

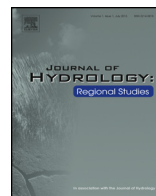


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Assessing dissolved methane patterns in central New York groundwater



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ABSTRACT

Study region: Groundwater in Chenango County (central New York State, USA), which is underlain by Devonian sedimentary bedrock. This region has conventional natural gas wells and is under consideration for future shale gas development using high-volume hydraulic fracturing.

Study focus: The study examines current patterns of dissolved methane in groundwater, based on 113 samples from homeowner wells in the spring of 2012. Samples were analyzed for methane and other water quality parameters, and each well characterized by its landscape position and geology. Statistical testing and regression modeling was used to identify the primary environmental drivers of observed methane patterns.

New hydrological insights for this region: There was no significant difference between methane concentrations in valleys versus upslope locations, in water wells less than or greater than 1 km from a conventional gas well, and across different geohydrologic units. Methane concentrations were significantly higher in groundwater dominated by sodium chloride or sodium bicarbonate compared with groundwater dominated by calcium bicarbonate, indicating bedrock interactions and lengthy residence times as controls. A multivariate regression model of dissolved methane using only three variables (sodium, hardness, and barium) explained 77% of methane variability, further emphasizing the dominance of geochemistry and hydrogeology as controls on baseline methane patterns.

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1. Introduction

1.1. Summary of Marcellus Shale gas issue in New York

Natural gas development is not an entirely new issue in New York State, with the first United States natural gas well installed in 1821 in Fredonia, NY (Kappel and Nystrom, 2012). Currently there are several thousand active natural gas wells, primarily located in the western and central regions of the state (NYSDEC, 2010). However, portions of the state that are underlain by the Marcellus Shale are being considered for extensive natural gas development. The Marcellus Shale underlies several states, including Pennsylvania, Ohio, and West Virginia, and contains approximately 141 trillion cubic feet of gas – enough to sustain current national energy needs for several years (USEIA, 2012). However, the extremely low permeability of this formation requires the use of unconventional technologies, horizontal drilling and high-volume hydraulic fracturing, to extract economically viable gas yields (Soeder and Kappel, 2009). While these methods are being utilized in many states, New York currently (as of May 2014) has a moratorium on the use of high-volume hydraulic fracturing as the New York State Department of Environmental Conservation (NYSDEC) develops regulations to be included in a supplement to the current Generic Environmental Impact Statement that governs oil and gas exploration (NYSDEC, 2011).

1.2. Concern of possible groundwater contamination

Potential environmental impacts being assessed by NYSDEC include the risk of contamination of groundwater resources due to shale gas development and hydraulic fracturing (NYSDEC, 2011). One concern is that high-pressure injection of large volumes of fracturing fluids could lead to contamination of aquifers. There is additional concern that methane could seep through or along improperly cemented gas well casings and into groundwater (Vidic et al., 2013). In other states currently allowing the use of these technologies, there have been reported instances of groundwater contamination. In Pennsylvania, between 2008 and 2011, there were two major cases of stray gas migration into groundwater, each affecting more than 15 drinking-water wells, though neither of these cases was specifically linked to hydraulic fracturing; rather the problem was deemed to be faulty casing of gas wells (Considine et al., 2012). A recent study in Pennsylvania found increased amounts of dissolved methane in groundwater within a kilometer of hydraulically fractured gas wells, however, no evidence of chemical contamination of groundwater due to drilling fluids was found (Osborn et al., 2011). Several replies to the paper by Osborn et al. (2011) contested the conclusion that methane contamination was due to hydraulic fracturing, noting there were a lack of baseline data and that much of the sampling occurred in the Dimock region of Pennsylvania, which was known to have methane migration issues from faulty gas well casings (Davies, 2011; Saba and Orzechowski, 2011; Schon, 2011). A follow-up study that included a more extensive dataset distributed across several counties in northeastern Pennsylvania similarly found increased methane concentrations with proximity to shale gas wells (Jackson et al., 2013). Two other studies in Pennsylvania found no evidence of increased methane in drinking-water wells as a result of natural gas drilling (Boyer et al., 2012; Molofsky et al., 2013), though one noted a few instances of water quality changes during pre-drilling and post-drilling (Boyer et al., 2012). In 2011, the U.S. Environmental Protection Agency found evidence of hydraulic fracturing chemicals in drinking-water wells in Pavillion, Wyoming, though the geology and hydrology of this site is considerably different than the Marcellus Shale region in the eastern part of the U.S. (USEPA, 2011). In another region of shale gas development in the U.S. – the Fayetteville Shale region of Arkansas – geochemical investigations did not find evidence that methane or major ion chemistry in shallow groundwater had been influenced in any way by shale gas drilling activities (Kresse et al., 2012; Warner et al., 2013).

1.3. Necessity of an understanding of baseline conditions

As New York considers lifting its moratorium on high-volume hydraulic fracturing, it is important to be able to accurately assess any potential cases of groundwater contamination due to these drilling technologies. Thus it is essential that there is an understanding of the existing baseline conditions

with regards to groundwater quality in New York ([Riha and Rahm, 2010](#)). Such a baseline would ideally include assessment of total suspended solids and a broad range of solutes, particularly chemicals known to be included in most fracturing fluid additives, as well as dissolved methane. Other parameters such as dissolved oxygen and volatile organic compounds could be informative baseline metrics as well, but these are not addressed in this paper.

With regard to methane monitoring, it is particularly useful to measure its isotopic composition ($\delta^{13}\text{C-CH}_4$ and/or $\delta^2\text{H-CH}_4$); this can provide information on the source reservoir of methane, and whether it was created biologically or thermogenically ([Schoell, 1980](#); [Laughrey and Baldassare, 1998](#); [Revesz et al., 1980](#)). Often, biologically produced methane is present in shallower geologic formations and unconsolidated deposits and thermogenic methane more in deeper, thermally mature formations. There can be wide variation of isotopic signatures among various methane-bearing formations ([Baldassare et al., 2014](#)). A survey of gas wells across western and central New York found that gas from wells tapping Upper and Middle Devonian formations had an average $\delta^{13}\text{C-CH}_4 = -44.7 \pm 3.9\%$ ($n = 8$) while wells finished in Lower Devonian or Silurian formations produced gas with a considerably different signature, averaging $\delta^{13}\text{C-CH}_4 = -36.3 \pm 3.0\%$ ($n = 9$) ([Jenden et al., 1993](#)). Isotopic signatures of dissolved methane, particularly in shallow aquifers, can represent mixing of gases from multiple source reservoirs ([Osborn and McIntosh, 2010](#); [Baldassare et al., 2014](#)).

1.4. Review of other studies examining dissolved methane patterns

There has been some work in some areas of New York and nearby states to characterize dissolved methane patterns in aquifers. One U.S. Geological Survey (USGS) study found that 9% of wells sampled in New York had methane concentrations above the recommended level of 10 mg L^{-1} ([Kappel and Nystrom, 2012](#)). Many of these wells were finished in Devonian-aged black shale or in confined glacial sand and gravel aquifers overlying the shale. Black shales are rich in organic carbon, typically leading to thermogenic methane production as the sediments are buried ([NYSDEC, 2011](#)). In this case, the black shale was presumed to be the source of the methane in the sampled water ([Kappel and Nystrom, 2012](#)). A recent USGS investigation focused specifically on isolating geologic and topographic controls on groundwater methane in south-central New York. Sampling locations in valleys had a higher proportion of methane concentrations in excess of 0.1 mg L^{-1} compared to upland wells and had predominantly thermogenic isotope signatures. Confined valley aquifers had the highest methane concentrations. The authors concluded that the likely source of the valley methane was underlying saline groundwater ([Heisig and Scott, 2013](#)). A USGS study in West Virginia found that groundwater methane levels over 10 mg L^{-1} were also linked to geology and topography; water wells in valleys and in regions dominated by low-sulfur coal deposits tended to have higher methane levels ([Mathes and White, 2006](#)).

In neighboring Pennsylvania, investigations of dissolved methane patterns yielded mixed results. Studies by one group found higher groundwater methane concentrations and very thermogenic isotope signatures in close proximity to existing gas wells ([Osborn et al., 2011](#); [Jackson et al., 2013](#)) but no correlation to other factors such as topographic position or tectonic deformation ([Jackson et al., 2013](#)). Another group found no relationship between dissolved methane in groundwater and proximity to gas wells, but did find topographic and geochemical relationships where methane concentrations were higher in valleys as well as in groundwater dominated by sodium chloride or sodium bicarbonate ([Molofsky et al., 2013](#)). In northeastern Pennsylvania, a multivariate regression of methane patterns using landscape and hydrogeologic factors found gas well proximity, groundwater residence time, and well depth relative to certain geologic strata to be most dominant, though only 28% of variation in methane was explained with the regression ([Pelepko, 2013](#)). A fourth study found no correlation between groundwater methane and proximity to gas wells, but did not examine other landscape characteristics that might be driving observed values ([Boyer et al., 2012](#)).

1.5. Objectives of this study

The objectives of this study were to obtain groundwater quality data from domestic wells in central New York in order to (1) investigate baseline distributions of dissolved methane and other water

quality parameters, including major cations and anions, and (2) to analyze dissolved methane patterns using a variety of statistical techniques in order to understand environmental drivers of the observed patterns.

2. Methods

2.1. Study area

The chosen study area was Chenango County, which is a 2315 km² (894 mi²) region (US Census, 2012) located in the glaciated Appalachian Plateau portion of central New York State (McPherson, 1993). The county is dominated by agricultural and forested land (Crandall, 1985). Surficial geology is characterized by unconsolidated glacial till that mantles the bedrock uplands except on hilltops, north-facing hillslopes, and truncated spur hillsides where the till is absent and bedrock crops out at the land surface; with major valleys containing thicker sediments comprised of alluvium and glacialfluvial outwash and glaciolacustrine fine sand, silt, and clay (Cadwell, 1991; Hetcher et al., 2003; Hetcher-Aguila and Miller, 2005). Bedrock in the county is dominated by Upper and Middle Devonian shale with sandstone, siltstone, limestone and black shale also present in some formations (Fig. 1). Underlying stratigraphy is shown in Fig. 1b.

As of April 2012, there were 93 natural gas wells in the county, with 33 of these wells considered active. Drilling density, considering all existing wells, varies across the county, from 0 in several townships to 0.48 wells km⁻² in Smyrna Township (Fig. 2). These wells primarily produce from the Oriskany and Herkimer Sandstones and Oneida Conglomerate (NYSDEC, 2012). However, advances in drilling technologies have resulted in interest by natural gas companies to produce natural gas from organic-rich shales. In south-central New York, two organic-rich shale formations that have been targeted are the Marcellus Shale and Utica Shale, with the Marcellus Shale becoming less desirable toward the northern portion of Chenango County where the formation is less than 1500 feet deep (Selleck, 2010a). Since unconventional drilling is significantly different than conventional drilling, New York has been in the process of developing supplemental regulations (Supplemental Generic Environmental Impact Statement, SGEIS) which are pending the approval of the NYSDEC as of May 2014 (NYSDEC, 2013).

Most county residents obtain their drinking water from groundwater, with residents in the major river valleys generally tapping the glaciofluvial sand and gravel aquifers, in which, some aquifers are confined. Residents in the uplands primarily tap into bedrock aquifers (McPherson, 1993).

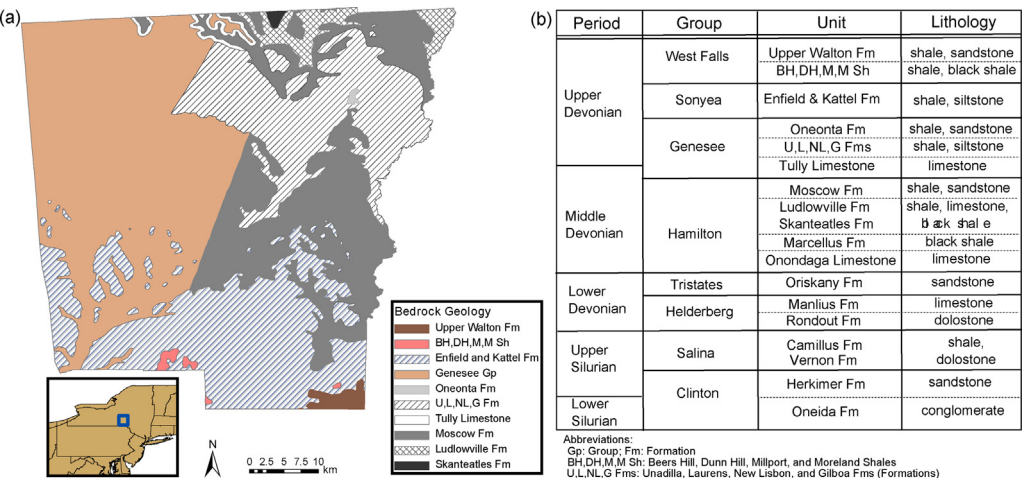


Fig. 1. Primary bedrock type (a) and generalized stratigraphy (b) for Chenango County, NY. Bedrock geology data was obtained from Fisher et al. (1970) and stratigraphy information was obtained from RCG (2013), Selleck (2010b), and USGS (2013).

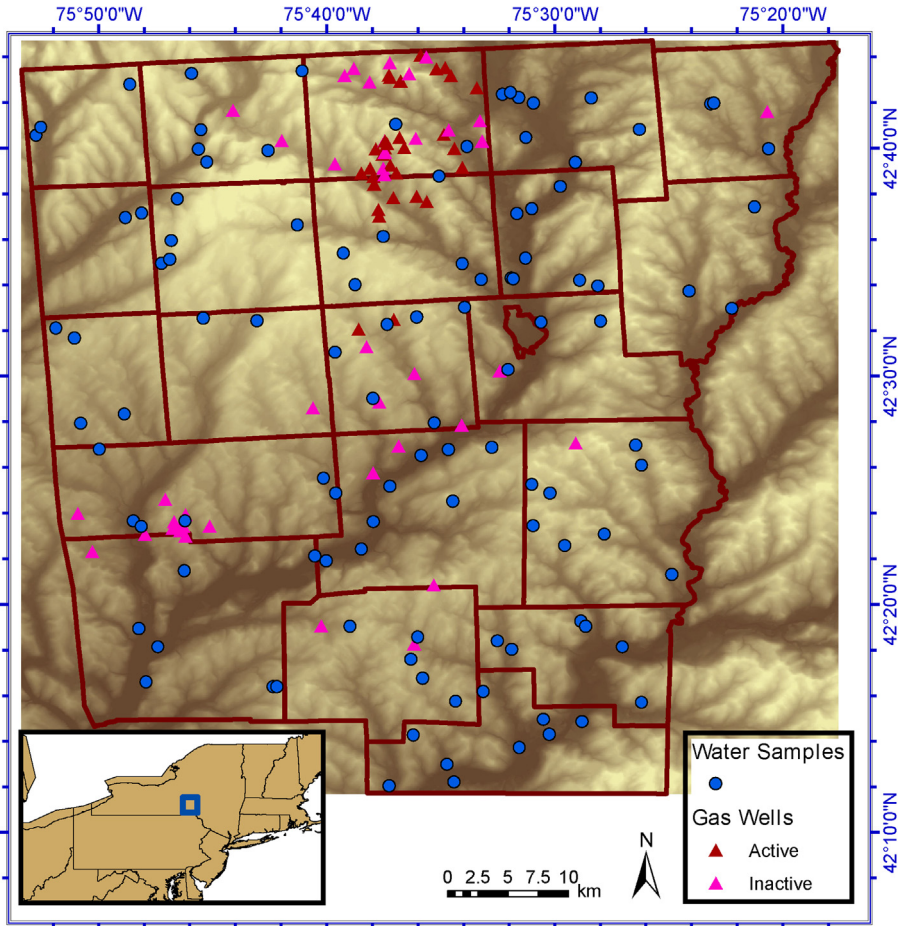


Fig. 2. Location of the 113 sample groundwater wells in Chenango County, NY with active and inactive gas wells (NYSDEC, 2012) also noted. Well locations are overlain on a Digital Elevation Model (DEM) (obtained from USGS) to show general topography. Town and City of Norwich boundaries are also denoted.

2.2. Field sample collection

In late 2011, Cornell Cooperative Extension collaborators placed newspaper ads in Chenango County newspapers to recruit residents who would allow us to obtain samples from their water wells in exchange for receipt of a free water quality report. Interested county residents who responded to the ad were accepted into the study; only drilled wells as opposed to dug wells or springs were included in this analysis. The 113 wells included in this analysis were distributed across the county (Fig. 2). Water samples were obtained from each of these homeowner wells between March and June 2012. The samples were taken from the closest accessible location to the well, which was often a spigot just past the water pressure tank in the basement. Water collection also occurred prior to the treatment system, if there was one. Water was initially run to purge the pipes and pressure tank of stagnant water, for at least five minutes. A one liter pre-cleaned amber glass bottle was filled with water to be used for sediment and solute analysis. A second water sample was then taken for dissolved gas analysis per standard methods of the USGS Reston Dissolved Gas Laboratory (Busenberg et al., 1998). For this method, flexible Masterflex Tygon tubing was attached to the spigot using a hose connector and water was run into a large bucket. The tubing was then inserted to the bottom of a 125 mL glass

serum bottle and the bottle filled with water. With the water still running, the bottle was lowered into the bucket and then the tube was removed. After making sure no bubbles were adhering to the inside of the bottle, a butyl rubber stopper was inserted in the bottle neck. A syringe needle was then inserted into the stopper that allowed the stopper to fully seal the bottle without having any remaining headspace. After sealing each bottle, the needle was removed, the bottle was removed from the full bucket, and the labeled sample bottles were stored in a cooler.

2.3. Sample processing

Upon return to the Cornell Soil and Water Lab, a subsample of water for anion and cation analysis was removed from the amber collection bottle after ensuring it was well-mixed. The subsample was filtered to 0.45 μm and all samples were stored at 4 °C until analysis. Analysis of total cations/metals was performed using a Jarrell Ash ICP-AES (Inductively Coupled Plasmography with Atomic Emission Spectrometer) for Ba, Ca, Cu, Fe, K, Mg, Na and ICP-MS (Inductively Coupled Plasmography with Mass Spectrometer) for As, Cd, Cr, Pb, Mn, Hg, and Se. Hardness was calculated as CaCO_3 equivalent based on calcium and magnesium concentrations. Analysis of anions (NO_3^- , NO_2^- , SO_4^{2-} , Cl^- , $\text{HCO}_3^-/\text{CO}_3^{2-}$) was performed on a Dionex ICS-2000 Ion Chromatograph with IonPac AS-18 analytical column, 25 μL sample loop, and 21 mM KOH eluent. Due to the high pH of the mobile phase, carbonate species were analyzed as CO_3^{2-} . Since the speciation cannot be resolved with this method, results are represented as ' $\text{HCO}_3^- + \text{CO}_3^{2-}$ '. Bromide data were not available due to interference from the end of the carbonate peak, which occurred with this chromatographic method. This issue was unable to be resolved at the time of analysis. Carbonate data were considered usable based on consistently good calibration curves ($R^2 > 0.98$) using peak height rather than peak area to deal with the interference with the bromide peak.

The unfiltered remainder from the amber collection bottle was analyzed within seven days for specific conductance and total suspended solids (TSS). Specific conductance was measured using a Fisher Scientific bench-top meter. TSS was determined by filtering 450 mL of sample through standard 934-AH glass fiber filters and determining the difference of oven-dry mass before and after filtration.

Water samples for dissolved gas extraction were stored at 4 °C until analysis, which occurred within two days of original sampling. The initial step was to remove a subsample of water to allow for sampling of headspace gas according to the phase equilibration technique ([Davidson and Firestone, 1988](#); [Kampbell and Vandegrift, 1998](#)). In order to be able to remove water from the full glass sampling bottle without contacting ambient air, a Tedlar bag filled with high purity helium was attached to tubing and a 21 gauge syringe needle, and the needle was inserted in the bottle stopper. A syringe was then inserted in the stopper and 20 mL of water sample was removed. The 20 mL water sample was injected into a pre-evacuated 125 mL serum bottle capped with a rubber septum. The headspace in this bottle was filled with high purity helium to equalize the internal pressure. The bottles were kept at 4 °C for 24 h, at which point they were removed and shaken vigorously for ten seconds to ensure gas equilibration. A gas sample was then removed from the headspace via syringe and injected into a pre-evacuated 12 mL Labco Exetainer. Gas samples were then sent to the UC Davis Stable Isotope Laboratory for analysis of methane concentration and $\delta^{13}\text{C}\text{-CH}_4$ using a Thermo Scientific GasBench-PreCon trace gas system interfaced to a Delta V Plus IRMS (Isotope Ratio Mass Spectrometer). The original concentration of dissolved gas in the water samples was then calculated using partition coefficients based on the temperature of sample incubation ([Lomond and Tong, 2011](#)).

2.4. Data analysis

ArcGIS 10 (ESRI, Inc.) geographic information system software was used to spatially analyze the data. Water sampling locations were classified according to their distance to the closest existing natural gas well, as well as their topographic position (valley vs. upslope). The samples were also classified by the geohydrologic units in which the water well was finished (bedrock formations vs. unconsolidated sand and gravel). Locations of existing natural gas wells in Chenango County were obtained from the NYSDEC ([NYSDEC, 2012](#)), and a threshold of 1000 m was used to group water wells into 'close' or 'far' from a gas well ([Osborn et al., 2011](#)). Topographic position was determined using two methods. Following [Molofsky et al. \(2013\)](#), one method determined location in a valley according

to distance to the nearest stream. Locations within 305 m (1000 feet) of a stream were considered to be valleys, where streams were defined using the USGS National Hydrography Dataset (NHD). A second approach focused on the geohydrologic setting and used surficial geology maps (Cadwell, 1991) and georeferenced USGS maps of valley-fill aquifers in Chenango County (McPherson, 1993) to classify 'valley' wells as those located in mapped valley-fill aquifers. These approaches were similar to the methodology used by a recent USGS study in south-central New York; however, their valley delineation factored in additional parameters including stream slope and elevation change between streams and adjacent uplands (Heisig and Scott, 2013). Well finishing geology in this study was determined as a specific bedrock formation or unconsolidated sand and gravel fill by using information on well depth (as reported by the homeowner) along with depth to bedrock estimated from USGS survey maps (McPherson, 1993) and bedrock geology maps (Fisher et al., 1970). Finishing geology was only determined for locations where well depth was reported by the homeowner.

R (The R Project for Statistical Computing) was used for statistical analysis of the data. For statistical analysis of all analytes, values below the method detection limit were treated as being equal to their analyzed values (Gilliom et al., 1984). The Mann–Whitney non-parametric test was used to analyze the dissolved gas data, as grouped according to proximity to gas wells and topographic position (valleys vs. upland). A non-parametric test was chosen due to the skewed distribution of the methane dataset and since log transformation of the data was not sufficient to normalize the distribution. For any analysis of $\delta^{13}\text{C}\text{-CH}_4$ data, values were excluded for samples where the methane concentration was below the method detection limit of 0.01 mg L^{-1} . The Kruskal–Wallis non-parametric test combined with a pairwise comparison ('kruskalmc' in R package 'pgirmess') was used where there were more than two groupings for methane data. It was used to evaluate differences between methane according to the geohydrologic units that the drinking-water wells tapped as well as across groundwater geochemical categories, as classified using major cation and anion data for the water samples (Deutsch, 1997). In order to classify the geochemical water type, a Piper diagram of major groundwater cations and anions that were detected in the samples was generated using Rockworks software (Rockware, Inc.). Multi-variate regression was used to determine what landscape setting or chemical parameters could best explain observed methane patterns. The factors initially included in the regression were chosen using a Pearson correlation analysis to assess what variables were most closely correlated with methane concentrations. Prior to regression analysis, methane and all other chemical analytes that were considered as explanatory variables were natural-log-transformed, due to their skewed distributions; the only variables considered in the regression that were not transformed were distance to streams and distance to active or existing gas wells.

3. Results and discussion

3.1. Baseline distribution of methane and dissolved solids

The tested groundwater samples from Chenango County met most federal drinking-water standards, with a few exceptions (Table 1). Among the measured constituents, manganese concentrations exceeded the USEPA SMCL (U.S. Environmental Protection Agency Secondary Maximum Contaminant Level) of $50\text{ }\mu\text{g L}^{-1}$ in 31 samples, chloride concentration exceeded the SMCL of 250 mg L^{-1} in one sample, and barium concentration exceeded the USEPA MCL (Maximum Contaminant Level) of 2 mg L^{-1} in one sample. 42 sampled wells yielded water that is considered 'hard' ($>120\text{ mg CaCO}_3\text{ L}^{-1}$) but this is a nuisance and not a health risk. For dissolved gas, there were no methane concentrations that exceeded the 10 mg L^{-1} 'watch' limit set by the Office of Surface Mining (Eltschlager et al., 2001) and 63 out of 113 total samples (56%) had methane concentrations less than 0.01 mg L^{-1} (the method detection limit). These results are comparable to the recent USGS study in south-central NY (primarily extending southwest of Chenango County), in which 34% of 65 groundwater samples had methane concentrations less than 0.01 mg L^{-1} and 65% had concentrations less than 0.1 mg L^{-1} . There were several samples in this USGS study that exceeded $10\text{ mg CH}_4\text{ L}^{-1}$ (Heisig and Scott, 2013).

With regards to $\delta^{13}\text{C}\text{-CH}_4$, 14 out of the 50 samples (28%) with methane concentrations over the detection limit had values more positive than -40‰ , 2 of 50 samples (4%) were below -60‰ , and the remaining 34 samples (68%) fell between -40 and -60‰ . $\delta^{13}\text{C}\text{-CH}_4$ values above -40‰ are

Table 1Summary of measured groundwater quality parameters^a

	Median	Min.	Max.	Established limit
CH ₄ (mg L ⁻¹)	0.01	0.01 ^f	8.26	10 ^b
δ ¹³ C-CH ₄ (‰ VPDB)	-44.4	-68.2	-10.1	n/a
Specific conductance (μS)	218	36	1390	n/a
TSS (mg L ⁻¹)	0.78	0.00	48.8	n/a
As (μg L ⁻¹)	0.50	0.05 ^f	5.22	10 ^c
Ba (mg L ⁻¹)	0.08	0.05 ^f	2.52	2 ^c
Ca (mg L ⁻¹)	29.2	1.42	99.1	n/a
Cl (mg L ⁻¹)	4.03	0.30 ^f	555	250 ^d
Cu (mg L ⁻¹)	0.05	0.05 ^f	0.44	1 ^c
Fe (mg L ⁻¹)	0.05	0.05 ^f	0.09	0.3 ^d
Hardness (mg CaCO ₃ L ⁻¹)	94.3	4.88	303	180 ^e
HCO ₃ ⁻ + CO ₃ ²⁻ (mg L ⁻¹)	116	11.3	311	n/a
K (mg L ⁻¹)	1.52	0.05 ^f	9.38	n/a
Mg (mg L ⁻¹)	5.59	0.32	22.1	n/a
Mn (μg L ⁻¹)	5.12	1.00	1010	50 ^d
Na (mg L ⁻¹)	9.46	0.69	156	n/a
NO ₃ ⁻ -N (mg L ⁻¹)	0.60	0.45	5.58	10 ^c
SO ₄ ²⁻ (mg L ⁻¹)	8.86	3.00	97.3	250 ^d

^a Cd, Cr, Pb, Hg, NO₂⁻-N, and Se were all measured and all values were at or below method detection limits (and thus also below any recommended limits).

^b Recommended 'action' level as defined by US Office of Surface Mining (Eltschlager et al., 2001).

^c EPA-mandated Maximum Contaminant Level (MCL) (USEPA, 2013).

^d EPA-recommended Secondary Maximum Contaminant Level (SMCL) (USEPA, 2013).

^e 120 mg L⁻¹ is the level considered 'hard' (WHO, 2011).

^f Method detection limit.

considered to be thermogenic in origin, those below -60‰ are considered biogenic, and those in the middle cannot be confidently designated without additional information and may represent mixing of sources (Schoell, 1980; Whiticar, 1999; Revesz et al., 1980). Median δ¹³C-CH₄ was -44.4‰. This is very similar to the isotopic signatures observed for gas produced from Upper and Middle Devonian geologic formations in New York (average = -44.7 ± 3.9‰) (Jenden et al., 1993), which means that the methane in many groundwater samples had an isotopic signature similar to that of the formations from which the groundwater was primarily sourced. Fig. 3 depicts kriged spatial distributions of dissolved methane concentration (a) and δ¹³C-CH₄ (b) in groundwater across Chenango County.

3.2. Statistical comparison of methane and environmental characteristics

3.2.1. Proximity to existing natural gas wells

Statistical comparison of methane concentration and δ¹³C-CH₄ using the Mann-Whitney non-parametric test indicated no significant difference ($p=0.29$; $p=0.48$) (Fig. 4a and e) between the distribution of samples less than 1 km ($n=8$) and greater than 1 km ($n=105$) from an existing natural gas well. The number of samples within 1 km of gas wells was small ($n=8$) and statistical analysis was influenced by one particularly high methane concentration. Highlighted in Fig. 5, this sample had a relatively high methane concentration (though still below the action level), a fairly thermogenic isotopic signature (δ¹³C-CH₄ = -43.1‰), and was within one kilometer of an existing (and in this case, active) gas well. While there are not data available on the isotopic signature of gas from that gas well or others in the county, we can look to data from wells in neighboring counties that produce from the same formations as many of the wells in Chenango County. To the north in Madison County, a gas well producing from the Herkimer Formation had a δ¹³C-CH₄ = -34.8‰, while to the southwest, a Steuben County gas well producing from the Oriskany Formation had a δ¹³C-CH₄ = -37.4‰ (Jenden et al., 1993). While these are only two points, both are notably less negative than the isotopic signature of the water sample of interest.

While it is possible that methane has migrated through or along the casings of this gas well and made it into the aquifer being tapped by the nearby water well (Osborn et al., 2011), it is also possible

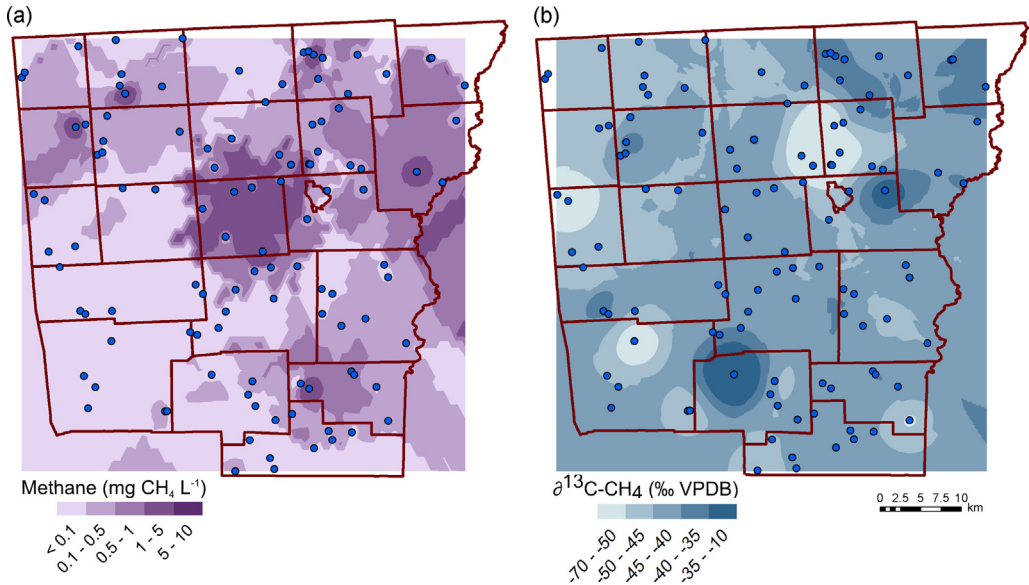


Fig. 3. Interpolated surfaces created by ordinary kriging for (a) dissolved methane concentration (mg L^{-1}) in groundwater and (b) $\delta^{13}\text{C-CH}_4$ (‰ VPDB) for the dissolved methane, Chenango County, NY. Sampling locations are also indicated.

that this water well simply taps an aquifer elevated in methane because it is in or overlying one of the many gas-yielding geologic strata in this region (Kappel and Nystrom, 2012). Pinpointing the source of the methane would require a 'multiple lines of evidence approach' (Molofsky et al., 2013) including analyses of additional methane isotopes ($^2\text{H-CH}_4$) and higher chain hydrocarbons (Revesz et al., 1980; Osborn et al., 2011; Baldassare et al., 2014) for the dissolved gas in the water samples as well as groundwater from the potential methane sources, along with investigation of local fractures, faults, casing logs for the gas wells, etc.

3.2.2. Topographic position

For wells grouped according to their distance from streams, statistical comparison of methane concentration and $\delta^{13}\text{C-CH}_4$ using the Mann–Whitney test revealed no significant difference ($p=0.38$; $p=0.30$) (Fig. 4b and f) between the distribution of methane for water samples located in valleys ($n=67$) compared to those taken at upslope locations ($n=46$). This is contrary to recent results observing significantly higher dissolved methane concentrations in valleys than in uplands in northeastern Pennsylvania (Molofsky et al., 2013). Our study covered a ten-fold greater area (2315 km^2 vs. 207 km^2) with much lower sampling density (0.05 wells/km^2 vs. 8.3 wells/km^2), so it is possible that not enough samples were obtained to discern the valley-methane relationship, but it is also possible that other factors are driving methane patterns in this particular region.

Our second method for classifying topographic position, which relied on location in valley-fill aquifers, led to different grouping compared to the first method that used distance to streams as an indicator of topographic position. Since wells were only considered to be located in valleys when they were in a mapped valley-fill aquifer, there were fewer ($n=29$) valley wells compared to the 67 identified using the stream-based method. Despite the difference in groupings, overall results were similar. Statistical comparison of methane concentration and $\delta^{13}\text{C-CH}_4$ using the Mann–Whitney test revealed no significant difference ($p=0.72$; $p=0.27$) (Fig. 4c and g) between the distributions of methane for water samples located in valleys ($n=29$) compared to those taken at upslope locations ($n=84$).

These findings are different from those of the recent USGS study in south-central NY (Heisig and Scott, 2013), in that they did observe a statistically significant difference in methane concentrations

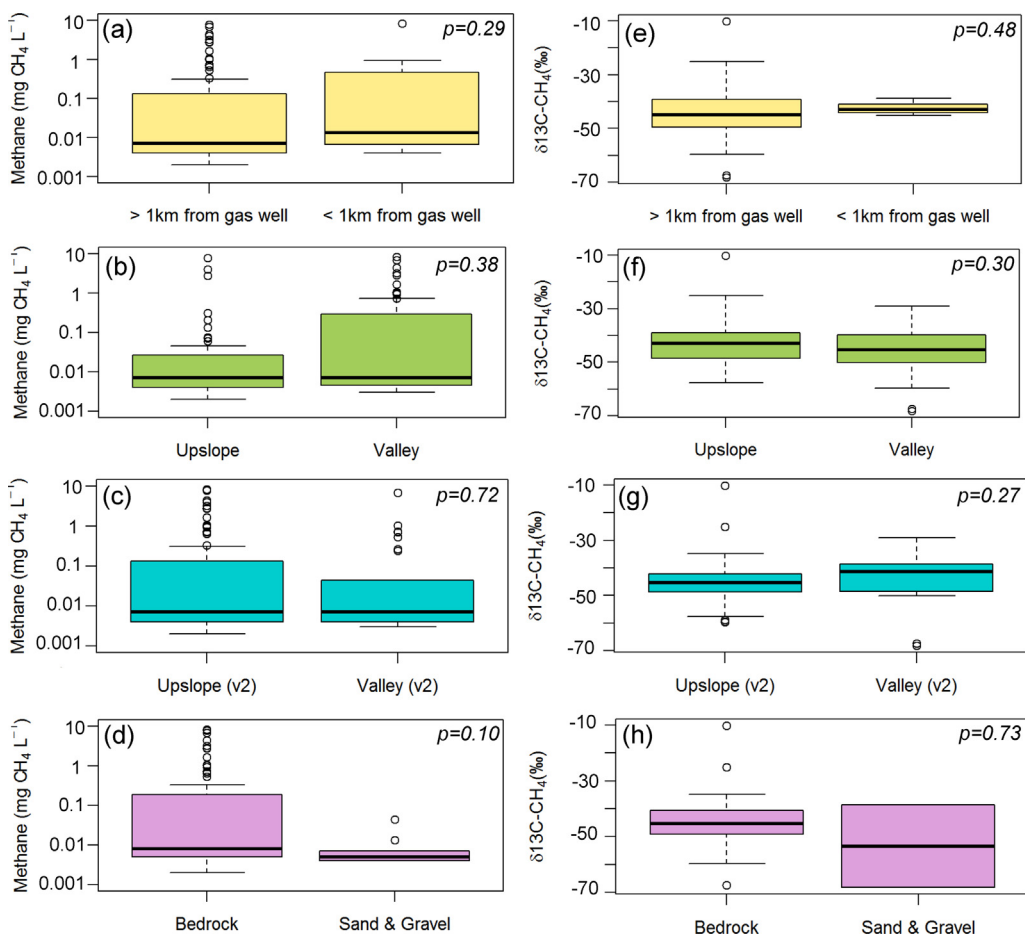


Fig. 4. Boxplots with p -values from a Mann–Whitney non-parametric test for dissolved methane (a) by proximity to gas wells, (b) by topographic position according to stream proximity, (c) by topographic position according to valley-fill aquifer mapping, and (d) by finishing geology. Boxplots for methane isotope fractionation (e) by proximity to gas wells, (f) by topographic position according to stream proximity, (g) by topographic position according to valley-fill aquifer mapping and (h) by finishing geology. All boxplots demonstrate the data median with the box denoting 1st and 3rd quartiles, the whiskers denoting 1.5 times the interquartile range, and the points representing extreme values (outliers).

by topographic setting. However, it was specifically wells located in confined valley aquifers that had statistically higher methane concentrations; methane concentrations in unconfined valley aquifers were not significantly different than those from upland sites.

3.2.3. Finishing geology

Boxplots showing distributions of dissolved methane from wells finished in sand and gravel aquifers ($n=9$) compared to those from wells finished in Devonian sedimentary rock ($n=76$) indicated a distribution skewed toward higher methane concentrations in bedrock wells. However, statistical comparison of methane concentration and $\delta^{13}\text{C-CH}_4$ using the Mann–Whitney test revealed no significant difference ($p=0.10$; $p=0.73$) (Fig. 4d and h) between the distributions from wells finished in sand and gravel aquifers compared to those from wells finished in Upper Devonian sedimentary rocks. The remaining 28 wells were not included in this comparison because they did not have available information on water-well depth or unit in which the well was finished. Separating out the 76 bedrock

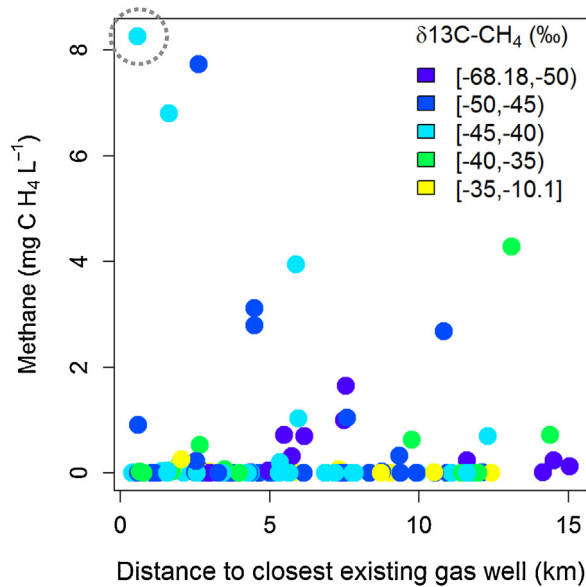


Fig. 5. Dissolved methane in sampled water wells and its relationship to distance to existing (active and inactive) natural gas wells, with a dotted circle around the highest concentration. Dissolved methane is characterized by overall concentration (mg L^{-1}) and $\delta^{13}\text{C-CH}_4$ (‰ VPDB).

wells according to the particular geologic formation in which they were finished (which included five shale-dominated formations), there were still no significant differences (Kruskal–Wallis $p > 0.05$) across methane concentration or $\delta^{13}\text{C-CH}_4$ (Fig. S1). The USGS study in south-central NY provides additional insight to finishing geology effects; similarly to ours, they observed higher methane in water wells tapping bedrock aquifers, as opposed to sand and gravel, but they found that the difference was significant specifically in unconfined valley settings (Heisig and Scott, 2013).

A key limitation to our analysis is the lack of detailed well logs for the sampled wells, since most wells that were sampled were drilled prior to 2000 when well drilling records were not required to be filed with the NYSDEC. These logs would have allowed us to better determine the geohydrologic unit in which wells were finished and whether the unit is confined or unconfined. In this way, our work is complemented by the USGS study (Heisig and Scott, 2013), which only selected water wells with detailed well logs so that they could specifically assess the geohydrologic setting of the well and its subsequent relationship to methane patterns.

3.2.4. Groundwater geochemistry

Assessment of major anion and cation chemistry (Fig. 6) revealed that the majority, 81 of 113, or 72%, of water samples fell into the calcium-bicarbonate (Ca-HCO_3) groundwater type. While only one of 81 samples of calcium-bicarbonate (Ca-HCO_3) groundwater type exceeded $1 \text{ mg CH}_4 \text{ L}^{-1}$, 11 of 19 (58%) sodium-dominated samples (including sodium-chloride (Na-Cl), sodium-bicarbonate-chloride ($\text{Na-HCO}_3\text{-Cl}$), and sodium-bicarbonate (Na-HCO_3) groundwater categories) exceeded $1 \text{ mg CH}_4 \text{ L}^{-1}$. A Kruskal–Wallis test combined with a pairwise comparison confirmed that methane concentrations in the Ca-HCO_3 groundwater type were significantly different ($p < 0.05$) than observed methane concentrations in the Na-Cl , $\text{Na-HCO}_3\text{-Cl}$, and Na-HCO_3 groups (Fig. S2).

These results are consistent with recent findings by Molofsky et al. (2013) in Pennsylvania, where Ca-HCO_3 was also the dominant groundwater type but 38% of samples from Na-Cl , $\text{Na-HCO}_3\text{-Cl}$, and Na-HCO_3 groundwater type exceeded $1 \text{ mg CH}_4 \text{ L}^{-1}$, compared to 0% of Ca-HCO_3 samples. In another Pennsylvania study, methane concentrations were found to be highest in more saline (defined as $>20 \text{ mg Cl L}^{-1}$) groundwater (Warner et al., 2012). Geochemical analysis by Warner et al. (2012)

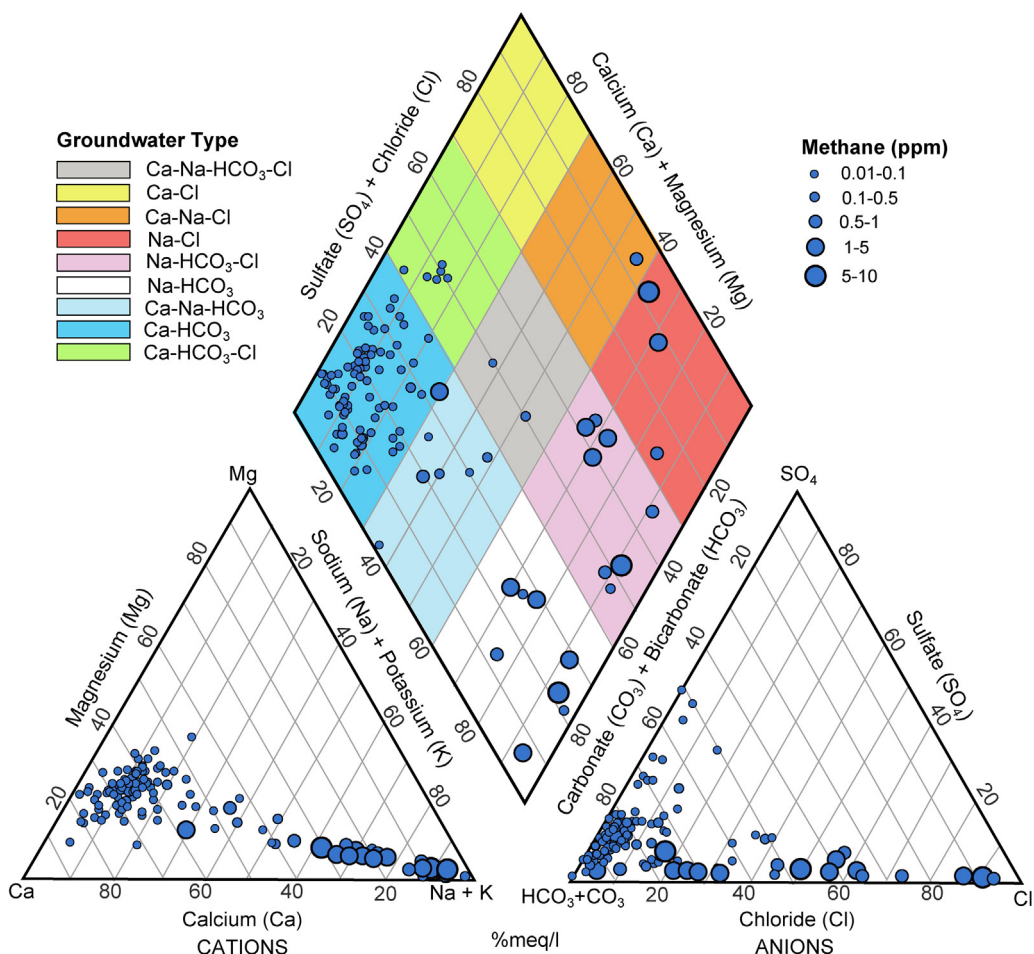


Fig. 6. Piper diagram showing groundwater type using major cations and anions in sampled wells. Samples are represented with circles scaled according to methane concentration. Groundwater types are categorized according to Deutsch (1997).

indicated that the saline water was migrating into shallow groundwater from deeper underlying formations through naturally occurring pathways such as faults and fractures.

In this study, there are several potential sources or formation mechanisms for the Na-Cl, Na-HCO₃-Cl, and Na-HCO₃ shallow groundwater. Na-Cl-type shallow groundwater may result from application of road salt (Kincaid and Findlay, 2009); however the rural nature of this county makes contributions of road salt to groundwater salinity less pervasive and does not explain the observed Na-Cl relationship with methane. Another possible anthropogenic source is septic system effluent. Most homes in Chenango County have septic systems, and use of water softeners could introduce sodium-dominated water back into the shallow groundwater via the septic system; however, none of the sampling locations with methane concentrations greater than 1 mg CH₄ L⁻¹ indicated water softener use (as reported by homeowners during the sampling visit).

A potential natural source of Na-Cl groundwater is interaction with Devonian bedrock or migration of more saline water from deeper underlying formations (Cheung et al., 2010). For the latter possibility, Na-Cl water could have been present in shallow groundwater as a result of natural hydraulic connections to underlying strata and the idea of such connections is supported by the documentation of natural fractures (Jacobi, 2002), particularly J1 and J2 joint sets, in the Genesee Shale (of the

Genesee Group) which underlies the western portion of the county (Fig. 1) (Engelder et al., 2009). The lack of differences in methane concentrations across different bedrock formations in which water wells were finished also supports the possibility that methane-rich Na-Cl water is migrating from deeper formations. In either case, this water chemistry is indicative of increased interaction with bedrock and less contribution of meteoric (precipitation-derived) water that would have infiltrated through overlying calcareous sediments (Fleisher, 1993). This extended residence time and potential interaction with methane-rich strata (e.g. black shale) could have led to relatively higher methane concentrations (Molofsky et al., 2013).

The Na-HCO₃ groundwater and its associated dissolved methane likely resulted from groundwater residence time and rock-water interaction as well as redox processes. Longer residence times typically lead to increased concentrations of Na and HCO₃ due to cation exchange between calcium and sodium and oxidation of organic matter, and can also promote biological methane production as oxygen is used up and methanogenesis is thermodynamically favored (Thorstenson et al., 1979; Kresse et al., 2012). The methane isotopic signatures also support the presence of some microbial methane, with the majority of $\delta^{13}\text{C-CH}_4$ values falling between –40 and –60‰, indicating likely mixing of biogenic and thermogenic methane (Whiticar, 1999).

3.3. Multivariate regression of methane patterns

To better predict patterns in dissolved methane, it is useful to model the relationship between methane and readily measurable environmental parameters. Such parameters could be GIS-derived characteristics described in previous sections or water quality and geochemical characteristics like specific conductance or sodium concentration. It is also important that such parameters be continuous, rather than classifications like ‘valley’ vs. ‘upslope’.

Table 2 displays the results of the best multivariate regression models using selected variables from the full suite of landscape and chemical parameters. An initial model was developed using nine variables that were selected based on their Pearson correlation with methane. Using the six variables found to be significant ($p < 0.05$) – hardness, barium, chloride, sodium, sulfate and distance from active gas wells – a regression model was created that could explain 82% of variation in observed methane patterns (Fig. S3). This was the best overall model, in that it had the highest adjusted *R*-squared value, and was also the model that resulted from an automated stepwise regression in *R*. While this model revealed distance to active gas wells as exhibiting a negative control on methane concentrations, this does not indicate that gas wells are definitively causing higher methane concentrations; since

Table 2
Results of dissolved methane regression models.

# Variables	Model <i>R</i> -squared	Intercept	Included variables	Coefficient	<i>P</i> -value
3	0.772	1.37	Hardness (mg CaCO ₃ L ⁻¹) ^a	–1.23	<0.001
			Ba (mg L ⁻¹) ^a	0.86	<0.001
			Na (mg L ⁻¹) ^a	1.02	<0.001
6	0.820	1.36	Hardness (mg CaCO ₃ L ⁻¹) ^a	–1.05	<0.001
			Ba (mg L ⁻¹) ^a	0.67	<0.001
			Na (mg L ⁻¹) ^a	0.88	<0.001
			Cl (mg L ⁻¹) ^a	0.22	0.009
			SO ₄ ²⁻ (mg L ⁻¹) ^a	–0.37	0.04
			Distance to active well (km)	–0.02	0.008
9	0.818	2.33	Conductivity (μS) ^a	–0.32	0.43
			Hardness (mg CaCO ₃ L ⁻¹) ^a	–0.94	<0.001
			Ba (mg L ⁻¹) ^a	0.64	<0.001
			Na (mg L ⁻¹) ^a	0.99	<0.001
			Cl (mg L ⁻¹) ^a	0.24	0.01
			NO ₃ ⁻ -N (mg L ⁻¹) ^a	–0.03	0.89
			SO ₄ ²⁻ (mg L ⁻¹) ^a	–0.38	0.03
			Distance to stream (km)	–1.55	0.26
			Distance to active well (km)	–0.03	0.01

^a A natural log transformation was applied to these variables.

these gas wells are inherently producing from methane-rich strata this may indicate that methane concentrations are higher in close proximity to these particular formations, but it is not possible to discern the cause of the relationship without further investigation. Sulfate was also found to be negatively correlated to methane in this model, providing further evidence for some biologically driven methane production. This follows thermodynamic principles given that sulfate reduction yields more energy than methanogenesis; thus methane is produced when sulfate concentrations are reduced (Schlesinger, 1997).

The three most significant variables in the model ($p < 0.001$) – hardness, sodium, and barium – together could explain 77% of the observed variation in dissolved methane. We acknowledge that including both sodium and hardness could introduce some multicollinearity into the model since sodium and hardness (as the sum of magnesium and calcium) tend to be negatively correlated; however, we find that removing either sodium or hardness from the model strongly reduces its predictive power, indicating that they are both contributing to it. These results are informative for better understanding the drivers of observed methane patterns. Sodium was positively correlated with methane concentrations and hardness was negatively correlated with methane. This is consistent with previously described geochemical patterns that indicated that methane likely resulted from bedrock-groundwater interactions and lengthy residence times. The positive correlation between barium and methane concentrations also indicates that there is a geologic relationship with methane patterns. While barium can be present due to human activities, including use in gas well drilling mud, it also is naturally present in geologic formations. Barium has been found in western New York to be primarily sourced from the mineral barite (BaSO_4) (Moore and Staubitz, 1984), which may also be present in formations underlying this study region.

Using measured environmental variables, regression models for methane were developed with high explanatory power. While these models were developed using data from Chenango County, New York, they could have similar predictive power in nearby areas of New York and Pennsylvania with similar shale-dominated bedrock geology. With other studies in New York observing some higher methane concentrations than here (Kappel and Nystrom, 2012; Heisig and Scott, 2013), it will be important to refine this model to try to better capture these patterns. In the future, it would also be beneficial to work toward creating improved regression models based on more easily quantified parameters (e.g. GIS-quantifiable landscape parameters rather than measured chemical variables) to aid in characterizing baseline groundwater methane across New York State.

4. Conclusion

With the potential for unconventional technology (high-volume hydraulic fracturing of horizontal wells) being used to access Marcellus Shale gas resources in New York State, it is important to gather baseline information on water quality before this contentious technology is implemented. In this study in central New York State, we analyzed 113 groundwater samples from across Chenango County for dissolved methane and a suite of cations and anions. Most measured dissolved solids were below federal drinking-water standards and no methane concentrations exceeded recommended action levels. The majority of methane samples exhibited a mixed isotopic signature based on analysis of $\delta^{13}\text{C}\text{-CH}_4$. When examining possible environmental drivers of the methane patterns, methane was not significantly correlated to proximity to gas wells, location in valleys, or the geohydrologic unit in which wells were finished. Statistical analysis of geochemical data revealed that significantly higher methane concentrations were found in groundwater classified as sodium-chloride, sodium-bicarbonate-chloride, and sodium-bicarbonate, which likely resulted from interactions with surrounding or underlying bedrock and long residence times. Multivariate regression models of dissolved methane concentrations revealed hardness, barium, and sodium to be the best predictors of observed methane patterns, further emphasizing the connection between dissolved methane and hydrogeology.

This study makes an important contribution to better understanding patterns of groundwater methane in central New York and complements existing studies, particularly adding geochemical insight to the geohydrologic and topographic controls investigated in the USGS study (Heisig and Scott, 2013). Better understanding the source and residence time of groundwater for a given drinking-water well could provide important insight into methane dynamics. The knowledge that some methane in

groundwater in this area could be originating from deeper geologic formations highlights the need to better understand the natural fractures and connectivity patterns among the geologic formations, particularly when considering future development of natural gas wells. Additionally, the heterogeneity visible in the observed water quality patterns emphasizes the importance of collecting baseline data from individual water wells in close proximity to potential future disturbances, such as in the event of expanded natural gas drilling in New York.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ejrh.2014.06.002.

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