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Distribution and Origin of Groundwater Methane in the Wattenberg Oil and Gas Field of Northern Colorado

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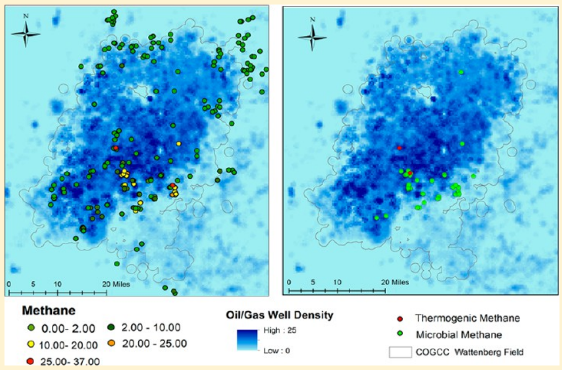
S Supporting Information

ABSTRACT: Public concerns over potential environmental contamination associated with oil and gas well drilling and fracturing in the Wattenberg field in northeast Colorado are increasing. One of the issues of concern is the migration of oil, gas, or produced water to a groundwater aquifer resulting in contamination of drinking water. Since methane is the major component of natural gas and it can be dissolved and transported with groundwater, stray gas in aquifers has elicited attention. The initial step toward understanding the environmental impacts of oil and gas activities, such as well drilling and fracturing, is to determine the occurrence, where it is and where it came from. In this study, groundwater methane data that has been collected in response to a relatively new regulation in Colorado is analyzed. Dissolved methane was detected in 78% of groundwater wells with an average concentration of 4.0 mg/L and a range of 0–37.1 mg/L. Greater than 95% of the methane found in groundwater wells was classified as having a microbial origin, and there was minimal overlap between the C and H isotopic characterization of the produced gas and dissolved methane measured in the aquifer. Neither density of oil/gas wells nor distance to oil/gas wells had a significant impact on methane concentration suggesting other important factors were influencing methane generation and distribution. Thermogenic methane was detected in two aquifer wells indicating a potential contamination pathway from the producing formation, but microbial-origin gas was by far the predominant source of dissolved methane in the Wattenberg field.



■ INTRODUCTION

There has been increasing attention directed toward the potential for environmental contamination associated with horizontal drilling and hydraulic fracturing, the key technologies employed during the extraction of unconventional oil and gas resources.[1] Hydraulic fracturing is utilized to increase formation permeability through introduction of large amounts of injection fluid under high pressure.[2] In addition to increasing the recovery of oil and gas from the producing formation, it has been suggested that hydraulic fracturing could create seepage pathways of natural gas (methane) and deep formation water (with high TDS) migrating to the shallow formation, resulting in aquifer contamination and green house gas emissions.[3,4]

Methane is formed in nature through two primary types of processes: microbial and thermogenic. Microbial methane is produced by subsurface bacteria and is a common natural source of methane gas in groundwater aquifers, usually found in water wells, swamps, and other environments with high carbon concentrations and low redox potential.[5] Microbial or biogenic methane can be produced through two pathways, acetate fermentation and CO_2 reduction. Thermogenic methane gas is produced at greater depths through high pressure and temperature processes, characteristic of deep oil and gas reservoirs that conventional and unconventional hydrocarbon wells tap.[6] Methane migration from deep underground formations to the surface can be achieved by several mechanisms including advective transport (gas migrates from areas of high pressure to areas of low pressure) through or around the protective casing that surrounds the production piping.[7]

Significant oil and gas development has occurred recently in the Denver-Julesburg (DJ) basin of northeast Colorado.[8] Intensive well drilling and fracturing in the Wattenberg field, located in the DJ basin,[9] first discovered in 1970, has resulted in greater than 19 000 producing oil and/or gas wells and 7500 abandoned wells through August, 2013.[9] The Colorado Oil and Gas Conservation Commission (COGCC) has compiled oil and/or gas extraction and production information and, more recently, has required groundwater monitoring at a minimum of two groundwater sources before and after drilling an oil and gas well (Rule 318A.e.(4)).[10] The objective of this paper is to understand the occurrence and distribution of methane in groundwater in the Wattenberg field. In addition, the

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relationship between methane and oil/gas activity is studied with chemical and spatial analysis of COGCC groundwater baseline data.

■ MATERIALS AND METHODS

The COGCC Baseline Groundwater Sampling Program requires oil and gas operators to sample two groundwater wells, springs, or seeps on opposite sides of one drilling location from the deepest aquifer within a half-mile radius of the surface location.[10] A subsequent sample needs to be taken between 12 and 18 months after the well completion or facility installation and again between 60 and 78 months after the initial sampling event (dry holes are exempt from this requirement). Isotopic and gas compositional analysis needs to be collected if the methane concentration exceeds 1.0 mg/L.

The study area, the Wattenberg field, is located on a 1 280 000-acre parcel in northeast Colorado.[11] Groundwater and gas composition data were collected in the area of the Wattenberg field and at COGCC groundwater well points. The components of water and gas were analyzed by standard methods (Supporting Information Table 1).[12−14]

A total of 223 data points from 176 drinking water wells were included in this analysis, with replicate samples collected from 45 groundwater wells that encountered a methane change, and 131 single sample wells. Within the 176 groundwater wells, 60 isotopic test results (carbon and hydrogen) from 40 wells were obtained to determine the composition of dissolved gases in water (such as methane), including 19 wells that were sampled multiple times.

■ RESULTS AND DISCUSSION

The origin of methane is related to the microbial and thermal alteration of organic matter. Carbon and hydrogen isotopic compositions of methane can be used to examine the different origins due to distinct characteristics of the two types, thermogenic and biogenic.[15]

^{13}C in CH_4 is depleted in the primary microbial dissimilation reactions, acetate fermentation and carbon dioxide reduction (shown below), and is accompanied by minimal C_2 and C_3 production.[16] However, thermogenic methane production will result in the production of heavier hydrocarbons (C_2, C_3; etc.),[17] and the stable isotope ^{13}C in CH_4 is closer to the isotope of the substrate that produced methane but more enriched via the thermogenic process than microbial mechanisms.[18]

Acetate fermentation pathway:

$$CH_3COOH = CH_4 + CO_2$$

CO_2 reduction pathway:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

Most microbial methane is generated in shallow aquifers while thermogenic methane is found in deep formations exceeding 3000 feet[19] due to the elevated temperature and pressure required. Therefore, the occurrence of thermogenic methane in groundwater can be indicative of upward migration of methane from deeper sections of the earth's crust. Rice and Ladwig[20] reported that Wattenberg field natural gas methane, that came from greater depths (usually 6000−8000 feet deep), contained significant amounts of heavier hydrocarbons (C_1/C_{1-5} values range from 0.83 to 0.87) and was isotopically heavier ($\delta\ ^{13}C{-}CH_4$ values range from −49 to −43 ‰). The chemical and isotopic composition of the gases indicated a thermogenic origin and were generated by thermal cracking processes during intermediate stages of thermal maturity in the deeper part of the Denver basin, consistent with the level of maturation determined by source rock studies.

Stable carbon and hydrogen isotope test results were plotted in Figure 1 to define the various sources of CH_4, and all the data points could be divided into two classifications, thermogenic and microbial, using a CD-diagram.[21] Of the 60 samples in our study, most of the samples could be classified as microbial methane and only 4 samples from 2 well sites were characterized as thermogenic-origin in the early mature stage. Average "thermogenic" methane concentration was 3.5 mg/L, and average methane concentration designated microbial in origin was 3.2 mg/L. Occurrence of microbial methane is ubiquitous accounting for over one-fifth of the world's gas accumulations[22] and is influenced by vegetation and soil conditions, or other anthropogenic activities.[23]

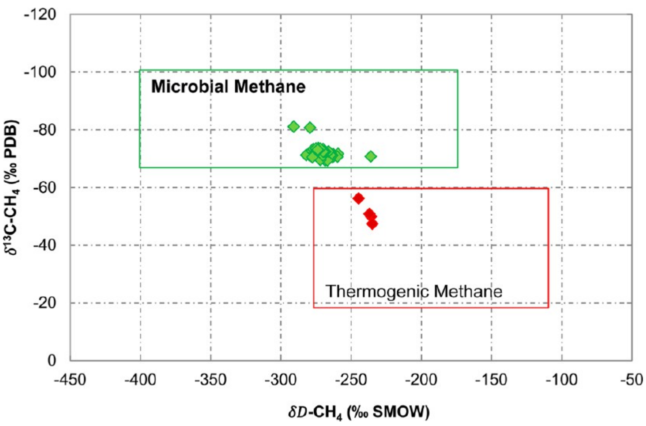

Figure 1. Carbon and hydrogen isotopic compositional ranges of methane from different sources.[21]

$$*\delta^{13}C - CH_4 = \left[\frac{\left(\frac{^{13}C}{^{12}C}\right)}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} - 1 \right] \times 10^3,$$

$$\delta D - CH_4 = \left[\frac{\left(\frac{D}{H}\right)}{\left(\frac{D}{H}\right)_{standard}} - 1 \right] \times 10^3$$

($*^{13}C/^{12}C$) is 0.0112372 for carbon standard as PDB and D/H is 0.00015576 for hydrogen standard as SMOW as hydrogen standard.[26]

A clear illustration of the different methane sources is shown in Figure 2, a comparison of isotopic characteristics (* listed definitions of $\delta^{13}C$ and δD) between dissolved methane found in aquifer wells (blue tilted squares) and gas phase methane from natural gas production wells (red triangles). Two distinct data point clusters are observed indicating that methane from the groundwater wells was formed with a different mechanism than methane from oil and gas wells. Samples from oil and gas wells were isotopically heavier than the samples from groundwater wells, implying thermogenic methane in origin. Oil/gas wells are much deeper than groundwater wells and produce methane by thermal cracking due to extremely high temperatures and abundant organic carbon sources during the early or intermediate thermal maturity stages.[24] Microbial and thermogenic methane, with distinct isotopic characteristics, are separated by low-permeability formations between groundwater

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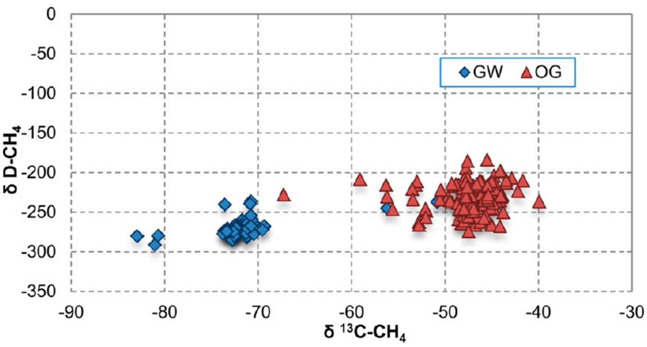

Figure 2. Plot of carbon and hydrogen isotopic results from a groundwater well (blue) and gas from an oil/gas well (red).

wells (up to 1000 feet (300 m) deep) and oil/gas wells (average 6500 feet (1980 m) deep).

Methane characteristics including concentration, C_1/C_{2+}, and $\delta\ ^{13}CH_4$ are plotted versus groundwater well depth in Figure 3. None of the methane characteristics has a significant correlation with water well depth, and concentration appears random. Figure 3b shows that most of the methane is considered "dry" or relatively devoid of C_{2+} compounds, another indication of a predominant biogenic origin.[25] In addition, most of the values of $\delta\ ^{13}CH_4$ below −60‰ (Figure 3c) suggest a microbial methanogenesis process.[26] Figure 3a shows the variation in the concentrations of dissolved methane in groundwater at different depths, that the methane concentration was low close to the surface (depth less than 150 m) while methane began to increase with depth. In groundwater with a low redox potential, anaerobic organisms such as *Methanogens* can produce methane. Jenden and Kaplan[27] observed that increasing depth could cause the change from fermentation to CO_2 reduction. Rich deposits of organic carbon in the shale

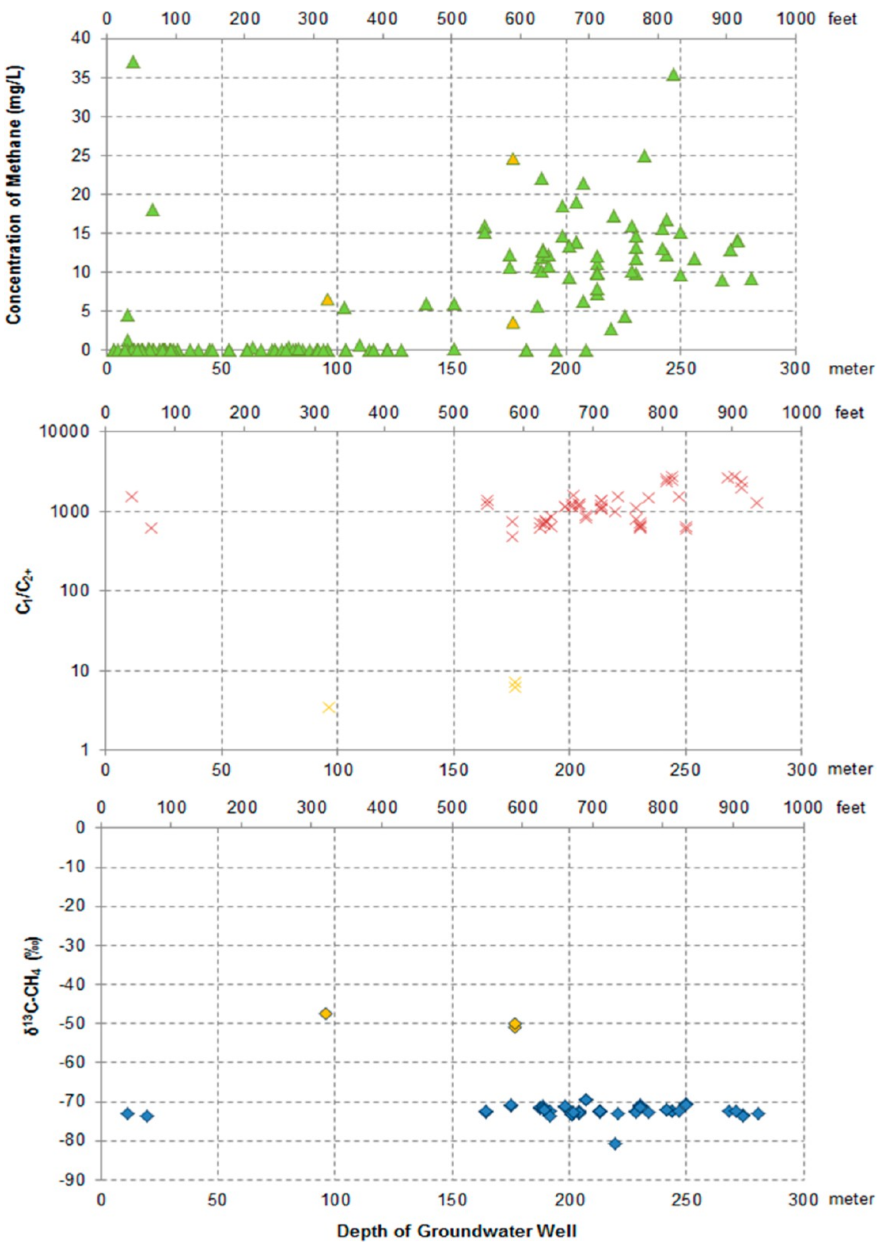

Figure 3. Plot of methane concentration, C_1/C_{2+}, and $\delta\ ^{13}CH_4$ with well depth.

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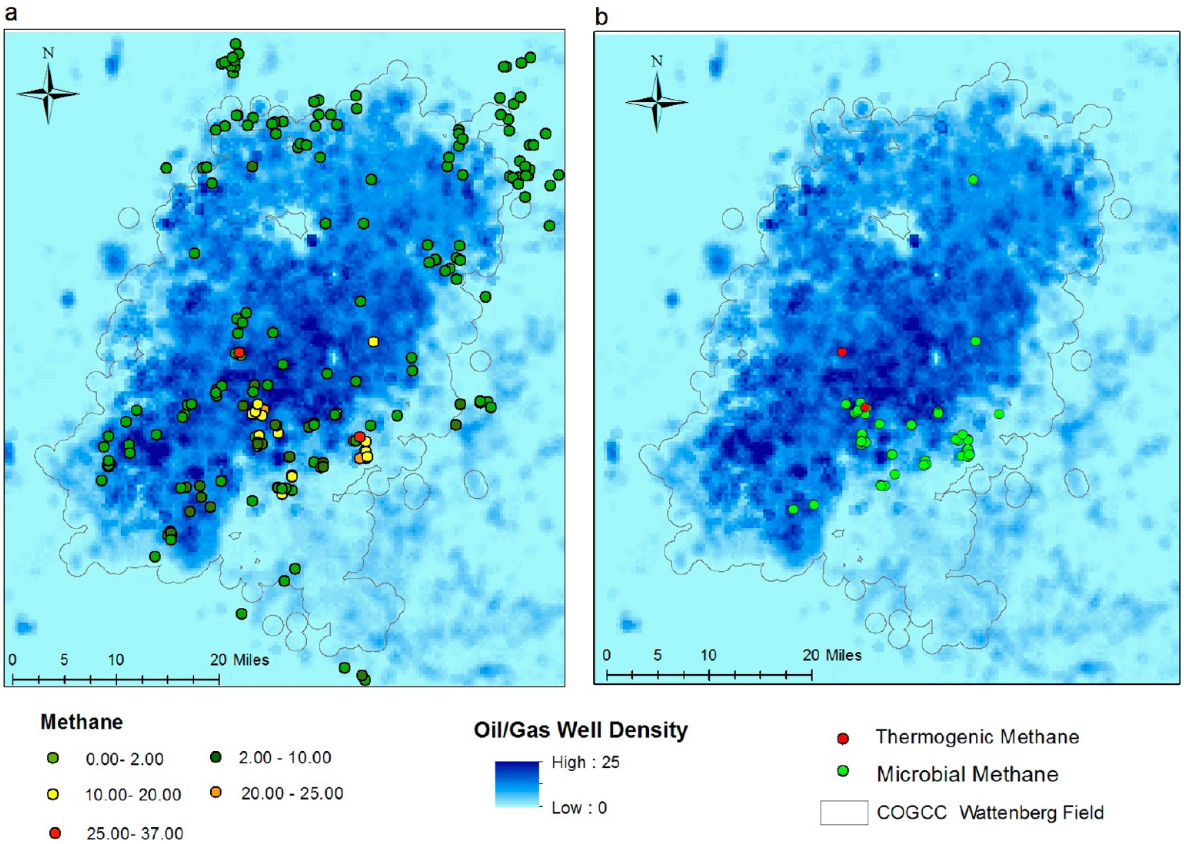

Figure 4. Location of COGCC groundwater wells in Wattenberg Field and distribution of dissolved methane in groundwater (from January 2012 to August 2013): (a) water matrix showing methane concentrations; (b) dissolved methane compositional analysis and isotopic results.

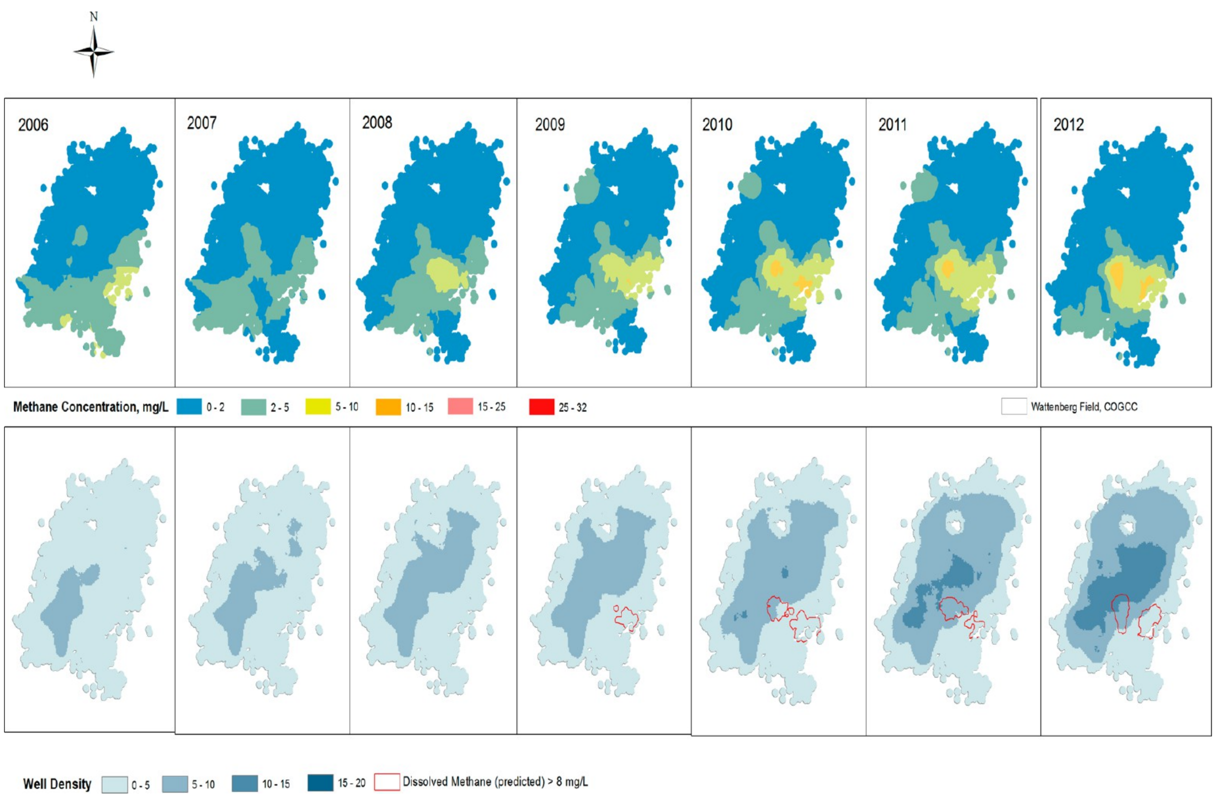

Figure 5. Distribution of methane and cumulative oil/gas well density in Wattenberg Field from 2006 to 2012 (well density was the number of oil/gas wells in a square kilometer).

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formations not only provides a large amount of hydrocarbons at greater depths but also favors anaerobic organisms to generate microbial methane in shallower formations. The presence of microbial methane coincident with deep natural gas deposits is a likely occurrence since the microorganisms could use the released energy with organic matter being oxidized to support their growth.[28]

To investigate the impact of oil and gas activities in the Wattenberg field on aquifer well methane concentrations, well density was examined. The evolution of oil and gas well density was explored to understand if the increased occurrence of drilling through groundwater aquifers and shallow reservoirs of microbial methane could result in a higher occurrence of stray gas migrating around casing leading to contamination of drinking water. For water samples collected between January 2012 and August 2013, Figure 4 illustrates the distributions of methane concentration, methane of different origins (biogenic or thermogenic), and oil/gas well density. The well density is based on total wells drilled (wellbores were completed) in and before 2012 to account for potential delayed effects related to drilling activity. Because isotopic components are only measured if dissolved methane exceeded 1.0 mg/L, the number of data points with isotope results are less than that shown in Figure 4a.

The average methane concentration was 4.0 mg/L ranging from 0 to 37.1 mg/L with a standard deviation of 6.6 mg/L. Over 20% of 223 samples had methane concentrations under the detection limit; 47% of the total samples had methane levels between 0 and 2 mg/L, and 2% of total sample points had methane in a range between 2 and 5 mg/L. Therefore, 70.5% of the overall samples had methane concentrations below 5 mg/L and only 3 out of 223 smaples had values exceeding 25 mg/L (1.2%). As shown in Figure 4b, the two groundwater wells that had "thermogenic" concentrations of methane were not located in the higher-density drilling areas.

Cumulative interpolation maps are shown in Figure 5 for both methane distribution and well density. Figure 5a shows the evolution of methane distribution and well density from 2006 to 2012 based on data provided by COGCC that includes all wells drilled.

Figure 5 shows spatial interpolation maps of methane concentration and well density incorporating all of the valid data associated with predicted areas with methane concentration exceeding 8 mg/L through the designated year in the analysis. A key assumption is that methane measured in one year will remain at that concentration in subsequent years if no more observations were available; otherwise, the mean concentration would be used. Methane in the northern Wattenberg field stayed at a low level which might be due to sufficient sulfate content in the water preventing microbial reduction of carbonate to methane.[20,29] Figure 5 illustrates the evolution of high methane areas (concentration of methane exceeded 8 mg/L), the growth of oil and gas activities, and the overlap of the high density areas. For the year 2008, the area with methane concentrations of 2−5 mg/L expanded in the south and began to have a small region exhibiting methane above 10 mg/L in the north edge of this 2−5 mg/L methane area. Locations of relatively high methane (above 10 mg/L) remained the same after 2008 but expanded slightly from 2008 to 2012. In contrast, methane in the northern Wattenberg field remained at a low level, distinct from areas to the south. The reason for this could be explained by methane or groundwater transport and heterogeneity of geological structure.

Potential transfers of methane involved two different migration mechanisms in the unsaturated and saturated zones. In the saturated zone, most of the methane would dissolve in water and transfer with groundwater flow; while in the unsaturated zone, methane partitions into three compartments, methane gas, dissolved methane, and sorbed methane on the soil surface.[30] Methane will preferentially dissolve in the water instead of partitioning to gas or solid phases when below saturation concentrations.[31]

The groundwater wells in the Wattenberg field for this analysis were located in the Laramie-Fox Hills aquifer[32,33]. Two opposite flow directions form in the north and south Wattenberg field due to an uplifting of the aquifer in the north part of the basin. This flow direction prevents the groundwater flow from south to north and along with the shallower buried depth of the aquifer contributes to the relative absence of dissolved methane in the northern section of the Wattenberg field. The lack of an available carbon source and/or the presence of higher redox conditions (higher sulfate concentrations) could also contribute to the lower incidence of elevated dissolved methane concentrations.

The area (km^2) and fraction (%) of the high methane areas (above 8 mg/L) in Figure 5b that overlap with different well density regions is shown in Table 1. Even in the latest year for which data was analyzed (2012), there is no overlap between the highest well density regions (15−20 wells within 500 m) and the high methane areas. The lack of overlap between the two high-density areas may indicate the absence of a correlation between oil and gas well drilling and the occurrence of biogenic methane. There does appear to be an increase in the overlap of the 10−15 wells within the 500 m density and the high methane concentration, but this is accompanied by a reduction in overlap with lower density areas (111 km^2 in 2010, 91 km^2 in 2012).

Table 1. Overlap between High Methane Areas (above 8 mg/L) and Areas of Different Well Densities: 2006 to 2012

	well density (number of wells within 500 m radius area)								
	0−5		5−10		10−15		15−20		total
year	area (km^2)	%	area (km^2)	%	area (km^2)	%	area (km^2)	%	area (km^2)
2006	55	83	11	17	0	0	0	0	66
2008	48	97	1	3	0	0	0	0	49
2010	111	87	16	13	<1	<1	0	0	127
2012	91	49	51	27	44	24	0	0	186

Plots of methane concentration versus the number of oil/gas wells within 500 and 1000 m are shown in Figure 6 for the water samples collected in 2012 and 2013. The figures represent the total number of oil/gas wells (since January 2012) in a circle area centered at the COGCC groundwater well with 500 and 1000 m radii, respectively. Methane concentration was randomly distributed with increasing numbers of oil/gas wells, and no obvious trend was observed.

For the 500 m radius, there is a decrease of methane concentration when the number of oil/gas wells within 500 m changed from 0−10 to 10−20 as the average methane concentration dropped from 5.8 to 2.5 mg/L (p = 0.03). For a 1000 m radius, there was no difference of methane concentration when the number of oil/gas wells changed from 0 to 40 (p = 0.4483). In summary, increasing well density did not correspondingly increase the methane concentration.

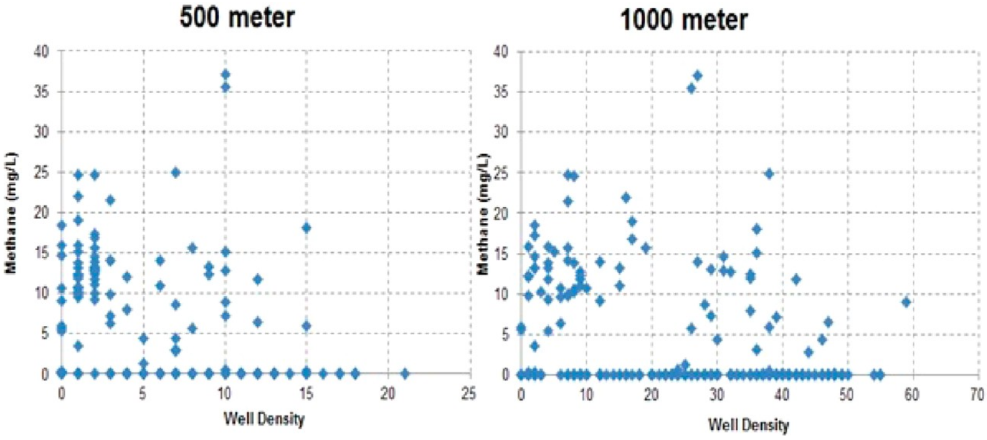

Figure 6. Histogram of methane in different well density areas for 500 and 1000 m distances.

Table 2. Frequency Distribution of Sample Sites by Distance

	distance (m)						
	0−100	100−200	200−300	300−400	400−500	500−1000	>1000
frequency	8	52	42	30	17	21	6
cumulative %	4.55	34.09	57.95	75	84.66	96.59	100

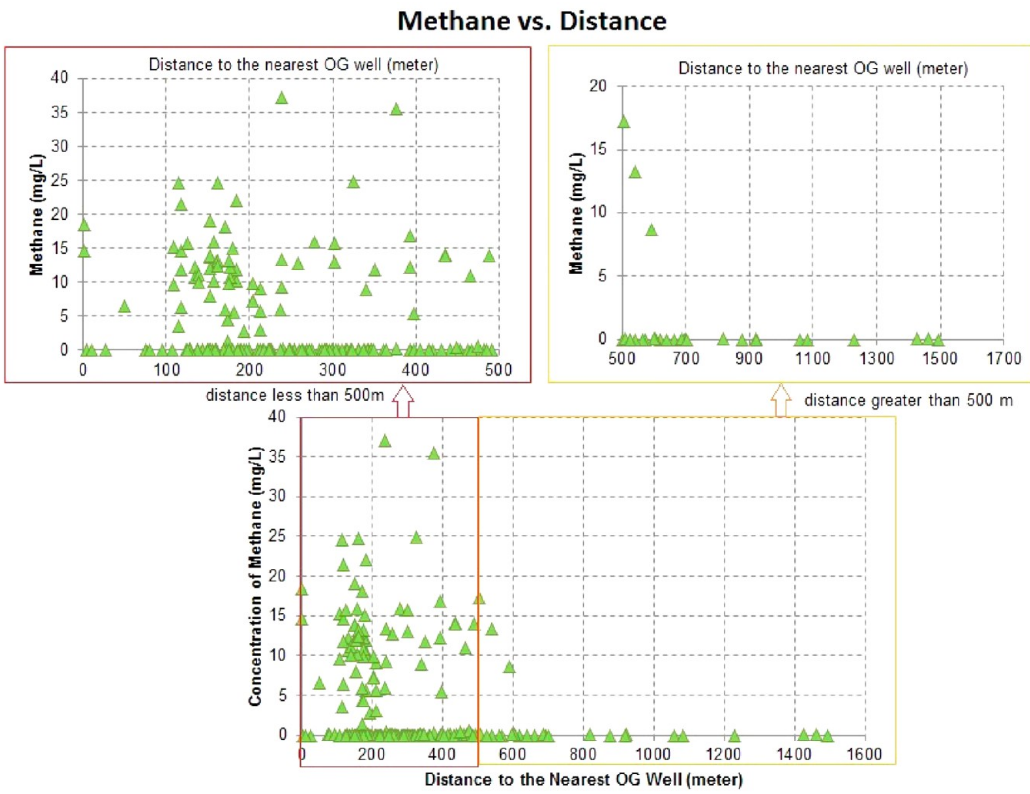

Figure 7. Plot of methane concentration versus distances to the nearest OG (oil/gas) well.

Distance from a groundwater well to the nearest oil/gas well is another factor used by Robert[34] and other studies to analyze the impact of oil and gas activities on methane occurrence. Since the Wattenberg field has been extensively developed over the past decades, there are high-density oil and gas producing areas at those distances. The majority of data points analyzed had distances to the nearest oil/gas wells less than 1000 m (96.6% from Table 2) and 84.7% of the total 223 data points within 500 m. Only 6 out of 223 samples (3.4%) were greater than 1000 m away from an oil and/or gas well. Since 150 feet was the minimum setback from an oil/gas well to a building (Rule 604),[35] few sampling wells were located within this limit.

Distance to the nearest oil and gas well was also used in our study to understand the contributing factors to methane occurrence in the Wattenberg field. Data were grouped by distance and average methane concentrations for each group and are shown in Figure 7. Methane concentration did not correlate with distance although the occurrence of methane

Table 3. Statistical Analysis Results (P Value) of Differences of Methane Concentration Classified by Distance

	distance to nearest oil/gas well (meters)					
P (t test)	0–100	100–200	200–300	300–400	400–500	500–1000
100–200	0.3073					
200–300	0.5694	0.0014				
300–400	0.9485	0.0874	0.4396			
400–500	0.6667	0.0220	0.8625	0.6048		
500–1000	0.3873	0.0008	0.5571	0.2309	0.5208	
>1000	0.1077	2.81×10^{-11}	0.0045	0.0065	0.0393	0.0962

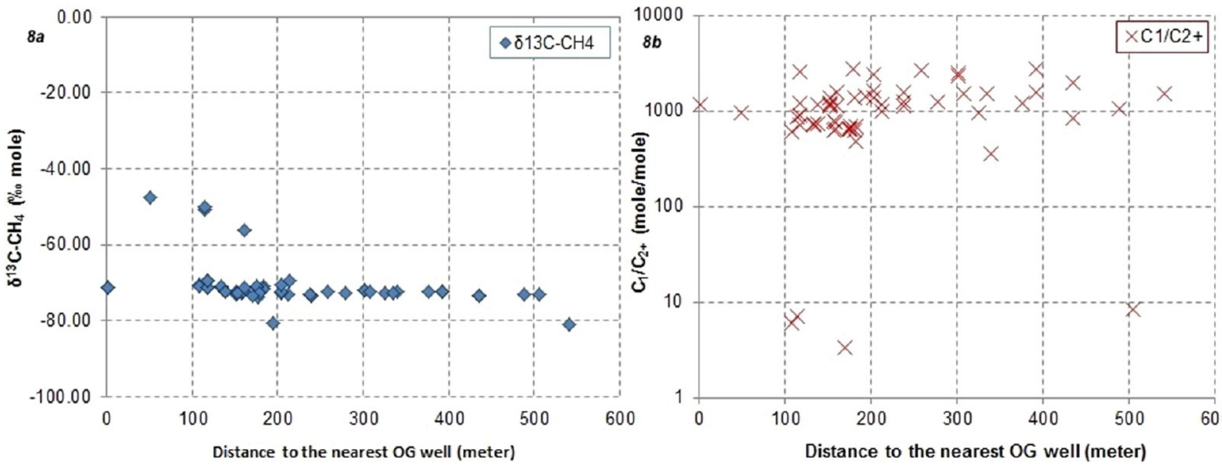

Figure 8. Plot of distances vs $\delta^{13}CH_4$ and C_1/C_{2+}.

levels above 5 mg/L appeared to decrease at distances greater than 700 m. The highest mean methane concentration (6.5 mg/L) occurred in groundwater wells between 100 and 200 m from oil and gas wells, and 42.2% of the wells in this range had methane concentrations greater than 8 mg/L. The groundwater wells having oil/gas wells between 0 and 100 m had a mean concentration of methane of 4.0 mg/L, lower than that within the 100–200 m range, without a statistical difference (p = 0.3073). The methane concentrations did not change significantly when the distance decreased from 500 to 200 m (t test results shown in Table 3 by comparison of concentrations of methane grouped by distance).

Figure 8 shows $\delta^{13}C-CH_4$ and ratio of C_1 to C_{2+} plotted versus distances to the nearest oil and gas wells. Methane sources (biogenic versus thermogenic) can be inferred on the basis of only the isotopic carbon component ($\delta^{13}C$). An isotopic signature of $\delta^{13}C-CH_4 \geq -40$‰ (reference to Vienna Pee Dee Belemnite standard[36]) generally suggests a thermogenic origin for methane, whereas $\delta^{13}C-CH_4 \leq -60$‰ indicates a microbial derived methane source. $\delta^{13}C-CH_4$ falling in between −40 and −60 ‰ refers to a mixed or transition status.[6]

Neither $\delta^{13}C-CH_4$ or gas dryness (ratio of C_1 to C_{2+}) appeared to correlate with the distance to the nearest oil/gas well. These results coupled with observations from Figure 7 indicate that distance from nearest oil and gas wells does not have an obvious effect on the methane concentration or methane source. However, in both Figures 7 and 8, there are fewer data points within 100 m of an oil and gas well, potentially due to regulated setback distances. Since thermogenic methane would be expected to have a low C_1/C_{2+}, the three points with a ratio less than 10 in Figure 8b being closer to the water well may be an expected observation.

Methane is pervasive in groundwater wells in the Wattenberg field with widely varying concentrations. Greater than 98% of dissolved methane measurements appear to have been generated from microbial processes, and the concentration and occurrence increased with increasing water well depth. The results of the study did not indicate systematic contamination of aquifers with methane due to oil and gas activities in the Wattenberg field, and elevated methane levels do not appear to be the result of increased drilling and fracturing. More likely, increased methane occurrence is due to aquifer utilization in areas with abundant sources of naturally occurring biogenic methane.

■ ASSOCIATED CONTENT

Supporting Information

Table of laboratory analyses and analytical methods. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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