Supporting Information

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Geological Setting. The study area (Fig. S1) was chosen because of its rapid expansion of drilling for natural gas from the Marcellus Shale (Pennsylvania); also, it has a limited history of prior oil and gas exploration. Additionally, the study area represents portions of both the upper Susquehanna and upper Delaware watersheds that provide drinking water to >15 million people. The geological setting and methods for the work have been described previously in the works by Osborn et al. (1) and Warner et al. (2). Briefly, the sedimentary geology represents periods of deposition, burial, lithification, uplift, and subsequent erosion that form relatively simple sets of horizontal strata dipping 1° to 3° to the south and east derived from depositional environments that ranged from proposed deep to midbasin black shales to terrestrial red beds (3–5). The monocline is bounded on the north by the Precambrian Canadian Shield and Adirondack uplift (north to northeast), the west by the Algonquin and Findlay arches, and the south and east by the Appalachian fold belt (the Valley and Ridge Province) (6, 7). In general, sedimentary deposition in the northern Appalachian Basin was relatively continuous throughout the Paleozoic era. However, several unconformities erase sequence records regionally, such as the Tri-States unconformity that removed Lower Devonian strata in western New York, but complete sequences are generally found in central New York and our study region of northeastern Pennsylvania (3).

The Appalachian Basin consists primarily of sedimentary sequences of Ordovician to Pennsylvanian age that are derived from the Taconic (~450 Ma), Acadian (~410–380 Ma), and Alleghanian (~330–250 Ma) orogenic events (8). Exposed at its northern extent near Lake Ontario is the Upper Ordovician–Lower Silurian contact (Cherokee unconformity). Younger deposits (Upper Silurian, Devonian, and Mississippian) occur in successive outcrop belts to the south to the Appalachian structural front (4, 9), whereas erosion has removed most post-Pennsylvanian deposition within western-central New York and most of our study area within northeastern Pennsylvania. Bedrock thickness within the basin ranges from ~920 m along the southern shore of Lake Ontario in northern New York to ~7,600 m along the Appalachian structural front to the south. A simplified stratigraphic reconstruction is presented in Fig. S2 for the study area, which constitutes a transition from the Valley and Ridge to the Plateau Province. Compared with the Valley and Ridge Province or the region near the Appalachian Structural Front, the plateau portion of the Marcellus Formation is significantly less deformed (10). Deformation began during the onset of the Alleghanian orogeny. In the plateau physiographic province, deformation is accommodated by a combination of layer parallel shortening, folding that led to low-amplitude anticline/syncline sequences, low angle thrust faulting structures, lineaments, joints, and natural fractures observable in northeastern Pennsylvania (4, 11, 12).

The Marcellus Formation is an organic-rich, hydrocarbon-producing, siliciclastic-rich black shale present beneath much of Pennsylvania, New York, West Virginia, and other northeastern states. It constitutes the stratigraphically lowest subgroup of the Middle Devonian Hamilton Group (5, 9) and was deposited in the foreland basin of the Acadian Orogeny (~385–375 Ma). The Marcellus Formation includes two distinct calcareous and iron-rich black shale members [i.e., the Union Springs (lower) and Mount Marion/Oatka Creek (upper)) interrupted by the Cherry Valley limestone].

Like the Marcellus, the upper part of the Devonian sequence is deposited in the foreland basin of the Acadian Orogeny and consists of material sourced from the Acadian orogeny as part of the Catskill Deltaic sequence. Above the Marcellus, the Hamilton Group consists of the Mahantango gray shale locally interbedded by limestones and the Tulley limestone. The Upper Devonian consists of thick synorogenic sequences of gray shales (i.e., the Brallier Formation) beneath the Lock Haven Formation sandstone and Catskill Formation clastic deltaic red sandstones. The Lock Haven and Catskill Formations constitute the two primary aquifer lithologies in northeastern Pennsylvania along with the overlying glacial and sedimentary alluvium, which is thicker in valleys than the uplands.

Additional geological information is in the work by Osborn et al. (1) and references therein and the work by Warner et al. (2) and references therein.

1. Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108(20):8172–8176.
2. Warner NR, et al. (2012) Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proc Natl Acad Sci USA* 109(30):11961–11966.
3. Brett CE, Goodman WM, LoDuca ST, Lehmann DF (1996) Upper Ordovician and Silurian strata in western New York: Sequences, cycles and basin dynamics. *New York State Geological Association Field Trip Guide, 1996*, ed Brett CE (University of Rochester, Rochester, NY), pp 71–120.
4. Lash GG, Engelder T (2011) Thickness trends and sequence stratigraphy of the Middle Devonian Marcellus Formation, Appalachian Basin: Implications for Acadian foreland basin evolution. *Am Assoc Pet Geol Bull* 95(1):61–103.
5. Brett CE, Baird GC, Bartholomew AJ, DeSantis MK, Straeten CAV (2011) Sequence stratigraphy and a revised sea-level curve for the Middle Devonian of eastern North America. *Palaeogeogr Palaeoclimatol Palaeoecol* 304(1-2):21–53.
6. Milici RC, de Witt W, Jr. (1988) *The Appalachian Basin*, ed Sloss LL (Geological Society of America, Boulder, CO), The Geology of North America, pp 427–469.
7. Jenden PD, Drazan DJ, Kaplan IR (1993) Mixing of thermogenic natural gases in Northern Appalachian Basin. *Am Assoc Pet Geol Bull* 77(6):980–998.
8. Rast N, ed (1989) *The Evolution of the Appalachian Chain* (Geological Society of America, Boulder, CO), Vol A, pp 347–358.
9. Straeten CAV, Brett CE, Sageman BB (2011) Mudrock sequence stratigraphy: A multi-proxy (sedimentological, paleobiological and geochemical) approach, Devonian Appalachian Basin. *Palaeogeogr Palaeoclimatol Palaeoecol* 304(1-2):54–73.
10. Faill RT (1997) A geologic history of the north-central Appalachians. 1. Orogenesis from the mesoproterozoic through the taconic orogeny. *Am J Sci* 297(6):551–619.
11. Jacobi RD (2002) Basement faults and seismicity in the Appalachian Basin of New York State. *Tectonophysics* 353(1–4):75–113.
12. Alexander S, Cakir R, Doden AG, Gold DP, Root SI (2005) Basement depth and related geospatial database for Pennsylvania. *4th Open-File General Geology Report 05-01.00* (Pennsylvania Geological Survey, Middletown, PA).

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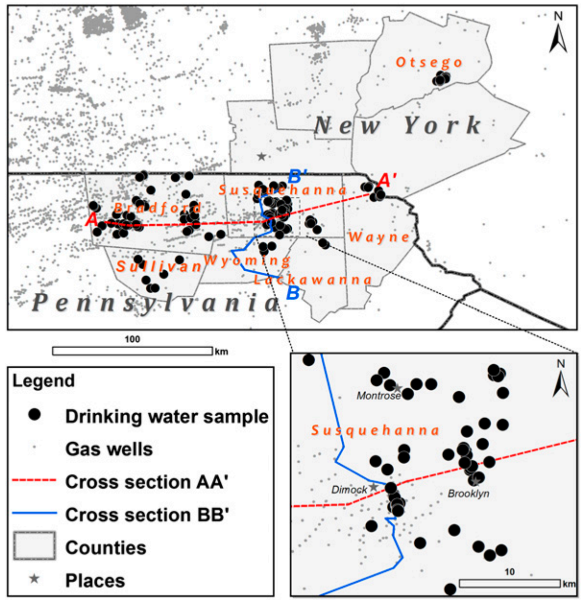

Fig. S1. Map of well water sampling locations in Pennsylvania and New York. The star in *Upper* represents the location of Binghamton, New York. (*Lower Right*) A close-up view of Susquehanna County, Pennsylvania. The stars in *Lower Right* represent the towns of Dimock, Brooklyn, and Montrose, Pennsylvania. The red and blue lines represent the approximate location of the cross-sections in Fig. S2.

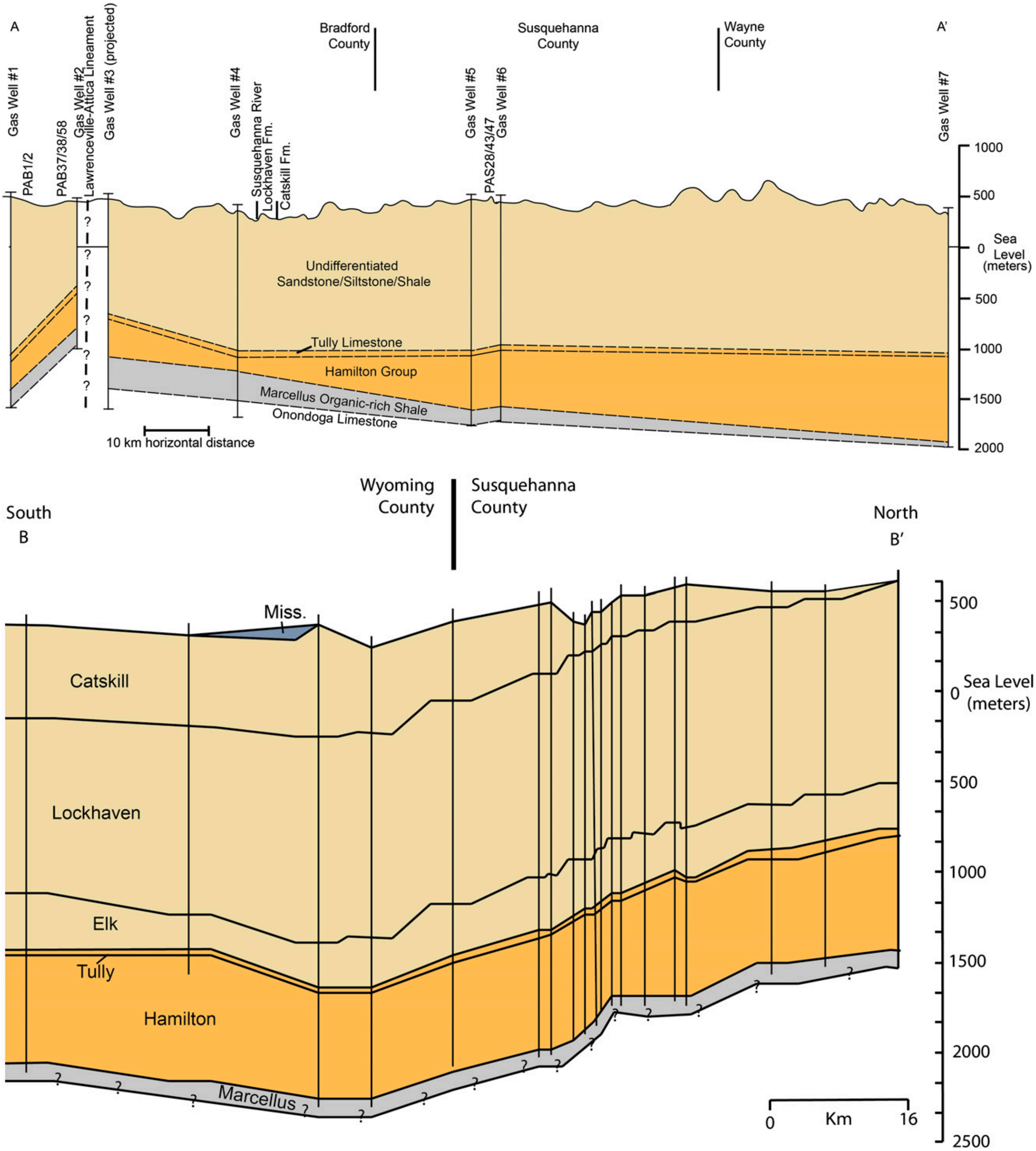

Fig. S2. Generalized stratigraphic section of the study region from the work by Osborn et al. (1), Molofsky et al. (2), and Warner et al. (3) and references therein. The cross sections shown here refer to the locations identified in Fig. S1.

1. Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108(20):8172–8176.
2. Molofsky LJ, Connor JA, Wylie AS, Wagner T, Farhat SK (2013) Evaluation of methane sources in groundwater in northeastern Pennsylvania. *Groundwater* 51(3):333–349.
3. Warner NR, et al. (2012) Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proc Natl Acad Sci USA* 109(30): 11961–11966.

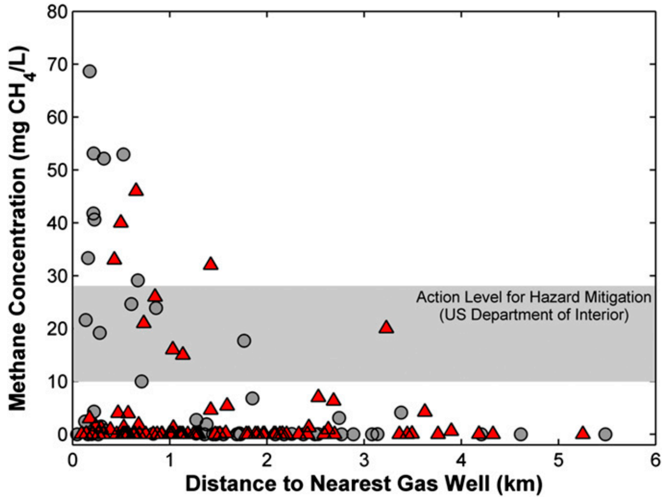

Fig. S3. Methane concentrations (milligrams per liter) vs. distance to nearest gas wells (kilometers) with data from the initial study (1) in filled circles and new observations in red triangles.

1. Osborn SG, Vengosh A, Warner NR, Jackson RB (2011) Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proc Natl Acad Sci USA* 108(20):8172–8176.

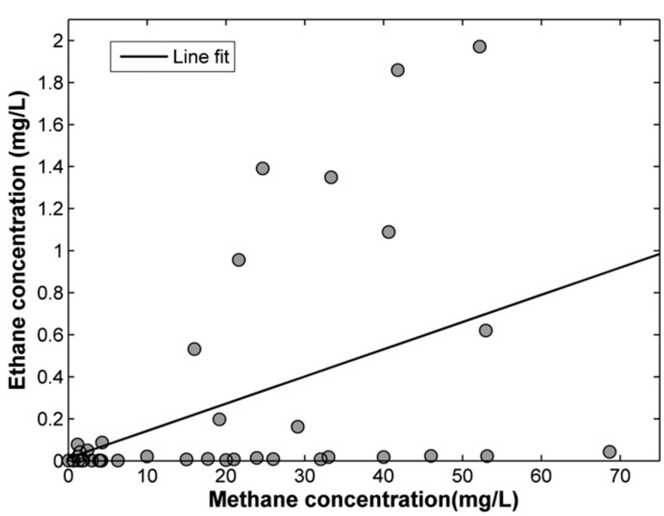

Fig. S4. Concentrations of ethane vs. methane across the groundwater dataset ($P = 0.0034$; $R^2 = 0.205$).

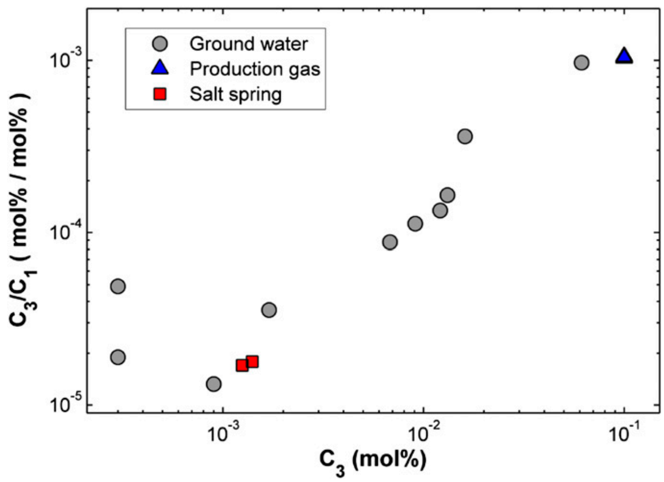

Fig. S5. The ratio of propane to methane concentrations vs. propane concentrations (mol%) for our data from drinking water wells (filled circles), the salt spring at Salt Springs State Park in Franklin Forks, Pennsylvania (red squares), and Marcellus production gas (blue triangle) (1).

1. Jenden PD, Drazan DJ, Kaplan IR (1993) Mixing of thermogenic natural gases in Northern Appalachian Basin. *Am Assoc Pet Geol Bull* 77(6):980–998.

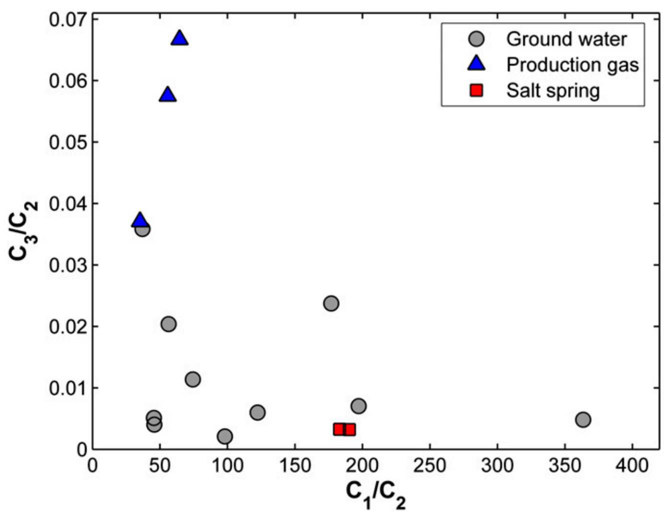

Fig. S6. The ratios of propane to ethane (C_3/C_2) and methane to ethane (C_1/C_2) concentrations for our data from drinking water wells (filled circles), the salt spring at Salt Springs State Park in Franklin Forks, Pennsylvania (red squares), and Marcellus production wells across the study area (blue triangles) (1, 2).

1. Jenden PD, Drazan DJ, Kaplan IR (1993) Mixing of thermogenic natural gases in Northern Appalachian Basin. *Am Assoc Pet Geol Bull* 77(6):980–998.
2. Laughrey CD, Baldassare FJ (1998) Geochemistry and origin of some natural gases in the Plateau province, central Appalachian basin, Pennsylvania and Ohio. *Am Assoc Pet Geol Bull* 82(2):317–335.

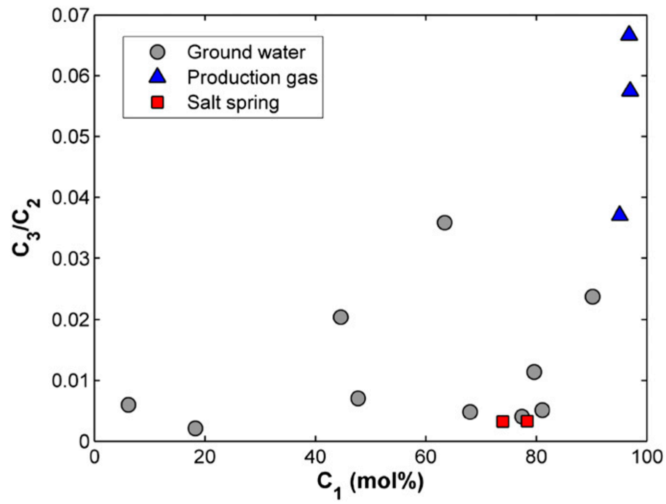

Fig. S7. The ratio of propane to ethane concentrations vs. methane concentrations (mol%) for our data from drinking water wells (filled circles), the salt spring at Salt Springs State Park in Franklin Forks, Pennsylvania (red squares), and production gases in the area (blue triangles) (1, 2).

1. Jenden PD, Drazan DJ, Kaplan IR (1993) Mixing of thermogenic natural gases in Northern Appalachian Basin. *Am Assoc Pet Geol Bull* 77(6):980–998.
2. Laughrey CD, Baldassare FJ (1998) Geochemistry and origin of some natural gases in the Plateau province, central Appalachian basin, Pennsylvania and Ohio. *Am Assoc Pet Geol Bull* 82(2):317–335.

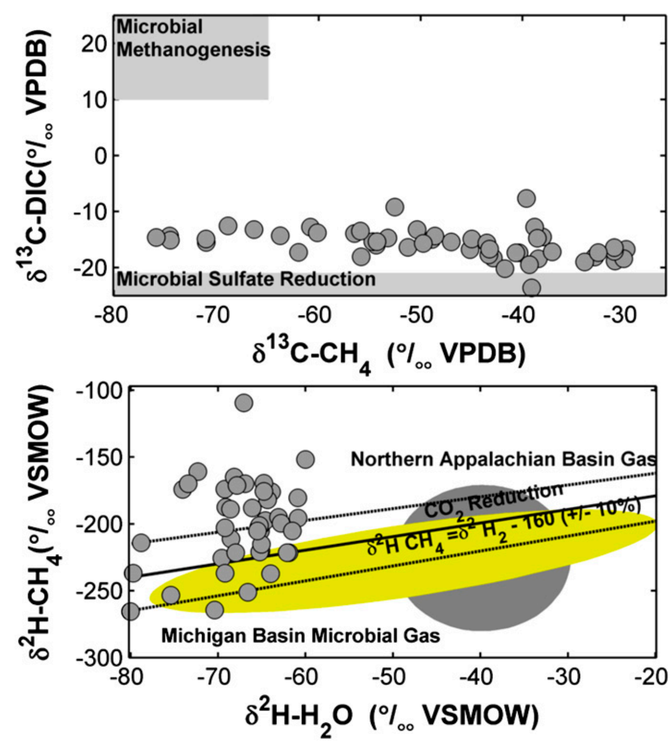

Fig. S8. (*Upper*) Plot of the carbon isotopes in $\delta^{13}C$ dissolved inorganic carbon ($\delta^{13}C$-DIC) in groundwater vs. carbon isotopes in coexisting methane ($\delta^{13}C$-CH_4), which illustrates that samples do not plot within methanogenesis or sulfate reduction zones. Ranges in $\delta^{13}C$-DIC for methanogenesis and sulfate reduction are taken from the work by Clark and Fritz (1). VPDB, Vienna Pee Dee belemnite. (*Lower*) Plot of $\delta^{2}H$-CH_4 of dissolved methane in groundwater vs. $\delta^{2}H$-H_2 of the groundwater. The fractionation line for microbial methanogenesis by CO_2 reduction depicted is from the work by Whiticar et al. (2). Microbial methane from the Michigan and Illinois Basins is depicted with the yellow oval (3, 4). Northern Appalachian Basin data are depicted in the gray oval (5). The lack of positive correlation between the two hydrogen sources indicates that microbial methane is negligible in the shallow groundwater. VSMOW, Vienna Standard Mean Ocean Water.

1. Clark ID, Fritz P (1997) *Environmental Isotopes in Hydrogeology* (Lewis, New York).
2. Whiticar MJ, Faber E, Schoell M (1986) Biogenic methane formation in marine and freshwater environments: CO_2 reduction vs. acetate fermentation—isotope evidence. *Geochim Cosmochim Acta* 50(5):693–709.
3. 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(10):1699–1720.
4. McIntosh JC, Walter LM, Martini AM (2002) Pleistocene recharge to midcontinent basins: Effects on salinity structure and microbial gas generation. *Geochim Cosmochim Acta* 66(10):1681–1700.
5. Osborn SG, McIntosh JC (2010) Chemical and isotopic tracers of the contribution of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl Geochem* 25(3):456–471.

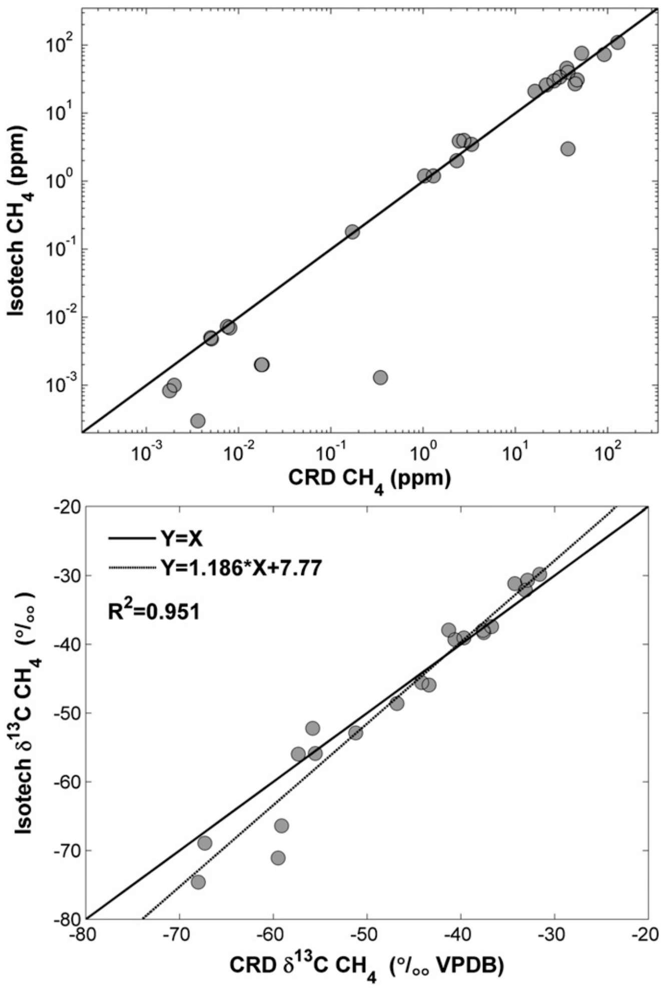

Fig. S9. Comparisons of Isotech Laboratories and cavity-ring down (CRD) spectrometry analyses for (*Upper*) [CH_4] and (*Lower*) $\delta^{13}C$-CH_4 analyzed in duplicate at both Isotech Laboratories and the Duke Environmental Stable Isotope Laboratory. These results show statistically indistinguishable differences between the two data analysis methods.