Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing

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Directional drilling and hydraulic-fracturing technologies are dramatically increasing natural-gas extraction. In aquifers overlying the Marcellus and Utica shale formations of northeastern Pennsylvania and upstate New York, we document systematic evidence for methane contamination of drinking water associated with shale-gas extraction. In active gas-extraction areas (one or more gas wells within 1 km), average and maximum methane concentrations in drinking-water wells increased with proximity to the nearest gas well and were 19.2 and 64 mg CH_4 L^{-1} ($n = 26$), a potential explosion hazard; in contrast, dissolved methane samples in neighboring nonextraction sites (no gas wells within 1 km) within similar geologic formations and hydrogeologic regimes averaged only 1.1 mg L^{-1} ($P < 0.05$; $n = 34$). Average $\delta^{13}C$-CH_4 values of dissolved methane in shallow groundwater were significantly less negative for active than for nonactive sites (−37 ± 7‰ and −54 ± 11‰, respectively; $P < 0.0001$). These $\delta^{13}C$-CH_4 data, coupled with the ratios of methane-to-higher-chain hydrocarbons, and $\delta^{2}H$-CH_4 values, are consistent with deeper thermogenic methane sources such as the Marcellus and Utica shales at the active sites and matched gas geochemistry from gas wells nearby. In contrast, lower-concentration samples from shallow groundwater at nonactive sites had isotopic signatures reflecting a more biogenic or mixed biogenic/thermogenic methane source. We found no evidence for contamination of drinking-water samples with deep saline brines or fracturing fluids. We conclude that greater stewardship, data, and—possibly—regulation are needed to ensure the sustainable future of shale-gas extraction and to improve public confidence in its use.

groundwater | organic-rich shale | isotopes | formation waters | water chemistry

Increases in natural-gas extraction are being driven by rising energy demands, mandates for cleaner burning fuels, and the economics of energy use (1–5). Directional drilling and hydraulic-fracturing technologies are allowing expanded natural-gas extraction from organic-rich shales in the United States and elsewhere (2, 3). Accompanying the benefits of such extraction (6, 7) are public concerns about drinking-water contamination from drilling and hydraulic fracturing that are ubiquitous but lack a strong scientific foundation. In this paper, we evaluate the potential impacts associated with gas-well drilling and fracturing on shallow groundwater systems of the Catskill and Lockhaven formations that overlie the Marcellus Shale in Pennsylvania and the Genesee Group that overlies the Utica Shale in New York (Figs. 1 and 2 and Fig. S1). Our results show evidence for methane contamination of shallow drinking-water systems in at least three areas of the region and suggest important environmental risks accompanying shale-gas exploration worldwide.

The drilling of organic-rich shales, typically of Upper Devonian to Ordovician age, in Pennsylvania, New York, and elsewhere in the Appalachian Basin is spreading rapidly, raising concerns for impacts on water resources (8, 9). In Susquehanna County, Pennsylvania alone, approved gas-well permits in the Marcellus formation increased 27-fold from 2007 to 2009 (10).

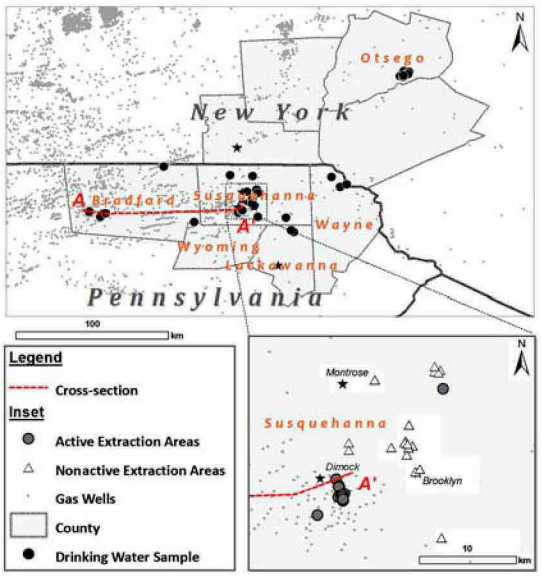

Fig. 1. Map of drilling operations and well-water sampling locations in Pennsylvania and New York. The star represents the location of Binghamton, New York. (*Inset*) A close-up in Susquehanna County, Pennsylvania, showing areas of active (closed circles) or nonactive (open triangles) extraction. A drinking-water well is classified as being in an active extraction area if a gas well is within 1 km (see *Methods*). Note that drilling has already spread to the area around Brooklyn, Pennsylvania, primarily a nonactive location at the time of our sampling (see inset). The stars in the inset represent the towns of Dimock, Brooklyn, and Montrose, Pennsylvania.

Concerns for impacts to groundwater resources are based on (*i*) fluid (water and gas) flow and discharge to shallow aquifers due to the high pressure of the injected fracturing fluids in the gas wells (10); (*ii*) the toxicity and radioactivity of produced water from a mixture of fracturing fluids and deep saline formation waters that may discharge to the environment (11); (*iii*) the potential explosion and asphyxiation hazard of natural gas; and (*iv*) the large number of private wells in rural areas that rely on shallow groundwater for household and agricultural use—up to one million wells in Pennsylvania alone—that are typically unregulated and untested (8, 9, 12). In this study, we analyzed groundwater from 68 private water wells from 36- to 190-m deep in

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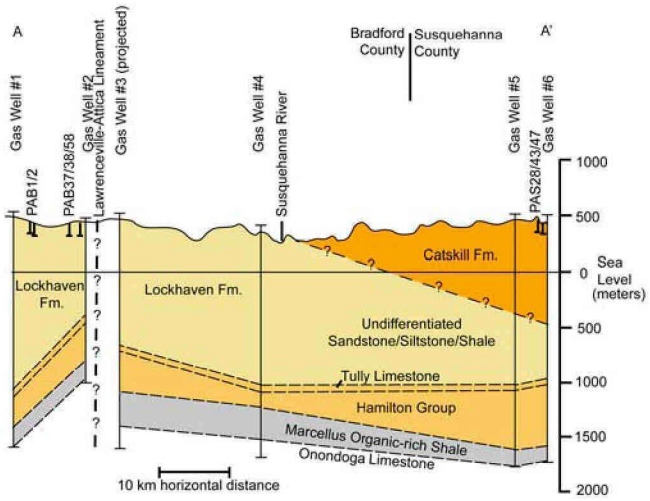

Fig. 2. Geologic cross-section of Bradford and western Susquehanna Counties created from gas-well log data provided by the Pennsylvania Department of Conservation and Natural Resources. The approximate location of the Lawrenceville-Attica Lineament is taken from Alexander et al. (34). The Ordovician Utica organic-rich shale (not depicted in the figure) underlies the Middle Devonian Marcellus at approximately 3,500 m below the ground surface.

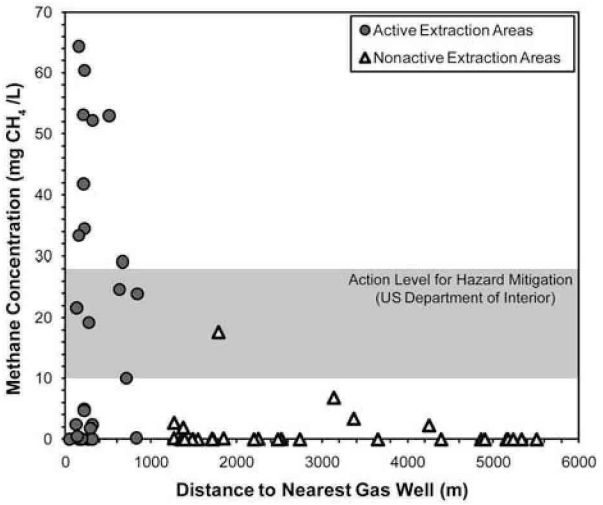

Fig. 3. Methane concentrations (milligrams of CH_4 L^{-1}) as a function of distance to the nearest gas well from active (closed circles) and nonactive (open triangles) drilling areas. Note that the distance estimate is an upper limit and does not take into account the direction or extent of horizontal drilling underground, which would decrease the estimated distances to some extraction activities. The precise locations of natural-gas wells were obtained from the Pennsylvania Department of Environmental Protection and Pennsylvania Spatial Data Access databases (ref. 35; accessed Sept. 24, 2010).

northeast Pennsylvania (Catskill and Lockhaven formations) and upstate New York (Genesee formation) (see Figs. 1 and 2 and *SI Text*), including measurements of dissolved salts, water isotopes (^{18}O and ^{2}H), and isotopes of dissolved constituents (carbon, boron, and radium). Of the 68 wells, 60 were also analyzed for dissolved-gas concentrations of methane and higher-chain hydrocarbons and for carbon and hydrogen isotope ratios of methane. Although dissolved methane in drinking water is not currently classified as a health hazard for ingestion, it is an asphyxiant in enclosed spaces and an explosion and fire hazard (8). This study seeks to evaluate the potential impact of gas drilling and hydraulic fracturing on shallow groundwater quality by comparing areas that are currently exploited for gas (defined as active—one or more gas wells within 1 km) to those that are not currently associated with gas drilling (nonactive; no gas wells within 1 km), many of which are slated for drilling in the near future.

Results and Discussion

Methane concentrations were detected generally in 51 of 60 drinking-water wells (85%) across the region, regardless of gas industry operations, but concentrations were substantially higher closer to natural-gas wells (Fig. 3). Methane concentrations were 17-times higher on average (19.2 mg CH_4 L^{-1}) in shallow wells from active drilling and extraction areas than in wells from nonactive areas (1.1 mg L^{-1} on average; $P < 0.05$; Fig. 3 and Table 1). The *average* methane concentration in shallow groundwater in active drilling areas fell within the defined action level (10–28 mg L^{-1}) for hazard mitigation recommended by the US Office of the Interior (13), and our maximum observed value of 64 mg L^{-1} is well above this hazard level (Fig. 3). Understanding the origin of this methane, whether it is shallower biogenic or deeper thermogenic gas, is therefore important for identifying the source of contamination in shallow groundwater systems.

The $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 values and the ratio of methane to higher-chain hydrocarbons (ethane, propane, and butane) can typically be used to differentiate shallower, biologically derived methane from deeper physically derived thermogenic methane (14). Values of $\delta^{13}C$-CH_4 less negative than approximately −50‰ are indicative of deeper thermogenic methane, whereas values more negative than −64‰ are strongly indicative of microbial methane (14). Likewise, $\delta^{2}H$-CH_4 values more negative than about −175‰, particularly when combined with low $\delta^{13}C$-CH_4 values, often represent a purer biogenic methane origin (14).

The average $\delta^{13}C$-CH_4 value in shallow groundwater in active drilling areas was -37 ± 7‰, consistent with a deeper thermogenic methane source. In contrast, groundwater from nonactive areas in the same aquifers had much lower methane concentrations and significantly lower $\delta^{13}C$-CH_4 values (average of −54± 11‰; $P < 0.0001$; Fig. 4 and Table 1). Both our $\delta^{13}C$-CH_4 data and $\delta^{2}H$-CH_4 data (see Fig. S2) are consistent with a deeper thermogenic methane source at the active sites and a more biogenic or mixed methane source for the lower-concentration samples from nonactive sites (based on the definition of Schoell, ref. 14).

Because ethane and propane are generally not coproduced during microbial methanogenesis, the presence of higher-chain hydrocarbons at relatively low methane-to-ethane ratios (less than approximately 100) is often used as another indicator of deeper thermogenic gas (14, 15). Ethane and other higher-chain hydrocarbons were detected in only 3 of 34 drinking-water wells from nonactive drilling sites. In contrast, ethane was detected in 21 of 26 drinking-water wells in active drilling sites. Additionally, propane and butane were detected (>0.001 mol %) in eight and two well samples, respectively, from active drilling areas but in no wells from nonactive areas.

Further evidence for the difference between methane from water wells near active drilling sites and neighboring nonactive sites is the relationship of methane concentration to $\delta^{13}C$-CH_4 values (Fig. 4*A*) and the ratios of methane to higher-chain hydro-

Table 1. Mean values ± standard deviation **of methane concentrations (as milligrams of CH_4 L^{-1}) and carbon isotope composition in methane in shallow groundwater $\delta^{13}C$-CH_4 sorted by aquifers and proximity to gas wells (active vs. nonactive)**

Water source, *n*	milligrams CH_4 L^{-1}	$\delta^{13}C$-CH_4, ‰
Nonactive Catskill, 5	1.9 ± 6.3	−52.5 ± 7.5
Active Catskill, 13	26.8 ± 30.3	−33.5 ± 3.5
Nonactive Genesee, 8	1.5 ± 3.0	−57.5 ± 9.5
Active Genesee, 1	0.3	−34.1
Active Lockhaven, 7	50.4 ± 36.1	−40.7 ± 6.7
Total active wells, 21	19.2	−37 ± 7
Total nonactive wells, 13	1.1	−54 ± 11

The variable *n* refers to the number of samples.

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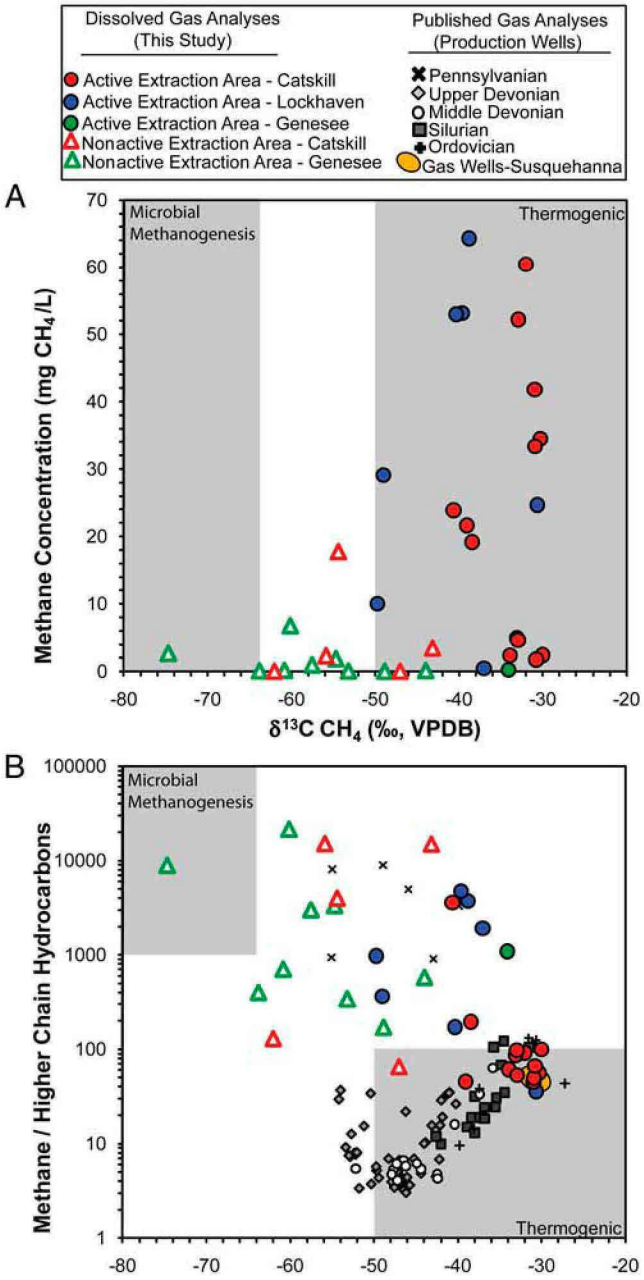

Fig. 4. (*A*) Methane concentrations in groundwater versus the carbon isotope values of methane. The nonactive and active data depicted in Fig. 3 are subdivided based on the host aquifer to illustrate that the methane concentrations and δ^{13}C values increase with proximity to natural-gas well drilling regardless of aquifer formation. Gray areas represent the typical range of thermogenic and biogenic methane taken from Osborn and McIntosh (18). VPDB, Vienna Pee Dee belemnite. (*B*) Bernard plot (15) of the ratio of methane to higher-chain hydrocarbons versus the δ^{13}C of methane. The smaller symbols in grayscale are from published gas-well samples from gas production across the region (16–18). These data generally plot along a trajectory related to reservoir age and thermal maturity (Upper Devonian through Ordovician; see text for additional details). The gas-well data in the orange ovals are from gas wells in our study area in Susquehanna County, Pennsylvania (data from Pennsylvania Department of Environmental Protection). Gray areas represent typical ranges of thermogenic and biogenic methane (data from Osborn and McIntosh, ref. 18).

carbons versus δ^{13}C-CH_4 (Fig. 4*B*). Methane concentrations not only increased in proximity to gas wells (Fig. 3), the accompanying δ^{13}C-CH_4 values also reflected an increasingly thermogenic methane source (Fig. 4*A*).

Using a Bernard plot (15) for analysis (Fig. 4*B*), the enriched δ^{13}C-CH_4 (approximately $> -50‰$) values accompanied by low ratios of methane to higher-chain hydrocarbons (less than approximately 100) in drinking-water wells also suggest that dissolved gas is more thermogenic at active than at nonactive sites (Fig. 4*B*). For instance, 12 dissolved-gas samples at active drilling sites fell along a regional gas trajectory that increases with reservoir age and thermal maturity of organic matter, with samples from Susquehanna County, Pennsylvania specifically matching natural-gas geochemistry from local gas wells (Fig. 4*B*, orange oval). These 12 samples and local natural-gas samples are consistent with gas sourced from thermally mature organic matter of Middle Devonian and older depositional ages often found in Marcellus Shale from approximately 2,000 m below the surface in the northern Appalachian Basin (14–19) (Fig. 4*B*). In contrast, none of the methane samples from nonactive drilling areas fell upon this trajectory (Fig. 4*B*); eight dissolved-gas samples in Fig. 4*B* from active drilling areas and all of the values from nonactive areas may instead be interpreted as mixed biogenic/thermogenic gas (18) or, as Laughrey and Baldassare (17) proposed for their Pennsylvanian gas data (Fig. 4*B*), the early migration of wet thermogenic gases with low-δ^{13}C-CH_4 values and high methane-to-higher-chain hydrocarbon ratios. One data point from a nonactive area in New York fell squarely in the parameters of a strictly biogenic source as defined by Schoell (14) (Fig. 4*B*, upper-left corner).

Carbon isotopes of dissolved inorganic carbon (δ^{13}C-DIC $> +10‰$) and the positive correlation of δ^2H of water and δ^2H of methane have been used as strong indicators of microbial methane, further constraining the source of methane in shallow groundwater (depth less than 550 m) (18, 20). Our δ^{13}C-DIC values were fairly negative and show no association with the δ^{13}C-CH_4 values (Fig. S3), which is not what would be expected if methanogenesis were occurring locally in the shallow aquifers. Instead, the δ^{13}C-DIC values from the shallow aquifers plot within a narrow range typical for shallow recharge waters, with the dissolution of CO_2 produced by respiration as water passes downward through the soil critical zone. Importantly, these values do not indicate extensive microbial methanogenesis or sulfate reduction. The data do suggest gas-phase transport of methane upward to the shallow groundwater zones sampled for this study (<190 m) and dissolution into shallow recharge waters locally. Additionally, there was no positive correlation between the δ^2H values of methane and δ^2H of water (Fig. S4), indicating that microbial methane derived in this shallow zone is negligible. Overall, the combined gas and formation-water results indicate that thermogenic gas from thermally mature organic matter of Middle Devonian and older depositional ages is the most likely source of the high methane concentrations observed in the shallow water wells from active extraction sites.

A different potential source of shallow groundwater contamination associated with gas drilling and hydraulic fracturing is the introduction of hypersaline formation brines and/or fracturing fluids. The average depth range of drinking-water wells in northeastern Pennsylvania is from 60 to 90 m (12), making the average vertical separation between drinking-water wells and the Marcellus Shale in our study area between approximately 900 and 1,800 m (Fig. 2). The research area, however, is located in tectonically active areas with mapped faults, earthquakes, and lineament features (Fig. 2 and Fig. S1). The Marcellus formation also contains two major sets of joints (21) that could be conduits for directed pressurized fluid flow. Typical fracturing activities in the Marcellus involve the injection of approximately 13–19 million liters of water per well (22) at pressures of up to 69,000 kPa. The majority of this fracturing water typically stays underground and could in principle displace deep formation water upward into shallow aquifers. Such deep formation waters often have high concentrations of total dissolved solids >250,000 mg L^{-1}, trace

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toxic elements, (18), and naturally occurring radioactive materials, with activities as high as 16,000 picocuries per liter (1 pCi L^{-1} = 0.037 becquerels per liter) for ^{226}Ra compared to a drinking-water standard of 5 pCi L^{-1} for combined ^{226}Ra and ^{226}Ra (23).

We evaluated the hydrochemistry of our 68 drinking-water wells and compared these data to historical data of 124 wells in the Catskill and Lockhaven aquifers (24, 25). We used three types of indicators for potential mixing with brines and/or saline fracturing fluids: (*i*) major inorganic chemicals; (*ii*) stable isotope signatures of water ($\delta^{18}O$, $\delta^{2}H$); and (*iii*) isotopes of dissolved constituents ($\delta^{13}C$-DIC, $\delta^{11}B$, and ^{226}Ra). Based on our data (Table 2), we found no evidence for contamination of the shallow wells near active drilling sites from deep brines and/or fracturing fluids. All of the Na^{+}, Cl^{-}, Ca^{2+}, and DIC concentrations in wells from active drilling areas were consistent with the baseline historical data, and none of the shallow wells from active drilling areas had either chloride concentrations >60 mg L^{-1} or Na-Ca-Cl compositions that mirrored deeper formation waters (Table 2). Furthermore, the mean isotopic values of $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$-DIC, $\delta^{11}B$, and ^{226}Ra in active and nonactive areas were indistinguishable. The ^{226}Ra values were consistent with available historical data (25), and the composition of $\delta^{18}O$ and $\delta^{2}H$ in the well-water appeared to be of modern meteoric origin for Pennsylvania (26) (Table 2 and Fig. S5). In sum, the geochemical and isotopic features for water we measured in the shallow wells from both active and nonactive areas are consistent with historical data and inconsistent with contamination from mixing Marcellus Shale formation water or saline fracturing fluids (Table 2).

There are at least three possible mechanisms for fluid migration into the shallow drinking-water aquifers that could help explain the increased methane concentrations we observed near gas wells (Fig. 3). The first is physical displacement of gas-rich deep solutions from the target formation. Given the lithostatic and hydrostatic pressures for 1–2 km of overlying geological strata, and our results that appear to rule out the rapid movement of deep brines to near the surface, we believe that this mechanism is unlikely. A second mechanism is leaky gas-well casings (e.g., refs. 27 and 28). Such leaks could occur at hundreds of meters underground, with methane passing laterally and vertically through fracture systems. The third mechanism is that the process of hydraulic fracturing generates new fractures or enlarges existing ones above the target shale formation, increasing the connectivity of the fracture system. The reduced pressure following the fracturing activities could release methane in solution, leading to methane exsolving rapidly from solution (29), allowing methane gas to potentially migrate upward through the fracture system.

Methane migration through the 1- to 2-km-thick geological formations that overlie the Marcellus and Utica shales is less likely as a mechanism for methane contamination than leaky well casings, but might be possible due to both the extensive fracture systems reported for these formations and the many older, uncased wells drilled and abandoned over the last century and a half in Pennsylvania and New York. The hydraulic conductivity in the overlying Catskill and Lockhaven aquifers is controlled by a secondary fracture system (30), with several major faults and lineaments in the research area (Fig. 2 and Fig. S1). Consequently, the high methane concentrations with distinct positive $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 values in the shallow groundwater from active areas could in principle reflect the transport of a deep methane source associated with gas drilling and hydraulic-fracturing activities. In contrast, the low-level methane migration to the surface groundwater aquifers, as observed in the nonactive areas, is likely a natural phenomenon (e.g., ref. 31). Previous studies have shown that naturally occurring methane in shallow aquifers is typically associated with a relatively strong biogenic signature indicated by depleted $\delta^{13}C$-CH_4 and $\delta^{2}H$-CH_4 compositions (32) coupled with high ratios of methane to higher-chain hydrocarbons (33), as we observed in Fig. 4*B*. Several models have been developed to explain the relatively common phenomenon of rapid vertical transport of gases (Rn, CH_4, and CO_2) from depth to the surface (e.g., ref. 31), including pressure-driven continuous gas-phase flow through dry or water-saturated fractures and density-driven buoyancy of gas microbubbles in aquifers and water-filled fractures (31). More research is needed across this and other regions to determine the mechanism(s) controlling the higher methane concentrations we observed.

Based on our groundwater results and the litigious nature of shale-gas extraction, we believe that long-term, coordinated sampling and monitoring of industry and private homeowners is needed. Compared to other forms of fossil-fuel extraction, hydraulic fracturing is relatively poorly regulated at the federal level. Fracturing wastes are not regulated as a hazardous waste under the Resource Conservation and Recovery Act, fracturing wells are not covered under the Safe Drinking Water Act, and only recently has the Environmental Protection Agency asked fracturing

Table 2. Comparisons of selected major ions and isotopic results in drinking-water wells from this study to data available on the same formations (Catskill and Lockhaven) in previous studies (24, 25) and to underlying brines throughout the Appalachian Basin (18)

	Active		Nonactive		Previous studies (background)		
	Lockhaven formation $N = 8$	Catskill formation $N = 25$	Catskill formation $N = 22$	Genesee group $N = 12$	Lockhaven formation (25) $N = 45$	Catskill formation (24) $N = 79$	Appalachian brines (18, 23) $N = 21$
Alkalinity as HCO_3^-,							
mg L^{-1}	285 ± 36	157 ± 56	127 ± 53	158 ± 56	209 ± 77	133 ± 61	150 ± 171
mM	[4.7 ± 0.6]	[2.6 ± 0.9]	[2.1 ± 0.9]	[2.6 ± 0.9]	[3.4 ± 1.3]	[2.2 ± 1.0]	[2.5 ± 2.8]
Sodium, mg L^{-1}	87 ± 22	23 ± 30	17 ± 25	29 ± 23	100 ± 312	21 ± 37	33,000 ± 11,000
Chloride, mg L^{-1}	25 ± 17	11 ± 12	17 ± 40	9 ± 19	132 ± 550	13 ± 42	92,000 ± 32,000
Calcium, mg L^{-1}	22 ± 12	31 ± 13	27 ± 9	26 ± 5	49 ± 39	29 ± 11	16,000 ± 7,000
Boron, μg L^{-1}	412 ± 156	93 ± 167	42 ± 93	200 ± 130	NA	NA	3,700 ± 3,500
$\delta^{11}B$ ‰	27 ± 4	22 ± 6	23 ± 6	26 ± 6	NA	NA	39 ± 6
^{226}Ra, *p*Ci L^{-1}	0.24 ± 0.2	0.16 ± 0.15	0.17 ± 0.14	0.2 ± 0.15	0.56 ± 0.74	NA	6,600 ± 5,600
$\delta^{2}H$, ‰, VSMOW	−66 ± 5	−64 ± 3	−68 ± 6	−76 ± 5	NA	NA	−41 ± 6
$\delta^{18}O$, ‰, VSMOW	−10 ± 1	−10 ± 0.5	−11 ± 1	−12 ± 1	NA	NA	−5 ± 1

Some data for the active Genesee Group and nonactive Lockhaven Formation are not included because of insufficient sample sizes (NA). Values represent means ±1 standard deviation. NA, not available.

N values for $\delta^{11}B$ ‰ analysis are 8, 10, 3, 6, and 5 for active Lockhaven, active Catskill, nonactive Genesee, nonactive Catskill, and brine, respectively. *N* values for ^{226}Ra are 6, 7, 3, 10, 5, and 13 for active Lockhaven, active Catskill, nonactive Genesee, nonactive Catskill, background Lockhaven, and brine, respectively. $\delta^{11}B$ ‰ normalized to National Institute of Standards and Technology Standard Reference Material 951. $\delta^{2}H$ and $\delta^{18}O$ normalized to Vienna Standard Mean Ocean Water (VSMOW).

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firms to voluntarily report a list of the constituents in the fracturing fluids based on the Emergency Planning and Community Right-to-Know Act. More research is also needed on the mechanism of methane contamination, the potential health consequences of methane, and establishment of baseline methane data in other locations. We believe that systematic and independent data on groundwater quality, including dissolved-gas concentrations and isotopic compositions, should be collected before drilling operations begin in a region, as is already done in some states. Ideally, these data should be made available for public analysis, recognizing the privacy concerns that accompany this issue. Such baseline data would improve environmental safety, scientific knowledge, and public confidence. Similarly, long-term monitoring of groundwater and surface methane emissions during and after extraction would clarify the extent of problems and help identify the mechanisms behind them. Greater stewardship, knowledge, and—possibly—regulation are needed to ensure the sustainable future of shale-gas extraction.

Methods

A total of 68 drinking-water samples were collected in Pennsylvania and New York from bedrock aquifers (Lockhaven, 8; Catskill, 47; and Genesee, 13) that overlie the Marcellus or Utica shale formations (Fig. S1). Wells were purged to remove stagnant water, then monitored for pH, electrical conductance, and temperature until stable values were recorded. Samples were collected "upstream" of any treatment systems, as close to the water well as possible, and preserved in accordance with procedures detailed in *SI Methods*. Dissolved-gas samples were analyzed at Isotech Laboratories and water chemical and isotope (O, H, B, C, Ra) compositions were measured at Duke University (see *SI Methods* for analytical details).

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Supporting Information

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SI Methods

Dissolved gas samples were collected in the field using procedures detailed by Isotech Laboratories (1), stored on ice until delivery to their facilities, and analyzed for concentrations and isotopic compositions of methane and higher-chain hydrocarbons. Analytical procedures for gas analyses are detailed in Osborn and McIntosh (2). The detection limits for methane and ethane were 0.0005 and 0.001 mol %, respectively, with a conservative ethane detection limit used for a few samples from nonactive areas in order to calculate the methane-to-higher-hydrocarbon ratios in Fig. 4*B*. Methane concentrations in some nonactive areas were estimated in milligrams of CH_4 L^{-1} from a correlation with mol % ($R^2 = 0.95$). Water sampling for elemental and isotopic analyses strictly followed US Geological Survey protocols (3) after filtration of samples in the field (0.45 μm syringe filters), with samples stored on ice for transport to Duke University and held in cold storage prior to analyses.

Major cations (Na^+, Ca^{+2}, Mg^{+2}) were analyzed using direct-current plasma optical emission spectrometry; major anions (Cl^-, Br^-, NO_3^-, and SO_4^{-2}) were determined by ion chromatography. In both cases, sample signals/concentrations were bound by matrix standards and reproducibility was compared to external standards. Trace metal concentrations were determined by a VG PlasmaQuad-3 inductively coupled plasma mass-spectrometer calibrated to the National Institute of Standards and Technology (NIST) 1643e standard. Alkalinity concentrations were determined by the Gran-Alk titration method (4) in duplicate. Values of $\delta^{13}C$, δ^2H, and $\delta^{18}O$ were determined by a Thermofinnigan Delta+XL gas-source isotope ratio mass spectrometer at the Duke Environmental Isotope Laboratory. Boron isotopes were analyzed by negative thermal ionization mass spectrometer on a ThermoFisher Triton at Duke University using a B-free seawater loading solution (5). Boron isotope ratios are reported in the conventional $\delta^{11}B$ notation as relative values to the NIST Standard Reference Material 951 boric acid standard. Radium isotope analyses (^{226}Ra) were measured at the Laboratory for Environmental Analysis of RadioNuclides at Duke University using a Durridge RAD7 radon-in-air monitor (6).

Hydrogeology

The study area consists of sites in northeastern Pennsylvania and upstate New York, northwest of Binghamton, that lie within the Appalachian Plateaus and Valleys complex (Fig. S1). The surficial geology is dominated by unconsolidated glacial sand, gravel, and till that range from a few meters on mountain tops to tens of meters in the valleys (7). The glacial deposits are underlain by an Upper Devonian sedimentary sequence that contains the Catskill and Lockhaven formations as well as the Genesee Group. The Catskill aquifer in northeastern Pennsylvania is composed of various amounts of gray to red shale, siltstone, sandstone, and conglomerate (8, 9) and overlies the Lockhaven Formation, with interbedded units of finely grained sandstone, siltstone, and silty shale (10). The Genesee Group, interbedded shale, sandstone, and siltstone, is part of the Upper Devonian stratigraphic sequence in New York. Both the Genesee Group in New York and the Lockhaven Formation in Pennsylvania overlie the Middle Devonian Hamilton Group, which includes Tully Limestone and the Marcellus Shale. Groundwater flow in all three aquifers is dominated by fracture flow through secondary porosity with variable flow rates from topographic highs to the lowland discharge areas (11). Generally, there are low total dissolved solids (<500 mg/L) and Ca-HCO_3 composition (7, 8), although local areas of high salinity (Na and Cl > 1,000 mg/L) in the Lockhaven Formation are rare (7). The area contains multiple faults and lineaments as mapped by ref. 11 (Fig. 2 and Fig. S1). The Marcellus formation slopes to the east and lies 1–4 km below the ground surface in the western and eastern portions of the study area, respectively. The study area was chosen because of its rapid expansion of drilling for natural gas from the Marcellus Shale (Pennsylvania) and Utica Shale (New York), and because it represents portions of both the upper Susquehanna and upper Delaware watersheds that combined provide drinking water to more than 15 million people.

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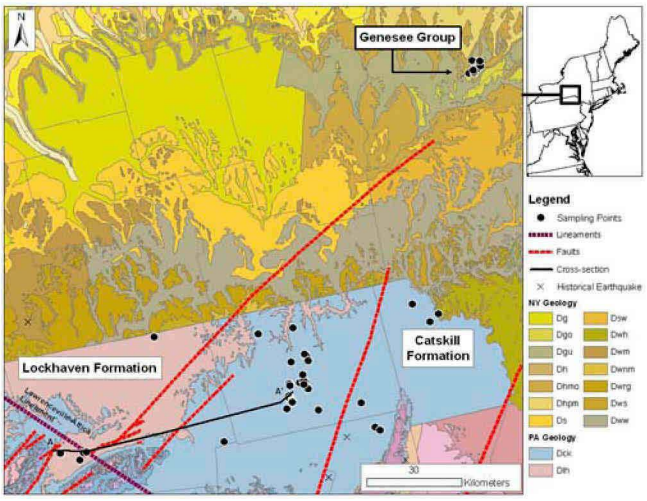

Fig. S1. Sampling locations in relation to bedrock geology for northeastern Pennsylvania and New York. Geological maps were obtained from United States Geological Survey state maps of New York (http://tin.er.usgs.gov/geology/state/state.php?state=NY) and Pennsylvania (http://tin.er.usgs.gov/geology/state/state.php?state=PA). Faults and lineaments mapped from data available through the Pennsylvania Department of Conservation and Natural Resources (1). New York Geologic Formations: Dwh = Honesdale; Dws = Slide Mountain; Dwm = Beers hill shale; Dww = upper Walton; Ds = Kattel; Dsw = lower Walton; Dgo = Oneonta Genesee Group; Dgu = Unadilla Genesee Group; Dhmo = Moscow(Hamilton Group); Dhpm = Panther Mountain; Dh = undifferentiated Hamilton Group; Dg = undifferentiated Genesee Group; Dwrg = Upper Devonian; Dwnm = Upper Devonian Pennsylvania Geologic Formations; Dck = undifferentiated Catskill; Dlh = Lockhaven.

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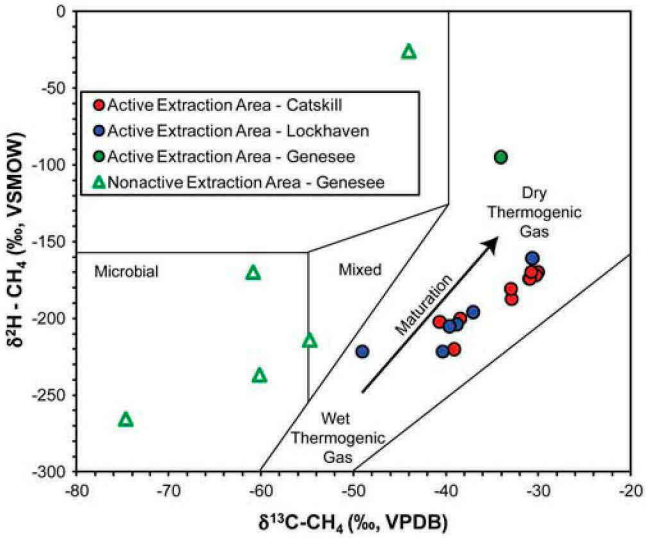

Fig. S2. Plot of (δ^2H-CH_4) versus (δ^{13}C-CH_4) in dissolved gas in shallow groundwater samples collected in the study area. Note that active area samples from all three aquifers plot within the thermogenic zone as defined by ref. 1 and nonactive samples within the mixed or microbial zones. VSMOW, Vienna Standard Mean Ocean Water; VPDB, Vienna Pee Dee belemnite .

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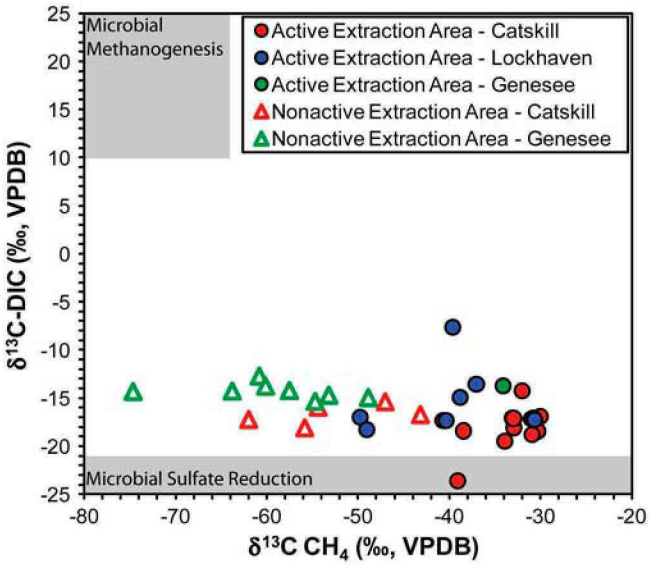

Fig. S3. Plot of the carbon isotopes in dissolved inorganic carbon (δ^{13}C-DIC) in groundwater versus carbon isotopes in coexisting methane (δ^{13}C-CH_4), illustrating that samples do not plot within methanogenesis or sulfate-reduction zones. Ranges in δ^{13}C-DIC for methanogenesis and sulfate reduction are taken from Clark and Fritz (1). VPDB, Vienna Pee Dee belemnite.

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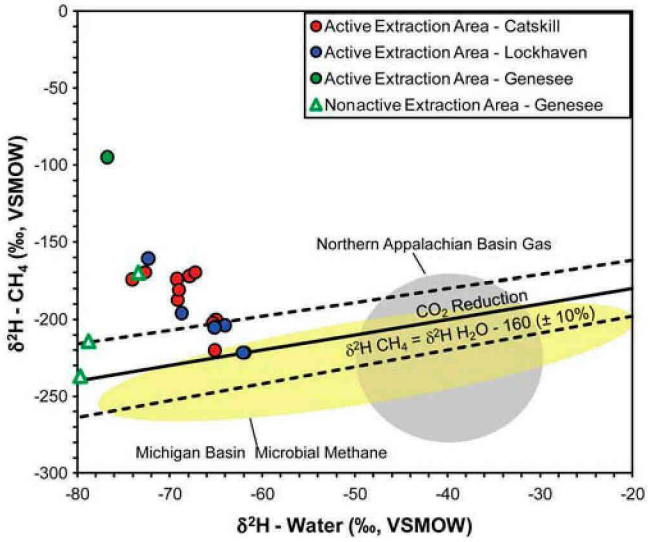

Fig. S4. Plot of the hydrogen isotope values of dissolved methane (δ^2H-CH_4) versus hydrogen isotope values of groundwater (δ^2H-water). The fractionation line for microbial methanogenesis via CO_2 reduction is depicted from Whiticar et al. (1). Microbial methane from the Michigan and Illinois basins are depicted with the yellow oval (2, 3). Appalachian basin data are depicted in the gray oval (4). The lack of positive correlation between the two sources of hydrogen indicates that microbial methane is negligible in the shallow groundwater. VSMOW, Vienna Standard Mean Ocean Water.

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2 Martini AM, et al. (1998) Genetic and temporal relations between formation waters and biogenic methane: Upper Devonian Antrim Shale, Michigan Basin, USA. *Geochim Cosmochim Acta* 62:1699–1720.
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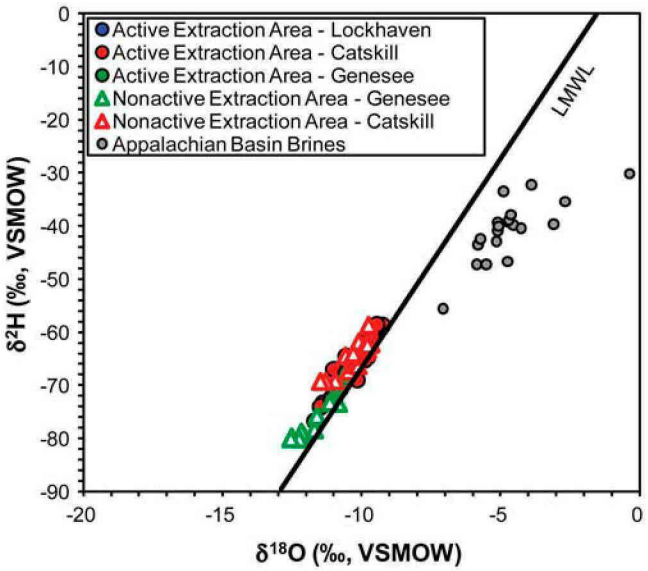

Fig. S5. Hydrogen versus oxygen isotope ratios [‰, Vienna Standard Mean Ocean Water (VSMOW)] in Appalachian brines, groundwater from active gas extraction areas, groundwater from nonactive gas extraction areas, and the local meteoric water line (LMWL; from ref. 1). There were no significant differences ($p > 0.05$) between the active and nonactive samples, indicating little to no mixing with deeper brines.

1 Kendall C, Coplan TB (2001) Distribution of oxygen-18 and deuterium in river waters across the United States. *Hydrol Processes* 15:1363–1393.

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