Frequently asked questions about the study "Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development" by Llewellyn GT, Dorman F, Westland JL, Yoxtheimer D, Grieve P, Sowers T, Humston-Fulmer E, Brantley SL, 2015 (PNAS, doi: 10.1073/pnas.1420279112). The information presented below was developed by several of the study's co-authors including Garth Llewellyn (Appalachia Hydrogeologic and Environmental Consulting, LLC), Frank Dorman (Penn State), Dave Yoxtheimer (Penn State), and Susan Brantley (Penn State) to provide context for the information presented in the original study.

1. **Some newspapers reported that no conflict of interest (COI) was noted on the version of the paper that was released by the journal when it was under embargo. In contrast, the published version notes a conflict of interest, i.e. that Llewellyn was paid as a consultant by the homeowners prior to the new research reported in the paper. Why was the COI not on the original version?**

The original draft of the paper – "the galleys" –noted there was no COI by any of the authors. This was initially the result of not realizing there was a COI declaration option (i.e. a box to check) during the original submission process. If the COI box is not checked off then the default states there is no COI. The authors sent corrections to PNAS <u>before</u> release of the embargoed paper including a COI declaration when it was realized there was a COI declaration option. It was felt that Mr. Llewellyn's previous consulting work for the homeowners could be construed as a COI and hence was declared as such. Nonetheless, the paper released under embargo to the media by PNAS did not contain the corrected description of the COI. The official published version of the paper notes correctly that Garth Llewellyn worked for the homeowners as a consultant. There was no intentional "misleading" by the authors or by PNAS. It should be noted that Mr. Llewellyn was no longer working for the homeowners at the time of sampling in Summer and Fall 2012, and that none of the other seven co-authors had any COI with the study. PNAS released a statement acknowledging the inconsistency to the media that had received the pre-released version of the paper on May 11, 2015.

The PNAS statement reads, "*We apologize for the confusion regarding the conflict of interest statement for the PNAS article "Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development," published online May 4, 2015. When the paper was first received by PNAS, it had no conflict of interest statement. When the authors returned their proofs, they added a conflict of interest statement for the first author. The embargoed version of papers that we prepare for EurekAlert do not include author corrections to proofs. We regret that our process did not relay this conflict of interest information to the media. We are closely examining our process to ensure that such updates are relayed to the media in a timely fashion in the future. The published article with the updated conflict of interest statement is attached.*"

2. **Does this study implicate high-volume hydraulic fracturing (HVHF) at depth for the observed natural gas, foam, UCM and 2-BE observed in the homeowner wells?**

No. On the contrary, we explicitly state in the paper that there is no evidence that HVHF of the Marcellus Shale at depths of approximately 6000-7000 feet was the cause of impacts. In fact, we provide strong evidence that this did not happen. When HVHF fluids are injected into the target formation (e.g. Marcellus Shale), they mix with natural formation fluids that contain high levels of dissolved solids (e.g. salt, metals, etc.). Of these, chloride and bromide tend to persist in water and their ratio is an excellent tracer of the chloride source. Examination of the impacted household water well chemistry did not have ratios of chloride:bromide that would indicate impacts from fluids that had migrated from the Marcellus Shale.

3. Why did you write this paper? How is this work different from articles already in the public domain discussing these types of issues?

We analyzed this incident largely because foam was consistently observed emanating from household Wells 1 – 6, but commercial laboratory chemical analyses of groundwater samples from the household wells did not detect any typical compounds that would explain the foam. Foam that was observed in the water indicated the presence of compound(s) that warranted further investigation. The authors evaluated existing case data, in addition to conducting further groundwater studies.

We demonstrate the application of a very sophisticated analytical tool, "two-dimensional gas chromatography with a time-of-flight mass spectrometer" (GCxGC-TOFMS) that provides significant improvements in evaluating alleged cases of oil and gas drilling impacts. This tool allows investigators to detect organic compounds in water at much lower detection limits (parts per trillion) and also to identify them more easily than conventional methods currently used. The development and use of GCxGC-TOFMS should be considered by others who want <u>to either confirm or refute</u> alleged oil and gas industry impacts to water resources.

We also wanted to illustrate the concept of a "multiple lines of evidence approach" for investigating alleged contamination from oil and gas drilling activities. In this case, the PA Department of Environmental Protection (PADEP) determined that adjacent Marcellus shale gas wells (Welles series) had impacted water resources, including the private wells with natural gas. However, no explanation or cause was assigned to the foam identified in the water wells. As a result, we used GCxGC-TOFMS to further investigate potential causes for the water foaming. Multiple lines of evidence, such as hydrogeologic characterization, the timeline of the gas well construction and remedial activities, GCxGC-TOFMS analytical results, natural gas isotopic measurements, and methane migration data were used to draw reasonable conclusions.

Lastly, we felt that public disclosure of such incidents will help scientists <u>and</u> non-scientists understand potential impacts, enabling more informed decision-making by stakeholders.

4. Aside from isolated cases, there have not been many reported problems with shale gas wells causing significant water quality problems: why highlight issues that do not appear to be widespread in areas undergoing unconventional shale gas development?

Several of the coauthors on the Llewellyn et al. (2015) paper previously published a peer-reviewed article emphasizing the rarity of significant, large water quality-related problems associated with shale gas development as documented in publicly available data (Brantley et al., 2014). However, even these relatively uncommon problems should be investigated thoroughly and discussed openly to make them even less common. An analogy can be drawn to the airline industry: crashes are extremely rare -- but when they happen, their cause(s) are evaluated to the fullest extent. Given ongoing unconventional oil and gas development, the public controversy surrounding it, and questions about its environmental impacts, the authors argue that information and data describing such events should be communicated to the public and openly discussed. The "social license" of unconventional gas development ultimately depends on the public's awareness and understanding.

5. Aside from natural gas impacts, your paper discusses the presence of a targeted compound, 2-BE and a "UCM" from samples collected from the household water wells. Why did you specifically look for 2-BE and what is a "UCM"?

The compound 2-butoxyethanol (2-BE) is known to be commonly used in drilling and HVHF fluids. It is an ingredient in at least one common drilling additive (Airfoam HD) as confirmed by the GCxGC-TOFMS analysis described in the paper. Further, there are confirmed cases as reported by the PADEP of Airfoam HD/2-BE impacts to water resources as a result of Marcellus gas drilling operations. Airfoam HD was cited by the PADEP as the cause of foam discharging from a spring above the Pine Creek canyon wall in Lycoming Co., PA in 2010. More recently in 2014, drilling fluid additives were also cited by the PADEP for the presence of foam, 2-BE, glycols and volatile organic compounds (VOCs) identified in a private water well in Springville Twp., Susquehanna Co., PA. As such, we felt it prudent to evaluate for the presence of 2-BE, given the readily apparent foam emitting from the water wells present at the three households described in the paper.

Besides the presence of 2-BE in one of the impacted water wells we sampled, a "UCM" or unresolved complex mixture of hydrocarbons was identified in all samples we collected from the impacted households. The UCM is a mixture of ~1000 different hydrocarbons that comprise a "signature" observed in the GCxGC-TOFMS chromatograms. The hydrocarbon classes range from aliphatic (e.g. they contain no aromatic rings), aromatic (e.g. they contain 6-carbon aromatic rings), saturated (e.g. no double bonds between carbon atoms), unsaturated (e.g. double bonds between carbon atoms) and oxygen-substituted hydrocarbons (e.g. they contain –COH, CO and -COOH groups). We refer to the UCM as being unresolved since we have not identified each of the individual compounds that comprise the complete UCM signature – we just know that the compounds are present.

We also observed a similar "UCM" signature in various samples of flowback/production fluid samples taken from gas wells throughout the Marcellus Shale region. We did not observe any 2-BE or "UCM" in background groundwater samples we collected from private water wells in the region that were not impacted by gas drilling activities.

6. Are there other potential sources of 2-BE?

Yes, 2-BE is used in various products that could be a potential source of the compound. Other uses are described in our article's Supporting Information. However, given the observed foam from the impacted water wells, the co-occurrence of 2-BE, thermogenic methane, and UCM as well as the other lines of evidence presented in our paper and amplified below, we argue that it is highly unlikely that it is derived from a source other than shale gas development.

7. **A recent peer-reviewed article by Smith et al. (2014) documents the leaching of 2-BE from Portland cement used in well construction. Isn't that a better explanation for the presence of low concentrations (ng/L) of 2-BE in the well? Why didn't you cite this paper?**

This paper was published in Fall 2014 at approximately the same time we submitted our paper for peer-reviewed publication and we were unfortunately unaware of it; otherwise, we would have cited it in our article.

Some have made the point that the water well where we identified 2-BE was a replacement well provided to the homeowners by the gas company. This well was emplaced in an effort to provide the household with potable water immediately following the initial impacts. The well was installed by a local water well driller hired by the gas company. The driller grouted the casing in place with cement using good practice. Given the findings of Smith et al. (2014), we acknowledge that it is possible – but highly unlikely -- that the foam in this replacement well and the 2-BE may have originated from this source. For example, in contrast to the small amount of cement used in the replacement well, approximately 42,500 gallons of cement was used to remediate the gas wells at the nearby Welles 3, 4 and 5 pads to alleviate methane migration and casing pressure/well integrity issues. Further, even if the 2-BE came from the grouting, such a scenario does not explain the presence of the UCM (~1000 hydrocarbon compounds) nor the foam that was observed in both the replacement wells and in the original water wells that had not been cemented. Furthermore, state regulations for public water supply wells actually require cement grout -- and of course most water wells do not foam as a result.

8. **What did the foam look like and when was it observed?**

All the authors observed the abundant, white, frothy foam that had a consistency somewhere between foam that one sees when doing the laundry and the foam used as shaving cream. We have included a number of photographs (see Figures 1, 2 & 3) as an addition to the photograph we published in the original paper. The homeowners indicated that foam was not present in their original wells prior to the initial sediment and natural gas impacts observed in July 2010. After the initiation of impacts on the wells, the three households utilized water buffalos that they had been given as a source of potable water; therefore, they cannot recount exactly when the foaming began in their wells. Once the families were given water buffalos, the wells were only used by environmental consultants for the purpose of sampling and we do not have documentation pertaining to all of the observations by the gas company's consultants. However, first author Garth Llewellyn served as an environmental consultant through his firm for one of the households (owners of Wells 1 and 2) beginning in Spring 2011. During that period Well 2 was not operational and therefore sampling was only conducted for Well 1. Foam was observed in Well 1 during every sampling event on a quarterly basis through Spring 2012. In Spring 2012, Garth Llewellyn and his firm were retained by all three households for consulting services and observed foam in household Wells 1 through 6, when sampling was conducted by his firm at the same time that samples were taken by the gas company's environmental consultants. Sampling by the authors commenced in Summer/Fall 2012 at which point we observed foam from all the wells we sampled (i.e. Wells 1, 3 and 6). At that point, first author Garth Llewellyn was no longer contracted by the families as a consultant and was helping to conduct the research at his own expense.

Figure 1. Photograph of foamy water emanating from Well 1 in Summer 2012, while authors of Llewellyn et al., 2015 prepared the well for sampling.

Figure 2. Photo-documentation of foam emanating from Well 2, while the gas company's environmental consultants prepared the well for sampling.

Figure 3. Photo-documentation of foam emanating from Well 3, while the gas company's environmental consultants prepared the well for sampling.

9. Isn't it very reasonable that the foam may have originated from equipment used to pump/sample the household water wells?

No. From Spring 2011 through Spring 2012, Garth Llewellyn and his firm, Appalachia Hydrogeologic and Environmental Consulting used dedicated equipment installed by the gas company to pump and sample Well 1. The only additional equipment used was a standard rubber garden hose that was connected to a sampling spigot in order to pump the well prior to sampling and direct water away from the sampling point. Notably, he and his firm have sampled in excess of 1000 households throughout Susquehanna, Bradford and Wyoming counties in PA using this hose or similar hoses for pre-sample purging without foaming (including wells that did have natural gas impacts). Further, concurrent sampling (split-sampling) was conducted by his firm and a consulting firm contracted by the gas company in late Spring 2012 (Figures 2, 3). During this time, the gas company's consultant used their own equipment for pumping and sampling the wells and the presence of foam was always observed in all sampled wells (Wells 1 – 6). Finally, the authors observed similar impacts in Fall 2012, when sampling Wells 1, 3 and 6. Given the numerous parties collecting samples at various times with different equipment, it is not reasonable to conclude that equipment was the cause for foam. Notably, the hoses are used for purging (pumping) the well prior to sampling but are not used in the sample collection process itself.

10. If the purging/sampling equipment didn't cause the foam, isn't the most probable source onsite, given that the impacted households are rural and use onsite septic systems? Couldn't septic systems also reasonably explain the presence of the UCM and 2-BE?

No, septic systems are not a probable source for a number of reasons. The possibility of septic system-derived contaminants was one of the first scenarios the authors examined to explain the foam, UCM and 2-BE in the impacted household wells.

- First of all, two of the authors are professional geologists (PGs) and have extensive practical consulting experience throughout PA. Some private wells in northeast PA do have impacts from onsite septic systems, but none have been observed to "foam", even with naturally occurring methane that would serve to "agitate" the water.
- The three background wells (outside the area affected by gas drilling impacts) we analyzed exhibited no evidence of foam, the UCM or 2-BE, despite all having onsite septic systems.
- Septic system impacts to groundwater are characterized by elevated nitrate (>2-3 mg/L; Panno et al., 2006). Tables 1 – 6 provide water quality data for Wells 1 – 6, respectively, pertaining to chloride, bromide and nitrate concentrations. Notably, Wells 1, 2, 3, 4 and 5 had non-detectable to low nitrate concentrations (maximum of 1.4 mg/L for Well 5). Well 6 had concentrations of non-detectable to 4.9 mg/L in May and November 2012, respectively. The single elevated nitrate concentration of 4.9 mg/L in November 2012 (Well 6) is inconsistent with septic waste impacts as a plausible explanation because: (1) ubiquitous foam was observed from Wells 1 – 6, (2) the UCM was identified in all sampled wells (e.g. Wells 1, 3 and 6) and (3) 2-BE was identified in Well 1.
- Figure 3 in Llewellyn et al. (2015) illustrates samples for which Cl:Br ratios are available. The cross-plot can be used to assist in evaluating the source of chloride present in groundwater. The collective data indicates halite as the probable source (e.g. road salt), which is applied throughout the study area for winter road deicing.

Table 1: Well 1 (replacement well)

Date	Sampled by:	Chloride (mg/L)	Bromide (mg/L)	Nitrate (mg/L)
9/14/2010	OG	28.8	--	--
3/1/2011	OG	18.6	--	--
4/7/2011	OG	11.2	--	--
5/23/2011	OG	13.5	--	--
5/26/2011	App	11.4	<0.0025	0.30
10/31/2011	OG	13.5	--	--
11/29/2011	App	12.8	0.028	0.08
3/26/2012	App	11.8	0.012	0.29
3/28/2012	OG	10.3	--	--
5/9/2012	OG	14.5	ND	ND
7/12/2012	PSU (post-purge)	13	<0.1	<0.4

Notes: OG = oil & gas company's environmental consultant; App = Appalachia Hydrogeologic and Environmental Consulting, LLC; PSU = Penn State; Dashed line = analysis unavailable; ND = Not Detected.

Table 2: Well 2 (original well)

Date	Sampled by:	Chloride (mg/L)	Bromide (mg/L)	Nitrate (mg/L)
4/8/2010	PL (baseline)	20.7	--	--
7/15/2010	PADEP or OG	51.0	--	--
7/21/2010	PADEP or OG	54.9	--	--
8/3/2010	OG	44.3	--	--
9/15/2010	OG	57.3	--	--
10/31/2010	OG	26.2	--	--
5/8/2012	OG	39.0	ND	ND
5/15/2012	App	36.6	0.022	--

Notes: PL = PA certified private laboratory that provided baseline; PADEP = Pennsylvania Department of Environmental Protection; OG = oil & gas company's environmental consultant; App = Appalachia Hydrogeologic and Environmental Consulting, LLC; Dashed line = analysis unavailable; ND = Not Detected.

Table 3: Well 3 (original well)

Date	Sampled by:	Chloride (mg/L)	Bromide (mg/L)	Nitrate (mg/L)
7/15/2010	PADEP or OG	8.8	--	--
7/21/2010	PADEP or OG	12.7	--	--
8/2/2010	OG	7.5	--	--
8/4/2010	OG	5.2	--	--
5/9/2012	OG	12.4	ND	ND
11/7/2012	PSU	6.6	<0.1	<0.7

Notes: PADEP = Pennsylvania Department of Environmental Protection; OG = oil & gas company's environmental consultant; PSU = Penn State; Dashed line = analysis unavailable; ND = Not Detected.

Table 4: Well 4 (replacement well)

Date	Sampled by:	Chloride (mg/L)	Bromide (mg/L)	Nitrate (mg/L)
9/13/2010	OG	13.6	--	--
2/17/2011	OG	13.3	--	--
4/7/2011	OG	13.1	--	--
5/23/2011	OG	13.5	--	--
5/9/2012	OG	14.6	ND	ND

Notes: OG = oil & gas company's environmental consultant; Dashed line = analysis unavailable; ND = Not Detected.

Table 5: Well 5 (original well)

Date	Sampled by:	Chloride (mg/L)	Bromide (mg/L)	Nitrate (mg/L)
7/21/2010	PADEP or OG	29.5	--	--
8/3/2010	OG	29.6	--	--
9/15/2010	OG	33.3	--	--
5/7/2012	OG	28.0	ND	1.4
5/14/2012	App	27.4	0.018	--

Notes: PADEP = Pennsylvania Department of Environmental Protection; OG = oil & gas company's environmental consultant; App = Appalachia Hydrogeologic and Environmental Consulting, LLC; Dashed line = analysis unavailable; ND = Not Detected.

Table 6: Well 6 (replacement well)

Date	Sampled by:	Chloride (mg/L)	Bromide (mg/L)	Nitrate (mg/L)
9/13/2010	OG	26.5	--	--
2/17/2011	OG	27.7	--	--
4/7/2011	OG	18.2	--	--
5/23/2011	OG	26.5	--	--
5/9/2012	OG	24.1	ND	ND
11/7/2012	PSU	19	<0.1	4.9

Notes: OG = oil & gas company's environmental consultant; PSU = Penn State; Dashed line = analysis unavailable; ND = Not Detected.

11. In your paper, you document very low concentrations (e.g. ng/L or parts-per-trillion) of organic compounds (e.g. UCM & 2-BE). How could such low concentrations of organic compounds cause foaming and are they a health risk?

We cannot comment on the toxicity of the identified UCM and 2-BE as none of the authors are toxicologists. Furthermore, before health risks can be assessed, one must identify the actual compounds and corresponding concentrations using a broad exploratory approach.

In addition to 2-BE being identified at ng/L concentrations in Well 1, the UCM (comprised of ~1000 individual hydrocarbon compounds) was identified at all wells we sampled (e.g. Wells 1, 3 & 6). Each of the individual compounds that comprise the UCM are also at ng/L concentrations, indicating that the total hydrocarbon concentration is likely at least on the order of µg/L (parts-per-billion). Based upon the research of Frank Dorman (coauthor), many natural and synthetic organic compounds can cause foaming at these levels. This is especially the case in the presence of natural gas, because gas facilitates foaming as it bubbles out of the water.

12. Is it possible or even likely that the natural gas and the organic compounds (e.g. UCM, 2-BE) came from separate sources?

Yes, it is indeed likely that these impacts are derived from different sources. We state this explicitly in the paper. There is overwhelming evidence that natural gas migrated from Welles 3-2H or multiple gas wells present on the Welles 3, 4 and 5 pads: for example, these wells were reported to have excessive annular pressures due to poor construction and subsequent remedial activities (e.g. "cement squeezes") were successful in reducing sustained annular gas pressures that had contributed to the gas migration to the impacted water wells. Additionally, we summarized three reasonable scenarios for the UCM and the 2-BE (but also see FAQ 6 above pertaining to 2-BE). First, the gas company was cited for a pit leak on the Welles 1 pad, and this could therefore implicate a surface-related release. Second, drilling fluids could have leaked out of one of the gas well boreholes at shallow to intermediate depths. The final scenario is leakage at shallow to intermediate depths of HVHF fluids prior to or during injection at the Welles 1 gas wells – well above the depth of hydraulic fracturing in the shale. We explain the scenarios in our paper.

13. For this study, you indicate that you sampled Wells 1, 3 and 6 for GCxGC-TOFMS analysis. Why did you sample these wells and not the others (i.e. Wells 2, 4 and 5)?

This project was largely unfunded. The National Science Foundation indirectly supported one graduate student (co-author Paul Grieve), whose overall job was to populate a database of water quality (www.shalenetwork.org). Leco Corporation supported the GCxGC-HR-TOFMS analysis. The rest of the work was supported by Penn State seed funds (used to establish new research) and by Appalachia Hydrogeologic and Environmental Consulting, LLC (Garth Llewellyn's time, transportation and equipment).

Given the limited funding, we decided to sample Wells 1 and 6 since they are located on the northern and southern-most ends of the households and have pre-existing and operational infrastructure. We also wanted to sample an original well and decided to select Well 3 since it is centrally located. (see Llewellyn et al., 2015, Figure 1B). In addition to the impacted household wells, we selected three water wells that were outside of the impacted area, but were within a reasonable distance (~5 km) to evaluate natural background water quality using GCxGC-TOFMS. If we had more funding, we would have sampled all the affected wells (e.g. Wells 1 – 6) and also more private household wells to evaluate background water quality to a further extent.

14. Has the gas company improved its well construction practices since this incident?

Representatives of the gas company communicated to us that since 2010, significant improvements have been made to gas well construction practices, including the use of a 3-string casing design that generally extends down to a depth of approximately 2400 feet and is fully cemented in place. In contrast, at the time of the incident, the implicated gas wells only had protective surface casing down to a depth of approximately 1000 feet. This casing design met regulations at the time of emplacement, but the regulations were strengthened in 2011 to include intermediate casing whenever natural gas occurs at a pressure that could cause migration in the upper several thousand feet of the borehole.

15. Why did you write a sensationalized paper?

It is not sensationalized given that the paper provides a substantial amount of factual information related to the case. We have also taken care to indicate uncertainty where it is warranted. We state unequivocally that we cannot unambiguously identify the exact source of the UCM and 2-BE. However, we know with certainty that: (1) natural gas impacts were the result of adjacent, upgradient Marcellus shale gas wells; (2) foam was observed multiple times in the original and replacement water wells; (3) 2-BE was identified in Well 1; (4) a UCM comprised of approximately 1000 different hydrocarbon compounds was identified in all the samples we collected from the impacted wells (i.e., Wells 1 ,3, 6); (5) the background water wells we sampled had no UCM nor 2-BE; and (6) the UCMs identified from the impacted homeowner water wells were similar to the approximately 30 samples we analyzed from Marcellus Shale flowback/production fluids.

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