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.

1. Isotech Laboratories (2011) Collection of Groundwater Samples from Domestic and Municipal Water Wells for Dissolved Gas Analysis (Isotech Laboratories, Champaign, IL), http://www.isotechlabs.com/customersupport/samplingprocedures/IsoBagSM.pdf.
2. 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* 25:456–471.
3. US Geological Survey (2011) National Field Manual for the Collection of Water-Quality Data (US Geological Survey, Washington, DC), http://water.usgs.gov/owq/FieldManual/.
4. Gieskes JM, Rogers WC (1973) Alkalinity determination in interstitial waters of marine sediments. *J Sediment Petrol* 43:272–277.
5. Dwyer GS, Vengosh, A (2008) Alternative filament loading solution for accurate analysis of boron isotopes by negative thermal ionization mass spectrometry. *EOS Trans Am Geophys Union* 89, p 53.
6. Kim G, Burnett WC, Dulaiova H, Swarzenski PW, Moore WS (2001) Measurement of ^{224}Ra and ^{226}Ra activities in natural waters using a radon-in-air monitor. *Environ Sci Tech* 35:4680–4683.
7. Williams JH, Taylor L, Low D (1998) Hydrogeology and Groundwater Quality of the Glaciated Valleys of Bradford, Tioga, and Potter Counties, Pennsylvania: Water Resources Report 68 (Commonwealth of Pennsylvania Dept of Conservation and Natural Resources, Harrisburg, PA), p 89.
8. Taylor LE (1984) Groundwater Resources of the Upper Susquehanna River Basin, Pennsylvania: Water Resources Report 58. (Pennsylvania Dept of Environmental Resources-Office of Parks and Forestry—Bureau of Topographic and Geologic Survey, Harrisburg, PA), p 136.
9. Lohman, SW (1957) Ground water in northeastern Pennsylvania. (Pennsylvania Dept of Conservation and Natural Resources, Harrisburg, PA), p 312.
10. Lohman SW (1973) Ground water in north-central Pennsylvania. (Pennsylvania Dept of Conservation and Natural Resources, Harrisburg, PA), p 219.
11. Geyer A, Wilshusen, JP (1982) Engineering characteristics of the rocks of Pennsylvania; environmental geology supplement to the state geologic map, 1982 Pennsylvania Geological Survey (Dept of Environmental Resources, Office of Resources Management, Harrisburg, PA), p 300

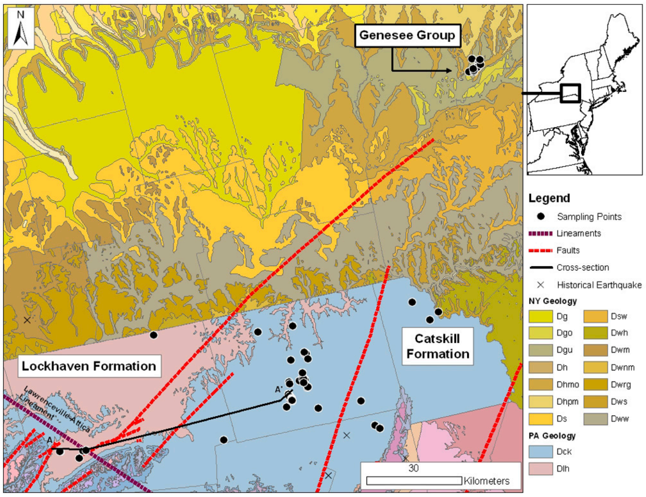

Fig. S1. Sampling locations in relation to bedrock geology for northeastern Pennsylvania and New York. Geological maps were obtained from United States Geological Survey state maps of New York (http://tin.er.usgs.gov/geology/state/state.php?state=NY) and Pennsylvania (http://tin.er.usgs.gov/geology/state/state.php?state=PA). 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.

1 Alexander SS, Cakir R, Doden AG, Gold DP, Root SI (2005) Basement depth and related geospatial database for Pennsylvania: Pennsylvania Geological Survey, 4th ser., Open-File General Geology Report 05-01.0 (Middletown, PA, Pennsylvania Dept of Conservation and Natural Resources), http://www.dcnr.state.pa.us/topogeo/openfile.

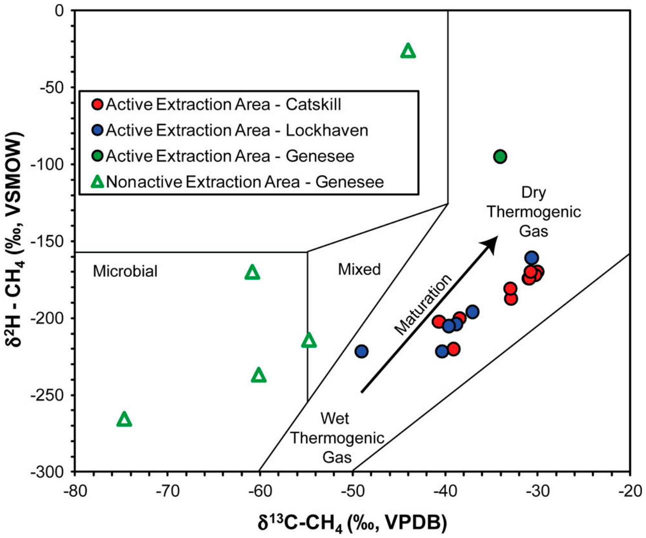

Fig. S2. Plot of (δ^2H-CH$_4$) versus (δ^{13}C-CH$_4$) in dissolved gas in shallow groundwater samples collected in the study area. Note that active area samples from all three aquifers plot within the thermogenic zone as defined by ref. 1 and nonactive samples within the mixed or microbial zones. VSMOW, Vienna Standard Mean Ocean Water; VPDB, Vienna Pee Dee belemnite .

1 Ryder RT, Zagorski WA (2003) Nature, origin, and production characteristics of the Lower Silurian regional oil and gas accumulation, central Appalachian basin, United States. *AAPG Bull* 87:847–872.

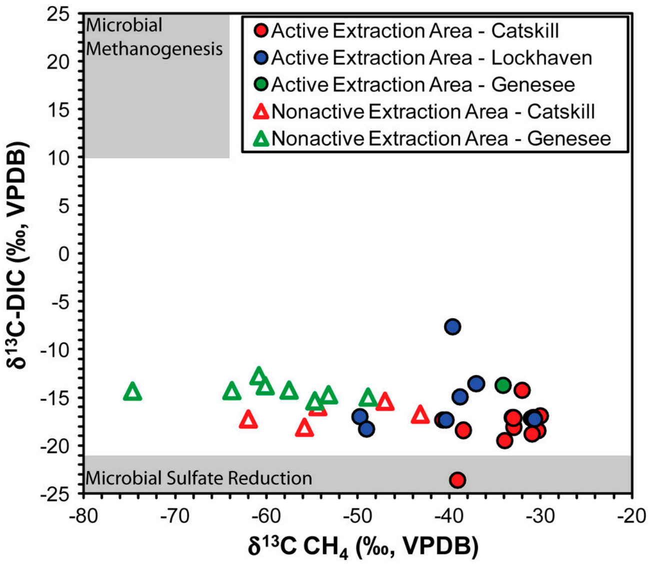

Fig. S3. Plot of the carbon isotopes in dissolved inorganic carbon (δ^{13}C-DIC) in groundwater versus carbon isotopes in coexisting methane (δ^{13}C-CH_4), illustrating that samples do not plot within methanogenesis or sulfate-reduction zones. Ranges in δ^{13}C-DIC for methanogenesis and sulfate reduction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

1 Clark ID, Fritz P (1997) *Environmental Isotopes in Hydrogeology* (Lewis Publishers, New York).

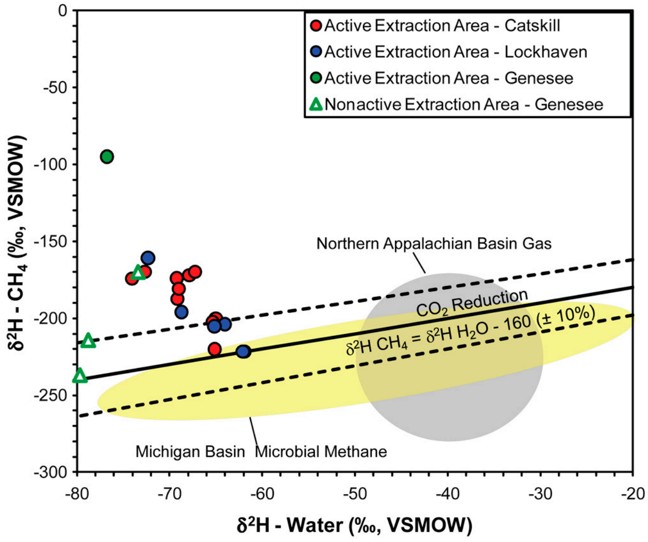

Fig. S4. Plot of the hydrogen isotope values of dissolved methane (δ^2H-CH_4) versus hydrogen isotope values of groundwater (δ^2H-water). The fractionation line for microbial methanogenesis via CO_2 reduction is depicted from Whiticar et al. (1). Microbial methane from the Michigan and Illinois basins 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.

1 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* 50:693–709.
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.
3 McIntosh JC, Walter LM, Martini AM (2002) Pleistocene recharge to midcontinent basins: Effects on salinity structure and microbial gas generation. *Geochim Cosmochim Acta* 66:1681–1700.
4 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* 25:456–471.

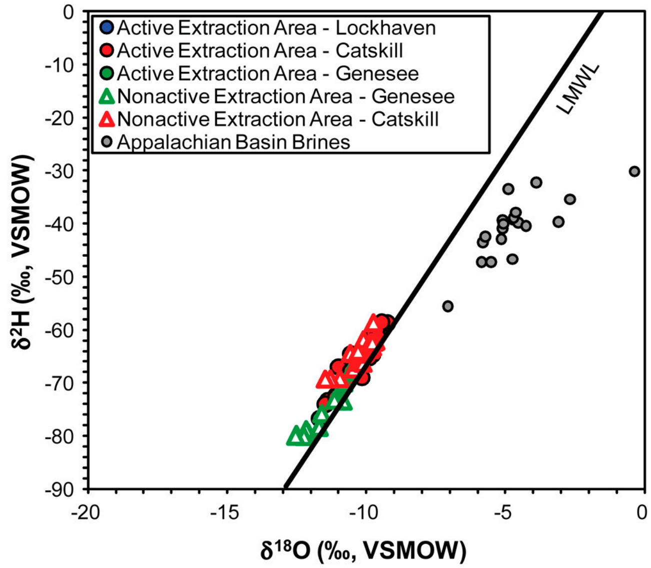

Fig. S5. Hydrogen versus oxygen isotope ratios [‰, Vienna Standard Mean Ocean Water (VSMOW)] in Appalachian brines, groundwater from active gas extraction areas, groundwater from nonactive gas extraction areas, and the local meteoric water line (LMWL; from ref. 1). There were no significant differences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