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DISSOLVED-METHANE CONCENTRATIONS IN WELL WATER IN THE APPALACHIAN PLATEAU PHYSIOGRAPHIC PROVINCE OF MARYLAND

by

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ABBREVIATIONS USED IN THIS REPORT

General

commun.	communication
COMAR	Code of Maryland Regulations
DNR	Maryland Department of Natural Resources
GPS	global positioning system
MDE	Maryland Department of the Environment
MGS	Maryland Geological Survey
NWIS	National Water Information System (database)
U/M Devonian	Upper/Middle Devonian
USGS	United States Geological Survey
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water

Units of Measurement

bcf	billion cubic feet
ft	feet
mg/L	milligrams per liter
µg/L	micrograms per liter
µS/cm	microsiemens per centimeter at 25 degrees Celsius
<	less than
>	greater than
ºC	degrees Celsius
‰	per mil
±	plus/minus
BLS	below land surface
RSD%	relative standard deviation percent

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KEY RESULTS

Dissolved-methane concentrations were measured in 87 drinking-water wells in the Appalachian Plateau Physiographic Province of Maryland between 2012 and 2014. The objectives of the study were to measure baseline dissolved-methane concentrations in well water in the region where natural gas from the Marcellus shale may eventually be produced, and (to the extent possible) evaluate factors associated with the occurrence and distribution of dissolved methane. Wells were sampled for dissolved methane, ethane, propane, and ethene; most samples were also tested for *n*-butane and isobutane. Field-measured parameters included pH, specific conductance, dissolved oxygen, alkalinity, chloride, and total hardness. The key results of this investigation are:

- Dissolved-methane concentrations ranged from less than the reporting limit of 1.5 micrograms per liter (µg/L) to 8,550 µg/L (0.0015 to 8.55 milligrams per liter [mg/L]). Seven samples exceeded 1,000 µg/L (1 mg/L) dissolved methane.
- Dissolved-methane concentrations were below the reporting level of 1.5 µg/L (0.0015 mg/L) in more than half of all sampled wells (47 of 87 wells). Dissolved ethane was detected in six wells; no higher-chain organic compounds were detected.
- Dissolved methane was detected in 26 of the 41 wells located in valleys (about 63 percent), compared with 14 of 46 wells (about 30 percent) located in upland settings. There was a significant difference in dissolved-methane concentrations between the two topographic positions (Mann-Whitney rank-sum test, $p<0.001$). Fifteen of the 16 wells that exceeded 20 µg/L (0.020 mg/L) methane were located in valleys.
- Dissolved methane was detected in 20 of 37 wells (about 54 percent) in areas underlain by coal, compared with 20 of 50 wells (40 percent) in areas without coal. However, there was no statistically significant difference between the groups.
- Valley wells in areas underlain by coal had the highest proportion of dissolved-methane detections (13 of 17 wells, about 76 percent), followed by valley wells in non-coal areas (13 of 24 wells; 54 percent), upland wells in coal areas (7 of 20 wells; about 35 percent), and upland wells in non-coal areas (7 of 26 wells; about 27 percent).
- Dissolved methane was detected in all nine geologic formations in which sampled wells were located.
- Monthly dissolved-methane samples collected from three wells showed considerable variation. The average percent difference from the median monthly methane concentration in each well was between 20 and 30 percent, although individual variations in each well were frequently larger. The data indicate that a single methane analysis from a well is insufficient to characterize dissolved-methane levels in individual wells.
- Isotopic data from two wells suggest a thermogenic origin for methane. However, methane-to-ethane ratios from these wells and six others suggest both a thermogenic and biogenic origin. More data are needed to better evaluate methane sources in the region.
- Dissolved-methane concentrations from 14 wells in the vicinity of the Accident Dome natural gas storage field are more closely correlated with topographic position than with the number of natural gas production or injection wells within a one-half mile radius of the water wells.

- Dissolved-methane concentrations from this study were compared to county-level studies in Pennsylvania, statewide assessments in West Virginia and New York, and a study of the Upper Delaware River Basin (Pennsylvania and New York). The vast majority of samples in each of these studies had methane concentrations that were either less than 1 milligram per liter (mg/L) or were reported as non-detections. The Maryland study is the only study in which no methane concentration exceeded 28 mg/L; however, methane concentrations above 28 mg/L are uncommon in the other studies, even in areas of extensive natural gas development. These studies show that low-level methane concentrations in well water are common throughout the region, even in areas where gas development has not occurred.

INTRODUCTION

The Appalachian Plateau in Maryland consists of Garrett County and the westernmost part of Allegany County (fig. 1). This part of Maryland is underlain by the Marcellus shale, which has more than 84 billion cubic feet (bcf) of undiscovered natural gas and more than 3 billion barrels of undiscovered natural gas liquids throughout its entire extent (Coleman and others, 2011). Advances in directional drilling and hydraulic fracturing (also called hydrofracturing, or “fracking”) have made possible the widespread development of the Marcellus shale and other organic-rich shales that had previously been considered uneconomical. Reports of methane gas explosions allegedly resulting from leaking gas wells have raised concerns that development of the Marcellus shale may increase the risk of explosion to those living near gas wells. However, other studies in northeastern Pennsylvania have determined that groundwater methane is naturally occurring and predates development of the Marcellus shale (Baldassare and others, 2014; Wilson, 2014).

Methane in well water has occasionally been reported over the years in the Appalachian Plateau of Maryland (S. Sherrard, Garrett County Health Department, oral commun., 2012). However, no systematic study of well-water methane occurrence and distribution has been conducted in Maryland; well water in the state is not routinely tested for methane, which does not have a Federal or State drinking-water standard.

In order to obtain data on well-water methane concentrations prior to the development of the Marcellus shale, the Maryland Geological Survey (MGS) collected water samples from 87 private and public drinking-water wells between 2012 and 2014 in Garrett County and western Allegany County, Maryland. The purpose of this study was to measure baseline dissolved-methane concentrations in water wells in the region and, to the extent possible, evaluate factors associated with the occurrence and distribution of methane in well water.

Methane is a colorless, odorless, flammable gas that can occur naturally in well water. Methane has a solubility of about 28 milligrams per liter (mg/L) (28,000 micrograms per liter [µg/L]) in water at atmospheric pressure and 25 degrees Celsius. At this concentration, methane will easily escape water as a gas. Although methane is not a regulated constituent in drinking water, the U.S. Department of the Interior, Office of Surface Mining recommends that methane levels between 10 and 28 mg/L (10,000 and 28,000 µg/L) be carefully monitored, and if concentrations exceed 28 mg/L, the area should be vented in order to prevent methane gas buildup that can lead to asphyxiation and explosive conditions in confined spaces (Eltschlager and others, 2001).

Methane is generated in the subsurface by microbial decomposition of organic material (biogenic methane) and by thermal decomposition of organic material due to increased temperature and pressure during burial (thermogenic methane). Biogenic and thermogenic processes can impart chemical and isotopic characteristics to dissolved gases and other groundwater constituents that can provide clues to the source(s) of organic material (Schoell, 1980; Aravena and Wassenaar, 1993; Jenden and others, 1993; Laughrey and Baldassare, 1998; McMahon and Chapelle, 2008; Osborn and McIntosh, 2010; Molofsky and others, 2013). Biogenic methane can be produced either by carbon dioxide reduction or fermentation reactions. Naturally occurring potential sources of methane in the study area include Devonian black shales (including the Marcellus shale), silty gray shales in shallow aquifers, Pennsylvanian-age coal deposits, and modern valley alluvium. Black and dark gray Devonian shales are common above the Marcellus shale in the Appalachian Basin (De Witt, 1986; Milici and Swezey, 2006; D. Brezinski, Maryland Geological Survey, written commun., 2014). Anthropogenic sources of methane include landfills, and leakage from gas wells and gas transmission lines.

PURPOSE AND SCOPE

This report presents the results of a study of dissolved methane in well water in the Appalachian Plateau Physiographic Province of Maryland. (In this report, all methane concentrations refer to dissolved methane, unless otherwise noted. Methane gas that may have accumulated in the well headspace was not measured.) This information is important for establishing baseline methane concentrations prior to any drilling, hydraulic fracturing, or production of natural gas from the Marcellus shale. The report describes the study components (study design, sample collection protocols, and analytical methods), site data, and methane and other water-quality data. Methane concentrations are discussed in relation to geologic set-

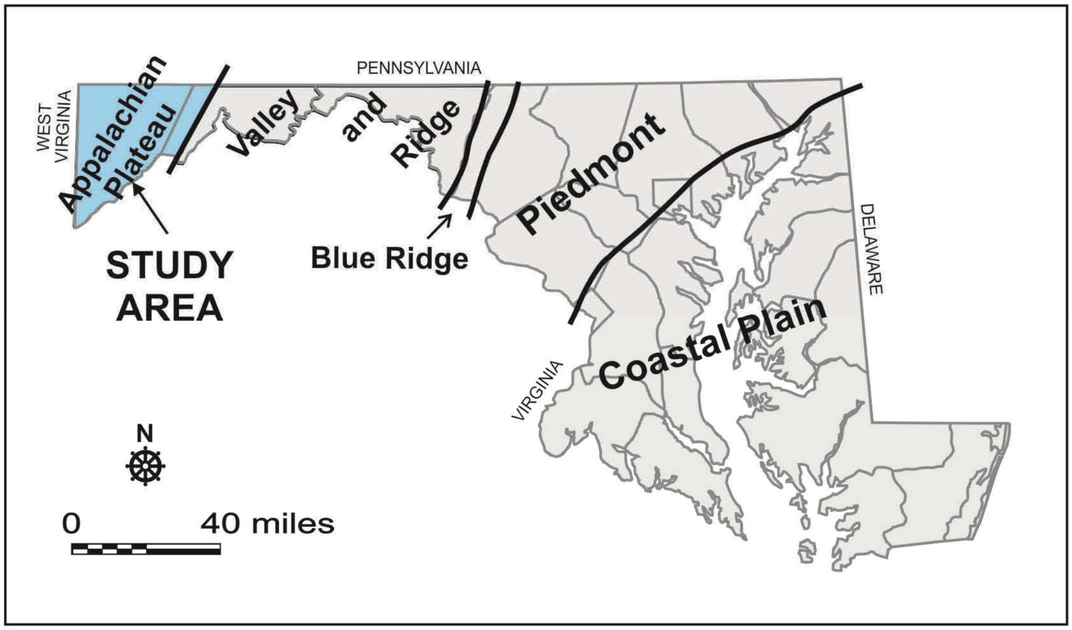

Figure 1. Location of the study area.

ting, topographic position, well depth, and other factors. Variation in monthly methane concentrations from three wells are discussed. Stable-isotope data ($^{13}C_{CH4}$ and $^{2}H_{CH4}$) from two wells are presented. Methane concentrations from a subset of the wells are examined with respect to proximity to gas storage wells in the Accident Dome gas storage field. The data are also compared with several wellwater methane studies in the Marcellus shale region.

LOCATION OF STUDY AREA

The study area is the Appalachian Plateau of Maryland, which includes all of Garrett County and the area in Allegany County located west of Dans Mountain (fig. 1). The region encompasses approximately 780 square miles, of which about 84 percent is in Garrett County and 16 percent is in Allegany County. Elevations range from approximately 850 feet (ft) above sea level at the Potomac River at the southeastern edge of the study area to 3,360 ft at Backbone Mountain (the highest point in Maryland) in southwestern Garrett County. The area is about 85 percent rural and 15 percent urban. The population of Garrett County, which comprises most of the study area, was approximately 30,000 in 2012 (U.S. Census Bureau, 2013).

ACKNOWLEDGMENTS

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HYDROGEOLOGIC SETTING

The geologic formations of the Appalachian Plateau Physiographic Province are Paleozoic sandstones, siltstones, shales, limestones, and coal beds (tab. 1). The gently folded strata form synclines and anticlines that are the source regions for coal and natural gas, respectively (Nutter and others, 1980). Coal beds are present in the Pennsylvanian-age rocks found in the major synclinal basins of the region, which include the Lower Youghiogheny Basin, Upper Youghiogheny Basin, Castleman Basin, Upper Potomac Basin, and Georges Creek Basin (fig. 2). At least 11 individual coal seams have been identified in the Pennsylvanian-age rocks (Amsden, 1953). Minor amounts of coal and coaly shale are occasionally present in the Devonian and Mississippian rocks. Coal basins underlie about 56 percent of the study area. Coal mining is not as prominent today as it was in the past in Garrett County; however, both strip- and deep-mining operations still exist.

Several gas fields have produced natural gas in the study area. In 1944, a well drilled on the Accident anticline was the first well in Maryland to encounter natural gas, although not in commercially viable amounts (Schwarz, 1996). In 1949, natural gas was found in commercial quantities near Mountain Lake Park in southern Garrett County. The natural gas was produced from the (Devonian) Oriskany Formation, likely from structural traps on the flanks of anticlines. Three well fields in Garrett County have produced natural gas: the Mountain Lake Park field (23 producing wells), the Accident field (19 producing wells), and the Negro Mountain field (3 wells) (Schwarz, 1996). Only the Deer Park Anticline currently contains active natural gas-producing wells (G. Day, Maryland Department of the Environment, oral commun., 2012). In 1962, the Accident field was acquired by the Texas Eastern Gas Transmission Company (now Spectra Energy) and was converted to a natural gas storage facility.

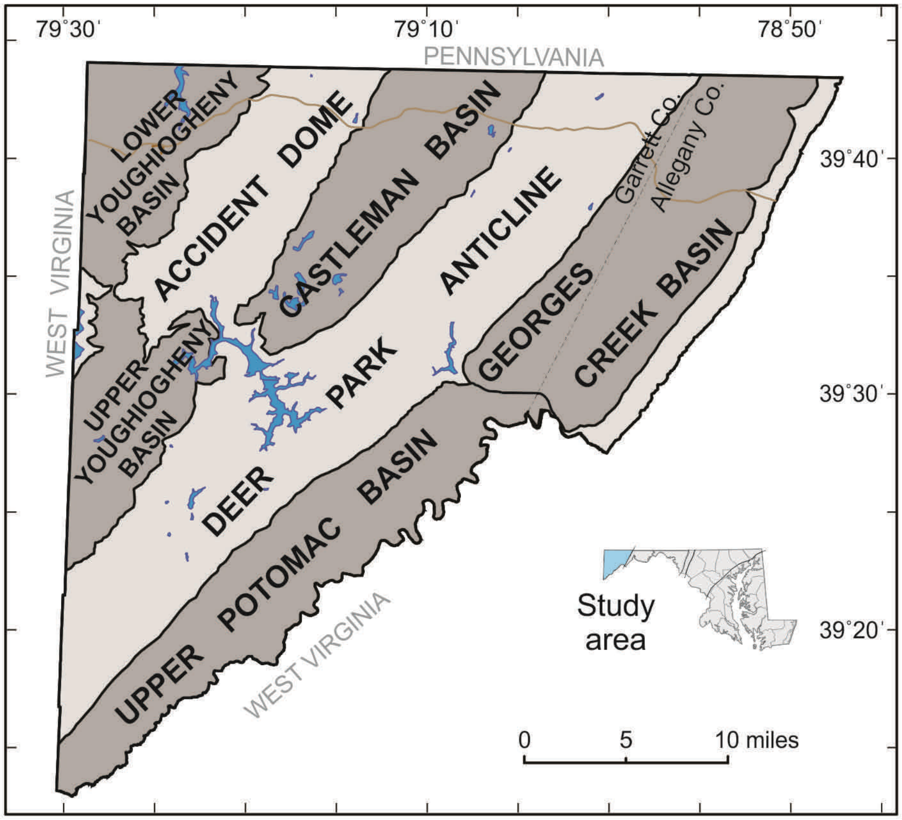

Figure 2. Geologic structure of the Appalachian Plateau Physiographic Province in Maryland. Synclines (coal areas) are shown in dark shading, and anticlines are in light shading. Modified from Overbeck (1954).

Table 1. Descriptions of geologic formations in the Appalachian Plateau Physiographic Province of Maryland. Modified from Brezinski and Conkwright (2013).

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

METHODS OF INVESTIGATION

WELL SELECTION

Wells were selected based on topographic position and geologic setting. Topographic position was investigated because well-water methane concentrations were found to be higher in water wells located in valleys than in those located in upland areas in Pennsylvania and New York (Heisig and Scott, 2013; Molofsky and others, 2013). Stream valleys often develop on zones of structural weaknesses such as joints and faults; these features may serve as pathways for upward migration of methane and other gases from the deeper part of the groundwater flow system. Wells were also selected in areas underlain by coal and in areas without coal. Coal basins comprise approximately 56 percent of the study area. Methane is one of the main types of gases found in coal seams, and coalbed methane is a significant energy source in some parts of the United States and elsewhere in the world (U.S. Geological Survey, 2000). Reports of well-water methane have occasionally been received by the Garrett County Health Department (S. Sherrard, Garrett County Health Department, oral commun.), mostly from wells that have penetrated coal seams.

Candidate wells were identified using several methods, including requesting participation at outreach events and public meetings, placing an advertisement in a local newspaper, and making "cold calls" at houses in underrepresented or targeted areas. The following well-selection criteria were used:

- Well-permit applications and well-completion reports were available.
- Wells were not equipped with jet pumps (which draw water by suction and can cause degassing of methane from water).
- Wells were being used on a regular basis (in order to ensure water had not been standing for a long period of time).
- Samples of untreated well water could be obtained.
- Water could be run for about 30 minutes (for purging and sample collection).
- Well locations provided a reasonable spatial distribution throughout the study area.
- There were no obvious or potential sources of contamination (e.g., the well cap was installed securely; the well was located upgradient of the septic system; the well had not been recently chlorinated, etc.).

Eighty-seven wells (mostly residential wells) were selected for sampling (fig. 3). Forty-one wells were located in valleys; 46 wells were located in upland settings. Thirty-seven wells were located in coal basins; 50 wells were located in non-coal areas. (tab. 2).

Well-construction information was obtained from the well-drilling permit application and the well-completion report for each well. Well construction information, site characteristics, and water quality data are given in appendixes A and B.

Wells in this report are identified by an alphanumeric system utilized by the U.S. Geological Survey as part of their National Water Information System (NWIS). The first two letters (both uppercase) indicate the county where the well is located (GA for Garrett County; AL for Allegany County). The next two letters (the first uppercase, the second lowercase) correspond to a 5-minute by 5-minute block of a grid superimposed over each county: the first letter corresponds to the row and the second letter corresponds to the column within the grid. Wells within each 5-minute by 5-minute block are numbered sequentially as they are inventoried. Thus well GA Bc 69 refers to the sixty-ninth well inventoried in the 5-minute by 5-minute block located at the intersection of row "B" and column "c" in Garrett County. Wells sampled during this project were inventoried and entered into the USGS NWIS.

SAMPLING PROCEDURES

Water samples were collected at the pressure-tank spigot or another tap source that dispensed untreated well water (fig. 4a). A Y-valve was attached to the spigot; a hose was attached to one branch of the Y-valve, and the well water was purged through the hose into a bucket in which pH, specific conductance, temperature, and dissolved oxygen probes were submerged. Field measurements were recorded at 5-minute intervals until measurements stabilized as follows: pH, ± 0.1 pH unit; temperature, ± 0.2 degree Celsius; specific conductance, ± 5 percent (if value was less than 100 microsiemens per centimeter at 25 degrees Celsius [µS/cm]), or ± 3 percent (if value was greater than 100 µS/cm); dissolved oxygen, ±0.3 mg/L. In some cases not all readings stabilized. Measurements were made using an Orion Star A329 portable multiparameter meter. Equipment calibra-

Table 2. Number of wells sampled with respect to geologic setting and topographic position.

	Valleys	Uplands	Total
Coal areas (synclines)	17	20	37
Non-coal areas (anticlines)	24	26	50
All wells	41	46	87

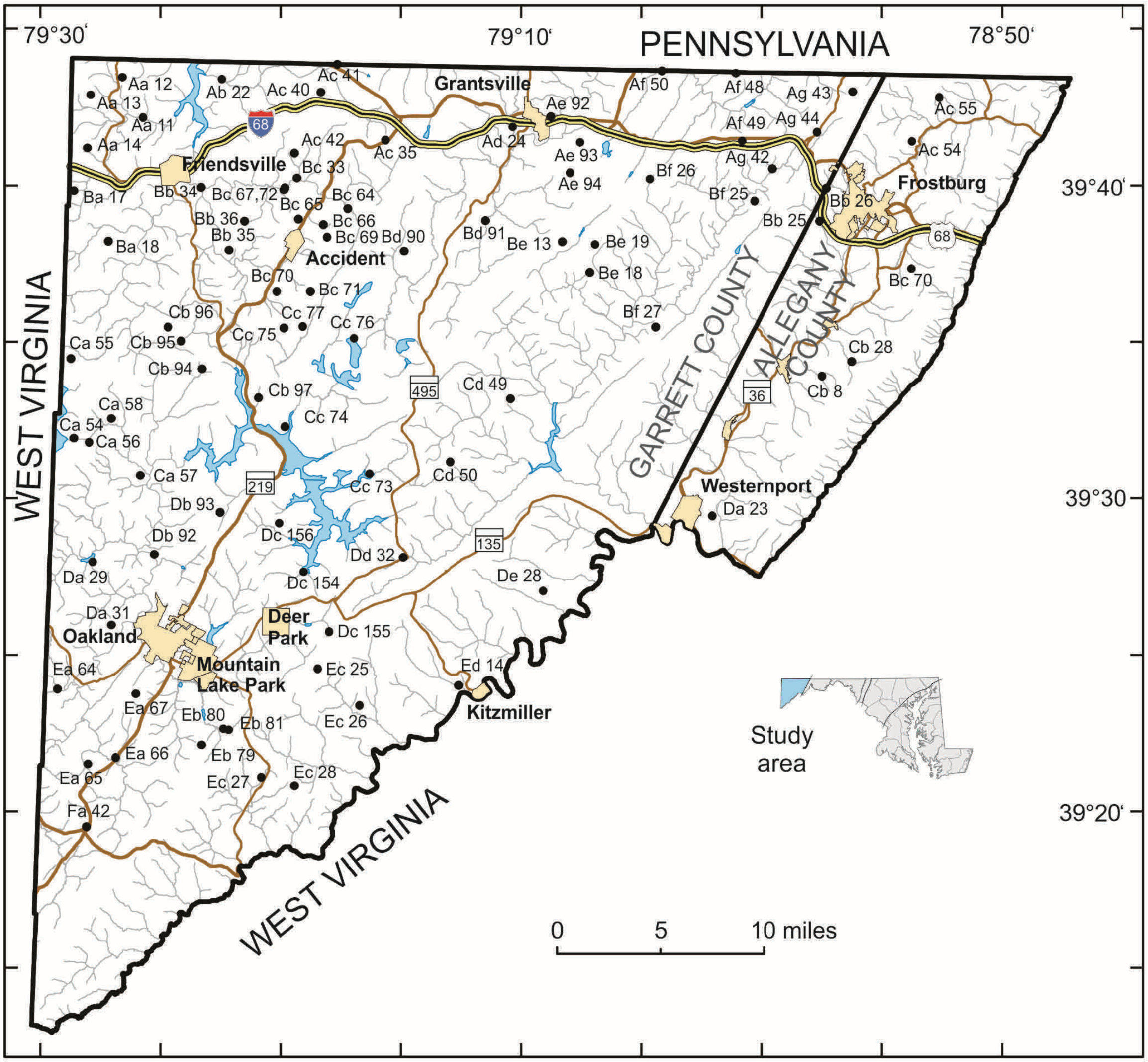

Figure 3. Locations of wells sampled during this study. "GA" and "AL" have been omitted from the Garrett and Allegany County well number labels, respectively.

tions were performed daily using appropriate standards and buffers[1].

To collect the methane sample after purging the well, the water was run through clear plastic tubing attached to the other branch of the Y-valve. The other end of the clear plastic tubing ran into a bucket through a J-shaped piece of 2-inch PVC pipe (fig. 4b). Water was then allowed to fill the bucket, resulting in the top of the clear plastic tubing being below the level of the water. To collect a water sample for methane analysis, a 40-milliliter glass vial was inverted over the clear plastic tubing. Water then flowed for at least 30 seconds, after which the vial was slowly pulled up and off the tubing and the vial was capped while still inverted and underwater. After being removed from the water, the vial was briefly uncapped, and hydrochloric acid was added to preserve the sample to pH less than 2. The vial was then re-capped, inverted several times, and stored on ice. Samples were transported by ground transportation to ALS Environmental Laboratories in Middletown, Pennsylvania.

ANALYTICAL METHODS

The samples were analyzed for dissolved methane, propane, ethane, and ethene concentrations using the headspace method (RSK-175) (Kampbell and Vandegrift, 1998). Samples collected after September 1, 2012 were also analyzed for *n*-butane and isobutane (due to a change in the laboratory's reporting procedures). The laboratory's reporting detection limits for samples analyzed prior to August 23, 2012 were 1 µg/L for methane and propane and 3 µg/L for ethane and ethene. Samples analyzed after August 23, 2012 had new reporting detection limits as a result of the laboratory's yearly instrumental checks. They were 1.5, 3.3, 2.4, 3.2, 4.3, and 4.6 µg/L for methane, ethane, ethene, propane, *n*-butane, and isobutane, respectively. Quality-control samples for methane consisted of duplicate samples, samples with known methane concentrations, and inter-laboratory comparison of samples. Quality-control samples are discussed in appendix C.

Alkalinity, chloride, and total hardness were measured by MGS personnel in the field on unfiltered water samples collected after purging was complete. Alkalinity was measured by digital titration with sulfuric acid and reported as milligrams per liter (mg/L) of $CaCO_3$ (Hach Company, 2008).

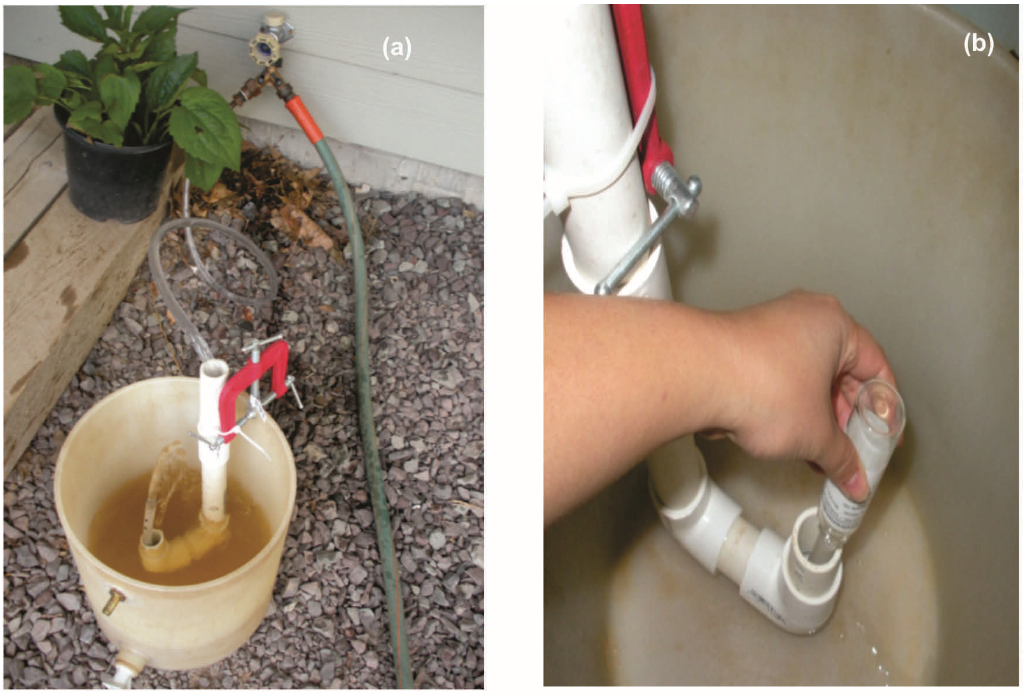

Figure 4. Photographs illustrating set-up for sample collection. (a) Configuration of purge hose and methane sampling hose. (b) Inverted bottle technique (water not shown in order to better illustrate the collection method).

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[1] The use of trade names, product names, and laboratories in this report is for identification purposes only, and does not constitute endorsement by the Maryland Geological Survey or other agencies associated with this study.

Chloride concentration was analyzed colorimetrically by titration using a test kit with a minimum reporting detection limit of 10 mg/L (Hach Company, 2012a). Total hardness was also analyzed colorimetrically by titration (Hach Company, 2012b). These constituents were analyzed primarily because the tests could be quickly and inexpensively performed at the site. It was beyond the scope of this study to characterize overall water chemistry at each site.

In addition to the water-quality measurements, photographs were taken of the purging and sampling area and the wellhead. Latitude and longitude of each well were recorded using a handheld global positioning system (GPS) unit (or in some cases using Google Earth). Additional documentation, including well permits and completion reports, were compiled for each well.

Forty-nine wells were sampled from June through September 2012; 28 wells were sampled between April and July, 2013; and 10 wells were sampled in April and May, 2014. Seventy-four wells were residential wells; the remaining 13 wells were public, institutional, or commercial water-supply wells. Three wells (GA Ba 17, GA Cb 95, and GA Ea 65) were sampled monthly for methane and other dissolved gases from December, 2012 to August, 2013, in addition to their initial sampling earlier in 2012. These samples were collected to determine variations in methane concentrations with time at individual wells. The wells were selected because they each had detectable levels of methane in the initial sample, and also represented a range of methane concentrations. Two wells (GA Ba 17 and GA Ed 14) were tested for stable isotopes of carbon and hydrogen in the methane molecule (^{13}C and ^{2}H, reported as $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$). Isotopic analysis can help determine whether the methane has a thermogenic (generated by organic decomposition over millions of years at great depth and pressure) or biogenic (generated recently by biological activity at shallow depths) origin. Isotopic analysis was performed by Isotech Laboratories (Champaign, Illinois) using dual-inlet isotope ratio mass spectrometry. A third well (GA Dc 156) was also sampled for isotopic analysis, but did not contain the minimum 1 mg/L methane required for isotopic analysis (in contrast to an earlier sample collected from the well).

RESULTS AND DISCUSSION

Dissolved-methane concentrations in the 87 untreated well-water samples collected from wells in the Maryland Appalachian Plateau ranged from less than 1.5 to 8,550 µg/L (figs. 5 and 6a; app. B). All samples were well below 28,000 µg/L, the level at which immediate venting of the wellhead is recommended (Eltschlager and others, 2001). Methane concentrations from 47 of the 87 wells (about 54 percent) were less than the reporting detection limit of 1.5 µg/L (median value: less than 1.5 µg/L). Forty samples (about 46 percent) had methane concentrations greater than 1.5 µg/L. (In this report, a methane detection is defined as methane greater than or equal to 1.5 µg/L (0.0015 mg/L). Eighty percent of all wells had less than 15 µg/L methane. Samples from seven wells (about 8 percent) exceeded 1,000 µg/L methane. Samples from six wells (GA Aa 14, GA Ae 92, GA Bc 33, GA Bc 67, GA Bc 72, and GA Ed 14) had dissolved ethane concentrations ranging from 3.6 to 191 µg/L, (app. B). No other wells had detectable ethane. None of the samples in this study contained any detectable ethene, propane, *n*-butane, or isobutane.

METHANE CONCENTRATIONS IN RELATION TO SITE CHARACTERISTICS

Topographic Position and Geologic Setting

Wells were classified as being in either valley or upland topographic positions, based on whether they were located within 1,000 ft of a major National Hydrography Dataset flowline (valley setting) or more than 1,000 ft from such a flowline (upland setting). Using this methodology, 41 wells were in valley settings; 46 wells were in upland settings. Methane concentrations from wells in uplands ranged from less than 1.5 µg/L to 1,720 µg/L (median: less than 1.5 µg/L) (fig. 6b). Methane was detected in 14 of 46 upland wells (tab. 3). Methane concentrations from wells in valleys ranged from less than 1.5 µg/L to 8,550 µg/L (median: 6.1 µg/L). Methane was detected in 26 of the 41 wells in valley settings (about 63 percent), compared with 14 of 46 wells in upland settings (about 30 percent) (fig. 6b). There was a statistically significant difference between methane concentrations in the two settings (Mann-Whitney rank sum test, $p<0.001$). The cumulative-percentage

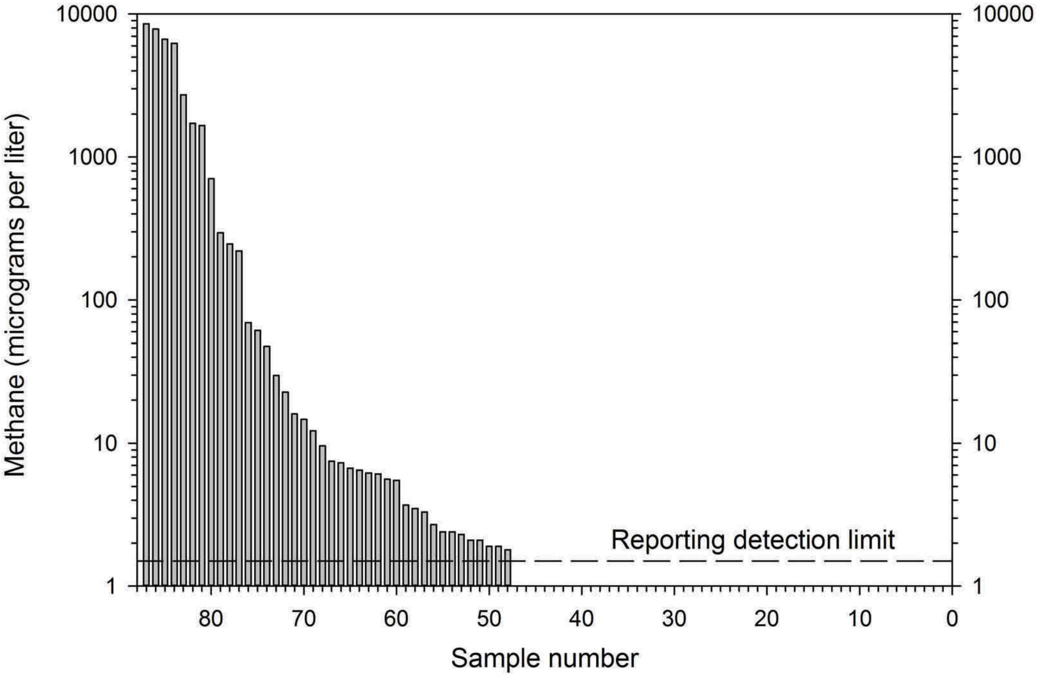


Figure 5. Methane concentrations for samples collected in this study. Each bar represents an individual sample. Samples are plotted in order of increasing methane concentration. Samples with methane concentrations less than the reporting detection limit are not plotted.

plots for the valley wells and upland wells illustrate the difference in methane distribution (fig. 7). Six of the seven wells in the study with more than 1,000 µg/L methane were located in valleys (tab. 3). Fifteen of the 16 wells with more than 20 µg/L methane were also located in valley settings.

Approximately 56 percent of the study area is underlain by sedimentary rocks containing one or more coal seams. Wells were categorized as being either in coal areas or non-coal areas; in this report, "coal-area wells" are defined as those completed in the (Pennsylvanian) Conemaugh, Allegheny, and Pottsville formations. Mississippian-age and older rock formations do not contain significant amounts of coal, and wells constructed in these formations are referred to in this report as "non-coal-area wells." Parts of the (Mississippian) Purslane Formation and (Devonian) Rockwell formation contain coaly shale beds; however, none of the wells in these formations have coal indicated on the driller's logs. In most wells in the coal areas, coal seams were identified by the driller on the well completion report. Wells in coal areas that did not have coal mentioned in the well completion report likely encountered coal that was not identified by the driller, or may not have been deep enough to penetrate underlying coal seams. Coal was not indicated on the well completion reports in any of the wells in the non-coal areas.

Methane was reported in 20 of the 37 samples (about 54 percent) for wells in the coal areas, with concentrations ranging from less than 1.5 µg/L to 8,550 µg/L (median: 2.1 µg/L) (fig. 6c). Methane was detected in 20 of the 50 samples in non-coal areas (40 percent); concentrations ranged from less than 1.5 µg/L to 6,650 µg/L (median: less than 1.5 µg/L). There was no statistically significant difference between these groups. The cumulative-percentage plot of methane concentrations for wells in the coal areas and non-coal areas shows a smaller separation than that for the valley versus upland methane concentrations (fig. 8). Methane concentrations exceeded 1,000 µg/L in similar proportions between the coal and non-coal groups (about 8 percent for each) (tab. 3). Three of the seven wells having more than 1,000 µg/L methane were from coal areas (one in each of the Lower Youghiogheny, Upper Potomac, and Castleman Basins). Two or more coal seams were noted by the drillers on the well-completion reports for these three wells. During purging, water from these three wells showed a slightly cloudy appearance in the purge bucket from many small gas bubbles in the water. Well GA Ba 17 is located approximately 1,000 ft from a well where a buildup of methane gas had reportedly blown the cap off the top of the well (L. Brenneman, Brenneman Well Drilling, personal commun., 2012).

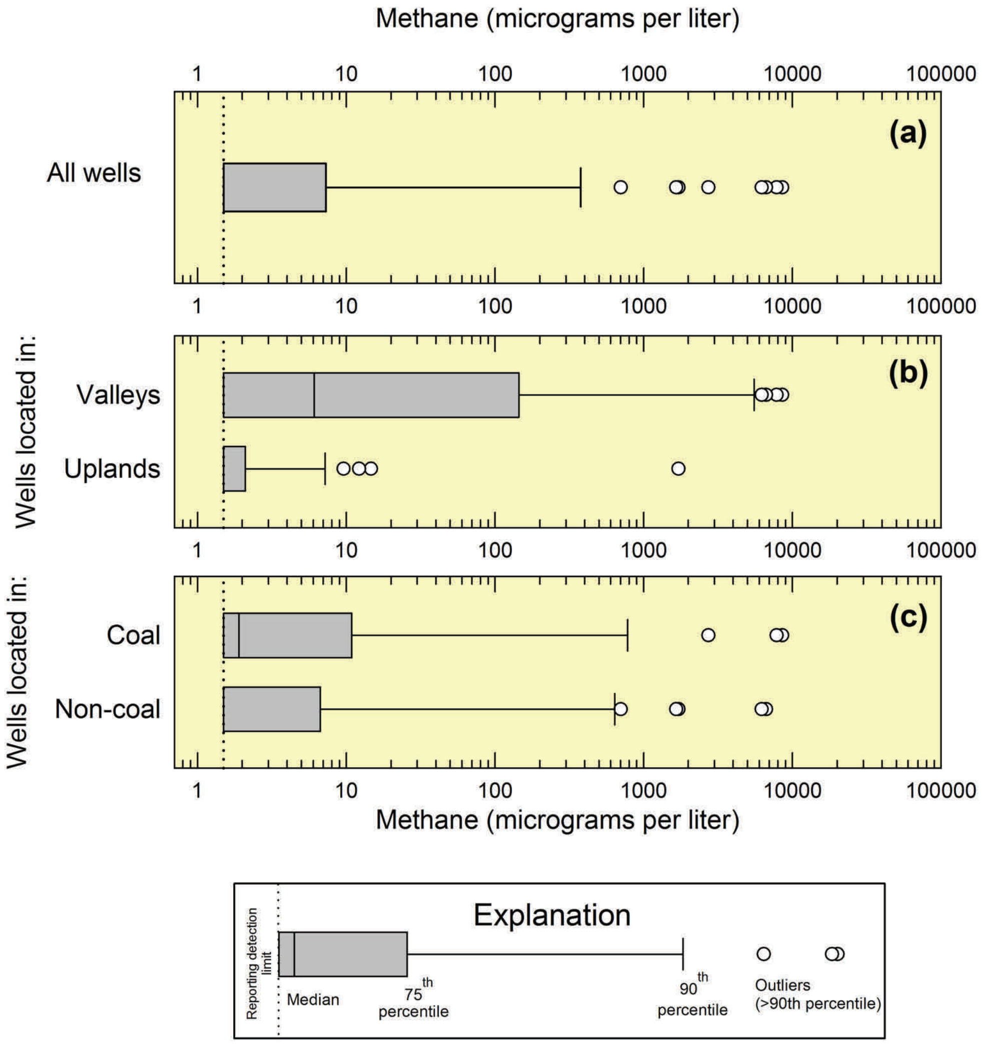


Figure 6. Boxplots showing distribution of methane concentrations in: (a) all wells; (b) wells in valleys and uplands; and (c) wells in coal areas and non-coal areas.

The well was remediated by isolating and packing off a coal seam in the well, after which there were no additional problems with methane buildup.

Sampled wells were located in nine geologic formations. The geologic formation for each well was determined using well locations combined with ArcGIS to plot the well locations on top of the georeferenced geologic map of Brezinski and Conkwright (2013), in conjunction with information on the driller's well completion report (primarily to confirm the presence or absence of coal beds). The majority of wells sampled were in either the (Pennsylvanian) Conemaugh Formation (29 wells) or the (Devonian) Hampshire Formation (23 wells); two to eight wells were sampled in each of the other formations (figs. 9 and 10). Methane was detected in all formations (tab. 4). Methane concentrations greater than 1,000 µg/L were measured in wells in the Conemaugh (2 of 29 samples), Allegheny (1 of 4 samples), and the Hampshire Formations (4 of 23 samples).

The geologic and topographic categories enable the wells to be grouped into one of four categories: valley/coal, upland/coal, valley/non-coal, or upland/non-coal. Valley wells in coal basins had the highest proportion of detections (13 of 17 wells, about 76 percent), followed by valley wells in non-coal basins (13 of 24 wells; 54 percent), upland wells in coal basins (7 of 20 wells; about 35 percent), and upland wells in non-coal basins (7 of 26 wells; about 27 percent) (tab. 5). Methane concentrations with respect to both topographic position and geologic setting are shown in figures 11 and 12.

Table 3. Summary of methane concentrations with respect to individual geologic setting and topographic position.

[<, less than; >, greater than]

Geologic setting or topographic position	Number of wells with dissolved-methane concentrations (in micrograms per liter): <1.5	1.5 – 1,000	>1,000	Total number of wells in each
Coal	17	17	3	37
Non-coal	30	16	4	50
All wells	47	33	7	87
Valleys	15	20	6	41
Uplands	32	13	1	46
All wells	47	33	7	87

Well Depth

Wells sampled during this study ranged in depth from 45 to 1,200 ft (median: 207 ft), as reported on the well completion report (fig. 13). Ninety percent of the wells were less than 450 ft deep. Current regulations for wells in Hydrogeologic Area 4 (non-carbonate sedimentary rock aquifers) require casing to extend through the weathered material and be seated at least two feet into bedrock, with a minimum of 40 ft of casing (Code of Maryland Regulations [COMAR] 26.04.04.17). Most of the wells were completed as open holes below the bottom of casing, although some wells have ungrouted liners installed to prevent sediment from accumulating in the bottom of the hole. Because water can enter the open hole through more than one fracture, the water samples often represent a composite sample from more than one water-producing zone. There was no significant relationship between well depth and methane concentrations (fig. 14), likely at least in part because of mixing of waters entering from different parts of the borehole.

Other Water-Quality Constituents

Methane concentrations are plotted against water quality constituents that were measured in the field (pH, alkalinity, dissolved oxygen, specific conductance, total hardness, and chloride) (fig. 15). Methane was negatively correlated with dissolved-oxygen levels (Spearman rank-order correlation, $P<0.01$). Methane was detected in only about 12 percent (4 of 34) of samples with dissolved-oxygen concentrations greater than 1 mg/L, compared with about 68 percent of wells having less than 1 mg/L dissolved oxygen. This is consistent with methanogenesis occurring in anaerobic (oxygen-depleted) environments. The presence of methane in oxygenated waters may reflect mixing of water from different zones within these wells. There appear to be some weak correlations between methane and other field measurements; however, the large number of methane samples less than 1.5 µg/L preclude rigorous statistical analysis. Water-quality constituents are summarized by topographic position and geologic setting in table 6.

Median values for specific conductance (a surrogate for dissolved solids), alkalinity, and total hardness were higher in wells located in coal/valley settings than from the other three categories. This may reflect longer residence times for groundwater in valley settings, differences in land use, or other factors.

VARIATION IN METHANE CONCENTRATIONS IN INDIVIDUAL WELLS

Groundwater methane has been shown to vary by 30 to 50 percent, due to differences in atmospheric, hydrologic, pumping, and sampling conditions (Gorody and others, 2005; Coleman and McElreath, 2012). To gage the amount of methane variation in individual wells, three wells (GA Ba 17, GA Cb 95, and GA Ea 65) were resampled for methane and

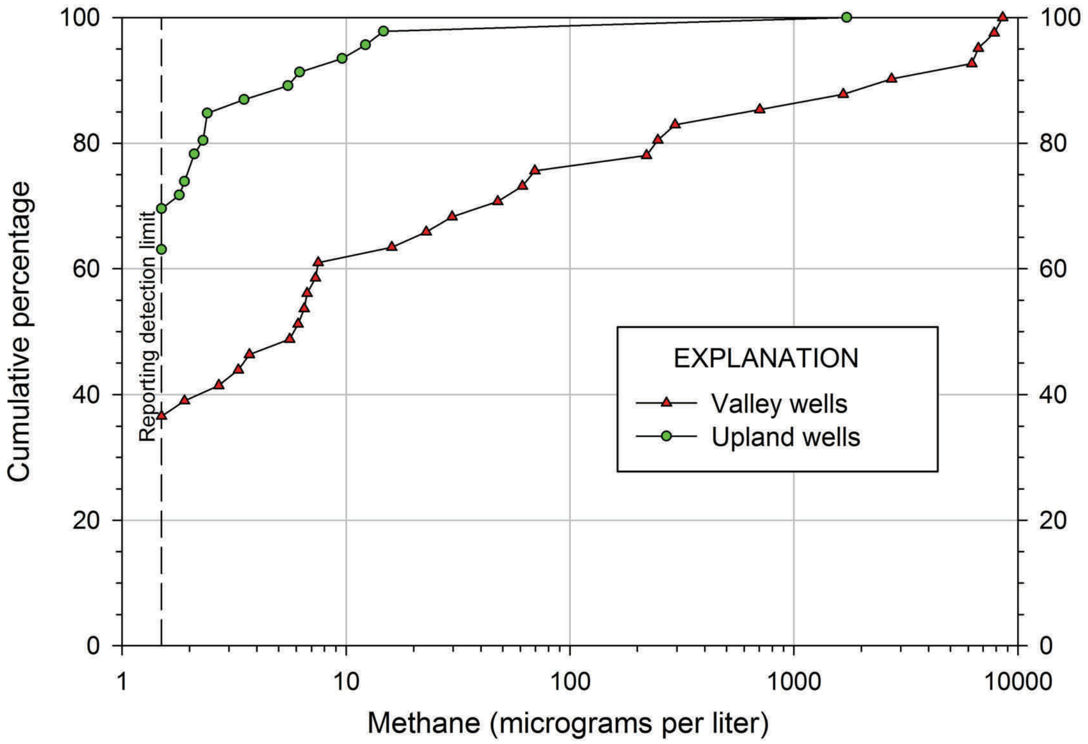


Figure 7. Cumulative percentage plots of methane concentrations with respect to topographic position. The cumulative percentage represents the percentage of samples less than or equal to the specified methane concentration.

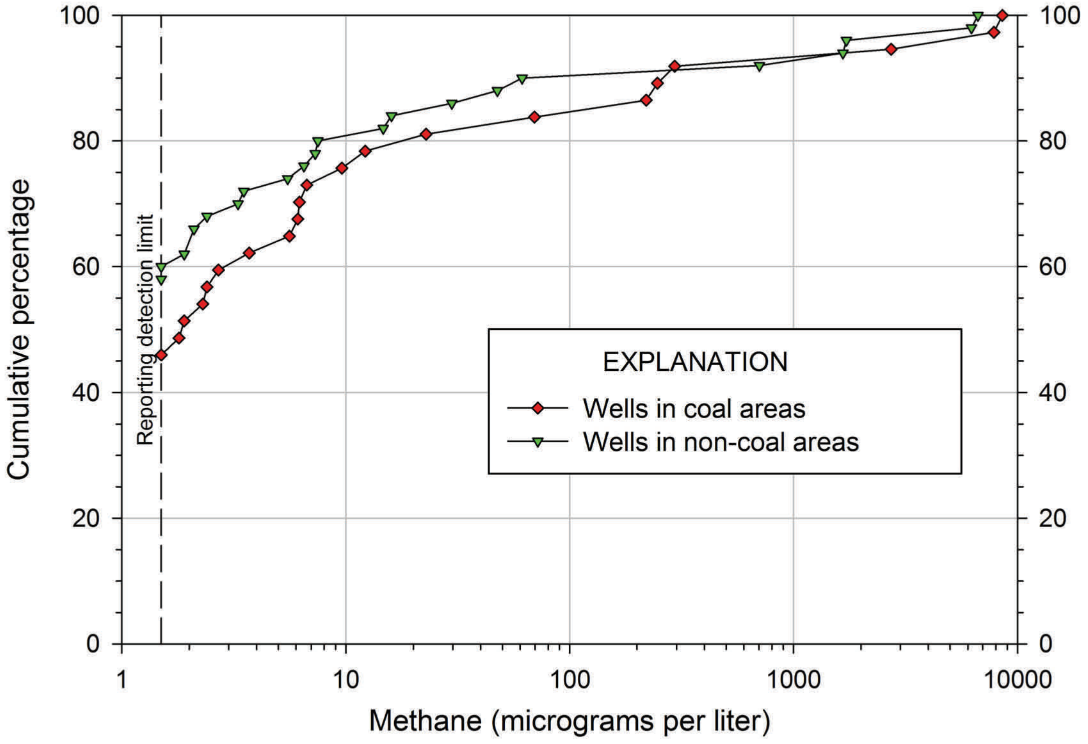


Figure 8. Cumulative percentage plots of methane concentrations with respect to geologic setting (coal versus non-coal areas). The cumulative percentage represents the percentage of samples less than or equal to the specified methane concentration.

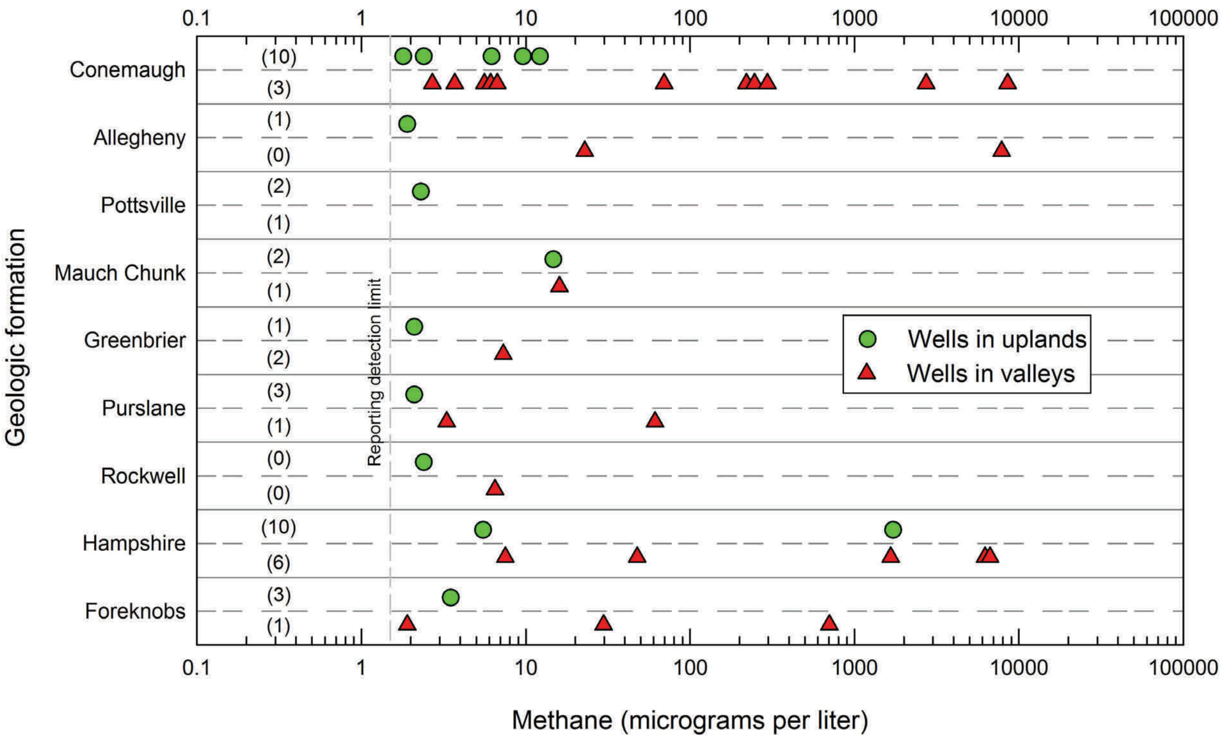


Figure 9. Methane concentrations from valley and upland wells with respect to geologic formation. Number of samples having less than 1.5 micrograms per liter methane is shown in parentheses.

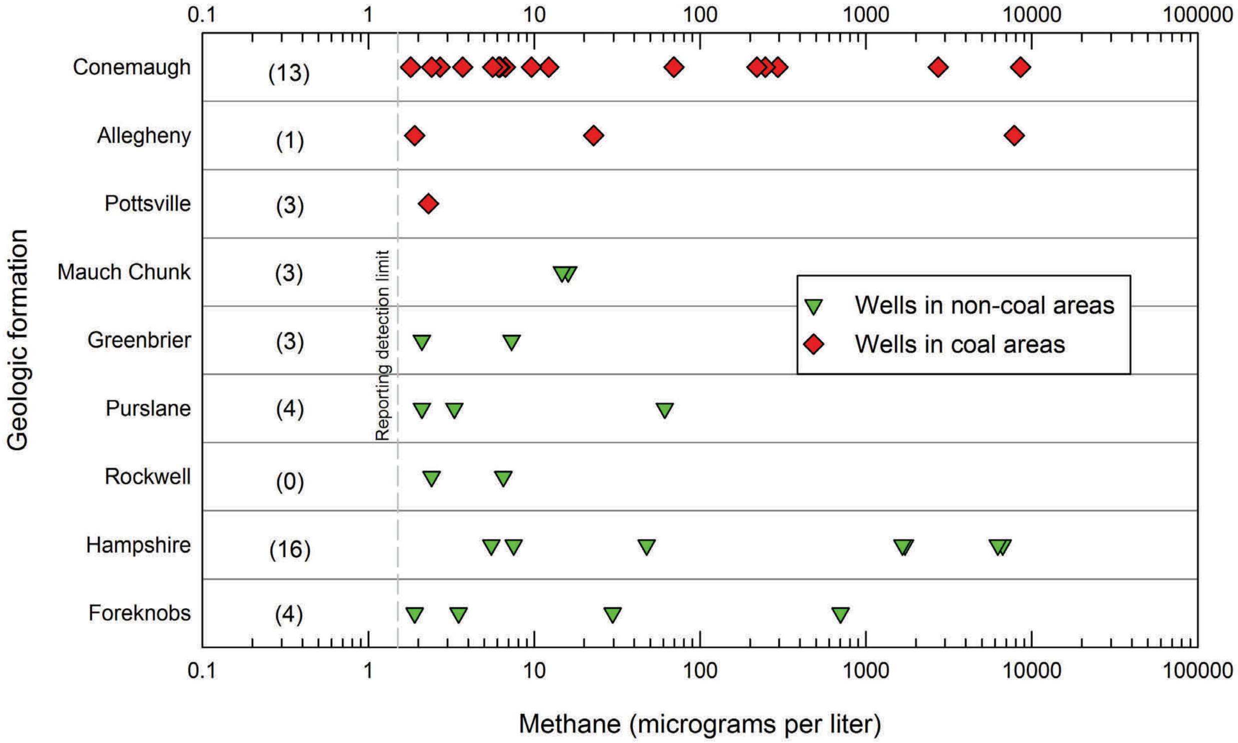


Figure 10. Methane concentrations from wells in coal and non-coal areas with respect to geologic formation. Number of samples having less than 1.5 micrograms per liter methane is shown in parentheses.

Table 4. Summary of methane concentrations with respect to geologic formations.

[<, less than; >, greater than]

Series	Geologic formation or group	Number of wells with dissolved-methane concentrations (in micrograms per liter):			Total number of wells
		<1.5	1.5 – 1,000	>1,000	
Pennsylvanian	Conemaugh	13	14	2	29
	Allegheny	1	2	1	4
	Pottsville	3	1	0	4
Mississippian	Mauch Chunk	3	2	0	5
	Greenbrier	3	2	0	5
	Purslane	4	3	0	7
Devonian	Rockwell	0	2	0	2
	Hampshire	16	3	4	23
	Foreknobs	4	4	0	8
TOTAL		47	33	7	87

Table 5. Summary of methane concentrations by topographic position within each geologic setting. Top number in each box is the number of wells; bottom number is percent of wells in each category.

[<, less than; >, greater than; µg/L, micrograms per liter; %, percent. Individual percentages may not add to 100 percent due to rounding errors.]

Geologic setting	Topographic position	Number of wells with dissolved-methane concentrations (in micrograms per liter):			Total number of wells in setting
		<1.5	1.5 – 1,000	>1,000	
Coal	Valleys	4 24%	10 59%	3 18%	17 20%
	Uplands	13 65%	7 35%	0 0%	20 23%
Non-coal	Valleys	11 54%	10 42%	3 13%	24 28%
	Uplands	19 73%	6 23%	1 4%	26 30%
TOTAL		47 54%	33 38%	7 8%	87 100%

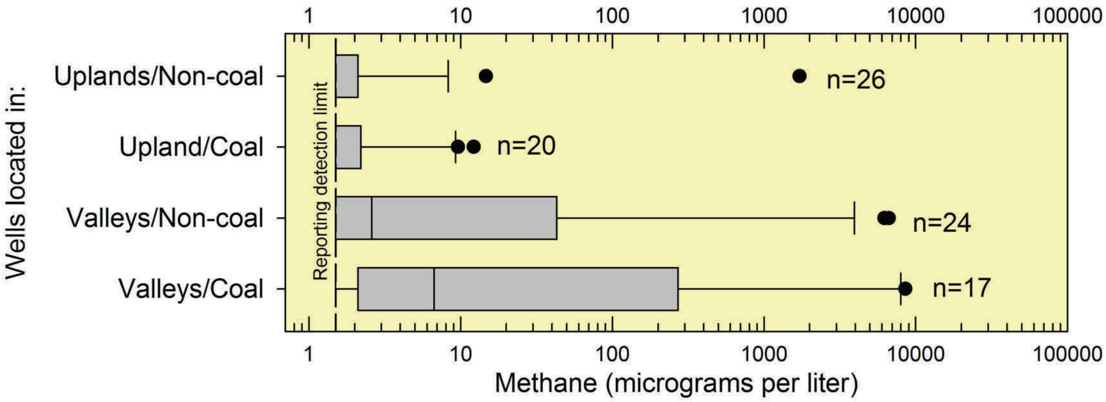


Figure 11. Boxplots showing distribution of methane concentrations in relation to both geologic setting and topographic position. See Figure 6 for explanation.

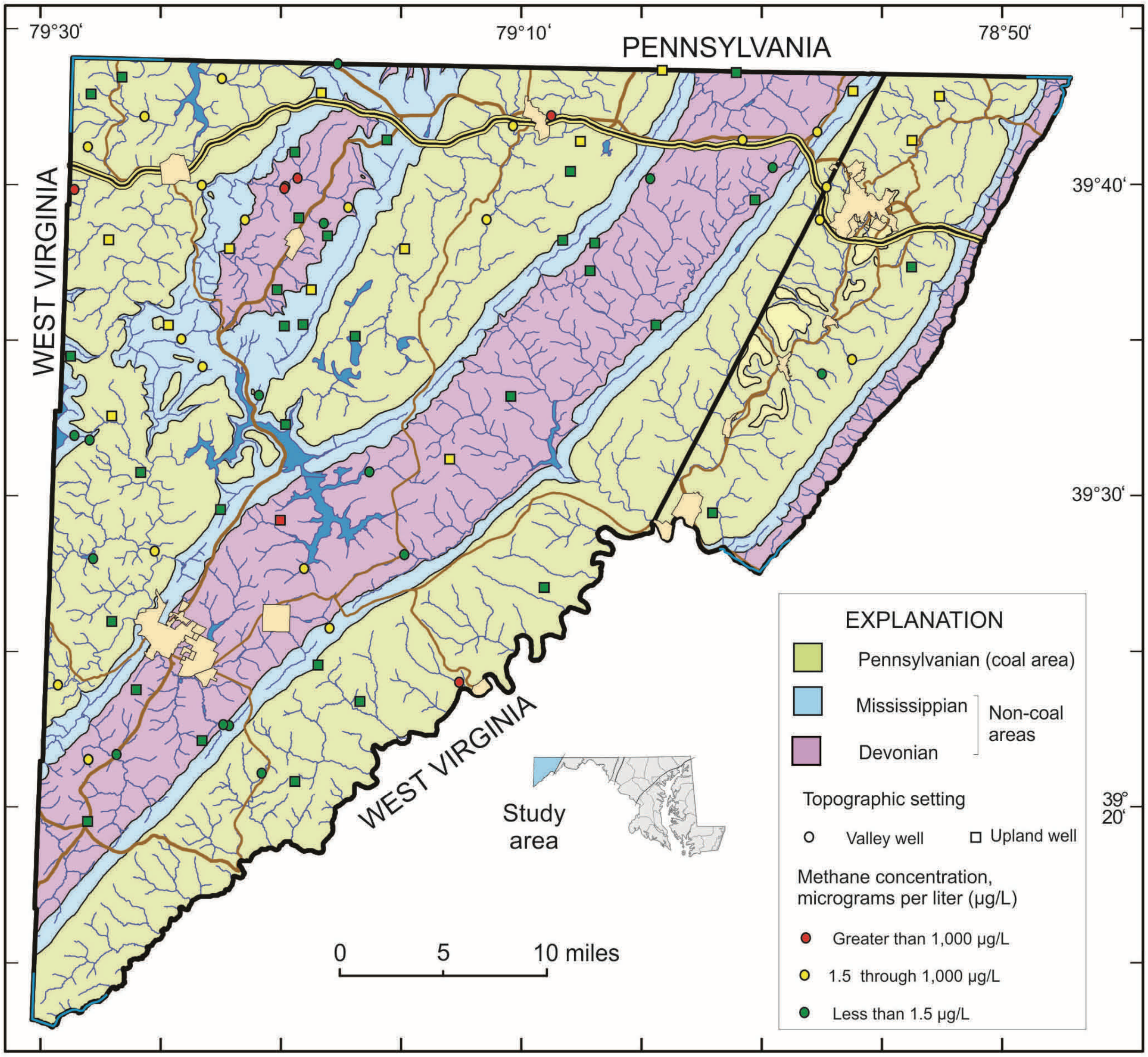


Figure 12. Map showing well-water methane concentrations with respect to geologic setting and topographic position.

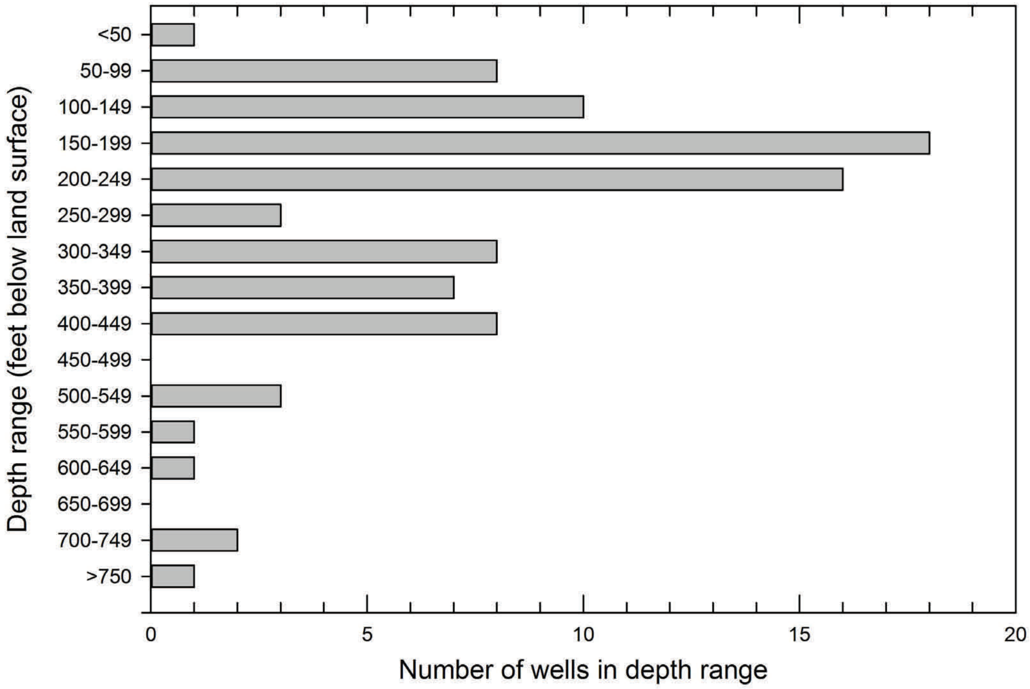


Figure 13. Frequency distribution of well depths sampled in this study.

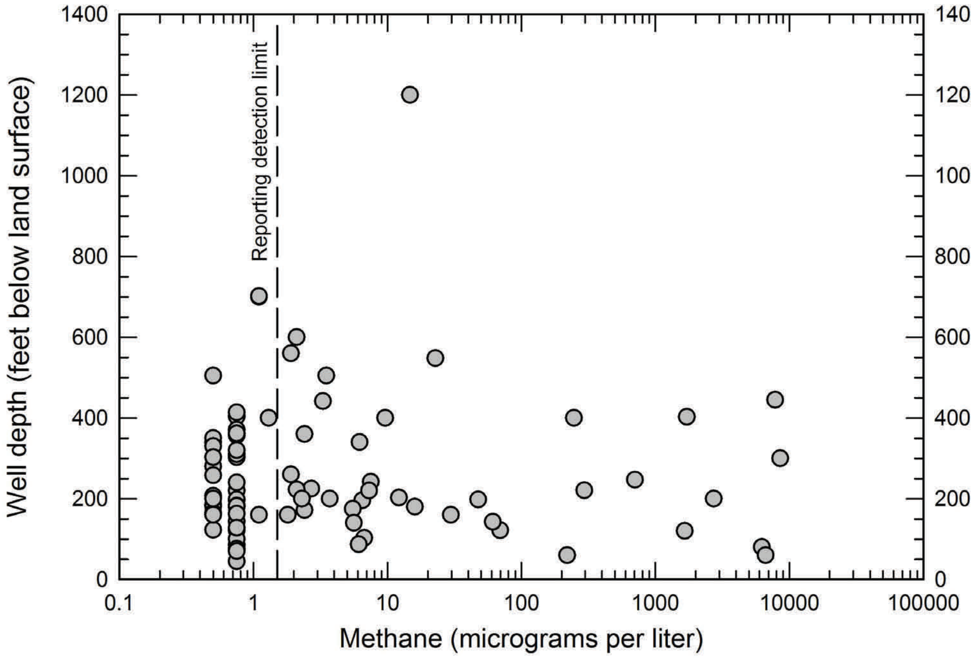


Figure 14. Relation between methane concentrations and well depth. Values reported as less than reporting detection limits (dashed line) are plotted at 1/2 the limit (either 0.5 of 0.75 micrograms per liter).

Table 6. Water-quality data summarized by geologic setting and topographic position. Top number is median value; values in parentheses contain the range.

[µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; <, less than]

Geologic setting	Topographic position	Number of wells	Dissolved methane (µg/L)	pH	Specific conductance (µS/cm)	Dissolved oxygen (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Chloride (mg/L)	Total hardness (mg/L as $CaCO_3$)
Coal	Valleys	17	6.7 (<1.5 – 8,550)	7.5 (6.3 – 8.9)	346 (58 – 898)	<1 (<1 – 4.6)	147 (20 – 213)	<10 (<10 – 210)	169 (<10 – 413)
	Uplands	20	<1.5 (<1.5 – 12.2)	7.0 (5.5 – 7.8)	249 (51 – 1,960)	<1 (<1 – 7.0)	109 (8 – 242)	<10 (<10 – 18)	122 (10 – 1,385)
Non-Coal	Valleys	24	2.6 (<1.5 – 6,665)	7.7 (5.4 – 8.7)	199 (30 – 655)	<1 (<1 – 9.1)	83 (11 – 134)	<10 (<10 – 119)	50[1] (12 – 198)
	Uplands	26	<1.5 (<1.5 – 1,720)	7.6 (5.9 – 9.4)	195 (55 – 545)	<1 (<1 – 9.8)	82 (9 – 149)	<10 (<10 – 85)	82[2] (21 – 220)

[1] Three wells were not tested for total hardness.
[2] Four wells were not tested for total hardness.

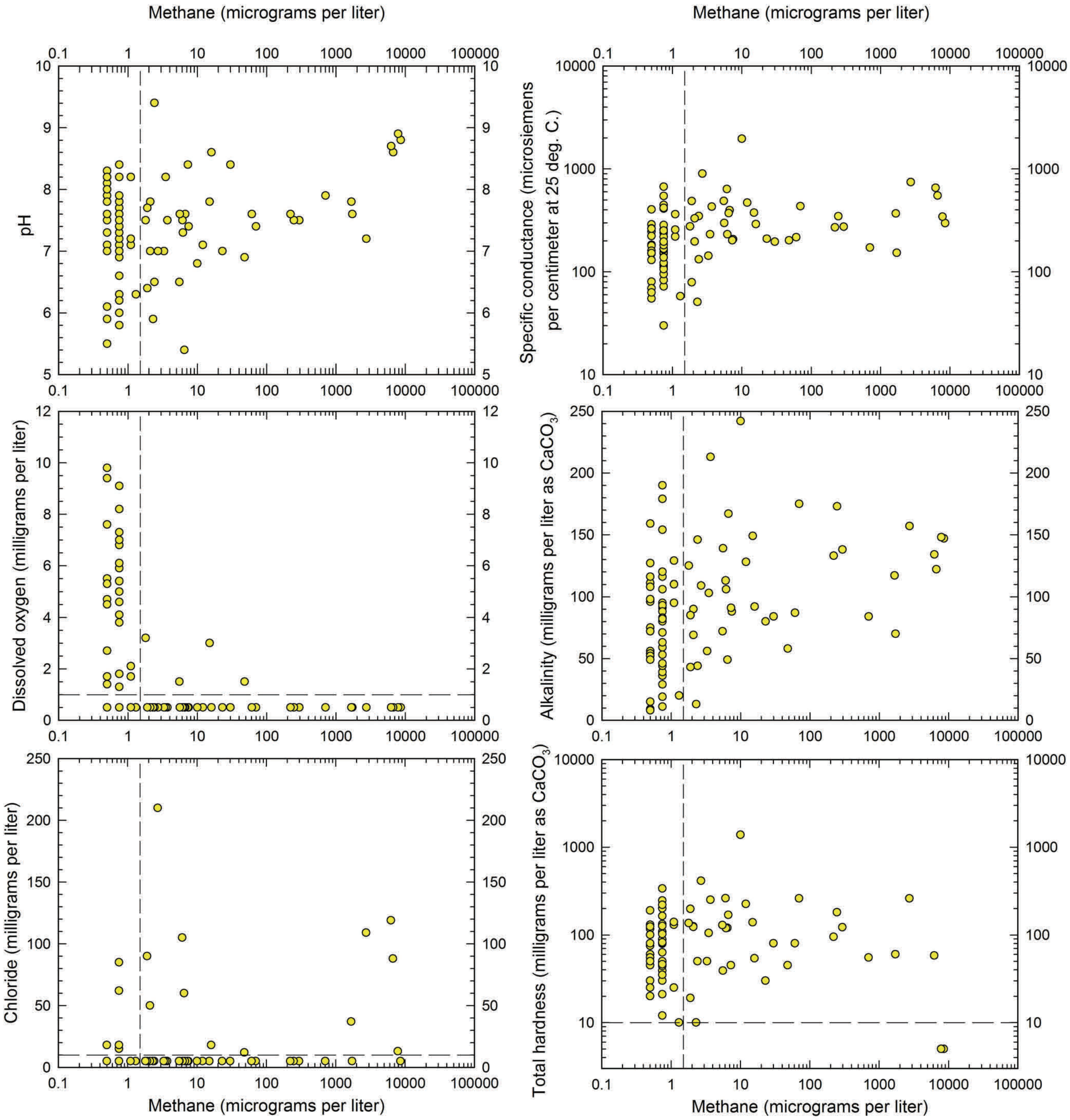


Figure 15. **Relation between methane concentrations and pH, specific conductance, dissolved oxygen, alkalinity, chloride, and total hardness. Values reported as less than reporting detection limits (dashed lines) are plotted at 1/2 the limit.**

other constituents at approximately monthly intervals between December, 2012 and August, 2013 (fig. 16; app. D). These particular wells were selected because the initial samples indicated that they represented a range of methane concentrations. The ranges and median methane concentrations in the three wells are shown in table 7. The average percent difference from the median monthly methane concentration in each well was between 20 and 30 percent, although individual variations in each well were frequently larger. Methane concentrations were noticeably lower in the samples collected on January 24, 2013 from GA Cb 95 and GA Ea 65 (GA Ba 17 could not be sampled on that date due to inaccessibility of the sampling site). The lower methane concentrations in these two wells do not appear to be caused by dilution from recharge water, as specific conductance values in these samples were similar to those collected on other dates. Furthermore, there had been little precipitation in the week prior to sampling, and subfreezing temperatures prevented snowmelt infiltration at this time. The decreases also do not correlate with changes in atmospheric pressure. It is unlikely that the changes observed in methane concentrations were due to differences in the sample collection process, since the differences in the duplicate samples from these sites were much less than the monthly changes.

Factors that may have affected methane concentrations in the monthly samples include the amount of time since last being pumped, water volume and rate of pumping by the homeowner, and static water level in the well (which was not measured). The variations observed in methane concentrations in these wells indicate that a single methane analysis is insufficient to characterize dissolved methane in well water. Multiple samples collected over a period of time would provide a range of methane concentrations to a particular well.

Table 7. Summary of methane and specific conductance data from multiple samples at three wells between August, 2012 and August, 2013.

[µg/L, micrograms per liter; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Well	Number of samples	Methane (µg/L)		Specific conductance, (µS/cm)	
		Range	Median	Range	Median
GA Ba 17	10	3,020--8,550	6,375	217-301	288
GA Cb 95	10	31.9--109	79	201-217	205.5
GA Ea 65	10	<1.5--795	570	161-172	162.5

SOURCES OF METHANE

Identification of methane source(s) in a particular water well is best done with multiple lines of evidence, including isotopic analysis, ratios of methane to higher-chain hydrocarbons, and evaluation of inorganic constituents. Although a detailed investigation of methane sources was not a primary objective of this study, a limited number of methane-to-ethane ratios and isotopic data from this study provide some information as to whether the methane was produced by thermogenic (increased temperature and pressure during burial) or biogenic (microbial) breakdown of organic matter.

The ratio of methane (C_1) to the sum of ethane and other higher-chain hydrocarbons (collectively referred to as $C_{2\text{-}5}$) can be used to help determine whether these gases are thermogenic, biogenic, or a combination of both. Because $C_{2\text{-}5}$ are not generally produced by microbial processes, water samples with $C_1/C_{2\text{-}5}$ values less than 100 suggest a thermogenic origin for methane; those with $C_1/C_{2\text{-}5}$ values greater than 1000 are considered to be biogenic (Schoell, 1980). Methane-to-ethane ratios between 100 and 1,000 may represent a combination of the two processes.

The six wells in the study that had detectable ethane had methane-to-ethane ratios ranging from 33 to

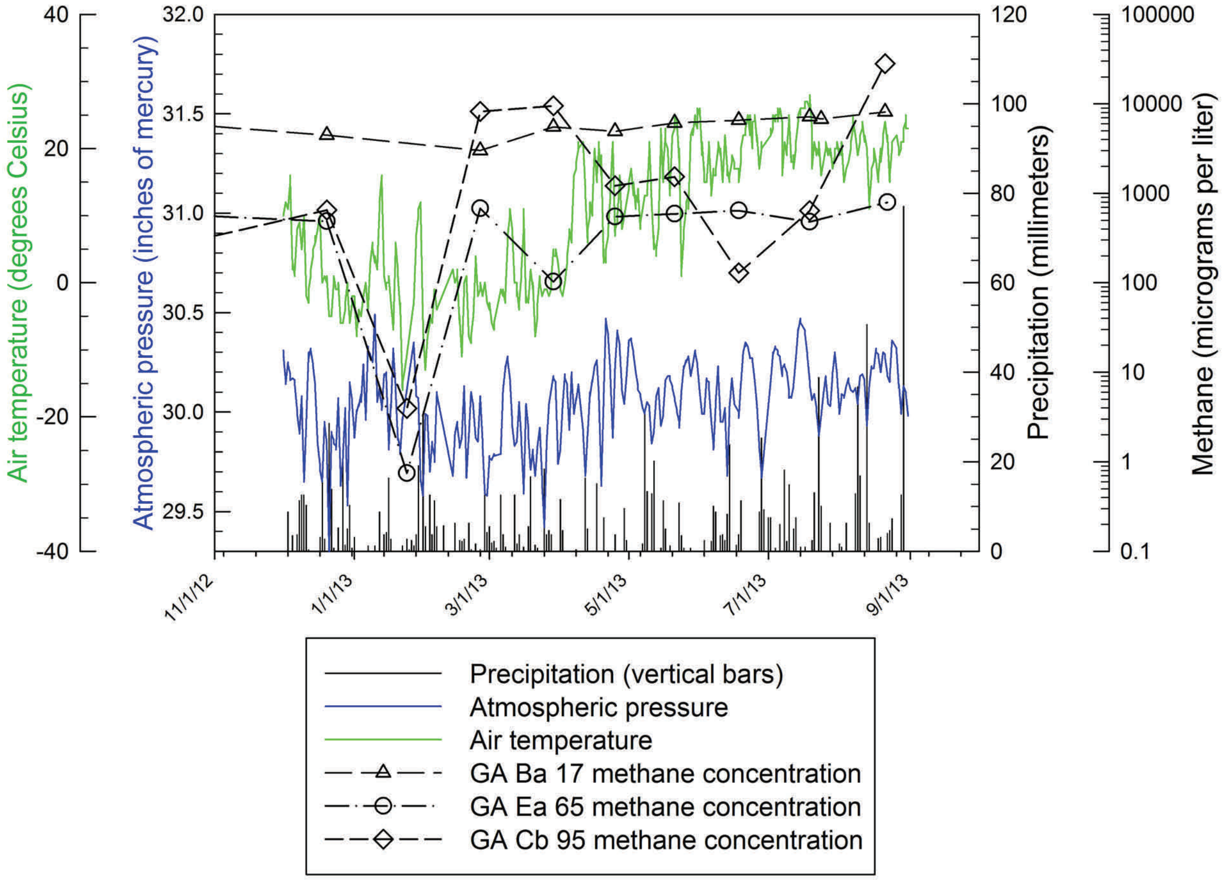


Figure 16. Monthly methane concentrations from wells GA Ba 17, GA Cb 95, and GA Ea 65 with respect to air temperature, atmospheric pressure, and precipitation. Temperature and pressure data recorded at Garrett County Airport. Precipitation data from Sines Deep Creek station (Station 3755). Source of data: National Oceanic and Atmospheric Administration, National Centers for Environmental Information (2015a; 2015b).

145 (tab. 8). (Because no other higher-chain hydrocarbons were detected in this study, the $C_1/C_{2\text{-}5}$ ratio equals the methane-to-ethane ratio.) Additionally, two other wells with elevated methane (GA Ba 17 and GA Dc 156, with methane concentrations of 6,800 and 1,720 µg/L respectively) each had less than 3 µg/L ethane, giving minimum methane-to-ethane ratios of 2,061 and 521, respectively. (The low methane concentrations in other wells, in conjunction with the lack of ethane detections, result in methane-to-ethane ratios that are meaningless for this purpose.) The methane-to-ethane ratios suggest that methane in four of the wells has a thermogenic origin, two are in the mixed thermogenic/biogenic range, one is partially or completely biogenic, and one is solely biogenic (tab. 8). The non-coal-area wells tended to have lower methane-to-ethane ratios (suggesting a more thermogenic origin) than coal-area wells (more biogenic). Seven of the eight wells in table 8 were located in valleys; all 6 wells having detectable ethane were located in valleys. The three wells in valley/non-coal settings are in the thermogenic range, while the one well in an upland/non-coal setting appears to have a partial biogenic source.

Stable isotopes of carbon and hydrogen in the methane molecule ($^{13}C_{CH4}$ and $^{2}H_{CH4}$, respectively) have also been used to identify sources of methane in the Appalachian Basin and elsewhere (Schoell, 1980; Laughrey and Baldassare, 1998; Osborn and McIntosh, 2010; Révész and others, 2010; Molofsky and others, 2013; Baldassare and others, 2014). Because stable isotopes of the same element have different masses, transformations will cause the reactants and products to become preferentially enriched or depleted in a particular isotope. Stable isotopes of carbon and hydrogen are reported as $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4,}$ and are calculated as a ratio to a standard as follows:

Table 8. $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$ values and methane-to-ethane ratios for selected wells.

[‰, per mil; µg/L, micrograms per liter; --, no data]

Well number	Date	$\delta^{13}C_{CH4}$ (‰)	$\delta^{2}H_{CH4}$ (‰)	Methane (µg/L)	Ethane (µg/L)	Methane-to-ethane ratio	Valley or upland	Coal or non-coal
GA Aa 14	5/15/2013	--	--	247	3.6	69	Valley	Coal
GA Ae 92	8/14/2012	--	--	2,730	4.4	621	Valley	Coal
GA Ba 17	7/24/2013	-52.54	-209.2	6,800	<3.3	>2,061	Valley	Coal
GA Bc 33	4/23/2014	--	--	1,660	26.2	63	Valley	Non-coal
GA Bc 67	4/23/2014	--	--	6,230	189	33	Valley	Non-coal
GA Bc 72	5/2/2014	--	--	6,665	191	35	Valley	Non-coal
GA Dc 156	5/2/2013	--	--	1,720	<3.3	>521	Upland	Non-coal
GA Ed 14	7/24/2013	-52.89	-214.5	8,010	55.1	145	Valley	Coal

$$\delta^{13}C_{CH4}\,(‰) = ([{}^{13}C_{sample}/{}^{13}C_{VPDB}] - 1) \times 1{,}000$$

and

$$\delta^{2}H_{CH4}\,(‰) = ([{}^{2}H_{sample}/{}^{2}H_{VSMOW}] - 1) \times 1{,}000$$

where:

VSMOW = Vienna Standard Mean Ocean Water
VPDB = Vienna Pee Dee Belemnite

Samples from two wells (GA Ba 17 and GA Ed 14) were analyzed for $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$. (A sample was also collected from a third well [GA Dc 156] but there was insufficient methane (less than 1 mg/L) for the analysis, despite an earlier sample with a methane concentration of 1,720 µg/L.) The data are shown in figure 17 with respect to fields corresponding to sources of methane. The two samples plot in the thermogenic zone. This is somewhat consistent with the methane-to-ethane ratio (145) for well GA Ed 14, which suggests a mixed biogenic-thermogenic origin for the methane. However, the methane-to-ethane ratio (at least 2,061) for well GA Ba 17 suggests a biogenic origin. Well-completion reports indicate that both wells penetrated coal seams. Both wells are located in valleys, although GA Ed 14 is in a larger valley, is located closer to the bottom of the valley, and is deeper than GA Ba 17. Well GA Ba 17 is within 1,000 ft of a water well that had a coal seam packed off because methane was entering the water lines (L. Brenneman, Brenneman Well Drilling, Inc., personal commun, 2011). Not all thermogenic gases contain ethane; ethane may have been removed by bacterial decomposition, thus giving a higher methane-to-ethane ratio than would otherwise be expected, a process that has been documented in subsurface hydrocarbon reservoirs (James and Burns, 1981; Coleman and others, 1993).

These data underscore the need for multiple lines of evidence when attempting to identify methane sources, which cannot always be conclusively determined from isotopic ratios and methane-to-ethane ratios. Source identification is enhanced by a larger sample size, as well as a comprehensive geological evaluation (e.g., Baldassare and others, 2014).

METHANE CONCENTRATIONS IN RELATION TO THE ACCIDENT DOME NATURAL GAS STORAGE FIELD

A major concern among residents living in areas where the Marcellus shale and other hydrocarbon-producing shales are being developed is the potential for methane to migrate from gas wells or producing formations to shallow fresh-water aquifers that often are the sole-source water supply in rural areas. Methane can migrate from gas wells to shallow aquifers via several routes. Wells that have not been properly grouted or that have damaged casing can provide a path for methane to travel up the well annulus (the space between the casing and the drilled hole) and enter into shallow groundwater. Improperly plugged and abandoned wells can provide a hydraulic connection between deeper gas zones and shallow aquifers. Methane may also be capable of

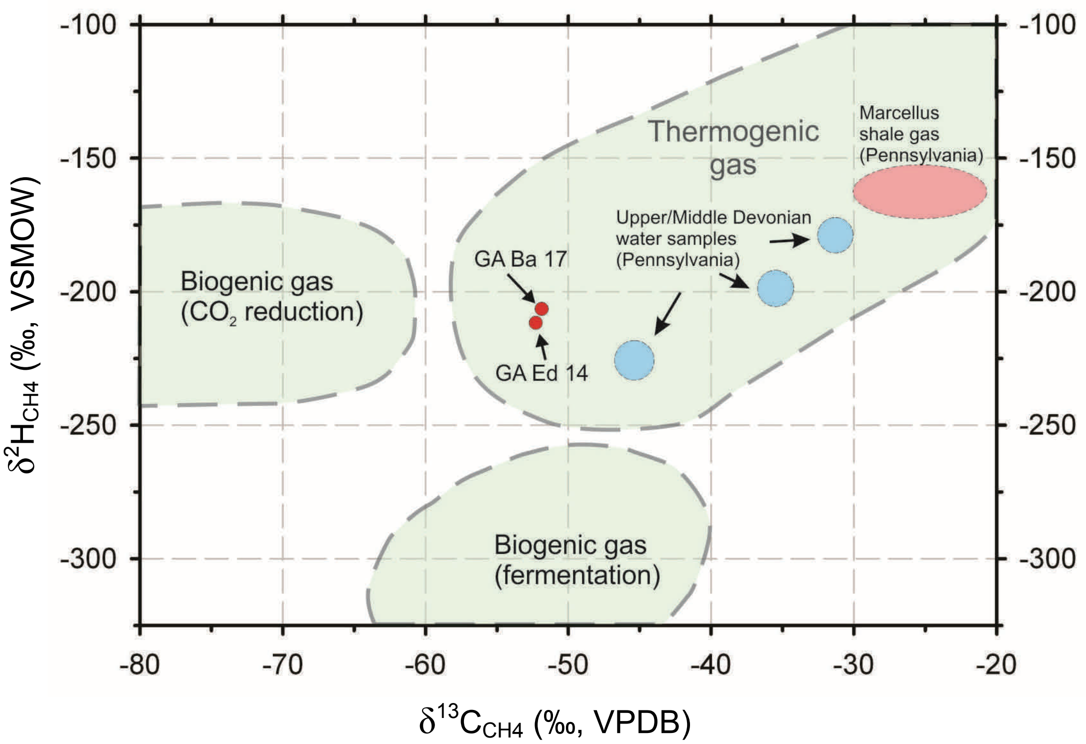


Figure 17. **$\delta^{13}C_{CH4}$ and δ^2H_{CH4} values from wells GA Ba 17 and GA Ed 14 in relation to isotopic fields for biogenic and thermogenic methane. Fields for biogenic and thermogenic gas modified from Coleman and others (1993). Marcellus shale gas and Upper and Middle Devonian water sample data from Molofsky and others (2011).**

migrating upward via naturally occurring fracture zones into the shallow subsurface.

The relation between methane concentrations in water-supply wells and proximity to Marcellus shale gas wells has been examined in several studies, often resulting in conflicting conclusions. Osborn and others (2011) presented evidence for methane contamination in drinking water due to gas-development activities in Pennsylvania and New York. Molofsky and others (2013), in a study of more than 1,700 wells in Susquehanna County, Pennsylvania, concluded that well-water methane is more closely associated with topographic position (higher methane in wells in valleys rather than uplands) than with proximity to gas wells. Another study in northeastern Pennsylvania, examining more than 11,300 methane analyses from domestic wells, found no statistically significant relationship between methane in private water wells and distance to existing oil or gas wells (Siegel and others, 2015).

As of 2015, no Marcellus shale gas wells have been drilled in Maryland. However, natural gas has been produced from three fields in Garrett County beginning in the 1950s: the Accident field, the Mountain Lake Park field, and the Negro Mountain field (fig. 18). The Accident field, located near the town of Accident in northern Garrett County, was discovered in 1953; 25 wells were drilled, of which 19 produced gas (Edwards, 1970). More than 2 bcf of natural gas was produced, with most production ceasing by 1965 (Schwarz, 1996). The (Devonian) Oriskany Sandstone, the geologic formation from which natural gas was produced, is approximately 200 ft below the Marcellus shale, which is thought to be the source of hydrocarbons for the Oriskany Sandstone (Brezinski, 2012). The Accident gas field was purchased by the Texas Eastern Gas Transmission Company (now Spectra Energy Corporation) in 1962 and was converted to a natural gas storage field, with 63 additional wells being drilled for gas injection and extraction (Schwarz, 1996). Natural gas gathered from elsewhere in the United States is injected into the field during the low-demand months and extracted during the winter when demand is higher.

Fourteen water wells sampled during this project are located in the vicinity of the Accident field (fig. 19). To evaluate the relation between gas wells and well-water methane concentrations, the locations of current and former gas-production and gas-storage

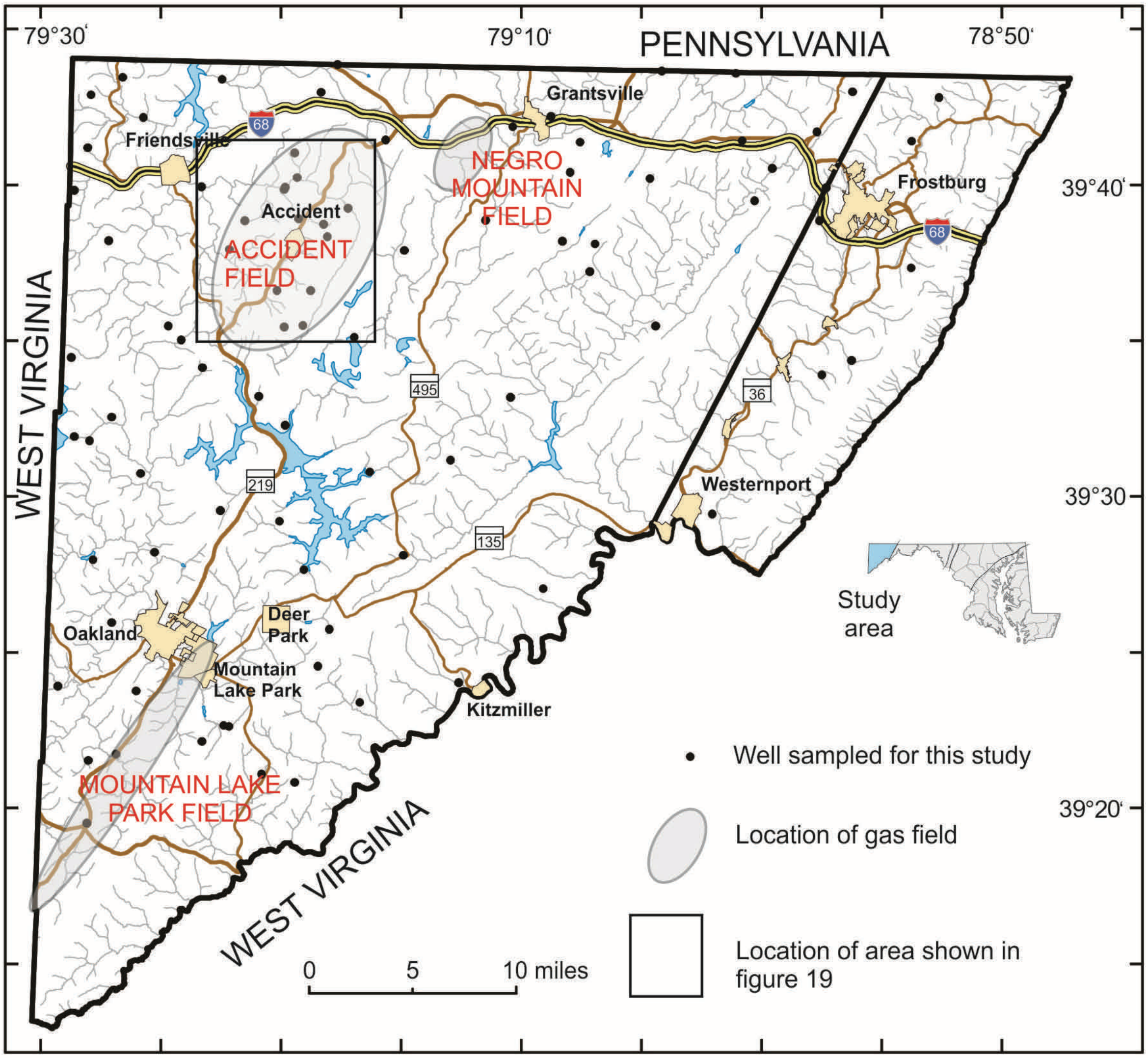
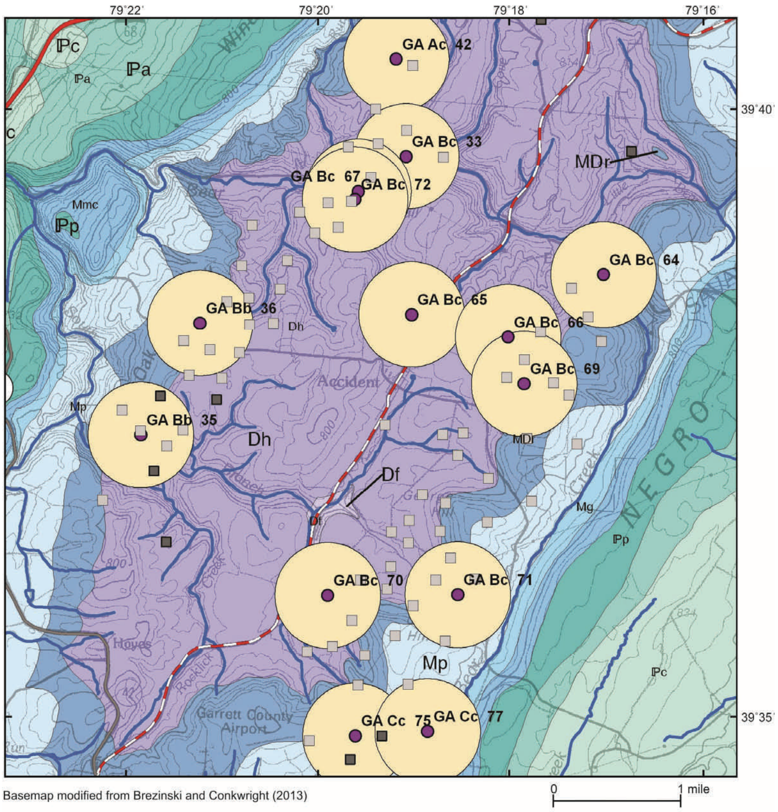


Figure 18. Locations of the Accident, Mountain Lake Park, and Negro Mountain gas fields.

injection/recovery wells (collectively referred to as gas wells) were obtained from MGS Basic Data Reports Nos. 5 and 11 (Edwards, 1970; Nutter and others, 1980). A half-mile-radius buffer zone was established around each of the 14 water wells (fig. 19). The number of gas wells contained within the buffer zone around each water well was plotted against methane concentrations from each well (fig. 20).

Methane concentrations in the 14 water wells ranged from less than 1.5 to 6,665 µg/L. There were between zero and 6 gas wells within 1/2 mile of the wells. Seven of the 14 wells had less than 1.5 µg/L methane; these wells had from zero to 5 gas wells within the buffer zone. All but one of the seven wells with less than 1.5 µg/L methane was located in an upland setting. The seven water wells having more than 1.5 µg/L methane had between two and six gas wells within each well's buffer zone. Significantly, five of these seven wells are located in valley settings, including the three samples with methane greater than 1,000 µg/L, whereas the maximum methane concentration for upland wells is 7.5 µg/L. The three wells having more than 1,000 µg/L methane are all located in the Bear Creek Valley, the major drainage route on the northern part of the Accident field. There are no coal beds underlying the area. The data suggest that topographic position plays a more significant role with regard to well-water methane than does proximity to gas wells. Furthermore, the highest methane concentration in the area was less than 10,000 µg/L, the recommended action limit for methane. These data do not suggest that well-water methane levels are higher due to proximity to current and former Accident field wells than they are elsewhere in the study area.



Basemap modified from Brezinski and Conkwright (2013)

Figure 19. Locations of gas wells (square symbols) and 1/2-mile buffer zones around water wells (round symbols) in the Accident Dome natural gas storage field. See figure 18 for map location.

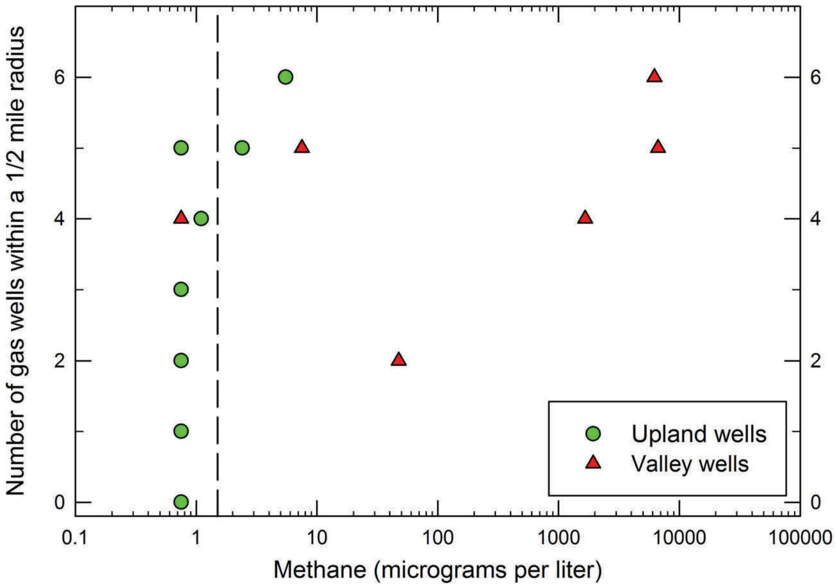


Figure 20. Relation between well-water methane concentrations and number of gas wells within 1/2-mile radius of sampled water wells in the Accident Dome natural gas storage field. Values reported as less than reporting detection limits (dashed line) are plotted at 1/2 the limit.

METHANE CONCENTRATIONS IN MARYLAND COMPARED WITH OTHER AREAS

Well-water methane concentrations have been evaluated in several areas throughout the Marcellus shale region, including county-level studies in Pennsylvania and statewide assessments in West Virginia and New York, and the Upper Delaware River Basin (Pennsylvania and New York). Some studies were conducted after development of the Marcellus shale and/or other formations had occurred (Mathes and White, 2006; Kappel and Nystrom, 2012; Molofsky and others, 2013), while others were conducted to document baseline groundwater-quality conditions prior to development (or extensive development) of the Marcellus shale (Senior, 2014; Sloto, 2013; 2014). Although the sample sizes are small in some of the studies, several observations can be made. Methane concentrations from the majority of samples in each of these studies were either less than 1 mg/L or were reported as non-detections (fig. 21; tab. 9). Overall, the distribution of methane concentrations in studies from Pennsylvania and New York is similar to those found in this study (referred to as the Maryland study), even though the geological settings and levels of gas development differ greatly between the areas. The Maryland study is the only study that had no methane concentrations greater than 28 mg/L; however, such samples are relatively uncommon in the other studies, even in areas of extensive natural gas development. West Virginia had a lower percentage of methane detections either below 1 mg/L or non-detections (66 percent) than other studies (73 to 92 percent), and a higher percentage of methane concentrations above 1 mg/L (including 8 percent of samples above 28 mg/L) than the other studies. This may be related to the widespread presence of coal, which underlies 53 of 55 counties in West Virginia (West Virginia Office of Miners'

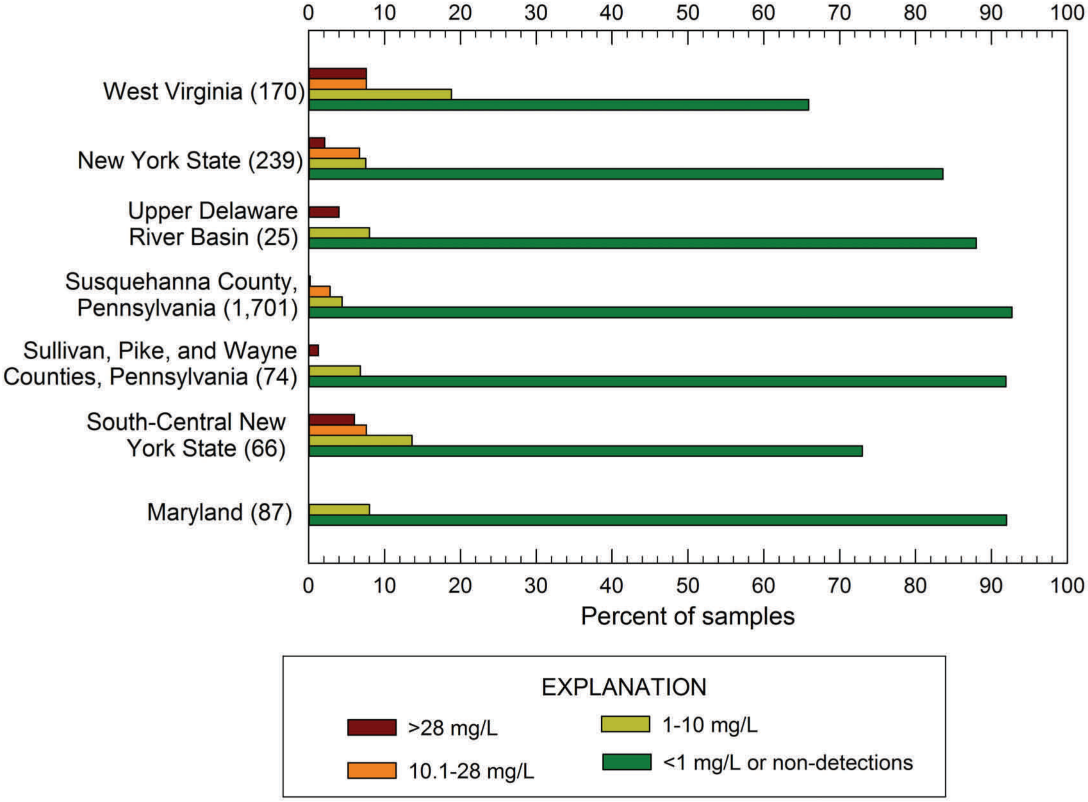


Figure 21. **Methane detection percentages in Maryland compared with other studies in the Marcellus shale region. Numbers in parentheses indicate total number of samples. Sources: Mathes and White (2006), West Virginia; Kappel and Nystrom (2012), New York State; Kappel (2013), Upper Delaware River Basin (Pennsylvania and New York); Molofsky and others (2013), Susquehanna County, Pennsylvania; Senior (2014) and Sloto (2013, 2014), Sullivan, Pike, and Wayne Counties, Pennsylvania (data combined from three reports); and Heisig and Scott (2013), South-Central New York State.**

Health, Safety and Training, 2015). In the West Virginia study, most of the highest methane concentrations were from south of the "hinge line" that separates low-sulfur coal in southern West Virginia from the higher-sulfur coal to the north (Mathes and White, 2006). Coal beds have been shown to be a likely source of thermogenic gas in groundwater in northeast Pennsylvania prior to gas-well drilling (Wilson, 2014). Microbial and mixed microbial and thermogenic gas have also been shown to be present prior to the commencement of Marcellus shale well drilling (Baldassare and others, 2014). These studies show that methane is a common component of well water throughout the region, even in areas where gas development has not occurred, and that the vast majority of methane concentrations are below levels at which additional monitoring or mitigation is recommended.

Table 9. Comparison of groundwater methane data in the Maryland Appalachian Plateau with other studies in the Marcellus shale region. Top number in each box is the number of wells; bottom number is percent of wells in each category.

[mg/L, milligrams per liter; %, percent. Individual percentages may not add to 100 percent due to rounding errors.]

		Methane concentration range				
Location	**Source**	**>28 mg/L**	**10.1–28 mg/L**	**1–10 mg/L**	**Detections <1 mg/L or non-detects**	**Total**
West Virginia	Mathes and White (2006)	13 8%	13 8%	32 19%	112 66%	170 100%
New York	Kappel and Nystrom (2012)	5 2%	16 7%	18 8%	200 84%	239 100%
Upper Delaware River Basin, Pennsylvania and New York	Kappel (2013)	1 4%	0	2 8%	22 88%	25 100%
Susquehanna County, Pennsylvania	Molofsky and others (2013)	3 <1%	47 3%	74 4%	1,577 93%	1,701 100%
Sullivan, Pike, and Wayne Counties, Pennsylvania (combined)	Senior (2014); Sloto (2013; 2014)	1 1.3%	0	5 6.8%	68 92%	74 100%
South-central New York	Heisig and Scott (2013)	4 6%	5 8%	9 14%	48 73%	66 100%
Maryland	this study	0	0	7 8%	80 92%	87 100%

SUMMARY AND CONCLUSIONS

The Maryland Geological Survey, in cooperation with the Maryland Department of the Environment, conducted a study of dissolved methane in well water in the Appalachian Plateau Province of Maryland. This study was undertaken to provide baseline methane data on well water prior to Marcellus shale natural gas development, and to evaluate factors associated with well-water methane.

Water samples were collected from 87 wells in 2012 through 2014 and were analyzed for methane, propane, ethane, and ethene via method RSK-175 (headspace method); most samples were also analyzed for *n*-butane and isobutane. Specific conductance, pH, temperature, chloride, alkalinity, and total hardness were measured in the field. Samples from two wells were analyzed for stable isotopes of carbon and hydrogen in methane (^{13}C and ^{2}H, reported as $\delta^{13}C_{CH4}$ and $\delta^{2}H_{CH4}$), to help identify the origin of methane.

Methane concentrations from 87 untreated well-water samples ranged from less than 1.5 to 8,550 µg/L (0.0015 to 8.55 mg/L). None of the samples exceeded 28,000 µg/L (28 mg/L), the level at which immediate venting of the wellhead is recommended. Methane concentrations from 47 of the 87 wells (about 54 percent) were less than the reporting limit of 1.5 µg/L (0.0015 mg/L). Samples from seven wells (about 8 percent) exceeded 1,000 µg/L (1 mg/L). Dissolved ethane was detected in samples from six wells; concentrations ranged from 3.6 to 191 µg/L (0.0036 to 0.191 mg/L). None of the samples contained any detectable ethene, propane, *n*-butane, or isobutane. Methane concentrations were significantly higher in valley wells than in wells in upland areas. Fifteen of the 16 wells with more than 20 µg/L methane were located in valleys. Methane was detected in about 54 percent of wells in areas underlain by coal, compared with about 40 percent of wells in non-coal areas. There was no significant difference in methane concentrations between the coal and non-coal areas. Methane was detected in well water from all geologic formations that were tested. There was no correlation between methane and well depth, likely in part because of mixing of waters entering from different parts of these open-hole wells.

Three wells that were initially sampled in August, 2012 were sampled monthly for methane and other dissolved gases between December, 2012 and August, 2013. The average percent difference from the median monthly methane concentration in each well was between 20 and 30 percent, although individual variations in each well were frequently larger. The variation in methane concentrations indicate that individual methane analyses may not adequately characterize methane concentrations in any given well.

Carbon and hydrogen stable isotopes were analyzed in two samples to help determine the origin of methane. $\delta^{13}C_{CH4}$ values (-52.54 and -52.89 per mil) and $\delta^{2}H_{CH4}$ values (-209.2 and -214.5 per mil) suggest a thermogenic origin for methane. Methane-to-ethane ratios evaluated from eight wells (range: 33 to more than 2,061) mostly suggest a thermogenic or mixed thermogenic/biogenic origin. More data are needed to fully evaluate the origin of methane in the region.

Fourteen of the sampled wells were in the vicinity of the Accident field, a former natural-gas well field that has been converted to a gas-storage facility. The 14 water wells have from zero to 6 gas wells within a ½-mile radius. The results suggest that the higher methane concentrations in water wells near the Accident field are more closely related to topographic position (i.e., valleys) than to proximity to gas wells.

Data from this study were compared to county and statewide evaluations of methane elsewhere in the Marcellus shale region in Pennsylvania, New York, and West Virginia. Methane concentrations from the vast majority of samples in all the studies (including this study) were either less than 1 mg/L or were reported as non-detections. This study was the only study (of those cited) in which none of the methane concentrations exceeded 28 mg/L. However, such samples were uncommon in the other studies, even in areas of extensive natural gas development. These studies show that methane is a common component of well water throughout the region, even in areas where gas development has not occurred. However, methane concentrations were overwhelmingly less than concentrations at which mitigation steps should be implemented to prevent methane gas buildup.

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Appendix A. Well information and site data for wells sampled in this study.

[BLS, below land surface; U, upland; V, valley]

Local well number	Well permit number	Altitude (ft)	Topo-graphic setting	Coal or non-coal area	Geologic formation at surface	Well depth (ft BLS)
AL Ac 54	AL-66-0059	1,520	U	Coal	Conemaugh	203
AL Ac 55	AL-94-0645	1,750	U	Coal	Conemaugh	400
AL Bb 25	AL-94-1377	2,090	V	Coal	Conemaugh	200
AL Bb 26	AL-94-0679	2,400	V	Coal	Conemaugh	225
AL Bc 70	AL-73-0726	2,180	U	Coal	Conemaugh	75
AL Cb 8	AL-01-2926	2,000	V	Coal	Conemaugh	86
AL Cb 28	AL-81-0233	2,020	V	Coal	Conemaugh	122
AL Da 23	AL-81-0400	1,560	U	Coal	Conemaugh	404
GA Aa 11	GA-73-1030	1,540	V	Coal	Conemaugh	60
GA Aa 12	GA-94-0550	2,090	U	Coal	Conemaugh	197
GA Aa 13	GA-88-1374	2,250	U	Coal	Conemaugh	220
GA Aa 14	GA-95-1620	2,260	V	Coal	Conemaugh	400
GA Ab 22	GA-81-0703	1,490	V	Coal	Conemaugh	103
GA Ac 35	GA-94-0709	2,920	U	Non-coal	Purslane	303
GA Ac 40	GA-95-0879	2,520	U	Non-coal	Greenbrier	600
GA Ac 41	GA-94-0014	2,400	V	Non-coal	Greenbrier	122
GA Ac 42	GA-94-1529	2,340	U	Non-coal	Hampshire	360
GA Ad 24	GA-81-0177	2,200	V	Coal	Conemaugh	87
GA Ae 92	GA-88-0320	2,140	V	Coal	Conemaugh	200
GA Ae 93	GA-94-2679	2,680	U	Coal	Conemaugh	172
GA Ae 94	GA-73-2449	2,690	U	Coal	Conemaugh	185
GA Af 48	GA-73-2720	2,630	U	Non-coal	Hampshire	144
GA Af 49	GA-95-1099	2,600	V	Non-coal	Foreknobs	560
GA Af 50	GA-95-1768	2,480	U	Coal	Allegheny	260
GA Ag 42	GA-88-1031	2,430	V	Non-coal	Hampshire	207
GA Ag 43	GA-94-0887	2,780	U	Non-coal	Purslane	223
GA Ag 44	GA-81-1150	2,760	V	Non-coal	Rockwell	196
GA Ba 17	GA-95-1128	2,170	V	Coal	Conemaugh	300
GA Ba 18	GA-95-1744	2,250	U	Coal	Conemaugh	340
GA Bb 34	GA-88-0314	1,650	V	Non-coal	Mauch Chunk	180
GA Bb 35	GA-02-7632	2,320	U	Non-coal	Hampshire	175
GA Bb 36	GA-95-0585	2,350	V	Non-coal	Hampshire	242
GA Bc 33	GA-73-0149	1,990	V	Non-coal	Hampshire	120
GA Bc 64	GA-88-0903	2,150	V	Non-coal	Hampshire	198
GA Bc 65	GA-94-0354	2,520	U	Non-coal	Hampshire	340
GA Bc 66	GA-95-0203	2,400	V	Non-coal	Hampshire	360
GA Bc 67	GA-94-1924	1,940	V	Non-coal	Hampshire	80
GA Bc 69	GA-73-1981	2,810	U	Non-coal	Hampshire	198
GA Bc 70	GA-95-1616	2,490	U	Non-coal	Hampshire	240
GA Bc 71	GA-94-1400	2,780	U	Non-coal	Rockwell	360
GA Bc 72	GA-72-0258	2,000	V	Non-coal	Hampshire	60
GA Bd 90	GA-88-0019	2,760	U	Coal	Conemaugh	160
GA Bd 91	GA-94-0666	2,200	V	Coal	Conemaugh	140
GA Be 13	GA-73-0358	2,560	U	Non-coal	Mauch Chunk	123

Appendix A (continued)

Local well number	Well permit number	Altitude (ft)	Topo-graphic setting	Coal or non-coal area	Geologic formation at surface	Well depth (ft BLS)
GA Be 18	GA-88-0961	2,520	U	Non-coal	Hampshire	350
GA Be 19	GA-94-0647	2,500	U	Non-coal	Hampshire	207
GA Bf 25	GA-94-0412	2,490	U	Non-coal	Hampshire	200
GA Bf 26	GA-95-0448	2,540	V	Non-coal	Hampshire	182
GA Bf 27	GA-94-1283	2,540	U	Non-coal	Hampshire	183
GA Ca 54	GA-94-1345	2,550	V	Non-coal	Greenbrier	100
GA Ca 55	GA-94-1347	2,650	U	Non-coal	Mauch Chunk	280
GA Ca 56	GA-94-2286	2,690	V	Coal	Pottsville	400
GA Ca 57	GA-88-1211	2,430	U	Coal	Allegheny	310
GA Ca 58	GA-95-0636	2,600	U	Coal	Pottsville	200
GA Cb 94	GA-81-1419	2,420	V	Non-coal	Greenbrier	220
GA Cb 95	GA-94-1667	2,210	V	Non-coal	Purslane	143
GA Cb 96	GA-94-2428	2,610	U	Non-coal	Mauch Chunk	1,200
GA Cb 97	GA-95-0336	2,550	V	Non-coal	Mauch Chunk	371
GA Cc 73	GA-88-0646	2,540	V	Non-coal	Hampshire	258
GA Cc 74	GA-92-0258	2,750	U	Coal	Pottsville	165
GA Cc 75	GA-94-0734	2,780	U	Non-coal	Purslane	700
GA Cc 76	GA-95-1612	2,690	U	Coal	Conemaugh	160
GA Cc 77	GA-94-1434	2,640	U	Non-coal	Purslane	180
GA Cd 49	GA-69-0056	2,420	U	Non-coal	Foreknobs	330
GA Cd 50	GA-94-1551	2,640	U	Non-coal	Foreknobs	505
GA Da 29	GA-73-1708	2,480	V	Coal	Conemaugh	357
GA Da 31	GA-94-0406	2,590	U	Coal	Conemaugh	160
GA Db 92	GA-92-0420	2,410	V	Coal	Allegheny	548
GA Db 93	GA-94-2289	2,590	U	Non-coal	Greenbrier	182
GA Dc 154	GA-81-1093	2,500	V	Non-coal	Foreknobs	160
GA Dc 155	GA-94-2145	2,550	V	Non-coal	Purslane	442
GA Dc 156	GA-94-2459	2,630	U	Non-coal	Hampshire	403
GA Dd 32	GA-66-0029	2,400	V	Non-coal	Hampshire	76
GA De 28	GA-95-0939	2,230	U	Coal	Conemaugh	505
GA Ea 64	GA-95-1011	2,390	V	Coal	Conemaugh	221
GA Ea 65	GA-88-0716	2,480	V	Non-coal	Foreknobs	247
GA Ea 66	GA-94-1278	2,420	V	Non-coal	Foreknobs	163
GA Ea 67	GA-95-0227	2,670	U	Non-coal	Foreknobs	320
GA Eb 79	GA-94-1319	2,600	U	Non-coal	Hampshire	303
GA Eb 80	GA-95-0987	2,470	V	Non-coal	Hampshire	414
GA Eb 81	GA-95-1211	2,530	V	Non-coal	Purslane	45
GA Ec 25	GA-94-1767	2,940	U	Coal	Pottsville	200
GA Ec 26	GA-95-0800	2,630	U	Coal	Conemaugh	702
GA Ec 27	GA-95-1686	2,590	V	Coal	Conemaugh	128
GA Ec 28	GA-95-0988	2,810	U	Coal	Conemaugh	362
GA Ed 14	GA-94-0821	1,750	V	Coal	Allegheny	445
GA Fa 42	GA-88-1078	2,530	U	Non-coal	Foreknobs	70

Appendix B. Groundwater quality data for wells sampled in this study.

[ºC, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius;
mg/L, milligrams per liter; <, less than; --, no data; µg/L, micrograms per liter]

Local well number	Date sampled	pH	Temperature (°C)	Specific conductance (µS/cm)	Dissolved oxygen (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Chloride (mg/L)	Total hardness (mg/L)
AL Ac 54	5/3/2013	7.1	12.7	470	<1	128	<10	225
AL Ac 55	7/24/2013	6.8	13.4	1,960	<1	242	<10	1385
AL Bb 25	7/9/2013	7.5	12.3	429	<1	213	<10	251
AL Bb 26	7/31/2013	7.0	11.0	898	<1	109	210	413
AL Bc 70	7/8/2013	6.6	10.8	116	<1	44	<10	88
AL Cb 8	6/19/2013	7.7	10.3	410	4.6	190	<10	200
AL Cb 28	7/23/2013	7.4	12.0	434	<1	175	<10	260
AL Da 23	7/8/2013	6.9	13.5	446	1.8	179	<10	246
GA Aa 11	6/27/2012	7.6	11.9	270	<1	133	<10	95
GA Aa 12	6/27/2012	7.5	12.7	403	<1	159	18	190
GA Aa 13	4/24/2013	6.6	11.6	110	<1	59	<10	49
GA Aa 14	5/15/2013	7.5	12.8	346	<1	173	<10	181
GA Ab 22	9/21/2012	7.6	12.0	396	<1	167	<10	169
GA Ac 35	5/15/2013	7.7	10.8	545	<1	106	85	220
GA Ac 40	7/20/2012	7.0	13.9	330	<1	69	50	125
GA Ac 41	5/3/2013	5.8	11.2	30	9.1	11	<10	12
GA Ac 42	4/24/2013	7.2	11.6	193	<1	95	<10	79
GA Ad 24	8/23/2012	7.5	11.5	636	<1	113	105	261
GA Ae 92	8/14/2012	7.2	16.8	743	<1	157	109	260
GA Ae 93	7/20/2012	6.5	10.4	132	<1	44	<10	50
GA Ae 94	8/13/2012	7.3	11.5	247	5.3	111	<10	117
GA Af 48	4/23/2013	6.0	10.3	72	6.8	19	<10	21
GA Af 49	5/3/2013	7.7	11.4	486	<1	85	90	198
GA Af 50	4/23/2013	6.4	10.5	79	<1	43	<10	19
GA Ag 42	7/18/2012	8.0	13.3	183	1.4	75	<10	75
GA Ag 43	7/9/2013	7.8	12.2	197	<1	90	<10	123
GA Ag 44	4/23/2013	5.4	11.2	371	<1	49	60	120
GA Ba 17	8/2/2012	8.8	12.7	297	<1	147	<10	<10
GA Ba 18	5/15/2013	7.3	12.5	231	<1	106	<10	119
GA Bb 34	8/14/2012	8.6	12.6	291	<1	92	18	54
GA Bb 35	4/22/2014	6.5	11.8	488	1.5	72	<10	129
GA Bb 36	4/23/2014	7.4	11.4	207	<1	88	<10	--
GA Bc 33	4/23/2014	7.8	11.5	369	<1	117	37	--
GA Bc 64	8/23/2012	6.9	12.7	202	1.5	58	12	45
GA Bc 65	6/14/2012	7.9	11.8	289	<1	116	<10	--
GA Bc 66	4/23/2014	7.1	10.8	257	5.9	91	<10	132
GA Bc 67	4/23/2014	8.7	10.1	655	<1	134	119	58
GA Bc 69	4/24/2014	7.6	10.0	239	8.2	93	<10	108
GA Bc 70	4/24/2014	7.9	10.9	285	<1	120	<10	126
GA Bc 71	5/2/2014	9.4	10.7	348	<1	146	<10	--
GA Bc 72	5/2/2014	8.6	11.0	550	<1	122	88	--
GA Bd 90	9/21/2012	7.5	11.2	276	3.2	125	<10	136
GA Bd 91	9/20/2012	7.6	11.3	298	<1	139	<10	39
GA Be 13	7/20/2012	8.3	13.4	179	5.5	72	<10	80

Appendix B (continued)

Local well number	Date sampled	Ethane (µg/L)	Ethene (µg/L)	Methane (µg/L)	Propane (µg/L)	n-Butane (µg/L)	Isobutane (µg/L)
AL Ac 54	5/3/2013	<3.3	<2.4	12	<3.2	<4.3	<4.6
AL Ac 55	7/24/2013	<3.3	<2.4	10	<3.2	<4.3	<4.6
AL Bb 25	7/9/2013	<3.3	<2.4	3.7	<3.2	<4.3	<4.6
AL Bb 26	7/31/2013	<3.3	<2.4	2.7	<3.2	<4.3	<4.6
AL Bc 70	7/8/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
AL Cb 8	6/19/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
AL Cb 28	7/23/2013	<3.3	<2.4	70	<3.2	<4.3	<4.6
AL Da 23	7/8/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Aa 11	6/27/2012	<3	<3	220	<1	--	--
GA Aa 12	6/27/2012	<3	<3	<1	<1	--	--
GA Aa 13	4/24/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Aa 14	5/15/2013	3.6	<2.4	247	<3.2	<4.3	<4.6
GA Ab 22	9/21/2012	<3.3	<2.4	6.7	<3.2	<4.3	<4.6
GA Ac 35	5/15/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ac 40	7/20/2012	<3	<3	2.1	<1	--	--
GA Ac 41	5/3/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ac 42	4/24/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ad 24	8/23/2012	<3.3	<2.4	6.1	<3.2	--	--
GA Ae 92	8/14/2012	4.4	<3	2,730	<1	--	--
GA Ae 93	7/20/2012	<3	<3	2.4	<1	--	--
GA Ae 94	8/13/2012	<3	<3	<1	<1	--	--
GA Af 48	4/23/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Af 49	5/3/2013	<3.3	<2.4	1.9	<3.2	<4.3	<4.6
GA Af 50	4/23/2013	<3.3	<2.4	1.9	<3.2	<4.3	<4.6
GA Ag 42	7/18/2012	<3	<3	<1	<1	--	--
GA Ag 43	7/9/2013	<3.3	<2.4	2.1	<3.2	<4.3	<4.6
GA Ag 44	4/23/2013	<3.3	<2.4	6.5	<3.2	<4.3	<4.6
GA Ba 17	8/2/2012	<3	<3	8,550	<1	--	--
GA Ba 18	5/15/2013	<3.3	<2.4	6.2	<3.2	<4.3	<4.6
GA Bb 34	8/14/2012	<3	<3	16	<1	--	--
GA Bb 35	4/22/2014	<3.3	<2.4	5.5	<3.2	<4.3	<4.6
GA Bb 36	4/23/2014	<3.3	<2.4	7.5	<3.2	<4.3	<4.6
GA Bc 33	4/23/2014	26.2	<2.4	1,660	<3.2	<4.3	<4.6
GA Bc 64	8/23/2012	<3.3	<2.4	48	<3.2	--	--
GA Bc 65	6/14/2012	<3	<3	<1	<1	--	--
GA Bc 66	4/23/2014	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Bc 67	4/23/2014	189	<2.4	6,230	<3.2	<4.3	<4.6
GA Bc 69	4/24/2014	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Bc 70	4/24/2014	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Bc 71	5/2/2014	<3.3	<2.4	2.4	<3.2	<4.3	<4.6
GA Bc 72	5/2/2014	191	<2.4	6,665	<3.2	<4.3	<4.6
GA Bd 90	9/21/2012	<3.3	<2.4	1.8	<3.2	<4.3	<4.6
GA Bd 91	9/20/2012	<3.3	<2.4	5.6	<3.2	<4.3	<4.6
GA Be 13	7/20/2012	<3	<3	<1	<1	--	--

Appendix B (continued)

Local well number	Date sampled	pH	Temperature (°C)	Specific conductance (µS/cm)	Dissolved oxygen (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Chloride (mg/L)	Total hardness (mg/L)
GA Be 18	6/14/2012	6.1	12.3	55	9.4	9	<10	--
GA Be 19	6/21/2012	7.1	12.0	263	<1	96	<10	100
GA Bf 25	6/21/2012	5.9	10.4	80	9.8	15	<10	30
GA Bf 26	6/21/2012	8.1	11.5	160	2.7	56	<10	60
GA Bf 27	5/16/2013	7.3	11.0	151	8.2	63	<10	63
GA Ca 54	9/19/2012	6.6	10.4	83	5.4	36	<10	35
GA Ca 55	8/1/2012	7.0	11.5	150	7.6	54	<10	55
GA Ca 56	7/19/2012	6.3	12.0	58	<1	20	<10	10
GA Ca 57	8/28/2012	6.3	12.4	95	7.0	39	<10	39
GA Ca 58	5/17/2013	5.9	11.0	51	<1	13	<10	10
GA Cb 94	7/19/2012	8.4	12.1	202	<1	91	<10	45
GA Cb 95	8/15/2012	7.6	11.8	217	<1	87	<10	80
GA Cb 96	8/9/2012	7.8	13.9	375	3.0	149	<10	139
GA Cb 97	9/20/2012	6.9	11.4	106	4.1	44	<10	45
GA Cc 73	8/15/2012	7.6	10.7	152	1.4	52	<10	45
GA Cc 74	7/19/2012	5.5	12.4	69	4.7	8	<10	20
GA Cc 75	8/2/2012	8.2	12.2	220	2.1	95	<10	25
GA Cc 76	6/27/2012	7.1	11.3	257	<1	129	<10	130
GA Cc 77	4/24/2014	7.2	10.7	155	<1	71	<10	--
GA Cd 49	6/20/2012	8.0	11.8	223	<1	98	<10	100
GA Cd 50	5/16/2013	8.2	11.5	231	<1	103	<10	105
GA Da 29	8/28/2012	7.8	12.1	218	<1	88	<10	102
GA Da 31	8/13/2012	7.8	14.0	264	<1	127	<10	130
GA Db 92	6/15/2012	7.0	11.9	209	<1	80	<10	30
GA Db 93	5/17/2013	8.2	10.7	165	9.1	83	<10	81
GA Dc 154	6/20/2012	8.4	11.1	196	<1	84	<10	80
GA Dc 155	9/20/2012	7.0	13.9	143	<1	56	<10	50
GA Dc 156	5/2/2013	7.6	11.2	153	<1	70	<10	60
GA Dd 32	9/19/2012	7.9	11.0	167	6.1	46	15	30
GA De 28	8/9/2012	7.0	13.0	262	5.3	108	<10	124
GA Ea 64	8/29/2012	7.5	11.0	274	<1	138	<10	122
GA Ea 65	8/1/2012	7.9	13.3	172	<1	84	<10	55
GA Ea 66	5/2/2013	7.0	11.7	418	1.3	116	62	44
GA Ea 67	4/24/2013	7.3	11.7	181	<1	80	<10	82
GA Eb 79	7/18/2012	8.2	11.9	130	1.7	49	<10	50
GA Eb 80	8/29/2012	8.4	10.8	196	<1	82	<10	35
GA Eb 81	8/29/2012	6.2	10.0	122	7.3	29	18	50
GA Ec 25	6/15/2012	5.9	13.6	63	4.5	15	<10	25
GA Ec 26	6/15/2012	7.2	13.3	362	1.7	110	<10	140
GA Ec 27	9/21/2012	7.4	12.3	671	3.8	154	<10	337
GA Ec 28	7/29/2013	7.5	12.4	251	5.0	120	<10	164
GA Ed 14	8/29/2012	8.9	13.0	343	<1	148	13	<10
GA Fa 42	5/2/2013	6.6	11.8	138	<1	53	<10	46

Appendix B (continued)

Local well number	Date sampled	Ethane (µg/L)	Ethene (µg/L)	Methane (µg/L)	Propane (µg/L)	n-Butane (µg/L)	Isobutane (µg/L)
GA Be 18	6/14/2012	<3	<3	<1	<1	--	--
GA Be 19	6/21/2012	<3	<3	<1	<1	--	--
GA Bf 25	6/21/2012	<3	<3	<1	<1	--	--
GA Bf 26	6/21/2012	<3	<3	<1	<1	--	--
GA Bf 27	5/16/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ca 54	9/19/2012	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ca 55	8/1/2012	<3	<3	<1	<1	--	--
GA Ca 56	7/19/2012	<3	<3	1.3	<1	--	--
GA Ca 57	8/28/2012	<3.3	<2.4	<1.5	<3.2	--	--
GA Ca 58	5/17/2013	<3.3	<2.4	2.3	<3.2	<4.3	<4.6
GA Cb 94	7/19/2012	<3	<3	7.3	<1	--	--
GA Cb 95	8/15/2012	<3	<3	61	<1	--	--
GA Cb 96	8/9/2012	<3	<3	15	<1	--	--
GA Cb 97	9/20/2012	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Cc 73	8/15/2012	<3	<3	<1	<1	--	--
GA Cc 74	7/19/2012	<3	<3	<1	<1	--	--
GA Cc 75	8/2/2012	<3	<3	1.1	<1	--	--
GA Cc 76	6/27/2012	<3	<3	1.1	<1	--	--
GA Cc 77	4/24/2014	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Cd 49	6/20/2012	<3	<3	<1	<1	--	--
GA Cd 50	5/16/2013	<3.3	<2.4	3.5	<3.2	<4.3	<4.6
GA Da 29	8/28/2012	<3.3	<2.4	<1.5	<3.2	--	--
GA Da 31	8/13/2012	<3	<3	<1	<1	--	--
GA Db 92	6/15/2012	<3	<3	23	<1	--	--
GA Db 93	5/17/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Dc 154	6/20/2012	<3	<3	30	<1	--	--
GA Dc 155	9/20/2012	<3.3	<2.4	3.3	<3.2	<4.3	<4.6
GA Dc 156	5/2/2013	<3.3	<2.4	1,720	<3.2	<4.3	<4.6
GA Dd 32	9/19/2012	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA De 28	8/9/2012	<3	<3	<1	<1	--	--
GA Ea 64	8/29/2012	<3.3	<2.4	295	<3.2	--	--
GA Ea 65	8/1/2012	<3	<3	704	<1	--	--
GA Ea 66	5/2/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ea 67	4/24/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Eb 79	7/18/2012	<3	<3	<1	<1	--	--
GA Eb 80	8/29/2012	<3.3	<2.4	<1.5	<3.2	--	--
GA Eb 81	8/29/2012	<3.3	<2.4	<1.5	<3.2	--	--
GA Ec 25	6/15/2012	<3	<3	<1	<1	--	--
GA Ec 26	6/15/2012	<3	<3	1.1	<1	--	--
GA Ec 27	9/21/2012	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ec 28	7/29/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ed 14	8/29/2012	55.2	<2.4	7,840	<3.2	--	--
GA Fa 42	5/2/2013	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6

Appendix C. Quality-control samples

1. Duplicate methane analyses

Fourteen duplicate samples from ten wells were analyzed for methane and other gases. Methane concentrations in nine of the eleven duplicate pairs having detectable methane were within 15 percent of each other (tab. C1). Variability could originate from one or more sources, including natural methane fluctuations due to atmospheric pressure and/or water level at the time of sampling, instrumental error, and/or human error. The largest difference (2,130 and 3,920 µg/L, or 44 percent) was from a well that had small bubbles visible in the sample bottle, and the results may represent small differences in the time when each bottle was uncapped in order to acidify the sample. In the report, methane concentrations for wells with duplicate samples refer to the average of the duplicate samples.

Table C1. Duplicate sample analyses for methane and other gases.

[µg/L, micrograms per liter ; <, less than; --, not analyzed]

Local Well Number	Sample date	Ethane (µg/L)	Ethene (µg/L)	Methane (µg/L)	Propane (µg/L)	n-Butane (µg/L)	Isobutane (µg/L)
GA Ba 17	2/25/13	<3.3	<2.4	2,120	<3.2	<4.3	<4.6
		<3.3	<2.4	3,920	<3.2	<4.3	<4.6
	4/25/13	<3.3	<2.4	4,960	<3.2	<4.3	<4.6
		<3.3	<2.4	4,930	<3.2	<4.3	<4.6
	6/18/13	<3.3	<2.4	6,700	<3.2	<4.3	<4.6
		<3.3	<2.4	6,480	<3.2	<4.3	<4.6
GA Bc 64	8/23/2012	<3.3	<2.4	42.8	<3.2	--	--
		<3.3	<2.4	52.2	<3.2	--	--
GA Cb 95	2/25/13	<3.3	<2.4	105	<3.2	<4.3	<4.6
		<3.3	<2.4	91.6	<3.2	<4.3	<4.6
	3/29/13	<3.3	<2.4	103	<3.2	<4.3	<4.6
		<3.3	<2.4	96.2	<3.2	<4.3	<4.6
GA Dd 32	9/19/2012	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
		<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Ea 64	8/29/2012	<3.3	<2.4	304	<3.2	--	--
		<3.3	<2.4	286	<3.2	--	--
GA Ea 65	1/24/13	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
		<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
	4/25/13	<3.3	<2.4	661	<3.2	<4.3	<4.6
		<3.3	<2.4	436	<3.2	<4.3	<4.6
GA Ed 14	8/29/2012	55.2	<2.4	7,810	<3.2	--	--
		54.4	<2.4	7,870	<3.2	--	--
GA Bc 72	5/2/2014	191	<2.4	6,270	<3.2	<4.3	<4.6
		214	<2.4	7,060	<3.2	<4.3	<4.6
GA Cc 77	4/24/2014	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
		<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
GA Bc 66	4/23/2014	<3.3	<2.4	1.5	<3.2	<4.3	<4.6
		<3.3	<2.4	<1.5	<3.2	<4.3	<4.6

2. Samples with known concentrations of methane

All methane samples were analyzed using the headspace method (RSK-175) (Kampbell and Vandegrift, 1998). Although RSK-175 is not a U.S. Environmental Protection Agency- approved method, it is widely used in studies of methane in water. There are no certified reference materials for methane for compliance monitoring. In order to gage the accuracy of the method, five samples with known concentrations of methane were prepared by the Pennsylvania Department of Environmental Protection Department of Laboratories and were submitted to ALS Environmental. Duplicate samples were analyzed for four known methane concentrations ranging from 5.8 to 11,600 µg/L. Results are given in table C2 and figure C1. In general, the analytical results agree well with the known concentrations, although known concentrations tend to be greater than the analyzed concentrations as overall concentrations increase.

Table C2. Results of analysis of samples with known concentrations of methane

[µg/L, micrograms per liter; RSD%, relative standard deviation percent]

Sample	Known concentration (µg/L)	Measured result (µg/L)	Average measured result (µg/L)	RSD% (measured result)
A1	5.8	6.5	7.2	-19.4%
A2	5.8	7.9		
B1	174	171	168.5	3.0%
B2	174	166		
C1	6,960	6,020	6,135	-3.7%
C2	6,960	6,250		
D1	11,600	10,500	10,500	0.0%
D2	11,600	10,500		

Appendix C (continued)

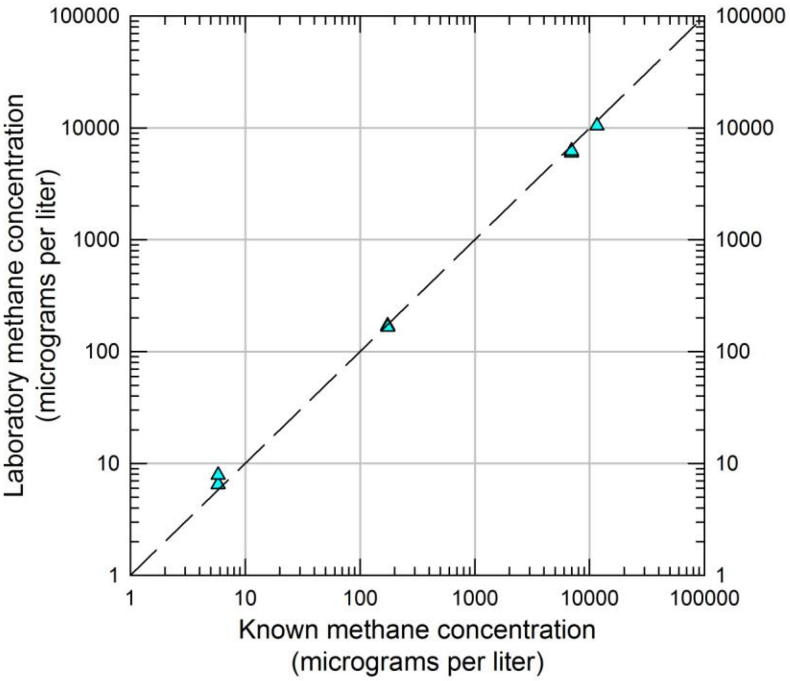

Figure C1. Relation between known and laboratory-measured methane concentrations.

3. Inter-laboratory comparison

Three samples that were analyzed for carbon and hydrogen isotopes were also tested for methane by Isotech Laboratories. A separate sample was also analyzed by ALS Environmental. Methane in one sample was less than 1.5 µg/L as reported by both laboratories. In the other two samples (GA Ba 17 and GA Ed 14), the methane concentrations from Isotech Laboratories were almost twice as high as the analyses from ALS Laboratories (tab. C3). This likely reflects a difference in sample collection protocols. In both these samples, bubbles were observed in the sample bottles. Samples analyzed by the RSK-175 method (ALS Environmental) were briefly uncapped when the samples were acidified, and methane likely escaped at that time. In contrast, the Isotech samples were collected in pre-treated plastic bags such that the samples were never exposed to the air. This suggests that for samples with bubbles observed in the sample bottles, the dissolved-methane concentrations may be less than the actual concentrations due to methane escaping when the samples were uncapped and acidified. Bubbles were observed in three other samples whose methane concentrations exceeded 2,000 µg/L. Thirteen other samples with bubbles observed during well purging all had methane concentrations less than 50 µg/L.

Table C3. Comparison of methane concentrations from Isotech Laboratories and ALS Environmental.

[µg/L, micrograms per liter; <, less than]

Local well number	Date	Methane concentration (µg/L)	
		Isotech Laboratories	ALS Environmental
GA Ba 17	7/24/2013	12,000	6,800
GA Dc 156	7/25/2013	1.3	<1.5
GA Ed 14	7/24/2013	14,000	8,010

Appendix D. Monthly methane and other water-quality data from selected wells in Garrett County, Maryland.

[ºC, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; --, not analyzed]

Well number and date sampled	pH	Temperature (°C)	Specific conductance (µS/cm)	Dissolved oxygen (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Chloride (mg/L)	Total hardness (mg/L)
GA Ba 17							
8/2/2012	8.8	12.7	297	<1	147	<10	<10
12/20/2012	8.7	11.4	287	<1	154	<10	10
2/25/2013[1]	7.6	10.6	217	<1	119	<10	18
3/29/2013	8.4	11.3	260	<1	151	<10	10
4/25/2013[1]	7.9	12.0	236	<1	134	<10	17
5/21/2013	8.8	12.8	287	<1	147	<10	<10
6/18/2013[1]	8.8	12.5	301	<1	158	<10	<10
7/19/2013	8.8	13.1	289	<1	146	<10	<10
7/24/2013	8.7	12.9	291	<1	149	<10	--
8/21/2013	9.0	12.9	300	<1	161	<10	--
GA Cb 95							
8/15/2012	7.6	11.8	217	<1	87	<10	80
12/20/2012	7.6	10.6	209	<1	92	<10	71
1/24/2013	7.5	9.8	204	<1	102	<10	78
2/25/2013[1]	7.6	10.4	207	<1	91	<10	73
3/29/2013[1]	7.6	10.4	203	<1	84	<10	73
4/25/2013	7.6	11.1	201	<1	94	<10	74
5/21/2013	7.6	11.7	205	<1	86	<10	73
6/18/2013	7.5	11.3	212	<1	86	<10	72
7/19/2013	7.5	12.6	201	<1	87	<10	72
8/21/2013	7.6	12.0	206	<1	87	<10	--
GA Ea 65							
8/1/2012	7.9	13.3	172	<1	84	<10	55
12/20/2012	7.8	10.7	165	<1	94	11	53
1/24/2013[1]	7.9	10.5	162	<1	95	<10	53
2/25/2013	7.9	10.4	163	<1	88	<10	52
3/29/2013	7.9	10.5	161	<1	91	<10	52
4/25/2013[1]	7.9	11.3	161	<1	96	<10	47
5/21/2013	7.9	11.8	162	<1	84	<10	52
6/18/2013	7.9	12.1	168	<1	89	<10	50
7/19/2013	7.8	12.4	161	<1	81	<10	54
8/22/2013	7.8	12.8	166	<1	87	<10	--

[1] Ethane, ethene, methane, propane, n-butane, and isobutane values are averages of two replicate values.

Appendix D (continued)

Well number and Date sampled	Ethane (µg/L)	Ethene (µg/L)	Methane (µg/L)	Propane (µg/L)	n-Butane (µg/L)	Isobutane (µg/L)
GA Ba 17						
8/2/2012	<3	<3	8,550	<1	--	--
12/20/2012	<3.3	<2.4	4,470	<3.2	<4.3	<4.6
2/25/2013[1]	<3.3	<2.4	3,020	<3.2	<4.3	<4.6
3/29/2013	<3.3	<2.4	5,530	<3.2	<4.3	<4.6
4/25/2013[1]	<3.3	<2.4	4,945	<3.2	<4.3	<4.6
5/21/2013	<3.3	<2.4	6,160	<3.2	<4.3	<4.6
6/18/2013[1]	<3.3	<2.4	6,590	<3.2	<4.3	<4.6
7/19/2013	<3.3	<2.4	7,190	<3.2	<4.3	<4.6
7/24/2013	<3.3	<2.4	6,800	<3.2	<4.3	<4.6
8/21/2013	<3.3	<2.4	8,140	<3.2	<4.3	<4.6
GA Cb 95						
8/15/2012	<3	<3	61.3	<1	--	--
12/20/2012	<3.3	<2.4	76.3	<3.2	<4.3	<4.6
1/24/2013	<3.3	<2.4	31.9	<3.2	<4.3	<4.6
2/25/2013[1]	<3.3	<2.4	98.3	<3.2	<4.3	<4.6
3/29/2013[1]	<3.3	<2.4	99.6	<3.2	<4.3	<4.6
4/25/2013	<3.3	<2.4	81.7	<3.2	<4.3	<4.6
5/21/2013	<3.3	<2.4	83.7	<3.2	<4.3	<4.6
6/18/2013	<3.3	<2.4	62.2	<3.2	<4.3	<4.6
7/19/2013	<3.3	<2.4	76.1	<3.2	<4.3	<4.6
8/21/2013	<3.3	<2.4	109	<3.2	<4.3	<4.6
GA Ea 65						
8/1/2012	<3	<3	704	<1	--	--
12/20/2012	<3.3	<2.4	487	<3.2	<4.3	<4.6
1/24/2013[1]	<3.3	<2.4	<1.5	<3.2	<4.3	<4.6
2/25/2013	<3.3	<2.4	677	<3.2	<4.3	<4.6
3/29/2013	<3.3	<2.4	103	<3.2	<4.3	<4.6
4/25/2013[1]	<3.3	<2.4	549	<3.2	<4.3	<4.6
5/21/2013	<3.3	<2.4	591	<3.2	<4.3	<4.6
6/18/2013	<3.3	<2.4	643	<3.2	<4.3	<4.6
7/19/2013	<3.3	<2.4	479	<3.2	<4.3	<4.6
8/22/2013	<3.3	<2.4	795	<3.2	<4.3	<4.6

[1] Ethane, ethene, methane, propane, n-butane, and isobutane values are averages of two replicate values.

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A message to Maryland's citizens

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

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