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Monitoring concentration and isotopic composition of methane in groundwater in the Utica Shale hydraulic fracturing region of Ohio

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Abstract Degradation of groundwater quality is a primary public concern in rural hydraulic fracturing areas. Previous studies have shown that natural gas methane (CH_4) is present in groundwater near shale gas wells in the Marcellus Shale of Pennsylvania, but did not have pre-drilling baseline measurements. Here, we present the results of a free public water testing program in the Utica Shale of Ohio, where we measured CH_4 concentration, CH_4 stable isotopic composition, and pH and conductivity along temporal and spatial gradients of hydraulic fracturing activity. Dissolved CH_4 ranged from 0.2 μg/L to 25 mg/L, and stable isotopic measurements indicated a predominantly biogenic carbonate reduction CH_4 source. Radiocarbon dating of CH_4 in combination with stable isotopic analysis of CH_4 in three samples indicated that fossil C substrates are the source of CH_4 in groundwater, with one ^{14}C date indicative of modern biogenic carbonate reduction. We found no relationship between CH_4 concentration or source in groundwater and proximity to active gas well sites. No significant changes in CH_4 concentration, CH_4 isotopic composition, pH, or conductivity in water wells were observed during the study period. These data indicate that high levels of biogenic CH_4 can be present in groundwater wells independent of hydraulic fracturing activity and affirm the need for isotopic or other fingerprinting techniques for CH_4 source identification. Continued monitoring of private drinking water wells is critical to ensure that groundwater quality is not altered as hydraulic fracturing activity continues in the region.

Keywords Hydraulic fracturing · Groundwater · Methane · Natural gas · Radiocarbon · Stable isotopes

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Introduction

Oil and natural gas extraction from unconventional shale reservoirs has intensified, making the United States the largest producer of oil and natural gas globally (Kerr 2010; EIA 2016). Although shale gas presents potential for a domestic, cleaner-burning fuel source in the midst of regulatory mandates for decreasing use of coal, environmental and health questions have been raised about horizontal drilling and hydraulic fracturing ("fracking"), including uncertainties of methane (CH_4) emission rates (Howarth et al. 2011; Townsend-Small et al. 2015, 2016c), increased seismic activity (Skoumal et al. 2015; Kozlowska et al. 2018), and toxic air

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emissions (Marrero et al. 2016). A primary public concern of expanding shale gas development is groundwater contamination by natural gas and/or fracking fluid in production areas (Revesz et al. 2010; Brantley et al. 2014; Darrah et al. 2014; Vengosh et al. 2014; USEPA 2016). Methane degassing from well and tap may combust at high concentrations and indicate the presence of toxic chemicals from natural gas and/or oil extraction (Department of the Interior 2001; Wilson and VanBriesen 2012; Llewellyn et al. 2015).

In the Middle Ordovician Utica Shale, over 2000 horizontal wells have been drilled to depths of up to 3.6 km at over 2500 permitted sites in Ohio since 2011 (Ohio Department of Natural Resources (ODNR) 2017). Many residents in this rural region rely on infrequently monitored private groundwater wells. Studies in the adjacent Devonian Marcellus Shale region of Pennsylvania found elevated CH_4 levels with an isotopic and alkane signature consistent with that of natural gas in groundwater wells within 1 km of active gas wells (Osborn et al. 2011; Jackson et al. 2013) linked to failed gas well casings (Darrah et al. 2014), although these studies had not analyzed groundwater prior to shale gas development. A later study indicated variously high levels of CH_4 in groundwater in the region before fracking activity began, but did not present CH_4 source indicators (Siegel et al. 2015). Other studies have also shown that produced water from oil and gas wells, including conventional wells, in the Marcellus Shale drilling region of Pennsylvania is very high in salinity (Akob et al. 2015; Rowan et al. 2015). Groundwater affected by hydraulic fracturing flowback water in the Marcellus Shale region would be expected to be lower in pH as compared to unaffected groundwater due to the use of hydrochloric acid, citric acid, and/or thioglycolic acid in the fracturing process (Vidic et al. 2013).

We made measurements of groundwater in the Utica Shale drilling region of Ohio over a 4-year period of increasing shale gas development (ODNR 2017) (Fig. 1). These data were collected during a free groundwater testing program offered to residents of this area by University of Cincinnati from 2012 to 2015. We present a dataset of dissolved CH_4 concentrations, $\delta^{13}C$-CH_4, $\delta^{2}H$-CH_4, pH, and electrical conductivity in shallow groundwater wells in this area, with a subset of samples ($n = 4$) also analyzed for $\Delta^{14}C$-CH_4. We hypothesized that CH_4 concentration would increase as the number of shale gas wells in the area increased, with the isotopic composition of CH_4 reflecting an increasingly fossil fuel derived natural gas source (Osborn et al. 2011; Jackson et al. 2013), and that pH of groundwater would decrease and electrical conductivity would increase due to the presence of acidic, salty hydraulic fracturing fluids in groundwater. We also predicted that groundwater wells located within 1 km of active shale gas wells would have elevated levels of dissolved CH_4 with isotopic ratios reflecting a natural gas source (e.g., Osborn et al. 2011; Jackson et al. 2013), and that groundwater within this "active zone" would have decreased pH and increased electrical conductivity.

Materials and methods

Study area The majority of groundwater monitoring in our study took place in Carroll County, eastern Ohio (Fig. 1). 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 (Ohio Division of Geological Survey 2003). The study began in January 2012, one year after the first hydraulic fracturing permit was issued for Carroll County (ODNR 2017). A lack of groundwater quality data existed in the region due to the recent start of unconventional gas extraction in Ohio, and at the time the study was initiated, Carroll County had been granted the greatest number of hydraulic fracturing permits in the state (ODNR 2017). At the onset of our study in January 2012, a total of 115 drilling permits had been issued in Ohio; by the end of February 2015, almost 1600 drilling permits had been issued (ODNR 2017). The study area also has a long legacy of conventional oil and gas extraction, with a high density of older active and abandoned conventional wells throughout the study area (ODNR 2018). There are no coalbed CH_4 wells in the study area.

Sampling methods We collected 180 groundwater samples in Eastern Ohio from January 2012 to February 2015 (Fig. 1). Of these samples, 118 were collected from 24 drinking water wells in Carroll, Harrison, and Stark counties from two to eight times over the study period, depending on homeowner availability and interest (dark blue triangles in Fig. 1). Other groundwater wells were sampled only once (light blue circles in

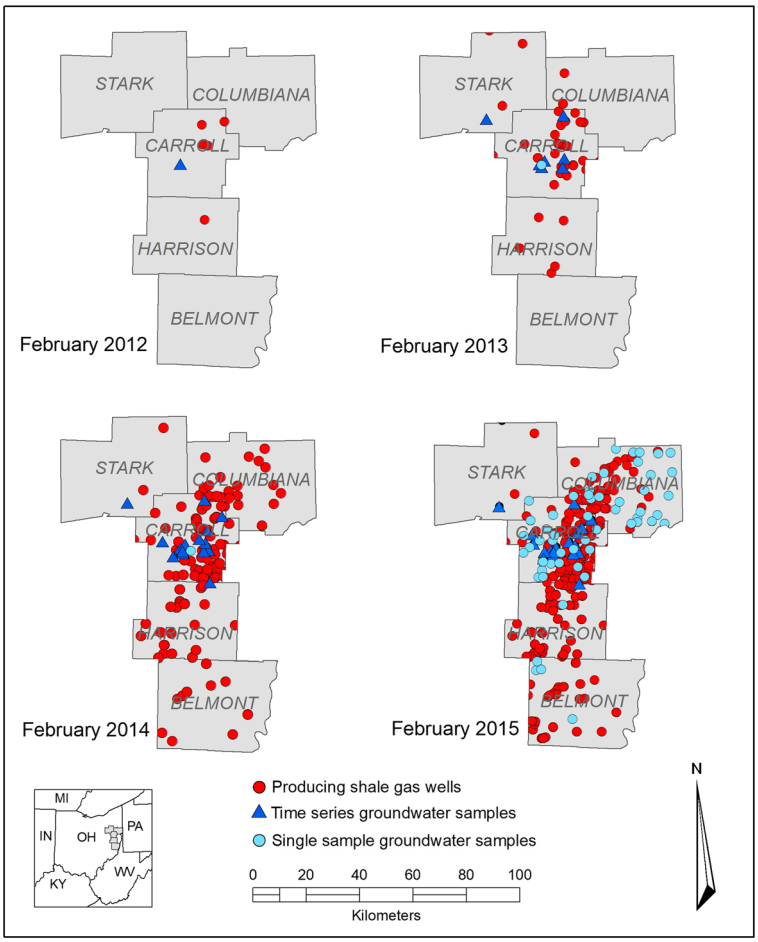

Fig. 1 Time-series map of Ohio counties where sampling occurred. Red circles are active natural gas wells. Blue diamonds are sites where time series groundwater samples were taken and light blue circles represent sites where single sample groundwater measurements were made. Groundwater sample locations are noted when samples were taken between the years noted in each map. There was a large increase in active natural gas wells from 2013 to 2014

Fig. 1), mostly as part of a sampling campaign in the broader area in May 2014, including Columbiana and Belmont counties, where increased hydraulic fracturing permitting and drilling was occurring at the time.

Sampling sites were chosen based on landowner interest in the study; all participation was voluntary. Sampling was exclusively conducted by the study's authors and not by homeowners. Wells were purged to remove stagnant water before sampling and measurement of pH, conductivity, and temperature (Yellow Springs Instruments Model 63, Yellow Springs, OH). All samples were taken prior to any form of water treatment or residence time in storage tanks and as close to the well as possible, typically from outdoor pumps, basement water pipes, garden hose spigots, 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. Water samples were preserved with 1-mL aliquots of saturated mercuric chloride ($HgCl_2$) solution, then capped with gray butyl rubber septa and sealed with aluminum crimps. Samples for radiocarbon analysis were collected in clean 1-L 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. This sampling technique may lead to slight underestimation of CH_4 concentration due to outgassing between sample collection and preservation and during the collection process, particularly in high concentration water samples.

We collected several samples of CH_4 sources in Carroll County for comparison to CH_4 in groundwater. We took one air sample downwind of a producing shale gas well and one sample of cow breath from a dairy farm in 5-L pre-evacuated stainless steel canisters filled to ~ 202 kPa pressure with an oil-free bellows pump. These

air samples were analyzed for CH_4 concentration and stable isotope composition as below, and the isotopic composition was corrected for the presence of background air as described in Townsend-Small et al. (2012). We further determined the isotopic composition of CH_4 from an abandoned conventional gas well that was sampled from a groundwater well that had been drilled into an abandoned conventional gas well shaft. This sample was taken in the same manner as other groundwater samples.

Sample analysis Sample analytes were chosen to limit the cost of the study and to keep the study running longer; therefore, we mostly chose analyses that could be done in the field or in-house at the University of Cincinnati. Dissolved CH_4 concentrations from water samples were acquired using headspace equilibrium methods at ambient temperature and pressure (Yamamoto et al. 1976; Beaulieu et al. 2014). A 30-mL headspace of ultra high-purity N_2 gas was inserted into each water sample, while another inserted needle and syringe captured the equally displaced volume of water. Samples were then agitated on a vortex shaker for 1 min and rested 5 min 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 two-way stopcock and 23-gauge needle (Ioffe and Vitenburg 1984). Extracted gas was then transferred to evacuated 20-mL clean dry glass vials sealed with butyl rubber septa and aluminum crimps, and containing silica gel desiccant beads to absorb water vapor.

The vials were then loaded into a GC-PAL AOC 5000 autosampler, and dissolved CH_4 concentrations were measured with an interfaced Shimadzu Scientific Instruments GC-2014 greenhouse gas analyzer for measurement of CH_4 concentration. Calibrated CH_4 standards were also analyzed alongside unknown samples. Standards were purchased from various suppliers and calibrated with a primary NOAA ESRL greenhouse gas standard. The standards ranged in concentration from below-ambient atmospheric CH_4 levels (1.5 ppm by volume) to 100,000 ppm CH_4, bracketing the CH_4 concentrations of unknowns. Headspace concentrations were used to calculate the original dissolved gas concentrations of sampled water using temperature-specific Bunsen solubility coefficients (Yamamoto et al. 1976; Townsend-Small et al. 2016a). The detection limit of this method is approximately 2.5 nmol CH_4/L. Variation in final dissolved CH_4 concentrations is approximately 6% using the headspace extraction method in our laboratory (Beaulieu et al. 2014).

The headspace equilibrium methods described above were also performed to acquire gas samples for stable isotope analysis of CH_4. Headspace gas samples were extracted and transferred to evacuated 12-mL glass vials (Exetainers®; Labco Ltd., Buckinghamshire, UK) containing silica gel desiccant beads. Samples were then analyzed for δ^{13}C-CH_4 and δ^{2}H-CH_4 at the University of Cincinnati via isotope ratio mass spectrometry (Yarnes 2013). Isotope standard concentrations were matched to sample concentrations to avoid linearity issues with the instrument. Stable isotope ratios were calibrated with standards from Isometrics, Inc. (Victoria, British Columbia) that were cross-calibrated with standards from the University of California, Irvine (Tyler et al. 2007; Townsend-Small et al. 2012) and the University of California, Davis (Yarnes 2013). Stable isotope ratios are expressed in standard delta notation with respect to the Vienna Pee Dee Belemnite (VPDB, for ^{13}C) and Vienna Standard Mean Ocean Water (VSMOW, for ^{2}H) standards. Samples were calibrated with a two-, three-, or four-point curve using standards bracketing the isotopic composition of the samples and ranging in δ^{13}C-CH_4 and δ^{2}H-CH_4 from −66.2‰ to −28.0‰ and −247‰ to −156‰, respectively. The reproducibility of the published method is ±0.2‰ and ±4‰ for δ^{13}C-CH_4 and δ^{2}H-CH_4 (Yarnes 2013), and this reproducibility is met or exceeded with daily analysis of multiple isotopic standards. Not all water samples analyzed for CH_4 concentrations were also analyzed for CH_4 isotopes.

Four groundwater samples with dissolved CH_4 concentrations above 1 mg/L were sent to the University of California–Irvine Keck Carbon Cycle AMS Facility for analysis of radiocarbon in CH_4. A headspace extraction technique was used to obtain CH_4 from these samples. The extracted gas samples were purified through a low-pressure zero air flow-through vacuum line and then combusted to produce CO_2 from CH_4. CO_2 samples were converted to graphite for ^{14}C analysis using the sealed tube zinc graphitization method (Xu et al. 2007; Pack et al. 2015). Radiocarbon contents are presented as Δ^{14}C in units of per mille, as fraction modern C (FM), and as conventional carbon age according to the

protocol of Stuiver and Polach (1977). Radiocarbon ages are calculated according to the following equations:

$$\text{Fraction Modern} = \frac{\frac{14C}{12C}\Big]sample, -25}{0.95\frac{14C}{12C}\Big]OX1, -19.}$$

Where "modern" is defined as 1950; the numerator refers to the $^{14}C/^{12}C$ ratio of the sample, corrected for a carbon stable isotope fractionation of − 25‰; and the denominator refers to the $^{14}C/^{12}C$ ratio of the standard, OX1 or oxalic acid, the primary modern radiocarbon standard used by the National Institute of Standards and Technology, which had an activity of 95% in the year 1950, and corrected for its $\delta^{13}C$ value of − 19‰ (Stuiver and Polach 1977). The Fraction Modern (FM) is used to calculate the radiocarbon age using the following equation:

$$^{14}\text{C Age} = -(1/\lambda_{14}) \times \ln(\text{FM}) = -8033 \times \ln(\text{FM})$$

Sample preparation backgrounds were subtracted based on measurements of ^{14}C-free coal. The precision of $\Delta^{14}C$ analysis is about 2‰ for modern samples based on long-term measurements of secondary standards.

Analytical framework The time-series data provide opportunities to evaluate changes in water well properties through time (CH_4 concentration, $\delta^{13}C$-CH_4, pH, conductivity). We evaluated these relationships using separate Pearson correlation coefficients between water well properties and the number of days between samples. In this context, 1.0 and − 1.0 indicate perfect positive or negative responses of a water well property with respect to time and 0.0 indicates a random association. Data collected to test for changes in water well properties as a function of distance to an active shale gas well were based on water wells sampled only once. Depending on the water well property, the data could be strongly right-skewed. To accommodate this, we used non-parametric Kruskal–Wallis analyses (Sokal and Rohlf 2012) to test for differences in CH_4 concentration and $\delta^{13}C$-CH_4 in water wells among different distance categories from the nearest active shale gas well (< 1 km, 1–2 km, 2–5 km, and more than 5 km). To report a measure of central tendency for these skewed distributions, we calculated bootstrapped estimates (run 10,000 times) of their median and 95% confidence intervals (CIs). The pH and conductivity datasets more closely approximated normal distributions. Thus, we tested for differences in pH and conductivity among distance categories using one-way ANOVA (Sokal and Rohlf 2012). Analyses were performed in R version 3.4.1 (R Core Team 2017).

Results

Figure 2 shows concentrations of CH_4 measured in groundwaters from sites visited two or more times throughout the study period ("time series sites"). Concentrations of dissolved CH_4 in time series sites ranged from 0.2 μg/L to 25.3 mg/L (Fig. 2). Of the 24 groundwater wells in the time series, three sites were measured for dissolved CH_4 concentration only twice: sites "A", "L", and "U" (Fig. 2), and, thus, do not have sufficient time series to evaluate secular correlations of CH_4 concentration. Of datasets with three or more observations, the majority showed negative Pearson correlations (CH_4 concentration decreasing with time). However, only four datasets had sample sizes greater than five and only the largest dataset (well "J", $n = 8$) had a significant correlation (cor = − 0.71, $p = 0.049$).

The $\delta^{13}C$-CH_4 of samples collected during the time series are shown in Fig. 3, plotted versus dissolved CH_4 concentration (symbols are coded according to site the same as in Fig. 2). Although we do not present the isotopic data in time series format, it is clear that isotopic composition was mostly similar in our sampling sites throughout the study, despite some variation in concentration (Fig. 3). Also shown in vertical lines in Fig. 3 are $\delta^{13}C$-CH_4 values for natural gas produced in the region from a shale gas well ($\delta^{13}C$-CH_4 = − 47.3‰; $\delta^{2}H$-CH_4 = − 171‰) and a conventional gas well ($\delta^{13}C$-CH_4 = − 41.3‰; $\delta^{2}H$-CH_4 = − 172‰). For comparison, our analysis of biogenic CH_4 from a cow's breath in Carroll County had a $\delta^{13}C$-CH_4 value of − 56.6‰ and a $\delta^{2}H$-CH_4 value of − 305‰. Finally, Fig. 3 also indicates radiocarbon content and ages of CH_4 in four water samples, in text next to each sample where radiocarbon age was measured. The complete record of CH_4 concentration and isotopic composition for these four samples is also shown in Table 1.

Results from samples from sites visited only once are shown in Fig. 4a and b. Figure 4a shows the relationship of dissolved CH_4 concentration in groundwater with

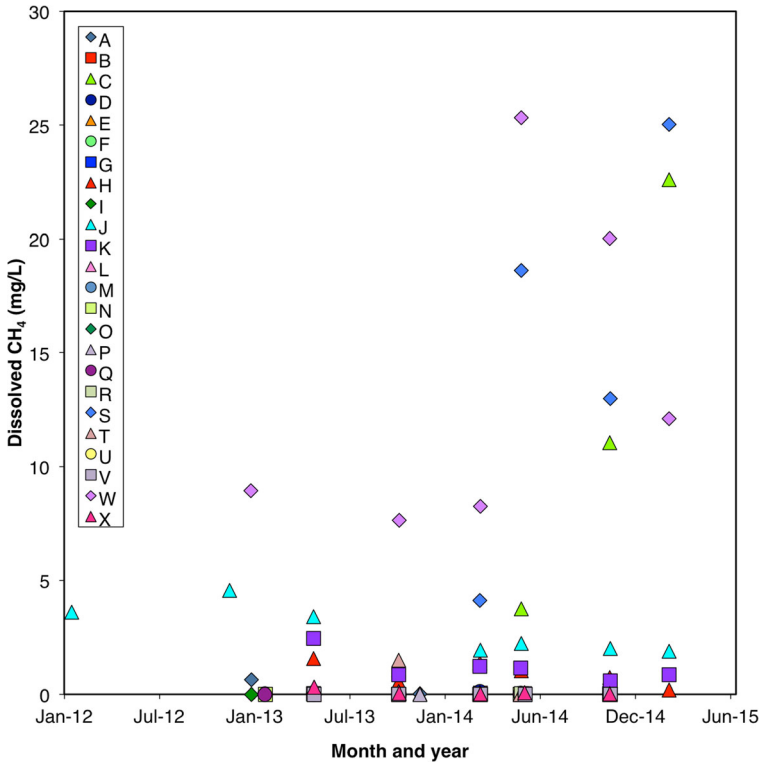

Fig. 2 CH_4 concentration in groundwater wells visited two or more times throughout the study, over a period of increasing shale gas permitting and drilling activity. Each symbol represents a different groundwater well

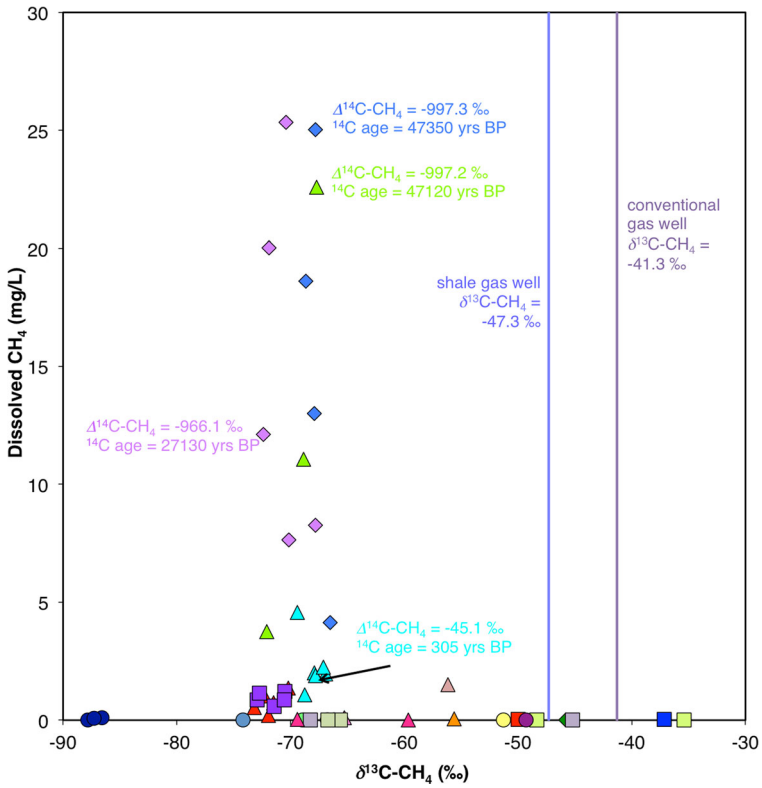

Fig. 3 Carbon stable isotopic composition of CH_4 versus CH_4 concentration in samples collected along the time series. Symbols are coded the same as in Fig. 2. Also included are measurements of the $\delta^{13}C$ of CH_4 from a shale gas well (−47.3‰) and a conventional gas well (−41.3‰) in the study area for comparison. The radiocarbon content of CH_4 ($\Delta^{14}C$-CH_4) and radiocarbon age (in years BP) of four water samples is also shown (Table 1)

Table 1 Summary of radiocarbon and stable isotope data of four groundwater samples containing elevated CH_4 concentrations (samples were taken in February 2015)

Sampling location	[CH_4] (mg/L)	δ^{13}C-CH_4 (‰)	δ^{2}H-CH_4 (‰)	Fraction modern C	Δ^{14}C-CH_4 (‰)	^{14}C Age (years BP)
Site W	12.1	− 72.4	− 227	0.0341	− 966.1	27,130
Site C	22.6	− 67.7	− 217	0.0028	− 997.2	47,120
Site S	25.0	− 67.8	− 219	0.0028	− 997.3	47,350
Site J	1.9	− 67.8	− 195	0.9625	− 45.1	305

distance from the nearest active shale gas well. A previous study in the Marcellus Shale drilling area of Pennsylvania defined an "active" shale gas drilling area as that with one or more producing horizontal wells within 1 km (Osborn et al. 2011). We found that the bootstrapped median and 95% CIs of CH_4 concentration within 1 km of an active shale gas well was 0.0010 (95% CI 0.00030, 0.0016) mg CH_4/L in contrast to 0.0042 (95% CI 0.00060, 0.012) CH_4/L farther than 1 km of an active shale gas well. There was no significant difference (compared using a Kruskal–Wallis test) of CH_4 concentrations 1 km, 1–2 km, 2–5 km, or more than 5 km from the nearest active shale gas well (Fig. 4a). Figure 4b shows the δ^{13}C-CH_4 of these samples, plotted versus their CH_4 concentration. The average δ^{13}C-CH_4 of samples with CH_4 concentrations less than 1 mg/L was − 60.9 (95% CI − 67.7, − 51.4), higher than those measured in samples with CH_4 concentrations higher than 1 mg/L (− 70.4; 95% CI − 76.7, − 61.15) (Wilcoxon test, $Z = 3.93$, $p < 0.05$). There was no significant difference (compared using a Kruskal–Wallis test) between average δ^{13}C-CH_4 values within 1 km, 1–2 km, 2–5 km, or more than 5 km from the nearest active shale gas well.

Figure 5 shows carbon and hydrogen stable isotopic compositions of all groundwater samples measured during this study, categorized according to whether they were sampled along the time series or only once, and also classified by dissolved CH_4 concentration. Also shown are isotope values for other CH_4 sources sampled during this study as well as CH_4 in clean background air (from Townsend-Small et al. 2016c). Finally, we show literature values for CH_4 source categories from Whiticar (1999).

Measurements of pH and conductivity from the time series sites are shown in Fig. 6a and b. No time-series sites with more than three measurements exhibited a significant change in pH over the study period (defined as a Pearson correlation with $p < 0.05$). We expected that pH would exhibit small natural temperature-related or other changes over seasonal and annual time scales, whereas we expected there would be fewer natural controls on CH_4 concentrations in groundwater. Three sites (D, J, and

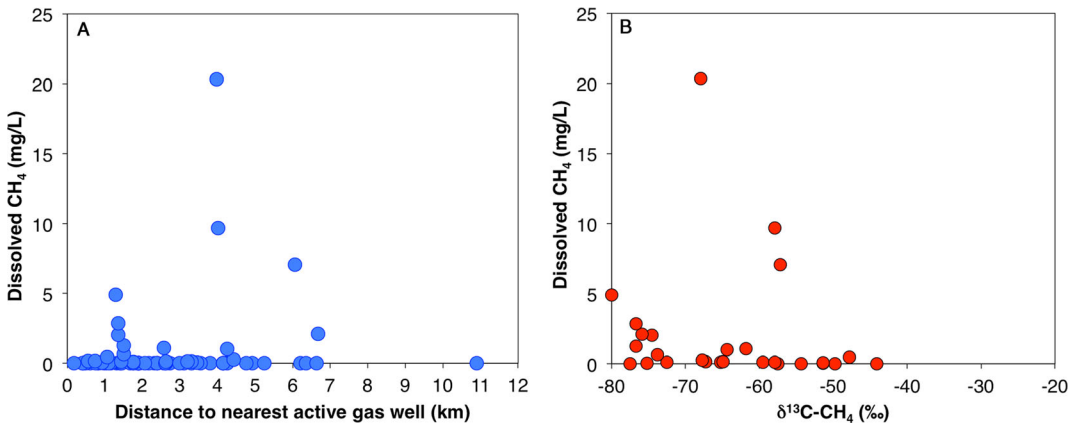

Fig. 4 **a** Relationship of dissolved CH_4 concentration with distance from the nearest active shale gas well in groundwater wells sampled only once. **b** Carbon stable isotopic composition of CH_4 in the same samples

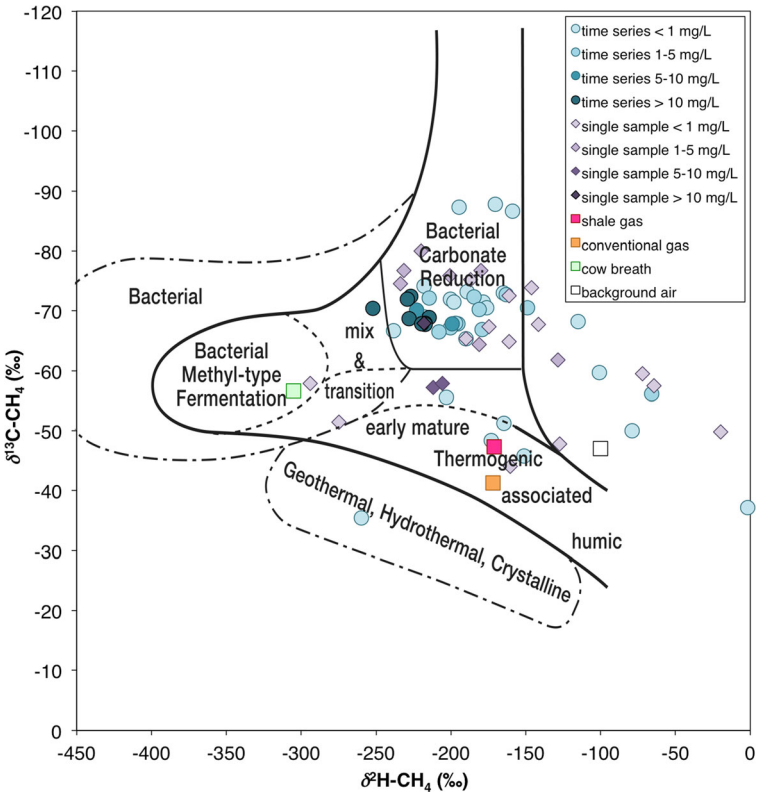

Fig. 5 Carbon and hydrogen isotopic compositions of groundwater samples taken during this study, along with isotopic composition of several sources (value for background air is from Townsend-Small et al. 2016c). Also shown are approximate literature values for different endmembers of CH_4 sources from Whiticar (1999). Groundwater samples are shown in blue circles, for time series samples, and purple diamonds, for single samples, with shading corresponding to sample CH_4 concentration, with increasing shading corresponding to increasing concentration

W) had a significant decrease in conductivity over the study period. Conductivity did not change significantly in any other regularly monitored well.

Data for pH and conductivity from sites sampled once are shown in Fig. 7a and b. The average (± standard deviation) pH of groundwater sampled within 1 km

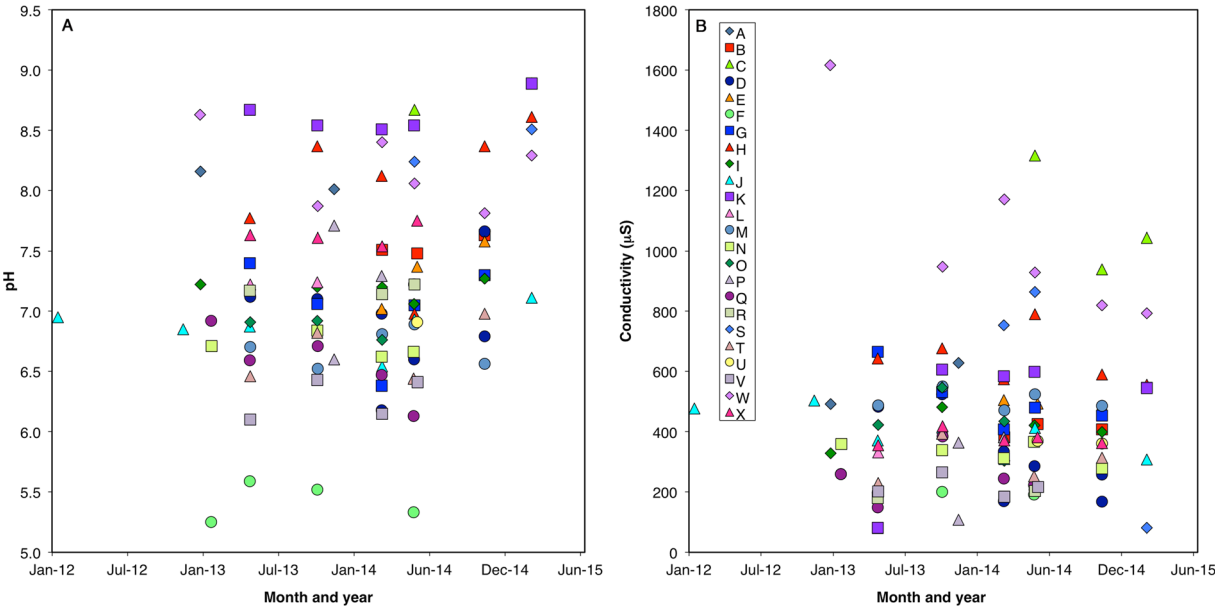

Fig. 6 pH and conductivity measurements from time series sites presented versus sampling date

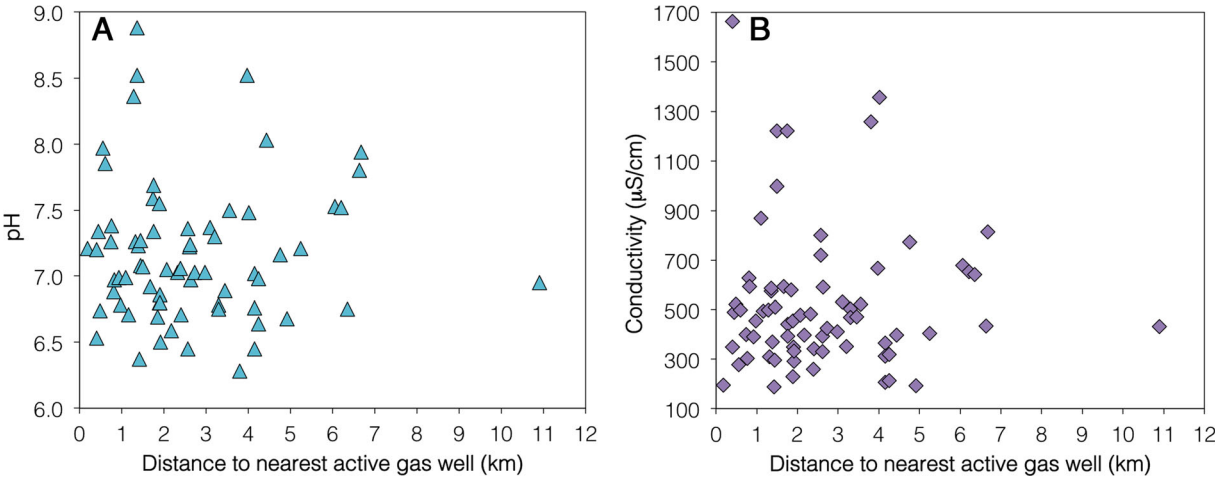

Fig. 7 pH and conductivity measurements from groundwater wells sampled only once, presented versus distance from the nearest active shale gas well

of an active shale well was 7.16 ± 0.42 and 7.17 ± 0.55 farther than 1 km from an active shale well. The average (± standard deviation) conductivity of groundwater sampled within 1 km of an active shale well was 520 ± 365 µS/cm and 524 ± 267 µS/cm farther than 1 km from an active shale well. There was no significant difference (evaluated using an ANOVA) in pH or conductivity of groundwater within 1 km, 1–2 km, 2–5 km, or more than 5 km from the nearest active shale gas well (Fig. 7a, b).

Discussion

Time series Contrary to our hypothesis, we did not see an increase in CH_4 concentration or change in isotopic composition of CH_4 in groundwater in regularly monitored wells over the study period (Figs. 2 and 3), despite a large increase in the number of producing shale gas wells in our study area (Fig. 1). In fact, we saw a decrease in CH_4 concentration in some of our regularly monitored wells, although the number of samples in our time series is relatively small. The low numbers of significant correlations indicate there may be natural variability in concentrations of biogenic CH_4 in groundwater in our study area (contrary to our expectation), and/or we may simply lack statistical power to uncover a robust signal. It is difficult to pinpoint exactly when shale gas wells were drilled, "fracked," or began producing in our study area, making it hard to relate dissolved CH_4 concentration to distance from the nearest active shale gas well for time series samples, although we have analyzed the relationship between CH_4 concentration and distance from the nearest active gas well for sites sampled only once (see below). We found that CH_4 concentrations in groundwater varied across several orders of magnitude in our study area (Fig. 2), from 0.2 µg/L to 25.3 mg/L. Three of our regularly monitored sites had CH_4 levels posing a fire or explosion hazard in enclosed spaces (above 10 mg/L; US Department of the Interior 2001).

As observed with CH_4 concentrations, isotopic concentration of CH_4 was consistent over time in regularly monitored groundwater wells, and the highest CH_4 concentrations had lower $\delta^{13}C$ values than known natural gas sources from the region (Fig. 3), indicating a biogenic CH_4 source. Biogenic CH_4 can be derived from anaerobic acetate fermentation from an organic matter source, such as soil or plant organic matter, or from reduction of carbon dioxide as in the case of coalbed CH_4 (Fig. 5). Radiocarbon dating of CH_4 from four samples indicates two of the four consist of fossil C (^{14}C age = 47,000 years; $\Delta^{14}C = -997‰$), the third consists of more modern C (^{14}C age = 305 years; $\Delta^{14}C = -45.1‰$), and the fourth has an intermediate age (^{14}C age = 27,000 years; $\Delta^{14}C = -966.1‰$) (Table 1; Fig. 5). All of the samples that were tested for radiocarbon age had stable isotope ratios indicating a bacterial carbonate reduction source signature. Some samples with very low dissolved CH_4 concentrations did have high $\delta^{13}C$ values near the range observed for natural gas sources (Fig. 3), but $\delta^{2}H$ analyses values indicate these may be attributed to in situ CH_4 oxidation (Fig. 5) (see further discussion of CH_4 sources below).

Two sites had changes in $\delta^{13}C$ values over the study period that might indicate the introduction of natural gas CH_4 in groundwater, but only two measurements of $\delta^{13}C$, which we considered insufficient to establish a statistical trend. The concentration of methane in well "N" ranged from 0.0002 to 0.0007 mg/L and there were two $\delta^{13}C$ measurements over the time series, one indicating a $\delta^{13}C$ of − 35.4‰ and one of − 48.3‰. The heavier carbon isotopic measurement, combined with its $\delta^{2}H$ measurement, puts it into the "geothermal, hydrothermal, crystalline" category in Fig. 5, but the other measurement is in the thermogenic range. The change in CH_4 source from geothermal to thermogenic was accompanied by a change in dissolved CH_4 concentration of 0.0002 mg/L, which is small compared to the range of concentrations observed throughout the study area. There was no change in the distance to the nearest active gas well between these two samples for well "N". The concentration of methane in well "V" ranged from 0.0003 to 0.0009 mg/L with two $\delta^{13}C$ measurements, one of − 68.2‰ and one of − 45.2‰. The change in CH_4 source from biogenic to thermogenic was accompanied by a change in dissolved CH_4 concentration of 0.0005 mg/L. There was no change in distance to the nearest active gas well during the study period for well "V". For both of these sites, small amounts of atmospheric CH_4 ($\delta^{13}C \sim -47$‰) dissolved in groundwater may also partially explain the results. Nevertheless, the change in isotopic composition of CH_4 in these wells may indicate that further changes in dissolved gas concentration, composition, and/or water quality are incipient.

Single samples Data collected from sites sampled only once were analyzed for the relationship of dissolved CH_4 concentration and $\delta^{13}C$-CH_4 with distance from the nearest producing shale gas well, similar to analyses done in the Marcellus Shale of Pennsylvania (Osborn et al. 2011; Jackson et al. 2013). Unlike in the previous studies, and contrary to our initial hypothesis, we did not observe increased CH_4 concentration in groundwater wells located within 1 km of a producing shale gas well (Fig. 4a). In fact, some of the highest concentrations (up to ~ 20 mg/L) were observed outside of this 1 km "active" zone (as defined by Osborn et al. 2011 and Jackson et al. 2013). Carbon stable isotopic data from these single sample sites also indicate that the highest CH_4 concentrations have a biogenic isotopic signature ($\delta^{13}C$-CH_4 between − 70 and − 60‰) (Fig. 4b). As also observed in our time series data, groundwater had a wide range of CH_4 concentrations.

Sources of CH_4 in groundwater Figure 5 compares C and H stable isotopic compositions of time series and single sample data, grouped by dissolved CH_4 concentration, and also showing biogenic and thermogenic endmembers from the same region. The majority of our samples, particularly in the highest concentrations, fall into the range defined by Whiticar (1999) as produced by bacterial carbonate reduction. A few samples with lower CH_4 concentrations fall in the range of bacterial methyl-type fermentation and thermogenic CH_4, similar to endmembers from cow breath and oil and gas wells, respectively (Fig. 5). Furthermore, we see evidence that oxidation of CH_4 in groundwater is occurring in our region, leading to high $\delta^{13}C$ and $\delta^{2}H$ signatures and decreased concentrations (Whiticar 1999; Townsend-Small et al. 2016a), as some low CH_4 concentration samples fall outside the range of known CH_4 sources (Fig. 5).

Other studies of thermogenic natural gas in Appalachia have found that it has $\delta^{13}C$-CH_4 values above − 52‰ (Jenden et al. 1993; Laughrey and Baldassare 1998), and $\delta^{13}C$-CH_4 values above − 50‰ in drinking water wells were interpreted as natural gas dissolved in groundwater near Pennsylvania gas wells (Osborn et al. 2011; Jackson et al. 2013). In contrast, biogenic coalbed CH_4 in Appalachia can be produced by microbial carbonate reduction and has a more ^{13}C- and ^{2}H-depleted isotopic signature than thermogenic natural gas (Laughrey and Baldassare 1998; Townsend-Small et al. 2016b). While some of our samples have isotope signatures similar to previous measurements of coalbed CH_4 in Appalachia ($\delta^{13}C$ from − 55.1 to − 39.9‰; $\delta^{2}H$ from − 121 to − 219‰; Laughrey and Baldassare 1998), many are even more depleted in ^{13}C and/or ^{2}H, similar to coalbed CH_4 in other regions (Rice 1990; Scott et al. 1994; Smith and Pallasser 1996; Clayton 1998; Martini et al. 1998; Schlegel et al. 2011). Production-scale coalbed CH_4 reservoirs are located in eastern Harrison County and east-central Carroll County, although there are no active coalbed CH_4 extraction wells in these counties (ODNR 2018). Appalachian Ohio in general has coal-bearing strata that could support methanogenesis via carbonate reduction, followed by CH_4 migration from coal seams into

selected groundwater wells (Ohio Division of Geological Survey 2004). Close examination of water well logs showed that some of our groundwater wells were drilled through coal seams (Ohio Division of Water and Soil Resources 2016), although the water well log database is incomplete in this area, particularly for older groundwater wells. Future studies may confirm the presence of biogenic rather than thermogenic CH_4 in these groundwater wells through analyses such as the ratio of CH_4 to higher chain hydrocarbons or dissolved inorganic C concentration and $\delta^{13}C$ measurements (Rice and Claypool 1981; Martini et al. 2003; Jackson et al. 2013).

A small number of groundwater samples fell within the mixed biogenic/thermogenic, methyl-type fermentation, or thermogenic source ranges based on stable isotopic analysis, mostly in water wells with dissolved CH_4 concentrations less than 1 mg/L (Fig. 5) (Whiticar 1999). We also had one sample that fell in the range of "geothermal" CH_4 (Fig. 5) (Whiticar 1999). Samples that fall to the right of the defined ranges in Fig. 5 are likely affected by partial CH_4 oxidation, which causes increased $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 values of residual CH_4 and is frequently observed in aquatic environments (Whiticar 1999; Townsend-Small et al. 2016a). Samples that fall into the range of thermogenic CH_4 or mixed biogenic/thermogenic CH_4 may represent groundwater wells that have small amounts of natural gas, perhaps because of nearby existing conventional or newly drilled unconventional oil and gas wells. There may also be a time lag between the onset of hydraulic fracturing in the region and the appearance of natural gas in groundwater, in which case these data may represent the first sign of thermogenic CH_4 in groundwater in the region. Clearly, additional monitoring is needed to determine whether CH_4 concentrations and source signals change in this region as the number of oil and gas wells continues to increase.

Radiocarbon analyses of CH_4 on samples from four groundwater wells containing dissolved CH_4 concentrations consistently > 1 mg/L were performed to determine whether biogenic CH_4 is derived from fossil or modern C (Aravena et al. 1995; Levin and Hesshaimer 2000; Townsend-Small et al. 2012; Garnett et al. 2013; Pack et al. 2015) (Table 1; Fig. 3). All of these samples had a stable isotopic composition indicative of a bacterial carbonate reduction CH_4 source. Three of these groundwater wells contained CH_4 in concentrations within the action level for mitigation (> 10 mg/L) and had ^{14}C ages between 27,000 and 47,000 years BP, indicating microbial reduction of ancient, "radiocarbon-dead" CO_2 (Table 1). In contrast, the $\Delta^{14}C$-CH_4 of − 45‰ for the fourth well, with the lowest CH_4 concentration, had a ^{14}C age of 305 years or approximately 96% modern C, indicating it is derived from carbonate reduction from a modern soil respiration or atmospheric CO_2 source (Table 1).

Previous studies of $\Delta^{14}C$-CH_4 in groundwater have found a similar range in radiocarbon ages that vary with the stable isotopic composition and therefore the CH_4 production pathway and/or C source. Groundwater CH_4 in the Alliston Aquifer, southern Ontario, Canada, was produced primarily by CO_2 reduction (as determined by $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4) and ranged in age from ~ 15,000 to 44,000 years BP (Aravena et al. 1995). A study of groundwater in central Iowa found that CH_4 was produced from methanogenesis of old organic C, producing CH_4 with ages from 14,000 and 17,000 years BP (Parkin and Simpkins 1995). Methane in arsenic-contaminated groundwater in Taiwan had a larger range of radiocarbon ages (~ 6200 to 42,000 years BP) and $\delta^{13}C$-CH_4 values that largely indicated a CO_2 reduction source (Liu et al. 2009).

Other studies in the Appalachian Basin have used additional tracers to distinguish between biogenic and thermogenic CH_4 sources or to determine gas intrusion pathways, including the concentration of ethane (C_2H_6) and higher alkanes (Jackson et al. 2013; Moritz et al. 2015; Humez et al. 2016a), concentrations of toxic hydrocarbons associated with oil and gas activity (Drollette et al. 2015), noble gases (Darrah et al. 2014, 2015), and/or isotopic analysis of C_2H_6, H_2O, CO_2, or other dissolved constituents (Warner et al. 2012, 2013). In the current study, we chose a smaller number of analytes that could be analyzed in our own laboratory at the University of Cincinnati in order to conserve funds to provide more water tests for more homeowners. This also allowed us to run our study for a longer period of time. Despite the relatively small number of analytes, our data indicate that the dominant source of CH_4 in groundwater in the Utica Shale region is biogenic, and that neither the CH_4 concentration nor its source change with an increasing number of shale gas wells or with changing distance to shale gas wells.

pH and conductivity As with concentration and isotopic composition of CH_4, conductivity did not change as shale gas drilling increased in the region in regularly monitored groundwater wells, nor was there a difference in

conductivity with distance from the nearest shale gas well (Figs. 6b and 7b), in contrast to our expectations. For the most part, conductivity levels in groundwater in our study were somewhat above the normal range for surface stream water for the northern Appalachian/Allegheny Plateau region, which is generally between about 50 and 350 μS/cm with other values recorded outside this range, up to 3000 μS/cm (Griffith 2014). However, groundwater is naturally more enriched in dissolved ions than surface water, and our data do not indicate any intrusion of high conductivity fracking fluids as the number of fracking wells increased in the region (Vidic et al. 2013; DiGuilio and Jackson 2016). In contrast, a stream in West Virginia next to a fracking wastewater injection well had elevated conductivity levels approximately five times greater than upstream of the injection well (Akob et al. 2016). Future studies of groundwater in the Utica Shale drilling region of Ohio may also consider including measurements of specific ions that may be indicative of hydraulic fracturing fluids or natural brines (Warner et al. 2012, 2013; Akob et al. 2016).

We did not see any major changes in pH levels in groundwater over time in our study area, or an indication that proximity to shale gas wells leads to reduced pH in groundwater due to the presence of acidic hydraulic fracturing fluids (Figs. 6a and 7a). At least one prior study in Appalachian West Virginia has shown that the accidental introduction of hydraulic fracturing wastewater to surface waters can lead to reduced pH (Akob et al. 2016). Our data indicate that pH values of groundwater in east-central Ohio vary widely, and that some groundwater wells have low pH values that may indicate the presence of acid mine drainage (site F, Fig. 6a). Our pH and conductivity measurements, along with our other data, provide a useful baseline for assessing future changes in groundwater quality in the region as more oil and gas development and its associated urbanization occur.

Implications While interactions of shale gas extraction and drinking water have been examined in the Marcellus Shale drilling area of Pennsylvania and West Virginia (Osborn et al. 2011; Jackson et al. 2013; Brantley et al. 2014; Darrah et al. 2014; Llewellyn et al. 2015; Harkness et al. 2017), our study is the first to characterize CH_4 sources in groundwater in the Utica Shale drilling region of Ohio, and is one of only a handful of time series studies of CH_4 concentration and associated isotopic composition in an oil and gas extraction area (e.g., Humez et al. 2016b). Continued monitoring will determine whether increased hydraulic fracturing activity will lead to natural gas or fracking fluid intrusion into groundwater, as has been shown elsewhere (Osborn et al. 2011; Jackson et al. 2013; Darrah et al. 2014; Llewellyn et al. 2015; Hildebrand et al. 2015; DiGuilio and Jackson 2010). More research is needed on the composition and sources of biogenic CH_4 in subsurface Appalachia, particularly on the interaction of this CH_4 source with current and past oil and gas extraction (Caulton et al. 2014; Townsend-Small et al. 2016b).

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References

Akob, D. M., Cozzarelli, I. M., Dunlap, D. S., Rowan, E. L., & Lorah, M. M. (2015). Organic and inorganic composition and microbiology of produced waters from Pennsylvania shale gas wells. *Applied Geochemistry, 60*, 116–125. https://doi.org/10.1016/j.apgeochem.2015.04.011.

Akob, D. M., Mumford, A. C., Orem, W., Engle, M. A., Klinges, J. G., Kent, D. B., & Cozzarelli, I. M. (2016). Wastewater disposal from unconventional oil and gas development degrades stream quality at a West Virginia injection facility. *Environmental Science & Technology, 50*, 5517–5525. https://doi.org/10.1021/acs.est.6b00428.

Aravena, R., Wassenaar, L. I., & Plummer, L. N. (1995). Estimating ^{14}C groundwater ages in a methanogenic aquifer. *Water Resources Research, 31*, 2307–2317. https://doi.org/10.1029/95WR01271.

Beaulieu, J. J., Smolenski, R. L., Nietch, C. T., Townsend-Small, A., & Elovitz, M. S. (2014). High methane emissions from a midlatitude reservoir draining an agricultural watershed. *Environmental Science & Technology, 48*, 11100–11108. https://doi.org/10.1021/es501871g.

Brantley, S. L., Yoxtheimer, D., Arjmand, S., Grieve, P., Vidic, R., Pollak, J., Llewellyn, G. T., Abad, J., & Simon, C. (2014). Water resource impacts during unconventional shale gas development: the Pennsylvania experience. *International Journal of Coal Geology, 126*, 140–156. https://doi.org/10.1016/j.coal.2013.12.017.

Caulton, D. R., Shepson, P. B., Santoro, R. L., Sparks, J. P., Howarth, R. W., Ingraffea, A. R., Cambaliza, M. O. L., Sweeney, C., Karion, A., Davis, K. J., Stirm, B. H., Montzka, S. A., & Miller, B. R. (2014). Toward a better understanding and quantification of methane emissions from shale gas development. *Proceedings of the National Academy of Sciences USA, 111*, 6237–6242. https://doi.org/10.1073/pnas.1316546111.

Clayton, J. L. (1998). Geochemistry of coalbed gas—a review. *International Journal of Coal Geology, 35*, 159–173. https://doi.org/10.1016/S0166-5162(97)00017-7.

Darrah, T. H., Vengosh, A., Jackson, R. B., Warner, N., & Poreda, R. J. (2014). Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett shales. *Proceedings of the National Academy of Sciences USA, 111*(39), 14076–14081. https://doi.org/10.1073/pnas.1322107111.

Darrah, T. H., Jackson, R. B., Vengosh, A., Warner, N. R., Whyte, C. J., Walsh, T. B., Kondash, A. J., & Poreda, R. J. (2015). The evolution of Devonian hydrocarbon gases in shallow aquifers of the northern Appalachian Basin: insights from integrating noble gas and hydrocarbon geochemistry. *Geochimica et Cosmochimica Acta, 17*, 321–355. https://doi.org/10.1016/j.gca.2015.09.006.

DiGuilio, D. C., & Jackson, R. B. (2016). Impact to underground sources of drinking water and domestic wells from production well stimulation and completion practices in the Pavilion, Wyoming, field. *Environmental Science & Technology, 50*, 4524–4536. https://doi.org/10.1021/acs.est.5b04970.

Drollette, B. D., Hoelzer, K., Warner, N. R., Darrah, T. H., Karatum, O., O'Connor, M. P., Nelson, R. K., Fernandez, L. A., Reddy, C. M., Vengosh, A., Jackson, R. B., Elsner, M., & Plata, D. L. (2015). Elevated levels of diesel range organic compounds in groundwater near Marcellus gas operations are derived from surface activities, Proceedings of the National Academy of Sciences USA., *112*, 13184–13189. https://doi.org/10.1073/pnas.11511474112.

Garnett, M. H., Hardie, S. M. L., Murray, C., & Billett, M. F. (2013). Radiocarbon dating of methane and carbon dioxide evaded from a temperate peatland stream. *Biogeochemistry, 14*, 213–223. https://doi.org/10.1007/s10533-012-9804-2.

Griffith, M. B. (2014). Natural variation and current reference for specific conductivity and major ions in wadeable streams of the conterminous USA. *BioOne, 33*, 1–17. https://doi.org/10.1086/674704.

Harkness, J. S., Darrah, T. H., Warner, T. H., Whyte, C. J., Moore, M. T., Millot, R., Kloppmann, W., Jackson, R. B., & Vengosh, A. (2017). The geochemistry of naturally occurring methane and saline groundwater in an area of unconventional shale gas development. *Geochimica et Cosmochimica Acta, 208*, 302–334. https://doi.org/10.1016/j.gca.2017.03.039.

Hildebrand, Z. L., Carlton, D. D., Fontenot, B. E., Melk, J. M., Walton, J. L., Taylor, J. T., Thacker, J. B., Korlie, S., Shelor, C. P., Henderson, D., et al. (2015). A comprehensive analysis of groundwater quality in the Barnett shale region. *Environmental Science & Technology, 49*, 8254–8262. https://doi.org/10.1021/acs.est.5b01526.

Howarth, R. W., Santoro, R., & Ingraffea, A. (2011). Methane and the greenhouse-gas footprint of natural gas from shale formations. *Climatic Change, 106*(4), 679–690. https://doi.org/10.1007/s10584-011-0061-5.

Humez, P., Mayer, B., Ing, J., Nightingale, M., Becker, V., Kingston, A., Akbilgik, O., & Taylor, S. (2016a). Occurrence and origin of methane in groundwater in Alberta (Canada): gas geochemical and isotopic approaches. *Science of the Total Environment, 541*, 1253–1268. https://doi.org/10.1016/j.scitotenv.2015.09.055.

Humez, P., Mayer, B., Nightingale, M., Ing, J., Becker, V., Jones, D., & Lam, V. (2016b). An 8-year record of gas geochemistry and isotopic composition of methane during baseline sampling at a groundwater observation well in Alberta (Canada). *Hydrogeology Journal, 24*, 109–122. https://doi.org/10.1007/s10040-015-1319-1.

Ioffe, B. V., & Vitenburg, A. G. (1984). *Head-space analysis and related methods in gas chromatography*. New York: Wiley.

Jackson, R. B., Vengosh, A., Darrah, T. H., Warner, N. R., Down, A., Poreda, R. J., Osborn, S. G., Zhao, K., & Karr, J. D. (2013). Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction. *Proceedings of the National Academy of Sciences USA, 110*, 11250–11255. https://doi.org/10.1073/pnas.1221635110.

Jenden, P. D., Drazan, D. J., & Kaplan, I. R. (1993). Mixing of thermogenic natural gases in northern Appalachian basin. *AAPG Bulletin, 77*, 980–998 http://aapgbull.geoscienceworld.org/content/77/6/980.

Kerr, R. A. (2010). Natural gas from shale bursts onto the scene. *Science, 328*(5986), 1624–1626. https://doi.org/10.1126/science.328.5986.1624.

Kozlowska, M., Brudzinski, M. R., Friberg, P., Skoumal, R. J., Baxter, N. D., & Currie, B. S. (2018). Maturity of nearby faults influences seismic hazard from hydraulic fracturing. *Proceedings of the National Academy of Sciences USA, 115*, E1720–E1729. https://doi.org/10.1073/pnas.1715284115.

Laughrey, C. D., & Baldassare, F. J. (1998). Geochemistry and origin of some natural gases in the plateau province, central Appalachian basin, Pennsylvania and Ohio. *AAPG Bulletin, 82*, 317–335 http://aapgbull.geoscienceworld.org/content/82/2/317.

Levin, I., & Hesshaimer, V. (2000). Radiocarbon—a unique tracer of global carbon cycle dynamics. *Radiocarbon, 42*, 69–80 https://journals.uair.arizona.edu/index.php/radiocarbon/article/viewFile/3855/3280.

Liu, T. K., Chen, K. Y., Yang, T. F., Chen, Y. G., Chen, W. F., Kang, S. C., & Lee, C. P. (2009). Origin of methane in high-arsenic groundwater of Taiwan—evidence from stable isotope analyses and radiocarbon dating. *Journal of Asian Earth Sciences, 36*, 364–370. https://doi.org/10.1016/j.jseaes.2009.06.009.

Llewellyn, G. T., Dorman, F., Westland, J. L., Yoxtheimer, D., Grieve, P., Sowers, T., Humston-Fulmer, E., & Brantley, S. L. (2015). Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development. *Proceedings of the National Academy of Sciences USA, 112*, 6325–6330. https://doi.org/10.1073/pnas.1420279112.

Marrero, J. E., Townsend-Small, A., Lyon, D. R., Tsai, T., Meinardi, S., & Blake, D. R. (2016). Estimating emissions of toxic hydrocarbons from natural gas production sites in the Barnett shale region of northern Texas. *Environmental Science & Technology, 50*, 10756–10764. https://doi.org/10.1021/acs.est.6b02827.

Martini, A. M., Walter, L. M., Budai, J. M., Ku, T. C. W., Kaiser, C. J., & Schoell, M. (1998). Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim shale, Michigan basin, USA. *Geochimica et Cosmochimica Acta, 62*, 1699–1720. https://doi.org/10.1016/S0016-7037(98)00090-8.

Martini, A. M., Walter, L. M., Ku, T. C. W., Budai, J. M., McIntosh, J. C., & 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 Bulletin, 87*, 1355–1375. https://doi.org/10.1306/031903200184.

Moritz, A., Hélie, J. F., Pinti, D. L., Larocque, M., Barnetche, D., Retailleau, R., & Gélinas, Y. (2015). Methane baseline concentrations and sources in shallow aquifers from the shale gas-prone region of the St. Lawrence lowlands (Quebec, Canada). *Environmental Science & Technology, 49*, 4765–4771. https://doi.org/10.1021/acs.est.5b00443.

Ohio Department of Natural Resources (ODNR). (2017). Division of Oil and Gas Resources. Utica/Point Pleasant Shale cumulative permitting activity. http://oilandgas.ohiodnr.gov/shale. Last accessed 8/26/2017.

Ohio Department of Natural Resources (ODNR). (2018). Ohio Oil & Gas Well Locator. http://oilandgas.ohiodnr.gov/well-information/oil-gas-well-locator. Last accessed 2/16/2018.

Ohio Division of Geological Survey. (2003). Shaded bedrock-topography map of Ohio: Ohio Department of Natural Resources, Division of Geological Survey Map BG-3, generalized page-size version with text, 2 p., scale 1:2,000,000. http://geosurvey.ohiodnr.gov/portals/geosurvey/?PDFs/BedrockGeology/ShadedBedrock_Topo.pdf

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, generalized page-size version with text, 2 p., scale 1:2,000,000. [Updated 2014.] http://geosurvey.ohiodnr.gov/portals/geosurvey/PDFs/Misc_State_Maps&Pubs/pg01.pdf

Ohio Division of Soil and Water Resources. (2016). Water well log search by county, township, and road, or log number. Ohio Department of Natural Resources, Division of Soil and Water Resources. Available at: https://apps.ohiodnr.gov/water/maptechs/wellogs/app/

Osborn, S. G., Vengosh, A., Warner, N. R., & Jackson, R. B. (2011). Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences USA, 108*, 8172–8176. https://doi.org/10.1073/pnas.1100682108.

Pack, M. A., Xu, X., Lupascu, M., Kessler, J. D., & Czimczik, C. I. (2015). A rapid method for preparing low volume CH_4 and CO_2 gas samples for ^{14}C AMS analysis. *Organic Geochemistry, 78*, 89–98. https://doi.org/10.1016/j.orggeochem.2014.10.010.

Parkin, T. B., & Simpkins, W. W. (1995). Contemporary groundwater methane production from Pleistocene carbon. *Journal of Environmental Quality, 24*, 367–372. https://doi.org/10.2134/jeq1995.00472425002400020021x.

R Core Team. (2017). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/

Revesz, K. M., Breen, K. J., Baldassare, A. J., & Burruss, R. C. (2010). Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-Central Pennsylvania. *Applied Geochemistry, 25*(12), 1845–1859. https://doi.org/10.1016/j.apgeochem.2010.09.011.

Rice, D. D. (1990). Controls, habitat, and resource potential of ancient bacterial gas [abs]. In L.M.H. Carter, (Ed.), U.S. Geological Survey research on energy resources (p. 67). Washington, U.S. Geological Survey Circular 1060. Available at: http://pubs.usgs.gov/circ/1990/1060/report.pdf

Rice, D. D., & Claypool, G. E. (1981). Generation, accumulation, and resource potential of biogenic gas. *AAPG Bulletin, 65*(1), 5–25 http://aapgbull.geoscienceworld.org/content/65/1/5.

Rowan, E. L., Engle, M. A., Kraemer, T. F., Schroeder, K. T., Hammack, R. W., & Doughten, M. W. (2015). Geochemical and isotopic evolution of water produced from Middle Devonian Marcellus shale gas wells, Appalachian basin, Pennsylvania. *AAPG Bulletin, 99*(2), 181–206. https://doi.org/10.1306/07071413146.

Schlegel, M. E., McIntosh, J. C., Bates, B. L., Kirk, M. F., & Martini, A. M. (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. *Geochimica et Cosmochimica Acta, 75*, 1903–1919. https://doi.org/10.1016/j.gca.2011.01.016.

Scott, A. R., Kaiser, W. R., & Ayers, W. B. (1994). Thermogenic and secondary biogenic gases, San Juan basin, Colorado and New Mexico—implications for coalbed gas producibility. *AAPG Bulletin, 78*(2), 1186–1209 http://aapgbull.geoscienceworld.org/content/78/8/1186.

Siegel, D. I., Azzolina, N. A., Smith, B. J., Perry, E. A., & Bothun, R. L. (2015). Methane concentrations in water wells unrelated to proximity to existing oil and gas wells in northeastern Pennsylvania. *Environmental Science & Technology, 49*, 4106–4112. https://doi.org/10.1021/es505775c.

Skoumal, R. J., Brudzinski, M. R., & Currie, B. S. (2015). Earthquakes induced by hydraulic fracturing in Poland township, Ohio. *Bulletin of the Seismological Society of America, 105*(1), 189–197. https://doi.org/10.1785/0120140168.

Smith, J. W., & Pallasser, R. J. (1996). Microbial origin of Australian coalbed methane. *AAPG Bulletin, 80*, 891–897 http://aapgbull.geoscienceworld.org/content/80/6/891.

Sokal, R. S., & Rohlf, F. J. (2012). *Biometry: The principles and practice of statistics in biological research* (Fourth ed.). New York: W.H. Freeman and Company 937 pages.

Stuiver, M., & Polach, H. A. (1977). Discussion: reporting of ^{14}C data. *Radiocarbon, 19*, 355–363.

Townsend-Small, A., Tyler, S. C., Pataki, D. E., Xiaomei, X., & Christensen, L. E. (2012). Isotopic measurements of atmospheric methane in Los Angeles, California, USA: influence of "fugitive" fossil fuel emissions. *Journal of Geophysical Research, 117*, D07308. https://doi.org/10.1029/2011JD016826.

Townsend-Small, A., Marerro, J. E., Lyon, D. R., Simpson, I. J., Meinardi, S., & Blake, D. R. (2015). Integrating source apportionment tracers into a bottom-up inventory of methane emissions in the Barnett shale hydraulic fracturing region. *Environmental Science & Technology, 49*(13), 8175–8182. https://doi.org/10.1021/acs.est.5b00057.

Townsend-Small, A., Disbennett, D., Fernandez, J. M., Ransohoff, R. M., Mackay, R., & Bourbonniere, R. A. (2016a). Quantifying emissions of methane derived from anaerobic organic matter respiration and natural gas extraction in Lake

Erie. *Limnology & Oceanography, 61*, S356–S366. https://doi.org/10.1002/lno.10273.

Townsend-Small, A., Ferrara, T. W., Lyon, D. R., Fries, A. E., & Lamb, B. K. (2016b). Emissions of coalbed and natural gas methane from abandoned oil and gas wells in the United States. *Geophysical Research Letters, 43*, 2283–2290. https://doi.org/10.1002/2015GL067623.

Townsend-Small, A., Botner, E. C., Jimenez, K. L., Schroeder, J. R., Blake, N. J., Meinardi, S., Blake, D. R., Sive, B. C., Bon, D., Crawford, J. H., Pfister, G., & Flocke, F. M. (2016c). Using stable isotopes of hydrogen to quantify biogenic and thermogenic atmospheric methane sources: a case study from the Colorado front range. *Geophysical Research Letters, 43*, 11462–11471. https://doi.org/10.1002/2016GL071438.

Tyler, S. C., Rice, A. L., & Ajie, H. O. (2007). Stable isotope ratios in atmospheric CH_4: implications for seasonal sources and sinks. *Journal of Geophysical Research, 112*, D03303. https://doi.org/10.1029/2006JD007231.

United States Department of the Interior. (2001). *Technical measures for the investigation and mitigation of fugitive methane hazards in areas of coal mining*. Pittsburgh: Office of Surface Mining Reclamation and Enforcement http://www.osmre.gov/resources/library/ghm/methane.pdf.

United States Energy Information Administration. (2016). Shale in the United States. Washington, DC. http://www.eia.gov/energy_in_brief/article/shale_in_the_united_states.cfm.

United States Environmental Protection Agency. (2016). Hydraulic fracturing for oil and gas: Impacts from the hydraulic fracturing water cycle on drinking water resources in the United States (Final Report). Washington, DC. EPA/600/R-16/236F. https://cfpub.epa.gov/ncea/hfstudy/recordisplay.cfm?deid=332990

Vengosh, A., Jackson, R. B., Warner, N., Darrah, T. H., & Kondash, A. (2014). A critical review of the risks to water resources from unconventional shale gas development and hydraulic fracturing in the United States. *Environmental Science & Technology, 48*(15), 8334–8348. https://doi.org/10.1021/es405118y.

Vidic, R. D., Brantley, S. L., Vandenbossche, J. M., Yoxtheimer, D., & Abad, J. D. (2013). Impact of shale gas development on regional water quality. *Science, 340*, 1235009. https://doi.org/10.1126/science.1235009.

Warner, N. R., Jackson, R. B., Darrah, T. H., Osborn, S. G., Down, A., Zhao, K., White, A., & Vengosh, A. (2012). Geochemical evidence for possible natural migration of Marcellus formation brine to shallow aquifers in Pennsylvania. *Proceedings of the National Academy of Sciences USA, 109*(30), 11961–11966 http://www.pnas.org/cgi.doi/10.1073/pnas.1121181109.

Warner, N. R., Kresse, T. M., Hays, P. D., Down, A., Karr, J. D., Jackson, R. B., & Vengosh, A. (2013). Geochemical and isotopic variations in shallow groundwater in areas of the Fayetteville shale development, north-Central Arkansas. *Applied Geochemistry, 35*, 207–220. https://doi.org/10.1016/j.apgeochem.2013.04.013.

Whiticar, M. J. (1999). Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane. *Chemical Geology, 161*, 291–314.

Wilson, J. M., & VanBriesen, J. M. (2012). Oil and gas produced water management and surface drinking water sources in Pennsylvania. *Environmental Practice, 14*, 288–300. https://doi.org/10.1017/S1466046612000427.

Xu, X., Trumbore, S. E., Zheng, S., Southon, J. R., McDuffee, K. E., Luttgen, M., & Lui, J. C. (2007). Modifying a sealed tube zinc reduction method for preparation of AMS graphite targets: reducing background and attaining high precision. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 259*, 320–329. https://doi.org/10.1016/j.nimb.2007.01.175.

Yamamoto, S., Alcauskas, J. B., & Crozier, T. E. (1976). The solubility of methane in distilled water and seawater. *Journal of Chemical Engineering Data, 21*, 78–80. https://doi.org/10.1021/je60068a029.

Yarnes, C. (2013). $\delta^{13}C$ and $\delta^{2}H$ measurement of methane from ecological and geological sources by gas chromatography/combustion/pyrolysis isotope-ratio mass spectrometry. *Rapid Communications in Mass Spectrometry, 27*, 1036–1044. https://doi.org/10.1002/rcm.6549.