Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development

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High-volume hydraulic fracturing (HVHF) has revolutionized the oil and gas industry worldwide but has been accompanied by highly controversial incidents of reported water contamination. For example, groundwater contamination by stray natural gas and spillage of brine and other gas drilling-related fluids is known to occur. However, contamination of shallow potable aquifers by HVHF at depth has never been fully documented. We investigated a case where Marcellus Shale gas wells in Pennsylvania caused inundation of natural gas and foam in initially potable groundwater used by several households. With comprehensive 2D gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOFMS), an unresolved complex mixture of organic compounds was identified in the aquifer. Similar signatures were also observed in flowback from Marcellus Shale gas wells. A compound identified in flowback, 2-n-Butoxyethanol, was also positively identified in one of the foaming drinking water wells at nanogram-per-liter concentrations. The most likely explanation of the incident is that stray natural gas and drilling or HF compounds were driven ~1–3 km along shallow to intermediate depth fractures to the aquifer used as a potable water source. Part of the problem may have been wastewaters from a pit leak reported at the nearest gas well pad—the only nearby pad where wells were hydraulically fractured before the contamination incident. If samples of drilling, pit, and HVHF fluids had been available, GCxGC-TOFMS might have fingerprinted the contamination source. Such evaluations would contribute significantly to better management practices as the shale gas industry expands worldwide.

high-volume hydraulic fracturing | shale gas | natural gas | water quality | Marcellus Shale

Horizontal drilling and high-volume hydraulic fracturing (HVHF) are used in combination to extract natural gas, condensate, and oil from shale reservoirs in the United States at rates affecting the world economy (1–4). In the shale gas-rich Marcellus Formation, such slick water HVHF began in 2004, leading to >8,000 Marcellus wells drilled in Pennsylvania (PA) alone as of October 2014. Nearly 70% of these have been hydraulically fractured using large volumes of water and sand with relatively small volumes of gels, acids, biocide, and other compounds (5, 6). The fast rate of such shale development in the northeastern United States has led to several cases of water resource impacts, including surface discharges of contaminants as well as subsurface gas migration (6–12). Although media reports of incidents are common, published reports are few (10).

The most useful evidence for incidents links contaminants directly to the source with a high degree of certainty. To evaluate impacts, a "multiple lines of evidence" approach (13–16) is generally necessary, including (*i*) time series analyses of natural gas and organic and inorganic compound concentrations, (*ii*) comparisons of natural gas isotopic compositions between gas well annular gas and groundwater, (*iii*) assessments of gas well construction, (*iv*), chronology of events, (*v*) hydrogeologic characterization, and (*vi*) geospatial relationships.

Here we provide data for a contamination incident from PA where the regulator (PA Department of Environmental Protection, PADEP) concluded that stray natural gas derived from nearby Marcellus Shale gas wells contaminated the aquifer used by at least three households in southeastern Bradford County, PA (Fig. 1). In addition to gas, the well waters were also observed to foam (Fig. 1*C*), but no cause was determined. To investigate this and other contaminants present, we demonstrate an investigative approach to identify unique organic unresolved complex mixtures (UCMs) and a target compound linked to shale gas-related contamination (2-n-Butoxyethanol, 2-BE).

History

Between 2009 and 2010, five gas well pads, known as Welles 1 through 5, were constructed about 1–2.25 km north of a small valley along the north branch tributary of Sugar Run where several private homes used groundwater for drinking (Fig. 1 *A* and *B* and Table S1). On each well pad, two wells with horizontal sections at depth were drilled and surface casing was emplaced to about 300 meters below ground surface (m-bgs) on the vertical section. The vertical casing consists of steel pipe surrounded by cement. At intermediate depths, no casing was installed. Production casing was used through the zone of gas production in the Marcellus Shale at depths between 2,100 m-bgs and 2,300 m-bgs (horizontal section).

By the end of September 2009 after both gas wells on the Welles 1 well pad were drilled, no construction problems associated with gas migration (6) were noted; however, a drilling fluid
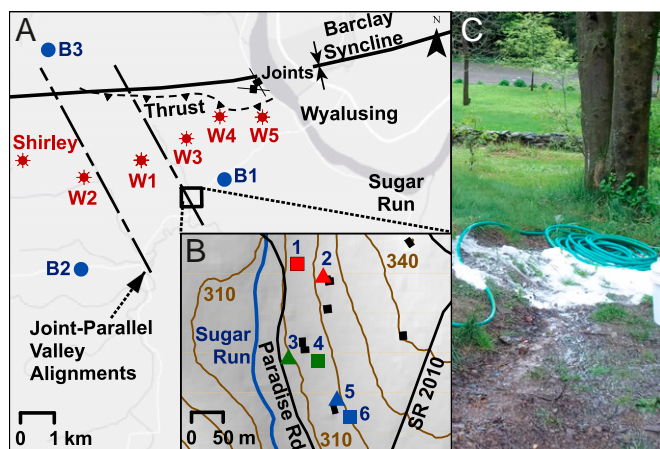
Fig. 1. (*A*) Study area showing the communities of Wyalusing and Sugar Run located on Susquehanna river (dark grey), gas wells (Shirley, Welles 1–5 well pads labeled as W1 through W5), domestic water wells not impacted by gas drilling activities (B1–B3), and notable geologic features (thrust fault surface expression, regional joint orientation, axis of syncline). (*B*) Expanded view of tributary of Sugar Run creek (blue line) showing domestic water Wells 1–6 impacted by gas drilling activities. Wells 2, 3, and 5 (triangles) are original impacted wells. Wells 1, 4, and 6 (squares) are replacement wells provided by gas company that also showed contamination. Brown lines are elevation contours (m-msl). Black squares are structures and lines are roads. (*C*) Foam emitted during purging of domestic water Well 2 in Spring, 2012.

leak from a pit was documented by the PADEP on 7 August 2009 (Table S1). HVHF was completed for Welles 1-3H and Welles 1-5H in February 2010. Gas well naming convention includes the propery owner (e.g., "Welles"), followed by the pad number (e.g., "1") and then the individual well designation (e.g., "3H" and "5H").

Gas wells on Welles 2–5 pads were drilled between September 2009 and May 2010. In May 2010, annular pressures measured in Welles 3-2H (∼64 atm), Welles 3-5H (∼48 atm), Welles 4-2H (∼33 atm), and Welles 4-5H (∼34 atm) exceeded the maximum allowable pressure of 24 atm (17). In July 2010, natural gas and sediment were reported in well water by at least three households along the north branch of Sugar Run (Fig. 1 and Table S1). White foam was also observed in the water from impacted wells (Fig. 1C). Further, vapor intrusion of natural gas was reported in one basement, requiring household evacuation as a safety precaution.

On 11 May 2011, the PADEP cited the gas company for violations of the PA Oil and Gas Act and Clean Streams Law for allowing natural gas to enter aquifers (Table S1). Although they did not admit culpability, the gas company complied with the PADEP consent order and agreement (COA). The company remediated gas wells present at the Welles 3–5 pads with cement squeezes and plugs (SI Text and Table S1) to reduce gas well annular pressures.

The impacted water wells (Fig. 1) were sampled by environmental consultants and the PADEP and analyzed by commercial laboratories between July 2010 and May 2012 (Fig. 2 and Table S2). The gas company installed replacement groundwater wells (e.g., Wells 1, 4, and 6 illustrated in Fig. 1B); however, these wells also exhibited impacts, and treatment systems were installed for each household in late summer of 2010.

A civil lawsuit initiated by the homeowners was settled in June 2012, and the gas company acquired the properties as part of a monetary settlement. No nondisclosure agreements were signed except for a subset of proprietary files. The Welles gas wells were identified by consultants working on the behalf of the homeowners as the most probable source of stray gas due to (*i*) nondetectable

concentrations of dissolved methane in a predrill analysis of Well 2 (Figs. 1B and 2), (*ii*) groundwater quality time series data, (*iii*) comparison of isotopic signatures of natural gas from gas well annular spaces and in the potable wells, (*iv*) timing of the issues after gas drilling (Fig. 2 and Table S1), (*v*) excessive gas well annular pressures, and (*vi*) documentation of hydrogeologic conditions conducive to gas migration.

PADEP correspondence with the gas company in August 2010 requested documentation on the gas company's implementation of a 3-string casing design to include intermediate casing that would provide greater shallow aquifer protection. Following the case settlement and compliance with the PADEP's COA, the PADEP allowed the company to hydraulically fracture the gas wells on Welles 2–5 pads between November 2012 and September 2013 (www.FracFocus.org).

Here, we report new analyses on additional samples from the household wells before ownership passed to the gas company (e.g., data plotted for November 2012 in Fig. 2 and Tables S3–S6). Also, to investigate the cause of foam (Fig. 1C) and impacts previously unidentified, we used an analytical technique, comprehensive 2D gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOFMS), that has not been previously used in similar cases. Although many attributes of the technique provide advantages for environmental forensics, few laboratories have GCxGC-TOFMS capabilities (14). We explored broad nontargeted organic compound classes at detection levels of nanograms per liter (e.g., detection limits lower than those achieved in most commercial laboratories). The method is amenable for forensic use in that it explores for broad classes of organic compounds and signatures rather than focusing on a specific list of target analytes that may or may not be present when impacts occur. No samples of HVHF fluid or flowback/production waters were available to us from the Welles series wells, but we investigated flowback and production waters from other similar unconventional gas wells in PA.

Methods

Samples were collected and analyzed from (*i*) ∼30 Marcellus Shale flowback/production waters sampled throughout PA and provided to us by commercial entities, (*ii*) one of the original household wells, (*iii*) two of the wells that were drilled as replacements for the homeowners that were still contaminated, (*iv*) one natural brine spring (Salt Springs) located about 50 km
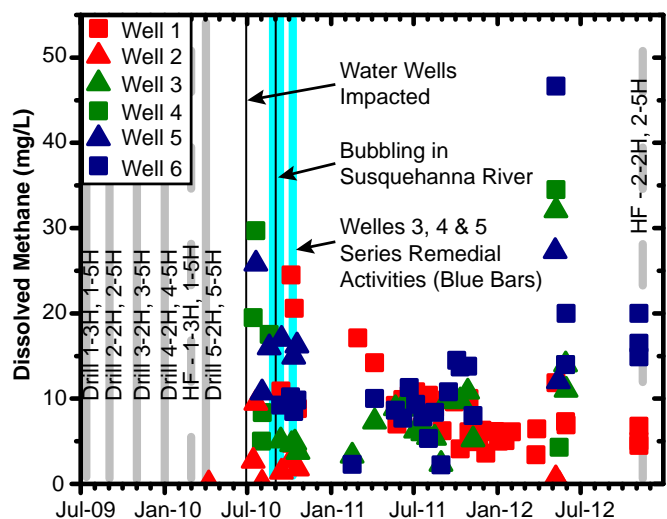

Fig. 2. Time series plot of dissolved methane concentrations with notable events, such as gas drilling, high-volume hydraulic fracturing (dashed grey lines labeled HF), gas well remedial activities, and onset of impacts to water Wells 1–6.

away in Susquehanna County, and (*v*) several potable water wells near the pollution incident that represent natural background. These background wells include a well from one of the relocated households, three non-impacted households located within 5 km of the impacted homes, and a private house near Salt Springs. We also obtained and analyzed one common drilling additive (Airfoam HD). Sampling methodologies are described in *SI Text*.

Subsets of these samples were analyzed via gas chromatographic separation, specifically using GCxGC-TOFMS, isotope ratio mass spectrometry, and inductively coupled plasma atomic emission spectrometry (ICP-AES) (see *SI Text* and Table S3). GCxGC-TOFMS has previously been successful in identifying hydrocarbons in crude oil forensics (13). Here, TOFMS was used to detect analytes as they eluted from the second column. Concentrations were quantified, when possible, by running samples with known compounds injected in tandem with the sample. Additionally, surrogate standards were added to all samples before extraction to account for sample extraction efficiency.

Available natural gas analyses completed during investigations before settlement (Table S2 and Figs. S1 and S2) and completed on a subset of the samples we collected in November 2012 (Table S5) are reported in *SI Text*.

Aquifer testing was also conducted using household Well 4 as a pumping well and the other original and replacement wells as monitoring wells to investigate shallow aquifer characteristics (Fig. S3).

Results

Dissolved Organic Analysis. Every flowback/produced water sample we analyzed had a similar UCM of hydrocarbons when evaluated with GCxGC-TOFMS (Fig. 3). All groundwater samples from impacted sites (Wells 1, 3, and 6; see Fig. 1) that were analyzed with GCxGC-TOFMS showed UCMs similar to those detected in the flowback/production waters (e.g., Fig. 4*A* and Figs. S4–S6). Well 1 was analyzed both before and after purging (at which time the water no longer foamed). Peak intensities for the UCM were generally greater after purging (compare Fig. 4*A* and Fig. S6).

Classes of analytes in GCxGC-TOFMS, such as aliphatic hydrocarbons or organic acids, align along a diagonal of the 2D cross-plot chromatograms. For the specific conditions used here, aliphatic hydrocarbons cluster near the origin, while compounds with increasing heteroatomic substitution or unsaturation lie further along the *y* axis. With the exception of the surrogate compounds (Table S7), only general classifications were determined from mass spectra. The detected molecules elute showing molecular weights <1,000 atomic mass units, and mass-to-charge

Fig. 4. GCxGC-TOFMS chromatograms for (*A*) Well 1 (PLG-12-67A) before purging and (*B*) background Well B1 (PLG-13-7A) that was not impacted by gas drilling activities. The hydrocarbon UCM observed in Well 1 is similar to that observed in flowback samples (e.g., Fig. 3). The 2-BE was positively identified in Well 1 (impacted by gas drilling activities), but not as part of background water quality. *B* is magnified to illustrate the absence of 2-BE.

ratios (*m/z*) of 50–550. Each flowback/production water sample had a similar but distinct pattern of saturated versus branched chain alkanes (compare Fig. 3 *A* and *C*).

A few of the ~30 flowback/production water samples were positively identified as containing 2-BE (Chemical Abstracts Service (CAS) number 111-76-2) and glycols—compounds commonly used during drilling and HVHF (Fig. 3*C*). For example, 2-BE was the only compound identified using GCxGC-TOFMS in the drilling additive and surfactant Airfoam HD (Fig. 5). The groundwater well analyzed before and after purging (Well 1) also contained detectable 2-BE. In contrast to the UCM, which increased in peak intensity with purging, concentrations of 2-BE decreased after purging: Sample PLG-12-67A before purge (Fig. 4*A*) contained ~0.42 ng/L 2-BE versus sample PLG-12-68A (after purging, Fig. S6) contained ~0.086 ng/L 2-BE (concentrations on as-received basis). No 2-BE was detected in the other two groundwater wells, although they contained the UCM [no 2-BE was detected in Well 3 (Fig. S4) or Well 6 (Fig. S5)].

To confirm the presence of 2-BE, sample extracts were reanalyzed using GCxGC with a high-resolution TOFMS (GCxGC-HR-TOFMS) at Leco Corporation. For example, the presence of 2-BE was confirmed in the accurate mass spectra for prepurge sample PLG-12-67A from Well 1 (e.g., one of the replacement wells) by comparison with the 2-BE standard (Fig. S7). Only 2-BE matched the molecular ion determined by the GCxGC-HR-TOFMS within 5 ppm. None of the field blanks or preparatory blanks contained

Fig. 3. GCxGC-TOFMS chromatograms of flowback water. (*A*) Example from a gas well in Connelsville, PA. (*B*) Magnified portion of *A* as indicated by white rectangle. (*C*) Example from a gas well in Kittanning, PA. (*D*) Magnified portion of *C* as indicated by white rectangle. General compound classes are illustrated in panels. Unresolved complex mixture (UCM) concentrations are relative to each panel, but increase in concentration from cool (e.g., blue) to bright (e.g., red) color.
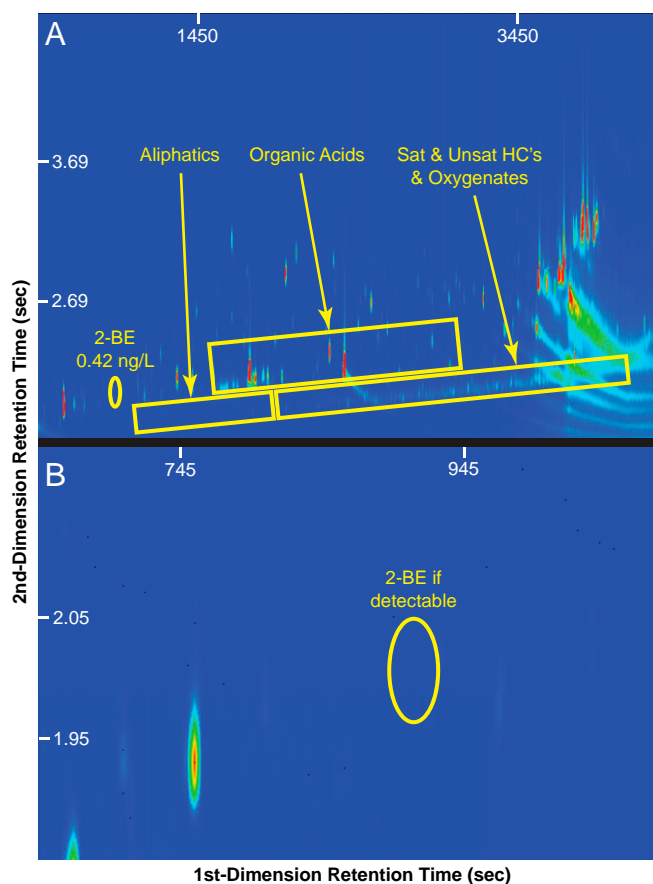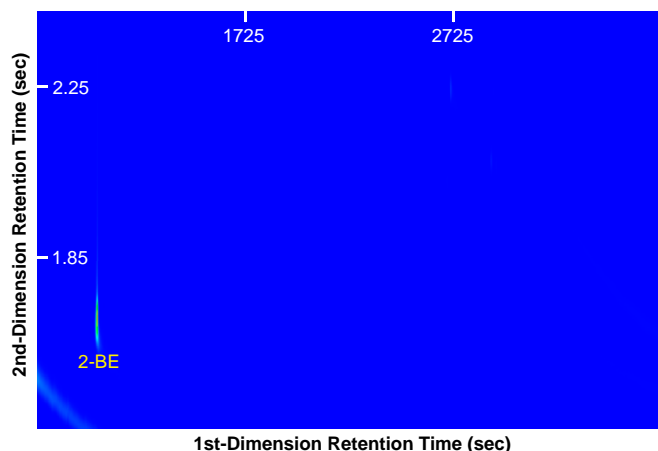
Fig. 5. GCxGC-TOFMS chromatogram for Airfoam illustrating 2-BE as the sole detectable component.

2-BE above detection (~0.01 ng/L). Likewise, neither UCM nor 2-BE were detected from groundwater (e.g., Fig. 4B and Fig. S8) sampled from three household wells (e.g., B1, B2, and B3 illustrated in Fig. 1) located outside of the impacted area and used to evaluate background conditions.

Inorganic Analysis. Conservative inorganic constituents (e.g., Cl and Br) can be used to determine if flowback or production waters have contaminated groundwater because these wastewaters can contain total dissolved solids in concentrations greater than 300,000 mg/L (6, 18). Further, if upward migration of HVHF fluids occurred after mixing with formation waters, dissolved Cl/Br mass ratios are more likely to be useful as effective fingerprints than the HVHF fluid components themselves, due to their more conservative behavior in groundwater (6, 10). Crossplots of Cl/Br (mass ratio) versus Cl concentration (Fig. 6) can help elucidate the source of Cl. For example, the natural water quality data for Salt Spring in Susquehanna County, PA, documents that Appalachian Basin brine (ABB) up-wells naturally into groundwater and surface water in Susquehanna County in that location as well as others (18). Although diluted, this spring water has a similar composition to flowback/production waters throughout PA and a few other brine springs and deep formation waters in the state (18–26) (Fig. 6 and Table S6). Conversely, Fig. 6 illustrates that the Cl concentrations and Cl:Br ratios of the impacted household waters from Bradford County are more likely gaining dissolved salts from sources with higher Cl:Br mass ratios than ABB.

Dissolved Gas and Isotopic Analyses. The dissolved methane concentrations measured in the impacted wells reached as high as 46.6 mg/L between 2010 and 2012 (Fig. 2 and Table S2). Such a high value is similar to methane concentrations we measured in three samples from Salt Springs State Park, where ABB is emitting naturally (Susquehanna County, 35.2 ± 1.53 mg/L, Table S5). In contrast, the predrill concentration in Well 2 was reported as <0.02 mg/L (e.g., plotting at the origin in Fig. 2). Likewise, the 1,701 drinking water wells collected by gas companies before drilling in adjacent Susquehanna County between 2008 and 2011 and analyzed in commercial laboratories (27) varied from a high (90th percentile) of 1.8 mg/L for valleys to a low of 0.017 mg/L for uplands. A steady decrease in dissolved methane was observed for at least one impacted household well (Well 1) with ample time series data, subsequent to the remediation of the Welles 3, 4, and 5 series gas wells (Fig. 2). An anomalous concentration spike was observed for all sampled wells in May 2012;

however, differences in well purging and sampling protocols from that event complicate comparison with those that preceded it.

A plot of δD versus $\delta^{13}C$ data for methane is illustrated in Fig. S1 for the (*i*) impacted household wells, (*ii*) annular space of Welles 2, 3, 4, and 5 gas wells, and (*iii*) predrill private household wells from the region (16). Notably, methane isotopic characteristics are consistent between gas sampled from the annular spaces of Welles 2, 3, 4, and 5 gas wells and groundwater sampled from the impacted homeowner wells. In contrast, methane characterized from predrill water wells in the region (16) illustrate generally different isotopic characteristics (Fig. S1). In addition, Fig. S2 illustrates that $\delta^{13}C$ for methane and ethane are also consistent among gas samples from Welles 3, 4, and 5 wells' annuli and the impacted groundwater wells.

Hydrogeologic Considerations. The impacted homeowner wells lie along the north branch of Sugar Run valley between the axes of two east−west aligned structural folds (Fig. 1 and Fig. S9). The concave Barclay fold (syncline), is located 1–3 km to the north of Welles 1–5 pads; the convex Wilmot fold (anticline) lies to the south at a distance of 5–7 km (Fig. S9). Under the impacted valley (between the folds), bedrock strata dip ~5–10 degrees downward to the northwest toward the Welles series gas wells.

In September 2010, significant gas bubbling commenced in the Susquehanna River near the community of Sugar Run southeast of the impacted homeowner wells (Fig. 1 and Fig. S9). When projected back to the Welles gas wells, bedding planes that outcrop near the river (and that presumably facilitate methane migration) intersect the boreholes at ~400–600 m-bgs (Fig. S9). In comparison, the gas wells were cased to ~300 m-bgs (Fig. S10).

Well-developed vertical to near-vertical fractures (joints) are observed in outcrop to trend NNW−SSE in the study area. A second, lesser-developed set is aligned E−W. Many stream valleys, such as the impacted north branch of Sugar Run, lie parallel to the NNW−SSE joints, consistent with joint-controlled valley development (Fig. 1). In addition to jointing, Fig. 1 and Fig. S9 also illustrate the surficial trace of a thrust fault identified from seismic reflection data. The fault plane dips ~16 degrees downward to the south: This dip intersects the Welles 1–5 series gas wells at depths between ~180 m-bgs and 580 m-bgs (Figs. S9 and S10). Thus, the thrust fault structural plane likely intersects some uncased portions of boreholes at the Welles 1, 2, and 3 pads. Of

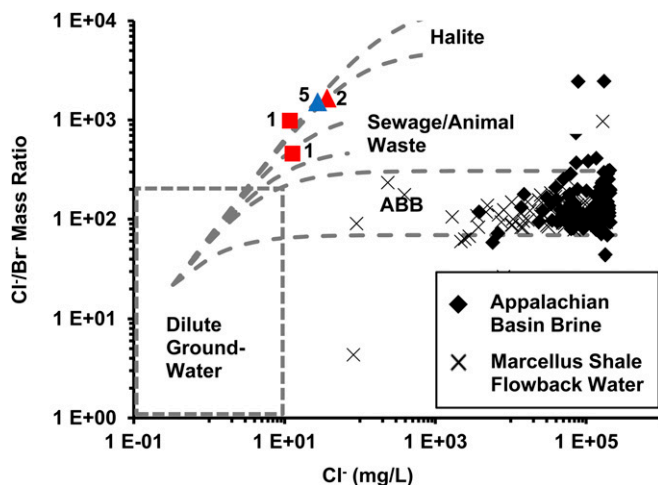**Fig. 6.** Crossplot of Cl/Br mass ratio vs. Cl concentrations for samples collected from Wells 1, 2, and 5 (labeled) with bounding upper and lower conservative mixing curves for various endmembers (e.g., Appalachian Basin brine, sewage and animal waste, and halite sources). Appalachian Basin brine samples (20–22, 24) and Marcellus Shale flowback samples (23, 25, 26) are also plotted for comparison.

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these three series, the Welles 1 and 2 wells did not reveal excessive, sustained annular gas pressures; however, elevated annular pressures of ~64 atm and ~48 atm were detected for Welles 3-2H and 3-5H, respectively. In response to the PADEP's COA with the gas company, cement was squeezed into boreholes for the Welles 3, 4, and 5 series (Table S1 and Fig. S10), with subsequent decreases in gas well annular pressure.

To evaluate the local bedrock aquifer used by the three impacted households, aquifer testing was conducted for 7 h in November 2012, using Well 4 as a pumping well (25.8 L/min). Static groundwater elevations near the three impacted households ranged from 303.5 m above mean sea level (m-msl) to 308.9 m-msl, with flow converging toward the north branch of Sugar Run (Fig. S3). The aquifer test results indicated preferential drawdown parallel to the valley alignment, suggesting aquifer anisotropy and/or heterogeneity. Additional aquifer characterization is provided in SI Text.

Discussion

Even though drinking water consistently foamed in three households in Bradford County (e.g., Fig. 1C), commercial laboratories reported no compounds other than natural gas present at concentrations above regulatory recommended action levels, and no constituents were detected above regulatory drinking water standards. However, commercial laboratory analyses did sporadically detect ethylene and propylene glycol and surfactants near microgram-per-liter detection limits (SI Text). When we analyzed a subset of the household waters with GCxGC-TOFMS in 2012, we detected very low concentrations of 2-BE. This compound is of special interest because the US Environmental Protection Agency (USEPA) has suggested that 2-BE could be an indicator of contamination from HVHF activities (29). Additional information on 2-BE is provided in SI Text. GCxGC-TOFMS also documented a UCM of organic contaminants in all three water wells analyzed. Background groundwater outside of the affected area had no such contamination (Fig. 4B and Fig. S8). It is not possible to prove unambiguously that the UCM and 2-BE were derived from shale gas-related activities. However, the timing (Fig. 2 and Table S1) and the presence of UCMs and 2-BE in flowback/production waters in PA (Fig. 3) are consistent with shale gas activity as the most probable source.

We also conclude that the foam identified from the homeowner wells was likely derived from either the UCM hydrocarbons (28) or 2-BE (a known surfactant). Methane degassing is exacerbated during the onset of household well pumping due to rapid water level drawdown and drop in hydrostatic pressure. The resulting effervescence and groundwater agitation then aids as a foaming facilitator. Given that 2-BE was only found in Well 1, despite foaming observed in all water wells, it might be reasonable to conclude that the UCM aided by gas effervescence was the most probable cause. Further, foaming and concentrations of 2-BE decreased with increasing well purging, unlike the UCM. On the other hand, 2-BE is a known surfactant, making it a more probable cause of foaming at low concentrations. Detection of 2-BE is difficult at these low concentrations in the presence of other organic compounds. Therefore, the compound may have been present in the foaming drinking waters even though we could not detect it in all wells.

There are no reports of 2-BE as a natural constituent in waters from shale (30). However, the common drilling additive Airfoam HD contains 2-BE as the only detectable organic component from our analyses (Fig. 5). Although we have no evidence that Airfoam HD was used in the Welles series gas wells in drilling fluids, this substance has been commonly used in northern and central PA. Indeed, it was cited by the PADEP as the cause of foam from a spring discharging to the canyon wall above Pine Creek in Lycoming County (PA) that began 15 March 2010. Further, a more recent PADEP contamination determination

letter, dated 14 May 2014, identified at least one private water well in Springville Township, Susquehanna County, PA, that was impacted by drilling fluids using Airfoam HD as a surfactant. Here, 2-BE in addition to volatile organic compounds and ethyl glycol were detected at microgram-per-liter concentrations in that household well and were deemed responsible for the foaming groundwater in the household well. This contamination was attributed to drilling fluid additives and not HVHF by the PADEP.

Notably, the Welles 1 gas well pad was the location of a drilling fluid pit leak in August 2009 (Table S1). Further, well construction issues required remedial efforts in the Welles 3–5 series gas wells. Therefore, drilling fluids used in their installation could reasonably account for the observed foam impacts to household Wells 1–6 (Fig. 1C). Since 2-BE and the UCM were identified together, drilling fluids might be the source of both.

Alternately, since the UCMs are similar in the well waters and flowback/production waters and 2-BE was only observed with the UCM, another scenario is that the UCM and 2-BE are derived from HVHF fluids. In fact, HVHF was initiated in February 2010 at the Welles 1 pad—5 mo before the turbidity and natural gas problems in the homeowner wells (Table S1 and Fig. 2). This well pad was also one of the two closest pads to the aquifer contamination incident. Notably, gas wells situated on the Welles 2–5 pads were hydraulically fractured in 2012 using fluids containing 2-BE (www.fracfocus.org; see Table S8). Although no data were reported online (www.fracfocus.org) regarding the compounds used during HVHF of Welles 1 pad wells, it is reasonable that the same nonemulsifier agent (which contained 2-BE) was likely used. Therefore, we conclude that it is possible that HVHF fluids used at the Welles 1 pad contaminated the drinking water aquifer.

If HVHF fluids did contaminate the water wells, it would be surprising if such contamination were due to fluids returning upward from deep strata, given that (i) this has never been reported (6), (ii) the time required to travel 2 km up from the Marcellus along natural fractures is likely to be thousands to millions of years (31), and (iii) Fig. 6 shows that the Cl:Br ratios in the drinking waters indicate the absence of salts that would be diagnostic of fluids from the Marcellus Shale (e.g., flowback/production waters). The most likely way for HVHF fluids to contaminate the shallow aquifers would therefore be through surface spillage of HVHF fluids before injection or by shallow subsurface leakage during injection.

It is possible that the provenance of the UCM and 2-BE was different from that of the stray gas. Indeed, the most reasonable explanation for the natural gas impacts to water wells is that gas migrated from Welles 3-2H or possibly from multiple gas wells drilled on the Welles 3–5 pads due to excessive annular pressures and lack of competent annular cement that allowed gas to move vertically upward along the wellbore and into shallow uncased portions of bedrock fractures, including an identified fault zone (Table S1, Fig. 1, and Figs. S9 and S10). Induced fracture propagation below the surface casing of Welles 3-2H is also possible given the recorded gas well annular pressures (see SI Text). In addition to potentially opening fracture pathways, excessive annular pressures and natural gas buoyancy likely drove gas up-dip along bedding-plane partings to the southeast, intermittently stair-stepping upward along near-vertical joints to Sugar Run (Fig. 1 and Figs. S3, S9, and S11). Well water turbidity was likely due to the entrainment of fine-grained sediment as a result of off-gassing and groundwater effervescence (32). The lower hydrostatic pressure of the shallow aquifer beneath the impacted valley, exacerbated by household pumping, likely drew in the contaminating fluids (Figs. S3 and S11).

Conclusions

We used comprehensive GCxGC-TOFMS to document that organic compounds derived from one or more shale gas wells in

PA were the likely cause of foaming and a complex suite of UCMs in three homeowner wells. In one well, 2-BE was positively identified and is a common constituent of both HVHF and drilling fluids. These impacts were likely caused by drilling or HVHF fluids used in the gas wells. Two of the closest shale gas wells were hydraulically fractured by the time of the impact, and the well pad was cited by the PADEP for a pit leak. Despite noticeable white foaming of groundwater, reported concentrations for dissolved organics were below applicable regulatory standards when investigated by both environmental consultants and the PADEP. Only natural gas was previously reported as a confirmed contaminant. If contaminants entered groundwater during HVHF or drilling, then they persisted 2.5 y in the subsurface, i.e., until the November 2012 sampling.

Importantly, the techniques we needed to identify the impacts, GCxGC-TOFMS and GCxGC-HR-TOFMS, are not readily available in most commercial laboratories. Investigating gas drilling impacts with these analytical methods may be more effective than using target compound lists that may or may not include appropriate analytes and appropriate laboratory detection limits.

Although much of the concern shown by the public focuses on the possibility that some of the 1,000 compounds (29, 33) used in HVHF could migrate upward from the target shale, such upward leakage has never been documented. This is probably because HVHF fluids remain trapped in deep rock strata. However, the public cannot ascertain the cause of most shale gas-related problems (10) because the full datasets are often not released publicly and explained.

The data released here do not implicate upward flowing fluids along fractures from the target shale as the source of contaminants but rather implicate fluids flowing vertically along gas well boreholes and through intersecting shallow to intermediate flow paths via bedrock fractures. Flow along such pathways is likely when fluids are driven by high annular gas pressure or possibly by high pressures during HVHF injection. Such shallow- to intermediate-depth contaminant flow paths are not limited to HVHF but rather have been previously observed with conventional oil and gas wells. As shale gas development expands worldwide, problems such as those that occurred in northeastern PA will only be avoided by using conservative well construction practices, such as intermediate casing strings, proper cementation, and mitigating overpressured gas well annuli.

1. MIT (2011) *The Future of Natural Gas* (MIT, Cambridge, MA).
2. Engelder T (2011) Should fracking stop? No, it's too valuable. *Nature* 477:272–275.
3. Arthur MA, Cole DR (2014) Unconventional hydrocarbon resources: Prospects and problems. *Elements* 10(4):257–264.
4. Blumsack S (2014) Dash for gas, 21st-century style! *Elements* 10(4):265–270.
5. King GE (2012) *Hydraulic Fracturing 101: What Every Representative, Environmentalist, Regulator, Reporter, Investor, University Researcher, Neighbor and Engineer Should Know About Estimating Frac Risk and Improving Frac Performance in Unconventional Gas and Oil Wells* (Soc Petrol Eng, Richardson, TX), Pap 152596.
6. Vidic RD, Brantley SL, Vandenbossche JM, Yoxtheimer D, Abad JD (2013) Impact of shale gas development on regional water quality. *Science* 340(6134):1235009.
7. Entrekin S, Evans-White M, Johnson B, Hagenbuch E (2011) Rapid expansion of natural gas development poses a threat to surface waters. *Front Ecol Environ* 9(9):503–511.
8. Wilson JM, VanBriesen JM (2012) Oil and gas produced water management and surface drinking water sources in Pennsylvania. *Environ Pract* 14(4):288–300.
9. 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.
10. Brantley SL, et al. (2014) Water resource impacts during unconventional shale gas development: The Pennsylvania experience. *Int J Coal Geol* 126:140–156.
11. Darrah TH, Vengosh A, Jackson RB, Warner NR, Poreda RJ (2014) Noble gases identify the mechanisms of fugitive gas contamination in drinking-water wells overlying the Marcellus and Barnett Shales. *Proc Natl Acad Sci USA* 111(39):14076–14081.
12. Jackson RB, et al. (2014) The environmental costs and benefits of fracking. *Annu Rev Environ Resour* 12(18):327–362.
13. Breen KJ, Revesz K, Baldassare FJ, McAuley SD (2007) *Natural Gases in Ground Water near Tioga Junction, Tioga County, North-Central Pennsylvania–Occurrence and Use of Isotopes to Determine Origins, 2005* (US Geol Surv, Reston, VA) Sci Invest Rep 2007-5085.
14. Revesz KM, Breen KJ, Baldassare FJ, Burruss RC (2010) Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania. *Appl Geochem* 25:1845–1859.
15. Molofsky LJ, Connor JA, Farhat SK, Wylie AS, Jr, Wagner T (2011) Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing *Oil Gas Dev* 109(19):54-67.
16. Baldassare FJ, McCaffrey MA, Harper JA (2014) A geochemical context for stray gas investigations in the northern Appalachian Basin: Implications of analyses of natural gases from Neogene- through Devonian-age strata. *AAPG Bull* 98(2):341–372.
17. General provision for well construction and operation, The Pennsylvania Code, Chapter 25, Sect. 78.73(c) (1989).
18. Llewellyn G (2014) Evidence and mechanisms for Appalachian Basin brine migration into shallow aquifers in NE Pennsylvania, U.S.A. *Hydrogeol J* 22(5):1055–1066.
19. 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.
20. Poth CW (1962) The occurrence of brine in western Pennsylvania. *Pa Geol Surv Bull* M47:1–53.
21. Dresel E (1985) The geochemistry of oilfield brines from western Pennsylvania, MSc thesis (Pennsylvania State University, University Park, PA).
22. Osborn SG, McIntosh JC (2010) Chemical and isotopic tracers of the contributions of microbial gas in Devonian organic-rich shales and reservoir sandstones, northern Appalachian Basin. *Appl Geochem* 25(20):456–471.
23. Hayes TD (2009) *Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas. Final Report Prepared for the Marcellus Shale Coaliton* (Gas Technol Inst, Des Plaines, IL).
24. Kelley D, DeBor D, Malanchak J, Anderson D (1973) *Subsurface brine analyses of Pennsylvania from deep formations, OFR 73-02* (Pa Bur Topogr Geol Surv, Harrisburg, PA).
25. Haluszcak LO, Rose AW, Kump LR (2013) Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Applied Geochemistry* 28(2013):55–61.
26. Pennsylvania Department of Environmental Protection (2010) *Frac and flowback water analyses* (Pa Dep Environ Prot, Harrisburg, PA). Available at www.shalenetwork.org.
27. Molofsky LJ, Connor JA, Wylie AS, Wagner T, Farhat SK (2013) Evaluation of methane sources in groundwater in northeastern Pennsylvania. *Ground Water* 51(3):333–349.
28. Lea JF, Nickens HV, Wells M (2008) *Gas Well Deliquification* (Elsevier, New York).
29. US Environmental Protection Agency (2012) *Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report* (US Environ Prot Agency, Washington, DC), EPA 601/R-12/011.
30. Leenheer JA, Noyes TI, Stuber HA (1982) Determination of polar organic solutes in oil-shale retort water. *Environ Sci Technol* 16(10):714–723.
31. Engelder T (2012) Capillary tension and imbibition sequester frack fluid in Marcellus gas shale. *Proc Natl Acad Sci USA* 109(52):E3625, and author reply (2012) 109(52):E3626.
32. Gorody AW (2012) Factors affecting the variability of stray gas concentration and composition in groundwater. *Environ Geosci* 19(1):17–31.
33. U.S. House of Representatives Committee of Energy and Commerce Minority Staff (2011) *Chemicals Used in Hydraulic Fracturing* (US House Rep, Washington, DC).

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 µg/L) and 5 (0.96 µg/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 µg/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 µg/L, respectively. Propylene glycol was also detected in Well 5 on 14 May 2012 at a concentration of 960 µg/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/customersupport/samplingprocedures/DGbottle.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 benzylkonium 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/uL 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 ±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 $\delta^{13}C$ 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 ±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 $\delta^{13}C$ (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 ±3% for all major elements and ±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. S3A).

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 (Tss) ~5.9 m²/d, and minimum transmissivity tensor (Tnn) ~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 (~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).

1. Kampbell DH, Vandegrift SA (1998) Analysis of dissolved methane, ethane, and ethylene in ground water by a standard gas chromatographic technique. *J Chromatogr Sci* 36(5):253–256.

2. Llewellyn G (2011) Structural and topographic assessment of shallow bedrock permeability variations throughout Susquehanna County, PA: A focus of Marcellus Shale gas development. *Geol Soc Am Abstr Prog* 43:567.

3. Llewellyn G (2014) Evidence and mechanisms for Appalachian Basin brine migration into shallow aquifers in NE Pennsylvania, U.S.A. *Hydrogeol J* 22(5):1055–1066.

4. 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.

5. Molofsky LJ, Connor JA, Farhat SK, Wylie AS, Jr, Wagner T (2011) Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing. *Oil Gas Dev* 109(19):54-67.

6. Molofsky LJ, Connor JA, Wylie AS, Wagner T, Farhat SK (2013) Evaluation of methane sources in groundwater in northeastern Pennsylvania. *Ground Water* 51(3):333–349.

7. Baldassare FJ, McCaffrey MA, Harper JA (2014) A geochemical context for stray gas investigations in the northern Appalachian Basin: Implications of analyses of natural gases from Neogene- through Devonian-age strata. *AAPG Bull* 98(2):341–372.

8. US Environmental Protection Agency (1984) *Operators Compliance Manual for Class II Injection Wells in Pennsylvania* (US Environ Prot Agency, Washington, DC).

9. US Department of Health and Human Services (1998) *Toxicological Profile for 2-Butoxy-ethanol and 2-Butoxyethanol Acetate* (US Dep Health Human Serv, Washington, DC).

10. Coleman DD, Liu CL, Hackley KC, Benson LJ (1993) Identification of landfill methane using carbon and hydrogen isotope analysis. *Proceedings of the Sixteenth International Madison Waste Conference* (Univ Wisconsin, Madison WI), pp 303-314.

11. Hsieh PA, Neuman SP, Stiles GK, Simpson ES (1985) Field determination of the three-dimensional hydraulic conductivty tensor of anisotropic media: 2. Methodology and application to fractured rocks. *Water Resour Res* 21(11):1667–1676.

12. Maslia ML, Randolph RB (1987) Methods and computer program documentation for determining anisotropic transmissivity tensor compoents of two-dimensional ground-water flow. *US Geol Surv Water Supply Pap* 2308:1–46.
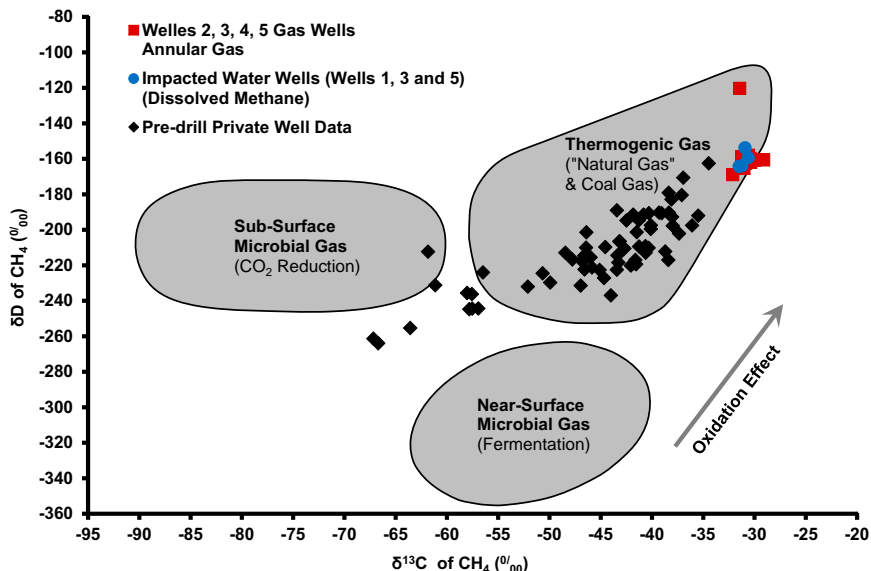
Fig. S1. Crossplot of δD of CH$_4$ vs. δ^{13}C of CH$_4$ (per mil) illustrating isotopic similarity between natural gas sampled from the annuli of gas wells (Welles 2, 3, 4, and 5 series) and impacted water wells (Wells 1, 3, and 5). Isotopic data were not available for other impacted water wells. Predrill 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).
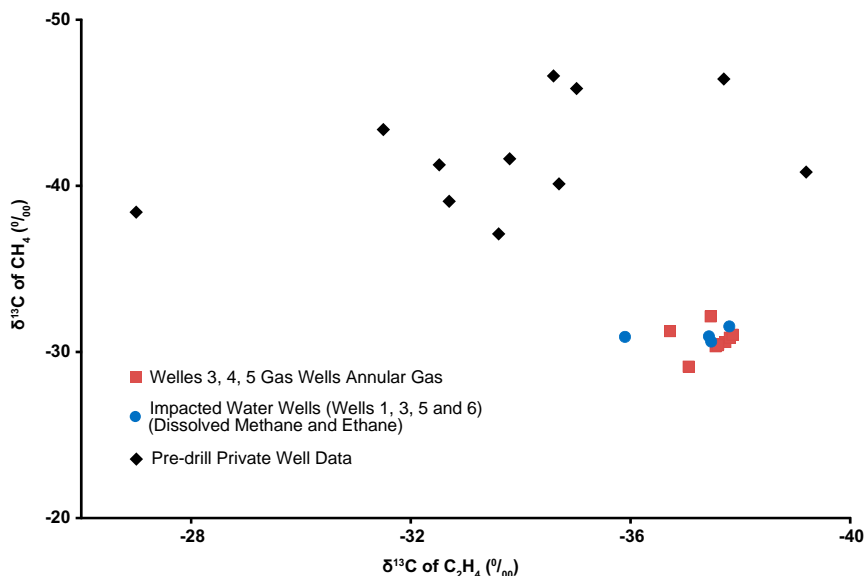
Fig. S2. Crossplot of δ^{13}C of CH$_4$ vs. δ^{13}C of C$_2$H$_6$ (per mil) illustrating isotopic similarity between natural gas sampled from annuli of gas wells (Welles 3, 4, and 5 series) and impacted water wells (Wells 1, 3, 5, and 6). Isotopic data were not available for other impacted water wells. Predrill private well data collected throughout Bradford, Sullivan, Susquehanna, and Tioga counties in NE Pennsylvania (7).

Fig. S3. (*A*) Groundwater elevation contours (meters above mean sea level) under ambient conditions illustrate groundwater convergence toward the valley center (Sugar Run tributary). (*B*) Drawdown (meters) induced by constant rate (25.8 L/min) 7-h aquifer test of Well 4. Using analysis methods outlined previously (11, 12), the maximum (T_{ss}) and minimum (T_{nn}) transmissivity components were estimated at 5.9 m^2/d and 2.6 m^2/d, respectively. The storage coefficient was estimated at 1.6×10^{-5}.

Fig. S4. GCxGC-TOFMS chromatogram illustrating UCM from Well 3 (PLG-12-60A), one of the original impacted household water wells. Compound classes are illustrated. Color variations indicate relative compound concentrations, with blue being the lowest and red being the highest.

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.
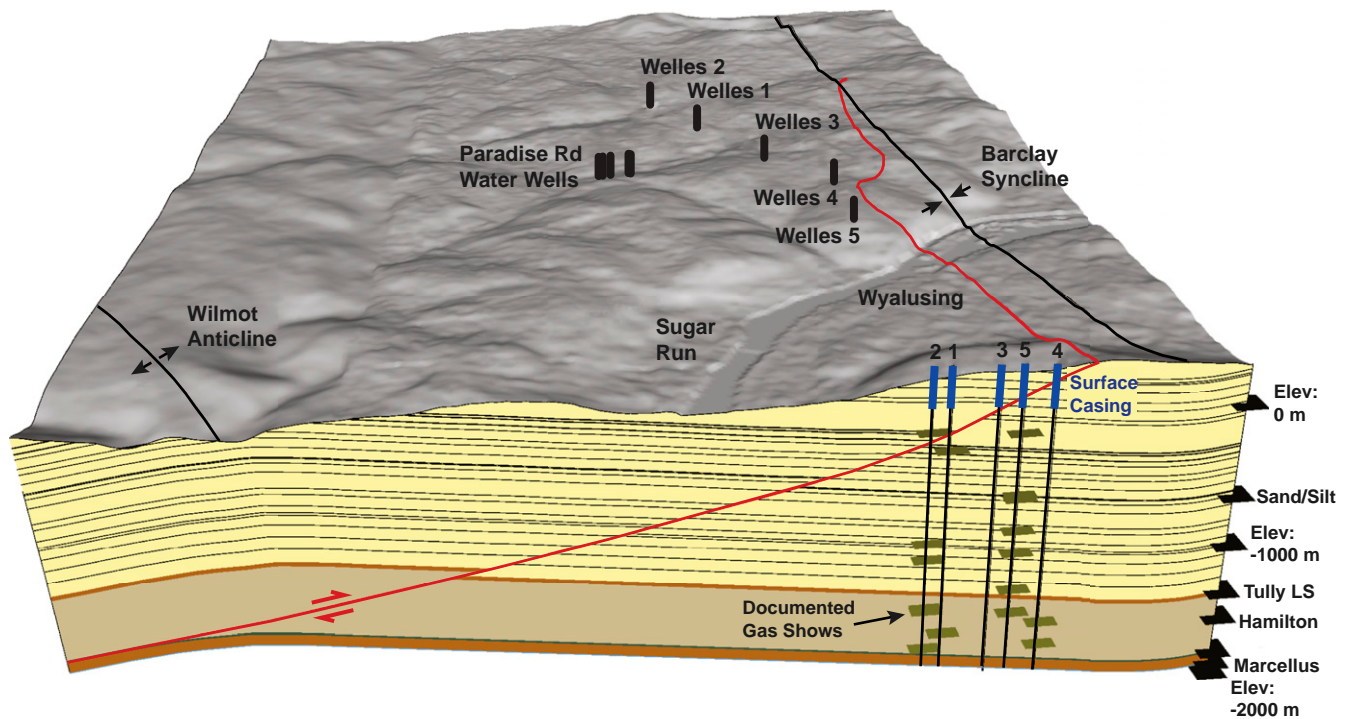
Fig. S9. Block diagram illustrating a shallow angle thrust fault (red line), Barclay and Wilmot structural fold surficial traces (surficial black lines), and bedding planes (subsurface black lines). Stratigraphic units and markers are illustrated on the right side. Viewpoint is toward the west. A light 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 (Welles 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.

Fig. S10. Schematic illustrating construction of Welles 1–5 series gas wells. Depth intervals of gas shows are illustrated in yellow, as documented in gas well logs. Intervals illustrated in red indicate remedial activities, including cement squeezes and plugs with known quantities of cement used. Originally emplaced cement is illustrated in dark gray, and "partially bonded" cement is illustrated in light gray. Highest recorded gas well annular pressures (pounds per square inch) are provided with record date.

Fig. S11. LIDAR hillshade digital elevation map illustrating land surface with bedrock elevation contours in meters above mean sea level (brown lines). Dashed lines indicate uncertainty. Welles 1 and 3 series gas wells are illustrated as red asterisks. Control points and corresponding bedrock elevations are illustrated for Wells 1 and 2 (red), Wells 3 and 4 (green), Wells 5 and 6 (blue), and additional domestic well records obtained from the Pennsylvania Topographic and Geologic Survey's PaGWIS database (black circles). Squares and triangles represent replacement and original household wells, respectively. Like colors represent each household.

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
05/2/21010	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 5-5Htreated 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 S1. Cont.

Date, m/d/y	Event
08/31/2010	Replacement water well started for a homeowner
09/01/2010	Another replacement water well started for a homeowner
09/02/2010	Second replacement water well finished for a homeowner
09/03/2010	Squeeze job at two shallow depths of Welles 3-5H with Na silicate and cement
09/03/1010	Ran temperature and audio log and performed squeeze job at an intermediate depth with cement (Welles 3-2H)
09/03/2010	Bubbles reported in Susquehanna River near Sugar Run, PA
09/04/2010	Ran temperature and audio log and did a cement squeeze job at intermediate depth at Welles 4-2H
09/04/2010	Ran temperature and audio log and did a cement squeeze job at intermediate depth at Welles 5-2H
09/07/2010	Replacement water well started for a homeowner
09/08/2010	Ran temperature and audio log and completed cement squeeze job at intermediate depth in Welles 5-5H
09/08/2010	Replacement water wells for two homeowners were completed
09/10/2010	Replacement water well completed for a homeowner
09/10/2010	Gas sensor and data logger installed in a residence
05/11/2011	PADEP cited gas company for violation of PA Oil and Gas Act and Clean Streams Law for allowing natural gas to enter aquifers; company had to identify, evaluate, and rehabilitate gas wells
09/29/2011	Welles 1-3H cited by PADEP for "failure to control residual waste to prevent water pollution"
11/29/2012	Welles 2-2H cited by PADEP for spill of high conductivity water on well pad
Fall 2012	Pumping test completed (Fig. S3)
11/11/2012 to 09/15/2013	Wells on Welles 2−5 well pads were hydraulically stimulated
10/18/2013	Spill on Welles 4–2H
11/04/2013	On PA DEP website under Welles 2-2H, Consent Agreements of Civil Penalty noted, $35,862 fine
10/18/2013	Spill on Welles 4-2H noted
10/25/2013	Spill associated with flowback fluids (10−15 gallons) noted on PA DEP website for Welles 5-6H

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 S3. GCxGC-TOFMS instrument parameters

	Parameter
GC instrument	
Carrier gas	helium
mode	split 10:1
Flow	1.00 mL/min
Septum purge flow	3.00 mL/min
Injection volume	1 μL
Injector temperature	250 °C
Transfer line temperature	300 °C
Oven equilibration time	0.5 min
First dimension oven*	
Initial temperature	40 °C
Hold time	0.20 min
Rate	1.60 °C/min
Final temperature	315 °C
Modulator	
Temperature offset	15 °C
Modulator period	5.00 s
Hot pulse time	0.6 s
Cool time	1.9 s
Second dimension oven[†]	
Initial temperature	55 °C
Hold time	0.20 min
Rate	1.60 °C/min
Final temperature	330 °C
Mass spectrometer	
Acquisition delay	320 s
Mass range	45–550 u
Acquisition rate	200 spectra/s
Detector voltage	2,000 V
Ionization energy	70 eV
Mass defect	0 mu/100 u
Ion source temperature	200 °C

*Rtx-Dioxin2, 60 m × 0.25 mm ID × 0.25 μm df.
[†]Rxi-17SilMS, 1.9 m × 0.15 mm ID × 0.15 μm df.

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. 1*B*	original well	41.642	−76.295	PLG-12–60 A	11/7/2012	sampled before purging
Well 6 (PLG 12-65)	Fig. 1*B*	replacement well	41.641	−76.294	PLG-12–64 A	11/7/2012	after purging ∼5 min
Well 1 (PLG 12-69)	Fig. 1*B*	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 *Methods*
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_2H_6, mg/L	STD%	$\delta^{13}CH_4$	$\delta^{13}C_2H_6$
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
p-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 lydrotreated Light	0.00025
Quaternary ammonium chloride (ammonium chloride)	0.00011
Alcohol ethoxylated C12−C16	0.00004
Ethoxylated alcohols	0.00004
Alchohol 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
Sobitan monooleate	Not available
Sorbitol tetraoleate	Not available

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