA SMCL | EPA HAL |
|---|---------------------------|--|---------|--------|---------|-------------------------------------|---------|----------|---------|
| Total dissolved solids | mg/L | 73 (97) | <20 | 132 | 1,687 | 3 (4) | -- | 500 | -- |
| Total solids | mg/L | 75 (100) | 32 | 131 | 1,800 | -- | -- | -- | -- |
| Hardness, total | mg/L as calcium carbonate | 75 (100) | 0.58 | 65.8 | 361 | -- | -- | -- | -- |
| Major ions (dissolved and total) | | | | | | | | | |
| Calcium, dissolved | mg/L | 75 (100) | 0.22 | 18.7 | 88.9 | -- | -- | -- | -- |
| Calcium, total | mg/L | 75 (100) | 0.18 | 18.8 | 88.0 | -- | -- | -- | -- |
| Magnesium, dissolved | mg/L | 75 (100) | 0.05 | 3.80 | 37.3 | -- | -- | -- | -- |
| Magnesium, total | mg/L | 75 (100) | 0.03 | 3.38 | 36.9 | -- | -- | -- | -- |
| Sodium, dissolved | mg/L | 75 (100) | 0.49 | 9.50 | 609 | 121 (28) | -- | 30–60 | 20 |
| Sodium, total | mg/L | 75 (100) | 0.5 | 9.6 | 639 | 121 (28) | -- | 30–60 | 20 |
| Potassium, dissolved | mg/L | 75 (100) | 0.22 | 0.74 | 2.98 | -- | -- | -- | -- |
| Potassium, total | mg/L | 59 (79) | <0.5 | 0.71 | 3.48 | -- | -- | -- | -- |
| Alkalinity, dissolved | mg/L as calcium carbonate | 75 (100) | 7.1 | 85.9 | 330.6 | -- | -- | -- | -- |
| Bromide, dissolved | mg/L | 12 (16) | <0.03 | <0.03 | 2.710 | -- | -- | -- | -- |
| Chloride, dissolved | mg/L | 75 (100) | 0.50 | 6.11 | 938 | 2 (3) | -- | 250 | -- |
| Chloride, total | mg/L | 69 (92) | <1 | 6.8 | 464 | 2 (3) | -- | 250 | -- |
| Fluoride, dissolved | mg/L | 75 (100) | 0.014 | 0.09 | 0.777 | 0 (0) | 4 | 2 | -- |
| Sulfate, dissolved | mg/L | 75 (100) | 0.27 | 8.80 | 62.6 | 0 (0) | -- | 250 | 500 |
| Sulfate, total | mg/L | 71 (95) | <1 | 9.6 | 64.1 | 0 (0) | -- | 250 | 500 |
| Silica, dissolved | mg/L as silica | 75 (100) | 3.54 | 8.91 | 21.4 | -- | -- | -- | -- |

Table 3. Minimum, median, and maximum of well characteristics, physical and chemical properties, major ions, nutrients, and bacteria determined in the laboratory for water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for dissolved concentrations in filtered samples done by U.S. Geological Survey National Water Quality Laboratory, and laboratory analysis for total concentrations in unfiltered samples done by Seewald Laboratories Incorporated.—Continued

[°C, degrees Celsius; mg/L, milligram per liter; μ S/cm, microsiemen per centimeter; MPN/100mL, most probable number per 100 milliliters; <, less than; --, not applicable; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HAL, health advisory level]

| Well characteristics and physical and chemical properties | Units | Number (percent) above reporting level | Minimum | Median | Maximum | Number (percent) exceeding standard | EPA MCL | EPA SMCL | EPA HAL |
|---|---------------------|--|---------|--------|---------|-------------------------------------|---------|----------|---------|
| Nutrients (dissolved or total) | | | | | | | | | |
| Kjehldahl nitrogen, total | mg/L as nitrogen | 75 (100) | <0.84 | <0.84 | 2.44 | -- | -- | -- | -- |
| Ammonia, dissolved | mg/L as nitrogen | 35 (47) | <0.01 | <0.01 | 0.556 | 0 (0) | -- | -- | 30 |
| Nitrite, dissolved | mg/L as nitrogen | 17 (23) | <0.001 | <0.001 | 0.127 | 0 (0) | 1 | -- | -- |
| Nitrate + Nitrite, dissolved | mg/L as nitrogen | 55 (73) | <0.04 | 0.412 | 8.84 | 0 (0) | 10 | -- | -- |
| Orthophosphate, dissolved | mg/L as phosphorous | 63 (84) | <0.004 | 0.013 | 0.127 | -- | -- | -- | -- |
| Bacteria (total) | | | | | | | | | |
| Total coliform | MPN/100mL | 39 (52) | <1 | 3 | 2,420 | 39 (52) | <1 | -- | -- |
| <i>Escherichia coli</i> | MPN/100mL | 10 (13) | <1 | <1 | 153 | 10 (13) | 0 | -- | -- |

¹21 samples (28 percent) exceed HAL of 20 mg/L and 6 samples (8 percent) exceed upper SMCL limit of 60 mg/L.

greater than 7.5. Low DO concentrations are related to chemical or biochemical reactions that consume oxygen and may be associated with reducing conditions that promote the release of iron, manganese, and associated metals to solution. The chemical reactions that consume oxygen generally involve organic carbon that can be naturally present in soil or aquifer materials or can be introduced from industrial, agricultural, or domestic wastes. Of the 75 well samples in this study, 19 percent were classified as “anoxic” (DO less than or equal to \leq 0.5 mg/L), 68 percent as “oxic” (DO >0.5 mg/L), and 13 percent as “mixed” (DO >0.5 mg/L with manganese >0.05 mg/L or iron >0.1 mg/L) based on criteria of McMahon and Chapelle (2008). Only 4 of the 14 samples classified as anoxic had chemical characteristics consistent with reducing conditions for iron and manganese oxides as defined by McMahon and Chapelle (2008); DO \leq 0.5 mg/L; nitrate <0.5 mg/L, manganese >0.05 mg/L, iron >0.1 mg/L, and sulfate >0.5 mg/L; none were identified with more strongly reducing conditions necessary for sulfate reduction or methanogenesis.

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 pipes and plumbing. The standard pH scale is 0 to 14, with 7 being neutral. Generally, pH

values of 6.5 to 7.5 are considered near neutral, values <6.5 are considered acidic, and values >7.5 are considered basic or alkaline. The pH of water samples collected in Lycoming County ranged from 5.3 to 9.15; the median pH was 7.33. The pH of 25 of the 75 samples (33 percent) was outside the EPA SMCL range of 6.5 to 8.5 (U.S. Environmental Protection Agency, 2012). Seventeen samples had a pH less than 6.5, and eight samples had a pH greater than 8.5 (table 3). Generally, the pH varied widely within and among the lithologic classes; median pH values were greatest for shale (7.69), least for sandstone (7.01), and intermediate for carbonate (7.33) and siltstone (7.18) classes (fig. 5).

The ALK of a solution indicates its capacity to neutralize acid and commonly results from dissolved carbonate and bicarbonate ions (Hem, 1985, p. 106). ALK, also referred to as the acid neutralizing capacity, is related to the pH of a water sample. In general, water samples with a higher pH have a higher ALK. ALK ranged from 7.1 to 331 mg/L as calcium carbonate; the median concentration was 85.9 mg/L (table 3). The estimated concentration of ALK to achieve ionic balance ranged from 9.8 to 300 mg/L as calcium carbonate (fig. 4). The highest alkalinities were from carbonate lithologies and the lowest were from sandstone.

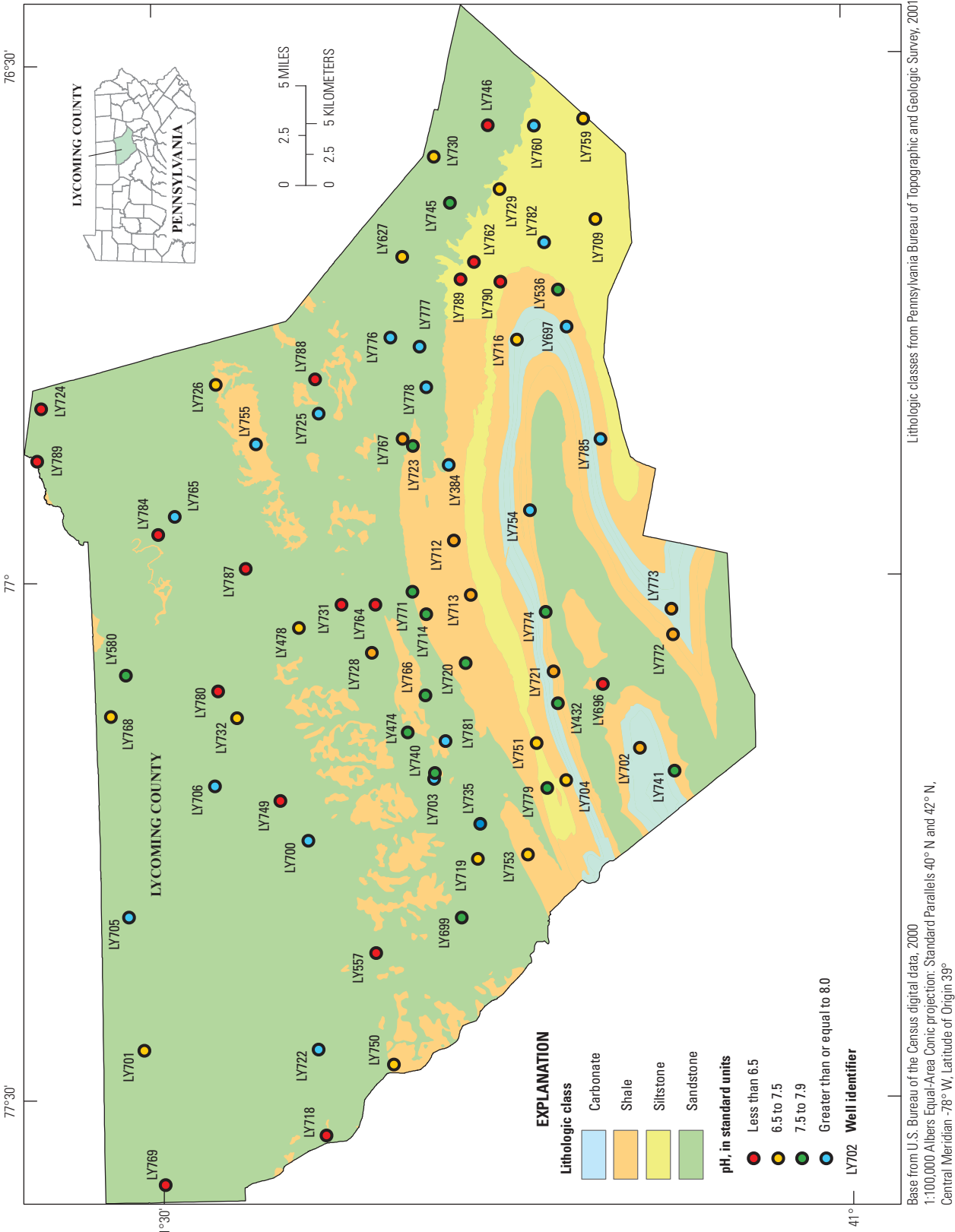


Figure 5. Lithologic classes and spatial distribution of pH concentrations in groundwater samples collected from 75 wells in Lycoming County, Pennsylvania.

Hardness of the 75 well-water samples (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) ranged from <0.58 to 361 mg/L as calcium carbonate, with a median value of 65.8 mg/L as calcium carbonate. Hardness generally results from the dissolution of calcium- and magnesium-bearing minerals, such as calcite and dolomite, that are commonly associated with limestone and other calcareous sedimentary rocks. Hard water decreases lathering of soap and increases accumulation of mineral deposits in plumbing and cooking utensils. Using a common hardness classification (Dufor and Becker, 1964), the measured values indicate that 34 (45 percent) of the 75 water samples are soft (<60 mg/L as calcium carbonate); 29 samples (39 percent) are moderately hard (61 to 120 mg/L as calcium carbonate); 7 samples (9 percent) are hard (121 to 180 mg/L as calcium carbonate); and 5 samples (7 percent) are classified as very hard (greater than 180 mg/L as calcium carbonate). Median hardness values were 329, 86, 73, and 44 mg/L as calcium carbonate for carbonate, shale, siltstone, and sandstone lithologies, respectively. Hardness varied with pH, with hardness generally greatest at near-neutral pH values (6.5 to 7.5). Water samples with low pH (<6.5) and very high pH (>8.0) typically had hardness <60 mg/L and were soft. The high-pH waters with low hardness typically have elevated sodium, which results from natural water-softening processes, described later in “Relations Among Constituents in Groundwater” section. There are no health-related standards established specifically for hardness in drinking water.

Hard water has greater potential than soft water to form scale or encrustations on plumbing and fixtures. Water resources engineers commonly identify the potential for encrustation or corrosion on the basis of the Langelier Index (LI), which provides an indication for the potential for lead and copper to enter water supplies from pipes and plumbing (Snoeyink and Jenkins, 1981). The LI, which is the difference between the measured pH and the pH at equilibrium with calcium carbonate, is equal in value to the calcite saturation index (SI_{CAL}), evaluated in more detail later. If the LI or SI_{CAL} is positive, the pH is greater than that at equilibrium with calcium carbonate and the water will tend to deposit calcium carbonate coating or scale that can insulate pipes, boilers and other components of a system from contact with water; however, if negative, then the water is undersaturated with calcium carbonate and will tend to be corrosive in the distribution system. The optimum condition is when the LI or SI_{CAL} is close to zero, whereby the water will be neither strongly corrosive nor scale forming. For the 75 groundwater samples, SI_{CAL} ranged from -5.0 to 0.2. Of the 75 samples, 31 (41 percent) had LI values that were <-1, indicating potentially strongly corrosive characteristics; the remaining samples would be considered neither strongly corrosive nor scale forming. Most samples characterized as strongly corrosive had pH values <7 and hardness <90 mg/L as calcium carbonate.

Specific conductance (SC) is a gross measure of the ability of ions in water to conduct an electrical current and is

expressed in units of microsiemens per centimeter. The higher the value for SC, the higher the concentrations of dissolved solids and associated ions in the water (fig. 4). The field-measured SC for the 75 groundwater samples ranged from 24.7 to 3,193 microsiemens per centimeter at 25 °C ($\mu\text{S}/\text{cm}$; fig. 4F); the median specific conductance was 214 $\mu\text{S}/\text{cm}$ (table 3). Values were similar for the laboratory-measured SC (fig. 4 and table 3). Explanations for ionic source of elevated SC are provided later.

Turbidity is a measure of the amount of solid particles suspended in water that block the transmission of light through the sample. Turbidity is expressed in Nephelometric Turbidity Ratio Units (NTRU), which quantify the degree to which light is scattered by solid particles suspended in water. When the NTRU is high, the turbidity of the water increases. Turbidity concentrations ranged from 0.13 to 180 NTRU; the median concentration was 1.12 NTRU (table 3). In general, samples with high turbidity could be expected to have total concentrations of constituents that include contributions from suspended particles, in addition to the dissolved concentration.

Major Ions

Major ions dissolved from soil and rock contribute most of the naturally present dissolved solutes in groundwater. The remainder comes mostly from constituents dissolved in precipitation. Anthropogenic sources, such as road-deicing chemicals, can also contribute to major ion concentrations. Major ions generally account for most of the dissolved constituents in groundwater and consist of positively charged cations (calcium, magnesium, sodium, and potassium) balanced by negatively charged anions (bicarbonate, chloride, nitrate, sulfate, and fluoride). Silica is a major constituent that is commonly an uncharged ion. Major ions were analyzed for filtered and unfiltered samples to represent both dissolved and total concentrations. Drinking-water standards have been established for only a few major ions and are commonly either a SMCL or HAL, both of which are recommended rather than regulatory standards. Of the major ions, only fluoride has an established MCL in drinking water because excessive consumption of fluoride can damage bone tissue. Summary statistics for major ions are given in table 3. Major ions, in order of decreasing median dissolved concentration, were calcium, sodium, silica, sulfate, chloride, magnesium, potassium, fluoride, and bromide.

Total dissolved solids (TDS) are a measurement of the total solute in water and are measured by evaporating the water and weighing the residue. The TDS concentration ranged from < 20 to 1,687 mg/L; the median concentration was 132 mg/L. Out of 75 samples, 3 samples (4 percent) exceeded 500 mg/L, which is the EPA SMCL for TDS in drinking water. The three samples with elevated TDS also had the highest concentrations of sodium and chloride out of all 75 samples and were from the Catskill and Lock Haven Formations (fig. 2). Elevated sodium and chloride concentrations could be caused by connate water in the formations and a zone

of restricted groundwater flow that limits flushing by fresh recharge, mixing of saline and freshwater, or by the introduction of salt from near-surface contaminant sources such as road-deicing salts, water softener additives, effluent from septic systems, or animal waste (Mullaney and others, 2009).

Dissolved concentrations of sodium ranged from 0.49 to 609 mg/L; the median concentration was 9.5 mg/L. The EPA has issued a taste threshold for sodium in public water supplies that recommends reducing sodium concentrations to between 30 and 60 mg/L (U.S. Environmental Protection Agency, 2003). This recommendation is a guideline that is not federally enforceable. The EPA HAL for sodium in drinking water is 20 mg/L. Out of 75 samples, 21 samples (28 percent) exceeded the HAL of 20 mg/L, whereas 6 samples (8 percent) exceeded the taste threshold upper limit of 60 mg/L. Salt used for food, road deicing, and other applications consists of sodium chloride. Thus, high concentrations of sodium and chloride may result from the addition of sodium chloride to the groundwater and may be related to land use as well as the lithology. Dissolved concentrations of chloride ranged from 0.5 to 938 mg/L; the median concentration was 6.11 mg/L (fig. 6). Out of 75 samples, 2 samples (3 percent) exceeded the EPA SMCL of 250 mg/L for chloride in drinking water.

Nutrients

Nutrients include nitrogen and phosphorous species. Nitrogen compounds in water include nitrate as nitrogen, nitrite, and ammonia, whereas phosphorus is present mainly as orthophosphate. Nutrients are essential for plant growth; however, the presence of elevated nutrient concentrations generally is an indicator of anthropogenic sources, which might include fertilizers, storm runoff, animal wastes, and effluent from septic systems. Summary statistics for nutrients are given in table 3. Nitrate is the most prevalent nitrogen species in oxic groundwater, but all nitrate concentrations were still less than the EPA MCL of 10 mg/L for nitrate as nitrogen (table 3). Excessive nitrate in drinking water causes a health threat, especially in infants, because it disrupts oxygen flow in the blood. Infants below the age of 6 months who drink water containing nitrate in excess of the MCL could become seriously ill, develop symptoms including shortness of breath and blue-baby syndrome, and may die if left untreated. Because concentrations of nitrite are so low, nitrate plus nitrite concentrations essentially represent nitrate concentrations. The concentration of nitrate ranged from <0.04 to 8.84 mg/L as nitrogen; the median concentration was 0.412 mg/L as nitrogen. The concentration of orthophosphate ranged from <0.004 to 0.127 mg/L with a median of 0.013 mg/L.

Bacteria

All samples were analyzed for total coliform and *Escherichia coli* (*E. coli*) to help to determine the associated human-health risk of potentially pathogenic (disease-causing) water-borne microorganisms. Coliform bacteria are ubiquitous in the environment and are not always pathogenic. Some strains of *E. coli*, such as O157:H7, can cause severe illness, and the presence of *E. coli* may indicate general fecal contamination because of the strong association of *E. coli* with the intestines of warm-blooded animals. 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), and these EPA criteria can be used to provide a reference point for domestic wells.

Total coliform bacteria were detected in 39 of the 75 groundwater samples (52 percent) (table 3). Total coliform concentrations ranged from <1 colonies per 100 milliliters (reported as most probable number per 100 milliliters [MPN/100mL]) to 2,420 MPN/100mL. Of the 39 samples that had total coliform bacteria, 10 samples had detectable *E. coli*, with concentrations ranging from 3 to 153 MPN/100mL.

Metals and Trace Elements

Metals and other trace elements are typically present in concentrations <1 mg/L in natural waters (Hem, 1985). Most metals and trace elements in groundwater are leached from soil or dissolved from underlying bedrock by groundwater, but some are present in precipitation. Summary statistics for metals and trace elements are listed in table 4.

The EPA has established MCLs, SMCLs, and HALs as the concentration of specific metals and trace elements in drinking water (tables 2 and 4). Samples from 9 wells (12 percent) exceeded the EPA MCL for arsenic, whereas 20 samples (27 percent) exceeded the SMCL for total iron or total manganese. Two samples (3 percent) exceeded 300 µg/L, which is the EPA HAL for total manganese (U.S. Environmental Protection Agency, 2012). If considering the dissolved concentration, the number of samples exceeding these criteria decreases (table 4). As mentioned previously, the replicate sample collected from LY789 had a copper concentration 36.95 µg/L greater than the environmental sample concentration (100-percent increase) and a zinc concentration 5.743 µg/L greater than the environmental sample concentration (272-percent increase). Out of the 75 wells sampled, if the highest resulting concentrations of copper and zinc were increased by 100 percent and 272 percent, respectively, the highest copper concentration would be 289.4 µg/L and the

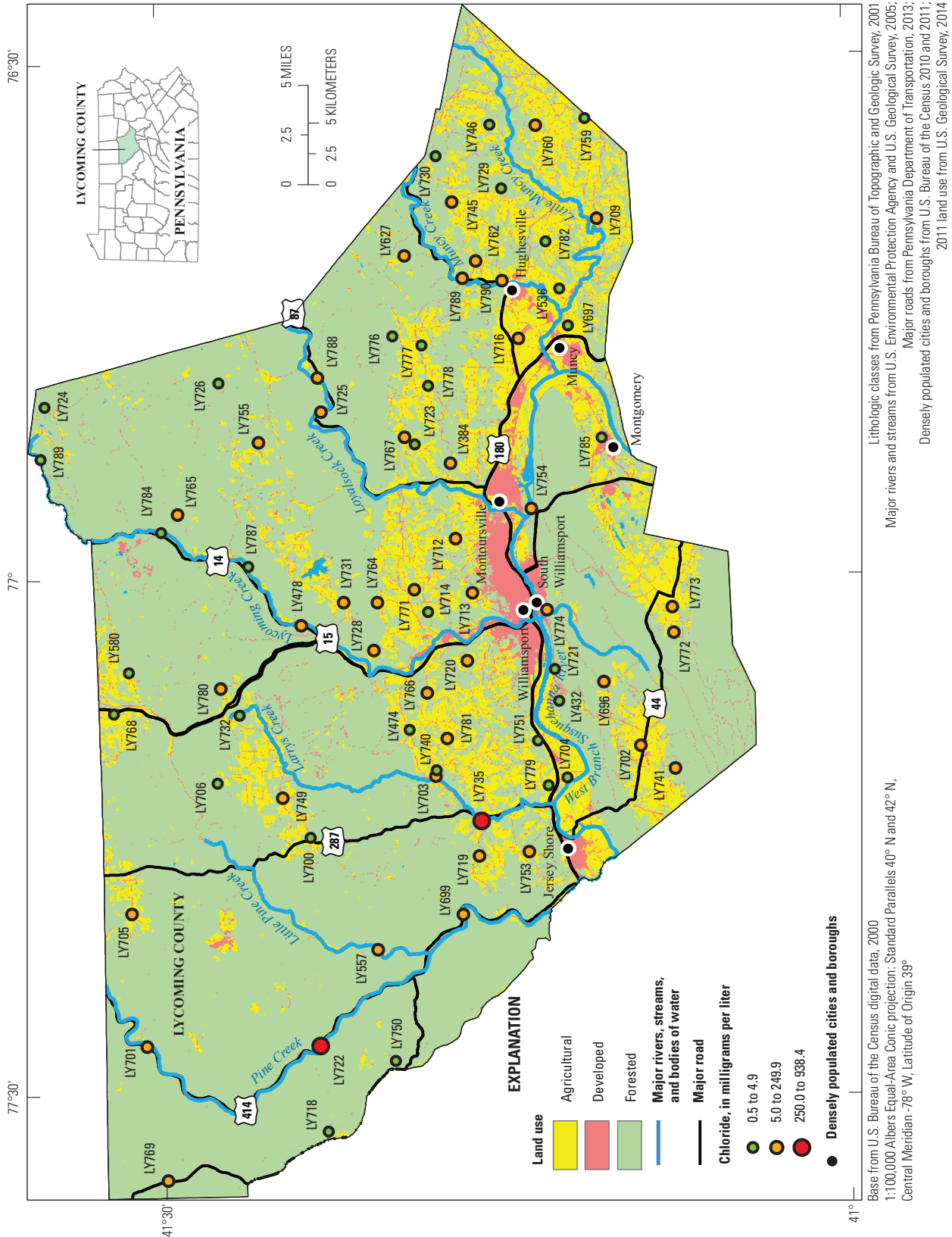


Figure 6. Spatial distribution of chloride concentrations in groundwater samples collected from 75 wells and land use in Lycoming County, Pennsylvania.

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Table 4. Minimum, median, and maximum concentrations of metals and trace elements for water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for dissolved concentrations in filtered samples done by U.S. Geological Survey National Water Quality Laboratory, and laboratory analysis for total concentrations in unfiltered samples done by Seewald Laboratories Incorporated.

[µg/L, microgram per liter; <, less than; --, no data or not applicable; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum level; HAL, health advisory level]

| Metals and trace elements | Units | Number (percent) above reporting level | Minimum | Median | Maximum | Number (percent) exceeding standard | EPA MCL | EPA SMCL | EPA HAL |
|--|-------|--|---------|--------|---------|-------------------------------------|---------|----------|---------|
| Dissolved constituent (filtered samples) | | | | | | | | | |
| Aluminum | µg/L | 34 (45) | <2.2 | <2.2 | 38.3 | 0 (0) | -- | 50–200 | -- |
| Antimony | µg/L | 36 (48) | <0.027 | <0.027 | 1.69 | 0 (0) | 6 | -- | -- |
| Arsenic | µg/L | 62 (83) | <0.10 | 0.85 | 23.6 | ¹ 9 (12) | 10 | -- | 2 |
| Beryllium | µg/L | 6 (8) | <0.020 | <0.020 | 0.09 | 0 (0) | 4 | -- | -- |
| Boron | µg/L | 68 (91) | <5 | 16.7 | 561 | 0 (0) | -- | -- | 7,000 |
| Cadmium | µg/L | 4 (5) | <0.030 | <0.030 | 0.06 | 0 (0) | 5 | -- | -- |
| Chromium | µg/L | 2 (3) | <0.30 | <0.30 | 0.98 | 0 (0) | 100 | -- | -- |
| Cobalt | µg/L | 27 (36) | <0.050 | <0.050 | 5.82 | -- | -- | -- | -- |
| Copper | µg/L | 53 (71) | <0.80 | 2.48 | 145 | 0 (0) | 1,300 | -- | 1,000 |
| Lead, dissolved | µg/L | 58 (77) | <0.040 | 0.16 | 2.03 | 0 (0) | 15 | -- | -- |
| Lithium | µg/L | 75 (100) | 0.409 | 10.7 | 523 | -- | -- | -- | -- |
| Molybdenum | µg/L | 64 (85) | <0.05 | 0.316 | 6.52 | 0 (0) | -- | -- | 40 |
| Nickel | µg/L | 55 (73) | <0.20 | 0.376 | 7.25 | 0 (0) | -- | -- | 100 |
| Selenium | µg/L | 49 (65) | <0.05 | 0.088 | 6.13 | 0 (0) | 50 | -- | -- |
| Silver | µg/L | 1 (1) | <0.020 | <0.020 | 0.04 | 0 (0) | -- | 100 | -- |
| Zinc | µg/L | 54 (72) | <2.0 | 3.42 | 366.3 | 0 (0) | -- | 5,000 | 2,000 |
| Dissolved and total constituents (filtered and unfiltered samples) | | | | | | | | | |
| Barium, dissolved | µg/L | 75 (100) | 1.26 | 81.8 | 3,262 | 0 (0) | 2,000 | -- | -- |
| Barium, total | µg/L | 75 (100) | 1.7 | 88 | 3,460 | 0 (0) | 2,000 | -- | -- |
| Iron, dissolved | µg/L | 48 (64) | <4.0 | 7.16 | 8,340 | 3 (4) | -- | 300 | -- |
| Iron, total | µg/L | 59 (79) | <10.0 | 71.4 | 13,900 | 20 (27) | -- | 300 | -- |
| Manganese, dissolved | µg/L | 56 (75) | <0.40 | 2.08 | 1,100 | ² 12 (16) | -- | 50 | 300 |
| Manganese, total | µg/L | 64 (85) | <0.50 | 14.6 | 761 | ³ 20 (27) | -- | 50 | 300 |
| Strontium, dissolved | µg/L | 75 (100) | 4.919 | 232 | 3,872 | 0 (0) | -- | -- | 4,000 |
| Strontium, total | µg/L | 73 (97) | <10.0 | 240 | 4 | 1(1) | -- | -- | 4,000 |

¹4 samples exceed the MCL of 10 µg/L and 23 samples (31 percent) exceed the HAL of 2 µg/L for arsenic.

²12 samples (16 percent) exceed the SMCL level of 50 µg/L and 1 (1 percent) sample exceeds the HAL of 300 µg/L for dissolved manganese.

³20 samples (27 percent) exceed the SMCL level of 50 µg/L and 2 (3 percent) samples exceed the HAL of 300 µg/L for total manganese.

highest zinc concentration would be 1,362.6 µg/L, which are less than established drinking-water standards.

Arsenic concentrations ranged from < 0.10 to 23.6 µg/L with a median concentration of 0.85 µg/L (fig. 7). Arsenic concentration is related to pH (fig. 8). All nine samples with arsenic concentrations exceeding the EPA MCL of 10 µg/L had pH greater than 7.0; six had pH greater than 8.0. Arsenate and arsenite, 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 the 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 a later section of this report. Possible health effects associated with ingestion of drinking water with arsenic in excess of the MCL for many years include skin damage, circulatory system problems, and increased cancer risk.

Water samples with a pH of 8.0 or greater also had the highest concentrations of boron, bromide, lithium, fluoride, and sodium (figs. 9, 10). In addition, water samples with a pH greater than 8.67 had nickel and zinc concentrations less than the detection limit. Generally, the decreased concentrations of trace cations, such as nickel and zinc, with increased pH may be explained by their strong adsorption at alkaline pH by iron oxides, whereas the increased concentrations of trace anions, such as arsenic, may result from their desorption at alkaline pH. The increased concentrations of sodium and lithium could result from cation-exchange reactions. The potential effects of ion exchange and other geochemical processes on pH and associated constituent concentrations are developed more completely in the following sections of this report.

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. Large doses of manganese can cause headaches, whereas long-term heavy exposure may result in nervous-system disorders. Concentrations of total iron ranged from <10.0 to 13,900 µg/L, with a median of 71.4 µg/L; dissolved iron ranged from <4.0 to 8,340 µg/L, with a median of 7.16 µg/L. Concentrations of total manganese ranged from <0.50 to 761 µg/L, with a median of 14.6 µg/L; dissolved manganese ranged from <0.40 to 1,100 µg/L, with a median of 2.08 µg/L. Twenty of these samples (27 percent) exceeded the EPA SMCL of 300 µg/L for total iron; however, only three samples (4 percent) had dissolved iron concentrations greater than 300 µg/L. Likewise, 20 samples (27 percent) had total manganese concentrations that exceeded the EPA SMCL of 50 µg/L, but only 12 (16 percent) had dissolved manganese concentrations greater than the SMCL. Two samples (3 percent) had total manganese concentrations in excess of the 300 µg/L EPA HAL for manganese (U.S. Environmental Protection Agency, 2012).

Although none of the well-water samples had concentrations of lead or copper in excess of the respective MCL values of 15 and 1,300 µg/L, corrosive water, as previously described by the LI or $SI_{CAL} < -1$, could acquire metals from lead or copper pipes in the household water system. Long-term exposure to excess copper can cause liver or kidney damage, whereas lead can cause neurological problems, especially in young children. Depending on water treatment, the corrosive characteristics may or may not be mitigated. Sampling at the tap would produce results describing actual concentrations of constituents in the household drinking water and could be used to evaluate the potential effects of water treatment, but this study was designed to evaluate constituent concentrations within the aquifer where the household well is completed, rather than the tap water being expelled within the household.

Radionuclides

Radionuclides naturally present in rocks and soils may be dissolved or leached into groundwater. Analyses for radioactivity 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. Summary statistics for radioactive constituents are given in table 5. The EPA has established or proposed MCLs for some of these constituents in drinking water (table 2).

Radioactivity is the release of energy and energetic particles by changes in the structure of certain unstable elements as they break down to form more stable arrangements. Radioactive energy is released as (1) alpha radiation consisting of positively charged helium nuclei, (2) beta radiation consisting of electrons or positrons, and (3) gamma radiation consisting of electromagnetic waves. The most commonly used unit for radioactivity in water is picocuries per liter. One Curie is the activity of 1 gram of radium, which is equal to 3.7×10^{10} atomic disintegrations per second. Activity refers to the number of particles emitted by a radionuclide. The rate of decay is proportional to the number of atoms present and inversely proportional to half-life. The half-life is the amount of time it takes for a radioactive element to decay to one-half of its original quantity.

Naturally present radioactivity in groundwater is produced primarily by the radioactive decay of uranium-238 and thorium-232, which are present in minerals. These isotopes disintegrate in steps emitting either alpha or beta particles and forming a series of radioactive nuclide “daughter” products, mostly short-lived, until a stable lead isotope is produced. The uranium-238 decay series produces the greatest amount of radioactivity in natural groundwater (Hem, 1985, p. 147). Uranium-238 has a half-life of 4.5 billion years. Its daughter products include radium-226 (half-life of 1,620 years) and radon-222 (half-life of 3.8 days). Radon-222, a decay product of radium-226, is a colorless, odorless, chemically inert,

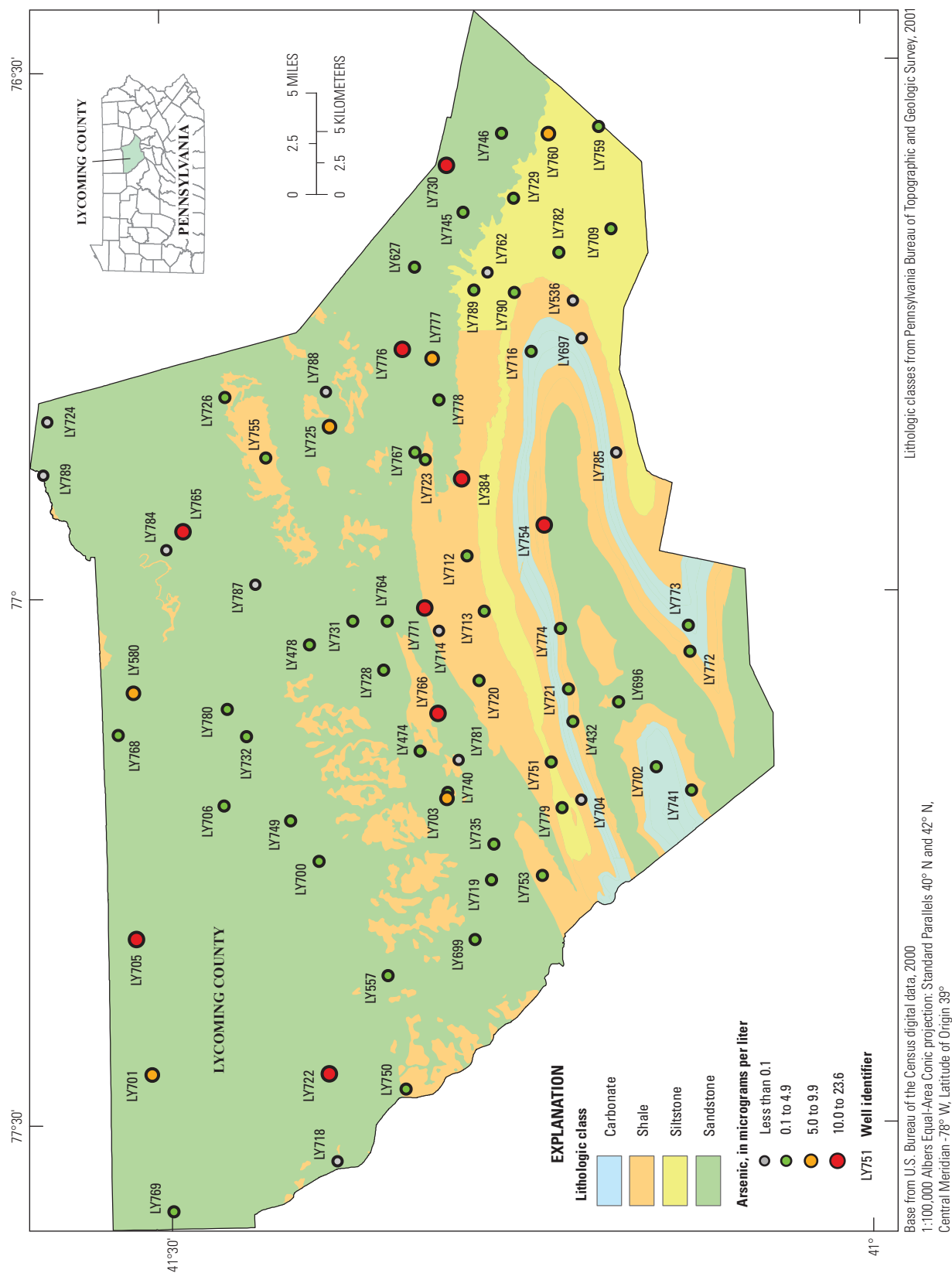


Figure 7. Spatial distribution of arsenic concentrations in groundwater samples collected from 75 wells and lithologic classes in Lycoming County, Pennsylvania.

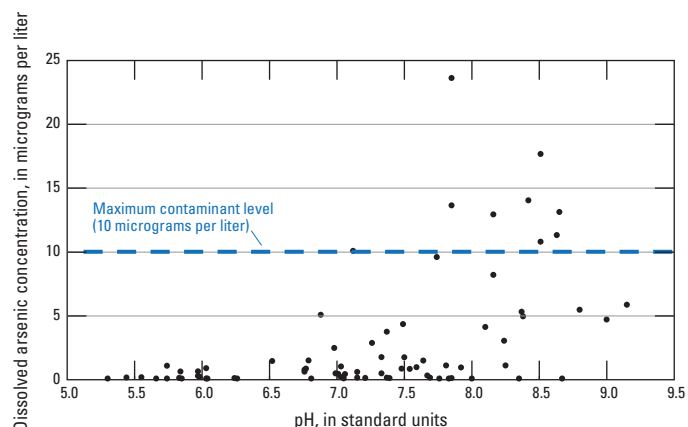


Figure 8. Relation between pH and arsenic concentration in groundwater samples collected from 75 wells in Lycoming County, Pennsylvania.

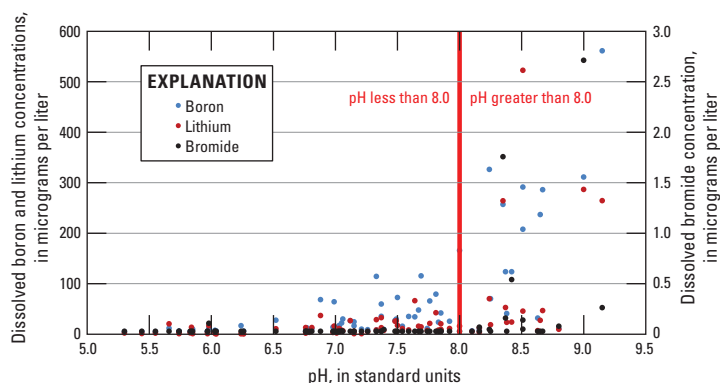


Figure 9. Relation between pH and boron, bromide, and lithium concentrations in groundwater samples collected from 75 wells in Lycoming County, Pennsylvania.

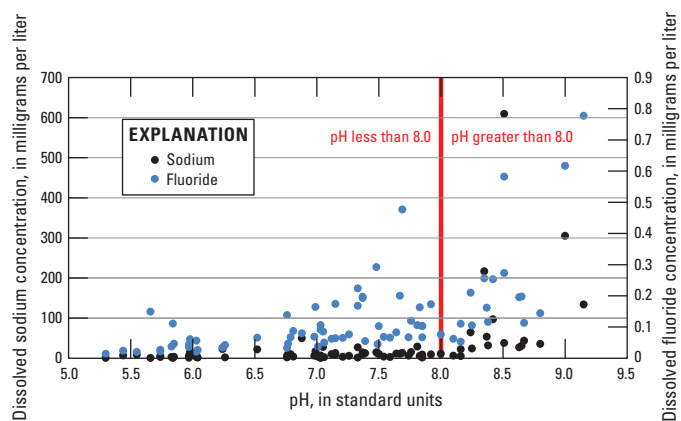


Figure 10. Relation between pH and fluoride and sodium concentrations in groundwater samples collected from 75 wells in Lycoming County, Pennsylvania.

alpha-particle-emitting gas, which is soluble in water. The end product of the decay series is the stable isotope lead-206.

Activities of radon-222 in water from the 75 sampled wells ranged from less than the detection limit to 7,420 pCi/L with a median activity of 863 pCi/L (table 5). 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. Because indoor air radon-222 is the second leading cause of lung cancer, the EPA proposed a drinking-water MCL of 300 pCi/L for radon-222 for States without an enhanced indoor air program. Water samples from 50 of the 75 wells sampled (67 percent) exceeded the proposed EPA MCL of 300 pCi/L, and 3 samples (4 percent) exceeded the proposed EPA AMCL of 4,000 pCi/L for radon-222.

The gross alpha-particle radioactivity (72-hour count) in water from the 75 sampled wells ranged from less than the detection limit to 6.4 pCi/L; the median activity level was 0.53 pCi/L (table 5). Alpha particles are counted at 72 hours and 30 days because some alpha-particle emitters, such as radium-224 (half-life of 3.6 days), would not be present in the 30-day count. Gross alpha-particle activity in the 30-day count was similar to the activity in the 72-hour count (table 5). No water samples exceeded the EPA MCL of 15 pCi/L for gross alpha-particle activity (table 2).

The gross-beta particle radioactivity (72-hour count) ranged from less than the detection limit to 11.0 pCi/L. Gross beta-particle activity in the 30-day count was similar to the activity in the 72-hour count in about one-half of the samples (table 5). The concentration of uranium ranged from <0.014 to 7.65 µg/L. The median concentration was 0.113 µg/L. No water samples exceeded the EPA MCL of 30 µg/L for uranium.

A subset of samples collected from 10 wells were analyzed for the radium isotopes radium-226 and radium-228. Concentrations (activities) of radium-226 ranged from 0.028 to 0.2 pCi/L in water samples, whereas activities of radium-228 ranged from non-detect to 0.5 from the 10 wells. Activities were less than the drinking-water standard of 5 pCi/L for combined radium-226 and radium-228. The highest activities of radium-226 and radium-228 were in water samples collected from the same well. Although the well with the highest radium-226 and radium-228 activities did also exhibit the highest 30-day gross alpha activity among the subset of 10 wells sampled, it did not exhibit correspondingly high 30-day gross beta activity or 72-day gross alpha or beta activities.

Table 5. Minimum, median, and maximum concentrations of radionuclides for water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for total concentrations of gross alpha and beta in unfiltered samples and radium-226 and radium-228 concentrations in filtered samples from a subset of wells done by TestAmerica, Inc. and dissolved concentrations in filtered samples done by U.S. Geological Survey National Water Quality Laboratory.

[nd, not detected; pCi/L, picocuries per liter; µg/L, microgram per liter; <, less than; --, no data or not applicable; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; HAL, health advisory level]

| Radionuclides | Units | Number (percent) above reporting level | Minimum | Median | Maximum | Number (percent) exceeding standard | EPA MCL | EPA HAL |
|---|-------|--|---------|--------|---------|--|----------------------|------------|
| Total (unfiltered sample) | | | | | | | | |
| Gross alpha radioactivity, 30-day recount | pCi/L | 40 (53) | nd | 0.77 | 6.7 | 0 (0) | 15 | -- |
| Gross alpha radioactivity, 72-hour count | pCi/L | 34 (45) | nd | 0.53 | 6.4 | 0 (0) | 15 | -- |
| Gross beta radioactivity, 30-day recount | pCi/L | 52 (69) | nd | 1.8 | 13.0 | 0 (0) | 4 millirems per year | -- |
| Gross beta radioactivity, 72-hour count | pCi/L | 44 (59) | nd | 1.5 | 11.0 | 0 (0) | 4 millirems per year | -- |
| Radon-222 | pCi/L | 72 (96) | nd | 863 | 7,420 | 50 (67) | ¹ 300 | -- |
| Dissolved (filtered sample) | | | | | | | | |
| Uranium (natural) | µg/L | 54 (72) | <0.014 | 0.113 | 7.65 | 0 (0) | 30 | 20 |
| Radium-226 and Radium-228 (filtered sample collected from a subset of 10 wells) | | | | | | | | |
| Radium-226 | pCi/L | 10 (100) | 0.028 | 0.07 | 0.2 | 0 (0) | ² 5 | -- |
| Radium-228 | pCi/L | 5 (50) | nd | nd | 0.5 | 0 (0) | ² 5 | -- |

¹50 samples (67 percent) exceed proposed MCL of 300 pCi/L and 3 samples (4 percent) exceed proposed alternative MCL of 4,000 pCi/L.

²MCL of 5 pCi/L is combined radium-226 and radium-228.

Dissolved Methane and Other Naturally Occurring Hydrocarbon Gases

Water sampled from the 75 wells had concentrations of dissolved methane (table 6) ranging from <0.01 to 16.8 mg/L, plus lower to non-detectable concentrations of other more complex hydrocarbon gases, including ethane, ethylene, propane, propylene, iso-butane, and N-butane. None of the samples had detectable concentrations of the dissolved hydrocarbons iso-pentane, N-pentane, and hexane.

Only 15 of the 75 wells sampled (20 percent) had dissolved methane concentrations greater than the reporting level of <0.01 mg/L (table 6). The median dissolved methane concentration was <0.01 mg/L, and the 15 detected concentrations ranged from 0.4 to 16.8 mg/L (table 6). Two of the samples (3 percent) had dissolved methane concentrations that exceeded the Pennsylvania action level of 7 mg/L (Commonwealth of Pennsylvania, 2014). Most samples with detectable concentrations of methane had alkaline pH; 13 of 15 water samples in which methane was detected had pH greater than 7.5 (fig. 11). Eight of these 13 samples also had low concentrations of DO (<0.5 mg/L; fig. 11).

Manmade Organic Compounds

All samples were analyzed for 77 selected manmade organic compounds, including 66 VOCs, 10 glycols and alcohols, and oil and grease (table 7). Out of these manmade organic compounds, five were measured in detectable concentrations in five of the 75 wells sampled (7 percent). The following four VOCs were detected in four wells: chloromethane, methyl *tert*-butyl ether, methyl ethyl ketone, and trichloromethane (the only trihalomethane detected). Also, oil and grease were detected in one well.

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 present in groundwater include industrial solvents, fuel hydrocarbons and oxidizers, fumigants, organic synthesis compounds, refrigerants, and disinfection byproducts (trihalomethanes) (Carter and others, 2007). VOCs are the most commonly found contaminant class associated with industrial and commercial sites, dumps,

Table 6. Minimum, median, and maximum concentrations of methane and ethane determined in the laboratory for water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for total concentrations in unfiltered samples done by Seewald Laboratories Incorporated.

[mg/L, milligram per liter; µg/L, microgram per liter; <, less than; --, no data or not applicable]

| | Units | Number (percent) above reporting level | Minimum | Median | Maximum | Number (percent) exceeding Penn- sylvania action level |
|---------|-------|--|---------|--------|---------|---|
| Methane | mg/L | 15 (20) | <0.01 | <0.01 | 16.8 | ¹ 2 (3) |
| Ethane | µg/L | 2 (3) | <10 | <10 | 47.8 | -- |

¹Two samples had methane concentrations (13.1 and 16.8 mg/L) exceeding the Pennsylvania action level of 7 mg/L (Commonwealth of Pennsylvania, 2014).

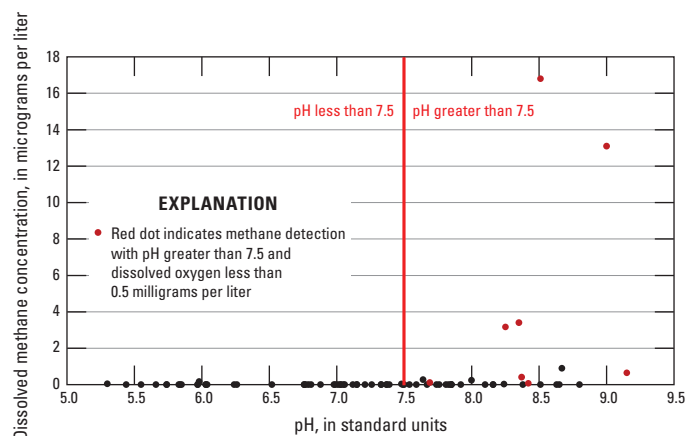


Figure 11. Relation between pH and dissolved methane concentration in groundwater samples collected from 75 wells in Lycoming County, Pennsylvania.

landfills, hazardous waste facilities, and military bases (Zogorski and others, 2006) and are widespread wherever human activities are present. Historically, many waste chemicals were disposed of indiscriminately, and the widespread use of VOCs has resulted in considerable mass of material released to the environment. Localized releases of VOCs can come from many sources, including leakage from storage tanks, direct application of pesticides containing VOCs (Barbash and Resek, 1996), septic systems, and leaking sewer systems. VOCs also are released to the atmosphere through engine exhausts, aerosol sprays, leakage of refrigerants, and application of fumigants and pesticides. Trihalomethanes (THMs) are frequently associated with chlorinated water and chlorinated cleaning products.

The reporting level for VOCs was 0.5 µg/L, which is lower than drinking-water MCLs established for 14 of the 68 analyzed VOCs (U.S. Environmental Protection Agency, 2012); however, drinking-water MCLs for two

compounds—1,2-dibromo-3-chloropropane and 1,2-dibromoethane—are less than the method reporting level as performed by the laboratory, so for these compounds, a more sensitive method is needed to determine if they are present in concentrations greater than the MCLs (although below the reporting level of 0.5 µg/L). Therefore, with the exception of these two compounds, if VOCs are present in groundwater at concentrations less than the reporting level of 0.5 µg/L, those concentrations would not exceed an established drinking-water standard. MCLs have not been established for VOCs where data are insufficient to evaluate human-health effects.

Of the 66 VOCs analyzed in the 75 groundwater samples, only 4 were detected at or above the reporting level: 2-Butanone (also known as methyl ethyl ketone or MEK) at 1.45 µg/L, methyl chloride (also known as chloromethane) at 1.68 µg/L, methyl tert-butyl ether (also known as MTBE) at 1.96 µg/L, and trichloromethane (considered a THM) at 24.8 µg/L. None of the detected VOCs were detected in samples from the same well, and concentrations of the detected VOCs did not exceed any established EPA drinking-water standard. MEK is a common laboratory contaminant, but this VOC was not detected in the field blank samples analyzed by SLI or USGS NWQL (Ohio Environmental Protection Agency, 2012). Although the measured VOC concentrations do not exceed established standards, the detection of these manmade compounds in groundwater indicates groundwater contamination by human activities.

The reporting level for the analyzed glycols and alcohols and oil and grease was 5 mg/L, a level that may not be low enough to detect possible presence of those compounds in groundwater; however, at the time of this study, a more sensitive approved method with lower reporting levels was not available. Therefore, these analyses only indicate that glycols and alcohols were not present in concentrations greater than 5 mg/L. Oil and grease were detected in one sample at a concentration of 11.1 mg/L. As of 2015, there are no established EPA drinking-water standards for oil and grease.

Table 7. Reporting levels and drinking-water standards (U.S. Environmental Protection Agency, 2012) for manmade organic compounds analyzed in water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for total concentrations in unfiltered samples done by Seewald Laboratories Incorporated.

[µg/L, microgram per liter; mg/L, milligram per liter; %, percent; --, no data or not applicable; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HAL, health advisory level]

| Constituent name | Units | Reporting limit | Number (percent) exceeding reporting limit | EPA MCL | EPA HAL |
|--|-------|-----------------|--|---------|---------|
| Volatile organic compounds | | | | | |
| 1,1,1,2-Tetrachloroethane | µg/L | 0.5 | 0 (0) | -- | 70 |
| 1,1,1-Trichloroethane | µg/L | 0.5 | 0 (0) | 200 | -- |
| 1,1,2,2-Tetrachloroethane | µg/L | 0.5 | 0 (0) | -- | 40 |
| 1,1,2-Trichloroethane | µg/L | 0.5 | 0 (0) | 5 | -- |
| 1,1-Dichloroethane | µg/L | 0.5 | 0 (0) | -- | -- |
| 1,1-Dichloroethene (1,1-Dichloroethylene) | µg/L | 0.5 | 0 (0) | 7 | -- |
| 1,1-Dichloropropene | µg/L | 0.5 | 0 (0) | -- | -- |
| 1,2,3-Trichlorobenzene | µg/L | 0.5 | 0 (0) | -- | -- |
| 1,2,3-Trichloropropane (1,2,3-TCP) | µg/L | 0.5 | 0 (0) | -- | 100 |
| 1,2,4-Trichlorobenzene | µg/L | 0.5 | 0 (0) | 70 | -- |
| 1,2,4-Trimethylbenzene | µg/L | 0.5 | 0 (0) | -- | -- |
| 1,2-Dichlorobenzene (<i>o</i> -Dichlorobenzene) | µg/L | 0.5 | 0 (0) | 600 | -- |
| 1,2-Dichloroethane | µg/L | 0.5 | 0 (0) | 5 | -- |
| 1,2-Dichloropropane | µg/L | 0.5 | 0 (0) | 5 | -- |
| 1,3,5-Trimethylbenzene | µg/L | 0.5 | 0 (0) | -- | -- |
| 1,3-Dichlorobenzene (<i>m</i> -Dichlorobenzene) | µg/L | 0.5 | 0 (0) | -- | 600 |
| 1,3-Dichloropropane | µg/L | 0.5 | 0 (0) | -- | -- |
| 1,4-Dichlorobenzene (<i>p</i> -Dichlorobenzene) | µg/L | 0.5 | 0 (0) | 75 | -- |
| 2,2-Dichloropropane | µg/L | 0.5 | 0 (0) | -- | -- |
| 2-Butanone (Methyl ethyl ketone, MEK) | µg/L | 1 | 1 (1) | -- | 4,000 |
| 2-Chlorotoluene | µg/L | 0.5 | 0 (0) | -- | 100 |
| 2-Hexanone (<i>n</i> -Butyl methyl ketone) | µg/L | 1 | 0 (0) | -- | -- |
| 4-Chlorotoluene | µg/L | 0.5 | 0 (0) | -- | 100 |
| 4-Methyl-2-Pentanone (MIBK) | µg/L | 1 | 0 (0) | -- | -- |
| Acetone | µg/L | 1 | 0 (0) | -- | -- |
| Benzene | µg/L | 0.5 | 0 (0) | 5 | -- |
| Bromobenzene | µg/L | 0.5 | 0 (0) | -- | 60 |
| Bromochloromethane | µg/L | 0.5 | 0 (0) | -- | 90 |
| Bromodichloromethane | µg/L | 0.5 | 0 (0) | 180 | -- |
| Bromoform (Tribromomethane) | µg/L | 0.5 | 0 (0) | 180 | -- |
| Bromomethane (Methyl bromide) | µg/L | 0.5 | 0 (0) | -- | 10 |
| Carbon Disulfide | µg/L | 0.5 | 0 (0) | -- | -- |
| Carbon Tetrachloride (Tetrachloromethane) | µg/L | 0.5 | 0 (0) | 5 | -- |
| Chlorobenzene | µg/L | 0.5 | 0 (0) | -- | -- |
| Chloroethane | µg/L | 0.5 | 0 (0) | -- | -- |
| <i>cis</i> -1,2-dichloroethene | µg/L | 0.5 | 0 (0) | 70 | -- |
| <i>cis</i> -1,3-dichloropropene | µg/L | 0.5 | 0 (0) | -- | 40 |

Table 7. Reporting levels and drinking-water standards (U.S. Environmental Protection Agency, 2012) for manmade organic compounds analyzed in water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for total concentrations in unfiltered samples done by Seewald Laboratories Incorporated.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; %, percent; --, no data or not applicable; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HAL, health advisory level]

| Constituent name | Units | Reporting limit | Number (percent) exceeding reporting limit | EPA MCL | EPA HAL |
|---|-------|-----------------|--|------------------|---------|
| Dibromochloromethane | µg/L | 0.5 | 0 (0) | ¹ 80 | -- |
| Dibromomethane | µg/L | 0.5 | 0 (0) | -- | -- |
| Dichlorodifluoromethane (Freon 12) | µg/L | 0.5 | 0 (0) | -- | 1,000 |
| Ethylbenzene | µg/L | 0.5 | 0 (0) | 700 | -- |
| Hexachlorobutadiene (1,3-Hexachlorobutadiene) | µg/L | 0.5 | 0 (0) | -- | 10 |
| Iodomethane (Methyl iodide) | µg/L | 0.5 | 0 (0) | -- | -- |
| Isopropylbenzene (Cumene) | µg/L | 0.5 | 0 (0) | -- | 4 |
| <i>m</i> + <i>p</i> -Xylene (<i>m</i> -Xylene plus <i>p</i> -xylene) | µg/L | 1 | 0 (0) | 10,000 | -- |
| Methyl chloride (Chloromethane) | µg/L | 0.5 | 1 (1) | -- | 400 |
| Methyl tert-butyl ether (MTBE) | µg/L | 0.5 | 1 (1) | -- | -- |
| Methylene Chloride (Dichloromethane, DCM) | µg/L | 0.5 | 0 (0) | 5 | -- |
| Naphthalene | µg/L | 0.5 | 0 (0) | -- | 100 |
| <i>n</i> -Butylbenzene | µg/L | 0.5 | 0 (0) | -- | -- |
| <i>n</i> -Propylbenzene | µg/L | 0.5 | 0 (0) | -- | -- |
| <i>o</i> -Xylene | µg/L | 0.5 | 0 (0) | 10,000 | -- |
| <i>p</i> -Isopropyltoluene (4-Isopropyltoluene) | µg/L | 0.5 | 0 (0) | -- | -- |
| <i>sec</i> -Butylbenzene | µg/L | 0.5 | 0 (0) | -- | -- |
| Styrene | µg/L | 0.5 | 0 (0) | 100 | -- |
| <i>tert</i> -Butylbenzene | µg/L | 0.5 | 0 (0) | -- | -- |
| Tetrachloroethene (Perchloroethylene, PCE) | µg/L | 0.5 | 0 (0) | 5 | -- |
| Toluene | µg/L | 0.5 | 0 (0) | 1,000 | -- |
| <i>trans</i> -1,2-Dichloroethene | µg/L | 0.5 | 0 (0) | 100 | -- |
| <i>trans</i> -1,3-Dichloropropene | µg/L | 0.5 | 0 (0) | -- | 40 |
| Trichloroethene (TCE, Trichloroethylene) | µg/L | 0.5 | 0 (0) | 5 (under review) | -- |
| Trichlorofluoromethane (Freon 11) | µg/L | 0.5 | 0 (0) | -- | 2,000 |
| Trichloromethane | µg/L | 0.5 | 1 (1) | ¹ 80 | -- |
| Total trihalomethanes (TTHMs) | µg/L | 0.5 | 1 (1) | ¹ 80 | -- |
| Vinyl Acetate | µg/L | 0.5 | 0 (0) | -- | -- |
| Vinyl Chloride (Chloroethene) | µg/L | 0.5 | 0 (0) | 2 | -- |
| Glycols and alcohols | | | | | |
| Ethanol | mg/L | 5 | 0 (0) | -- | -- |
| Ethylene glycol | mg/L | 5 | 0 (0) | 14 | -- |
| Isobutyl alcohol (2-Methyl-1-propanol) | mg/L | 5 | 0 (0) | -- | -- |
| Isopropyl Alcohol (2-Propanol) | mg/L | 5 | 0 (0) | -- | -- |
| Methanol | mg/L | 5 | 0 (0) | -- | -- |
| <i>n</i> -Butanol (1-Butanol, <i>n</i> -Butyl alcohol) | mg/L | 5 | 0 (0) | -- | -- |
| <i>n</i> -Propanol (1-Propanol) | mg/L | 5 | 0 (0) | -- | -- |
| Propylene glycol | mg/L | 5 | 0 (0) | -- | -- |

Table 7. Reporting levels and drinking-water standards (U.S. Environmental Protection Agency, 2012) for manmade organic compounds analyzed in water samples collected from 75 wells in Lycoming County, Pennsylvania, June–August 2014. Laboratory analysis for total concentrations in unfiltered samples done by Seewald Laboratories Incorporated.—Continued

[µg/L, microgram per liter; mg/L, milligram per liter; %, percent; --, no data or not applicable; EPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; HAL, health advisory level]

| Constituent name | Units | Reporting limit | Number (per-cent) exceed-ing reporting limit | EPA MCL | EPA HAL |
|---|-------|-----------------|--|---------|---------|
| sec-Butyl alcohol | mg/L | 5 | 0 (0) | -- | -- |
| tert-Butyl Alcohol (2-Methyl-2-propanol, TBA) | mg/L | 5 | 0 (0) | -- | -- |
| Oil and grease | | | | | |
| Oil and grease | mg/L | 5 | 1 (1) | -- | -- |

¹1998 Final Rule for Disinfectants and Disinfection By-products: The total for trihalomethanes (TTHMs) is 80 µg/L.

Relations Among Constituents in Groundwater

Dissolved constituents in groundwater may be derived from atmospheric, geologic, biologic, and anthropogenic sources as the aqueous solution interacts with various materials along transport pathways. Solute concentrations can range widely depending on the presence of constituent elements in the source(s), the extent of contact between water and the source, the aqueous solubility and interactions among the dissolved elements, and geochemical conditions such as pH and redox state that affect element form, mobility, and transport in the aqueous environment.

Major ions commonly are derived by 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 directly related 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 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.

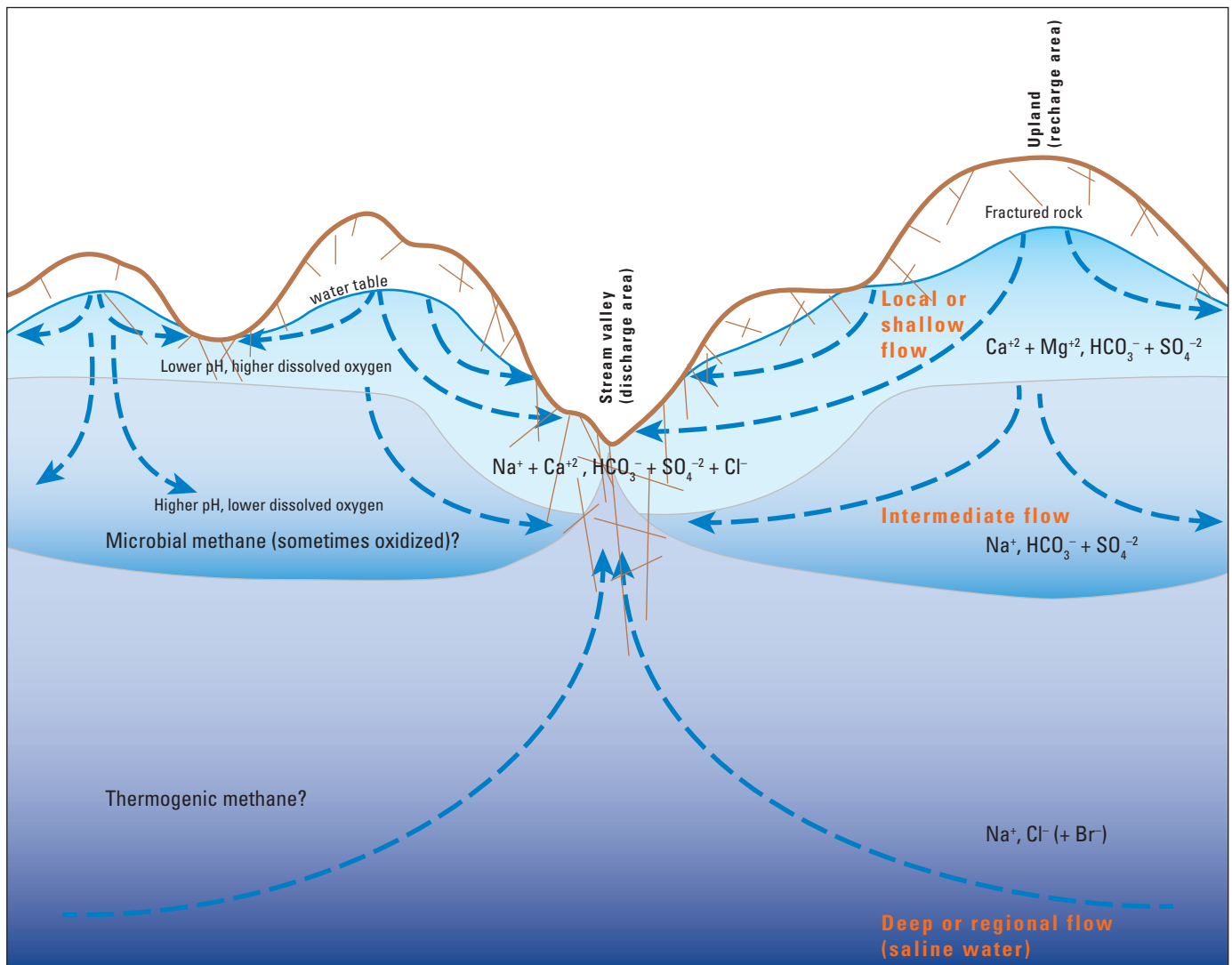
Major cations (positively charged ions such as calcium, magnesium, sodium, and potassium), major anions (negatively charged ions such as sulfate, chloride, fluoride, and bicarbonate), and nonionic solutes (uncharged solutes such as silica) typically are present in natural waters at concentrations >1 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 <1 mg/L (Hem, 1985). Concentrations of DO and nutrients (such as nitrogen and phosphorus compounds) commonly range from

values <1 mg/L to values >1 mg/L because of biological processes that involve the production or metabolism of organic carbon compounds that contain nitrogen and phosphorus. Although biological (biochemical) processes can affect the concentrations of nutrients and trace constituents in groundwater directly or indirectly because of changes to pH and redox, such processes generally have minor effects on major ion concentrations.

Conceptual Hydrogeochemical Setting

Brines with elevated concentrations of sodium, chloride, bromide, barium, strontium, and other solutes occupy pore spaces in deep-lying sedimentary rocks throughout Pennsylvania. The highly saline sodium chloride brines and overlying groundwaters of intermediate salinity generally are present 1,000 feet or more below the surface (Feth, 1965; Heisig and Scott, 2013). Such brine-influenced waters commonly are produced from gas or oil wells (Dresel and Rose, 2010; Hayes, 2009; Haluszczak and others, 2013), and may affect water quality of springs and domestic-supply wells (Llewellyn, 2014; Siegel and others, 2015).

The shallowest flow systems tend to be highly fractured aquifers where actively circulating freshwater has depleted sodium, chloride, and other vestiges of connate brines (fig. 12). Groundwater composition evolves from calcium-magnesium-bicarbonate-sulfate type with relatively lower pH and higher DO concentrations in recharge areas and local flow zones to predominantly sodium-bicarbonate-sulfate with higher pH and lower DO along intermediate flow paths. Deeper or regional groundwater that is relatively saline may be mixing with intermediate flow waters, especially in discharge areas, such as stream valleys, where methane from microbial and (or) thermogenic sources appears most frequently and in highest concentrations in northeastern Pennsylvania. In the shallow groundwater zone, water types of predominantly calcium-magnesium/bicarbonate and calcium-magnesium/bicarbonate-sulfate compositions are produced



This diagram is not drawn to scale, and actual flow system depths may vary in relation to topographic features.

EXPLANATION

| | |
|------------------------------|----------------------------------|
| Ca^{+2} — Calcium | Br^{-} — Bromide |
| Mg^{+2} — Magnesium | Cl^{-} — Chloride |
| Na^{+} — Sodium | HCO_3^{-} — Bicarbonate |
| SO_4^{-2} — Sulfate | |

Figure 12. Schematic diagram of generalized conceptual hydrogeochemical setting for fresh and saline groundwater in a fractured bedrock aquifer setting.

by the active weathering of moderately soluble carbonate minerals, and to a lesser extent sulfate and sulfide minerals. In the intermediate zone, groundwater of sodium/bicarbonate type and moderate salinity typically is present between the shallow, actively circulating freshwater and the deeper, slower moving sodium chloride type waters. Poth (1962) described the freshening process in the intermediate zone as chloride being readily removed by circulating groundwater with sodium being more difficult to remove because much of it is adsorbed on the clay in the rocks. The sodium, which occupies exchange sites on clay minerals, tends to be displaced by calcium and magnesium. Such cation-exchange processes lead to the formation of sodium/bicarbonate type waters, which are transitional between the sodium chloride waters at great depth and the calcium-magnesium/bicarbonate waters in the overlying freshwater zone.

Most wells constructed for domestic use are completed within the local, freshwater flow system. The wells sampled in Lycoming County for this study were completed to depths ranging from 40 to 620 feet, with one-half drilled to depths of 175 to 400 feet. Neither of the two deepest wells, LY745 and LY755, completed to depths of 600 and 620 feet below the surface, respectively, exhibited characteristics of brine-influenced waters; however, several wells about one-half that depth had characteristics indicative of such influence, notably elevated SC and TDS dominated by sodium and chloride, plus elevated concentrations of bromide, lithium, and methane, as explained in more detail below.

Correlations Among Major and Trace Constituents in Groundwater

Evaluation of the correlations among chemical constituents and environmental variables provides insight on hydrochemical processes affecting groundwater chemistry in the study area.

Relations Among pH, Specific Conductance, and Constituent Concentrations

The chemical compositions of the 75 groundwater samples collected in Lycoming County during 2014 ranged widely, as indicated by pH values from 5.3 to 9.2 and SC from 20 to 3,120 $\mu\text{S}/\text{cm}$ (fig. 13). Detection limits for bromide and arsenic were 0.03 and 0.0001 mg/L, respectively; symbols plotted at those values were below detection (fig. 13). Most of the samples had pH values from 6.7 to 8.0 and SC from 150 to 300 $\mu\text{S}/\text{cm}$. Only 3 of the 75 well-water samples in this study had SC values greater than 1,000 $\mu\text{S}/\text{cm}$; these samples had alkaline pH (>8) values and greater concentrations of sodium and chloride than those for the other samples. In addition to figure 13, which shows the relations among pH, SC, and multiple inorganic constituents, boxplots are included in appendix 3 that show the overall relations among individual

constituents with pH class interval (fig. 3-1) and SC class interval (fig. 3-2). Additional boxplots show the same constituents as a function of redox class interval (fig. 3-3) and lithology (fig. 3-4).

The pH for the 75 groundwater samples was positively correlated with SC and other measures of ionic strength, including TDS ROE, whereas the pH and SC were negatively correlated with the concentration of DO. With increased pH and SC, the concentrations of several major and trace constituents generally increased, including ALK, sodium, lithium, boron, fluoride, bromide, arsenic, and, to a lesser extent, strontium and barium (fig. 13). Despite positive correlations between SC and the concentration of chloride, sulfate, calcium, magnesium, or hardness (fig. 13), those constituents were not correlated with pH over the entire range of measured values. Concentrations of potassium were not correlated with pH or SC.

The relation between the pH and concentrations of calcium, magnesium, and hardness changes from positive to negative at about pH 7.5 (fig. 13). For pH values <7.5, the concentrations of hardness, calcium, magnesium, and other cations, including strontium, barium, sodium, potassium, and lithium, plus ALK, generally increased with pH; however, for pH values greater than 7.5, the concentrations of hardness, calcium, and magnesium decreased with increased pH, whereas the SC and concentrations of sodium, ALK, and TDS continued to increase. Such trends in pH, SC, and constituent concentrations are consistent with the dissolution of calcite over the range of pH combined with cation-exchange at pH greater than 7.5. Through cation-exchange reactions, the hardness is removed, or “softened,” as calcium and magnesium ions displace sodium ions from exchange sites on clay minerals (Appelo and Postma, 2005), as explained in more detail below.

Boxplots show the constituent concentrations for three different pH class intervals (fig. 3-1). As indicated by the scatter plots that showed constituent concentrations as a function of pH for all 75 samples (fig. 13), most constituent concentrations increased with pH to values of 7.4 (acidic to neutral range). The alkaline pH class (pH >7.5) had higher median values for SC, TDS, sodium, potassium, ALK, chloride, bromide, fluoride, boron, lithium, methane, barium, strontium, arsenic, and molybdenum than the acidic or near-neutral classes. In contrast, the alkaline pH class had lower or equal medians for hardness, calcium, magnesium, and DO.

Boxplots also show constituent concentrations for four different SC class intervals (fig. 3-2). As indicated by the scatter plots that showed constituent concentrations as a function of SC for all 75 samples (fig. 13), most constituent concentrations increased with SC to values approaching 700 $\mu\text{S}/\text{cm}$. The highest SC class (SC >700 $\mu\text{S}/\text{cm}$) had higher median values for pH, TDS, sodium, potassium, ALK, chloride, bromide, fluoride, boron, lithium, methane, ammonia, and arsenic, and lower median values for DO, nitrate, aluminum, and zinc than the lower SC classes. The concentrations of nitrate and zinc were below detection in the highest SC class. Constituents that

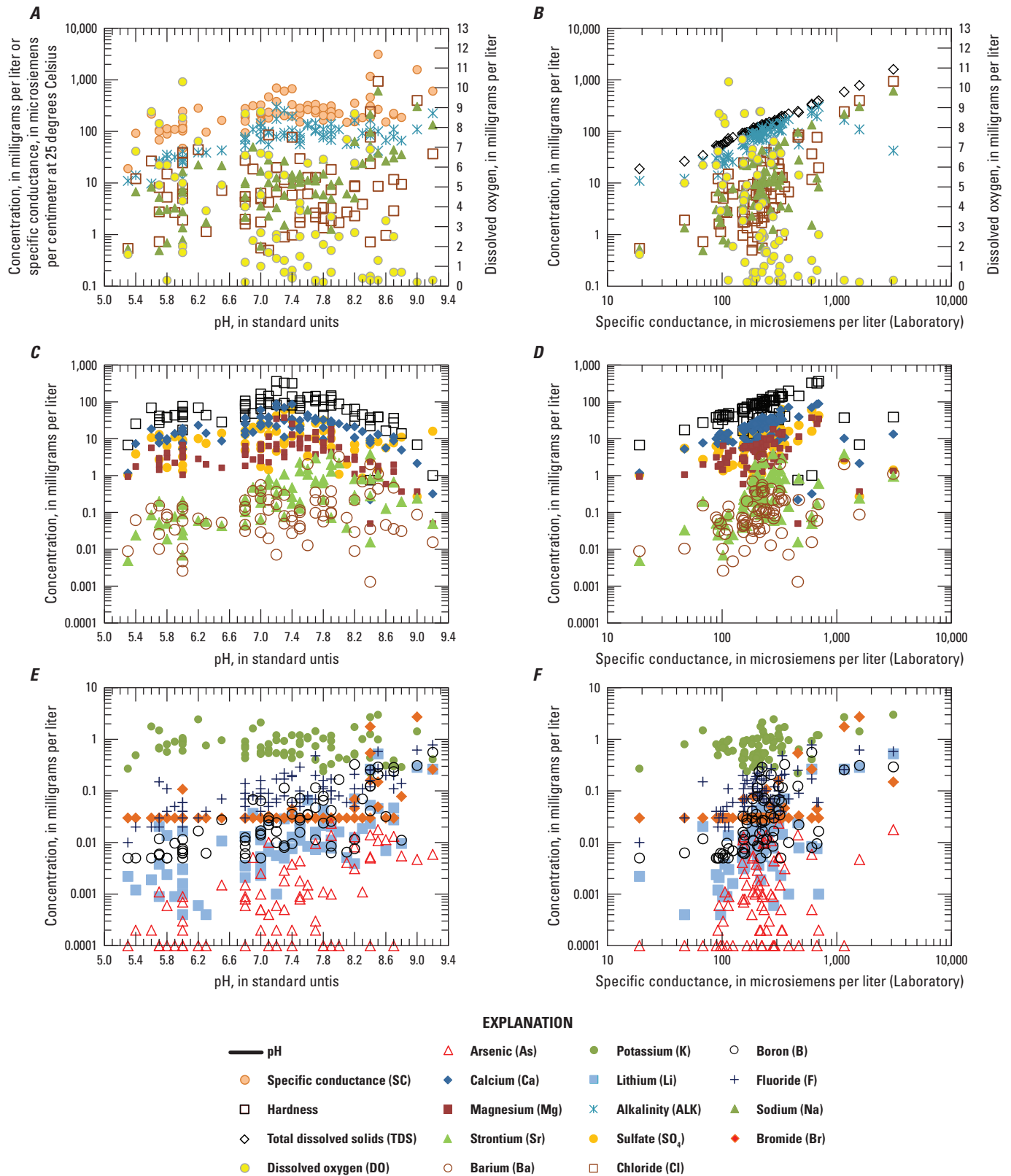


Figure 13. Concentrations of selected constituents in groundwater samples collected from 75 wells in Lycoming County, Pennsylvania, 2014, compared to A–C, pH; or D–F, specific conductance.

did not vary with SC and (or) pH may be controlled by other factors, such as redox state.

The constituent concentrations for anoxic, mixed, and oxic redox class intervals also are illustrated as boxplots in appendix 3 (fig. 3-3). Although most constituent 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, bromide, fluoride, boron, ammonia, molybdenum, iron, and manganese, and lower median values for DO, nitrate, uranium, and radon-222 than the oxic samples.

Ionic Contributions to Conductivity and Total Dissolved Solids

Despite general correlations between SC and major ion concentrations, the predominance of various ionic contributions to the SC varied widely for samples with comparable values of SC (fig. 14). Calcium and bicarbonate were the

predominant ions in most samples, considering the ionic contributions to SC or considering the ion concentrations in units of mass, moles, or equivalents. Although sodium and chloride were subordinate in most samples, these constituents were the predominant ions in a few samples, particularly those with SC greater than 1,000 $\mu\text{S}/\text{cm}$, but also in several samples with relatively low values of SC. Sulfate was subordinate to bicarbonate and chloride as a source of conductivity in the samples; its importance generally decreased with increased SC. Contributions by magnesium were comparable to sulfate; however, contributions by nitrate, potassium, hydrogen, hydroxyl, or carbonate ions were relatively minor.

Variations in the major ion species contributions to the SC values measured in the laboratory for six selected groundwater samples are illustrated as pie charts (fig. 15). To provide context, the samples illustrated in figure 14 are identified among all 75 samples in figure 15. Calcium, bicarbonate, magnesium, sodium, sulfate, and chloride ions are the predominant sources of conductivity for the average of the 75 samples and

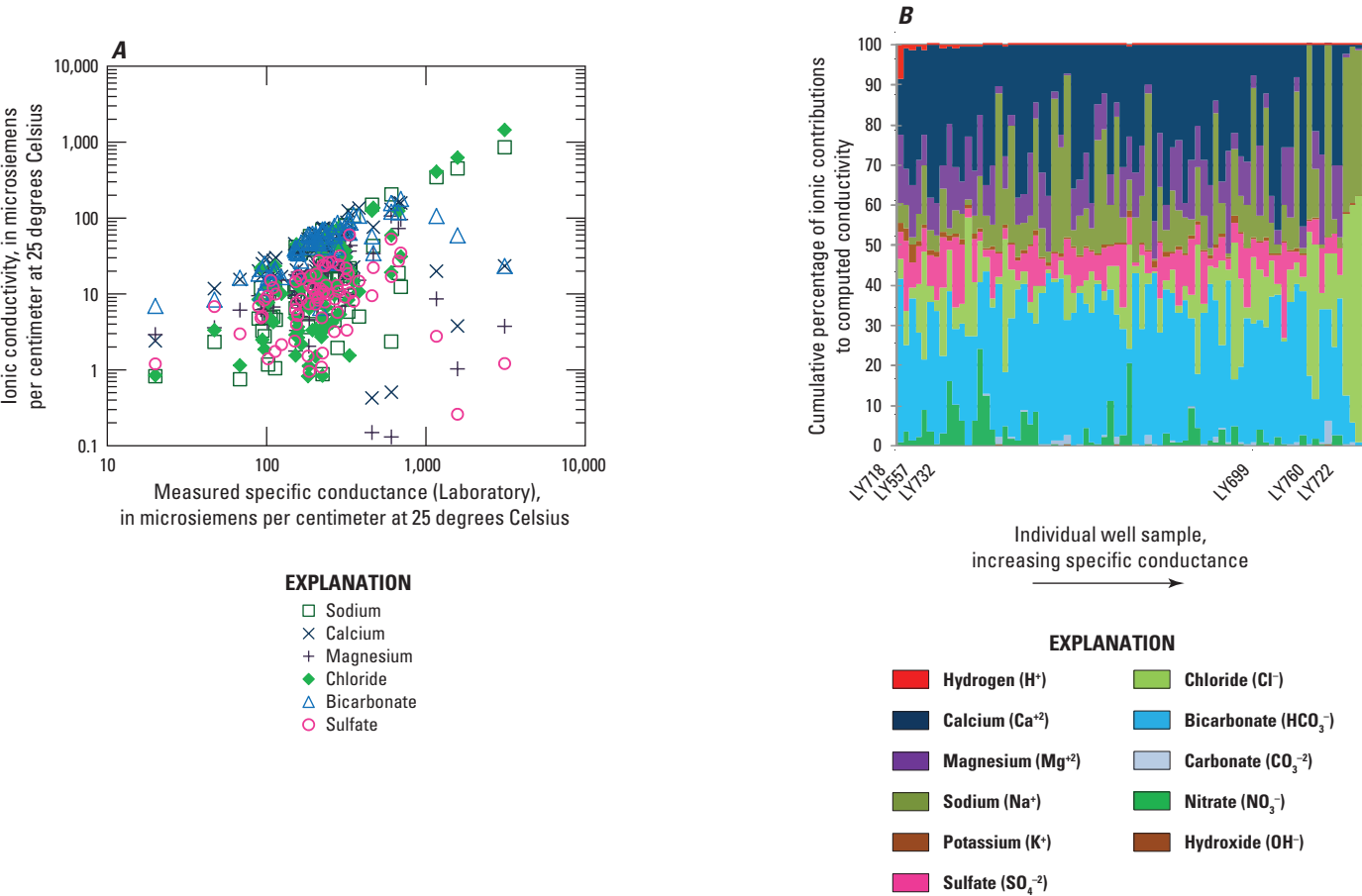
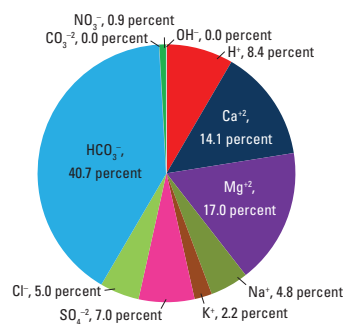
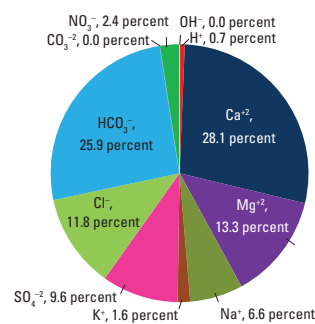
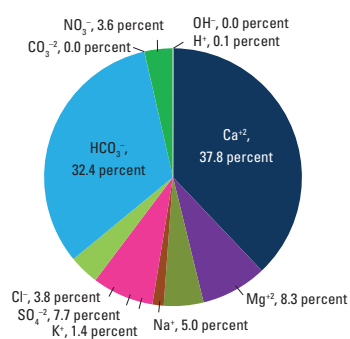
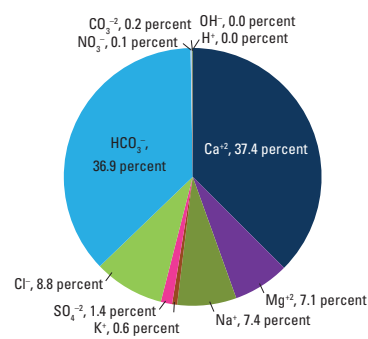
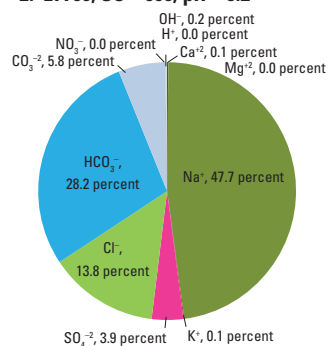
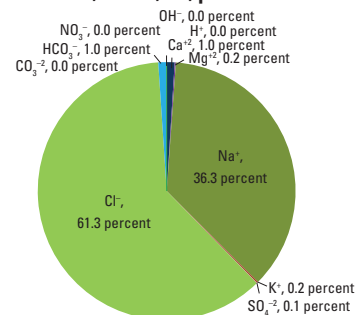
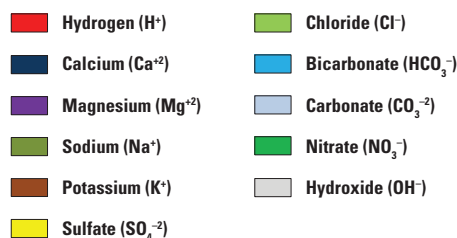


Figure 14. Major ion contributions to specific conductance (SC) for groundwater samples collected from 75 wells in Lycoming County, Pennsylvania, 2014. *A*, comparison of estimated ionic conductivity contributions by sodium, calcium, magnesium, chloride, bicarbonate, and sulfate to measured SC; and *B*, relative contributions by major ion species (hydrogen, calcium, magnesium, sodium, potassium, sulfate, chloride, bicarbonate, carbonate, nitrate, and hydroxide) to computed SC, expressed in percent, in order of increasing SC. Individual ion conductivities estimated from dissolved constituent concentrations as the “transport number” (relative contribution of a given ion to the overall conductivity, using methods of McCleskey and others, 2012) after aqueous speciation calculations with the aqueous geochemical computer program, PHREEQC (Parkhurst and Appelo, 2013).

A. LY718; SC = 20; pH = 5.3**B. LY557; SC = 89; pH = 5.8****C. LY732; SC = 94; pH = 6.8****D. LY699; SC = 319; pH = 7.6****E. LY760; SC = 606; pH = 9.2****F. LY722; SC = 3,120; pH = 8.5****EXPLANATION**

SC, specific conductance, in microsiemens per centimeter at 25 degrees Celsius

Figure 15. Ionic contributions to specific conductance (SC) computed for selected groundwater samples from Lycoming County, Pennsylvania, 2014 for wells, A, LY718, B, LY557, C, LY732, D, LY699, E, LY760; and F, LY722. Individual ionic conductivities estimated from dissolved constituent concentrations (using methods of McCleskey and others, 2012) after aqueous speciation calculations with the aqueous geochemical computer program, PHREEQC (Parkhurst and Appelo, 2013).

most other samples having low to moderate SC values, such as from wells LY718, LY557, LY732, and LY699, with minor contributions from nitrate, potassium, and hydrogen ions. Samples with higher than average SC values, such as from wells LY760 and LY722, generally have increased contributions from sodium and chloride.

The sample from well LY718 had a pH of 5.3 and SC of 20 $\mu\text{S}/\text{cm}$, which were the lowest values for all of the well-water samples from Lycoming County in 2014. These low pH and SC values were comparable to those for bulk precipitation

(rainwater) in the northeastern United States (Peters and Bonelli, 1982); the observation that hydrogen protons contributed significantly to the conductivity of this sample is consistent with its acidic pH and low ionic strength. Samples from wells LY557 and LY732 are representative of minimally evolved groundwater with relatively low, but comparable SC values of 89 and 94 $\mu\text{S}/\text{cm}$, respectively. The conductivity of both samples can be produced as the result of rainwater evaporation plus dissolution of various minerals and salts; however, these two samples differ in their ionic character.

The sample from well LY557 had a pH of 5.8 with important contributions to its conductivity by several ions, including calcium, magnesium, bicarbonate, chloride, and sulfate, and subordinate contributions by sodium, potassium, nitrate, and protons. In contrast, the sample from well LY732 had a higher pH of 6.8 and ionic conductivity contributions dominated by calcium and bicarbonate, which may reflect the interaction of recharge water or groundwater mainly with calcareous minerals. Although the sample from well LY699 had a higher pH of 7.6 and SC of 319 $\mu\text{S}/\text{cm}$ compared to LY732, both samples would be classified as calcium/bicarbonate water types. In contrast, the sample from well LY760, which had a pH of 9.2 and SC of 606 $\mu\text{S}/\text{cm}$, had predominant ionic conductivity contributions by sodium and bicarbonate, with lesser contributions by chloride, carbonate, and sulfate ions. Such sodium/bicarbonate waters can be produced as a result of cation-exchange processes, where sodium on mineral surfaces is exchanged from calcium. In the extreme, the sample from well LY722, which had a pH of 8.5 and the highest measured SC of 3,120 $\mu\text{S}/\text{cm}$, had predominant contributions by sodium and chloride, which indicate a salt source. The predominance of sodium and chloride ionic conductivities was exhibited mainly by those samples with elevated SC, but also by a few samples with intermediate SC values, such as the sample from well LY754, which had a pH of 8.7 and SC of 210 $\mu\text{S}/\text{cm}$.

Principal Components Analysis of Interrelations Among Constituents

Five principal components (PCs) explain nearly 75 percent of the variance in the Lycoming County groundwater dataset and consist of 22 routinely detected constituent loadings (table 8). As explained by Thyne and others (2004), the loading value is comparable to the correlation coefficient between a constituent and the PC, whereas the communality and eigenvalues indicate the degree to which the PCA explains the total variability of the elements considered in the analysis. Associations of additional chemical and physical variables excluded from the analysis are indicated by the Spearman-rank coefficient of correlation of these variables with the PC scores; significant correlations are listed below the five PCAs included in table 8, which are named PC1 through PC5.

PC1, which explains 31.7 percent of the variance in the data, has positive loadings by pH, molybdenum, boron, lithium, sodium, arsenic, strontium, ALK, SC, and bromide, with negative loading by DO and nitrate (table 8). Scores on PC1 are positively correlated with fluoride, TDS (ROE), and gross alpha radioactivity, and negatively correlated with zinc, copper, nickel, and total nitrogen (table 8). The negative associations of PC1 with DO and positive associations with pH and TDS are consistent with the depletion of oxygen as groundwater interacts with organic matter and minerals in the aquifer and becomes more mineralized, alkaline, and “softened” along flow paths from recharge areas in uplands to discharges in valleys. Although PC1 scores were not related

to lithology of the source aquifer, those samples classified as anoxic generally had higher, positive scores on PC1 compared to those classified as mixed or oxic, as shown by appendix figure 3-3. High positive scores on PC1 generally may be attributed to the progressive weathering of calcite and dolomite (carbonate minerals) *combined with* cation-exchange processes. The natural cation-exchange reactions liberate sodium and other alkali earth cations, such as lithium, while removing calcium and magnesium (hardness), much like a water-softening treatment system (Hem, 1985; Poth, 1962). The removal of calcium and magnesium from solution leads to undersaturation of the groundwater with respect to calcite and dolomite, thus promoting additional dissolution of the carbonate minerals and progressive increases in pH and ALK along the flow path. The resultant sodium-bicarbonate waters tend to have alkaline pH (>8) values and high positive scores on PC1. At alkaline pH, various trace elements are oxyanions in groundwater, including molybdenum, boron, and arsenic, tend to be poorly sorbed and become mobile; however, trace cations, such as zinc, copper, and nickel, tend to be adsorbed and removed from solution.

PC2, which explains 15.5 percent of the variance in the data, has positive loadings by manganese and iron, and negative loadings by DO, nitrate, radon-222, and arsenic (table 8). Scores on PC2 are positively correlated with ammonia, methane, and fluoride and negatively correlated with total nitrogen, uranium, selenium, lead, and copper. High scores on PC2 are interpreted to indicate isolation from the atmosphere, the depletion of oxygen, and the development of reducing conditions that may be attributed to the microbial decomposition of organic matter in the aquifer or introduced to the groundwater. Samples from aquifers consisting of shale or siltstone lithologies and (or) classified as having anoxic or mixed redox characteristics generally had positive scores on PC2, whereas samples from aquifers consisting of carbonate or sandstone lithologies and (or) classified as oxic generally had negative scores, as shown by appendix figure 3-3. The negative correlation of uranium with PC2 is consistent with its high mobility as uranyl-carbonate complexes under oxidizing conditions, whereas the negative correlations of lead, copper, arsenic, selenium, and radon-222 with PC2 indicate decreased mobility of these constituents where concentrations of dissolved iron and manganese are elevated, possibly because of adsorption by hydrous ferric oxide minerals including goethite or ferrihydrite. All but one of the anoxic samples and most of the samples classified as having oxic or mixed redox characteristics are supersaturated or saturated with respect to the hydrous ferric oxide minerals, which is further explained in the “Water Quality Variations and Water-Rock Interactions” section.

PC3, which explains 12.5 percent of the variance in the data, has positive loadings by chloride, strontium, calcium, magnesium, sulfate, ALK, silica, and SC. Scores on PC3 are positively correlated with hardness and TDS. High scores on PC3 can be attributed to the dissolution of calcite, dolomite, gypsum, and possibly pyrite or other sulfide minerals, without the cation-exchange softening effects (alkaline pH) indicated by high scores on PC1. Median PC3 scores decreased in the

Table 8. Principal components analysis of major factors controlling the chemistry of groundwater, Lycoming County, Pennsylvania, 2014.

[--, no data or not applicable; PC1–PC5, Principal components 1 through 5 with major factor indicated in parentheses; Varimax rotation pattern for rank-transformed data (SAS Institute, Inc., 2012); minimum eigenvalue less than 1; loading values for constituents included in model and Spearman correlation coefficients (p -value less than 0.001) multiplied by 100 and rounded; *, highly significant loading (p -value less than 0.001). Significant Spearman correlation coefficients are shown only for constituents excluded from the principal components analysis]

| | PC1 (pH) | PC2 (Redox) | PC 3 (Hardness) | PC4 (Chloride) | PC5 (Potassium) | Communality |
|---|-------------|----------------|--------------------|-------------------|--------------------|-------------|
| Constituent Loadings | | | | | | |
| pH (pH) | 89* | 11 | 2 | 3 | -11 | 0.820 |
| Molybdenum (Mo) | 84* | -19 | 4 | 10 | 6 | 0.762 |
| Boron (B) | 81* | 36 | 8 | 9 | 10 | 0.804 |
| Lithium (Li) | 77* | 38 | 4 | 12 | 2 | 0.762 |
| Sodium (Na) | 72* | 22 | -8 | 43* | -8 | 0.763 |
| Arsenic (As) | 69* | -37 | -21 | 12 | -4 | 0.676 |
| Strontium (Sr) | 65* | 19 | 39* | -21 | 40* | 0.813 |
| Alkalinity (ALK) | 58* | 19 | 54* | 6 | 16 | 0.703 |
| Manganese (Mn) | -13 | 85* | -13 | 3 | 16 | 0.784 |
| Iron (Fe) | -9 | 80* | -20 | 23 | -7 | 0.744 |
| Dissolved Oxygen (DO) | -41* | -64* | -18 | -18 | 10 | 0.651 |
| Radon-222 (Rn-222) | -23 | -70* | -30 | -6 | 1 | 0.634 |
| Nitrate (NO ₃ N) | -40* | -75* | 23 | 21 | 6 | 0.819 |
| Calcium (Ca) | -3 | -13 | 87* | -9 | 23 | 0.839 |
| Magnesium (Mg) | -14 | -2 | 87* | -6 | 11 | 0.791 |
| Sulfate (SO ₄) | 4 | -16 | 64* | 33 | -34 | 0.668 |
| Specific Conductance (SCL) | 51* | 15 | 55* | 52* | 22 | 0.905 |
| Silica (SiO ₂) | 29 | 15 | 53* | -35 | -38 | 0.650 |
| Chloride (Cl) | 10 | 9 | 8 | 85* | 17 | 0.769 |
| Bromide (Br) | 42* | 18 | -27 | 67* | 4 | 0.728 |
| Potassium (K) | -4 | -17 | 6 | 35 | 84* | 0.866 |
| Barium (Ba) | 31 | 38 | 28 | -7 | 55* | 0.631 |
| Eigenvalue | 6.982 | 3.412 | 2.749 | 2.095 | 1.345 | 16.582 |
| Cumulative Percent Variance Explained | 31.7 | 47.2 | 59.7 | 69.3 | 75.4 | -- |
| Significant Spearman Correlations (p -value less than 0.001) | | | | | | |
| pH, Lab (pHL) | 86 | -- | -- | -- | -- | -- |
| Fluoride (F) | 68 | 45 | -- | -- | -- | -- |
| Alkalinity, Incremental (ALKI) | 55 | -- | -- | -- | -- | -- |
| Gross alpha radioactivity (AlphaTh30) | 47 | -- | -- | -- | -- | -- |
| Nickel (Ni) | -47 | -- | -- | -- | -- | -- |
| Copper (Cu) | -53 | -46 | -- | -- | -- | -- |
| Zinc (Zn) | -59 | -- | -- | -- | -- | -- |
| Ammonia (NH ₃ N) | -- | 72 | -- | -- | -- | -- |
| Methane (Methane) | -- | 52 | -- | -- | -- | -- |
| Lead (Pb) | -- | -46 | -- | -- | -- | -- |
| Selenium (Se) | -- | -58 | -- | -- | -- | -- |

Table 8. Principal components analysis of major factors controlling the chemistry of groundwater, Lycoming County, Pennsylvania, 2014.—Continued

[--, no data or not applicable; PC1–PC5, Principal components 1 through 5 with major factor indicated in parentheses; Varimax rotation pattern for rank-transformed data (SAS Institute, Inc., 2012); minimum eigenvalue less than 1; loading values for constituents included in model and Spearman correlation coefficients (p -value less than 0.001) multiplied by 100 and rounded; *, highly significant loading (p -value less than 0.001). Significant Spearman correlation coefficients are shown only for constituents excluded from the principal components analysis]

| | PC1 (pH) | PC2 (Redox) | PC 3 (Hardness) | PC4 (Chloride) | PC5 (Potassium) | Communality |
|--------------------------------------|-------------|----------------|--------------------|-------------------|--------------------|-------------|
| Nitrogen, Total (NT) | -44 | -63 | -- | -- | -- | -- |
| Uranium (U) | -- | -70 | -- | -- | -- | -- |
| Hardness (Hard) | -- | -- | 93 | -- | -- | -- |
| Total Dissolved Solids (TDS) | 49 | -- | 56 | 47 | -- | -- |
| Specific Conductance, Field (SCF) | 48 | -- | 52 | 51 | -- | -- |
| Residue on Evaporation 180C (ROE180) | 44 | -- | 52 | 51 | -- | -- |

order of carbonate, shale, siltstone, and sandstone lithologies, as shown by appendix figure 3-4.

PC4, which explains 9.6 percent of the variance in the data, has positive loadings by chloride, bromide, sodium, and SC and is positively correlated with TDS (table 8). The positive association between chloride, bromide, and sodium could indicate the influence of Appalachian Basin brine or other sources of salinity, such as sewage, fertilizer, and (or) road-deicing salt, on the groundwater of associated samples.

PC5, which explains 6.1 percent of the variance in the data, has positive loadings by potassium, barium, and strontium (table 8). The positive associations of these cations could indicate a common origin or geochemical control. For example, potassium, barium, and strontium commonly substitute for calcium in carbonate (aragonite) minerals and one another in sulfate (barite-celestine) minerals, which could be possible sources or sinks of the cations (Hanor, 1968; Hanshaw and Back, 1979). Additionally, these cations may be retained more strongly than sodium and lithium by clay minerals involved in cation-exchange (Appelo and Postma, 2005) and, thus, may be released as the exchange sites become depleted in sodium and lithium and enriched in calcium and magnesium.

Relation Between Groundwater Quality, Geology, and Topographic Setting

Groundwater acquires solutes through natural and anthropogenic loading of constituents in the recharge area from precipitation, weathering reactions of minerals in the soil and aquifer materials, and constituents applied by human activities at or near the land surface. Additional solutes may be acquired as groundwater flows through the aquifer. Groundwater supplying 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.

Bedrock underlying Lycoming County mainly consists of clastic sedimentary lithologies that include shale, siltstone, and sandstone. Such clastic rocks mainly consist of silicate and aluminosilicate minerals, including quartz, feldspar, chlorite, muscovite, and illite, plus minor carbonate, sulfate, sulfide, and oxide minerals that are clasts, fracture filling, and cements. Geologic units with primarily carbonate lithologies, such as limestone and calcareous shale, are present in the southern part of the county (fig. 3), but only three wells in this study were completed in carbonate rock units.

The constituent concentrations for the four major lithologic classes, defined as carbonate, shale, siltstone, and sandstone, generally had comparable ranges (fig. 3-4). Although most constituent concentrations varied little with lithologic class, the medians for several constituents were significantly different between the carbonate and siliciclastic lithologies. The samples associated with carbonate bedrock had higher median values for SC, TDS, hardness, calcium, magnesium, potassium, ALK, sulfate, chloride, and nitrate, and lower median values for bromide, boron, methane, aluminum, orthophosphate, and arsenic than the samples from siliciclastic bedrock lithologies. Furthermore, the samples from carbonate and sandstone bedrock had higher median values for uranium and radon-222 than those from shale and siltstone lithologies.

Although mineralogy is expected to vary locally, the carbonate, sulfate, and sulfide minerals in the siliciclastic bedrock are prone to weathering in near-surface environments where they may be important sources of hardness, ALK, sulfate, and other solutes. Likewise, various clay minerals, which are hydrated aluminosilicates with layered crystal structures that readily accommodate ionic substitutions, are widely recognized to be involved in cation-exchange and sorption processes (Hem, 1985; Appelo and Postma, 2005). For example, chlorite, muscovite, illite, and kaolinite are common clay components of soils, shales, and siltstones and could influence solute concentrations in well-water samples from the study area.

Major Ion Compositions Indicated by Piper Diagrams

Trilinear diagrams and associated Piper diagrams indicate the percentage contributions of the major cations and anions, in equivalents (molar concentration multiplied by ionic charge), relative to the total equivalents for cations and anions in a sample. Although similar in concept to the pie charts showing ionic conductivity contributions to the SC, 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. 16). For the Lycoming County well-water samples, calcium/bicarbonate type waters were most abundant, with others classified as sodium/bicarbonate or mixed water types including calcium-sodium/bicarbonate, calcium-sodium/bicarbonate-chloride, sodium/bicarbonate-chloride, or sodium/chloride types (fig. 16).

Representative samples are identified on the Piper diagram in fig. 17A and B in order to explain their characteristics and possible origins. The sample from well LY557 is the low-pH, low ionic strength sample, described previously, which is similar in character to rainwater. Samples from wells LY732, LY721, and LY699 are classified as calcium/bicarbonate type, and samples from wells LY432 and LY718 are calcium-magnesium/bicarbonate type (fig. 17A), which can be produced by the dissolution of calcium carbonate and dolomite by rainwater (recharge) or groundwater (fig. 17B). Samples from wells LY700, LY755, LY703, and LY760 are classified as sodium/bicarbonate type. Such water types are likely to form by the dissolution of calcite and (or) dolomite combined with cation-exchange; these processes are described in more detail below. Samples plotting away from an apex or within the center part of the diagram are classified as mixed hydrochemical types. For example, the sample from well LY716 is classified as a mixed calcium/bicarbonate-chloride type, the sample from well LY719 is classified as a mixed sodium-calcium/bicarbonate-chloride type, and the sample from well LY731 is a mixed calcium-sodium/chloride-bicarbonate type. The mixed water types imply that multiple sources of constituents or processes may be important. Finally, samples from wells LY781, LY735, and LY722 are sodium-chloride type. The predominance of chloride implies the addition of salt (sodium chloride, calcium chloride) from road-deicing salts, sewage or animal waste, or possibly brine of geological origin.

As illustrated in figure 17B, possible evolution pathways are indicated for the various well-water samples. The dissolution of calcite by groundwater produces calcium/bicarbonate type (on the left corner of the Piper diagram). Calcite dissolution combined with cation-exchange produces the sodium/bicarbonate type (on the lower corner). Simple mixing of calcium/bicarbonate water with brine can explain waters of mixed calcium-sodium/bicarbonate-chloride types (upper right

track). Likewise, the addition of road-deicing salt to groundwater produces a range of mixed calcium-sodium/bicarbonate-chloride to sodium/chloride water types (ending on the right corner); however, the sodium/chloride type (right corner) also can be produced by mixing of groundwater with brine plus cation-exchange, with or without calcite dissolution. Although the origins and evolution pathways are very different, the points on a Piper diagram cannot be distinguished. Other characteristics, such as the pH, ionic strength, and the concentrations of bromide, lithium, strontium, and barium, could be helpful to distinguish the origins of the groundwater.

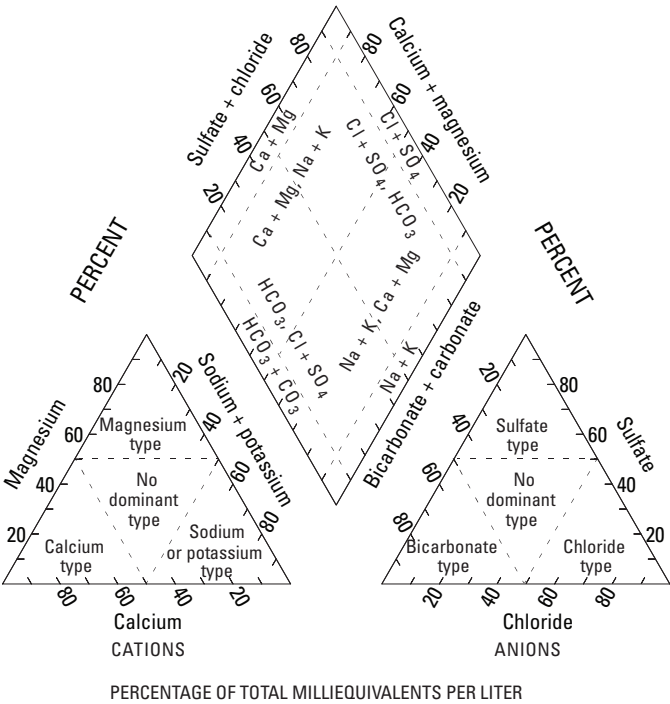
Water-Quality Variations and Water-Rock Interactions

To evaluate the potential for various minerals to be dissolved or precipitated by the groundwater, the SI values are displayed as a function of pH for the Lycoming County well-water samples (fig. 18). The samples that had $\text{pH} \leq 8$ were undersaturated ($\text{SI} < 0$) with respect to calcium carbonate and dolomite, indicating the groundwater could feasibly dissolve these carbonate minerals, if present. The SI_{CAL} increased linearly from pH of 5.3 ($\text{SI} -4.99$) to pH of 8 ($\text{SI} -0.04$), above which the SI value approximately equal to 0 was maintained. Despite the indicated equilibrium, dissolution of calcite could be anticipated to continue at pH values greater than 8 because of the removal of calcium in exchange of sodium. As the concentrations of calcium are depleted, the groundwater could dissolve more calcite with progressive increases in concentrations of ALK and pH to values as high as 9.2 (fig. 13).

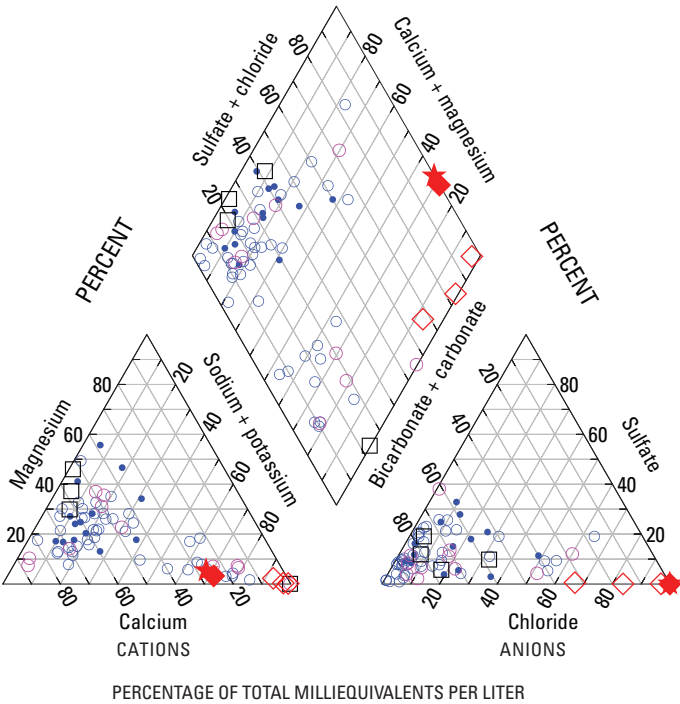
On the basis of negative SI values, feldspar minerals, represented by albite, were undersaturated and could feasibly dissolve in groundwater, albeit slowly. In addition to being sources of base cations (sodium, potassium, calcium), aluminum, and silicon, the feldspars commonly contain traces of phosphate and, thus, could be a potential natural source of phosphate in the sampled groundwater (Denver and others, 2010). Likewise, chlorite, which is a clay mineral, was indicated to be undersaturated and unstable. In contrast, quartz and kaolinite were saturated or supersaturated. Thus, over the range of pH for the samples of this study, the unstable aluminosilicates generally would be anticipated to dissolve incongruently, releasing cations to solution while silica and aluminum are retained in secondary solid phases, such as quartz and kaolinite. Other clay minerals, including beidellite, illite, and muscovite had SI values that ranged from negative to positive, indicating these or similar phases could potentially decompose where undersaturated, or such phases could participate in surface complexation or exchange reactions where saturated or supersaturated.

The major calcium and magnesium carbonate minerals commonly contain traces of other cations, including iron, manganese, strontium, and barium (Hanshaw and Back, 1979). These trace cations can also appear locally as pure carbonate phases. Over the range of pH, the SI values for siderite,

A. Water type or hydrochemical facies



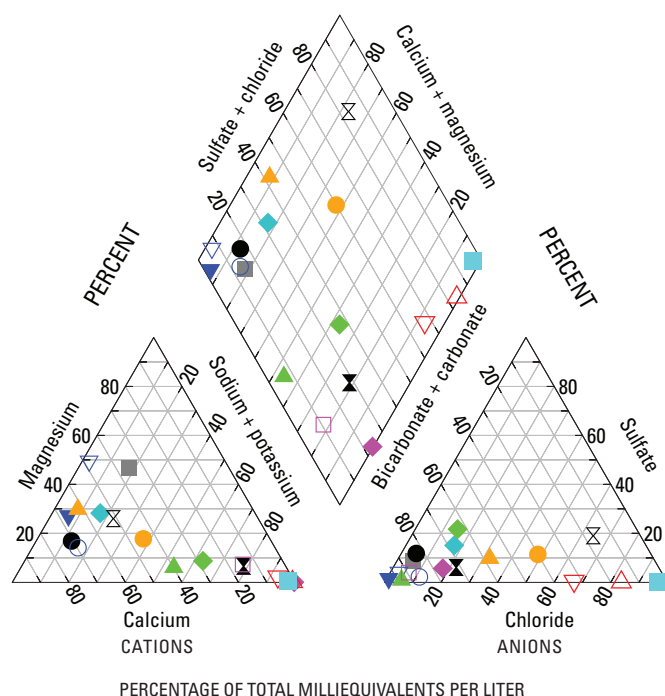
B. Lycoming County groundwater 2014



| EXPLANATION | |
|--|---|
| Groundwater | |
| Hydrogen (H ⁺) | • 20 < SC < 150 |
| Calcium (Ca ⁺²) | ○ 150 ≤ SC < 300 |
| Magnesium (Mg ⁺²) | ◌ 300 ≤ SC < 500 |
| Sodium (Na ⁺) | ◻ 500 ≤ SC < 700 |
| Potassium (K ⁺) | ◊ 700 ≤ SC < 3,120 |
| Sulfate (SO ₄ ⁻²) | ★ Oil and gas well brine |
| Chloride (Cl ⁻) | ◆ Flowback water |
| Bicarbonate (HCO ₃ ⁻) | SC Specific conductance, in microsiemens per centimeter |
| Carbonate (CO ₃ ⁻²) | < Less than |
| | ≤ Less than or equal to |

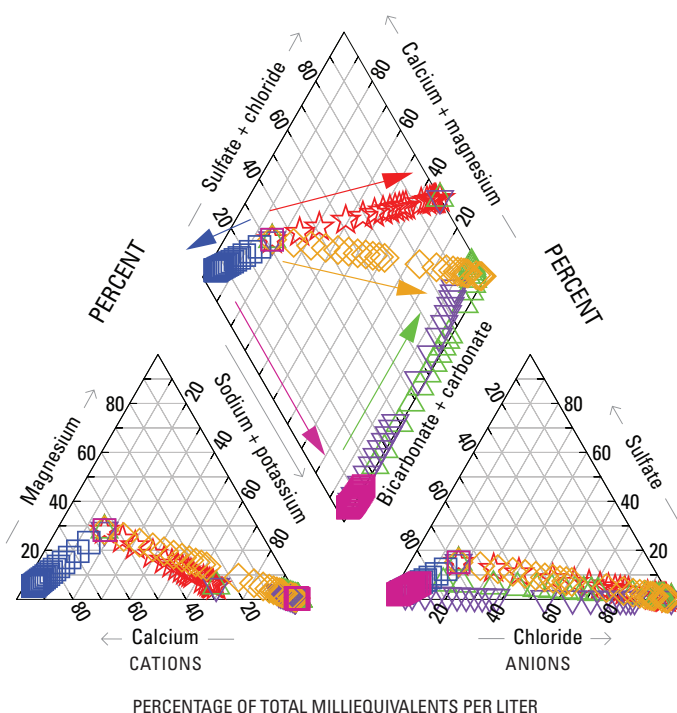
Figure 16. Trilinear diagrams showing *A*, predominant water types or hydrochemical facies; and *B*, data for groundwater samples collected from 75 wells in Lycoming County, Pennsylvania, 2014, plus median composition of brine from oil and gas wells in western Pennsylvania (Dresel and Rose, 2010) and flowback water from Marcellus Shale gas wells (Hayes, 2009). Symbols for groundwater scaled by specific conductance.

A. Lycoming County groundwater 2014



- EXPLANATION**
- Groundwater sample number
- LY718
 - LY732
 - ◆ LY557
 - ▼ LY721
 - ▽ LY432
 - LY432
 - ⊗ LY749
 - ▲ LY700
 - ◆ LY719
 - ⊗ LY703
 - LY731
 - ▲ LY716
 - LY755
 - ◆ LY760
 - ▽ LY781
 - △ LY735
 - LY722

B. Groundwater + road-deicing salt; groundwater + calcite ± exchange



- EXPLANATION**
- Groundwater plus calcite
 - Groundwater plus calcite plus exchange
 - ◇ Groundwater plus road salt
 - ★ Groundwater plus brine
 - △ Groundwater plus brine plus exchange
 - ▽ Groundwater plus brine plus calcite plus exchange

Figure 17. Trilinear diagrams showing A, data for 17 selected groundwater samples from Lycoming County, Pennsylvania, 2014; and B, evolution pathways for mixing of dilute calcium/bicarbonate groundwater with road-deicing salt, with brine, with brine combined with cation-exchange, or with brine plus calcite dissolution to saturation and then cation-exchange. Evolution pathways computed for groundwater sample LY557 mixed in varying proportions with median composition for brine and for the same initial groundwater sample with varying amounts of road-deicing salt.

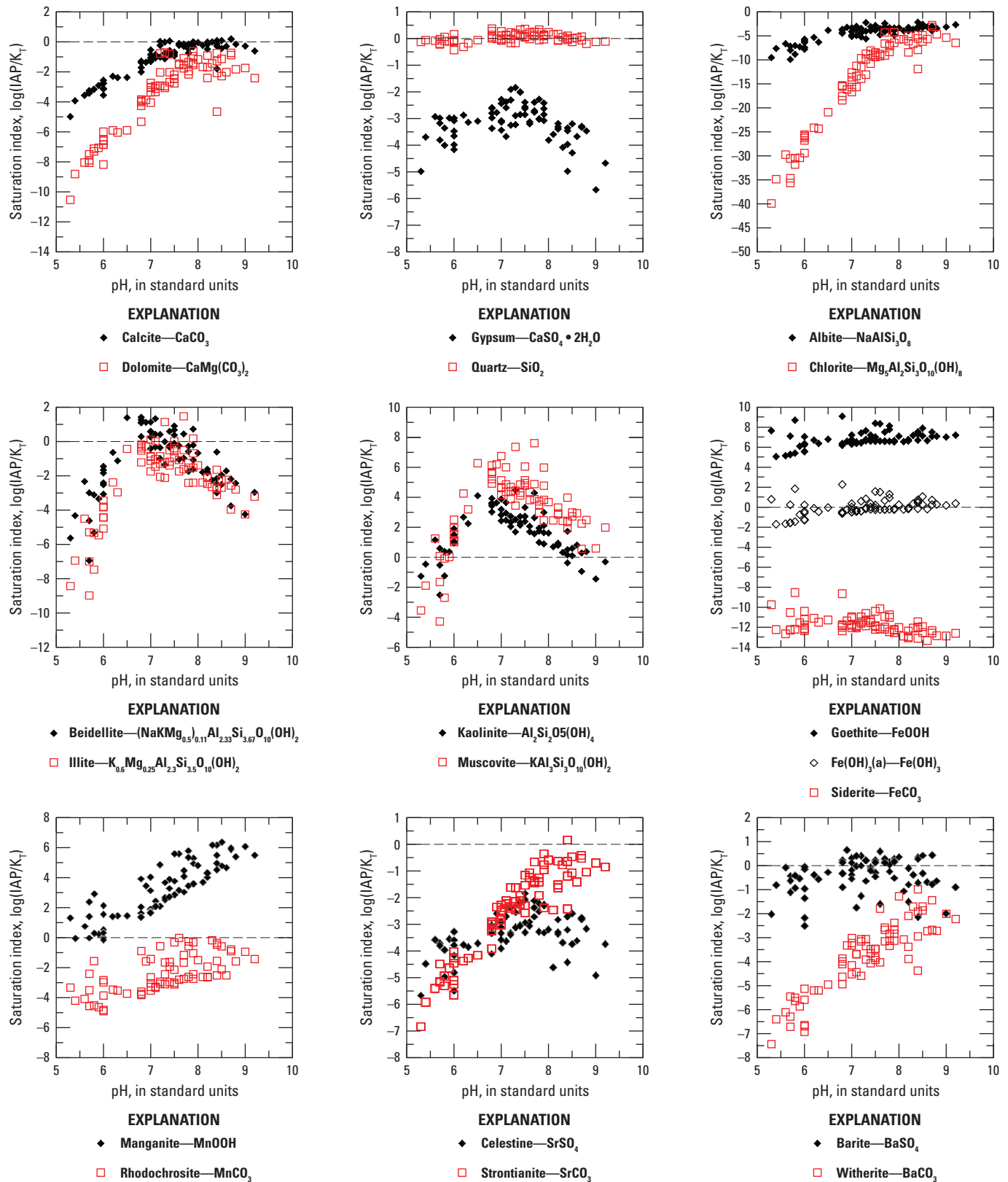


Figure 18. Saturation indices for minerals and other solids as a function of pH for groundwater samples collected from 75 wells in Lycoming County, Pennsylvania, 2014. Computations with PHREEQC aqueous geochemical computer program (Parkhurst and Appelo, 2013) using the wateq4f.dat database file derived from the WATEQ4F ion-association aqueous model (Ball and Nordstrom, 1991). [IAP, Ion Activity Product; K_f , equilibrium constant for reaction at temperature T]

rhodochrosite, strontianite, and witherite were negative, indicating these carbonate minerals, if present, could feasibly be dissolved by the groundwater (fig. 18). Hence, dissolution of calcite, dolomite, or other carbonates could release various trace cations to solution. However, the concentrations of trace elements may be limited by the formation of other solid phases. For example, the accumulation of sulfate from rainfall, sulfide mineral oxidation, or gypsum dissolution could promote the observed supersaturation of barite, which could precipitate and limit the concentrations of dissolved barium (fig. 18). In contrast, celestine was indicated to be undersaturated (fig. 18). Nevertheless, strontium concentrations could possibly be limited by coprecipitation with barium in barite (Hanor, 1968). Furthermore, strontium, barium, and other trace cations could participate in exchange reactions with clay minerals or adsorption processes.

Hydrous oxides of iron and manganese are common in soils and weathered bedrock. The groundwater sampled for the study generally is indicated to be saturated or supersaturated with respect to iron and manganese oxides, which indicates such phases could feasibly precipitate as stable secondary phases (although the redox state is uncertain) upon dissolution of carbonates or oxidation of sulfides containing iron and manganese. The hydrous iron and manganese oxides are widely recognized as potential sorbents of trace anions (arsenic, selenium, molybdenum, and boron) at acidic pH and cations (copper, lead, and zinc) at near-neutral to alkaline pH (Appelo and Postma, 2005; Dzombak and Morel, 1990; Hem, 1985). Adsorption, or surface complexation, can maintain trace-element concentrations at low levels compared to the solubilities of corresponding trace-element minerals; however, as the pH or redox conditions change, the trace ions could be released into solution by the oxides (Chapman and others, 2012). An illustration of the effects of changes in pH on the potential for adsorption and desorption of trace elements by hydrous iron oxide, or hydrous ferric oxide, is shown in figure 19. Hydrous ferric oxide was specified as 90 mg/L, with a specific surface area of 600 square meters per gram consisting of 5×10^{-6} moles of strong binding sites and 2×10^{-4} moles of weak binding sites. Relevant anion or cation was specified as 0.05 millimole per liter (mmol/L) in matrix consisting of 5 mmol/L chloride, sulfate, and dissolved inorganic carbon plus sodium to balance charge.

Chloride, Bromide, and Sodium in Groundwater

The concentrations of chloride (0.5 to 938 mg/L), bromide (<0.03 to 2.71 mg/L), and sodium (0.5 to 609 mg/L) for the 75 groundwater samples collected for this study ranged widely and were positively correlated with one another. In Lycoming County, chloride concentrations greater than a few mg/L in shallow groundwater may result from human activities or contributions from naturally present, deeper, more saline groundwater of regional extent. 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 elevated (but two or more orders of magnitude smaller) concentrations of bromide, which could indicate influence from residual brine of geologic origin.

Chloride/bromide ratios can be useful to distinguish different sources of chloride (Davis and others, 1998; Mullaney and others, 2009; Whittemore, 2007). 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 road-deicing salt (sodium chloride) or salt present in septic effluent, typically have low amounts of bromide and relatively high chloride/bromide mass ratios. Recent studies of groundwater quality in nearby Susquehanna County in northeastern Pennsylvania (Warner and others, 2012; Llewellyn, 2014; Siegel and others, 2015) have reported groundwater that has concentrations of chloride and chloride/bromide ratios that indicate possible mixing with higher salinity or brine-type waters; these brine-type waters are postulated to be discharging from undetermined depths below the freshwater aquifer and mixing with shallow, more dilute groundwater (fig. 12).

The chloride/bromide mass ratios for the 75 Lycoming County well-water samples are shown in relation to chloride concentrations in figures 20A and 20B, which also show curves representing compositions resulting from mixing of different proportions of dilute groundwater with (1) relatively pure sodium chloride salt containing only a trace of bromide (such as road-deicing salt, salt in water softeners, and salt present in human and animal waste) or (2) bromide-rich oil and gas well brines (such as that from wells producing gas from the Marcellus Shale). Most of the Lycoming County well-water samples, including the sample with the highest chloride concentration (from well LY722) of 938 mg/L, plotted on or near the mixing curve for relatively pure sodium chloride salt; however, several well-water samples (from wells LY760, LY384, LY781, and LY735) had relatively high bromide concentrations (greater than 0.1 mg/L) with low chloride/bromide mass ratios (about 120 to 150 mg/L) compared to their chloride concentrations of 20 mg/L and higher (fig. 20). These well-water samples plotted near or on the mixing curve for oil and gas well brines (figs. 20A, B, and C), indicating a possible small contribution of chloride from a brine-like source. Salt Spring, a natural saline spring in Susquehanna County, also plotted along the brine mixing curve. Mixing curves computed for initial fresh water with chloride of 0.5 to 0.6 mg/L and bromide of 0.025 to 0.035 mg/L mixed with road-deicing salt (fig. 20 upper curve, after Llewellyn, 2014) or with median composition of oil and gas well brine (fig. 20 lower curve, after Dresel and Rose, 2010). Selected samples having methane concentrations ≥ 0.7 mg/L, alkaline pH, or other chemical characteristics illustrate the variable compositions of the samples from Lycoming County, Pennsylvania (fig. 20).

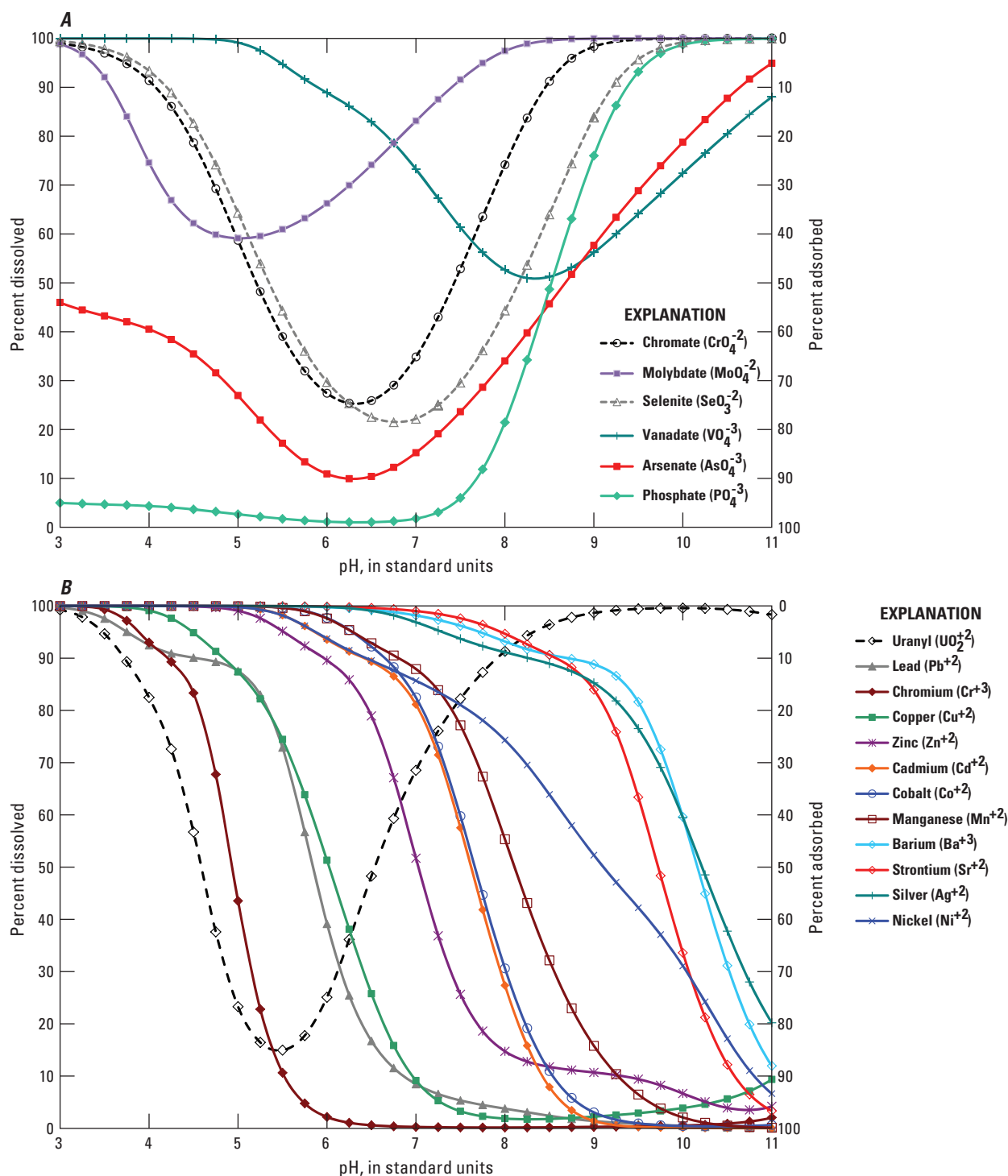


Figure 19. Equilibrium fractions of initial concentrations of *A*, anions or *B*, cations that may be dissolved or adsorbed on a finite amount of hydrous ferric oxide at 25 degrees Celsius as a function of pH. Area below curve indicates fraction that is not adsorbed; area above curve indicates fraction adsorbed. Simulations conducted using PHREEQC aqueous geochemical modeling program (Parkhurst and Appelo, 2013) with thermodynamic data from Ball and Nordstrom (1991), Duro and others (2012), and Dzombak and Morel (1990).

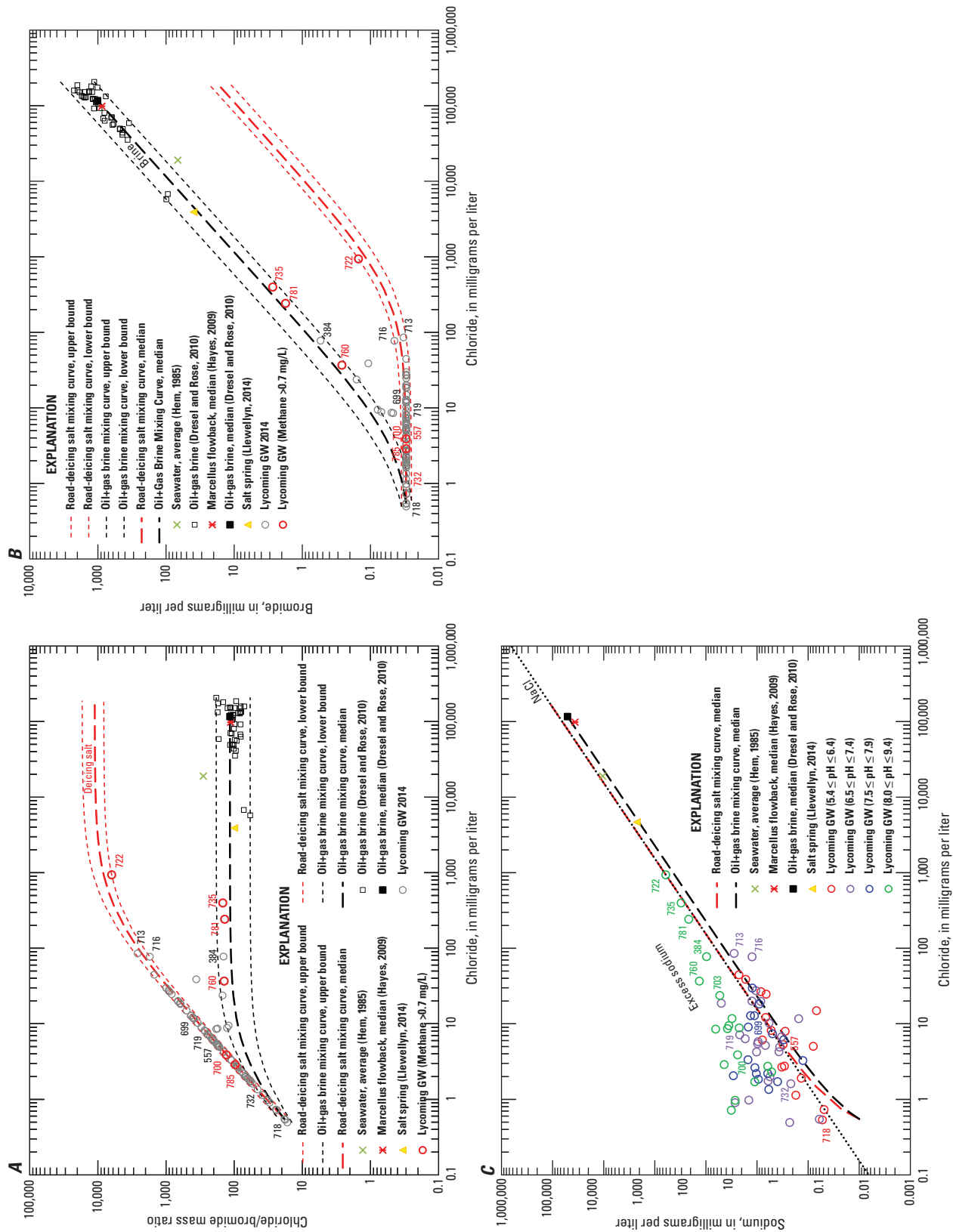


Figure 20. Chloride concentrations compared to *A*, chloride/bromide mass ratios; *B*, bromide concentrations; *C*, sodium concentrations for groundwater from Lycoming County, Pennsylvania, 2014, plus median values for Salt Spring (Llewellyn, 2014), flowback waters from Marcellus Shale gas wells (Hayes, 2009), and oil and gas well brines from Western Pennsylvania (Dresel and Rose, 2010). (GW, groundwater; mg/L, milligrams per liter)

Of the six water samples that had methane concentrations ≥ 0.7 mg/L, three samples (from wells LY785, LY700, and LY722) had chloride/bromide ratios that plotted on the road-deicing salt mixing curve, whereas the remaining samples (from wells LY735, LY781, and LY760) had chloride/bromide mass ratios that plotted on the brine mixing curve (figs. 20A–C). These six wells were located in valleys or on valley sides and had depths ranging from 149 to 500 feet below the land surface. Nevertheless, many other wells in the valley settings did not exhibit elevated methane concentrations.

Most of the samples had chloride/bromide ratios that plotted along the mixing curve for road-deicing salt, which is essentially sodium chloride that is also present in human and animal waste. For example, the water sample from well LY722, which had the highest concentration of chloride (938 mg/L = 26.5 mmol/L), had an equal molar concentration of sodium (609 mg/L = 26.5 mmol/L), which could result by the dissolution of pure sodium chloride by groundwater or recharge water (fig. 20C). Nevertheless, compared to the stoichiometry for sodium chloride, many other samples that had chloride and bromide compositions plotting on the chloride/bromide mixing curve for salt also contained excess sodium (greater than 1:1 [sodium]:[chloride] molar ratio or 22.99:35.45 mass ratio). The excess sodium, which can be derived from mineral sources that do not contain chloride, may result from the release of residual sodium on cation-exchange sites on clay minerals to the groundwater.

The chloride/bromide and associated constituent relations for the Lycoming County well-water samples collected for this study are similar to those for 20 groundwater samples collected in 2012 in Sullivan County (Sloto, 2013), 20 groundwater samples collected in 2012 in Pike County (Senior, 2014), and 121 groundwater samples collected in 2013–14 in Wayne County (Senior and others, 2016). These studies consistently indicate that groundwater in north-central and northeastern Pennsylvania has locally elevated concentrations of bromide, chloride, sodium, and methane.

Geochemical Models

The evolution pathways for the major ions indicated on the Piper diagram (fig. 17) and also as mixing curves on the bromide/chloride and sodium/chloride plots (fig. 20) were computed using the PHREEQC aqueous geochemical computer program to create geochemical models considering the various mixing scenarios with road-deicing salt or brine, plus reactions including calcite dissolution and (or) cation-exchange. In addition to determining the concentrations of major cations and bromide, the geochemical models indicated the effects of reactions and mixtures on the pH and the concentrations of minor elements including strontium, barium, potassium, and lithium.

Parallel sets of reaction models initially simulated the addition of road-deicing salt or brine to groundwater, without or with calcite dissolution, but did not consider

cation-exchange (fig. 21). The simplest models indicated the effect of increasing additions of road-deicing salt (fig. 21A) or brine (fig. 21C) to the initial groundwater. For both scenarios, the pH decreased progressively from the initial value of 5.8, whereas the concentrations of sodium, chloride, and bromide increased. Because the samples that had elevated sodium (53 to 610 mg/L) had alkaline pH (fig. 13A), these conservative mixing models were considered unsatisfactory and were enhanced by specifying that calcite would dissolve to equilibrium (figs. 21B and D). The resultant models that involved mixing and calcite dissolution produced results that could explain the formation of acidic to near-neutral waters of calcium-sodium/bicarbonate-chloride types, such as samples from wells LY731 or LY719, but not the sodium/bicarbonate types with pH values greater than 8.

The geochemical models were modified further to evaluate the potential effects of calcite dissolution plus cation-exchange on the pH and solute concentrations (fig. 22). For these models, instead of road-deicing salt, calcite is added progressively to the initial groundwater, without or with cation-exchange (figs. 22A and B). Likewise, the groundwater plus brine mixing scenarios are considered with cation-exchange, without or with calcite dissolution (figs. 22C and D). Generally, calcite dissolution alone could produce near-neutral calcium/bicarbonate waters, which were the most common types. Furthermore, a mixture of 0.01 percent to 0.07 percent brine plus groundwater could produce the observed concentrations of bromide and chloride plus other major and trace ions. However, calcite dissolution plus cation-exchange was required to produce the elevated pH, ALK, and sodium concentrations. The exchange sites were modeled as containing mostly sodium, with minor calcium, magnesium, strontium, barium, and lithium (instead of all sodium). Thus, observed concentrations of strontium, barium, and lithium could be maintained or increased through the exchange reactions.

Isotopic Composition of Methane and Origin of Methane Gas

Only the five samples (from wells LY700, LY735, LY781, LY785, and LY722) with the highest concentrations of methane (0.9 to 16.8 mg/L) were analyzed for the stable isotopic compositions of methane, deuterium and carbon, and the associated concentrations of higher-chain hydrocarbon gases (fig. 23). Ethane was detected at concentrations ranging from 0.67 to 60 $\mu\text{g/L}$ in all five samples, propane was detected at concentrations ranging from 0.2 to 0.5 $\mu\text{g/L}$ in four samples, and butane was detected at 0.2 $\mu\text{g/L}$ in one sample. The elevated ratios of methane to ethane plus higher-chain hydrocarbons for all five samples implies a microbial origin of the methane (fig. 23B), owing to the lack of significant microbial generation of the higher-chain hydrocarbon gases (Strapoć and others, 2011). However, the isotopic compositions of methane in four of the five groundwater samples are consistent with a predominantly thermogenic source of the methane (figs. 23A

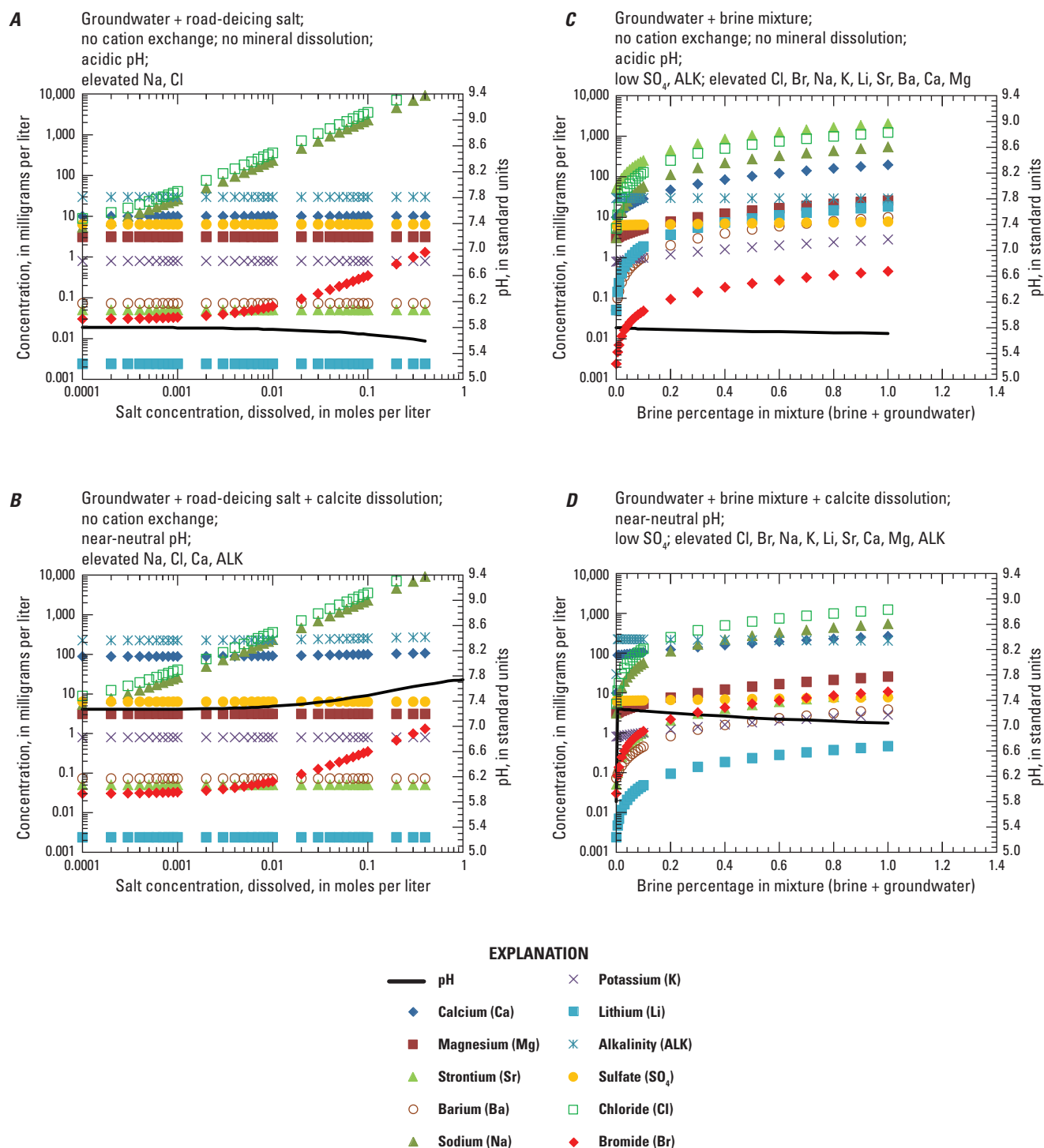


Figure 21. Computed compositions of waters resulting from dissolution of road-deicing salt and (or) calcite, but without cation-exchange. Low-ionic strength groundwater (LY557) *A*, dissolves road-deicing salt without other reactions; *B*, dissolves road-deicing salt plus dissolves calcite to equilibrium (saturation index = 0); *C*, mixes with median oil and gas well brine (Dresel and Rose, 2010) without reactions; and *D*, mixes with median oil and gas well brine with calcite dissolution to equilibrium. Computations conducted using the aqueous geochemical computer program, PHREEQC (Parkhurst and Appelo, 2013).

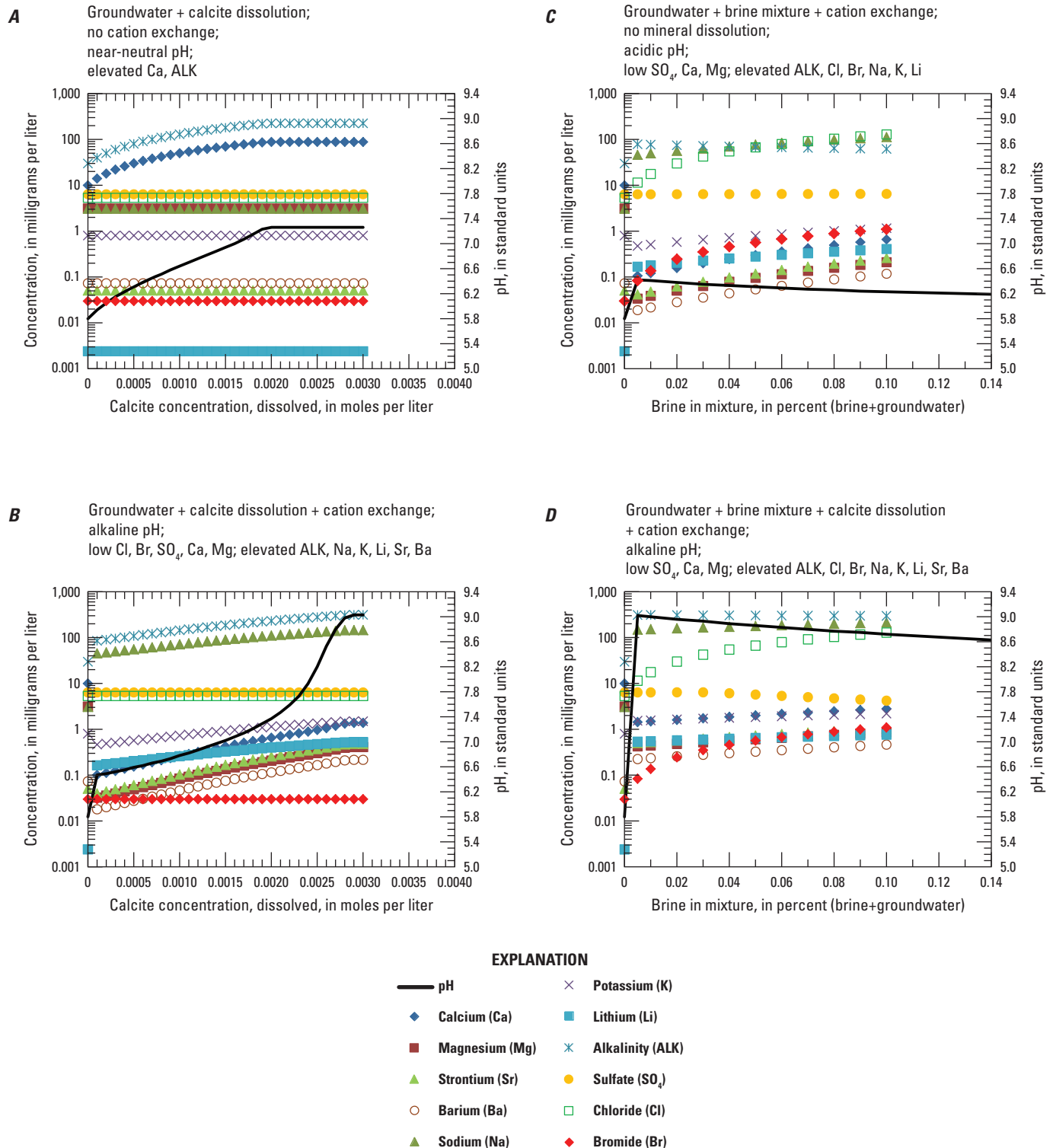


Figure 22. Computed composition of waters resulting from mixing of different solutions and (or) reactions including dissolution of calcite and cation-exchange. Low-ionic strength groundwater (LY557) dissolves incremental amounts of calcite until reaching equilibrium *A*, without cation-exchange; or *B*, with cation-exchange. Mixing of low-ionic strength groundwater with median oil and gas well brine (Dresel and Rose, 2010) *C*, with cation-exchange; and *D*, with calcite dissolution to equilibrium and cation-exchange. Computations conducted using the aqueous geochemical computer program, PHREEQC (Parkhurst and Appelo, 2013).

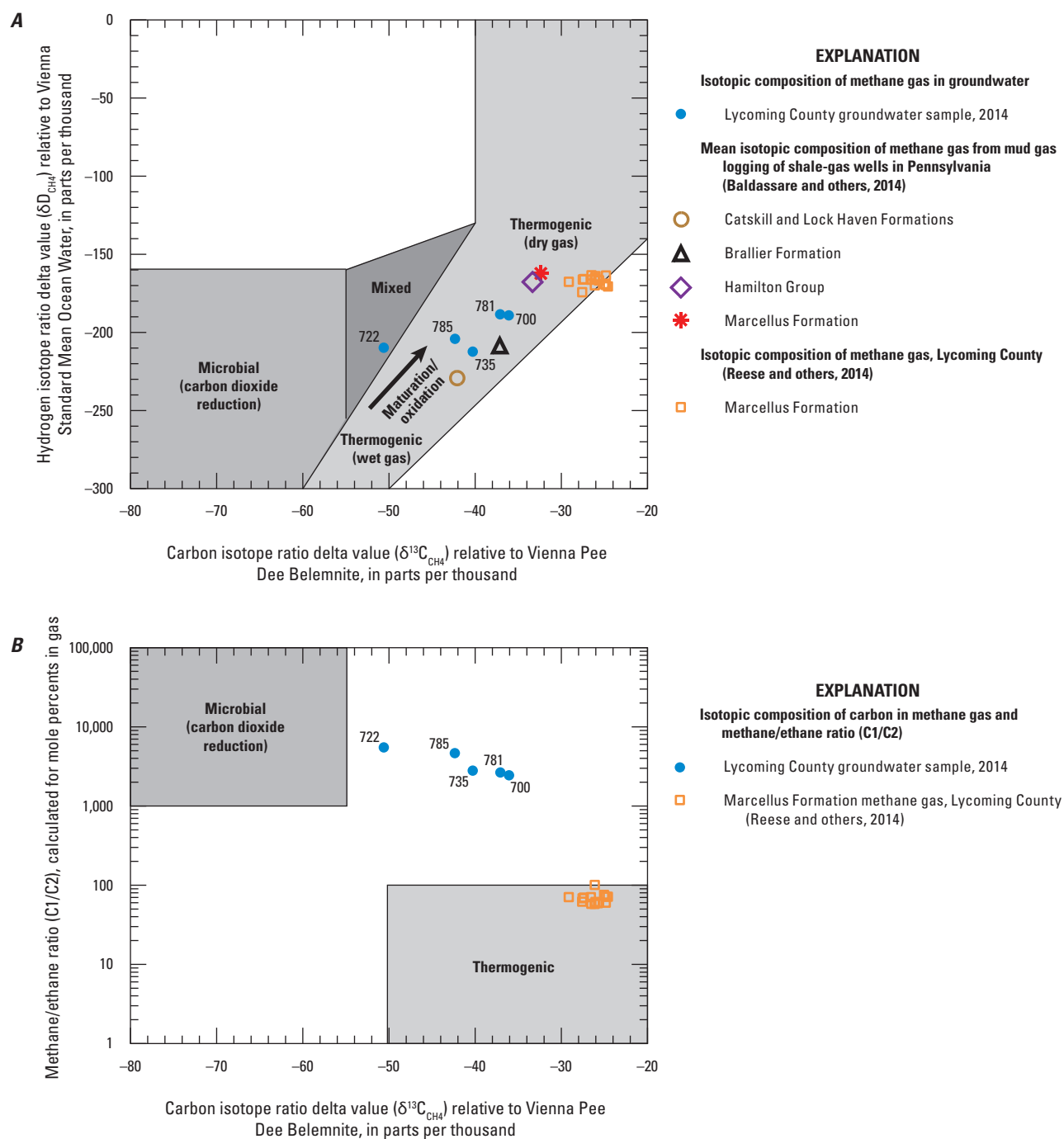


Figure 23. A, Isotopic composition of methane in groundwater samples collected from five wells in Lycoming County, Pennsylvania, 2014, and B, ratio of methane to higher-chain hydrocarbons in relation to carbon isotopic composition for methane in these samples. Boundaries for microbial and thermogenic gas types and compositional shift related to gas maturation/oxidation, shown by arrow, from Reese and others (2014, figure 30, p. 38). Marcellus Formation methane gas data for Lycoming County from Reese and others (2014, table 7), and mud-gas logging data by geologic formation from Baldassare and others (2014, table 1).

and 23B). These four samples, from the Catskill and Lock Haven Formations and the Hamilton Group, have carbon isotopic ratios delta values ranging from -42.36 to -36.08 ‰ and hydrogen isotopic ratios delta values ranging from -212.0 to -188.4 ‰, which are consistent with the isotopic compositions reported for mud-gas logging samples from these geologic units and a thermogenic source of the methane. The fifth sample had the highest concentration of methane, 16.8 mg/L, with a carbon isotopic ratio delta values of -50.59 ‰ and a hydrogen isotopic ratio delta values of -209.7 ‰, which are consistent with methane of mixed thermogenic and microbial origins or, possibly, microbial gas that subsequently underwent oxidation.

The methane in four of these five groundwater samples, from wells located in the Catskill and Lock Haven Formations (LY700, LY735, LY781) and wells located in the Hamilton Group (LY785), have carbon isotopic ratio delta values ranging from -42.36 to -36.08 ‰ and hydrogen isotopic ratio delta values ranging from -212.0 to -188.4 ‰, which are consistent with the isotopic compositions reported by Baldassare and others (2014) for mud-gas logging samples from these geologic units; however, the methane in these groundwater samples has lower (lighter) carbon isotopic ratio delta values than those reported by Reese and others (2014) for Marcellus Formation methane gas samples from Lycoming County. The fifth sample (from well LY722) had the highest concentration of methane, 16.8 mg/L, with a carbon isotopic ratio delta values of -50.59 ‰ and hydrogen isotopic ratio delta values of -209.7 ‰, which was closer than other samples identifying with a microbial origin of the methane. These characteristics could indicate a mixed thermogenic and microbial source (carbon-dioxide reduction process) of methane and also could imply that methane of microbial origin has been oxidized (becoming isotopically heavier).

Groundwater with relatively elevated methane concentrations (near or above 1 mg/L) also had a chemical composition that differed in some respects (pH, selected major ions and inorganic trace constituents) from groundwater with low methane concentrations. The five well-water samples with the highest methane concentrations also had among the highest pH values (8.25 to 9.0) and elevated concentrations of sodium, lithium, boron, fluoride, arsenic, and bromide. Relatively elevated concentrations of some other constituents, such as barium, strontium, and chloride, commonly were present in, but not limited to, those well-water samples with elevated methane.

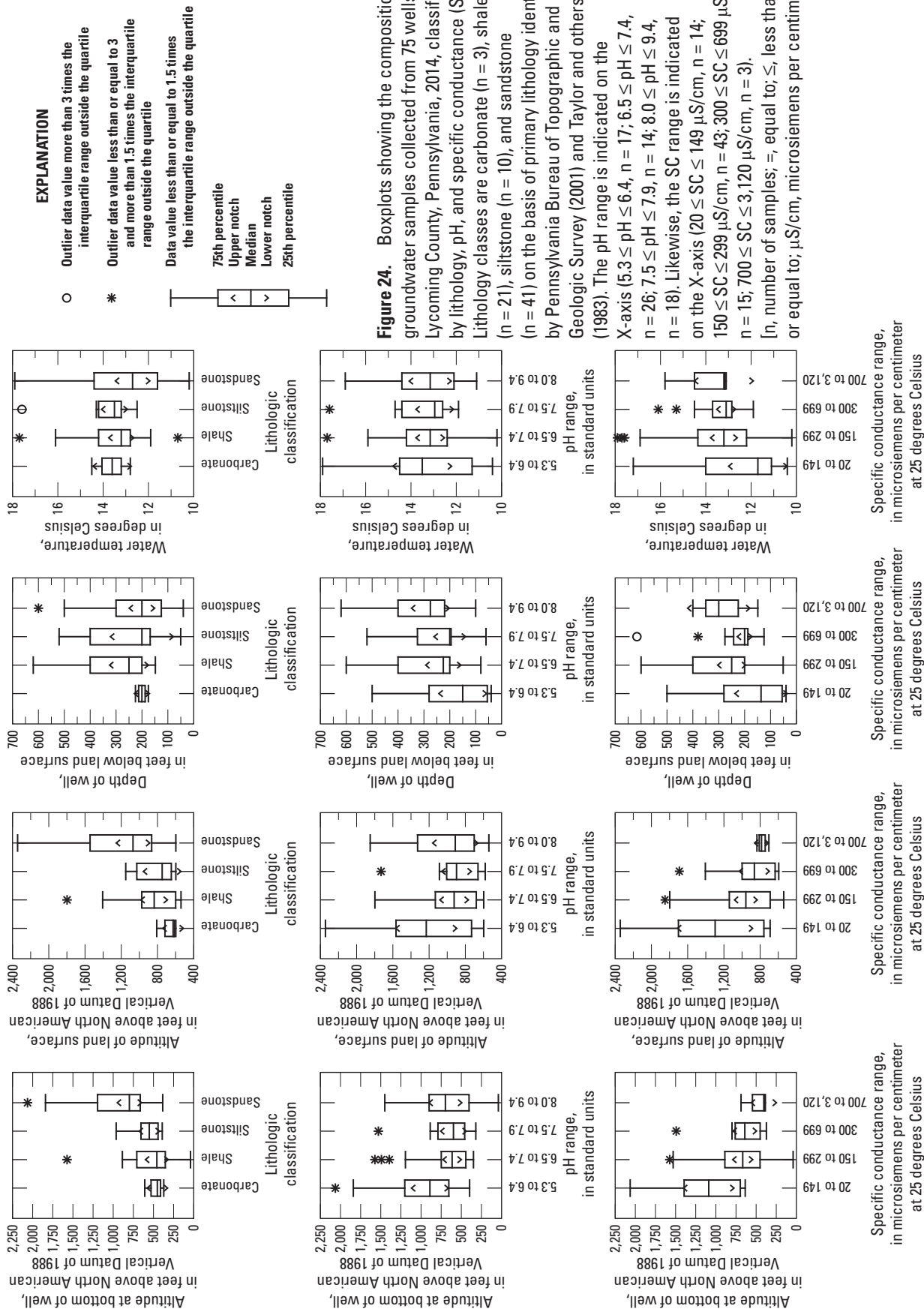
Spatial Distribution of Dissolved Methane and Associated Constituents

The spatial distribution of methane and associated groundwater-quality characteristics in Lycoming County is complex. Generally, the pH, SC, and associated concentrations of major and trace constituents are related to the predominant

bedrock lithology (fig. 3 and table 1), which influences the topography and hydrogeology (Taylor and others, 1984). Boxplots in the appendix (figs. 3–1 through 3–4) illustrate variations in dissolved methane and other constituents as a function of the pH, SC, redox, and lithology. Additionally, spatial relations of the water quality are illustrated by boxplots of the land surface elevation, well depth, well bottom elevation, and water temperature by major lithology, pH, and SC (fig. 24).

In general, the uplands in northern areas of Lycoming County, which are underlain predominantly by sandstone bedrock usually have dilute (low conductivity), slightly acidic, oxygenated, calcium-bicarbonate type waters. In contrast, areas of intermediate altitudes in southern areas of the county, which are underlain by shale and siltstone bedrock, usually have calcium-bicarbonate and sodium bi-carbonate groundwater with near-neutral to alkaline pH values and moderate to high conductivity. A subset of samples from the shale and siltstone lithologies is characterized as sodium-chloride type water, which generally had the highest pH values along with elevated arsenic, sodium, lithium, and bromide concentrations. Areas of low to intermediate altitudes in the southern areas where carbonate bedrock predominates generally have groundwater with near neutral pH and highest amounts of hardness (calcium and magnesium).

Llewellyn (2014) described possible associations between elevated methane or brine signatures with deep faulting and associated structural features; however, the available data for this study indicate that no one physical factor such as the topographic setting, well depth, or altitude at the bottom of the well was particularly useful for predicting those well locations with an elevated dissolved concentration of methane. The five samples that had methane concentrations near or greater than 1 mg/L were from four of the six topographic settings, including valleys, lower slopes, upper slopes, and gentle slopes (fig. 25). Elevated methane was not associated with the waters from ridge settings; no wells were sampled, if present, in the steep slope topographic setting. The wells from which the elevated-methane samples had been collected had depths ranging from 149 to 500 feet. The two samples with the highest methane concentrations (fig. 25) were collected from wells with depths of 300 and 400 feet and with bottom elevations of 404 and 385 feet above the NAVD 88, respectively, in order of increasing methane concentration. Furthermore, as previously discussed, the sample with the greatest methane concentration (LY722) and two other samples with elevated methane (LY700 and LY785) had chloride/bromide ratios and corresponding chloride/sodium ratios that were indicative of a sodium chloride source and not a brine source (fig. 20). Methane in sample LY722 had an isotopic composition that could result by the oxidation of a microbial source (fig. 23). In contrast, three of the other four samples analyzed for isotopic composition (LY735, LY760, and LY781) had sodium, chloride, and bromide characteristics that were consistent with mixing of a fresh groundwater with a deep brine source.



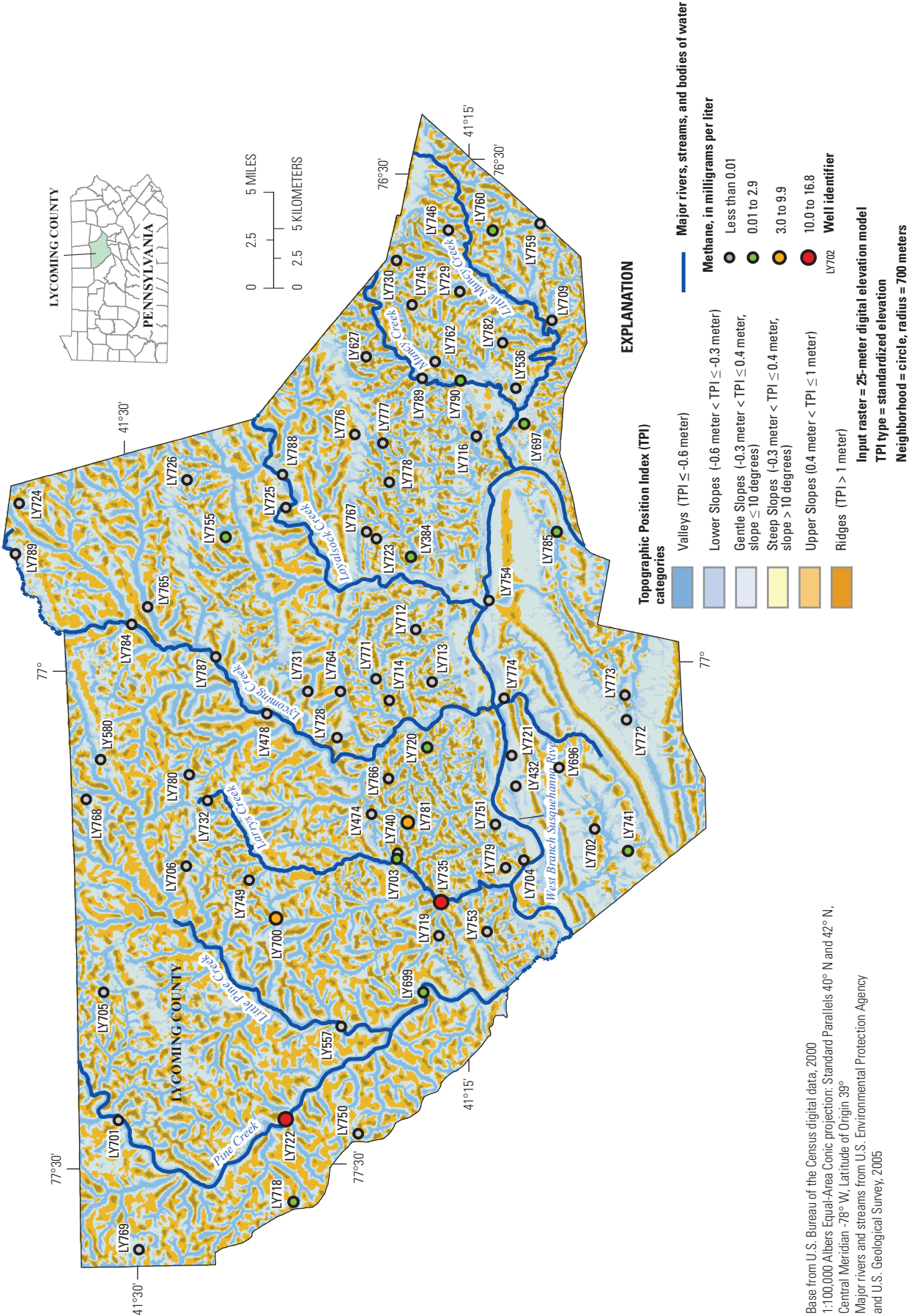


Figure 25. Spatial distribution of dissolved methane concentrations in 75 wells sampled and topographic position index categories in Lycoming County, Pennsylvania.

Summary and Conclusions

Approximately 43 percent of the population of Lycoming County, Pennsylvania, has a self-supplied drinking-water source, primarily groundwater. The groundwater used for water supply is mostly derived from wells completed in fractured bedrock (primarily sandstone, siltstone, shale, or limestone) and may also be derived from wells in alluvium and glacial outwash and drift overlying the bedrock in the stream valleys in the northern one-half of the county. This report, prepared in cooperation with Lycoming County, presents analytical data for groundwater samples from 75 domestic wells sampled throughout Lycoming County in June, July, and August 2014. The samples were collected using existing pumps and plumbing prior to any treatment and analyzed for physical and chemical properties, major ions, nutrients, radionuclides, metals and trace elements, manmade organic compounds, and dissolved gases, including methane and radon-222. Results for specific constituents are evaluated in relation to drinking-water standards established by the U.S. Environmental Protection Agency (EPA), which include maximum contaminant levels (MCLs), secondary maximum contaminant levels (SMCLs), and health advisory levels (HALs). These data are also used to indicate the variations among different bedrock lithologies (natural characteristics) and possible effects from human activities on the groundwater resource.

The groundwater quality generally met most drinking-water standards, but some samples exceeded MCLs, SMCLs, or HALs for arsenic, iron, manganese, total dissolved solids (TDS), chloride, pH, bacteria, or radon-222. Arsenic concentrations were higher than the MCL of 10 micrograms per liter ($\mu\text{g/L}$) in 9 of the 75 (12 percent) well-water samples, with concentrations as high as 23.6 $\mu\text{g/L}$; arsenic concentrations were higher than the HAL of 2 $\mu\text{g/L}$ in 23 samples (31 percent). Total iron concentrations exceeded the SMCL of 300 $\mu\text{g/L}$ in 20 of the 75 samples; total manganese exceeded the SMCL of 50 $\mu\text{g/L}$ in 20 of the 75 samples and the HAL of 300 $\mu\text{g/L}$ in 2 of those 20 samples. Two samples had chloride concentrations that exceeded the SMCL of 250 milligrams per liter (mg/L), and both of those samples exceeded the SMCL of 500 mg/L for TDS. The pH of water samples ranged from 5.3 to 9.15 and did not meet the SMCL range of 6.5 to 8.5 in 22 samples, with 17 samples having a pH less than 6.5, and 8 samples having pH greater than 8.5. Generally, samples that had elevated TDS, chloride, or arsenic concentrations had high pH. Total coliform bacteria were detected in 39 of 75 samples (52 percent), with *Escherichia coli* detected in 10 of those 39 samples. Radon-222 activities ranged from non-detect to 7,420 picocuries per liter (pCi/L), with a median of 863 pCi/L , and exceeded the proposed drinking-water standard of 300 pCi/L in 50 of the 75 samples (67 percent); radon-222 activities were higher than the alternative proposed standard of 4,000 pCi/L in 3 of the 75 samples.

Water from 15 of 75 (20 percent) wells had concentrations of methane greater than the reporting level of 0.01 milligrams per liter (mg/L), which ranged from 0.04 to

16.8 mg/L . Two samples had methane concentrations (13.1 and 16.8 mg/L) exceeding the action level of 7 mg/L . Low levels of ethane (up to 0.12 mg/L) were present in five samples with the highest methane concentrations. The occurrence of hydrocarbon gas composed of predominantly methane with minor concentrations of higher chain hydrocarbons (ethane, propane, and butane) could indicate a microbial source of the methane. Nevertheless, methane in four of these groundwater samples, from the Catskill and Lock Haven Formations and the Hamilton Group, had carbon isotopic ratio delta values ranging from -42.36 to -36.08 parts per thousand (‰) and hydrogen isotopic ratio delta values ranging from -212.0 to -188.4 ‰, which are consistent with the isotopic compositions reported for mud-gas logging samples from these geologic units and a thermogenic source of the methane. The fifth sample had the highest concentration of methane, 16.8 mg/L , with a carbon isotopic ratio delta values of -50.59 ‰ and a hydrogen isotopic ratio delta values of -209.7 ‰ that are consistent with methane of mixed thermogenic and microbial gas that subsequently underwent oxidation.

Groundwater with relatively elevated methane concentrations (near or above 1 mg/L) also had a chemical composition that differed in some respects (pH, selected major ions and inorganic trace constituents) from groundwater with low methane concentrations. The five well-water samples with the highest methane concentrations also had among the highest pH values (8.25 to 9.0) and elevated concentrations of sodium, lithium, boron, fluoride, arsenic, and bromide. Relatively elevated concentrations of some other constituents, such as barium, strontium, and chloride, commonly were present in, but not limited to, those well-water samples with elevated methane and pH.

Three of the six groundwater samples with the highest methane concentrations had chloride/bromide ratios that are consistent with mixing fresh groundwater with a small amount of brine (0.02 percent or less) similar in composition to those reported for gas and oil well brines in Pennsylvania. Such brines generally may be naturally present at undetermined depths below the freshwater aquifer. The sample with the highest methane concentration and most other samples with low methane concentrations (less than about 1 mg/L) have chloride/bromide ratios that indicate predominantly anthropogenic sources of chloride, such as road-deicing salt, septic systems, and (or) animal waste. Although brines may be naturally present and originate from deeper parts of the aquifer system, the anthropogenic sources are more likely to affect shallow groundwater.

The spatial distribution of groundwater compositions generally is related to the predominant bedrock. In general, (1) uplands underlain by sandstone bedrock in the northern area of Lycoming County usually have relatively dilute, slightly acidic, oxygenated, calcium-bicarbonate type waters; (2) the southern area of low to intermediate altitudes underlain by carbonate bedrock usually has calcium-bicarbonate water with moderate to high conductivity, near-neutral pH, and highest amounts of hardness (calcium and magnesium); and (3) the

southern area underlain by shale and siltstone bedrock usually has water with near-neutral to alkaline pH values ≥ 8 and highest arsenic, sodium, lithium, and bromide concentrations. Geochemical modeling indicated that for samples with elevated pH, sodium, lithium, bromide, and alkalinity, the water chemistry could have resulted by dissolution of calcite (calcium carbonate) combined with cation-exchange and mixing with a small amount of brine. Through cation-exchange reactions, which are equivalent to processes in a water softener, calcium ions released by calcite dissolution are exchanged for sodium ions on clay minerals. Consequently, the water becomes undersaturated with calcite and can dissolve additional calcite; through repeated exchange and dissolution steps, the pH can increase to values greater than 8. Constituents such as arsenic tend to be mobile at high pH. Thus, the current assessment of groundwater quality in Lycoming County generally meets drinking-water standards established by the EPA, but concentrations of arsenic may exceed MCLs and HALs. Some samples in various parts of the aquifer indicated groundwaters that can have elevated concentrations of iron and manganese and low to moderate concentrations of methane and some constituents that are typically found in high concentrations in natural brine and produced waters from gas and oil wells.

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Appendixes 1, 2, and 3

Appendix 1

Table: Compilation of data not available in the National Water Information System (doi <http://dx.doi.org/10.5066/F7P55KJN>), including station name, station identification number, lithologic class, and topographic position index, for wells sampled by the U.S. Geological Survey in Lycoming County, Pennsylvania, June–August 2014. (Appendix 1 available online as Excel file at <https://doi.org/10.3133/sir20165143>)

Appendix 2

Table: Spearman rank correlation coefficient (r) matrix for groundwater chemical data Lycoming County, Pennsylvania, 2014. (Appendix 2 available online as Excel file at <https://doi.org/10.3133/sir20165143>)

Appendix 3

Boxplots: Distributions of continuous variables were compared among different sample classifications using notched boxplots (Velleman and Hoaglin, 1981; Helsel and Hirsch, 2002). Statistically significant correlation coefficients and boxplots are presented. Where the median for a group is greater than the common reporting limit, it is displayed as a horizontal line within the box that is defined by the 25th and 75th percentiles for that group; otherwise, the median is displayed at the reporting limit. If the notched intervals around the medians for sample subsets do not overlap, the medians are statistically different at the 95-percent confidence interval.

Appendix 3. Boxplots

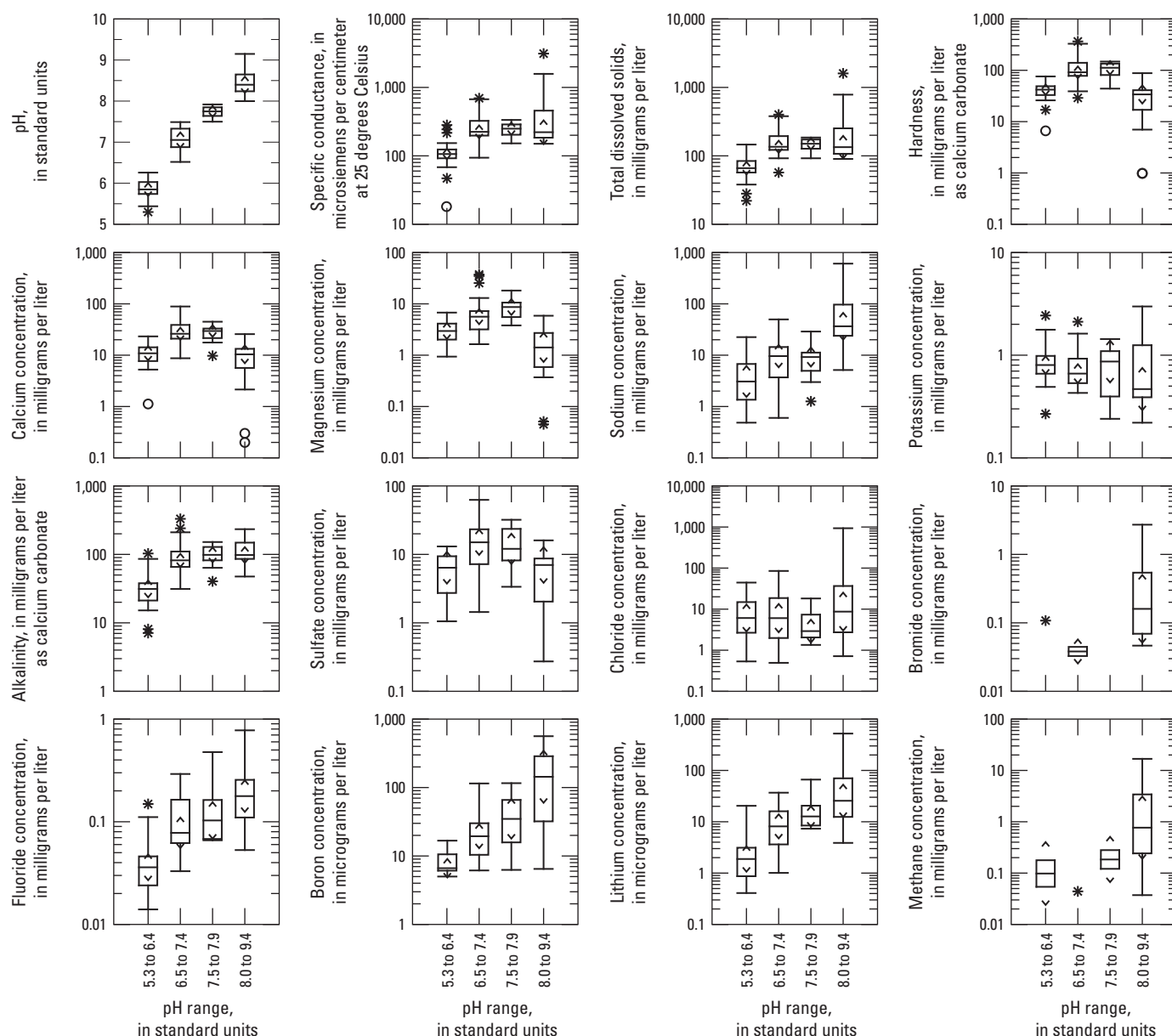
Distributions of continuous variables were compared among different sample classifications using notched boxplots (Velleman and Hoaglin, 1981; Helsel and Hirsch, 2002). Statistically significant correlation coefficients and boxplots are presented. Where the median for a group is greater than the common reporting limit, it is displayed as a horizontal line within the box that is defined by the 25th and 75th percentiles for that group; otherwise, the median is displayed at the reporting limit. 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 3-1: pH

Figure 3-2: Specific conductance

Figure 3-3: Redox

Figure 3-4: Lithologic class



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
- 75th percentile
- Upper notch
- Median
- Lower notch
- 25th percentile

Figure 3-1. Boxplots showing the composition of 75 groundwater samples from Lycoming County, Pennsylvania, 2014, classified by pH class interval. The pH range is indicated on the X-axis ($5.3 \leq \text{pH} \leq 6.4$, $n = 17$; $6.5 \leq \text{pH} \leq 7.4$, $n = 26$; $7.5 \leq \text{pH} \leq 7.9$, $n = 32$). (\leq , greater than or equal to; n , number of samples; $=$, equal to)

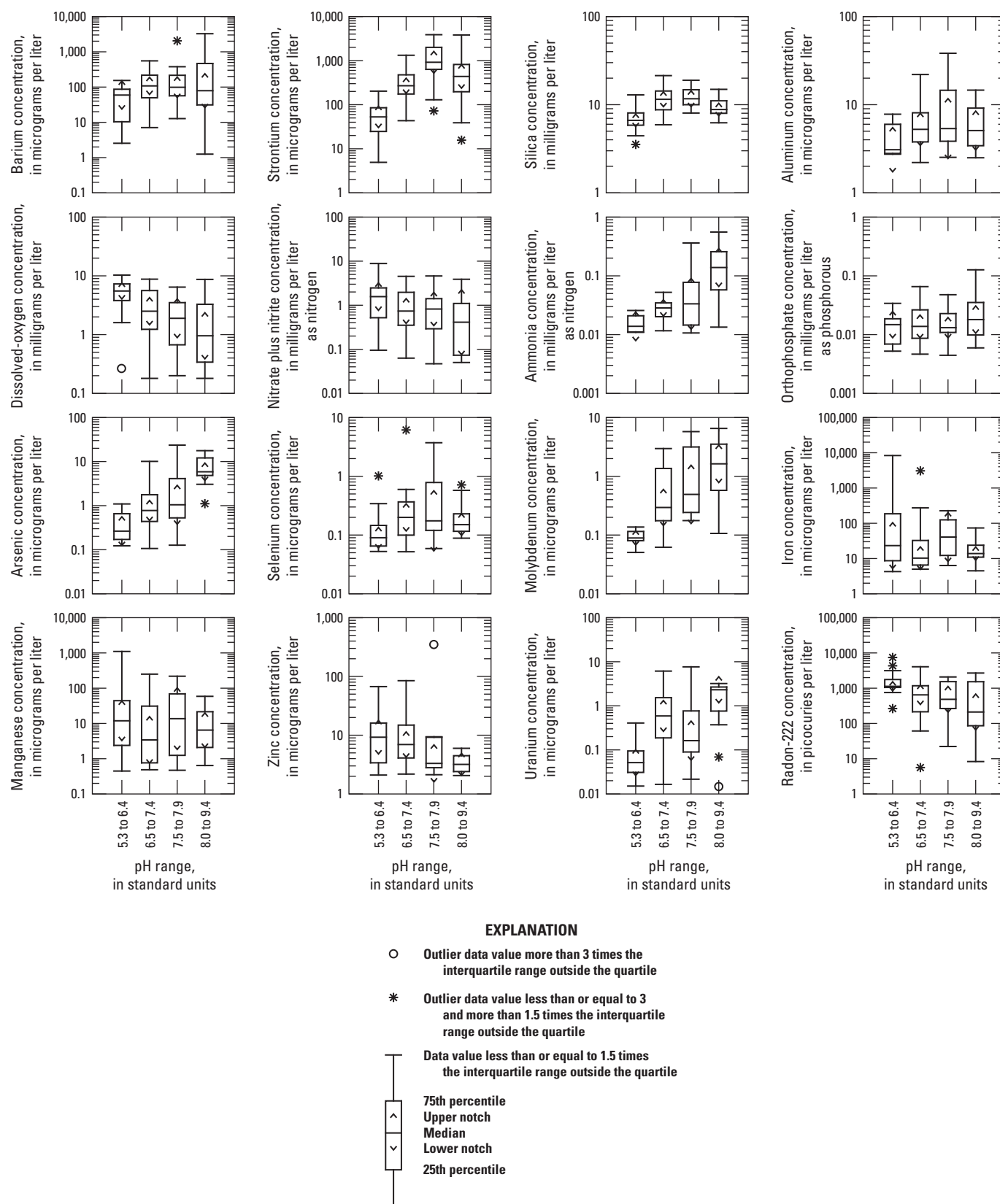


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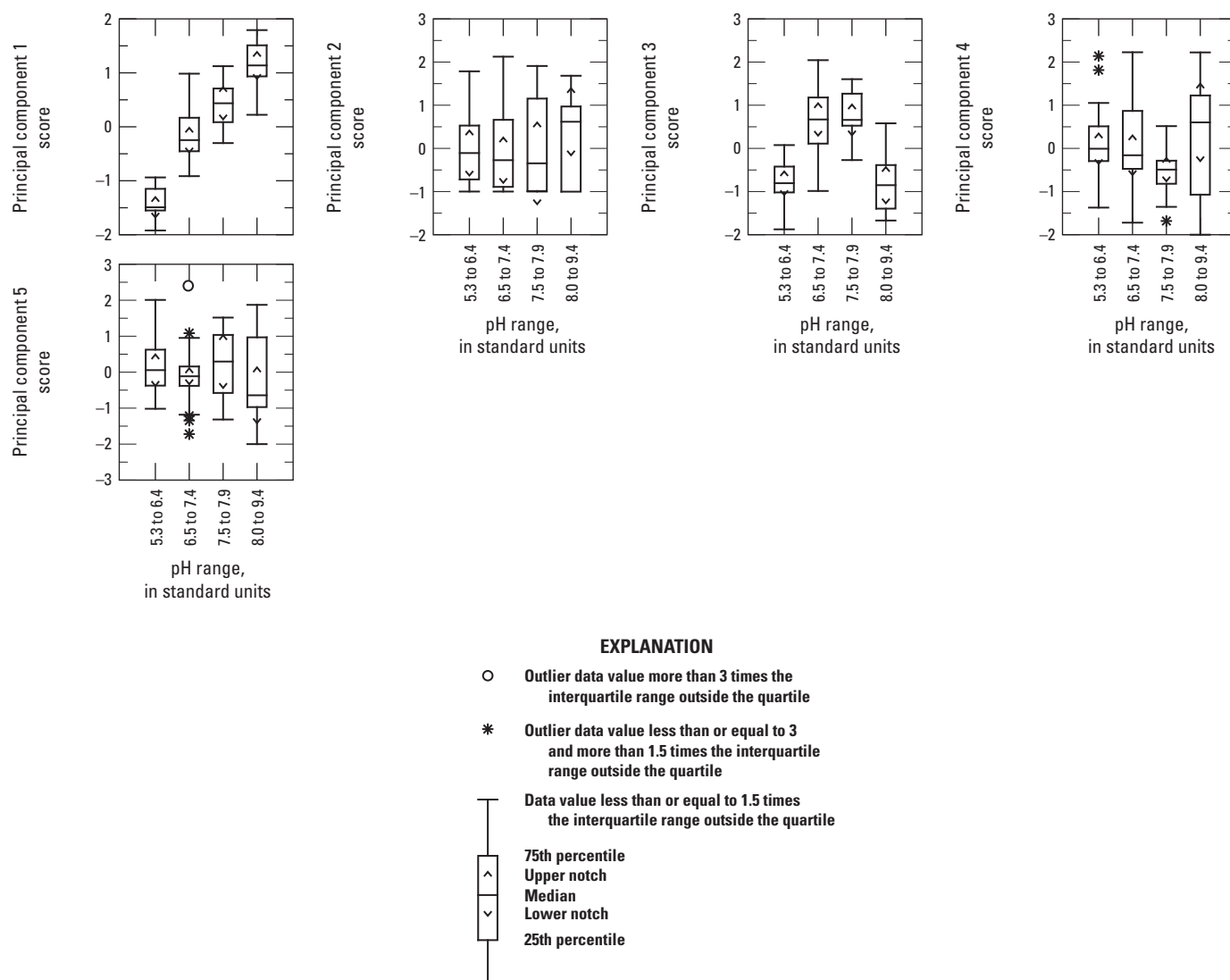


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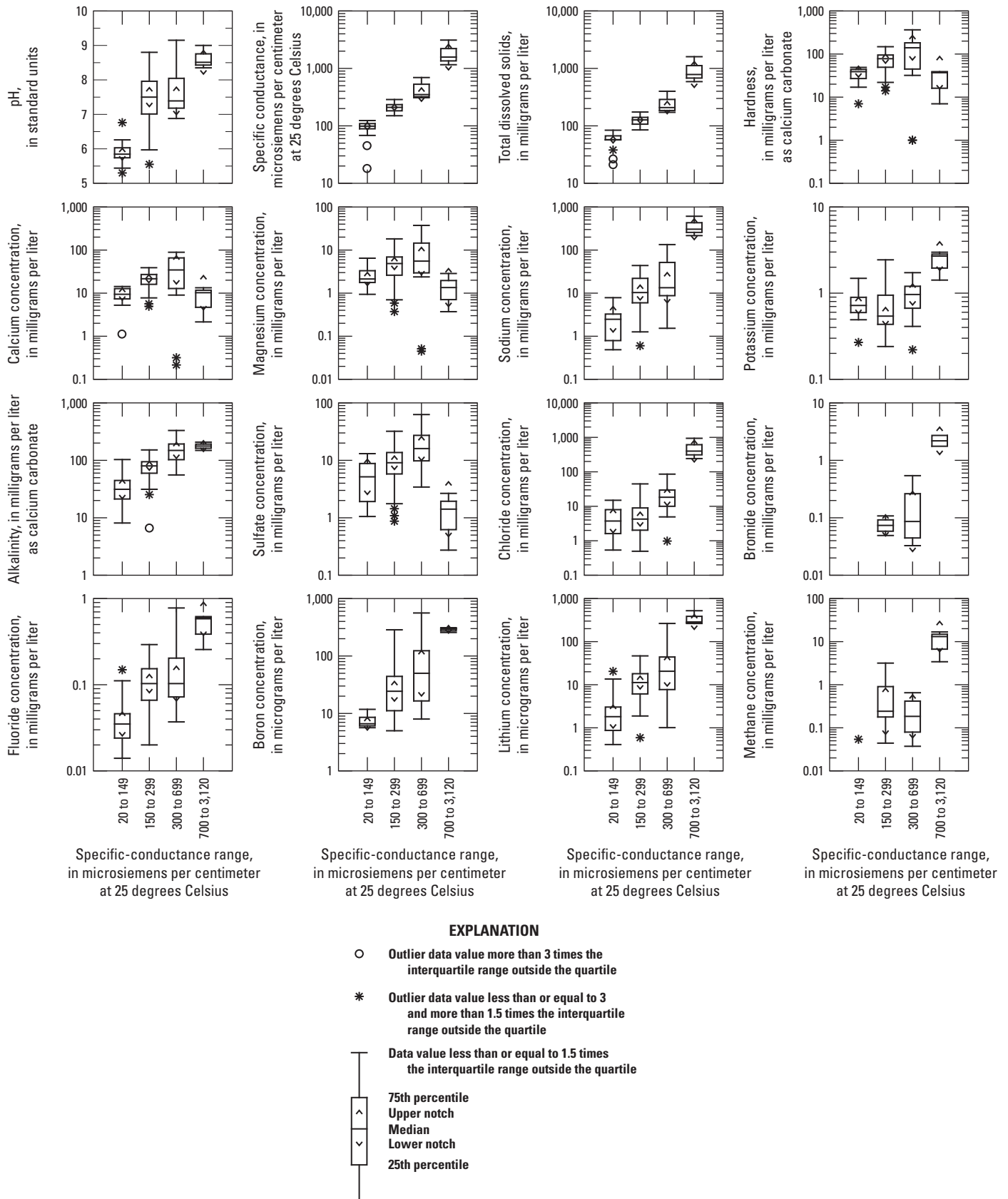


Figure 3-2. Boxplots showing the composition of 75 groundwater samples from Lycoming County, Pennsylvania, 2014, classified by specific conductance (SC) class interval. The SC range is indicated on the X-axis ($20 \leq SC \leq 149 \mu\text{S/cm}$, $n = 14$; $150 \leq SC \leq 299 \mu\text{S/cm}$, $n = 43$; $300 \leq SC \leq 699 \mu\text{S/cm}$, $n = 15$; $700 \leq SC \leq 3,120 \mu\text{S/cm}$, $n = 3$). Note that nitrate, aluminum, and zinc were not detected for the subset of samples in the highest SC class interval. (SC, specific conductance; \leq , greater than or equal to; $\mu\text{S/cm}$, microsiemens per centimeter; n , number of samples; $=$, equal to)

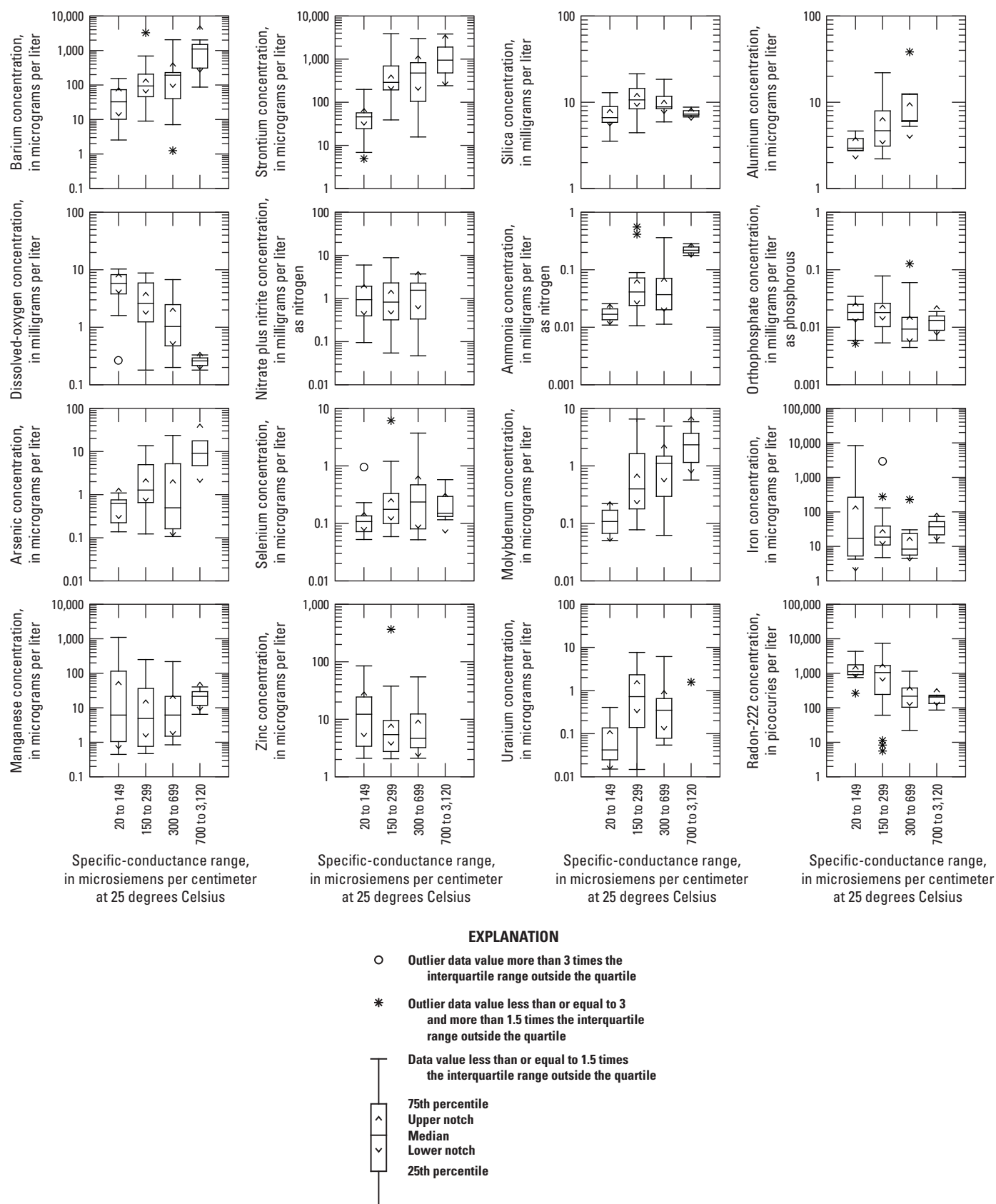
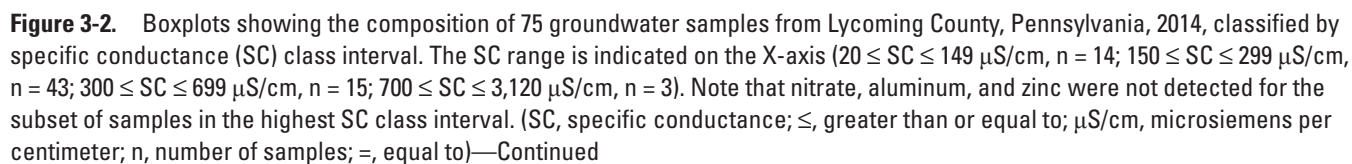


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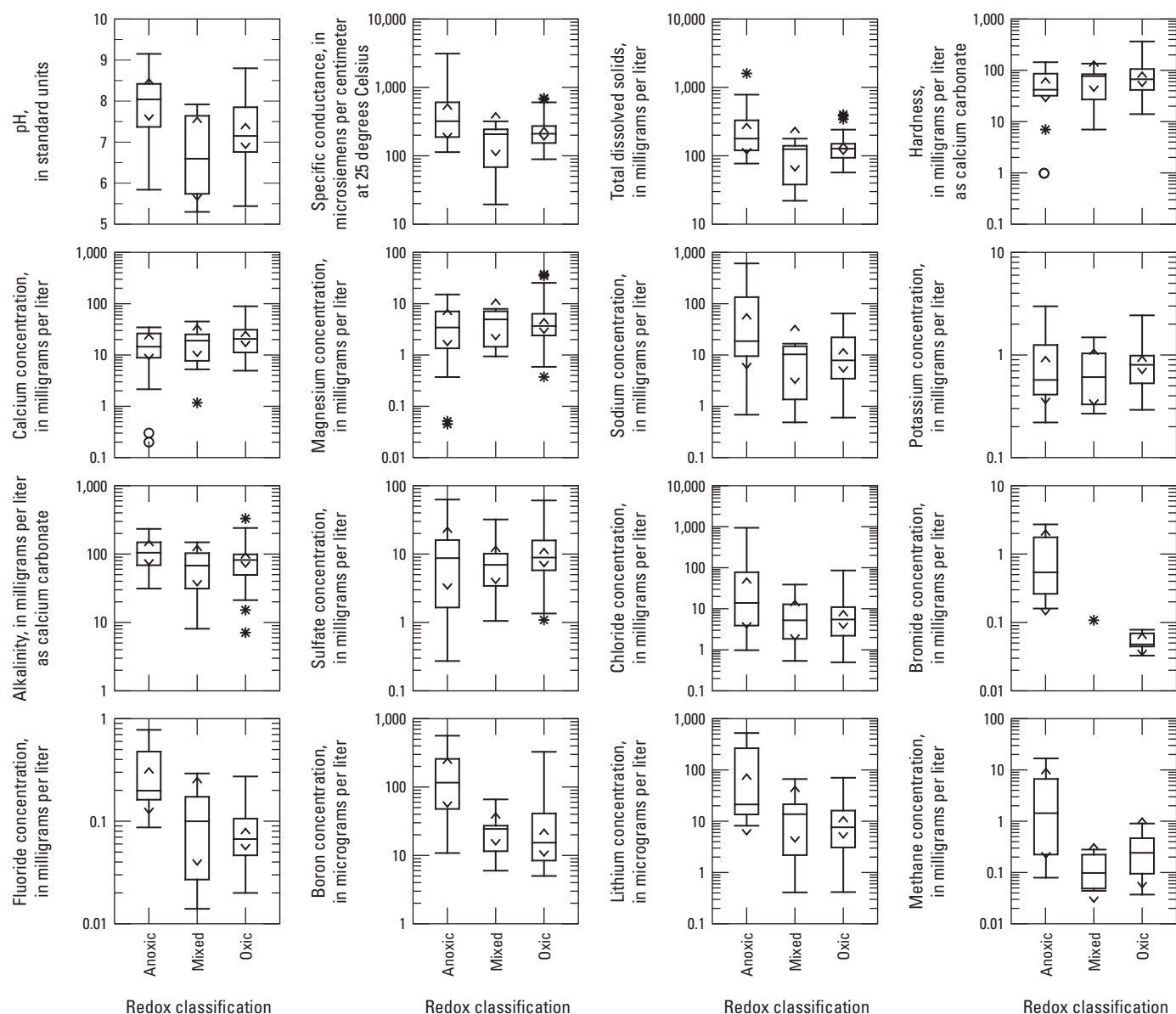


Figure 3-3. Boxplots showing the composition of 75 groundwater samples from Lycoming County, Pennsylvania, 2014, classified as anoxic ($n = 14$), mixed ($n = 10$), and oxic ($n = 51$) on the basis of dissolved oxygen concentration and other water-quality criteria of McMahon and Chapelle (2008). (n , number of samples; $=$, equal to)

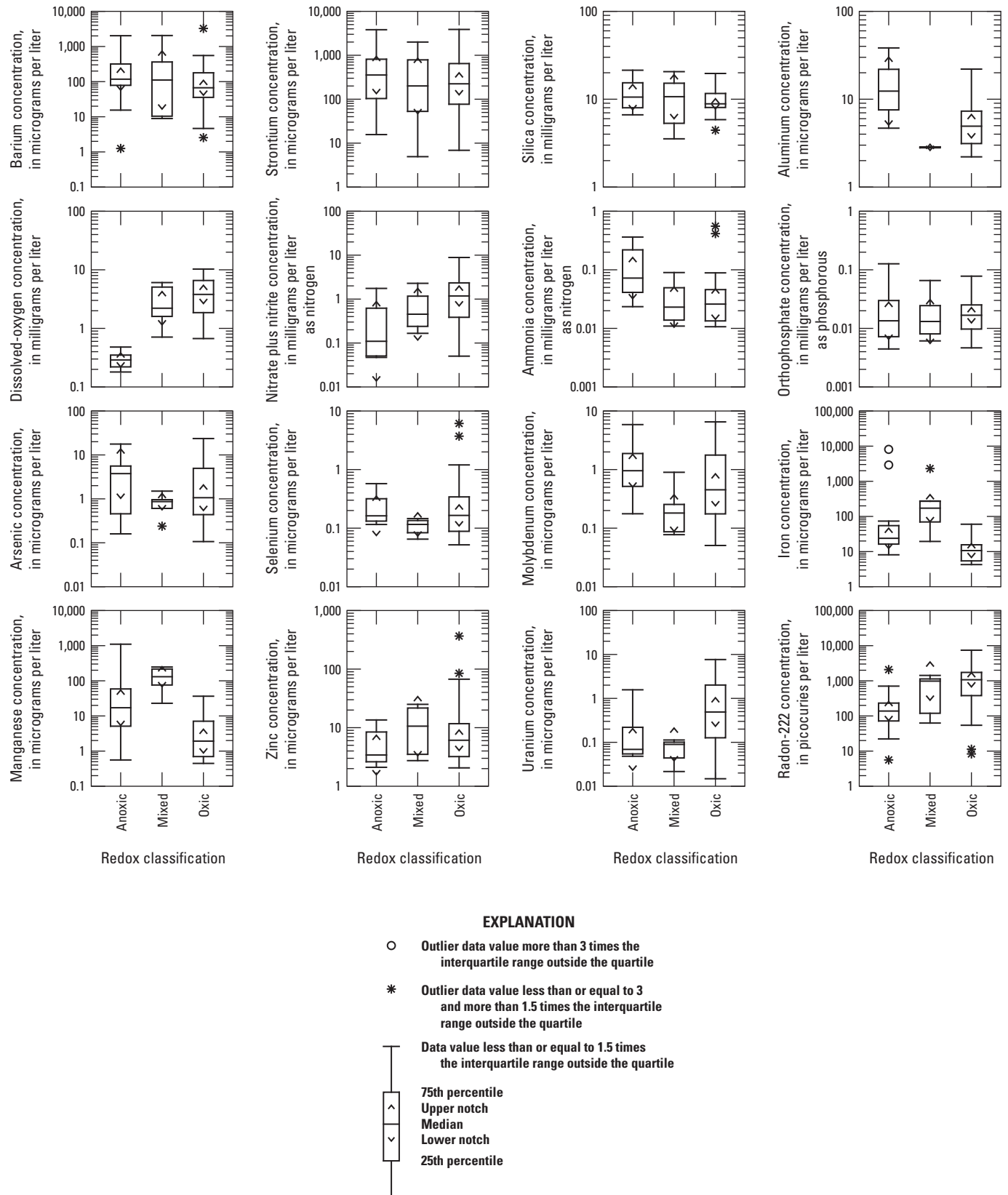


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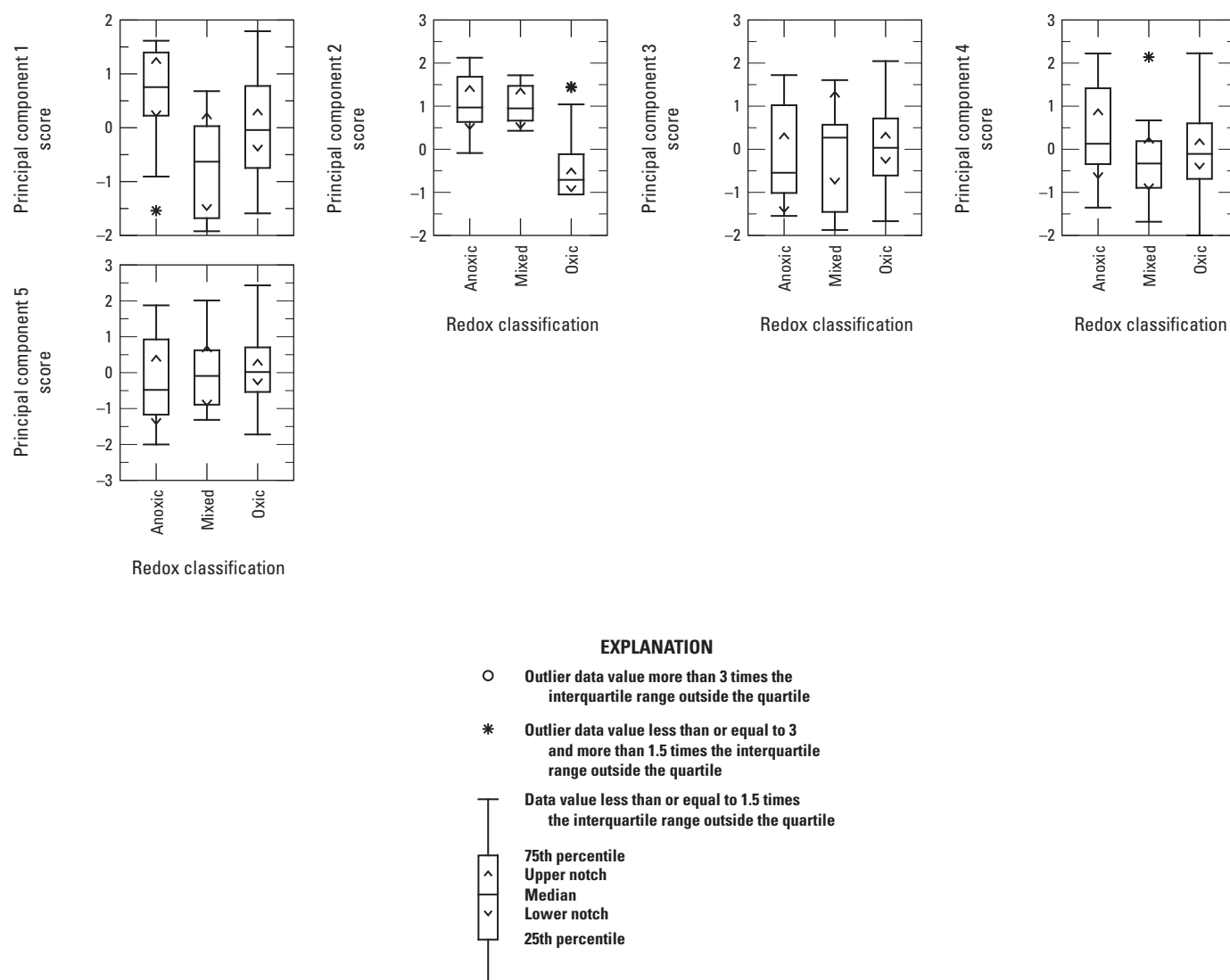


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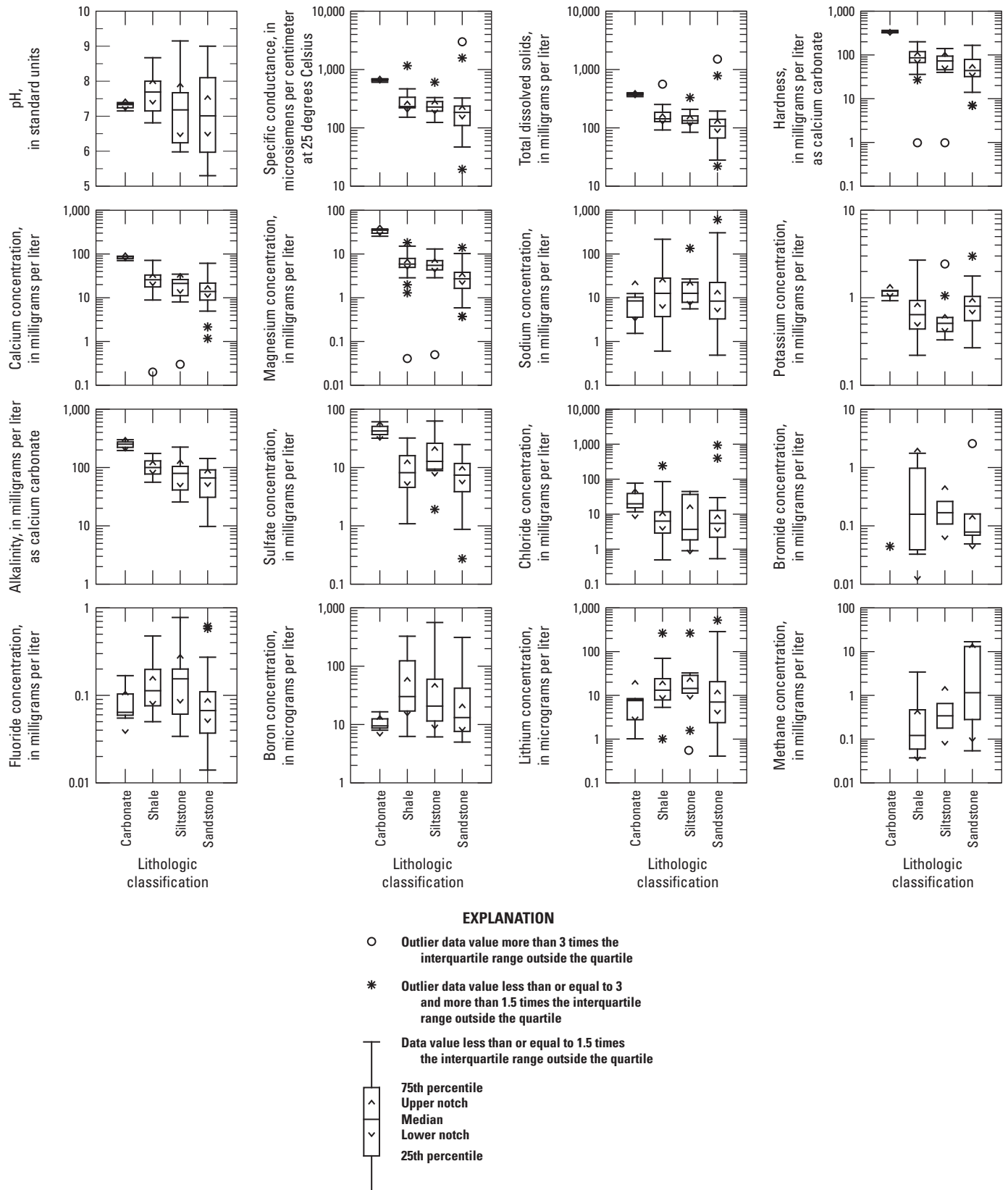


Figure 3-4. Boxplots showing the composition of 75 groundwater samples from Lycoming County, Pennsylvania, 2014, classified as carbonate ($n = 3$), shale ($n = 21$), siltstone ($n = 10$), and sandstone ($n = 41$) on the basis of lithologic class identified by Pennsylvania Bureau of Topographic and Geologic Survey (2001) and Taylor and others (1983). (n , number of samples; =, equal to)

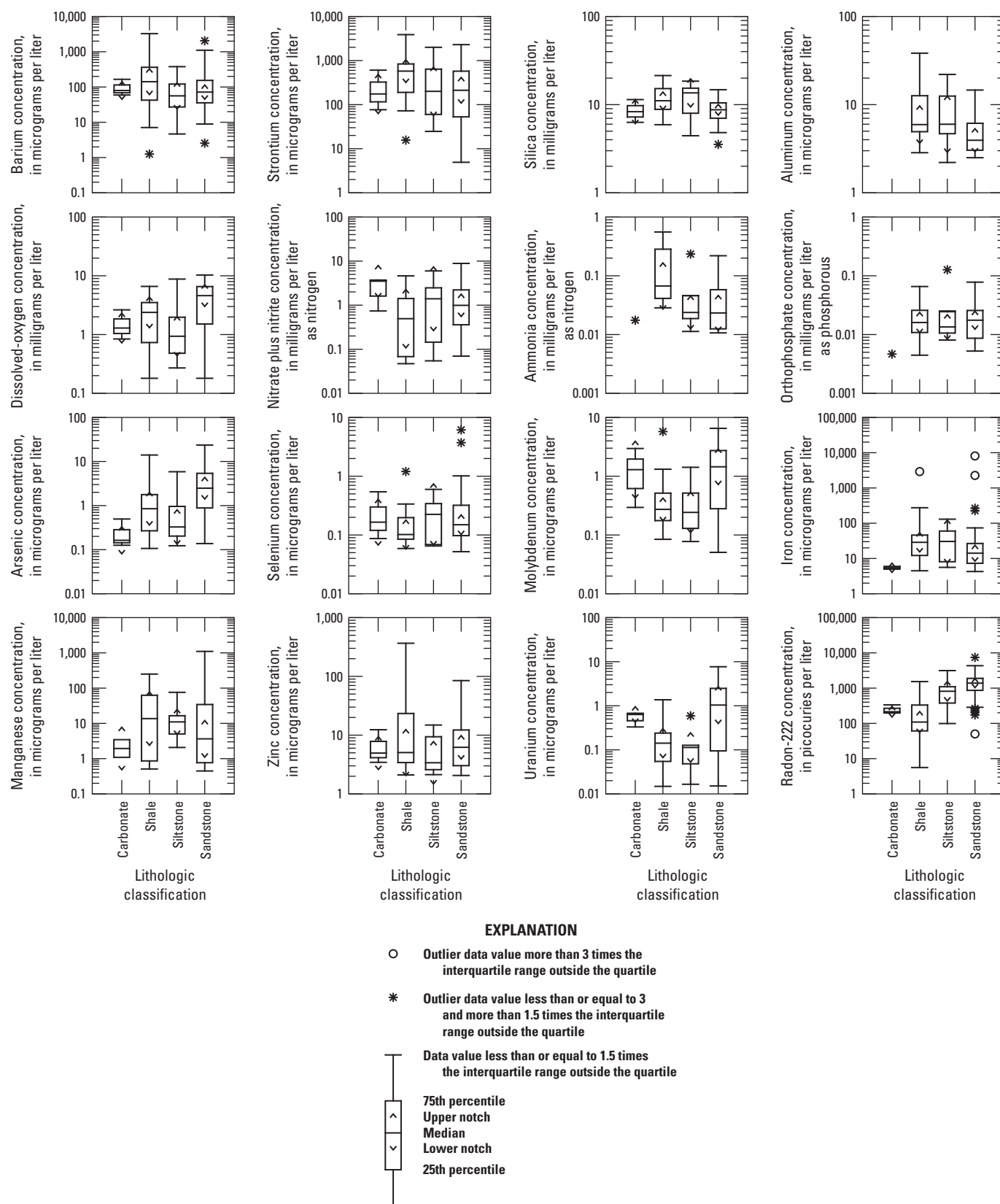


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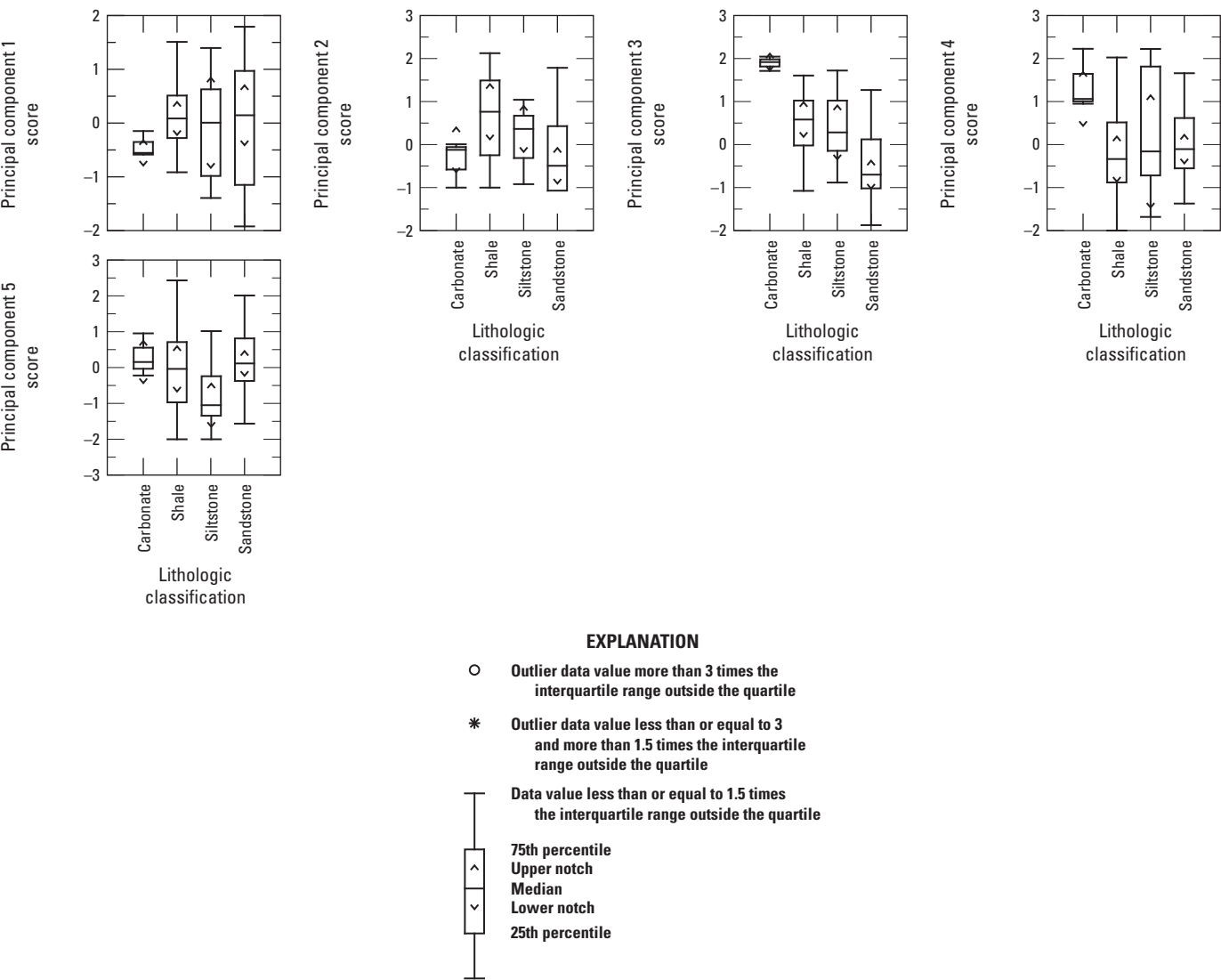


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