

Supporting Information

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SI Text

SI History

Given the early groundwater problems reported, venting of the annular spaces in the gas wells commenced in July 2010. Casings were perforated and cement was injected into the annular space (cement squeezing) from August to September 2010 to bolster the gas wells' integrity and reduce annular pressures in the Welles 3, 4, and 5 series gas wells (Table S1 and Fig. S10). The remedial cement squeezes were coincident with reports of natural gas bubbling in the Susquehanna River near the town of Sugar Run, ~3.5 km southeast of the Welles series gas wells (Fig. 1 and Fig. S9). The Welles series wells were the closest associated gas drilling activity at that time.

With commercial laboratory analyses, more than 250 target compounds were analyzed on at least one occasion (inorganics, volatile organics, semivolatile organics, glycols, radiologicals, and surfactants, among others). Despite visible foaming during initial purging, no analyte concentrations exceeded PADEP primary drinking water maximum contaminant levels or medium-specific concentrations as regulated under PA Act 2. Almost no targeted volatile or semivolatile organic compounds were detected, except for carbon disulfide in household Wells 2 (0.45 $\mu\text{g/L}$) and 5 (0.96 $\mu\text{g/L}$). This compound is not uncommonly found in such analyses and is not uniquely linked to gas drilling. Although not reported by the commercial laboratory, our evaluation of the laboratory reports (Method 8270C for Well 1 for semivolatile organics) revealed various nontargeted compounds with ~10–36 carbon atoms (estimated total concentration of ~25–50 $\mu\text{g/L}$) that were present in at least one groundwater sample collected. Surfactants (methylene blue active substances) were also detected at the detection limit (0.12 mg/L) by a commercial laboratory in one sample from Well 1 on 26 March 2012. Ethylene glycol was detected in Wells 1 and 5 on 26 March 2012 and 14 May 2012 at concentrations of 5,100 and 3,200 $\mu\text{g/L}$, respectively. Propylene glycol was also detected in Well 5 on 14 May 2012 at a concentration of 960 $\mu\text{g/L}$. All of these analytes and corresponding low concentrations were detected sporadically with intermittent “nondetections” when analyzed for. The civil case focused on the most obvious contamination–natural gas impacts.

SI Methods

Sampling. The new analyses reported here were measured on samples collected from outside spigots using pumps and infrastructure already in place and from a sample from Salt Springs. Before sampling, water was purged for the amount of time indicated in Table S4 with field water quality parameters noted (e.g., pH, conductivity, temperature). All samples were preserved on ice for transport, and were subsequently refrigerated.

Samples for dissolved gases were collected using two types of vessels: 125-mL glass serum bottles and 1-L sample bottles designed by Isotech, Inc. for natural gas isotopic analysis. In all cases, water was allowed to enter the bottles gently using vinyl tubing attached to an outside spigot (to minimize agitation and off-gasing). Isotech bottles (which contain biocide in a specially designed cap) were filled following Isotech protocol for collecting dissolved gas samples (www.isotechlabs.com/customer-support/sampling-procedures/DG-bottle.pdf). The bottles were filled with water, inverted, and submerged in a water-filled 5-gallon bucket. The source of water was allowed to keep flowing into the sample bottle until another two volumes of water had been displaced.

For the serum bottles, a slight headspace was left so the bottles could be capped with a 20-mm butyl rubber stopper. Then 1.25 mL of benzylnonium chloride (or, for some test bottles, sodium azide) were added, using a syringe, to kill microbiota. As the biocide was added, a second syringe was inserted into the septa cap and used to evacuate headspace. The water emitting at Salt Springs in Salt Springs Park (Susquehanna County, PA) was sampled by submerging three 125-mL glass serum bottles into the spring water, allowing the bottles to fill, and then capping them with a 20-mm blue butyl rubber stopper under water. Two syringes were then used to add 1.25 mL of sodium azide and to evacuate the remaining headspace.

Samples of almost 30 flowback or production waters were shared with us from natural gas wells drilled in the PA Marcellus before treatment at a brine wastewater remediation plant. Additionally, a sample of drilling foam (M-I SWACO Platinum AirFoam) was obtained.

GCxGC Analysis. An extended organic analysis was completed on the flowback/production waters and samples from three of the potable wells (one original and two replacement wells, bottles labeled PLG-12-60A, PLG-12-68A, and PLG-12-64A). In addition, one of the replacement wells that was sampled after purging (PLG-12-68A) was compared with water before purging (PLG-12-67A). Three background potable water samples were also analyzed from houses outside of the impacted area, but within 5 km of the incident: bottles PLG 13-5B, PLG 13-6A, and PLG 13-7A.

Samples were prepared using separatory funnel-based liquid/liquid extraction under both acidic and basic pH by extraction in dichloromethane following a modification of USEPA Method 3510C (www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3510c.pdf). Many of the flowback samples formed emulsions, especially during the first sample extraction, and were therefore separated using centrifugation. Samples were also spiked with control “surrogate” compounds to measure extraction efficiency (see Table S7).

Sample extracts from flowback and production waters were first characterized by GC-TOFMS. Spectra were very complex, resulting in large UCMs in every sample. To further identify compounds in the UCMs, analysis by GCxGC-TOFMS was used. The GCxGC-TOFMS was a Pegasus-4D system (Leco Corporation).

The sample of Airfoam HD was also analyzed with GCxGC-TOFMS. Additional preparatory blanks and a trip blank taken with the samples were also prepared and analyzed.

The potable waters were compared with the data from flowback/produced waters as well as reference standards. These standards, chosen from among the compounds used in hydraulic fracturing in PA (files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/MarcellusShale/Frac%20list%206-30-2010.pdf), were run under identical conditions at a concentration of 200 pg/ μL as a single-point calibration. When these compounds were detected in the potable water samples, concentrations were estimated from the area under the peak for a given fragment and mass/charge ratio.

Dissolved Gases. Samples were analyzed for dissolved hydrocarbons including methane and ethane within 1 wk of collection. To analyze the 1-L bottles for dissolved gases, ultra-high-purity helium was introduced to create headspace (10% by volume standard temperature and pressure) (1). Headspace hydrocarbons were then analyzed using an HP 5890 Series II Gas Chromatograph with a flame ionization detector and a custom vacuum inlet system. Daily standard curves were generated using 1.83 ppm,

14.9 ppm, and 1,000 ppm methane standards from Scott Specialty Gases. Analytical precision for measurement of these standards was better than $\pm 2\%$.

When headspace is created, gas in the water equilibrates between the aqueous phase and the gases in the headspace, and the concentration can be determined from

$$TC = C_{AH} + C_A,$$

where TC is the total concentration (in milligrams per liter) of the original aqueous sample, C_{AH} is the measured concentration in the gas phase (in milligrams per liter), and C_A is the concentration (in milligrams per liter) that has remained in the aqueous phase, as indicated by the Henry's Law constant at 21 °C.

To analyze $\delta^{13}\text{C}$ in methane and ethane, ~ 5 nmols of analyte were injected into a helium carrier stream and purified using a modified PreCon peripheral device before analysis on a MAT 252 mass spectrometer. Precision of measurements of daily standards (1.84 ppm) is $\pm 0.3\%$, with daily standards providing the means of accurately reporting data directly on the Vienna Pee Dee Belemnite scale.

A few samples were also sent to Isotech for analysis of $\delta^{13}\text{C}$ (in CH_4 and C_2H_6) and δD in CH_4 . Samples analyzed at Pennsylvania State University and Isotech varied between 0‰ and 0.7‰.

Inorganic Analysis. Anions were analyzed using a Dionex ICS 2500 ion chromatograph (IC) on filtered unacidified samples using an IonPac AS18 anion exchange column (4×250 mm) and IonPac AG18 guard column (4×50 mm) at Pennsylvania State University. Major elements were analyzed on a Perkin-Elmer Optima 5300 ICP-AES on filtered, acidified samples. Analytical precision on the ICP-AES is estimated to be $\pm 3\%$ for all major elements and $\pm 10\%$ for minor elements. Detection limits for the IC data were calculated as the concentration of the lowest standard used during analysis minus the relative SD for multiple analyses of that standard.

Hydrogeology. The impacted area (Fig. 1) lies within the Glaciated Low Plateau section of the Appalachian Plateau province. Bedrock consists of gently folded sandstone, siltstone, and shale overlain by glacial drift. In the study area, sandstone of the Upper Devonian Catskill Formation dominates the uppermost stratigraphic section, with siltstone and shale of the Lock Haven Formation outcropping infrequently in low-lying areas to the north (Fig. 1). Average elevation drop from ridge to valley is ~ 125 m. Drift and alluvial sediments vary in thickness from a thin veneer on hill slopes to 60 m in major valleys. Fig. S11 illustrates approximate bedrock elevations in meters above mean sea level. Groundwater discharges into the valley along the north branch of Sugar Run where the affected houses are located (Fig. 1 and Fig. S34).

Two principal aquifers are present. Shallow unconfined outwash acts as an aquifer in the major valleys, while confined bedrock units act as aquifers in the uplands. Groundwater flows from hilltops to valley discharge zones. Groundwater is largely of the Ca-HCO_3^- type; however, Na-Cl type groundwater, which occurs in some major valleys, has been attributed to upward seepage of ABB (2–4). For example, Cl-Br ratios are consistent with transport of ABB upward into shallow aquifers along permeable faults and topographic lineaments (3). Thermogenic natural gas is also common in shallow groundwater throughout the region (5–7).

In response to the groundwater quality problems, the gas company installed a replacement potable well for each household

in September 2010. However, these replacement wells exhibited elevated natural gas concentrations. Water wells 1–6 are cased to ~ 6.5 m-bgs and are completed as open rock wells to a maximum depth of ~ 60 m-bgs. We completed a pumping test in November 2012 to evaluate aquifer characteristics. Well 4 (a replacement well) was pumped for 7 h at a constant pumping rate of 25.8 L/min while evaluating the hydraulic responses of the original and replacement potable wells (Fig. S3). Water level monitoring revealed a maximum drawdown of 15.2 m in the pumping well, and the drawdown ellipse was aligned NNW–SSE along the dominant set of fractures (joints) and the valley orientation (Fig. 1 and Figs. S3 and S11), indicating aquifer anisotropy and/or heterogeneity.

Asymmetric drawdown observed could be due to the dominant vertical joints oriented NNW–SSE as observed in local bedrock outcrops. Alternately, asymmetric drawdown could be due to openings between bedding planes that terminate in the valley wall (e.g., stress relief fracturing). Consistent with bedrock heterogeneity, the steep hydraulic gradient observed east of the pumping well (e.g., into the bedrock valley wall) suggests lower permeability in the more upland areas away from the incised valley. Shallow valley aquifer parameters were estimated: storativity (S) $\sim 1.6 \times 10^{-5}$, maximum transmissivity tensor (T_{ss}) ~ 5.9 m²/d, and minimum transmissivity tensor (T_{nn}) ~ 2.6 m²/d with a NNW–SSE major axis orientation. The geometric mean of principal transmissivities was estimated at 3.9 m²/d; given a saturated well thickness of 23 m for Well 4, the hydraulic conductivity (K) is estimated at 2×10^{-6} m/s.

Welles 3-2H pressures and fracturing potential. Based upon the observed annular pressures recorded at gas well Welles 3-2H (~ 64 atm), it is possible that fracturing was induced near the well's surface casing shoe (base of surface casing), providing an additional migration pathway for contaminants. Although fracture gradients vary regionally, 0.16 atm/m is used as a guideline to avoid potential fracture propagation in PA injection wells (8). For gas well Welles 3-2H, the approximate threshold for fracture propagation would be an approximate pressure of 51 atm at the surface casing shoe—surface casing extends 320 m-bgs. Given the maximum recorded annular pressure of 64 atm in connection with Welles 3-2H, it is indeed possible that fracture propagation was induced, providing a pathway for contaminant migration. Notably, 196 bbl of cement ($\sim 31,100$ L) was reportedly squeezed at a relatively shallow depth interval (~ 500 – 600 m-bgs) at Welles 3-2H as part of its remediation (Fig. S10).

Uses and sources of 2-BE. In addition to being used in gas drilling and HVHF fluids, 2-BE is used in industry as a solvent for paints and surface coatings and as an ingredient for paint thinners, herbicides, degreasers, dyes, soaps, and cosmetics. It is a fully miscible, clear liquid with an ether-like odor at thresholds of 0.10–0.40 ppm in air. Domestic US production of 2-BE has steadily increased—reported amounts include 59 million kilograms, 123 million kilograms, 136 million kilograms, and 185 million kilograms for years 1975, 1984, 1986, and 1995, respectively, by producers such as Dow Chemical, Eastman Chemical Co., Occidental Petroleum Corp., and Shell Chemical Co., among others. Besides areas undergoing gas drilling development, areas most prone to water resource discharges of 2-BE include those near manufacturing or processing facilities that use 2-BE, municipal landfills, hazardous waste sites, and areas treated with herbicides that contain 2-BE. Although not expected to be significant, release of 2-BE could also result from consumer product use, such as outdoor use of liquid cleaners and paints (9).

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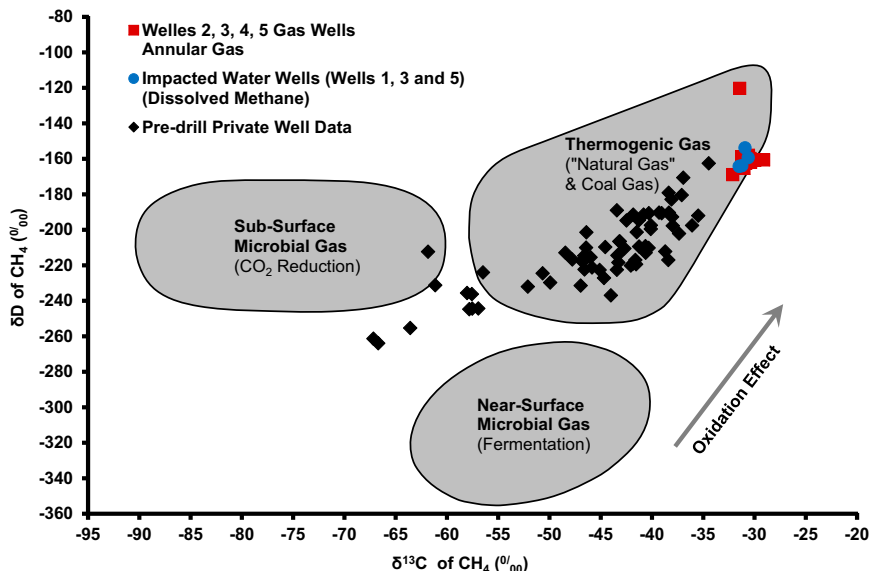


Fig. S1. Crossplot of δD of CH_4 vs. $\delta^{13}C$ of CH_4 (per mil) illustrating isotopic similarity between natural gas sampled from the annuli of gas wells (Welles 2, 3, 4, and 5 series) and impacted water wells (Wells 1, 3, and 5). Isotopic data were not available for other impacted water wells. Predrill private well data were collected throughout Bradford, Sullivan, Susquehanna, and Tioga counties in NE Pennsylvania (7). Regions for different types of microbial and thermogenic gas are illustrated (10).

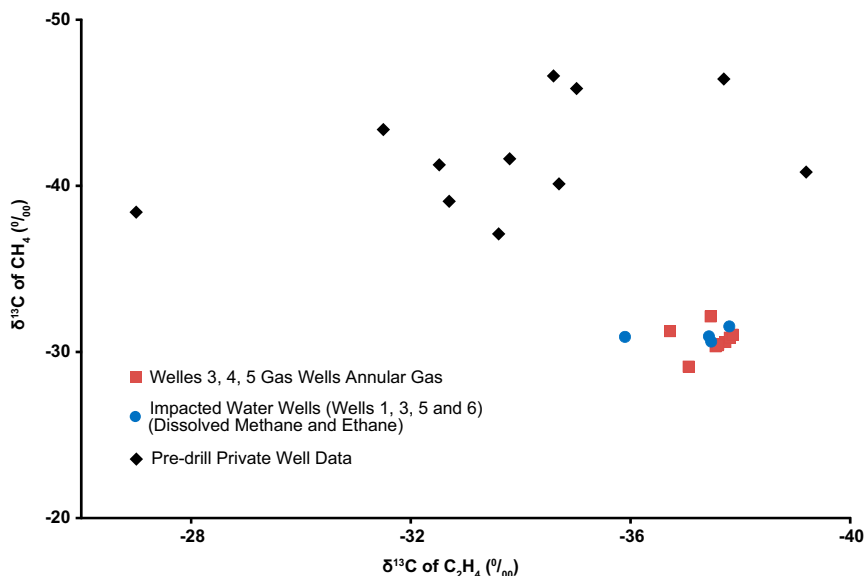


Fig. S2. Crossplot of $\delta^{13}C$ of CH_4 vs. $\delta^{13}C$ of C_2H_6 (per mil) illustrating isotopic similarity between natural gas sampled from annuli of gas wells (Welles 3, 4, and 5 series) and impacted water wells (Wells 1, 3, 5, and 6). Isotopic data were not available for other impacted water wells. Predrill private well data collected throughout Bradford, Sullivan, Susquehanna, and Tioga counties in NE Pennsylvania (7).

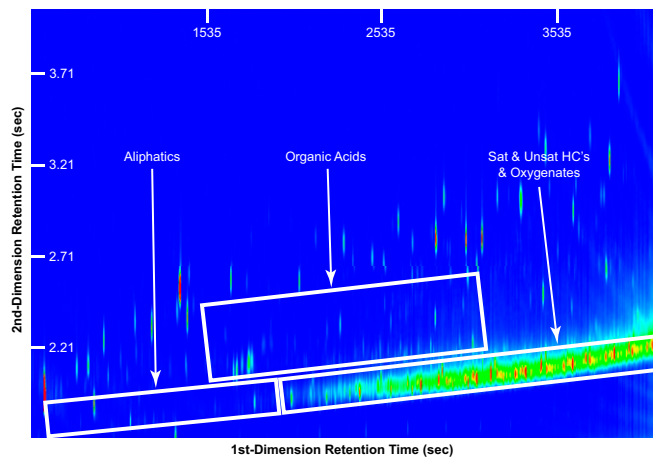


Fig. S5. GCxGC-TOFMS chromatogram illustrating UCM from Well 6 (PLG-12-64A), which was installed as a replacement for Well 5 by the gas company in August/September 2010 and exhibits impacts. Compound classes are illustrated. Color variations indicate relative compound concentrations, with blue being the lowest and red being the highest.

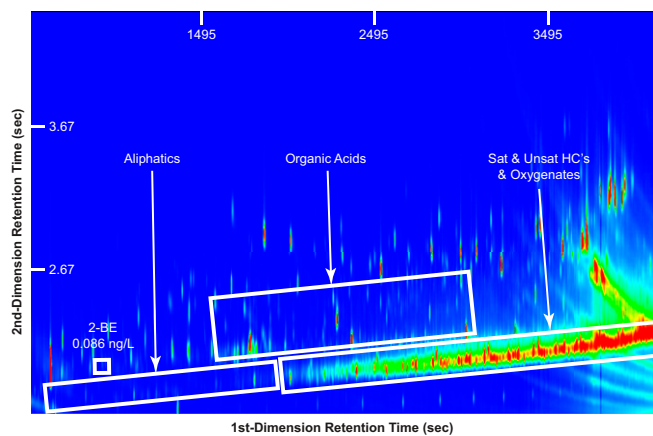


Fig. S6. GCxGC-TOFMS chromatogram illustrating UCM from Well 1 (PLG-12-68A) after purging, which was installed as a replacement for Well 2 by the gas company in August/September 2010 and exhibits impacts. The presence of 2-BE is still identified but at a lower concentration than prepurge Well 1 sample (compare Fig. 4A).

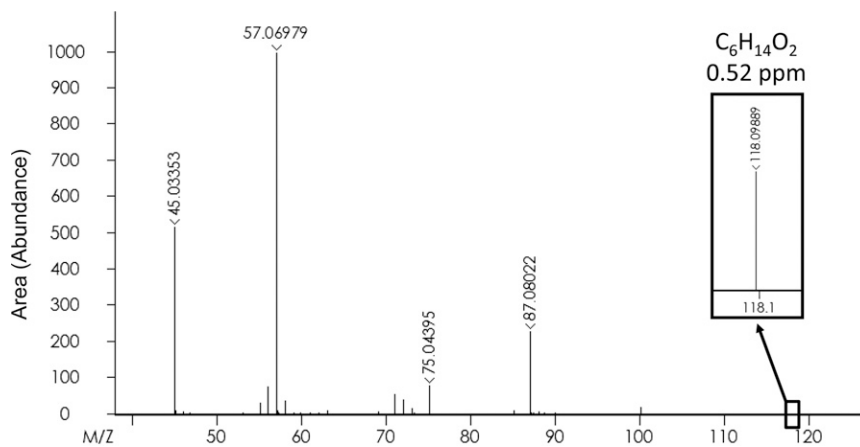


Fig. S7. The accurate high resolution mass spectrometer mass spectrum indicating presence of 2-BE in Well 1 (PLG-12-67A) before purging.

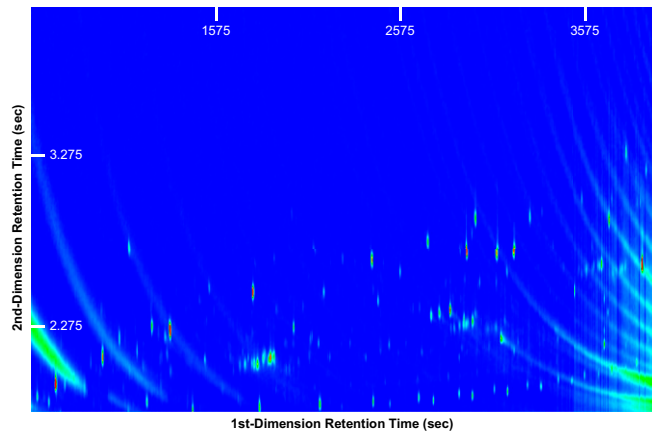


Fig. S8. GCxGC-TOFMS chromatogram illustrating absent UCM from background well B1 (bottle PLG-13-7A) that was not impacted by gas drilling activities. Other background wells (B2 and B3) produced similar GCxGC-TOFMS chromatograms, indicating the same.

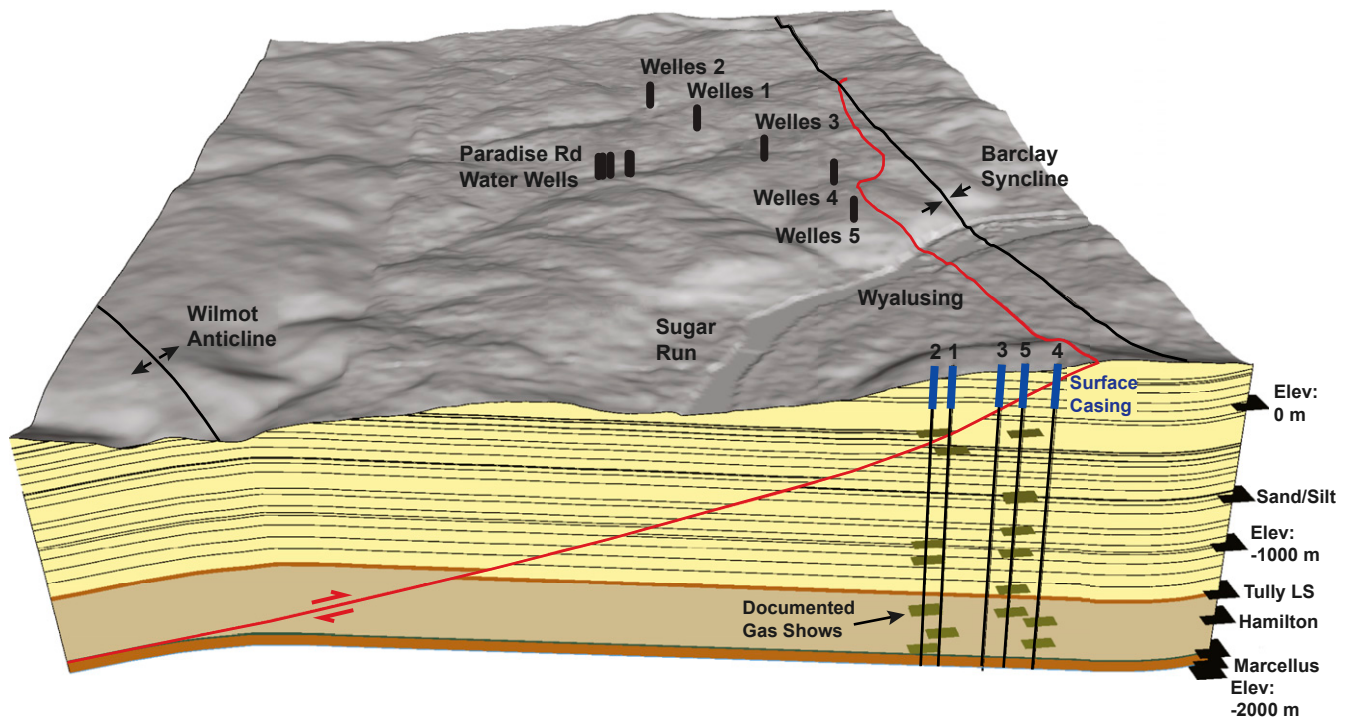


Fig. S9. Block diagram illustrating a shallow angle thrust fault (red line), Barclay and Wilmot structural fold surficial traces (surficial black lines), and bedding planes (subsurface black lines). Stratigraphic units and markers are illustrated on the right side. Viewpoint is toward the west. A light detection and ranging (LIDAR) digital elevation model (DEM) was used to construct the land surface. Water well positions (Wells 1 through 6) are illustrated. Generalized gas well depictions (Wells 1–5 series) are illustrated and projected to the front of the block for comparison with the thrust fault, bedding planes, and documented gas shows overlying the Marcellus Shale (see Fig. S10). In September 2010, gas was observed bubbling from the Susquehanna River in numerous locations between the communities of Sugar Run and Wyalusing. Gas bubbling ceased following gas well remedial activities conducted at the Welles 3, 4, and 5 well pads.

Table S1. Generalized timeline of events

Date, m/d/y	Event
04/23/2009	Welles 1 Pad constructed
05/15/2009	Welles 2 Pad constructed
06/15/2009	2 wells set on Welles 1 pad using 45 feet of conductor casing
06/28/2009	First spud of Welles 1-3H and 1-5H
08/07/2009	Leak out of a pit at Welles 1-3H, 1-5H
08/23/2009	Welles 3 Pad constructed
09/02/2009	Welles 1-3H, 1-5H cited by PADEP for discharge of contaminated fluids (from drilling or well) to ground
09/23/2009	Rig release from Welles pad 1
09/28/2009	First spud of Welles 2-2H and 2-5H
10/23/2009	Completion of Welles 2-2H
10/30/2009	First spud of Welles 3-2H and 3-5H
11/04/2009	Welles 4 Pad constructed
12/17/2009	Welles 5 Pad constructed
01/08/2010	First spud of Welles 4-2H and 4-5H
02/01/2010	Fracture stimulation (i.e., hydraulic fracturing), 20 stages, at Welles 1-3H and 1-5H
03/21/2010	Spud of Welles 5-2H and 5-5H
04/2/2010	1-3H initial annular gas pressure, 0 psi; 5-5H initial annular pressure, 0 psi; homeowner first notifies company of silt in a spring
04/14/2010	Drilling commences on Welles 5-2H
05/2/2010	Drilling finishes on Welles 5-2H
Early 05/2010	Homeowner notices sediment in water from well 3 (Fig. 1)
05/08/2010	Drilling completed for Welles 3-2H
05/12/2010	Rig release from Welles 3 pad
05/24/2010	Initial annular pressure on 3-2H, 950 psi, and for 3-5H, 700 psi
06/13/2010	Water pump has sediment in it at well 3
07/12/2010	Gas company notified of turbid water well 2 (Fig. 1); gas company observes sediment on filters in homeowner wells; registered water driller requested to investigate
07/12/2010	Homeowner at well 2 contacts gas company about turbidity; also turbidity issue at well 3
07/13/2010	Homeowner of well 2 notifies PA Department of Environmental Protection (DEP); company delivers water to both residences; homeowner tells gas company that their water from well 5 (Fig. 1) can be ignited, but gas company visits and ignition is not achieved; gas company delivers water for homeowners with wells 2 and 3
07/14/2010	DEP finds methane in well 3 but none in well 2
07/15/2010	DEP worker measures 3 vol.% methane in well 3 and none in well 2
07/17/2010	Water well driller retained by gas company notifies gas company that the water wells are bubbling at wells 3 and 2; gas company visits and observes the same
07/17/2010	Bubbling reported in well waters; well evacuated to allow recharge; lower explosive limit reported at 3% in well 3 and 68% in 2
07/19/2010	Letter sent to gas company by owner of well 3; gas company visits and sees no problems
07/20/2010	Welles 5-2H and 5-5H treated by gas company
07/21/2010	Inspection of well 5 reveals no issues although some effervescence was observed, but no turbidity; gas company notifies DEP of the complaints and waits for DEP to indicate path forward
07/22/2010	Gas company is informed that a natural spring has dried up; gas company visits well 5 where the homeowner has been advised by a physician to not drink, cook, or bathe in the water
07/24/2010	Diagnostic tests run on Welles 3-5H and 3-2H to find problems (includes cement logging)
07/25/2010	Backhoe used to dig out cellar of Welles 3-2H to correct eccentric wellhead; unable to dig past big rock
07/26/2010	Four residents experiencing gas in water at faucets
07/30/2010	Another resident notifies gas company of turbidity in water
07/31/2010	Environmental teams for gas company collect samples of groundwater from residences in a screening sweep within 1-mile radius of Welles 1 and 3 pads
08/02/2010	Gas company installs methane monitor in well 3 (Fig. 1)
08/04/2010	Methane monitor sounds off at well 3 (Fig. 1); gas company responds to secure safety of residence and notify emergency responders
08/05/2010	Gas company makes an offer to replace water wells
08/06/2010	Four residences are set up by gas company with water tanks
08/06/2010	Track hoe used at Welles 3-2H to excavate cellar and repair eccentric wellhead; perforated shallow casing and squeezed with cement
08/10/2010	Shallow squeeze job on Welles 3-2H
08/13/2010	Squeeze job at two shallow depths on Welles 3-2H
08/17/2010	Gas company initiated drilling of replacement water well for a homeowner
08/19/2010	Perforated Welles-3-5H at shallow depth and pumped in 10 bbls of Na silicate, but unable to place cement; perforated shallow casing and squeezed in cement
08/20/2010	Installed methane monitors
08/26/2010	Completed water well for a homeowner

Table S2. Methane data used in initial investigation

	Analyst	Date, m/d/y	Methane, µg/L	
Well 1	Unknown	9/14/2010	10,900	
	Unknown	10/6/2010	24,500	
	Unknown	10/13/2010	20,600	
	Unknown	10/20/2010	8,820	
	Unknown	3/1/2011	17,100	
	Unknown	4/7/2011	14,200	
	Unknown	5/23/2011	9,210	
	Property owners' consultant	5/26/2011	7,000	
	Unknown	6/8/2011	9,890	
	Unknown	6/22/2011	10,400	
	Unknown	7/6/2011	10,800	
	Unknown	7/20/2011	6,650	
	Unknown	8/3/2011	10,400	
	Unknown	8/17/2011	8,880	
	Unknown	9/2/2011	6,230	
	Unknown	9/14/2011	9,870	
	Unknown	9/29/2011	9,620	
	Unknown	10/12/2011	4,100	
	Unknown	10/31/2011	6,090	
	Unknown	10/31/2011	10,000	
	Unknown	11/9/2011	4,940	
	Unknown	11/22/2011	5,510	
	Property owners' consultant	11/29/2011	6,300	
	Unknown	12/7/2011	3,600	
	Unknown	12/27/2011	6,120	
	Unknown	1/4/2012	5,020	
	Unknown	1/18/2012	5,060	
	Unknown	2/1/2012	6,100	
	Property owners' consultant	3/26/2012	3,400	
	Unknown	3/28/2012	6,460	
Gas company's consultant	5/9/2012	11,850		
Property owner's consultant	5/30/2012	7,300		
Property owner's consultant	5/31/2012	6,900		
Well 2	Property owner's initial laboratory baseline	4/8/2010	<20	
	Unknown	7/15/2010	2,690	
	Unknown	7/21/2010	9,480	
	Unknown	8/3/2010	95.7	
	Unknown	9/15/2010	1,410	
	Unknown	10/6/2010	2,780	
	Unknown	10/13/2010	4,580	
	Unknown	10/20/2010	1,780	
	Unknown	10/31/2010	ND	
	Gas company's consultant	5/8/2012	630	
	Property owners' consultant	5/15/2012	15	
	Well 3	Unknown	7/15/2010	19,500
		Unknown	7/21/2010	29,700
Unknown		8/4/2010	8,360	
Unknown		8/2/2010	5,020	
Gas company's consultant		8/19/2010	17,510	
Gas company's consultant		5/9/2012	34,520	
Property owners' consultant		5/16/2012	4,300	
Property owner' consultant		5/30/2012	14,000	
Well 4	Unknown	9/13/2010	5,070	
	Unknown	10/7/2010	4,620	
	Unknown	10/14/2010	4,810	
	Unknown	10/21/2010	3,710	
	Unknown	2/17/2011	3,270	
	Unknown	4/7/2011	7,290	
	Unknown	5/23/2011	8,860	
	Unknown	6/8/2011	8,790	
Unknown	6/22/2011	10,400		

Table S2. Cont.

	Analyst	Date, m/d/y	Methane, µg/L
	Unknown	7/6/2011	6,240
	Unknown	7/22/2011	5,920
	Unknown	8/3/2011	5,490
	Unknown	8/17/2011	5,390
	Unknown	8/31/2011	2,330
	Unknown	9/16/2011	10,100
	Unknown	10/3/2011	9,670
	Unknown	10/12/2011	9,760
	Unknown	10/28/2011	10,800
	Unknown	11/9/2011	5,190
	Gas company's consultant	5/9/2012	32,060
	Property owners' consultant	5/30/2012	14,000
	Property owners' consultant	5/31/2012	11,000
Well 5	Unknown	7/21/2010	25,800
	Unknown	8/3/2010	10,700
	Unknown	9/15/2010	17,000
	Unknown	10/12/2010	14,900
	Unknown	10/19/2010	16,200
	Gas company's consultant	8/19/2010	16,000
	Gas company's consultant	5/7/2012	27,280
	Property owners' consultant	5/14/2012	12,000
Well 6	Unknown	9/13/2010	9,230
	Unknown	10/5/2010	10,200
	Unknown	10/12/2010	8,480
	Unknown	10/19/2010	9,820
	Unknown	2/17/2011	2,290
	Unknown	4/7/2011	10,000
	Unknown	5/23/2011	8,630
	Unknown	6/8/2011	7,710
	Unknown	6/22/2011	11,300
	Unknown	7/6/2011	9,310
	Unknown	7/22/2011	7,850
	Unknown	8/3/2011	5,330
	Unknown	8/17/2011	8,380
	Unknown	8/31/2011	2,210
	Unknown	9/16/2011	10,800
	Unknown	10/4/2011	14,500
	Unknown	10/12/2011	13,700
	Unknown	10/28/2011	13,800
	Unknown	11/9/2011	8,020
	Gas company's consultant	5/9/2012	46,640
	Property owners' consultant	5/30/2012	14,000
	Property owners' consultant	5/31/2012	20,000

ND, not determined.

Table S4. Site descriptions for PSU analyses

Site names	Sample site	Sample site	Latitude	Longitude	GCxGC-TOFMS bottle ID	Sample date, m/d/y	Sampling protocol
Analyzed with GCxGC: impacted houses							
Well 3 (PLG 12-60)	Fig. 1B	original well	41.642	-76.295	PLG-12-60 A	11/7/2012	sampled before purging
Well 6 (PLG 12-65)	Fig. 1B	replacement well	41.641	-76.294	PLG-12-64 A	11/7/2012	after purging ~5 min
Well 1 (PLG 12-69)	Fig. 1B	replacement well	41.643	-76.294	PLG 12-67 A	11/7/2012	before purging
					PLG 12-68 A	11/7/2012	after purging ~10 min
Analyzed with GCxGC: nonimpacted houses							
Well B1 (PLG 13-7)	5 km from incident	nonimpacted household well	41.646	-76.286	PLG 13-7 A	3/16/2013	water purged
Well B2 (PLG-13-5)	5 km from incident	nonimpacted household well	41.628	-76.324	PLG 13-5B	3/16/2013	water purged
Well B3 (PLG-13-6)	5 km from incident	nonimpacted household well	41.671	-76.332	PLG 13-6A	3/16/2013	water purged
Analyzed for inorganic solutes and/or dissolved gases							
PLG-12-33	on Route 29 near Salt Spring Park	private home, Susquehanna County	41.964	-75.819	NA	7/12/2012	water purged
PLG-12-34	Salt Spring State Park	Salt Springs, Susquehanna County	41.964	-75.819	NA	7/12/2012	see <i>Methods</i>
PLG-12-70	Wyalusing, PA	new house	41.708	-76.261	NA	11/7/2012	water purged
PLG-13-2	within 5 km of impacted valley	nonimpacted household well	41.643	-76.278	NA	3/16/2013	water purged
PLG-13-4	within 5 km of impacted valley	nonimpacted household well	41.648	-76.292	NA	3/2/2013	water purged

NA, not analyzed with GCxGC-TOFMS.

Table S5. Hydrocarbon analyses (Pennsylvania State University and Isotech)

Site ID	Bottle ID*	Sample date, m/d/y	Location of analysis	Bottle	Biocide	CH ₄ mg/L	STD%	C ₂ H ₆ , mg/L	STD%	δ ¹³ CH ₄	δ ¹³ C ₂ H ₆
Well 6 on Fig. 1 (replacement well)	1	11/7/2012	Penn State	Isotech	benzyl Cl	14.88	17.06	0.21	2.91	-31.9	—
	2	11/7/2012	Isotech	Isotech	benzyl Cl	20.00	—	0.36	—	-30.9	-35.6
	2	11/7/2012	PSU	Isotech	benzyl Cl	16.48	12.40	0.25	3.24	-30.8	—
Well 1 on Fig. 1 (replacement well)	1	11/7/2012	PSU	Isotech	benzyl Cl	6.76	19.28	0.11	8.53	-33.3	—
	2	11/7/2012	Isotech	Isotech	benzyl Cl	4.50	—	0.15	—	-31.5	-37.8
	2	11/7/2012	PSU	Isotech	benzyl Cl	5.00	19.34	0.13	5.27	-32.8	—
PLG 12-70 (new house)	70	11/7/2012	PSU	125 mL serum	benzyl Cl	0.80	0.21	—	—	-67.9	—
	70NB	11/7/2012	PSU	125 mL serum	no biocide	0.90	0.89	—	—	-64.0	—
PLG-12-34 (Salt Springs)	PLG-12-34A	7/12/2012	PSU	125 mL serum	Na azide	35.27	5.89	0.37	0.36	—	—
	PLG-12-34B	7/12/2012	PSU	125 mL serum	Na azide	36.66	5.19	0.36	7.22	—	—
	PLG-12-34C	7/12/2012	PSU	125 mL serum	Na azide	33.61	2.9	0.3	1.18	—	—

*Where a 1 or 2 are indicated, two bottles were collected at the site: one sent to Isotech (2) and then back to Pennsylvania State University (PSU) for analysis, the other (1) only analyzed at PSU.

Table S6. Inorganic analyses, mg/L

Site ID	Date, m/d/y	Ba (0.005)	Ca (0.01)	Fe (0.01)	K (0.01)	Mg (0.01)	Na (0.01)	P (0.01)	Si (0.01)	Sr (0.005)	Cl	SO ₄	NO ₃	Br
PLG 12-60	11/7/2012	0.2	26.1	0.18	1.46	4.40	31.3	0.02	4.59	0.49	6.6	9.4	<0.7	<0.1
PLG 12-65	11/7/2012	0.2	36.7	0.20	3.85	6.30	18.6	<0.01	4.52	0.95	19	11	4.9	<0.1
PLG 12-70	11/7/2012	0.1	43.3	<0.01	1.06	11.0	17.4	<0.01	4.88	0.25	0.98	19	<0.7	<0.1
PLG-12-33	7/12/2012	0.2	25.5	0.22	1.45	8.40	50.5	0.02	5.53	0.52	5.3	18	<0.4	<0.1
PLG-12-34	7/12/2012	110	367	1.61	13.5	55.0	1,800	0.70	3.75	65.8	2,680	<1.9	<0.4	48.1
PLG-12-69*	7/12/2012	0.2	28.8	0.04	1.62	4.20	30.3	0.06	4.77	1.33	14	6.8	<0.4	<0.1
PLG-12-69 [†]	7/12/2012	0.2	28.1	<0.01	1.68	4.10	30.1	0.20	4.69	1.31	13	7.5	<0.4	<0.1
PLG 13-2	3/2/2013	0.3	40.1	<0.01	2.03	5.22	20.4	0.01	5.35	2.06	5.7	14	0.3	0.01
PLG 13-4	3/2/2013	0.5	28.5	<0.01	2.72	3.02	28.2	<0.01	4.96	1.80	9.9	7.4	<0.4	0.02
PLG 13-5	3/2/2013	0.2	63.6	<0.01	1.13	9.26	12.1	<0.01	4.59	0.20	28	20	2.7	<0.01
PLG 13-7	3/16/2013	0.3	54.5	<0.01	1.41	7.53	9.1	<0.01	5.15	0.85	34	15	0.3	<0.01
PLG-13-6	3/2/2013	0.2	46.6	<0.01	1.20	6.48	8.2	0.06	4.87	0.41	8.3	16	1.3	<0.01

Detection limits are given in parentheses next to element, if applicable.

*Prepurge.

[†]Postpurge.

Table S7. List of surrogate compounds used in analyses

Compound name	CAS no.	Concentration in final extract, pg/uL
2-Fluorobiphenyl	321-60-8	200
Nitrobenzene-d5	4165-60-0	200
<i>p</i> -Terphenyl-d14	1718-51-0	200
2-Chlorophenol-d4	93951-73-6	200
2-Fluorophenol	367-12-4	200
Phenol-d6	13127-88-3	200
2,4,6-Tribromophenol	118-79-6	200
PCB 18	37680-65-2	200
PCB 28	7012-37-5	200
PCB 52	35693-99-3	200
Triphenylmethane	519-73-3	40
Triphenylphosphate	115-86-6	80
Tris-(1,3-dichloroisopropyl)phosphate	13674-87-8	200

Table S8. Reported hydrofracturing compounds used in Welles 2-5H

Compound	Maximum concentration in hydraulic fracturing fluid, % by mass
Hydrochloric acid	0.03543
Trisodium nitrilotriacetate	0.00056
Sodium sulfate	0.00003
Sodium hydroxide	0.00001
Methanol (methy alcohol)	0.00021
Ethoxylated alcohols (C14–15)	0.00011
Modified thiourea polymer	0.00011
Propargyl alcohol (2-propynol)	0.00004
Alkenes	0.00002
2-butoxyethanol (ethylene glycol monobutyl ether)	0.00006
Methanol (methyl alcohol)	0.00006
Diethanolamine	0.00001
Petroleum distillate hydrotreated light	0.01532
Ammonium acetate	0.00263
Sodium polyacrylate	0.00881
Glutararaldehyde	0.00719
Didecyl dimethyl ammonium chloride	0.00213
Quaternary ammonium compound	0.00147
Ethanol	0.00107
Petroleum distillate lydotreated Light	0.00025
Quaternary ammonium chloride (ammonium chloride)	0.00011
Alcohol ethoxylated C12–C16	0.00004
Ethoxylated alcohols	0.00004
Alcohol ethoxylate	0.00004
Alcohols, C12–C14—secondary, ethoxylated	Not available
Ethoxylated oleylamine	Not available
Polyacrylamide (acrylamide, ammonium acrylate copolymer)	Not available
Polyethylene glycol monnleate	Not available
Sorbitan monooleate	Not available
Sorbitol tetraoleate	Not available

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