

**Elevated Methane Levels from Biogenic Coalbed Gas in Ohio Drinking Water Wells near
Shale Gas Extraction**

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Elizabeth Claire Botner

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Thesis Committee

Dr. Amy Townsend-Small

Dr. David B. Nash

Dr. Arndt Schimmelmann

Abstract

Hydraulic fracturing and shale gas development have led to an abundance of domestic natural gas production, and the environmental impacts of these processes are under investigation. Previous studies in regions where the Marcellus Shale has been developed have shown that methane (CH₄) derived from natural gas was present in drinking water wells near gas wells, likely due to well casing failures. Here we present a 28-month time series of groundwater CH₄ concentration, CH₄ stable isotope composition ($\delta^{13}\text{C}$ and $\delta^2\text{H}$), pH, and specific electrical conductivity through a period of increasing shale gas extraction from the Utica Shale of eastern Ohio. The study period corresponded with an increase in the number of active Carroll County gas wells from 3 in late 2011 to 354 in 2015. CH₄ was detected in all groundwater wells, with concentrations ranging from below 0.2 $\mu\text{g L}^{-1}$ to above 25 mg L^{-1} . $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ measurements averaged $-65 \pm 11 \text{ ‰}$ (n=78) and $-180 \pm 61 \text{ ‰}$ (n=85), respectively, indicating a biogenic CH₄ source origin. Radiocarbon dating of four dissolved CH₄ samples indicates that coal formations are the source of elevated CH₄. We found no positive relationship between CH₄ concentration in groundwater and proximity to active gas well sites, and we found no significant change in CH₄ concentration, isotopic composition of CH₄, pH, or conductivity in water wells during the study period. Ongoing monitoring of private drinking water wells is critical to ensuring residents are not exposed to harmful levels of natural gas or other fracking contaminants.

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Introduction

Natural gas extraction from unconventional shale reservoirs has intensified in the U.S. and comprised 40% of total natural gas extraction in 2013 (1, 2). Within the next two decades, it is projected to become the largest contributor to the nation's natural gas supply (2). Although shale gas presents potential for a domestic, cleaner-burning fuel source in the midst of regulatory mandates for decreasing use of coal, the processes of horizontal drilling and hydraulic fracturing ("fracking") to acquire shale gas raise both environmental and health concerns.

Environmental issues surrounding the extraction and use of unconventional natural gas include uncertainties of greenhouse gas, particularly CH₄, emission rates from production and transport (3, 4), increased seismic activity during drilling activities (5), and localized reductions in air quality (6). The prevailing public concern of expanding shale gas development is groundwater contamination in areas of active drilling and production via stray gas migration and wastewater leakage (7-11). CH₄ from natural gas in groundwater can present an explosion hazard at certain concentrations, and may indicate the presence of other potentially harmful chemicals used in hydraulic fracturing or associated with natural gas and/or oil (12, 13).

Within the Utica Shale, directional drilling and hydraulic fracturing has led to the creation of over 1,400 horizontal wells in the state of Ohio (14). Many residents in this region rely on unregulated private groundwater wells, most of which are untested due to the high cost for analysis. While no studies have been performed in the Utica Shale of Ohio, previous studies in the Marcellus Shale regions of Pennsylvania have found elevated levels of CH₄ with an isotopic and alkane ratio signature consistent with that of natural gas in drinking water within 1 km of active gas wells (15, 16), although these studies did not collect baseline data before the onset of shale gas activity.

In this study, we seek to evaluate the impact of shale gas activity on groundwater resources in the Utica Shale of Ohio through time as development expands. We analyzed groundwater from 27 private drinking water wells, ranging from 35 to 115 meters in depth, in Carroll County, Ohio and the surrounding area over a period of sharply increasing shale gas development (17). These wells were sampled three to four times a year over a two-year period. We also performed a regional field campaign in May 2014, in which 96 groundwater wells were sampled within five counties.

Here, we present a dataset of dissolved CH₄ concentrations in shallow groundwater wells during the study period. We use isotopic data ($\delta^{13}\text{C-CH}_4$, $\delta^2\text{H-CH}_4$, and $\Delta^{14}\text{C-CH}_4$) to determine whether this CH₄ was derived from thermogenic natural gas or biogenic processes in underlying soils or rocks (anaerobic organic matter respiration or carbonate reduction), as well as to constrain the age of the carbon substrate. We also analyze the relationship of CH₄ concentration, $\delta^{13}\text{C-CH}_4$, and distance to the nearest active gas well, similar to the analyses done in previous studies (15, 16). Lastly, we examine dissolved CH₄ concentration, $\delta^{13}\text{C-CH}_4$, $\delta^2\text{H-CH}_4$, pH, and conductivity values over the duration of the study period to determine if trends or changes emerge.

Methods

Study Area

The majority of groundwater monitoring in our study took place in Carroll County, a rural farming region in eastern Ohio. Carroll County and the surrounding area reside in the Appalachian Plateau physiographic province; groundwater in the region is characterized by artesian springs in Pennsylvanian sandstones and small, shallow aquifers made up of sandstone and limestone in alluvial valleys (18). The study began here in November of 2012, 23 months after the first hydraulic fracturing permit was granted to Carroll County (14). This area was targeted for two reasons. First, a lack of water quality data exists in the region due to the recent start of unconventional gas extraction in Ohio. Secondly and perhaps most importantly, Carroll County has been granted the greatest number of hydraulic fracturing permits in the state (19). At the onset of our study, 161 natural gas wells were permitted in Carroll County; in May of 2015, over 400 gas wells were permitted (14).

Groundwater was also monitored in Belmont, Columbiana, Harrison, and Stark counties, although not at the frequency of sampling in Carroll County. These counties lack baseline groundwater data and continue to see a rise in unconventional natural gas wells. Figure 1 shows changes in the number of active natural gas wells and groundwater sampling sites in the five county study area over a 14-month period. Over time, both the number of sampling sites and active wells increased significantly.

Sample Collection

A total of 194 samples from drinking water wells and springs were collected in five counties of Ohio (Belmont, Carroll, Columbiana, Harrison, and Stark) from November 2012 to February 2015. Of these samples, 115 were collected from 27 drinking water wells and 2 springs

in Carroll, Harrison, and Stark counties that were regularly tested over the course of the two-year study period. Sampling sites were chosen based on landowner interest in the study, and all participation was voluntary.

At each site, wells were purged to remove stagnant water, then pH, specific electrical conductivity, and temperature were measured with a YSI Model 63 pH, salinity, conductivity, and temperature meter until stable measurements could be recorded. All samples were taken prior to any form of water treatment or storage tanks and as close to the well as possible, typically from outdoor pumps, basement water pipes, or less frequently, indoor faucets. Water samples were collected into 155 mL dry narrow neck glass serum vials, which were allowed to overfill to prevent headspace. Vials were preserved with 1000 μL of brine saturated with mercuric chloride (HgCl_2), then capped with grey butyl rubber septa and sealed with aluminum crimps.

A subset of four water samples was taken at groundwater wells with $\text{CH}_4 > 1 \text{ mg L}^{-1}$ for radiocarbon analysis. Three of these samples were collected in clean 1000 mL glass anaerobic media bottles capped with blue butyl rubber stoppers and preserved with HgCl_2 using the same methods as described above. One water sample collected in a 125 mL narrow neck glass serum vial treated with HgCl_2 was also used for radiocarbon analysis.

Methane Concentration Analysis

Dissolved CH_4 concentrations from water samples were acquired using headspace equilibrium methods (20) at 20°C and 101325 Pa. The bottled water samples were injected with 30 mL of ultra high purity N_2 gas, while another inserted needle and syringe captured the equally displaced volume of water. Samples were then agitated on a vortex shaker for one minute and rested five minutes before extraction was completed. To extract the headspace gas, the

previously displaced water was slowly injected back into the sample vial as the gas sample was simultaneously extracted with a 30-mL syringe equipped with a 2-way stopcock and 23-gauge needle. Extracted gas was then transferred to evacuated 20 mL clean dry glass serum vials sealed with butyl rubber septa and aluminum crimps, and containing desiccant to absorb water vapor.

The vials were then loaded into a GC-PAL AOC 5000 autosampler, and dissolved CH₄ concentrations were measured with an interfaced Shimadzu GC-2014 greenhouse gas chromatograph with Flame Ionization Detector (FID). Calibrated CH₄ standards were also prepared and placed intermittently into the autosampler to be analyzed alongside unknown samples. The standards represented a concentration range of ambient atmospheric CH₄ levels to 100,000 ppm CH₄, bracketing the CH₄ concentrations of water samples. Headspace concentrations were used to calculate the original dissolved gas concentrations of sampled water using temperature specific Bunsen solubility coefficients (21). Variation in final dissolved CH₄ concentrations is approximately 6% using the headspace extraction method (22).

Methane Isotope Analysis

The headspace equilibrium methods described above were also performed to acquire gas samples for stable isotope analysis of CH₄. Headspace gas samples were extracted and transferred to evacuated 12-mL glass vials (Exetainers[®], Labco Ltd., Buckinghamshire, UK) containing desiccating beads. Samples were then analyzed for $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ at the University of Cincinnati via isotope ratio mass spectrometry. CH₄ standards similar in concentration to samples were analyzed concurrently to calibrate the isotope ratio mass spectrometer. Stable isotope ratios were calibrated with standards from Isometrics, Inc (Victoria, British Columbia) that were cross-calibrated with standards from University of California, Irvine (23, 24) and University of California, Davis (25). Samples analyzed for $\delta^{13}\text{C}$ were calibrated

with a two, three, or four point curve using standards bracketing the isotopic composition of the samples and ranging in $\delta^{13}\text{C}$ and $\delta^2\text{H}$ from -66.2 ‰ to -28.5 ‰ and -247‰ to -156 ‰, respectively. The reproducibility of this method (25) is ± 0.2 ‰ and ± 4 ‰ for $\delta^{13}\text{C}$ and $\delta^2\text{H}$. By analyzing several replicates of CH_4 standards with each daily sample run, reproducibility parameters were met or surpassed.

Selected groundwater samples were sent to the University of California-Irvine Keck Carbon Cycle AMS Facility for radiocarbon dating analysis of CH_4 . A headspace extraction technique was used to obtain CO_2 and CH_4 gases from these samples. The extracted gas samples were purified through a low-pressure zero air flow-through vacuum line then combusted to produce CO_2 from CH_4 . CO_2 samples were then prepared for ^{14}C analysis using the sealed tube Zn graphitization method (26, 27). Radiocarbon concentrations are given as a fraction of the Modern carbon standard (FM), as $\Delta^{14}\text{C}$, and as conventional carbon age according to the protocol of Stuiver and Polach (28). Sample preparation backgrounds have been subtracted based on measurements of ^{14}C -free coal. The precision of $\Delta^{14}\text{C}$ analysis is about 2 ‰ for modern samples based on long-term measurement of secondary standards.

Results and Discussion

Dissolved CH₄ was detected in all sampled wells and concentrations spanned five orders of magnitude; however, no relationship was found between CH₄ concentration and proximity to natural gas wells (Figure 2). CH₄ concentration data coupled with CH₄ stable isotope ratios do not indicate high concentrations of natural gas in water wells near gas wells, unlike previous reports in Pennsylvania (15, 16). The highest levels of dissolved CH₄ were observed at sites in Carroll and Stark counties and were more than 5 km from active gas wells (Figure 2). The groundwaters from these high CH₄ sites bear stable isotopic signals consistent with biogenic CH₄. Subsequent radiocarbon dating of selected high CH₄ samples indicates the source of elevated CH₄ in three of the four sites analyzed is likely coalbed gas, whereas one lower CH₄ concentration sample had a relatively younger radiocarbon age consistent with anaerobic respiration of soil organic carbon. Underlying coal geology and previously reported coalbed deposits (29) support our discovery of coalbed CH₄ in certain groundwater aquifers.

Characterization of Methane Levels in Eastern Ohio

Dissolved CH₄ concentrations had a large range, but CH₄ concentrations within 27 consistently sampled drinking water wells did not experience significant changes during the two-year sampling window (Figure 5), except for minor variations in the CH₄ saturation ratio due to exposure of well water to air. The concentration of CH₄ in water at equilibrium with air from a monitored spring in Carroll County averaged $0.3 \pm 0.1 \mu\text{g L}^{-1}$ (n=6). Concentrations varied little throughout the study period exhibiting only seasonal (temperature- and pH-dependent) fluctuations (30). Variability in groundwater CH₄ concentrations within the region can depend on factors such as well depth, aquifer type, topography, groundwater chemistry, aeration, and other hydrogeologic features (30-33).

When considering all groundwater wells sampled during the study, the majority of wells (57%) had concentrations of dissolved CH₄ around or below 1 µg L⁻¹ CH₄ with a CH₄ saturation ratio below 25. Three regularly sampled drinking water wells were within 1.5 km of an active natural gas well during the study period. The water wells were sampled two or more times both before and after natural gas extraction activities began nearby. None of the measured parameters significantly varied in these groundwater wells before or after drilling or natural gas production.

The average dissolved CH₄ concentration in drinking water wells within an active gas extraction zone was 1.7 ± 4.5 mg L⁻¹ (n=81), while the average dissolved CH₄ concentration in drinking water wells outside of a gas extraction zone was 1.2 ± 4.0 mg L⁻¹ (n=112). We define an active gas extraction zone as the 1.5-km radius surrounding a producing unconventional natural gas well. A subset of three groundwater wells consistently contained dissolved CH₄ in concentrations above the action level for mitigation set by the U.S. Office of Surface Mining (10 mg L⁻¹ CH₄) (12), averaging 13.5 ± 0.8 mg L⁻¹ over a year of quarterly sampling. When we exclude these three individual water wells, average dissolved CH₄ concentrations are much lower both within and outside of active extraction zones at 0.54 ± 1.1 mg L⁻¹ and 0.54 ± 2.4 mg L⁻¹, respectively (Figure 6).

Groundwater CH₄ Isotopic Composition

Isotopic measurements played a key role in this study, allowing us to determine the origins of CH₄ in sampled groundwater and to identify any possible changes in CH₄ sources as shale gas development intensifies in the region. δ¹³C-CH₄ and δ²H-CH₄ measurements can signify one or both of the main sources of CH₄ in groundwater: biogenically-derived CH₄ from microbial respiration or carbonate reduction pathways, or deeper, thermogenic CH₄ produced from organic matter subject to intense heat and pressure over large time scales (34, 35).

Thermogenic CH₄ from Ordovician, Silurian, and Devonian shale and coal formations within the Appalachian Basin has been characterized with $\delta^{13}\text{C-CH}_4$ values generally above -52 ‰ (36-38). CH₄ with $\delta^{13}\text{C}$ values above -50 ‰ was interpreted as natural gas in drinking water wells near natural gas wells in Pennsylvania (15). $\delta^{13}\text{C-CH}_4$ values between -50 ‰ and -110 ‰ indicate a biogenic CH₄ source (24, 35). $\delta^2\text{H-CH}_4$ values less than -275 ‰ are generally consistent with biological CH₄ sources while measurements above this value can indicate a thermogenic or mixed biogenic-thermogenic source (24, 36, 37). Although unconventional gas samples from the sampling region could not be obtained, a gas sample from a conventional natural gas well in Carroll County yielded carbon and hydrogen isotopic signatures of -41.3 ‰ and -172 ‰, respectively. Air samples taken downwind of an unconventional gas well in the region were characterized by $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ values of -47.3 ‰ and -171 ‰, respectively. In contrast to regional thermogenic CH₄ sources, the breath of a local dairy cow was analyzed and yielded a biogenic $\delta^{13}\text{C}$ value of -56.6 ‰ and $\delta^2\text{H}$ value of -305 ‰.

Over the course of the study, regularly monitored groundwater wells did not undergo a significant change in either $\delta^{13}\text{C-CH}_4$ or $\delta^2\text{H-CH}_4$ values. Figure 2 compares the CH₄ concentration and $\delta^{13}\text{C-CH}_4$ values of all measured groundwater wells. Water wells containing CH₄ in concentrations above 1 mg L⁻¹ had $\delta^{13}\text{C}$ measurements averaging -68.9±5.1 ‰, signifying a biogenic CH₄ source. Similarly, $\delta^2\text{H-CH}_4$ data, averaging -197±35 ‰, indicated a biological CH₄ source in water wells containing elevated CH₄. Prior Marcellus Shale groundwater studies established a positive correlation between dissolved CH₄ concentrations and stable carbon isotope values in drinking water wells (15, 16); however, we did not find any relationship between measured CH₄ concentrations and $\delta^{13}\text{C-CH}_4$ data in this study. The average

$\delta^{13}\text{C-CH}_4$ values of groundwater wells within and outside of an active gas extraction zone were -66.5 ± 10.1 ‰ and -63.3 ± 11.8 ‰ respectively.

A small number of groundwater samples fell within the mixed biogenic/thermogenic or thermogenic source range based on $\delta^{13}\text{C-CH}_4$ analysis, but there are many plausible explanations for these values. As shown in Figure 2, samples with $\delta^{13}\text{C-CH}_4$ values between the biogenic and thermogenic range were from water wells with low levels of dissolved CH_4 . Most of the samples in this range were collected from artesian springs or very shallow groundwater wells. These wells likely contain a significant amount of dissolved atmospheric CH_4 due to greater contact with air compared to deeper wells. Atmospheric CH_4 has a $\delta^{13}\text{C}$ value around -47 ‰ (39), potentially increasing dissolved $\delta^{13}\text{C-CH}_4$ measurements. Intermediate $\delta^{13}\text{C-CH}_4$ and $\delta^2\text{H-CH}_4$ values in the mixed biogenic/thermogenic range can potentially be attributed to CH_4 oxidation in aerobic portions of underlying aquifers, thus dampening a strong biogenic signal (40). One groundwater sample contained CH_4 with a carbon isotopic signature (-32.7 ‰) consistent with those of thermogenic sources; however, the hydrogen isotopic value was -2 ‰ and the CH_4 concentration was low at 0.03 mg/L, making the sample a likely coalbed CH_4 source (41).

Additional parameters can be measured in future field studies to confirm the biogenic origin of CH_4 measured in Carroll County groundwater wells. Groundwater dissolved inorganic carbon (DIC) concentrations are elevated alongside exceptionally high $\delta^{13}\text{C-DIC}$ values in aquifer environments with significant amounts of microbially generated gases, such as CH_4 and CO_2 (42, 43). Comparisons of the ratio of CH_4 to higher chain hydrocarbons (C_{2+}), such as propane and ethane, can also be used to distinguish between thermogenic and biogenic gases (16, 35).

Figure 3 compares groundwater $\delta^{13}\text{C}-\text{CH}_4$ and $\delta^2\text{H}-\text{CH}_4$ values alongside previously reported natural gas and coalbed CH_4 isotope data in the Appalachian Basin (36, 37). While some samples are similar in isotopic composition to coalbed CH_4 , many are even more depleted in ^{13}C and ^2H . Certain samples have carbon isotope signatures indicative of a microbial origin; however, the sample hydrogen isotope signature is more ^2H -enriched than a typical biogenic CH_4 source (24). A likely explanation for these values is a coalbed gas source. The $\delta^2\text{H}-\text{CH}_4$ values of certain water samples fall in line with CH_4 originating from coal seams, or coal bed CH_4 (CBM), based on previous isotopic analysis of coalbed CH_4 sources (37, 41, 44, 45). More research is needed on the composition and abundance of coalbed CH_4 in subsurface Appalachia, particularly on the interaction of this CH_4 source with current and past oil and gas extraction (46).

Of particular interest are four individual drinking water wells, three of which were regularly monitored (sampled 3 to 4 times per year), which contained dissolved CH_4 at concentrations within the action level for hazard mitigation set by the U.S. Office of Surface Mining ($10 - 28 \text{ mg L}^{-1}$). One well consistently reached CH_4 concentrations near the upper limit of this level (12). This well was greater than 10 km away from an active well site for the entire duration of our study period. Stable isotope analysis of this well, as well as the other wells containing hazardous CH_4 levels, indicates a biogenic source of CH_4 . Closer examination of water well logs show that two of the wells containing 10 mg L^{-1} or more dissolved CH_4 are drilled through at least one coal formation (17). Coal deposits, common in the Appalachian Basin region, may be a contributor of high levels of CH_4 in groundwater from coalbed gases. Large reserves of coalbed CH_4 are documented south of our study area in eastern Harrison County, Ohio in addition to a small reserve in east-central Carroll County (29), providing evidence that

coalbed gas may be a potential source of elevated CH₄ in groundwater resources in Carroll County and the surrounding region.

Coalbed Gas – Potential CH₄ Source?

Coalbed CH₄, which can consist of both thermogenic and biogenic CH₄ sources, has been characterized in Australia as well as certain regions of the San Juan, Powder River, Michigan, Illinois, and Appalachian basins of the United States (37, 41, 47-49). Biogenic coalbed CH₄ originates from microbial carbonate reduction or acetate fermentation, either early in the formation of coal or typically during subsequent invasions of meteoric water within the coal deposits (44, 45).

Previous studies on coalbed CH₄ have been performed in northern Ohio and the Appalachian Basin, with geologic features quite similar to those found in our study area of Carroll County, Ohio. These studies found that gases were usually of thermogenic origin, with $\delta^{13}\text{C-CH}_4$ values ranging from -55.1 ‰ to -45.9 ‰ and $\delta^2\text{H-CH}_4$ ranging from -219 ‰ to -196 ‰ (37). While the hydrogen isotope values of many groundwater wells in our study fall within this range, carbon isotopic data of CH₄ samples are comparable to previously measured coalbed gases in Australia, characterized with by carbon stable isotope values of $-60 \pm 10\text{ ‰}$ (Figure 3), indicating that CH₄, if originating from coal deposits, was produced biologically and may have experienced secondary mixing with thermogenic coalbed CH₄ (37, 44, 45).

Based on stable isotopic analysis alone, biogenically derived coalbed CH₄ can be indistinguishable from CH₄ produced through microbial methanogenesis within an aquifer from soil organic carbon (50). Because CH₄ originating from both shallow soil aquifers and coal seams can have similar carbon and hydrogen isotopic signatures, radiocarbon dating can be used to discriminate between these two sources. CH₄ gas found in coal deposits, whether biogenic or

thermogenic, is devoid of measurable radiocarbon, as the carbon substrate for CH₄ formation is much greater than 60,000 years old and all radiocarbon has decayed away (24, 27). This lack of radiocarbon generates a fossil carbon $\Delta^{14}\text{C}$ signature approaching -1000 ‰ (24). Groundwater containing CH₄ originating from coalbed gas, therefore, will have a very small fraction of radiocarbon and will be depleted in ¹⁴C compared to atmospheric $\Delta^{14}\text{C}$ (51). In contrast, CH₄ produced from more recent organic matter decomposition will contain a higher level of ¹⁴C (24, 50), with a $\Delta^{14}\text{C}$ signature > 0‰ (27, 52).

In order to distinguish between these two sources of biological CH₄, radiocarbon dating of four groundwater samples from private drinking water wells containing consistently elevated (> 1 mg L⁻¹) dissolved CH₄ concentrations was performed. Table 1 overviews CH₄ concentration, stable isotope data, and radiocarbon abundances of the four samples. The water well in Stark County, Ohio (Well 1) was mostly fossil CH₄ based on $\Delta^{14}\text{C}$ value of -966.1 ‰. Wells 2 and 3 contained CH₄ concentrations at the upper action level limit (> 22 mg L⁻¹) and had extremely low $\Delta^{14}\text{C}$ values, indicating that coalbed CH₄ comprised the majority of dissolved CH₄ in the water wells. In contrast to Wells 1-3, Well 4 had a radiocarbon isotopic signal of -45 ‰, or about 96% modern C. Anaerobic decomposition in a large pond near the groundwater well at Well 4, particularly in the summer months, may be a contributor to modern CH₄.

Water wells containing the highest levels of CH₄ had the lowest $\Delta^{14}\text{C}$ values; therefore, ¹⁴C age positively correlates with CH₄ concentrations. This relationship suggests that biogenic coalbed CH₄, when present in an aquifer system, contributes to high levels of dissolved CH₄ in groundwater. When considered with the respective stable isotope data, the dead carbon comprising coalbed CH₄ was likely formed during microbial reduction of carbonates, characterized by $\delta^{13}\text{C}\text{-CH}_4$ values less than -70 ‰ and $\delta^2\text{H}\text{-CH}_4$ values above -250 ‰ (41).

These results indicate past CO₂ reduction in coal seams is a source of CH₄ in at least three groundwater wells of our study, and supplies large concentrations of dissolved CH₄ in two wells containing CH₄ levels well above the action level for hazard mitigation. Radiocarbon analyses of other groundwater samples from our study area containing biogenic CH₄ would provide a more detailed representation of coalbed CH₄ in the region and its prevalence in groundwater resources. Our data not only show that elevated CH₄ in sampled groundwater wells does not originate from hydraulic fracturing, but that coalbed CH₄ may be a major source of biogenic CH₄ to drinking water resources. Although our investigation of coalbed CH₄ in groundwater is preliminary, the results warrant additional studies of coalbed CH₄ in this region and in other major shale plays, particularly where natural gas extraction is dominant. Continuing research is needed to determine whether increased hydraulic fracturing activity will lead to natural gas or fracking fluid intrusion into groundwater wells, as has been shown elsewhere (9, 15, 16, 53, 54).

Characterization of Other Geochemical Parameters

On site measurements of pH and conductivity can indicate groundwater adulteration from hydraulic fracturing wastewater leaks or spills. Fracturing wastewater, also termed produced water, fracking fluid, or flowback, is acidic and contains high levels of dissolved salts (5, 13, 55). Figure 4 compares pH and conductivity of sampled groundwater wells. The majority of groundwater wells had pH values between 6-8, while conductivity values generally remained below 1000 microsiemens per centimeter. Both pH and conductivity values of most water wells fell within the normal range for freshwater in the U.S. (56).

Certain trends were observed, including a positive correlation between pH and conductivity. Analysis of the minerals present in groundwater of the region may provide an explanation for this trend, as the presence of certain mineral ions and carbonates are associated

with not only elevated conductivity and pH but also elevated CH₄ levels (33). Geographical patterns were also detected; most notably, Columbiana County groundwater wells were characterized by higher conductivity values than wells sampled in other counties (Table 1). Migration of briny source water into aquifer systems, particularly in lowland areas, could contribute to higher conductivity and pH levels in this area (30, 32). Proximity to coal mining activities may have lowered pH measurements in one regularly monitored water well (57).

Significance of Baseline Data

While the relationship between shale gas extraction and drinking water quality has been well studied in the Marcellus Shale (8,15, 16, 53, 55), little is known about groundwater quality in the Utica Shale drilling region eastern Ohio. Our study is the first to characterize CH₄ concentrations and sources in groundwater in this area both before and after the onset of widespread hydraulic fracturing and horizontal drilling. The steady increase in natural gas well permitting, drilling, and production over the duration of this study allowed us to establish baseline water quality data of drinking water in the area as well as monitor changes in groundwater quality as drinking water wells became in proximity to active gas extraction zones. As many permitted natural gas wells transition into the producing phase, our characterization of groundwater in eastern Ohio will allow further studies to monitor any significant changes in drinking water resources.

Conclusions

We have found that a small subset of groundwater wells in the Utica Shale region consistently contained elevated CH₄ levels, but stable isotope analysis indicated biological sources. Based on the carbon and hydrogen stable isotope data along with the relatively consistent measurements within individual wells over the study period, we have found no evidence for natural gas contamination from shale oil and gas mining in any of the sampled groundwater wells of our study. ¹⁴C analysis confirmed the presence of biogenic, coalbed CH₄ in three out of four water wells with remarkably high CH₄ concentrations. Additional geochemical parameters can be measured to further characterize coalbed CH₄ and its presence in groundwater in eastern Ohio.

While past studies have found evidence for Marcellus Shale-derived natural gas contamination in Pennsylvanian drinking water wells due to improper well construction and maintenance (8), shale gas development firms may be using safer well construction practices in the relatively newer drilling area of the Utica Shale to avoid leakage from well casings. As currently permitted natural gas wells undergo drilling, hydraulic fracturing, and production, the status of water quality in the region may change at any time. When unconventional gas well casings age, the integrity of the well structure may become compromised, causing leaks to develop. Although no evidence for natural gas contamination from shale gas extraction activities was found in this study, continual monitoring of groundwater quality, CH₄ concentration, and CH₄ sources is needed to assess the longer-term impacts of hydraulic fracturing on groundwater resources of the eastern Ohio region.

Tables

Sample ID	CH ₄ (mg/L)	$\delta^{13}\text{C-CH}_4$ (‰)	$\delta^2\text{H-CH}_4$ (‰)	Fraction Modern Carbon	$\Delta^{14}\text{C}$ (‰)	¹⁴ C Age (BP)
Well 1	12.1	-72.4	-227	0.0341	-966.1	27130
Well 2	22.6	-67.7	-217	0.0028	-997.2	47120
Well 3	25.0	-67.8	-219	0.0028	-997.3	47350
Well 4	1.9	-67.8	-195	0.9625	-45.1	305

Table 1. Summary of radiocarbon and stable isotope data of four groundwater samples containing elevated CH₄ from February 2015.

Figures

14-Month Time-Series of Active Gas Wells and Sampled Groundwater Wells in Eastern OH

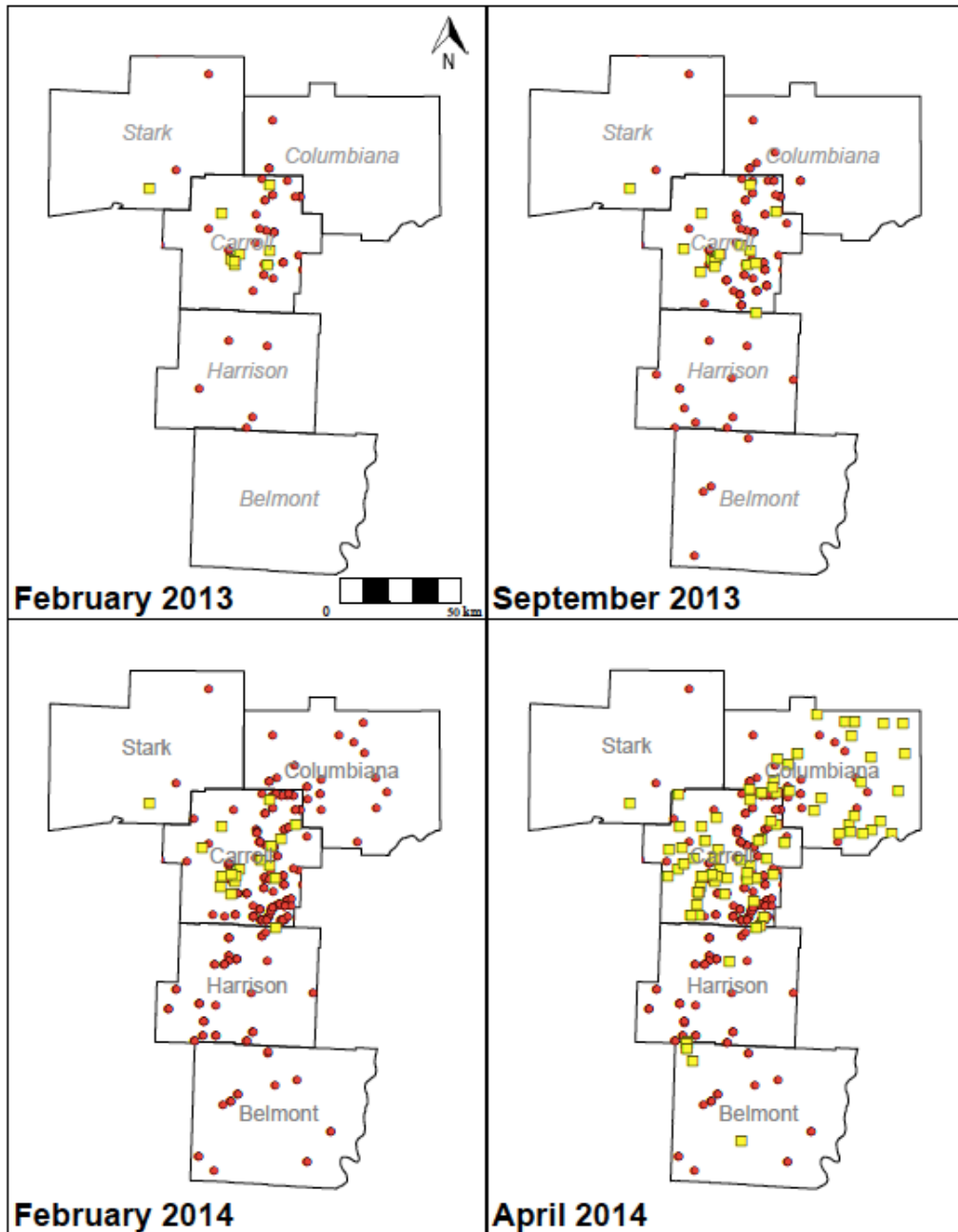


Figure 1. Map of Ohio counties in the study area over 14 months of the sampling period. Yellow squares are sampled groundwater sites. Red circles are active natural gas wells.

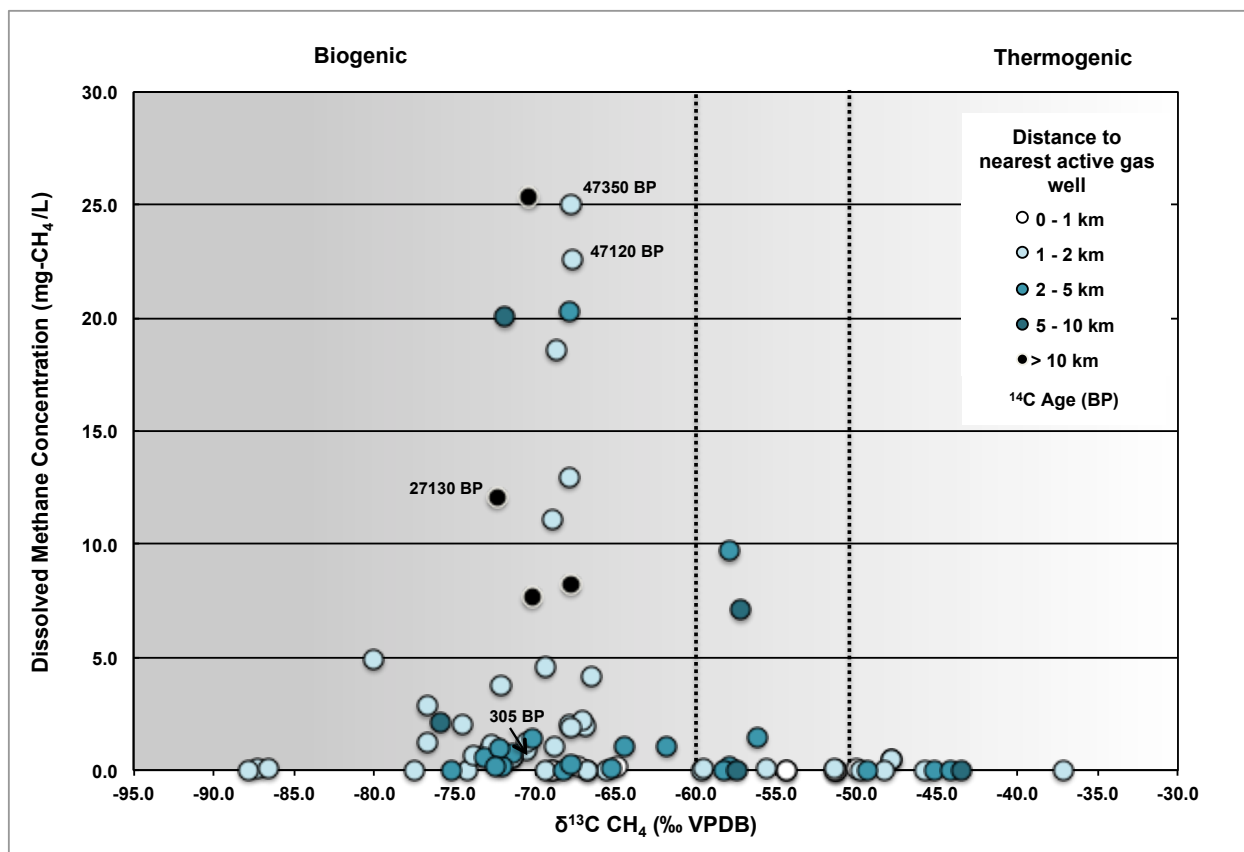


Figure 2. CH₄ concentration compared to the carbon stable isotope composition of groundwater samples. Symbol shade represents distance to the nearest active gas well in km, with lighter shades denoting a closer proximity to active wells. Four data points are labeled with ¹⁴C-CH₄ age (BP). Biogenic and thermogenic carbon isotopic signature ranges are separated by dotted lines. (Osborn et al., 2011, Jackson et al. 2013).

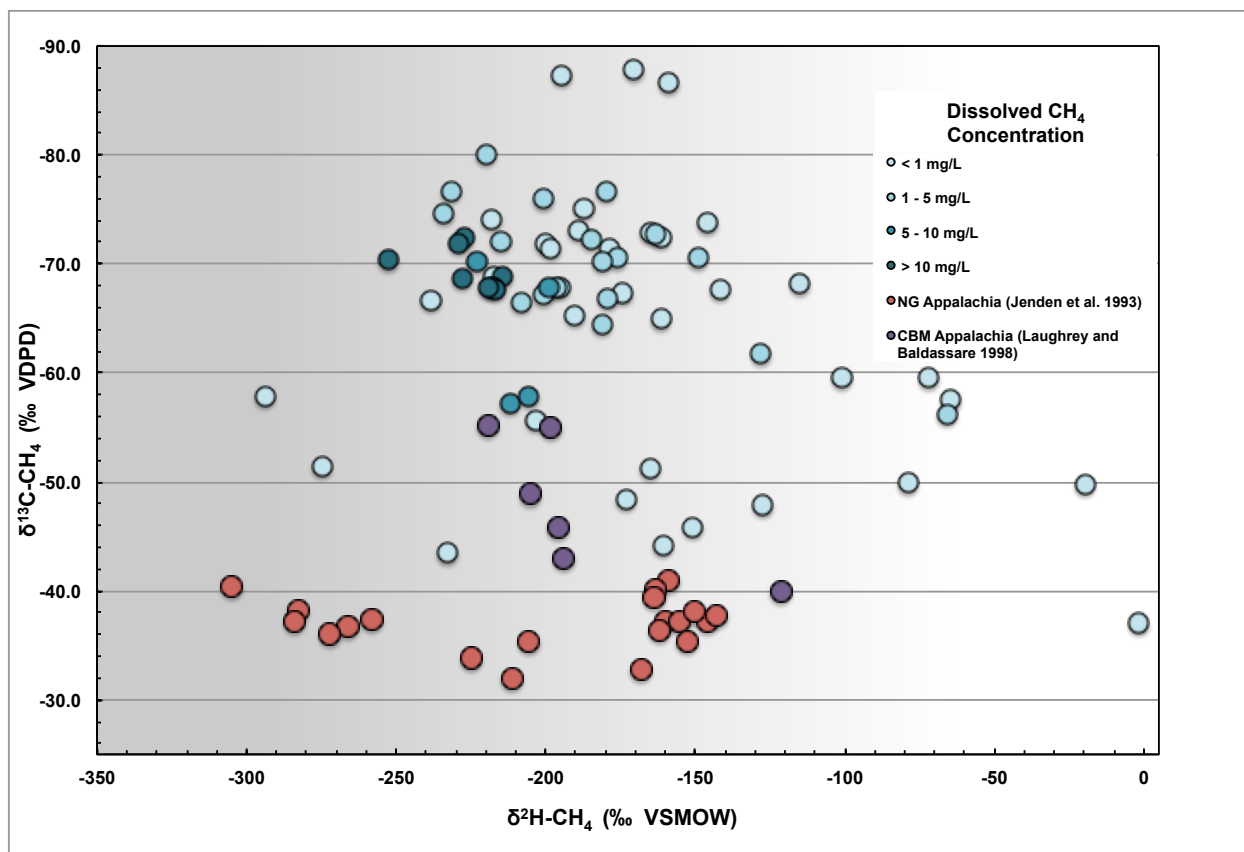


Figure 3. Carbon and hydrogen stable isotopic composition of CH₄ in groundwater (shown as symbols with a turquoise color scale). Symbol shade represents the relative dissolved CH₄ concentration, with higher concentrations represented by darker shades. Purple symbols represent the stable isotopic composition of coalbed methane in Appalachia from Laughrey and Baldassare (1998), while red data points characterize the stable isotopic composition of Appalachian natural gas samples (Jenden et al., 1993).

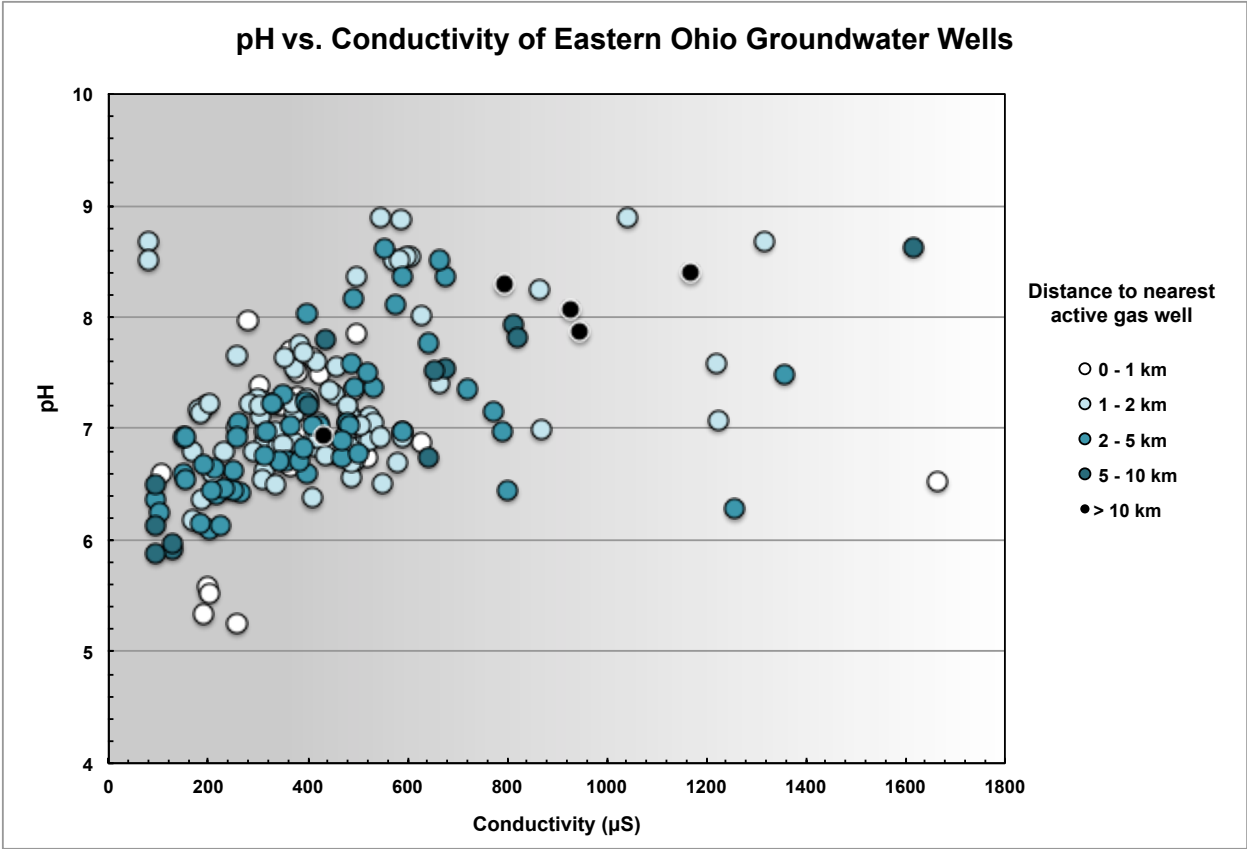


Figure 4. *pH and conductivity (in microsiemens) of groundwater sites. Symbol shade represents distance to the nearest active gas well in kilometers, with lighter shades denoting a closer proximity to active wells.*

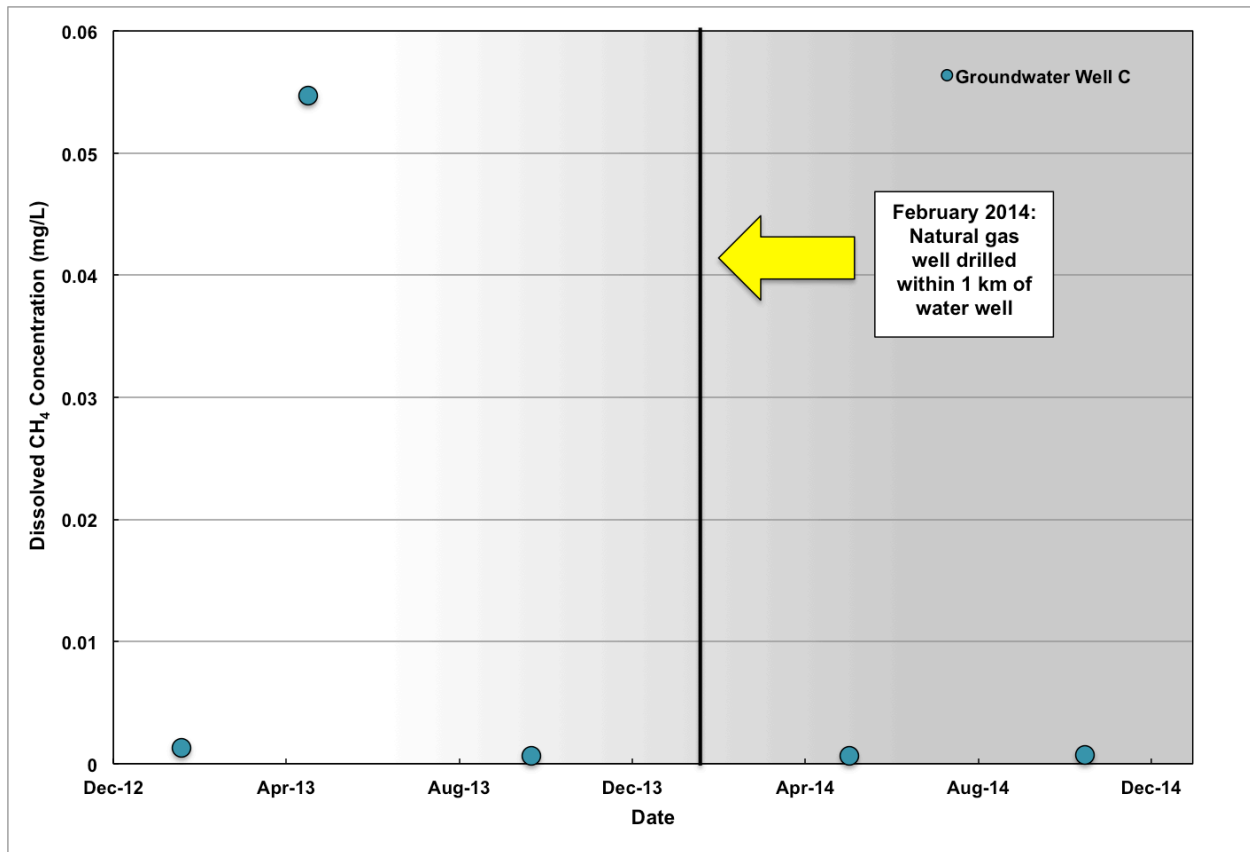


Figure 5. *The dissolved CH₄ concentration of groundwater well “C” in Carroll County, Ohio over two years of monitoring. In January 2013, a natural gas well was drilled within 1 kilometer of the water well, but no significant changes in groundwater CH₄ concentration were observed. Variability in CH₄ concentrations prior to nearby gas drilling is likely due to exposure of groundwater to air.*

Figure 6.

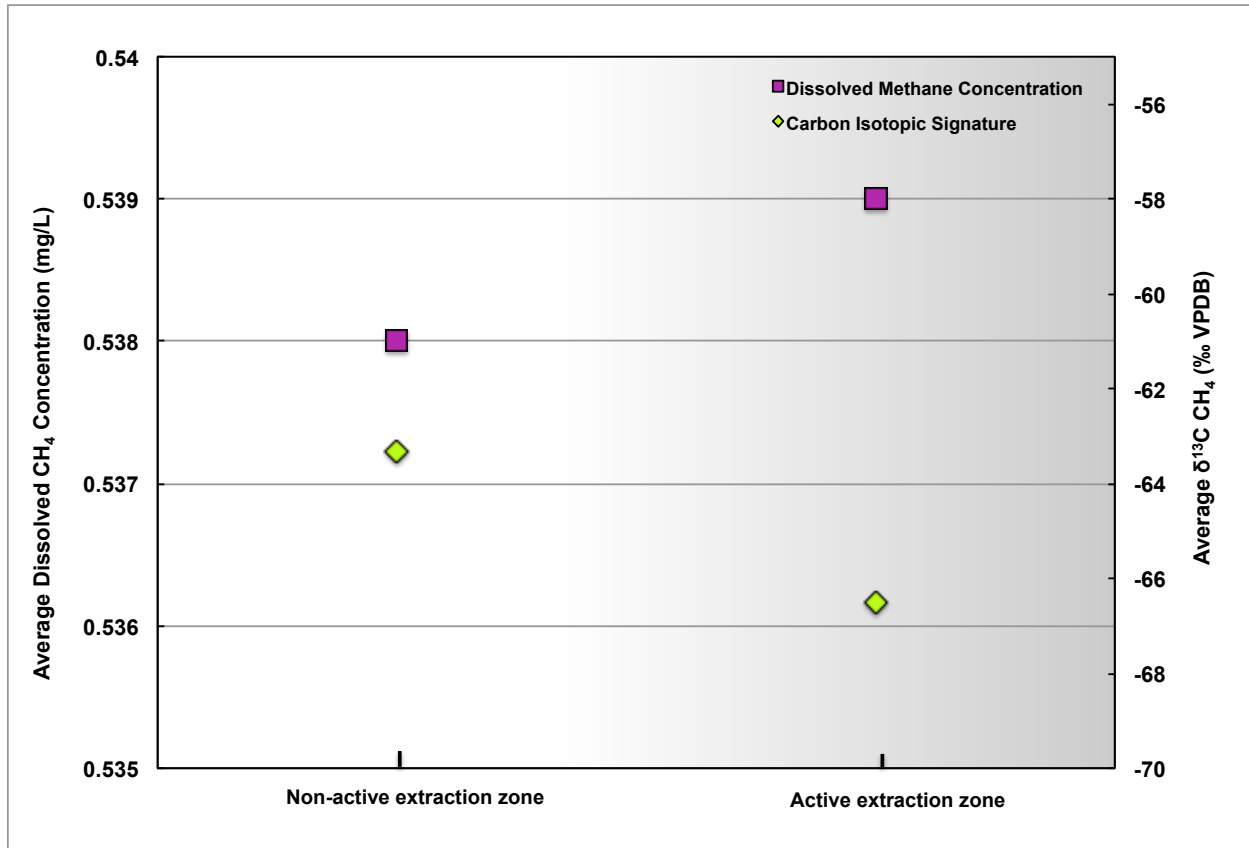


Figure 6. The average dissolved CH₄ concentration and average δ¹³C-CH₄ value of groundwater monitoring sites in active and non-active extraction zones of the study area. A water well within an active extraction zone is defined as being within 1 kilometer of an active natural gas well. Three groundwater samples containing dissolved CH₄ values consistently greater than 10 mg/L were not included in the average dissolved CH₄ calculation.

References

1. Kerr RA (2010) Natural gas from shale bursts onto the scene. *Science* 328 (5986): 1624-1626. doi:10.1126/science.328.5986.1624
2. U.S. Energy Information Administration (2014) Shale gas provides largest share of U.S. natural gas production in 2013. *Today in Energy* 2014(1/30): 1
<http://www.eia.gov/todayinenergy/detail.cfm?id=18951>
3. Howarth RW, Santoro R & Ingraffea A (2011) Methane and the greenhouse-gas footprint of natural gas from shale formations. *Climatic Change* 106(4): 679-690.
doi:10.1007/s10584-011-0061-5
4. Townsend-Small A, Marrero JE, Lyon DR, Simpson IJ, Meinardi S, & Blake DR (2015) Integrating source apportionment tracers into a bottom-up inventory of methane emissions in the Barnett Shale hydraulic fracturing region. *Environ. Sci. Technol.* 49(13): 8147-8182. doi:10.1021/acs.est.5b00057
5. Kargbo DM, Wilhelm RG & Campbell DJ (2010) Natural gas plays in the Marcellus Shale: Challenges and potential opportunities. *Environ. Sci. Technol.* 44(15): 5679-5684.
doi:10.1021/es903811p
6. Pétron G, Frost G, Miller BR, Hirsch AI, Montzka SA, Karion A, Trainer M, Sweeney C, Andrews AE, Miller L, Kofler J, Bar-Ilan A, Dlugokencky EJ, Patrick L, Moore Jr. CT, Ryerson TB, Siso C, Kolodzey W, Lang PM, Conway T, Novelli P, Masarie K, Hall B, Guenther D, Kitzis D, Miller J, Welsh D, Wolfe D, Neff W, & Tans P (2012) Hydrocarbon emissions characterization in the Colorado Front Range: A pilot study. *J. Geophys. Res.* 117 (D4): DO4304. doi:10.1029/2011JD016360

7. Revesz KM, Breen KJ, Baldassare AJ & Burruss RC (2010) Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania. *Appl. Geochem.* 25(12): 1845-1859.
doi:10.1016/j.apgeochem.2010.09.011
8. Brantley SL, Yoxtheimer D, Arjmand S, Grieve P, Vidic R, Pollak J, Llewellyn GT, Abad J, Simon C (2014) Water resource impacts during unconventional shale gas development: The Pennsylvania experience. *Int. J. Coal Geol.* 126: 140-156.
doi:10.1016/j.coal.2013.12.017
9. Darrah TH, Vengosh A, Jackson RB, Warner N & Poreda RJ (2014) Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales. *Pro. Natl. Acad. Sci. USA* 111(47): 14076-140811.
doi:10.1073/pnas.1322107111
10. Simon JA (2014) Editor's perspective – an update on the hydraulic fracturing groundwater contamination debate. *Remediation* 24(2): 1-9. doi:10.1002/rem.21390
11. Vengosh A, Jackson RB, Warner N, Darrah TH & Kondash A (2014) A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environ. Sci. Technol.* 48(15): 8334-8348. doi: 10.1021/es405118y
12. Eltschlager KK, Hawkins JW, Ehler WC & Baldassare F (2011) Technical measures for the investigation and mitigation of fugitive methane hazards in areas of coal mining. *US Dept. of the Interior, Office of Surface Mining Reclamation and Enforcement, Pittsburgh:* 1-124.

13. Wilson JM & VanBriesen JM (2012) Oil and gas produced water management and surface drinking water sources in Pennsylvania. *Environ. Pract.* 14(4): 288-300.
<http://dx.doi.org/10.1017/S1466046612000427>
14. Ohio Division of Oil and Gas Resources Management (4/4/2015) Utica/Point pleasant cumulative permitting activity. *Shale Development & Activity* 2015(5/11): 100.
15. Osborn SG, Vengosh A, Warner NR & Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Pro. Natl. Acad. Sci. USA* 108(20): 8172-8176. doi:10.1073/pnas.1100682108
16. Jackson RB, Vengosh A, Darrah TH, Warner NR, Down A, Poreda RJ, Osborn SG, Zhao K, Karr JD (2013) Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. *Pro. Natl. Acad. Sci. USA* 110(28): 11250-11255. doi:doi:10.1073/pnas.1221635110
17. Ohio Division of Soil and Water Resources (2015) Water well log search by county, township, and road, or log number. *Ohio Department of Natural Resources, Division of Soil and Water Resources* 2015(02/18).
18. Ohio Division of Geological Survey (2006) Bedrock geologic map of Ohio. *Ohio Department of Natural Resources, Division of Geological Survey Map BG-1* 1:2,000,000(Ohio, U.S.A.): 2 p.
19. Paulik LB, Donald CE, Smith BW, Tidwell LG, Hobbie KA, Kincl L, Haynes EN, Anderson KA (2015) Impact of natural gas extraction on PAH levels in ambient air. *Environ. Sci. Technol.* 49(8): 5203-5210. doi: 10.1021/es506095e
20. Ioffe BV, Vittenburg AG & Manatov IA (1984) *Head-space analysis and related methods in gas chromatography*, (John Wiley & Sons, Inc., New York), pp 304.

21. Yamamoto S, Alcauskas JB & Crozier TE (2002) The solubility of methane in distilled water and seawater. *J. Chem. Eng. Data* 21(1): 78-80. doi: 10.1021/je60068a029
22. Beaulieu JJ, Smolenski, RL, Nietch CT, Townsend-Small A, & Elovitz MS(2014) High methane emissions from a midlatitude reservoir draining an agricultural watershed. *Environ. Sci. Technol.* 48(19): 111000-11108. doi: 10.1021/es501871g
23. Tyler SC, Rice AL, & Ajie HO (2007) Stable isotope ratios in atmospheric CH₄: Implications for seasonal sources and sinks. *J. Geophys. Res.* 112(D3): D03303. doi:10.1029/2006JD007231.
24. Townsend-Small A, Stanley TC, Pataki DE, Xiaomei X & Christensen LE (2012) Isotopic measurements of atmospheric methane in Los Angeles, California, USA: Influence of “fugitive” fossil fuel emissions. *J Geophys Res Atmos* 117(D7): D07308. doi: 10.1029/2011JD016826
25. Yarnes C (2013) $\delta^{13}\text{C}$ and $\delta^2\text{H}$ measurement of methane from ecological and geological sources by gas chromatography/combustion/pyrolysis isotope-ratio mass spectrometry. *Rapid Commun. Mass Spectrom.* 27(9): 1036-1044. doi: 10.1002/rcm.6549
26. Xu X, Trumbore SE, Zheng S, Southon JR, McDuffee KE, Luttgen M, & Lui JC (2007) Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: Reducing background and attaining high precision. *Nucl. Instrum. Meth. B* 259(1): 320-329. doi:10.1016/j.nimb.2007.01.175
27. Pack MA, Xu X, Lupascu M, Kessler JD & Czimeczik CI (2014) A rapid method for preparing low volume CH₄ and CO₂ gas samples for ¹⁴C AMS analysis. *Org. Geochem.* 78: 89-98. doi:10.1016/j.orggeochem.2014.10.010

28. Stuvier M & Polach HA (1977) Discussion: Reporting of ^{14}C data. *Radiocarbon* 19: 355-363.
29. Ohio Division of Geological Survey (2004) Oil and gas fields map of Ohio. *Ohio Department of Natural Resources, Division of Geological Survey Map PG-1* 1:2,000,000.(Ohio, U.S.A.): 2 p.
30. Beeman RA & Sulflita JM (1991) Environmental factors influencing methanogenesis in a shallow anoxic aquifer: A field and laboratory study. *J. Ind. Microbiol.* 5(1): 45-58. DOI?
31. Zhang C, Grossman EL & Ammerman JW (1998) Factors influencing methane distribution in Texas ground water. *Ground Water* 36(1): 58-66. doi: 10.1111/j.1745-6584.1998.tb01065.
32. Heisig PM & Scott T (2013) Occurrence of methane in groundwater of south-central New York state, 2012 -- systematic evaluation of a glaciated region by hydrogeologic setting. *U.S. Geological Survey Scientific Investigations Report 2013-5190* : 1-32. <http://dx.doi.org/10.3133/sir20135190>.
33. Molofsky LJ, Connor JA, Wylie AS, Wagner T & Farhat SK (2013) Evaluation of methane sources in groundwater in northeastern Pennsylvania. *Ground Water* 51(3): 333-349. doi: 10.1111/gwat.12056
34. Whiticar MJ, Faber E & Schoell M (1986) Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation--isotope evidence. *Geochim. Cosmochim. Acta* 50(5): 693-709. doi:10.1016/0016-7037(86)90346-7
35. Schoell M (1980) The hydrogen and carbon isotopic composition of methane from natural gases of various origins. *Geochim. Cosmochim. Acta* 44(5): 649-661. doi:10.1016/0016-7037(80)90155-6

36. Jenden PD, Drazan DJ & Kaplan IR (1993) Mixing of thermogenic natural gases in northern Appalachian basin. *AAPG Bull.* 77(6): 980-998.
37. Laughrey CD & Baldassare FJ (1998) Geochemistry and origin of some natural gases in the Plateau province, central Appalachian basin, Pennsylvania and Ohio. *AAPG Bull.* 82(2): 317-335.
38. Baldassare FJ, McCaffrey MA & Harper JA (2014) A geochemical context for stray gas investigations in the northern Appalachian basin: Implications of analyses of natural gases from Neogene-through Devonian-age strata. *AAPG Bull.* 98(2): 341-372. doi: 10.1306/06111312178
39. Stevens CM & Rust FE (1982) The carbon isotopic composition of atmospheric methane. *J. Geophys. Res.* 87(C7): 4879-4882. doi: 10.1029/1998GB900006
40. Barker JF & Fritz P (1981) The occurrence and origin of methane in some groundwater flow systems. *Can. J. Earth Sci.* 18(12): 1802-1816. doi: 10.1139/e81-168
41. Clayton JL (1998) Geochemistry of coalbed gas -- A review. *Int. J. Coal Geol.* 35: 159-173. doi: 10.1016/S0166-5162(97)00017-7
42. Rice DD & Claypool GE (1981) Generation, accumulation, and resource potential of biogenic gas. *AAPG Bull.* 65(1): 5-25
43. Martini AM, Walter LM, Ku TCW, Budai JM, McIntosh JC, & Schoell M(2003) Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian shale gas play, Michigan basin. *AAPG Bull.* 87(8): 1355-1375. doi: 10.1306/031903200184
44. Rice DD (1992) Controls, habitat, and resource potential of ancient bacterial gas. *Bacterial Gas*: 91-118.

45. Scott AR, Kaiser WR & Ayers Jr. WB (1994) Thermogenic and secondary biogenic gases, San Juan basin, Colorado and New Mexico -- implications for coalbed gas producibility. *AAPG Bull.* 78(8): 1186-1209.
46. Caulton DR, *et al* (2014) Toward a better understanding and quantification of methane emissions from shale gas development. *Pro. Natl. Acad. Sci. USA* 111(17): 6237-6242.
47. Smith JW & Pallasser RJ (1996) Microbial origin of Australian coalbed methane. *AAPG Bull* 80(6): 891-897. doi: 10.1073/pnas.1316546111.
48. Martini AM, Walter LM, Budai JM, Ku TCW, Kaiser CJ, & Schoell M (1998) Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim shale, Michigan basin, USA. *Geochim. Cosmochim. Acta* 62(10): 1699-1720. doi: 10.1016/S0016-7037(98)00090-8
49. Schlegel ME, McIntosh JC, Bates BL & Kirk MF (2011) Comparison of fluid geochemistry and microbiology of multiple organic-rich reservoirs in the Illinois basin, USA: Evidence for controls on methanogenesis and microbial transport. *Geochim. Cosmochim. Acta* 75(7): 1903-1919. doi:10.1016/j.gca.2011.01.016
50. Aravena R, Wassenaar LI & Plummer LN (1995) Estimating ¹⁴C groundwater ages in a methanogenic aquifer. *Water Resour. Res.* 31(9): 2307-2317. doi: 10.1029/95WR01271
51. Levin I & Hesshaimer V (2000) Radiocarbon – a unique tracer of global carbon cycle dynamics. *Radiocarbon* 42(1): 69-80.
52. Garnett MH, Hardie SML, Murray C & Billett MF (2013) Radiocarbon dating of methane and carbon dioxide evaded from a temperate peatland stream. *Biogeochemistry* 14(1-3): 213-223.

53. Llewellyn GT, Dorman F, Westland JL, Yoxtheimer D, Grieve P, Sowers T, Humston-Fulmer E, & Brantley SL (2015) Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development. *Pro. Natl. Acad. Sci. USA* 112(20): 6325–6320. doi: 10.1073/pnas.1420279112
54. Hildebrand ZL, Carlton Jr. DD, Fontenot BE, Meik JM, Walton JL, Taylor JT, Thacker JB, Korlie S, Shelor CP, Henderson D, Kadjo AF, Roelke CE, Hudak PF, Burton T, Rifai HS, & Schug KA (2015) A comprehensive analysis of groundwater quality in the Barnett Shale region. *Environ. Sci. Technol.* 49(13): 8254-8262. doi: 10.1021/acs.est.5b01526
55. Vidic RV, Brantley SL, Vandenbossche JM, Yoxtheimer D & Abad JD (2013) Impact of shale gas development on regional water quality. *Science* 340(6134): 1235009. doi: 10.1126/science.1235009
56. Griffith MB (2014) Natural variation and current reference for specific conductivity and major ions in wadeable streams of the conterminous USA. *BioOne* 33(1): 1-17. <http://dx.doi.org/10.1086/674704>
57. Gray, NF (1996) Field assessment of acid mine drainage contamination in surface and groundwater. *Environ. Geol.* 27(4): 358-361. doi: 10.1007/BF00766705