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

by

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KEY RESULTS

Untreated water samples were collected from 49 wells in the Appalachian Plateau portion of Maryland and were analyzed for dissolved methane, ethane, ethene, propane, and field parameters (pH, specific conductance, dissolved oxygen, alkalinity, chloride, and total hardness). Wells were selected on the basis of whether they were in areas with or without coal, and whether they were located in valleys or hilltop+hillside topographic settings. The key results of this study are:

- Dissolved-methane concentrations ranged from less than 1.5 to 8,550 micrograms per liter (µg/L). Twenty-nine of the 49 samples had less than 1.5 µg/L of dissolved methane. Twenty of the 49 wells had dissolved-methane concentrations greater than 1.5 µg/L.
- Three wells exceeded 1,000 µg/L dissolved methane; all were below the recommended action level of 10,000 µg/L. These wells were located in valley settings in three different coal basins. Two of these wells had detectable levels of ethane; no other samples contained ethane. None of the 49 wells had detectable ethene or propane.
- Methane detections (defined as methane concentrations ≥1.5 µg/L) were observed in wells in both the coal basins and the non-coal areas, although a greater proportion of wells in the coal basins had methane detections (11 out of 21 wells, or about 52 percent) than in the non-coal areas (9 out of 28 wells, or about 32 percent).
- Methane was detected in a greater portion of valley wells (16 out of 29 wells, or about 55 percent) than hilltop+hillside wells (4 out of 20 wells, or 20 percent).
- Valley wells in coal basins had the highest proportion of detections (9 of 13 wells, or 69 percent), followed by non-coal/valley wells (7 of 16 wells, about 44 percent), coal/hilltop+hillside (2 of 8 wells; 25 percent), and non-coal/hilltop+hillside wells (2 of 12 wells, about 17 percent).

INTRODUCTION

Methane in well water has been reported anecdotally over the years in the Appalachian Plateau of Maryland; however, no systematic study has been conducted regarding methane occurrence and distribution. The potential development of the natural gas reserves in the Marcellus Shale in western Maryland has raised concerns about whether such development could result in methane contamination of the water-supply aquifers in the region. Methane is not routinely tested for in well water in Maryland, since it does not have an established Primary or Secondary Maximum Contaminant Level (MCL). Because of the concern over possible methane contamination of water wells resulting from Marcellus Shale gas-development activities, in 2012 the Maryland Geological Survey (MGS) collected samples from 49 wells in Garrett County in the Appalachian Plateau region of Maryland. The purpose of this preliminary study was to measure ambient methane concentrations in water wells in the region, and to begin to gain an understanding of the occurrence and distribution of methane in water wells.

Situated in the westernmost part of Maryland, Garrett County and parts of Allegany County lie within the Appalachian Plateau Physiographic Province, which is characterized by outcrops of sedimentary rocks of Carboniferous (Pennsylvanian and Mississippian) and Devonian periods. The gently folded strata form synclines and anticlines that are the source regions for coal and natural gas, respectively (Nutter and others, 1980). The five major coal basins in Garrett County are the Lower Youghiogheny Basin, Upper Youghiogheny Basin, Castleman Basin, Upper Potomac Basin, and Georges Creek Basin (fig. 1). Part of the Georges Creek Basin also extends into Allegany County.

Natural gas production and coal mining were once a large part of the economy in this region. The Accident Dome used to be an area of intensive natural gas extraction. Currently, the Accident Dome is being used for gas storage (fig. 2). The other anticlinal structure, the Deer Park Anticline, contains several active natural gas-producing wells (Gregory Day, Maryland Department of the Environment, oral commun., 2012).

From an economic standpoint, coal mining is not as prominent today as it was in the past for Garrett County; however, both strip and deep mining operations still exist. There are several economically viable coal seams within the Pennsylvanian System that underlie the basins. Among them are the Upper Freeport coal, Waynesburg coal, Pittsburgh coal, Kittanning coal group, and Bakerstown coal (fig. 3). From a water-quality standpoint, coal seams are among significant sources of methane production (Eltschlager and others, 2001).

Methane is a colorless, odorless, flammable gas that can occur naturally in well water with a solubility of about 28 milligrams per liter (mg/L) (28,000 µg/L). Even though methane is not a regulated constituent in drinking water, it is recommended that methane levels above 10 mg/L (10,000 µg/L) need to be addressed to prevent asphyxiation and explosive conditions in confined spaces (Eltschlager and others, 2001). Prior to the present study, no quantitative measurements for methane have been done for well waters in Maryland on a regional basis, although methane has been detected in wells in western Maryland, using a simple qualitative test (i.e. a flame test using well water placed in a jar) (Steve Sherrard, Garrett County Health Department, oral commun., 2012).

Methane has been identified in ground water in neighboring West Virginia and Pennsylvania. A study conducted in West Virginia from 1997 to 2005 by the U.S. Geological Survey (USGS) sampled 170 water wells for methane (Mathes and White, 2006) (fig. 4). They concluded that higher methane concentrations (greater than 10,000 µg/L) were found in wells completed in Pennsylvanian-age rock formations as well as those located in valleys and on hillsides. These findings suggest that topography and geology are contributing factors in the occurrence of methane. From sampling more than 1,700 wells in Susquehanna County, Pennsylvania, Molofsky and others (2011) also found that methane detection was linked to topography. A study conducted by Stoner and others (1987) in southwestern Pennsylvania showed that, particularly in Greene County, methane in ground water is ubiquitous with concentrations commonly exceeding 25,000 µg/L and as high as 74,000 µg/L.

METHODS

Well Selection

Forty-nine wells (mostly residential wells) were selected throughout the Appalachian Plateau Province and sampled for methane and other water-quality constituents. Wells were selected according to whether they were located in coal basins (21 wells) or non-coal regions (28 wells). This scheme was used because we felt it was reasonable to assume that wells in coal basins would have more methane than the non-coal wells. Additionally, the wells were identified as being located in valleys (29 wells) or hilltop/hillside topographic settings (20 wells). The topographic criterion was established because of evidence that valley wells have higher methane than other wells (Molofsky and others, 2011). Thus, the sampled wells fell into four groups: coal/valley (13 wells), coal/hilltop+hillside (8 wells), non-coal/valley (16 wells), and non-coal/hilltop+hillside (12 wells). A 50th coal/valley well was sampled but was eliminated from the analysis because the sample was later found to have gone through a water-treatment system.

The distinction between coal basins and non-coal areas was based on our classification that coal basins consist of areas underlain by Pennsylvanian-age rock formations. Mississippian and older rock formations generally do not contain coal, and thus, wells constructed in these formations are classified as non-coal. The geologic formation was assigned to each well site based on a Global Positioning System (GPS) location, a georeferenced geologic map by Amsden (1953), and examination of the well log description from drillers. The main formations are Conemaugh, Allegheny–Pottsville, Mauch Chunk, Greenbrier, Pocono, Hampshire, and Jennings (tab. 1). Of the 49 wells, 21 wells were completed in Pennsylvanian-age rock formations (mostly the Conemaugh Formation), 14 wells in Mississippian-age rock formations, and 14 wells in Devonian-age rock formations (fig. 5). The topographic setting and altitude of each well were determined using topographic maps and site inspections. For each well, the well-permit number was used to acquire well-construction data. Well-construction information, site characteristics, and water-quality data are shown in tables 2 through 4.

Other well-selection criteria were as follows:

- Wells had construction documentation (i.e. well-permit application and well completion report).
- Wells had submersible pumps that were being used on a regular basis.
- Samples of untreated well-water could be obtained.
- Well water could be run for about 30 minutes (i.e. purging and sample collection).
- Well locations provided a reasonable spatial distribution throughout the study area.
- No obvious or potential contamination sources were identified (e.g. well cap on securely; well located upgradient of septic system; well had not been recently chlorinated).

Site inspections were performed to determine suitability prior to sampling. Wells selected for this study are shown with their corresponding well-permit numbers in figure 6.

Sampling Procedures

Water samples were collected at the pressure tank spigot or another tap source that dispenses untreated well water (fig. 7). During well purging, the spigot was turned on, and water was allowed to run into a bucket wherein pH, specific conductance, and dissolved oxygen probes were submerged. Field measurements were recorded at 5-minute intervals until measurements stabilized (pH, ± 0.1 pH unit; temperature, ± 0.2 degree Celsius; specific conductance, ± 5 percent (if value was less than 100 μS/cm) and ± 3 percent (if value was greater than 100 μS/cm); dissolved oxygen, ± 0.3 mg/L). These measurements were made using a Orion Star A329 portable multiparameter meter[1]. Equipment calibrations were performed daily using appropriate standards and buffers.

Once the purge was completed, untreated well-water samples were collected in two 40-milliliter glass vials using the inverted bottle technique (fig. 8). Hydrochloric acid drops were then added to the vials to preserve the sample to pH less than 2, re-capped, shaken by hand, and stored on ice. For comparing reproducibility of results, four sets of duplicate samples were taken. The samples were brought back to the office, and arrangements were made for the private laboratory (ALS Environmental, Middletown, Pennsylvania) to pick up the samples for analysis. The constituents analyzed were dissolved methane, propane, ethane, and ethene concentrations using the headspace method (RSK-175). Towards the end of the sampling portion of the study, the laboratory analyses also included *n*-butane and isobutane. The laboratory's reporting detection limits for samples analyzed from June 14, 2012 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 a new set of reporting detection limits as a result of the laboratory's yearly instrumental checks. They are 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.

Alkalinity, chloride, and total hardness were measured in the field using unfiltered water samples collected in polyethylene bottles after purging had been completed. Alkalinity was measured using a digital titrator with sulfuric acid and reported as milligrams per liter of $CaCO_3$ (HACH Company, 2008). Chloride concentration was analyzed colorimetrically by titration using a test kit with a minimum reporting limit of 10 mg/L (HACH Company, 2012a). Total hardness was also analyzed colorimetrically by titration (HACH Company, 2012b).

In addition to the water-quality measurements, photographs were taken of the purging and sampling area as well as the wellhead for supplemental documentation. At each wellhead, the latitude and longitude were recorded using a handheld GPS unit. Each well site was given its own folder containing all related documentation, including well permits and completion reports along with field sheets.

Fifty wells were sampled from June through September 2012. Forty wells were residential wells; the remainder were State park and public drinking-water supply wells. Table 5 shows the number of wells sampled among the four geologic and topographic settings, and figure 9 illustrates the sampling sites with respect to geology and stream networks in Garrett County. A sample from one well, GA-94-0137, was determined after sample collection to have passed through a water-treatment system. Its location, well

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[1] The use of tradenames and product names in this report is for identification purposes only, and does not constitute endorsement.

information, and water-quality data are included on the location map (fig. 6) and in tables 2 through 4, but the data is otherwise not discussed or analyzed in this report.

Duplicate samples for laboratory analysis of the dissolved gas components were taken for four well sites as indicated in table 3. The percent difference ranged from 0.7 to 20. Dissolved-gas parameters for both the original and duplicate samples from one well site (GA-66-0029) were all below the minimum reporting limits. Variability could originate from one or more sources including natural methane fluctuations, instrumental error, or human error. Discussion of dissolved-gas concentrations for wells with duplicate samples refers to the average of the two samples.

RESULTS AND DISCUSSION

Methane

Dissolved methane concentrations in the 49 untreated well-water samples collected from Garrett County ranged from less than 1.5 to 8,550 µg/L (tab. 3 and fig. 10), all of which were below the recommended action limit of 10,000 µg/L (Eltschlager and others, 2001). Methane concentrations in samples from 29 of the 49 wells were less than 1.5 µg/L, whereas 20 samples had dissolved-methane concentrations greater than 1.5 µg/L. Samples from three wells exceeded 1,000 µg/L (fig. 11).

Methane data with respect to topographic setting (valley versus hillside+hilltop) and geology (coal versus non-coal areas) are presented in figure 12 and table 6. Wells in coal basins had a greater proportion of methane detections[2] (11 of 21 wells, or 52 percent) than wells in non-coal areas (9 of 28 wells, or 32 percent). Wells located in valleys had a higher proportion of methane detections (16 of 29 wells, or 55 percent) than wells located on hilltops and hillsides (4 of 20 wells, or 20 percent).

With respect to the four well-location categories targeted in this study (coal/valley; coal/hilltop+hillside; non-coal/valley; non-coal/hilltop+hillside), valley wells in coal basins had the highest proportion of detections (9 of 13 wells, or 69 percent), followed by non-coal/valley wells (7 of 16 wells, or 44 percent), coal/hilltop+hillside (2 of 8 wells, or 25 percent), and non-coal/hilltop+hillside wells (2 of 12 wells, or 17 percent) (tab. 7).

Three wells (GA-95-1128, GA-94-0821, and GA-88-0320) had dissolved methane concentrations of 8,550, 7,840, and 2,730 µg/L, respectively (fig. 10). These are valley wells located in coal basins (tab. 2 and fig. 12). Two or more coal seams were noted by the drillers on the well completion reports. Wells GA-95-1128, GA-94-0821, and GA-88-0320 are located in different coal basins (i.e. Lower Youghiogheny, Upper Potomac, and Castleman,Basins, respectively). Wells GA-95-1128 and GA-88-0320 were drilled through the Conemaugh Formation while well GA-94-0821 was drilled through the Allegheny and Pottsville Formations (tab. 2 and fig. 13). During purging, all three wells showed a somewhat cloudy appearance in the purging bucket from the numerous small gas bubbles exsolving.

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[2] For the purpose of this report, a methane detection is defined as any sample having a dissolved-methane concentration of greater than or equal to 1.5 µg/L. This represents the higher of the two minimum reporting levels (1 and 1.5 µg/L) reported by ALS Laboratory during the course of the project.

Wells GA-94-0821 and GA-88-0320 had detectable dissolved ethane concentrations of 54.8 µg/L and 4.4 µg/L, respectively (tab. 3). No other wells had detectable ethane. None of the 49 samples contained any detectable ethene or propane. The eight wells tested for *n*-butane and isobutane did not show any detection of these gases.

This preliminary study shows similar trends as the findings from the West Virginia study (Mathes and White, 2006). Wells located in valleys and completed in coal basins tend to have higher dissolved methane concentrations (fig. 12). The three highest dissolved-methane concentrations were measured in wells completed in the Pennsylvanian-age rock formations (tab. 8). When compared to hilltop+hillside wells, valley wells have higher detectable amounts of dissolved methane even in non-coal areas (fig. 12). The causative factors are not clear. It could be related to fracture density in the vicinity of valleys that influence gas migration within the subsurface, accumulation of organics in valleys that cause enhanced microbial activity in those areas, or other factors.

Other Chemical Constituents

Specific conductance appears to be higher in well-water samples collected from coal basins compared to non-coal areas (tab. 9). Alkalinity and total hardness values were higher in samples taken from coal/valley settings compared with non-coal/valley settings. Dissolved oxygen was less than 1 mg/L for most well-water samples collected in coal/valley settings, and tended to be higher in wells in the other three settings. This finding is consistent with the idea that methanogenesis occurs in anaerobic (i.e., oxygen-depleted) environments and, thus, where there is methane detection, the dissolved-oxygen concentration should be low (i.e., less than 1 mg/L). Dissolved-oxygen concentrations in topographically high areas could be reasonably expected to be higher than in low areas due to having shorter flow paths and, hence, less time to enter into oxygen-consuming reactions with aquifer minerals.

Valley wells in non-coal areas tend to have total hardness values less than 100 mg/L as $CaCO_3$, and wells located in coal/valleys areas have higher alkalinity (fig. 14). The two wells with the highest methane levels (GA-95-1128 and GA-94-0821) have similar water quality characteristics. Well GA-88-0320, which had the third highest dissolved-methane detection, shows very different water-quality characteristics from the other two high-methane wells. Alkalinity values are high for all three, but well GA-88-0320 has very hard water (260 mg/L as $CaCO_3$) compared to the very soft waters (8 mg/L as $CaCO_3$) from both wells GA-95-1128 and GA-94-0821 (fig. 14). Wells GA-95-1128 and GA-94-0821 have more basic waters (pH 8.8 and 8.9, respectively) compared to 7.2 from well GA-88-0320 (fig. 15). The specific conductance for well GA-88-0320 is more than 300 µS/cm greater than the other two wells, reflecting a higher chloride concentration (109 mg/L compared to <10 and 13 mg/L) (fig. 16). The hilltop+hillside well samples located in coal basins tend to show a marked relationship between specific conductance and total hardness so that with increasing specific conductance, the hardness increases linearly (fig. 16). When plotting the pH and total hardness for the 49 samples, a bell-shaped curve forms centered slightly above pH of 7, with the lowest pH of 5.5 and highest pH of 8.9 (fig. 17). Well GA-88-0320 had the highest chloride value (109 mg/L) of all the samples (fig. 18). One other valley well (GA-81-0177) located in a coal basin, had a chloride concentration of 105 mg/L; only seven other wells had chloride concentrations above the detection limit of 10 mg/L.

Unique Circumstances

Well GA-94-2428, located on a hilltop in a non-coal area, had a higher dissolved-methane concentration (14.7 µg/L) than other wells in the same category (tab. 3). Based on the well-completion report, the well depth is 1,200 feet (ft) below land surface (tab. 2), which makes it the deepest well among those sampled for this study. Consequently, the well likely goes through the Greenbrier Formation even though it is surficially located on the Mauch Chunk Formation. This determination coincides with the well-log description from the completion report. In addition, the well owner has had the well water tested in the past with positive methane detection.

Three of the wells sampled (GA-94-0354, GA-94-0734 and GA-88-0903) are in proximity to the Accident Dome gas-storage field. Two of the wells are in the non-coal/hilltop+hillside setting and had less than 1.5 µg/L of dissolved methane, but GA-88-0903 is in a valley setting with a dissolved-methane value of 47.5 µg/L (tab. 3). Here it seems likely that the topography plays a larger role in the methane levels than proximity to the gas wells. However, more sampling locations near the Accident Dome would be helpful to observe if methane concentrations follow this trend.

The southern portion of Deer Park Anticline has several active natural gas wells that trend northeast-southwest. The surface geology common among all these is the Jennings Formation. Well GA-88-0716 from this study is situated almost between two active gas wells (approximately 2 miles distant from each) and has the same surface geology. This well is located in a valley setting with a spring used as a standby water source. At this well site, the dissolved methane concentration was 704 µg/L (tab. 3). Three additional water wells (GA-94-1319, GA-95-0987, and GA-95-1211) are in proximity to the active gas wells, but are located on the flanks of the anticline on different surface geology (i.e. Hampshire and Pocono Formations). These wells are also in a valley setting; however, unlike well GA-88-0716, they did not show any methane detection. For this instance, it seems as though the geology was the overriding factor in the methane levels and not the topographic setting.

SUMMARY AND RECOMMENDATIONS

Forty-nine wells in the Appalachian Plateau region of Maryland were sampled for methane and other water-quality constituents from June through September, 2012. Wells were selected in four geologic and topographic settings: coal basins/valleys (13 wells), coal basins/hilltop+hillside (8 wells), non-coal areas/valleys (16 wells), and non-coal areas/hilltop+hillside (12 wells). Data obtained from this study indicate:

- Dissolved-methane concentrations ranged from less than 1.5 to 8,550 µg/L. Twenty-nine of the 49 samples had less than 1.5 µg/L of dissolved methane. Twenty of the 49 wells had dissolved-methane concentrations greater than 1.5 μg/L.

- Three wells exceeded 1,000 μg/L dissolved methane; all were below the recommended action level of 10,000 μg/L. These wells were located in valley settings in three different coal basins. Two of these wells had detectable levels of ethane; no other samples contained ethane. None of the 49 samples had detectable ethene or propane.
- Methane detections (defined as methane concentrations ≥1.5 μg/L) were observed in wells in both the coal basins and the non-coal areas, although a greater proportion of wells in the coal basins had methane detections (11 out of 21 wells, or about 52 percent) than in the non-coal areas (9 out of 28 wells, or about 32 percent).
- Methane was detected in a greater portion of valley wells (16 out of 29 wells, or about 55 percent) than hilltop+hillside wells (4 out of 20 wells; 20 percent).
- Valley wells in coal basins had the highest proportion of detections (9 of 13 wells, or 69 percent), followed by non-coal/valley wells (7 of 16 wells, about 44 percent), coal/hilltop+hillside (2 of 8 wells; 25 percent), and non-coal/hilltop+hillside wells (2 of 12 wells, about 17 percent).

The data collected during this study provides initial information to help determine the distribution and occurrence of methane in well water in the Appalachian Plateau Province of Maryland. These data are limited and the conclusions considered preliminary, as the sample size is small relative to the size of the study area; additional data are needed to improve our understanding of well-water methane in the region. The methane data collected can be used in conjunction with other water-quality data to establish baseline water-quality conditions prior to development of the Marcellus Shale, and to provide a basis for developing strategies to effectively monitor the groundwater quality. The following tasks are suggested as ways to build on the current understanding of ambient ground-water methane concentrations:

1. <u>Sample additional wells in the Appalachian Plateau Province of Maryland.</u> Considering the extent of the Appalachian Plateau Province, additional wells would need to be sampled to fill in data gaps and help provide a sound basis for statistical analysis.

2. <u>Evaluate well water for seasonal and other changes in methane concentrations.</u> Re-sampling is another important aspect of obtaining a representative baseline for methane in ground water. One of the wells sampled during this study had been independently tested for methane on three separate occasions. Those results give us an indication of the potentially wide variation in methane levels over a short period of time. An appropriate monitoring strategy for several wells can help constrain factors such as seasonality and give a more meaningful baseline.

3. <u>Identify sources of methane.</u> There are several potential sources of methane in ground water. Methane of thermogenic origin is produced from thermally altered organic materials that are millions of years old such as natural gas and coalbed methane (Eltschlager and others, 2001; Révész and others, 2010). Biogenic (microbial) methane is the product of bacterial decomposition of organic material within alluvium and glacial drift deposits (Molofsky and others, 2011). Landfills are a common anthropogenic

source. Other sources include abandoned and/or leaking gas wells and seismic activity which can alter the permeability of the bedrock and consequently create new pathways for methane migration (Révész and others, 2010). Distinguishing the sources of the methane can be facilitated by utilizing isotopic signatures (e.g. Molofsky and others, 2011).

For isotope analysis to be performed on a water sample, the dissolved-methane concentration of the sample needs to be at least 1 mg/L (Isotech Laboratories, Inc., personal commun., 2012). Only three of the wells sampled in 2012 meet this criterion. Re-sampling these wells specifically for stable isotope ratios (δ^{13}C-CH_4 and δ^{2}H-CH_4) may provide further information on source(s) of methane in the region.

4. <u>Sample for additional water-quality constituents besides methane and field parameters.</u> The methane study conducted by Mathes and White (2006) also demonstrated that low-sulfur coal regions located south of the hinge line were found to contain higher methane as opposed to high-sulfur coal (fig. 4). The Upper Freeport coal bed is classified as medium-sulfur (2.24 ±1.02 weight percent), and the Lower Kittanning coal beds contain high sulfur content (2.90 weight percent) (Ruppert, 2001). Even though the highest detected methane concentration in our study was 8,550 µg/L, this is less than those in low-sulfur coal areas in West Virginia which were in excess of 28,000 µg/L. As a continuation of this study, it would be useful to measure for more water-quality constituents (including major ions and trace elements) to determine if there is a geochemical "fingerprint" to the high-methane areas.

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Table 1. Geologic formations and their water-bearing properties (Nutter and others, 1980, p. 3)

[gal/min, gallons per minute]

System	Formation	Thickness (feet)	Lithology	Water-bearing properties
Quaternary	Deposits of Holocene and Pleistocene age	0 – 70	Alluvium, peat deposits, slide rock, sand and gravel	Not important aquifers owing to small areal extent and thickness.
Pennsylvanian	Monogahela	240 - 270	Shale, siltstone, sandy shale, sandstone, coal seams	Not an important aquifer because of small areal extent, and the formation is partly drained by mine shafts and drifts.
	Conemaugh	850 – 950	Sandstone, shale, siltstone, red beds, clay, shaley limestone, coal seams	Important aquifer in the coal basins. Well yields range from 1 to 200 gal/min; mean yield 13.3 gal/min and median yield 7 gal/min.
	Allegheny	275 – 325	Sandstone, sandy shale, siltstone, clay beds, coal seams	Important aquifer in the coal basins. Formation is not mapped separately in Garrett County.
	Pottsville	180 – 250	Sandstone (conglomeratic in lower part), siltstone, shale, claystone, a few thin discontinuous coal seams	Moderately important aquifer along the flanks of coal basins. Relatively few wells derive water from this formation, but it has potential for yield moderately large quantities. Well-yield data combined with Allegheny. Well yields range from 0.5 to 150 gal/min; mean yield 13.1 gal/min and median yield 7 gal/min.
Mississippian	Mauch Chunk	500 – 700	Red and green sandy shale, platy sandstone beds	Moderately important aquifer along the flanks of Deer Park and Accident anticlines. Well yields range from 3 to 51 gal/min; mean yield 11.8 gal/min and median yield 10 gal/min.
	Greenbrier	200 – 300	Red and green shale, lenticular limestone, limy sandstone	Moderately important aquifer along flanks of anticlinal structures. Well yields range from 1 to 300 gal/min; mean yield 32.6 gal/min and median yield 14 gal/min. Numerous springs used for water supplies.
	Pocono	700 – 1,300	Coarse-grained sandstone (locally conglomeratic), shale, sandy shale	Important aquifer in Deer Park and Accident anticlines. Many wells and springs in Pocono including several fairly high-yielding wells. Yields range from 0.8 to 130 gal/min; mean yield 13.1 gal/min and median yield 7.5 gal/min.
Devonian	Hampshire	1,400 – 2,000	Brown and green sandy shale, shale, thin-bedded sandstone, red beds	Important aquifer in the Deer Park and Accident anticlines. Well yields range from 1 to 60 gal/min; mean yield 12 gal/min and median yield 8 gal/min.
	Jennings	4,000 – 5,000	Gray and green shale and sandy shale, sandy siltstone, thin-bedded sandstone	Important aquifer in Deer Park anticline area. Well yields range from 0.2 to 50 gal/min; mean yield 8.7 gal/min and median yield 7 gal/min.

Table 2. Well-construction and geologic data for water samples collected during this study

[ft, feet; ASL, above sea level; BLS, below land surface]

Well-permit number	Topographic setting	Coal or Non-coal region	Geologic formation	Altitude (ft ASL)	Well depth (ft BLS)
GA-66-0029	Valley	Non-Coal	Hampshire	2,397	76
GA-69-0056	Hilltop+hillside	Non-Coal	Jennings	2,422	330
GA-73-0358	Hilltop+hillside	Non-Coal	Mauch Chunk	2,559	123
GA-73-1030	Valley	Coal	Conemaugh	1,541	60
GA-73-1708	Valley	Coal	Conemaugh	2,484	357
GA-73-2449	Hilltop+hillside	Coal	Conemaugh	2,688	185
GA-81-0177	Valley	Coal	Conemaugh	2,200	267
GA-81-0703	Valley	Coal	Conemaugh	1,497	103
GA-81-1093	Valley	Non-Coal	Jennings	2,503	160
GA-81-1419	Valley	Non-Coal	Greenbrier	2,419	220
GA-88-0019	Hilltop+hillside	Coal	Conemaugh	2,755	160
GA-88-0314	Valley	Non-Coal	Mauch Chunk	1,649	180
GA-88-0320	Valley	Coal	Conemaugh	2,139	200
GA-88-0646	Valley	Non-Coal	Hampshire	2,541	258
GA-88-0716	Valley	Non-Coal	Jennings	2,477	247
GA-88-0754	Valley	Coal	Allegheny-Pottsville	2,394	220
GA-88-0903	Valley	Non-Coal	Hampshire	2,151	198
GA-88-0961	Hilltop+hillside	Non-Coal	Hampshire	2,522	350
GA-88-1031	Valley	Non-Coal	Hampshire	2,418	207
GA-88-1211	Hilltop+hillside	Coal	Conemaugh	2,405	310
GA-92-0258	Hilltop+hillside	Non-Coal	Mauch Chunk	2,742	165
GA-92-0420	Valley	Coal	Conemaugh	2,407	548
GA-94-0137[1]	Valley	Coal	Allegheny-Pottsville	2,200	123
GA-94-0354	Hilltop+hillside	Non-Coal	Hampshire	2,520	340
GA-94-0406	Valley	Coal	Conemaugh	2,583	160
GA-94-0412	Hilltop+hillside	Non-Coal	Hampshire	2,491	200
GA-94-0550	Hilltop+hillside	Coal	Conemaugh	2,084	197
GA-94-0647	Hilltop+hillside	Non-Coal	Hampshire	2,488	207
GA-94-0666	Valley	Coal	Conemaugh	2,201	140
GA-94-0734	Hilltop+hillside	Non-Coal	Pocono	2,783	700
GA-94-0821	Valley	Coal	Allegheny-Pottsville	1,750	445
GA-94-1319	Valley	Non-Coal	Hampshire	2,589	303
GA-94-1345	Valley	Non-Coal	Mauch Chunk	2,551	100
GA-94-1347	Hilltop+hillside	Non-Coal	Mauch Chunk	2,650	280
GA-94-1667	Valley	Non-Coal	Pocono	2,208	143
GA-94-1767	Hilltop+hillside	Non-Coal	Mauch Chunk	2,939	200
GA-94-2145	Valley	Non-Coal	Pocono	2,557	442
GA-94-2286	Hilltop+hillside	Coal	Allegheny-Pottsville	2,694	400
GA-94-2428	Hilltop+hillside	Non-Coal	Greenbrier	2,617	1,200
GA-94-2679	Hilltop+hillside	Coal	Conemaugh	2,680	172
GA-95-0336	Valley	Non-Coal	Greenbrier	2,553	371
GA-95-0448	Valley	Non-Coal	Hampshire	2,535	182
GA-95-0800	Hilltop+hillside	Coal	Conemaugh	2,631	702
GA-95-0879	Hilltop+hillside	Non-Coal	Pocono	2,521	600
GA-95-0939	Hilltop+hillside	Coal	Conemaugh	2,217	505
GA-95-0987	Valley	Non-Coal	Hampshire	2,474	414
GA-95-1128	Valley	Coal	Conemaugh	2,173	300
GA-95-1211	Valley	Non-Coal	Pocono	2,525	45
GA-95-1612	Valley	Coal	Conemaugh	2685	160
GA-95-1686	Valley	Coal	Conemaugh	2,591	128

[1] GA-94-0137 was not included in the results and discussion of this report due to sample being post-treatment.

Table 3. Dissolved methane and other gas concentration data for water samples collected during this study.

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

Well- permit number	Sample date	Methane[1] (µg/L)	Ethane[1] (µg/L)	Ethene[1] (µg/L)	Propane[1] (µg/L)	n-butane[2] (µg/L)	Isobutane[2] (µg/L)
GA-66-0029	9/19/2012	<1.5	<3.3	<2.4	<3.2	<4.3	<4.6
GA-66-0029[3]	9/19/2012	<1.5	<3.3	<2.4	<3.2	<4.3	<4.6
GA-69-0056	6/20/2012	<1	<3	<3	<1	-	-
GA-73-0358	7/20/2012	<1	<3	<3	<1	-	-
GA-73-1030	6/27/2012	220	<3	<3	<1	-	-
GA-73-1708	8/28/2012	<1.5	<3.3	<2.4	<3.2	-	-
GA-73-2449	8/13/2012	<1	<3	<3	<1	-	-
GA-81-0177	8/23/2012	6.1	<3.3	<2.4	<3.2	-	-
GA-81-0703	9/21/2012	6.7	<3.3	<2.4	<3.2	<4.3	<4.6
GA-81-1093	6/20/2012	29.7	<3	<3	<1	-	-
GA-81-1419	7/19/2012	7.3	<3	<3	<1	-	-
GA-88-0019	9/21/2012	1.8	<3.3	<2.4	<3.2	<4.3	<4.6
GA-88-0314	8/14/2012	16	<3	<3	<1	-	-
GA-88-0320	8/14/2012	2,730	4.4	<3	<1	-	-
GA-88-0646	8/15/2012	<1	<3	<3	<1	-	-
GA-88-0716	8/1/2012	704	<3	<3	<1	-	-
GA-88-0754	8/29/2012	304	<3.3	<2.4	<3.2	-	-
GA-88-0754[3]	8/29/2012	286	<3.3	<2.4	<3.2	-	-
GA-88-0903	8/23/2012	42.8	<3.3	<2.4	<3.2	-	-
GA-88-0903[3]	8/23/2012	52.2	<3.3	<2.4	<3.2	-	-
GA-88-0961	6/14/2012	<1	<3	<3	<1	-	-
GA-88-1031	7/18/2012	<1	<3	<3	<1	-	-
GA-88-1211	8/28/2012	<1.5	<3.3	<2.4	<3.2	-	-
GA-92-0258	7/19/2012	<1	<3	<3	<1	-	-
GA-92-0420	6/15/2012	22.8	<3	<3	<1	-	-
GA-94-0137[4]	8/24/2012	46.2	<3.3	<2.4	<3.2	-	-
GA-94-0354	6/14/2012	<1	<3	<3	<1	-	-
GA-94-0406	8/13/2012	<1	<3	<3	<1	-	-
GA-94-0412	6/21/2012	<1	<3	<3	<1	-	-
GA-94-0550	6/27/2012	<1	<3	<3	<1	-	-
GA-94-0647	6/21/2012	<1	<3	<3	<1	-	-
GA-94-0666	9/20/2012	5.6	<3.3	<2.4	<3.2	<4.3	<4.6
GA-94-0734	8/2/2012	1.1	<3	<3	<1	-	-
GA-94-0821	8/29/2012	7,810	55.2	<2.4	<3.2	-	-
GA-94-0821[3]	8/29/2012	7,870	54.4	<2.4	<3.2	-	-
GA-94-1319	7/18/2012	<1	<3	<3	<1	-	-
GA-94-1345	9/19/2012	<1.5	<3.3	<2.4	<3.2	<4.3	<4.6
GA-94-1347	8/1/2012	<1	<3	<3	<1	-	-
GA-94-1667	8/15/2012	61.3	<3	<3	<1	-	-
GA-94-1767	6/15/2012	<1	<3	<3	<1	-	-
GA-94-2145	9/20/2012	3.3	<3.3	<2.4	<3.2	<4.3	<4.6
GA-94-2286	7/19/2012	1.3	<3	<3	<1	-	-
GA-94-2428	8/9/2012	14.7	<3	<3	<1	-	-
GA-94-2679	7/20/2012	2.4	<3	<3	<1	-	-
GA-95-0336	9/20/2012	<1.5	<3.3	<2.4	<3.2	<4.3	<4.6
GA-95-0448	6/21/2012	<1	<3	<3	<1	-	-
GA-95-0800	6/15/2012	1.1	<3	<3	<1	-	-
GA-95-0879	7/20/2012	2.1	<3	<3	<1	-	-
GA-95-0939	8/9/2012	<1	<3	<3	<1	-	-
GA-95-0987	8/29/2012	<1.5	<3.3	<2.4	<3.2	-	-
GA-95-1128	8/2/2012	8,550	<3	<3	<1	-	-
GA-95-1211	8/29/2012	<1.5	<3.3	<2.4	<3.2	-	-
GA-95-1612	6/27/2012	1.1	<3	<3	<1	-	-
GA-95-1686	9/21/2012	<1.5	<3.3	<2.4	<3.2	<4.3	<4.6

[1] Reporting Detection Limit (RDL) for samples analyzed after August 23, 2012.

[2] ALS Laboratory added two additional constituents to their analytical package for method RSK-175 for samples after 9/19/2012.

[3] Duplicate samples were taken.

[4] GA-94-0137 was not included in the discussion of this report due to sample being post-treatment.

Table 4. Water-quality data for well-water samples in this study

[mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; ft, feet; °C, degree Celsius; <, less than]

Well-permit number	pH	Temperature (°C)	Specific conductance (µS/cm at 25°C)	Dissolved oxygen (mg/L)	Alkalinity (mg/L as $CaCO_3$)	Chloride (mg/L)	Total hardness (mg/L as $CaCO_3$)
GA-66-0029	7.9	11	167	6	46	15	30
GA-69-0056	8.0	11.8	223	<1	98	<10	100
GA-73-0358	8.3	13.4	179	5.5	72	<10	80
GA-73-1030	7.6	11.9	270	<1	133	<10	95
GA-73-1708	7.8	12.1	218	<1	88	<10	102
GA-73-2449	7.3	11.5	247	5.3	111	<10	117
GA-81-0177	7.5	11.5	636	<1	113	105	261
GA-81-0703	7.6	12	396	<1	167	<10	169
GA-81-1093	8.4	11.1	196	<1	84	<10	80
GA-81-1419	8.4	12.1	202	<1	91	<10	45
GA-88-0019	7.5	11.2	276	3.2	125	<10	136
GA-88-0314	8.6	12.6	291	<1	92	18	54
GA-88-0320	7.2	16.8	743	<1	157	109	260
GA-88-0646	7.6	10.7	152	1.4	52	<10	45
GA-88-0716	7.9	13.3	172	<1	84	<10	55
GA-88-0754	7.5	11	274	<1	138	<10	122
GA-88-0903	6.9	12.7	202	1.5	58	12	45
GA-88-0961	6.1	12.3	55	9.4	9	<10	-
GA-88-1031	8.0	13.3	183	1.4	75	<10	75
GA-88-1211	6.3	12.4	95	7	39	<10	39
GA-92-0258	5.5	12.4	69	4.7	8	<10	20
GA-92-0420	7.0	11.9	209	<1	80	<10	30
GA-94-0137[1]	6.6	11.6	142	<1	61	<10	1
GA-94-0354	7.9	11.8	289	<1	116	<10	-
GA-94-0406	7.8	14	264	<1	127	<10	130
GA-94-0412	5.9	10.4	80	9.8	15	<10	30
GA-94-0550	7.5	12.7	403	<1	159	18	190
GA-94-0647	7.1	12	263	<1	96	<10	100
GA-94-0666	7.6	11.3	298	<1	139	<10	39
GA-94-0734	8.2	12.2	220	2.1	95	<10	25
GA-94-0821	8.9	13	343	<1	148	13	8
GA-94-1319	8.2	11.9	130	1.7	49	<10	50
GA-94-1345	6.6	10.4	83	5.4	36	<10	35
GA-94-1347	7.0	11.5	150	7.6	54	<10	55
GA-94-1667	7.6	11.8	217	<1	87	<10	80
GA-94-1767	5.9	13.6	63	4.5	15	<10	25
GA-94-2145	7.0	13.9	143	<1	56	<10	50
GA-94-2286	6.3	12	58	<1	20	<10	10
GA-94-2428	7.8	13.9	375	3	149	<10	139
GA-94-2679	6.5	10.4	132	<1	44	<10	50
GA-95-0336	6.9	11.4	106	4.1	44	<10	45
GA-95-0448	8.1	11.5	160	2.7	56	<10	60
GA-95-0800	7.2	13.3	362	1.7	110	<10	140
GA-95-0879	7.0	13.9	330	<1	69	50	125
GA-95-0939	7.0	13	262	5.3	108	<10	124
GA-95-0987	8.4	10.8	196	<1	82	<10	35
GA-95-1128	8.8	12.7	297	<1	147	<10	8
GA-95-1211	6.2	10	122	7.3	29	18	50
GA-95-1612	7.1	11.3	257	<1	129	<10	130
GA-95-1686	7.4	12.3	671	3.8	154	<10	337

[1] GA-94-0137 was not included in the analysis and discussion for this report due to the sample being post-treatment.

Table 5. Numbers of wells sampled in categories based on topography and geology

	Valley	Hilltop+hillside
Coal basin (syncline)	13	8
Non-coal basin (anticline)	16	12

Table 6. Summary of methane detections by individual geologic and topographic setting

[<, less than; µg/L, micrograms per liter; ≥, equal to or greater than]

	Number and percentage of wells with methane <1.5 µg/L		Number and percentage of wells with methane ≥1.5 µg/L		Total number of wells in setting
Setting	Number of wells	Percentage of wells	Number of wells	Percentage of wells	
Coal	10	48%	11	52%	21
Non-coal	19	68%	9	32%	28
Valley	13	45%	16	55%	29
Hilltop+hillside	16	80%	4	20%	20

Table 7. Summary of methane detections by topographic setting within each geologic setting

[<, less than; µg/L, micrograms per liter; ≥, equal to or greater than]

		Number and percentage of wells with methane <1.5 µg/L		Number and percentage of wells with methane ≥1.5 µg/L		Total number of wells in setting
Geologic setting	Topographic setting	Number of wells	Percentage of wells	Number of wells	Percentage of wells	
Coal	Valley	4	31%	9	69%	13
	Hilltop+hillside	6	75%	2	25%	8
Non-coal	Valley	9	56	7	44%	16
	Hilltop+hillside	10	83%	2	17%	12

Table 8. Dissolved-methane concentrations with respect to geologic formations in the Appalachian Plateau Province

[<, less than; >, greater than]

System	Geologic formation	Number of samples with the indicated dissolved methane concentrations (in micrograms per liter)		
		<1.5	**1.5 – 1,000**	**>1,000**
Pennsylvanian	Conemaugh	9	7	2
	Allegheny and Pottsville	1	1	1
Mississippian	Mauch Chunk	5	1	0
	Greenbrier	1	2	0
	Pocono	2	3	0
Devonian	Hampshire	10	1	0
	Jennings	1	2	0
	Total samples	**29**	**17**	**3**

Table 9. Water-quality data summarized by the four categories of geology and topography. 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]

Category	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/Valley	13	6.7 (<1.5 – 8,550)	7.6 (7 – 8.9)	297 (209 – 743)	<1 (<1 – 3.8)	138 (80 – 167)	<10 (<10 – 109)	122 (8 – 337)
Coal/Hilltop+Hillside	8	<1.5 (<1.5 – 2.4)	7.1 (6.3 – 7.5)	255 (58 – 403)	2.5 (<1 – 7)	109 (20 – 159)	<10 (<10 – 18)	121 (10 – 190)
Non-Coal/Valley	16	<1.5 (<1.5 – 704)	7.9 (6.2 – 8.6)	170 (83 – 291)	1.4 (<1 – 7.3)	57 (29 – 92)	<10 (<10 – 18)	50 (30 – 80)
Non-Coal/Hilltop+Hillside	12	<1.5 (<1.5 – 14.7)	7.1 (5.5 – 8.3)	200 (55 – 375)	3.8 (<1 – 9.8)	71 (8 – 149)	<10 (<10 – 50)	68[1] (20 – 139)

[1] Two wells were not tested for hardness.

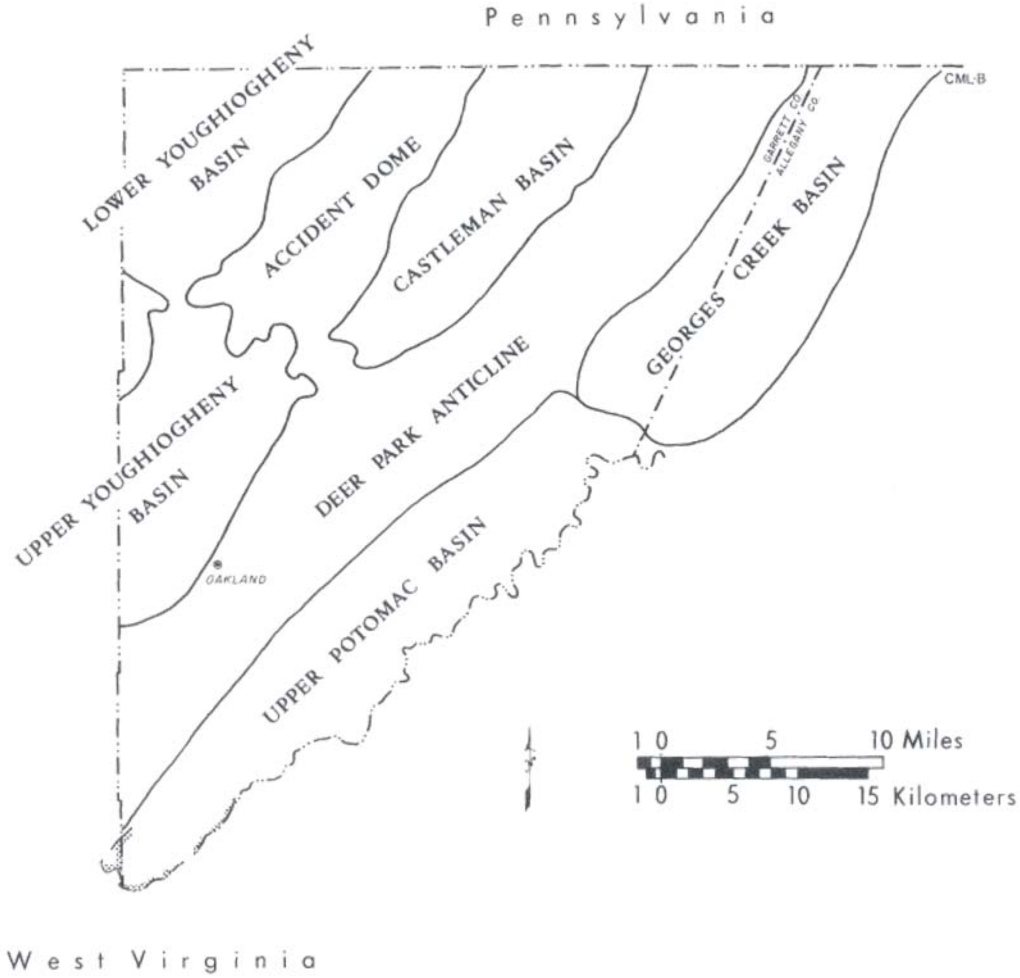

Figure 1. **Geologic structure of Garrett County showing synclinal basins (Lower and Upper Youghiogheny Basin, Castleman Basin, Upper Potomac Basin and Georges Creek Basin), the Accident Dome and Deer Park Anticline (from Duigon and Smigaj, 1985).**

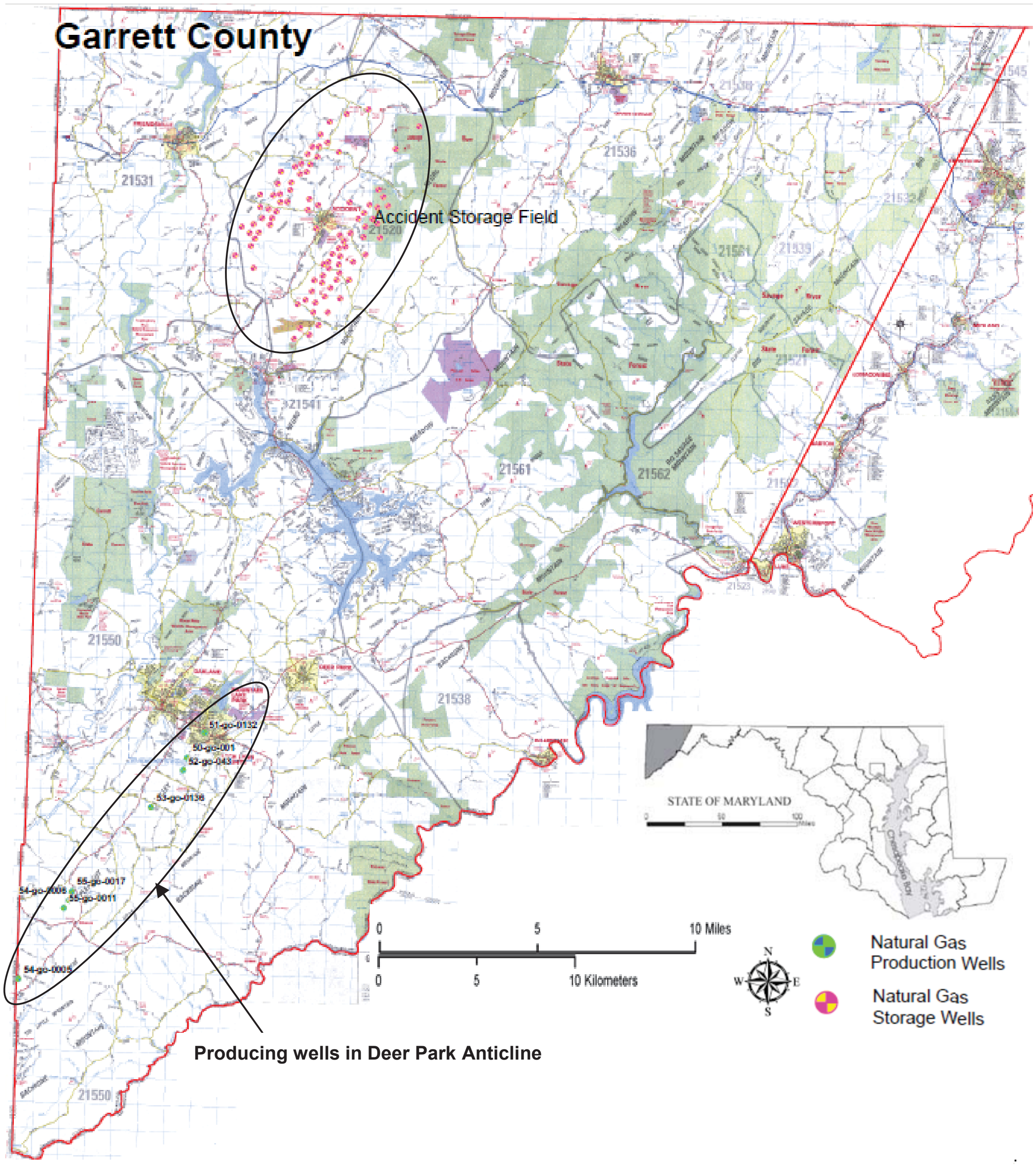

Figure 2. Location of natural gas producing and storage wells in Garrett County, Maryland (modified from MDE Mining Program, 2007).

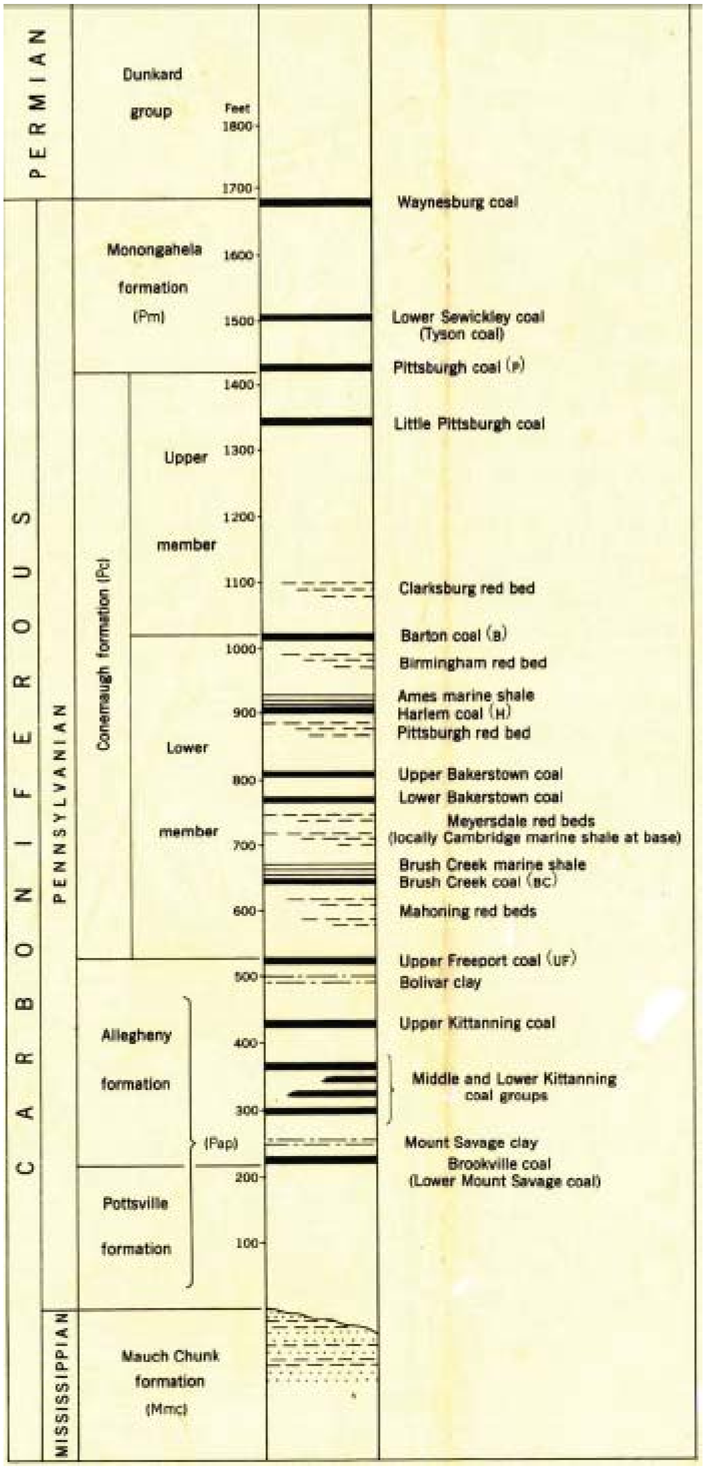

Figure 3. Subdivisions of the Pennsylvanian strata in Maryland (from Amsden, 1953).

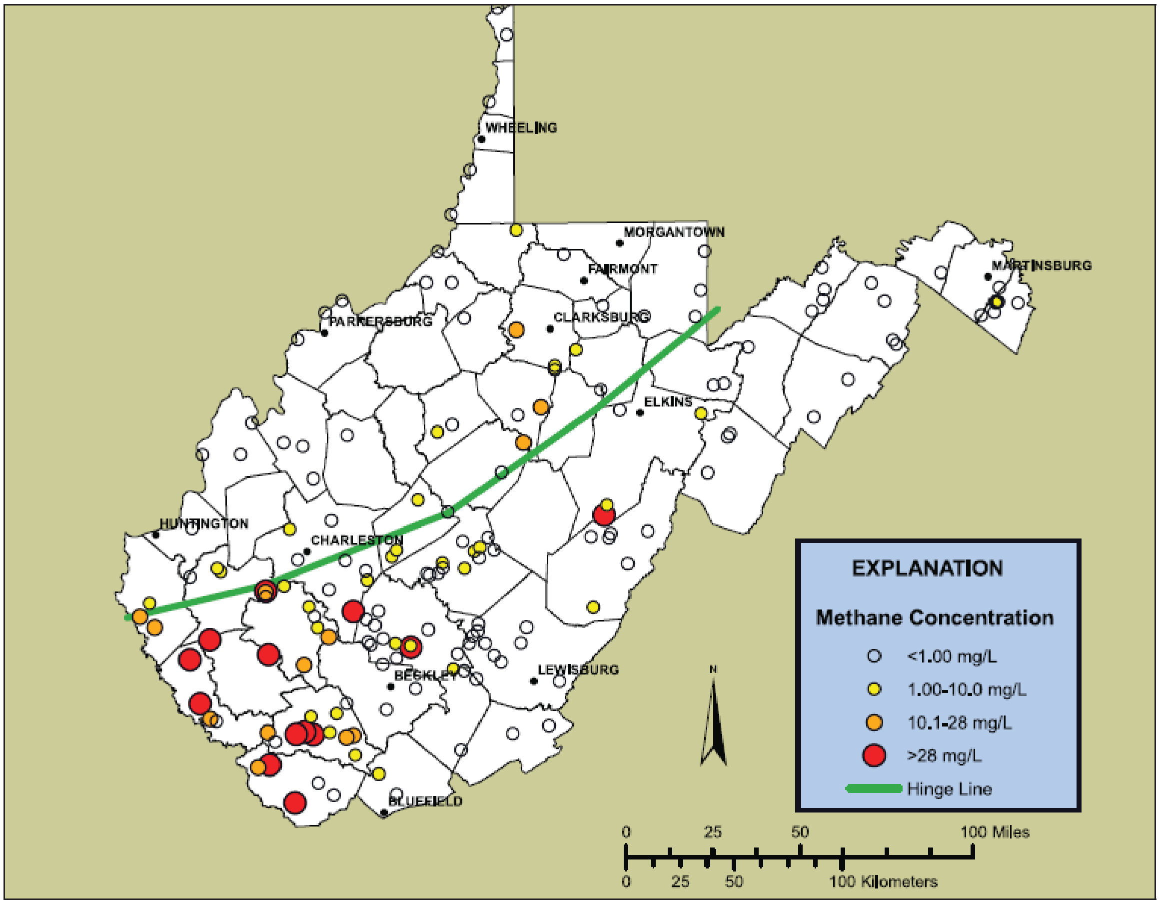

Figure 4. Methane concentrations in water wells of West Virginia. South of the hinge line is the low-sulfur coal; north of the hinge line is high-sulfur coal (Mathes and White, 2006).

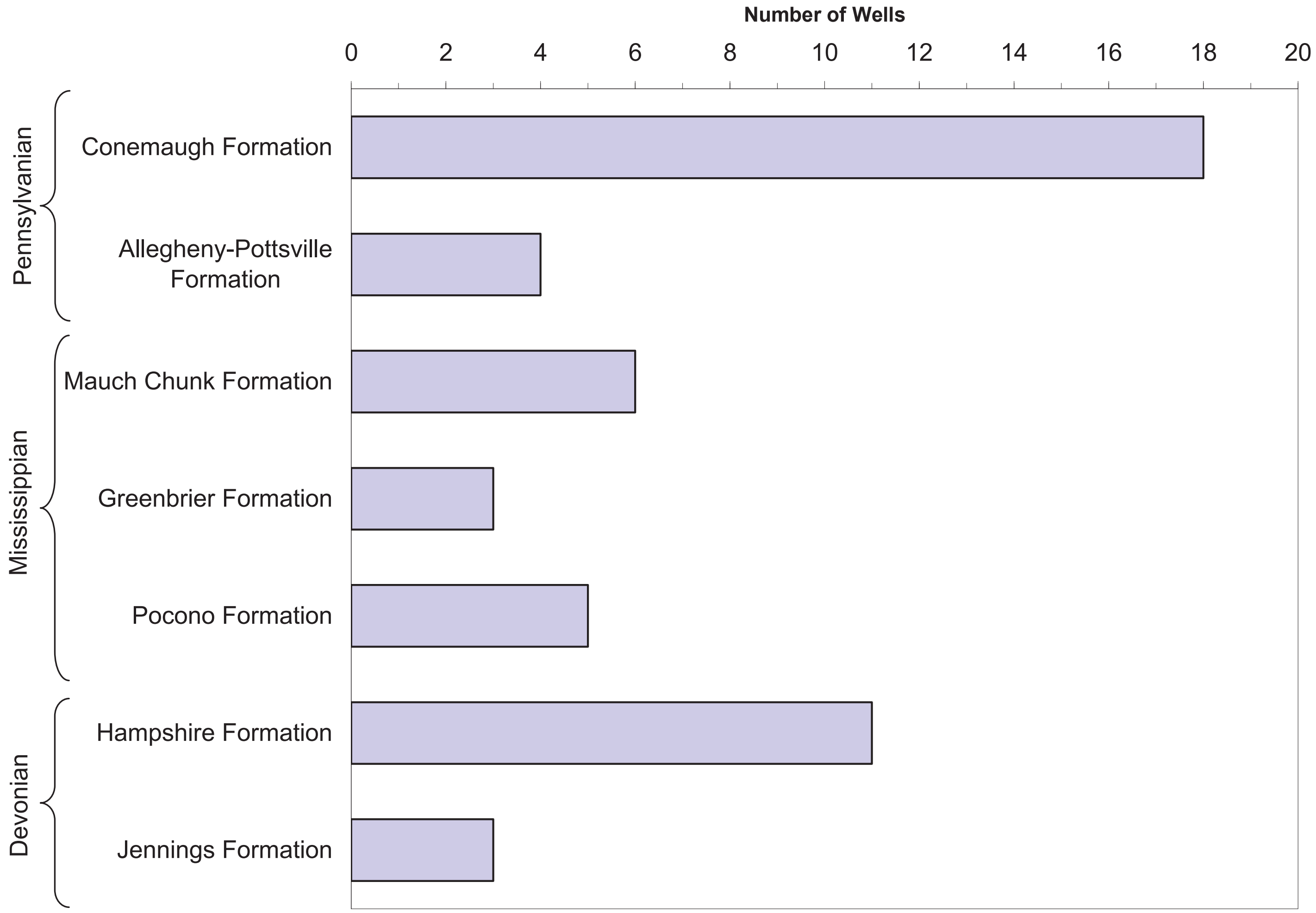

Figure 5. **Number of wells associated with each geologic formation in the Appalachian Plateau Province. Figure includes well GA-94-0137, which had a post-treatment water sample.**

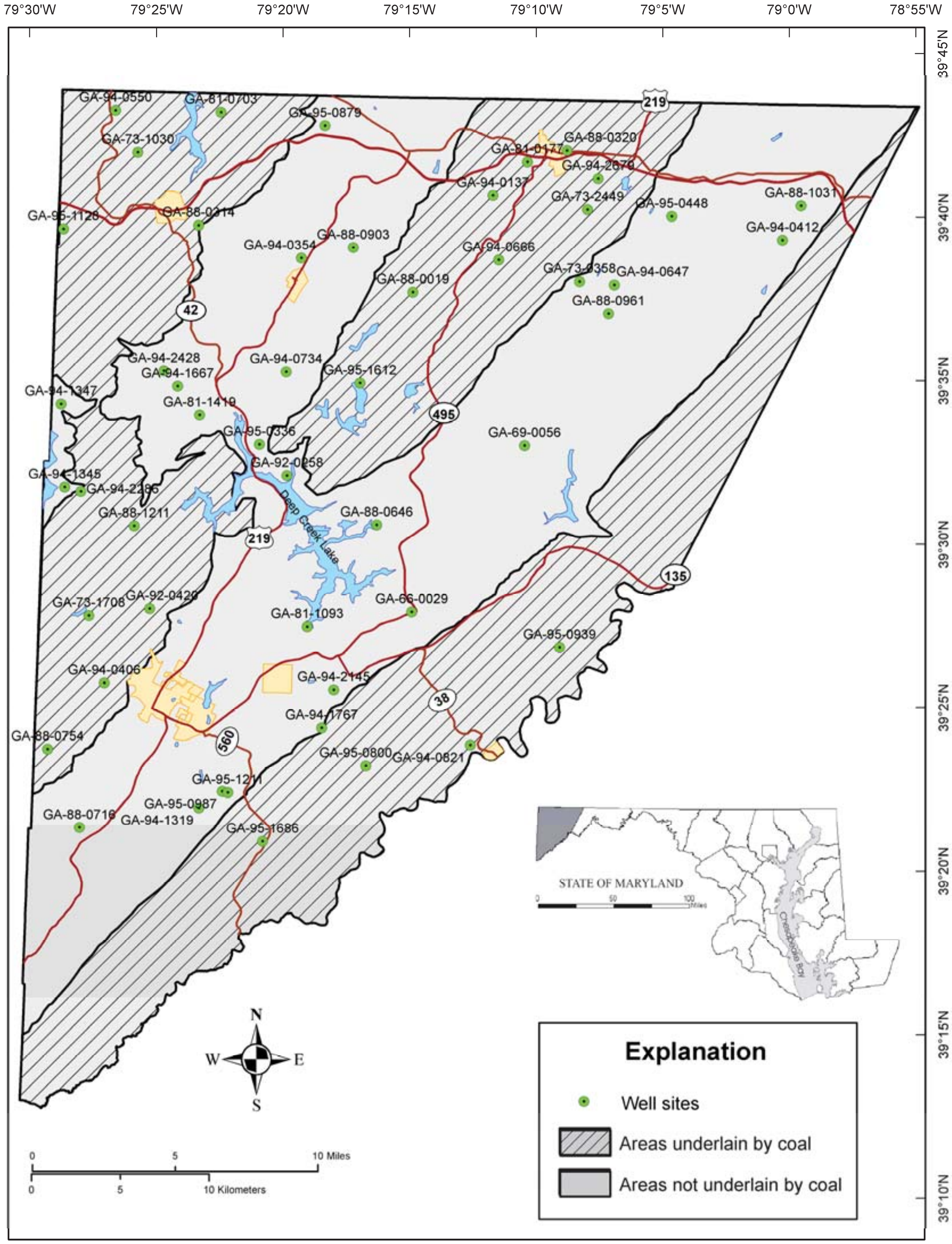

Figure 6. Well sites labeled with corresponding well permit numbers.

A B

Figure 7. Photographs showing different sampling ports for dissolved-methane collection. Water treatment systems, if present, were bypassed during purging and sampling.

A B C

Figure 8. Inverted bottle technique for dissolved-methane collection of well-water samples. Step A: Clear tubing is connected to untreated water source (e.g., pressure tank spigot), and the water is turned on to fill up the sampling bucket. Step B: Cap is removed from glass vial. Step C: Glass vial is inverted and placed over the clear tubing. Water fills the vial and is allowed to flush three vial volumes before the vial is capped underwater (modified from Hirsche and Mayer, 2009).

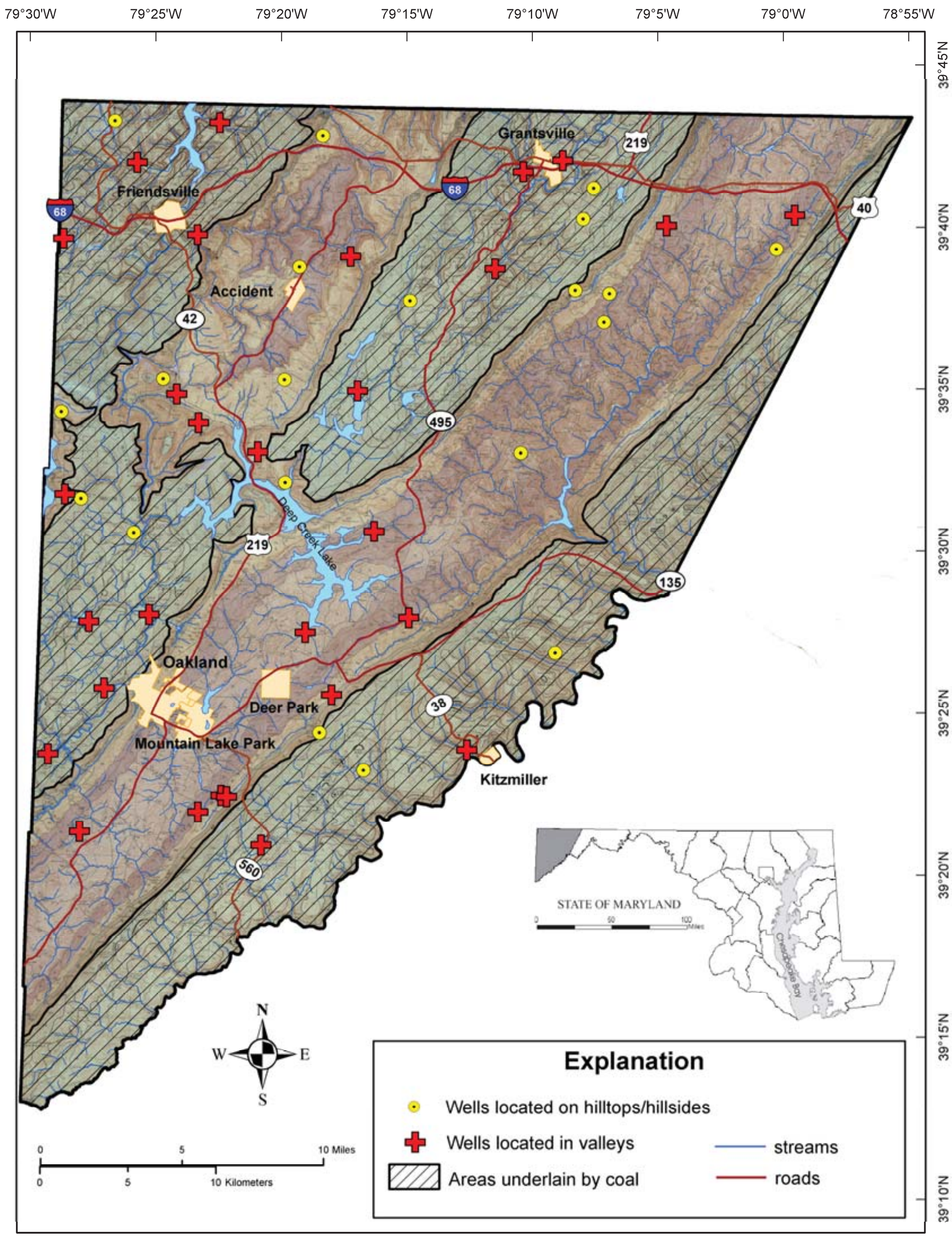

Figure 9. Locations of sampled well sites in Garrett County, Maryland with respect to streams, underlying geology, and topographic setting.

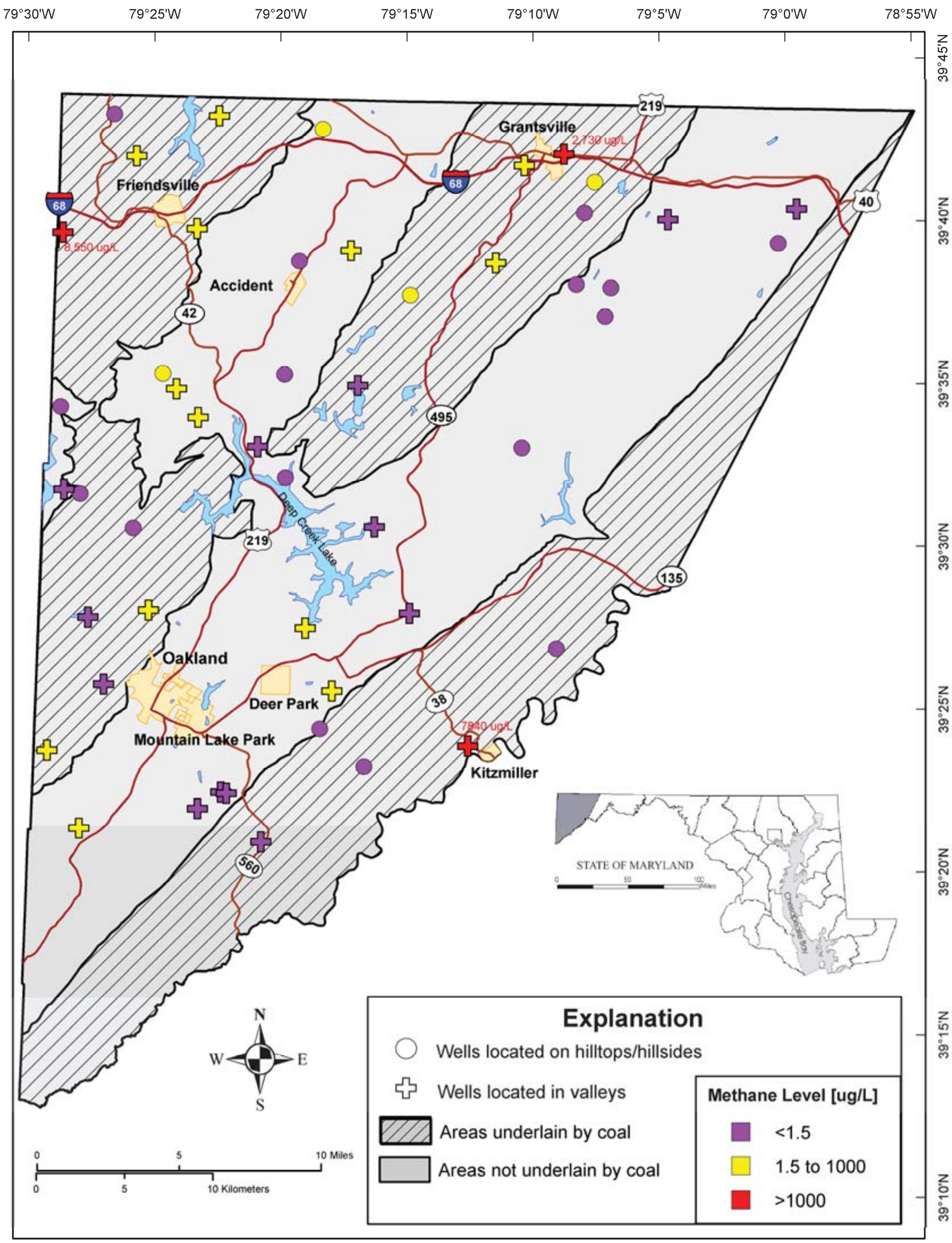

Figure 10. Map showing dissolved-methane concentrations with respect to geologic and topographic setting. The red labels display the dissolved methane concentration values.

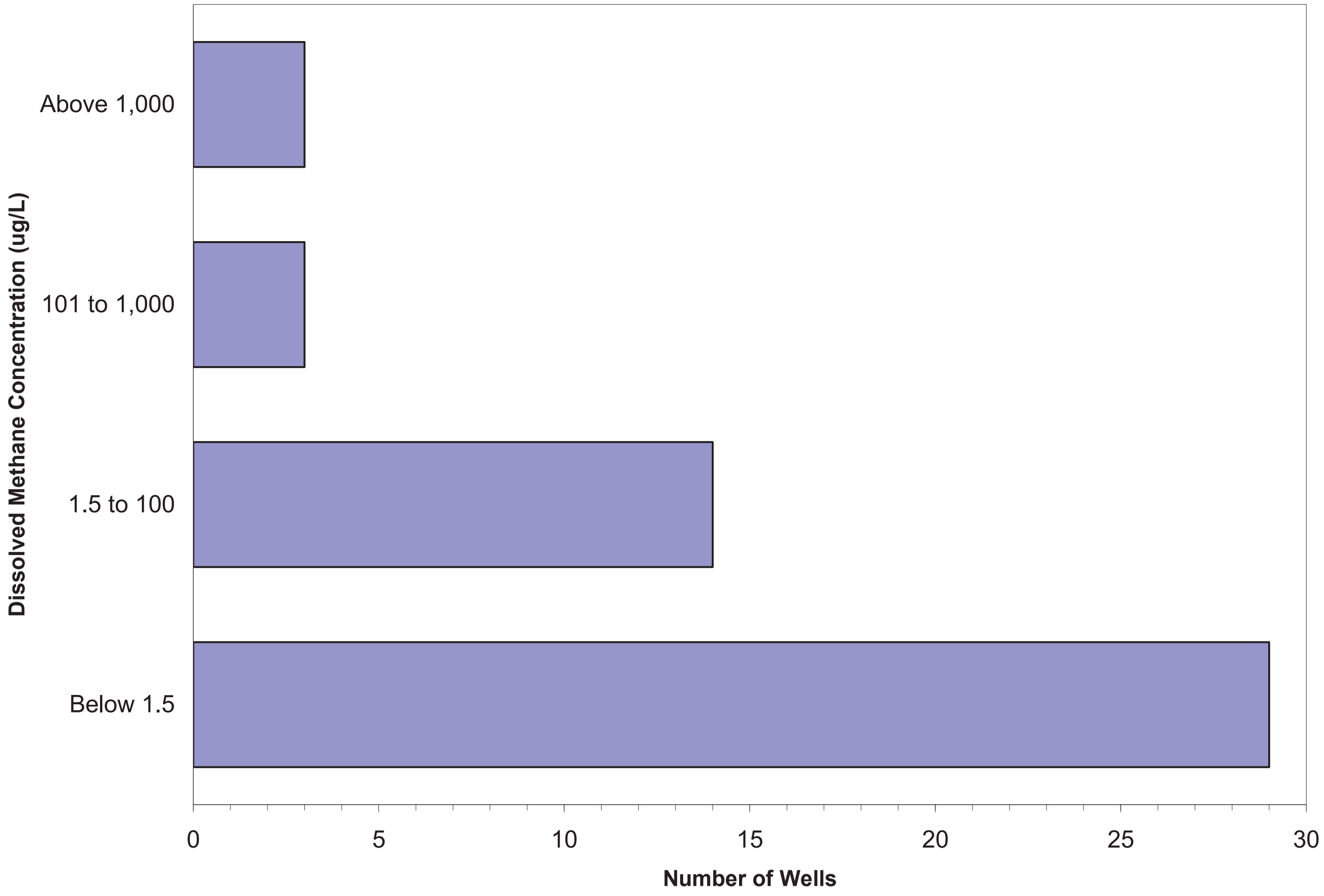

Figure 11. Number of wells associated with each range of dissolved-methane concentrations for well-water sampled in this study.

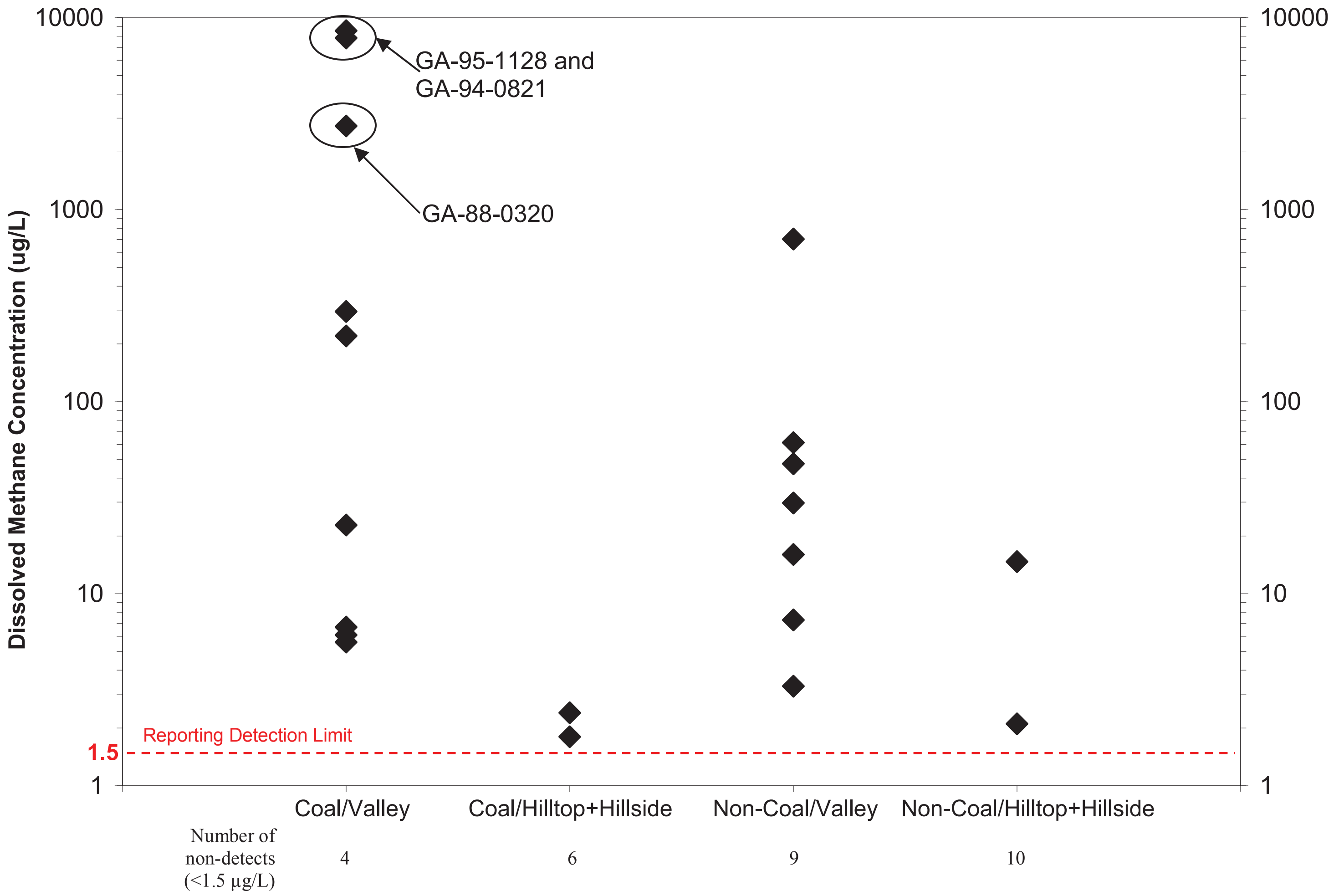

Figure 12. Relation of topographic setting (valley versus hilltop/hillside) and geologic feature (coal basin vs. non-coal basin) with the dissolved-methane concentration of each well. The number of non-detects per category is shown below the graph, but is not plotted.

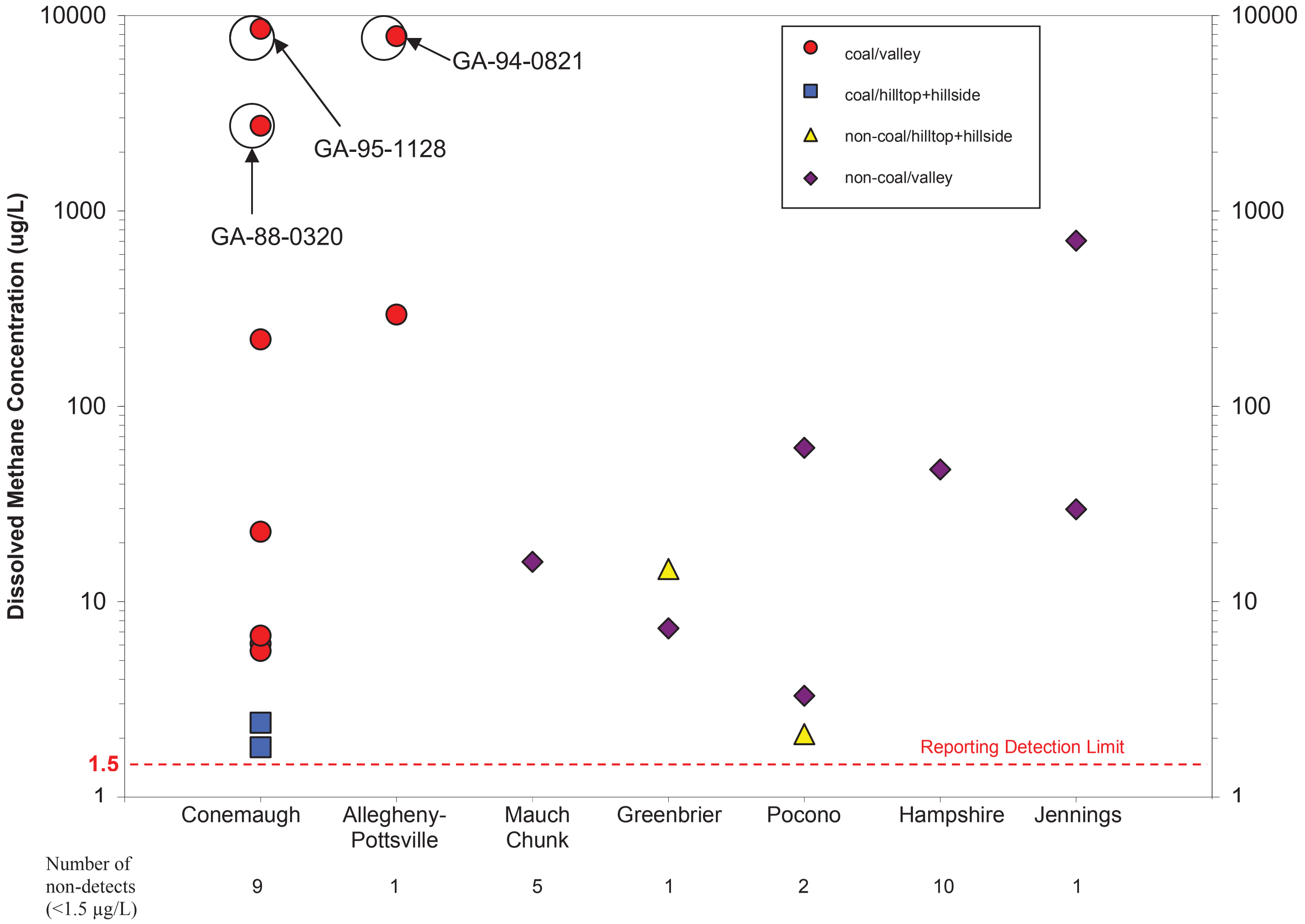

Figure 13. Relation of underlying geology, topographic setting, and dissolved-methane concentration of well-water samples. The number of non-detects per category is shown below the graph, but is not plotted.

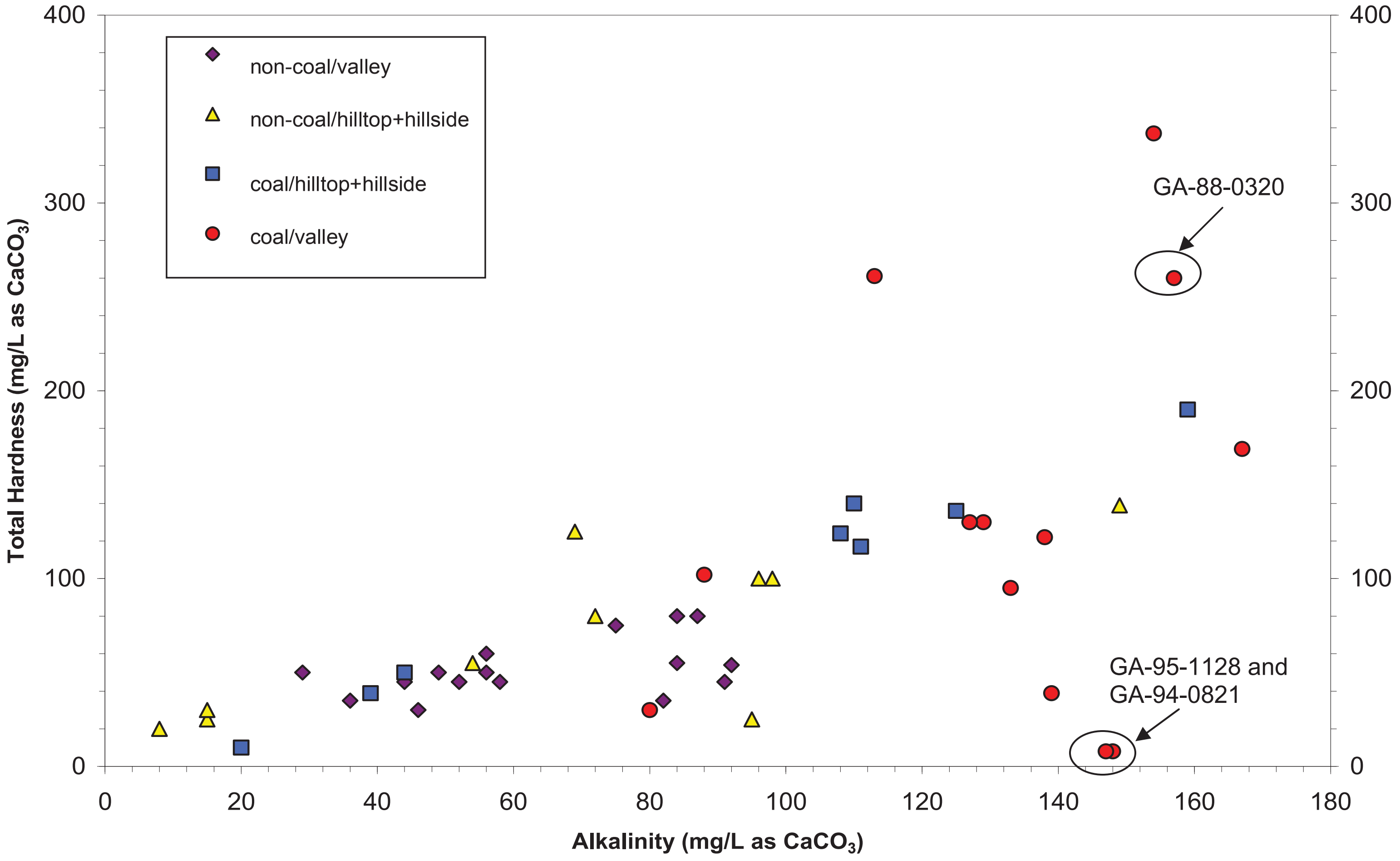

Figure 14. Relation of total hardness and alkalinity in well-water samples in the Appalachian Plateau Province. Two data points are not shown due to the lack of total hardness measurements.

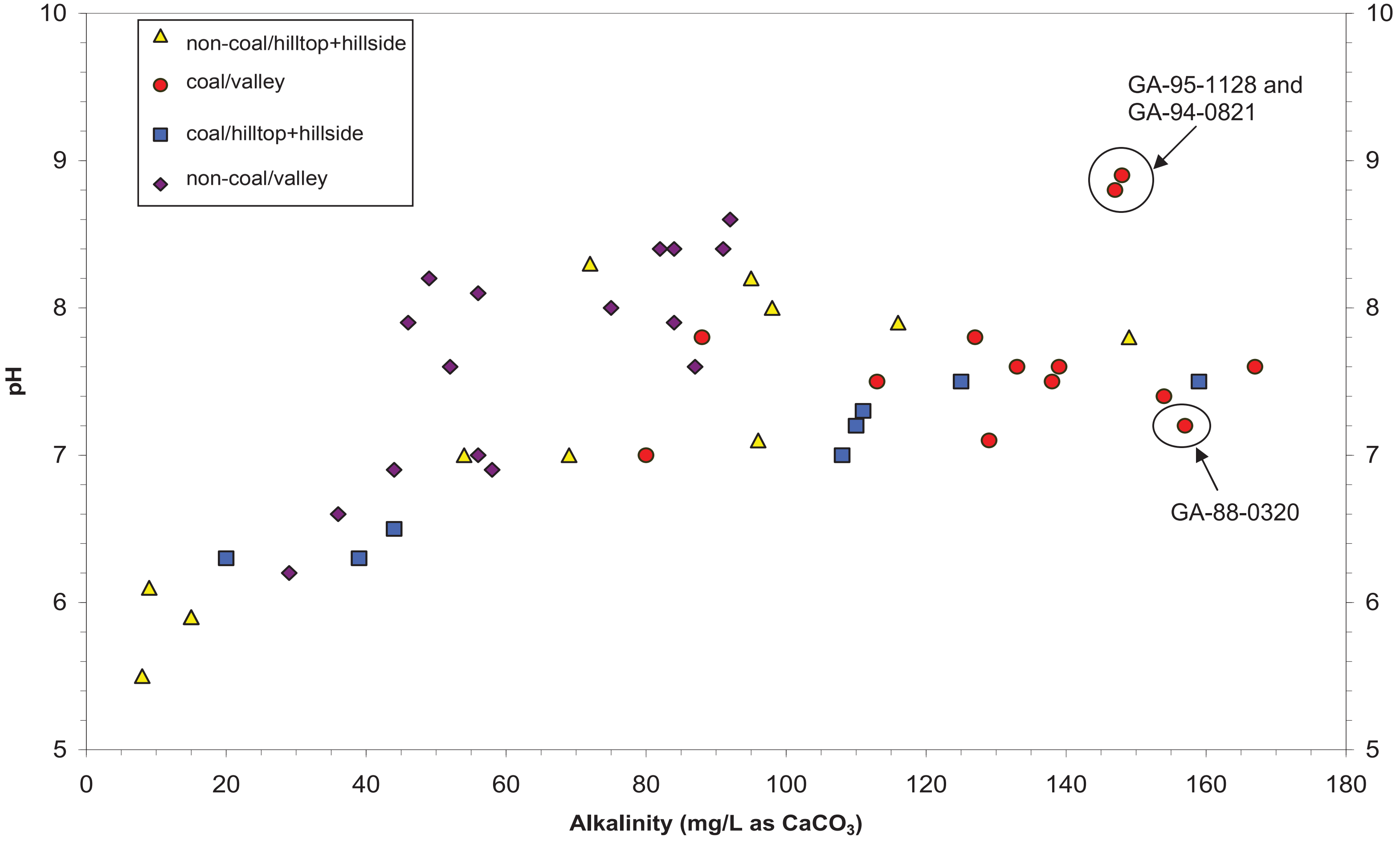

Figure 15. Relation of pH and alkalinity in well-water samples in the Appalachian Plateau Province.

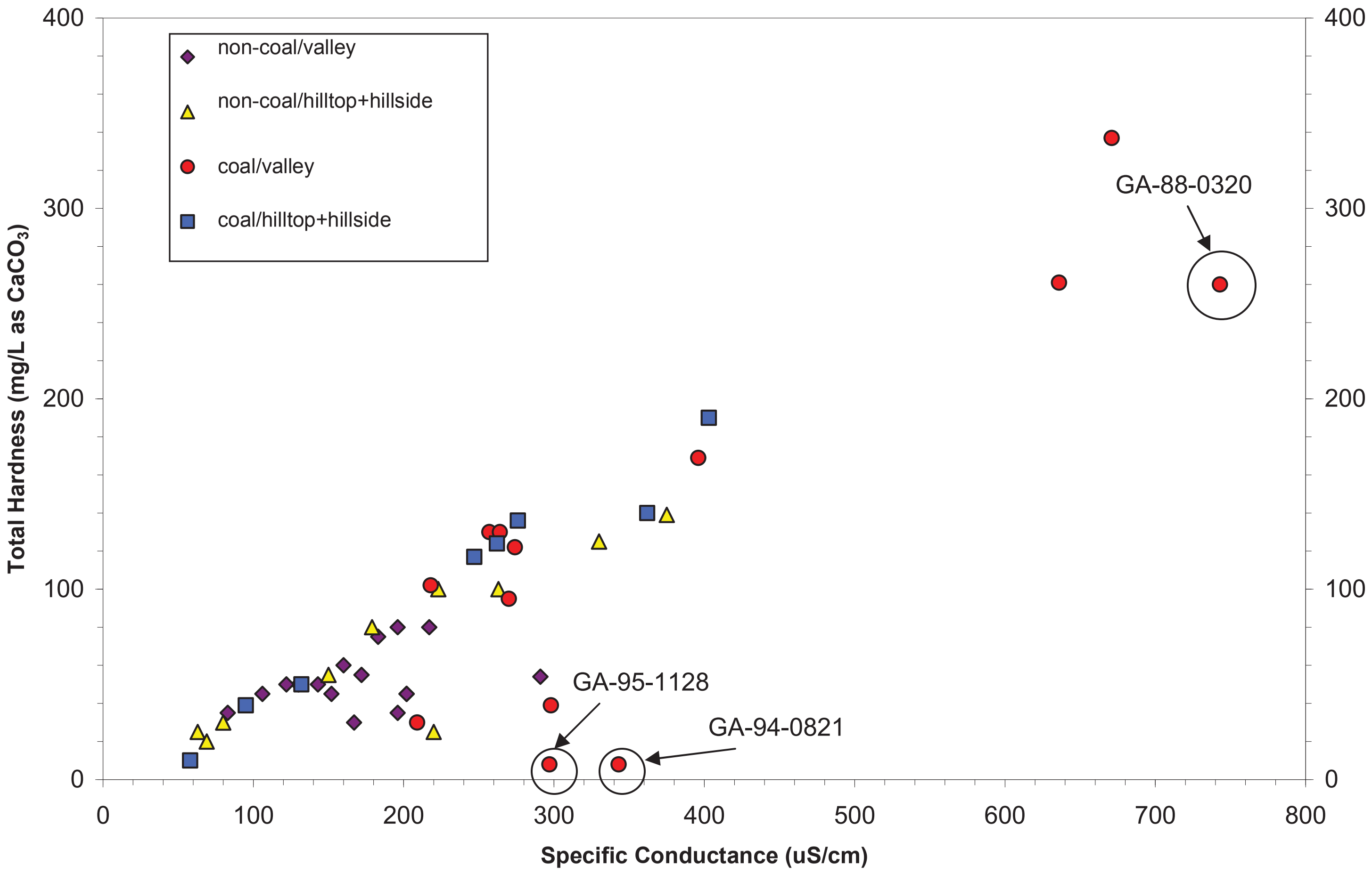

Figure 16. Relation of total hardness and specific conductance in well-water samples in the Appalachian Plateau Province. Two data points are not shown due to the lack of total hardness measurements.

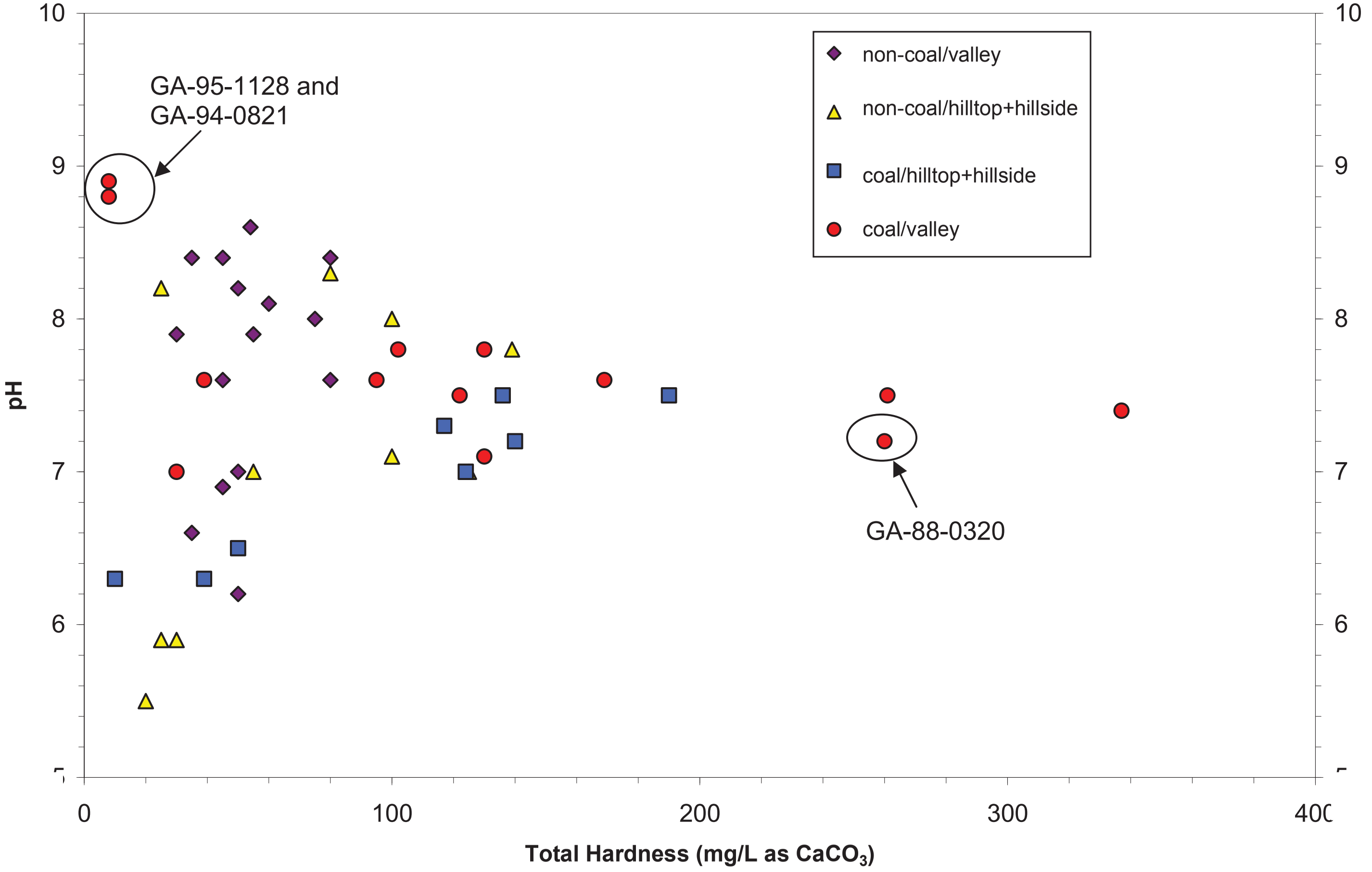

Figure 17. Relation of pH and total hardness in well-water samples in the Appalachian Plateau Province. Two data points are not shown due to the lack of total hardness measurements.

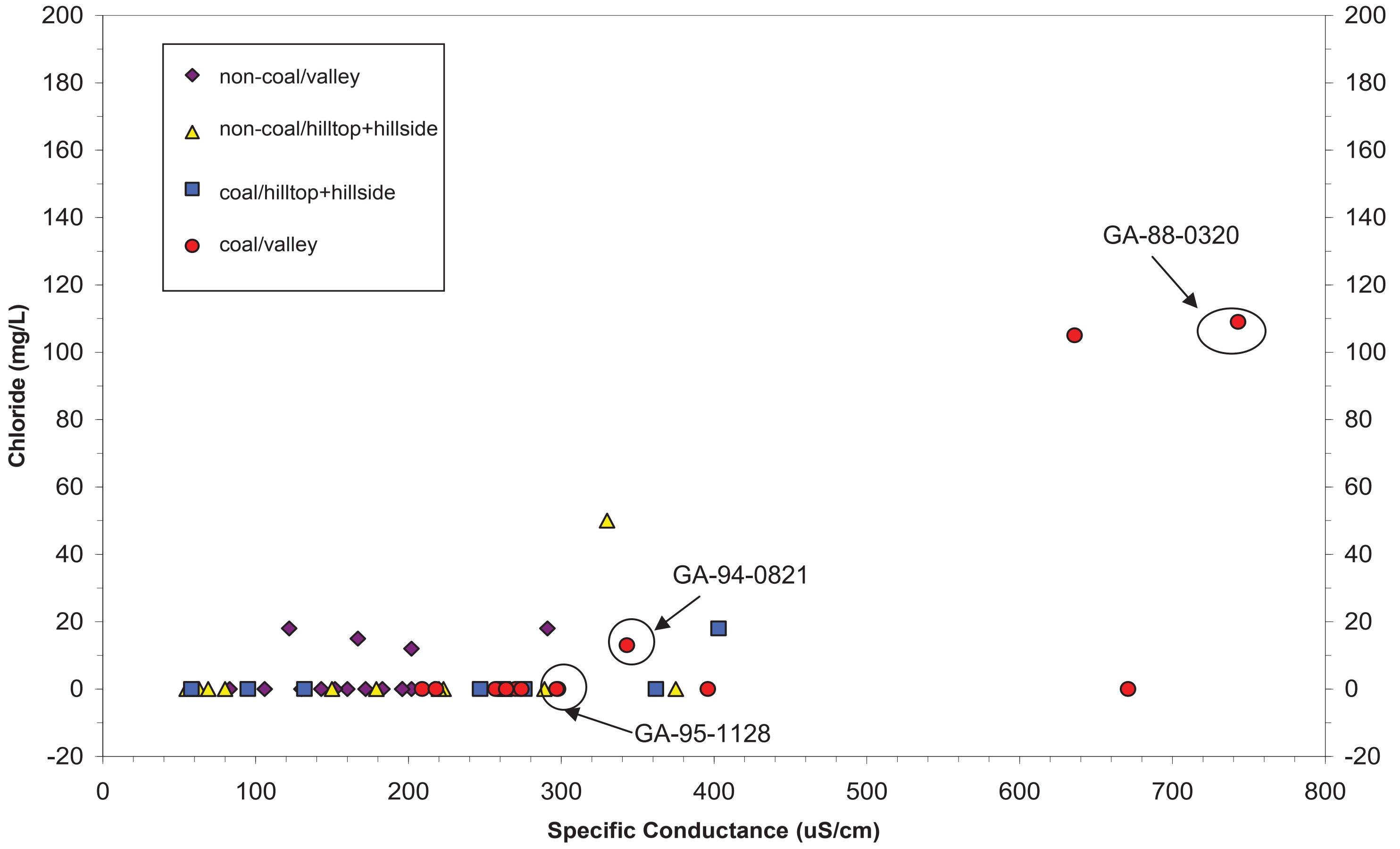

Figure 18. Relation of chloride and specific conductance in well-water samples in the Appalachian Plateau Province. Detection limit for chloride is 10 mgL; chloride non-detects (<10 mg/L) have been set to zero for the purpose of plotting.