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The relationship between methane migration and shale-gas well operations near Dimock, Pennsylvania, USA

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1.0 Additional Site Investigations

1.1 Gas Well 2 (GW-2) and Water Well E (WW-E)

GW-2 was completed and stimulated in 2008. Prior to its construction, lower explosive limit (LEL) measurements were taken in two house wells within 460 m of GW-2, with no detection of methane. Three wells were sampled in January 2009, two of which had methane levels less than 1 mg/L, and the third (WW-E) had a concentration of 17.9 mg/L. Isotopic analyses of a sample from WW-E produced results similar to those of the annular gas in nearby gas wells. Although the pressure in the annulus of GW-2 was 590 psig, there were no reported leaks from annular spaces. No record could be found that the well was vented; however, the LEL readings in WW-E decline from 50-55% on 1/20-21/2009 (i.e. 20-21 January 2009) to 23% on 1/27/2009, the same period that other gas wells in the area were vented.

Fig.S1 is a graph of methane chemistry and related operational records for WW-E. The record can be divided into several portions. During early 2009 the methane levels vary between 9 and 22.5 mg/L. After the gas well was squeezed the concentrations decline to about 10 mg/L for five months, then increase steadily to a peak of 25 mg/L on 12/14/2009, followed by a decline to 10 mg/L. The average concentrations at this point were 15.7 mg/L. After an 8-month gap, there is a substantial increase in the frequency of the sampling for about three months (9/19-12/7/2010) during which there is a rapid fluctuation in the methane concentrations. This may have been related to an additional attempt to remediate the gas well; however, no operator records were found to confirm such activity. The methane levels then decline to 0 mg/L and stay at less than 5.4 mg/L until October 2011, followed by two final data points of 16.7 and 9.2 mg/L. The average concentration during the later period is 6.0 mg/L. During 48-hour tests conducted on 9/2011, there was a minimal increase in pressure from 0 to 48 psig in the annulus of GW-2.

The methane in samples collected in 2010 and 2012 was substantially more depleted than that of the 2009 sample or gas leaking from annular spaces, suggesting that there were two sources for the methane. This water well is located in an upland area underlain by a thin layer of glacial till, where oxidizing conditions might be expected. Cultivation practices, however, may have reduced the oxidation potential of the soils at that site or the source was from a shallow, bedrock formation, both of which could produce the later, less mature, thermogenic methane signature.

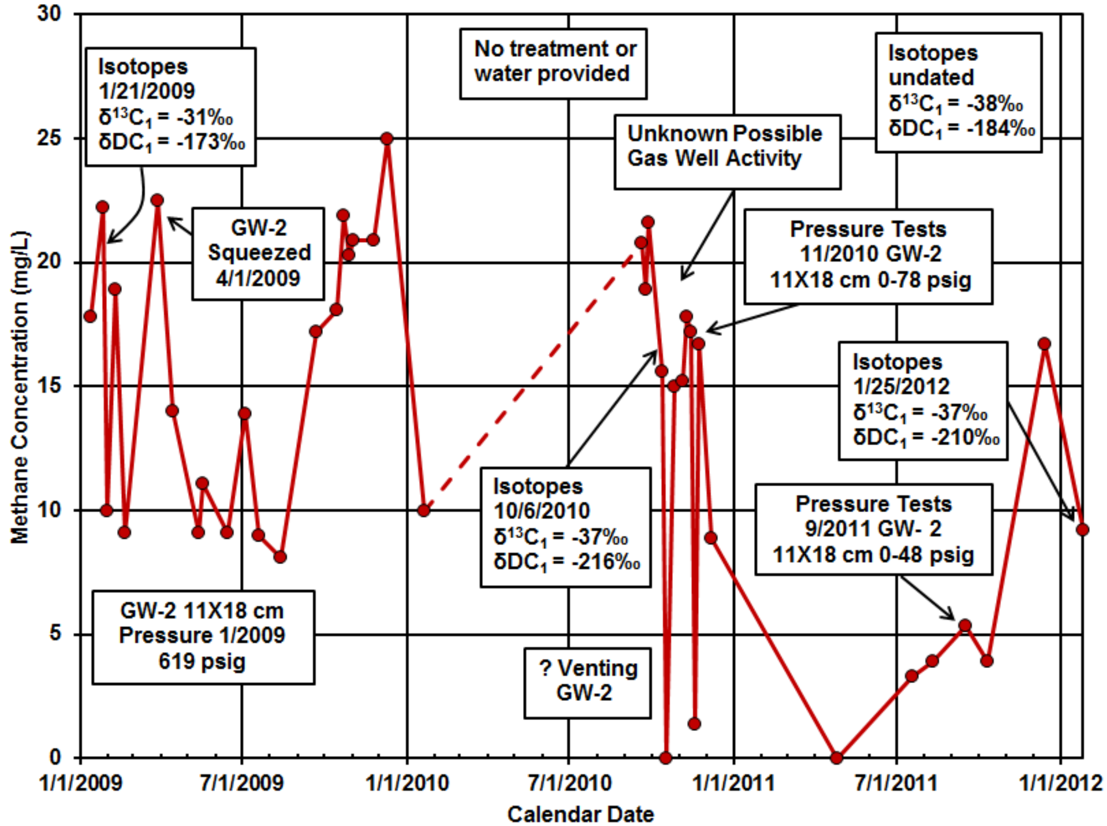

Fig. S1 Methane concentrations and stable isotope compositions of samples from WW-E, near GW-2

1.2 Gas Wells 4, 5 and 6 (GW-4, -5 and -6) and Water Wells J and K (WW-J and –K)

WW-J and -K are located within 762 m (2500 feet) of GW-4, -5 and -6. Methane and operational data are shown in Fig. S2. GW-4 was completed on 10/14/2008 and stimulated on 9/30/2008. GW-5 was completed on 10/31/2008 and stimulated on 10/13-15/2008. GW-6 well was completed on 4/14/2008 and stimulated on 10/6-8/2008. Prior to construction of the three gas wells, LEL measurements were taken in two nearby house wells, with no detection of methane. The annular pressure of GW-4 was 345 psig on 1/21/2009; but, there were no reported leaks. Venting of GW-4 started 1/22/2009. In 1/2009, the reported annular pressure in GW-5 was 707 psi; but, it was zero psi on 1/21/2009. The annular pressure in GW-6 was 1200 psig on 1/21/2009; but, there were no reported leaks or venting of that well. The methane concentrations on 1/26/2009 were 0.015 mg/L in WW-J and 0.395 mg/L in WW-K. This may have been due to venting of GW-4, but that could not be confirmed.

WW-J and -K are located 159 and 295 m from GW-4, 459 and 522 m from GW-5, and 724 and 493 m from GW-6, respectively. After GW-4 was squeezed, the methane concentrations in the two house wells increased and remained relatively high until mid- to late-2010. There was a gap of 7-8 months in the data during which GW-6 was squeezed (5/11/2010). Subsequently, the concentrations in WW-J and -K then declined to low levels during a period that included another data gap, during which GW-5 was squeezed (1/10-24/2011).

An isotopic analysis of water collected from WW-J on 11/20/2010 produced results similar to the values from the annular spaces of nearby gas wells. An isotopic analysis of water collected from WW-K on 11/9/2010, before GW-5 and after GW-6 were squeezed, produced results that were more depleted than the values from the annular spaces of nearby gas wells. After the remediation of GW-5, an US EPA sample collected from WW-J was more oxidized than any of the gas leaking from annular spaces. WW-J had a C1:C2 ratio that increased by 60 per cent relative the earlier sample, while the ratio for WW-K remained unchanged. The isotopic signatures and C1:C2 ratios indicate that the migrated methane in WW-J was due to GW-5 activity and in WW-K was due to GW-6/6a activity. This corresponds to the relative proximity of the water wells to each gas well. The water wells are located in a lowland area underlain by a fairly thick layer of glacial till where depleted methane might be expected. However, if wetlands existed in the area, then more oxidized conditions might exist, which could account for the enriched isotope compositions for the late-time sample from WW-J.

The isotope results for a sample taken on 1/8/2009 from a pond near water well K were $\delta^{13}C_1$ equal to -28.07‰ and δDC_1 equal to -156.6‰. While these values are similar to those of the production gases, isotope results for the pond on 2/15/2010 produced $\delta^{13}C_1$ equal to -36.03‰ and δDC_1 equal to -196.2‰ and were more reduced than the earlier sample, indicating that the methane compositions may have been controlled by variations of microbial activity within the pond.

The minimal, pre-drill LEL readings and low methane concentrations in the two house wells after possible venting indicate there may have been some initial methane migration that was corrected by squeezing of either or both GW-4 and -6. The following relatively high levels of methane concentrations and matching isotope results between water well J and leaking gas well annular spaces indicate that later migration may have occurred. The later squeezes of GW-5 and -6 correspond to declines in the methane concentrations of WW-J and -K.

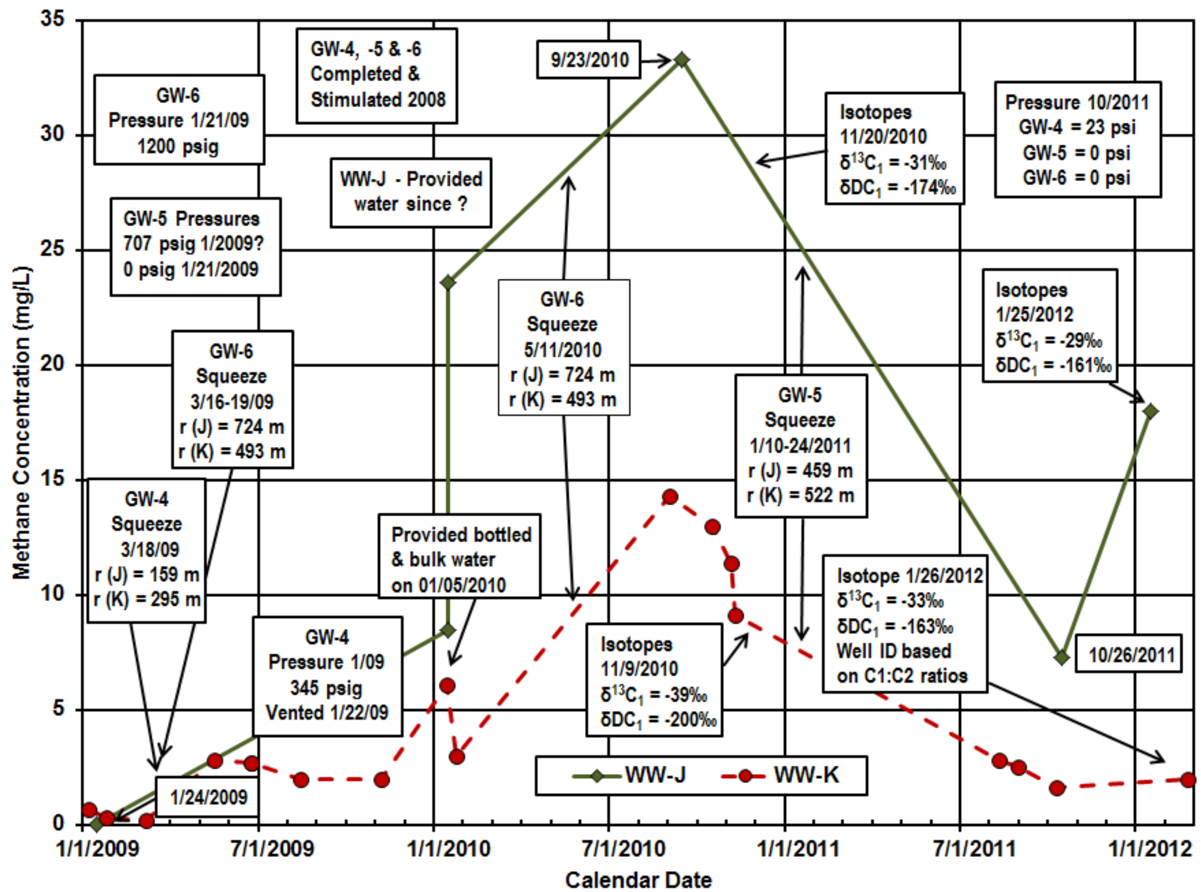

Fig. S2 Methane concentrations and stable isotope compositions of samples from WW-J and –K, near GW-4, -5 and-6

1.3 Gas Wells 6/6a (GW-6/-6a) and Water Well L (WW-L)

The methane and operational data for WW-L are given in Fig. S3. That well is located 427 m from GW-6 and -6a. The completion and simulation dates for GW-6 are given above. GW-6a was completed on 8/11/2008 and stimulated in six stages from 10/1/2008 to 11/4/2008. The annular pressure in GW-6 was 1200 psig on 1/21/2009; but, there were no reported leaks or venting of the well. After 2/28/2009, the concentrations in WW-L drop to near zero, during a period when GW-6 was squeezed, then increase sharply to about 4 mg/L, possibly due to recovery after gas well venting following the squeeze job. The concentrations remain low for the remainder of the record. GW-6a was squeezed on 8/27/08 and 3/6-9/2011. There were no methane data collected during the time of the first squeeze job and no change in the low levels after the last squeeze.

Isotopic analyses of the samples from WW-L produced results similar to those from samples taken from the annular space of GW-6. These results combined with the reduction in methane concentrations and the response to apparent venting after the squeeze job on GW-6 indicate that there was methane migration due to leakage from GW-6. Potential conflicting evidence is that no pressure was built up during post remedial testing of GW-6. One explanation for this contradiction is that squeezing of the annular space formed a cement seal above a channel that continued to provide a pathway for methane to migrate to the aquifer supplying the house well.

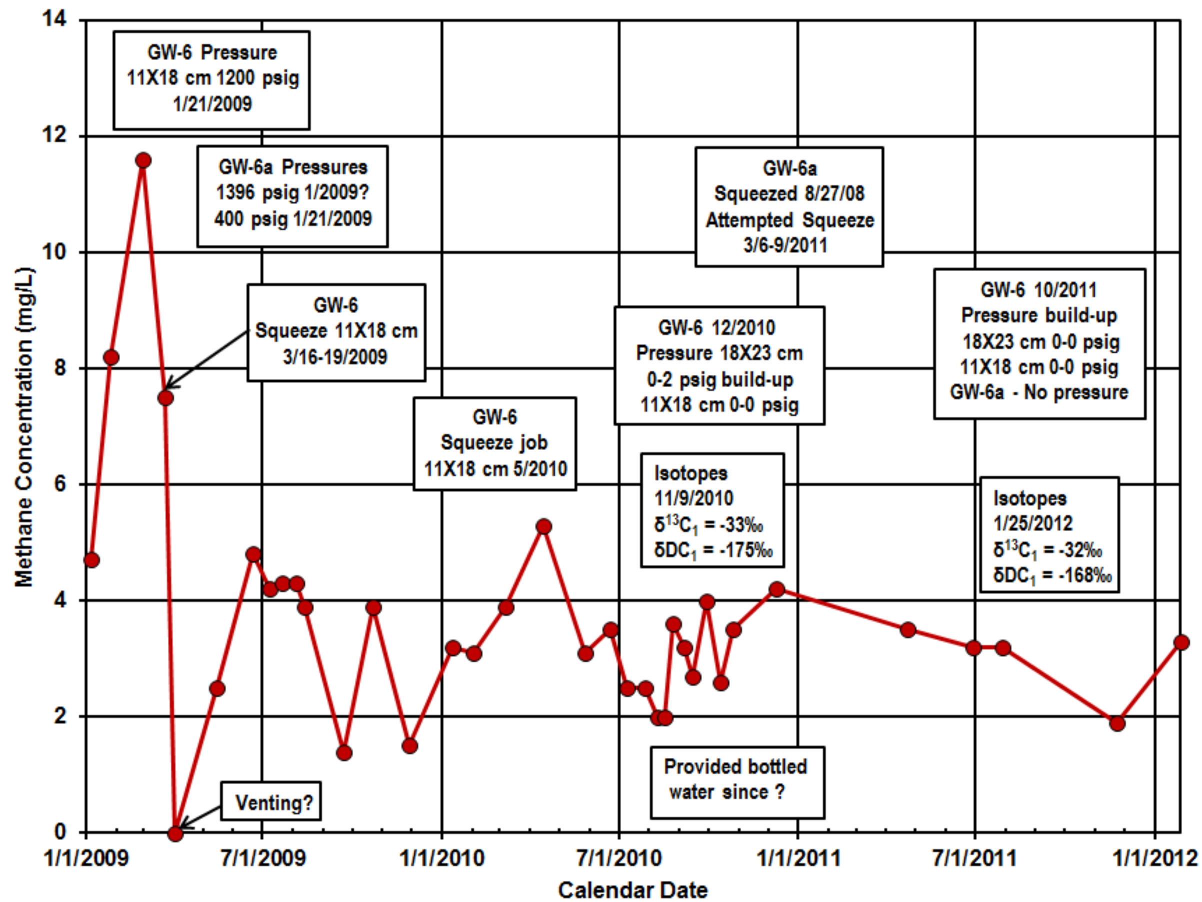

Fig. S3 Methane concentrations and stable isotope compositions of samples from WW-L, near GW-6 and -6a

1.4 Gas Well 7 (GW-7) and Water Wells M and N (WW-M and –N)

WW-M and N are located 564 and 503 m from GW-7, respectively, near Carter Road and the Meshoppen Creek basin, and the methane and operational data are shown in Fig. S4. In January 2009, the annular pressure recorded in GW-7 was 226 psi. Initial water samples in the house wells were not taken until late 2009 and early 2010. They varied from 14 to 32 mg/L until September and October 2010. At those points a new well replaced WW-M and an aeration treatment was installed on the WW-N system. No methane was detected in the final sample from WW-M, which was probably related to non-use from that water well. After the aeration system was installed on WW-N well, the initial methane concentration was 2.9 mg/L and the final one was 0.002 mg/L. GW-7 was squeezed on 2/14/2011; however, due to the non-use and treatment of the house wells, it is not possible to tell if remediation of the gas well had any effects on methane levels in WW-M and -N.

Isotope analyses were conducted on two samples taken from WW-M producing similar results, which were significantly more depleted than the annular space gases of nearby gas wells. One sample had a C1:C2 ratio of 6667 and the second detected no ethane. This suggests a thermogenic gas with a biogenic component, from an immature, shallow, bedrock source, possibly at a depth < 1000 m. The samples were collected prior to remediation of the gas well, drilling of the replacement water well, and installation of the aeration system. No samples were taken after the repairs and remediation were completed, so it is not possible to determine if two sources of methane existed; however, if more samples had been taken, this might have provided evidence of migration of shallow gas that could be identified as having a microbial origin.

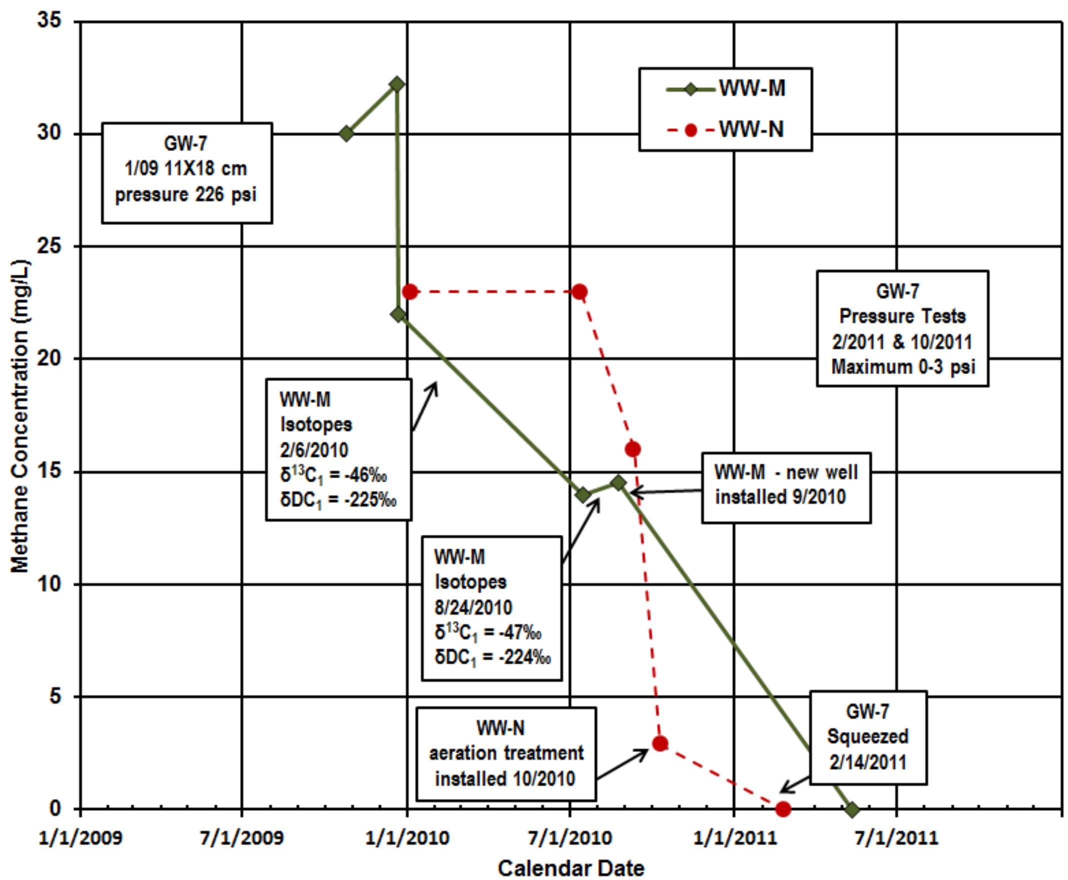

Fig. S4 Methane concentrations and stable isotope compositions of samples from WW-M and –N, near GW-7. Included are gas well operations and other activities possibly related to methane gas migration

Table S1 Gas Well Construction Data (All depths in meters)

GW	Direction	Depth TVD	Comp.	Stim.	Elev.	Depth casing	Depth Top of Cement	Depth of Gas Shows
1	V	2271	8/31/08	8/19/08	471	468	1673	1823, 2099
2	V	2189	10/14/08	12/10/08	440	480	1658	611, 730, 917, 1549, 1983
3	V	271	10/8/08	None	395	58	N/A	None
3a	V	2124	12/16/08	3/20/09	391	510	1613	445, 458, 1917-23
3b	V	582	N/R	None	393	437	N/A	None
4	V	2148	10/14/08	10/1/08	366	477	1813	None
5	V	2178	10/31/08	10/15/08	407	481	1813	1709
6	V	2208	4/14/08	11/8/08	369	454	1765	1275
6a	H	2153	8/11/08	11/4/08	369	1074	N/R	None
7	V	2194	7/21/09	8/9/08	326	463	1448	None
8	H	2927	4/8/09	8/8/09	347	464	808	13 shows 1190-9326
8a	H	2844	7/13/09	8/16/09	434	455	716	4150
8b	V	2127	4/08/09	8/15/09	347	455	213	None

Table S2 Gas Well Remediation Data (TOC = Top of Cement)

GW	Press. (psig)	Equivalent Depth (m)	Annulus (cm)	Date	Vent	Date	Remediation			Pressure Tests		
							Type	Date	Depth (m)	Date	Annulus (cm)	Pressures (psig)
1	520	739	11X18	1/09	Yes	1/21/09	Squeeze	10/28/08	TOC@1673, 2091			
							Squeeze	2/15/09	TOC@387, 1533			
							Plug	6/21/10	2091			
2	619	880	11X18	1/09	No?		Squeeze	4/1/09	1616, TOC@328	11/2010	18X23	0-78
										9/2011	18X23	0-48
3	Cmt Shut				No		Plug	10/8/08	N/A			
3a	286	406	11/18	1/09	Yes	1/22/09	Squeeze	4/3/09	1570, TOC@268			
							Plug	5/23/10				
3b	N/R				No		Plug	5/23/10	N/A			
4	345	490	11X18	1/09	Yes	1/22/09	Squeeze	3/18/09	1522, TOC@442	11/2010	11X18	0-2
										10/2011	11X18	0-23
5	707&0	1005&0	11X18	1/09	No		Squeeze	1/24/11	479, 484, 1658	10/2011		0
6	1200	1705	11X18	1/09	No		Squeeze	3/19/09	457	10/2011	11X18	0
							Squeeze	5/11/10	1753	9/2011	18X23	0
6a	400	568	11X18	1/09	No		Squeeze	9/27/08	190, 410, 447	10/2011		0
							Squeeze	3/9/11	0-170			
7	226	321	11X18	1/09	No		Squeeze	2/14/11	1402	2/2011	11X18	0
										10/2011	11X18	0-3
8	340	483	11X18	1/09	Yes	1/22/09	None			11/2010	11X18	0-225
										9/2011	11X18	0-69
8a	380	540	11X18	11/10	No?		Squeeze	10/16/10	256, 410	11/2010	11X18	0-380
											18X23	0-4
										9/2011	11X18	0-299
											18X23	0-6
8b	100	142	11X18	11/10	No?		None			11/2010	11X18	0-100
											18X23	0-15
										9/2011	11X18	0-2
											18X23	0

Table S3 Water Well Remediation Data

WW	Date	Type
A	N/R	Supplied bottled and bulk water
B	7/20/2009	Supplied water (bottled & /or bulk?)
C	5/2010	Aeration (bottled water date?)
D	6/2011	Treatment (type?), not primary residence
E	N/R	Supplied bottled and bulk water
F	N/R	Supplied bottled and bulk water
G	N/R	Supplied bottled and bulk water
H	4/22/2010	Bottled & bulk water
I	11/12/2009	Bottled & bulk water
J	N/R	Supplied bottled and bulk water
K	01/05/2010	Supplied bottled and bulk water
L	N/R	Supplied bottled water
M	9/2010	New well
N	10/2010	Aeration
O	10/2010	Treatment (type?)
P	8/2010	Treatment & RO
Q	11/30/2009	Provided water (ended 6/17/2010)
R		None

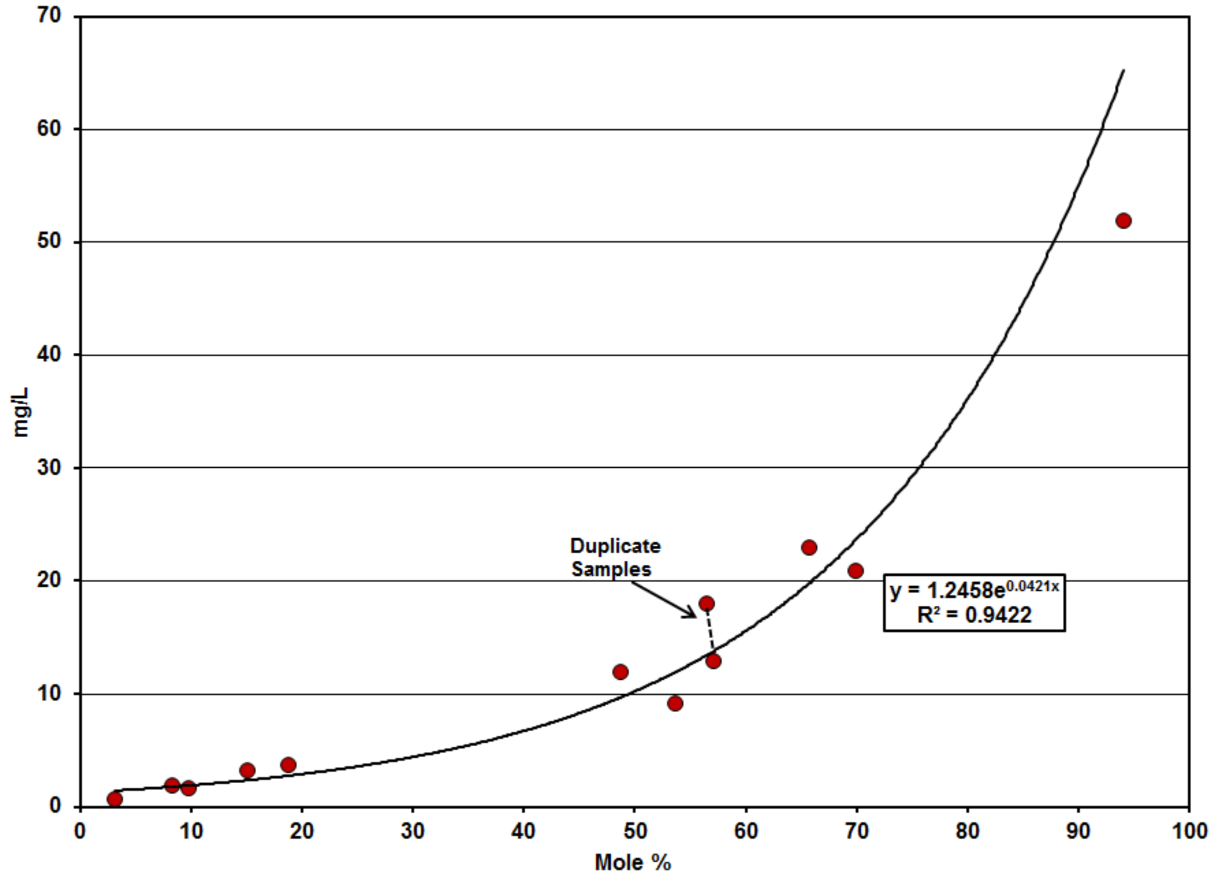

Fig. S5 US EPA methane concentrations

Note: The Molofsky et al. (2013) data only gave methane concentrations in mole%. The US EPA data expressed methane concentration in both mole% and mg/L units. From that data an equation was developed that was used to calculate the Molofsky data concentrations in mg/L units

Table S4 Isotopic and Molecular Data (all isotopic data in ‰)

					Ratio	Ratio	Water Well				Conc	Molar %	Water
	$\delta^{13}C$-CH_4	δ^2H-CH_4	$\delta^{13}C$-C_2H_6	δ^2H-C_2H_6	C1:C2	C1:C3	2011	2013	Date	Gas	mg/L	C1	Well
PA DEP and CEC	-32.04	-170.3	NA		63.4	35230	1	1	1/18/2009	Free	1.39	2.6	WW-H
	-33.2	-186.9	-34.69		59.2	32884	1	1	10/6/2010	Free	28.78	74.58	WW-H
	-32.04	-178.7	-35.21		52.8	-	3	1	11/13/2010	Dissolved	24.99	71.23	WW-H
	-30.53	-176.8	-34.46		44.2	36820	2	2	10/6/2010	Free	7.54	42.77	WW-I
	-31.51	-182.3	-35		50	-	4	2	11/9/2010	Dissolved	36.12	79.98	WW-I
	-31.24	-174.4	-34.77		72.6	7257	4	3	11/12/2010	Dissolved	41.82	83.46	WW-G
	-31.24	-174.1	NA		57.2	17347	4	4	1/21/2009	Free	1.52	4.74	WW-F
	-32.85	-175.4	-32.99		109	-	5	5	11/9/2010	Dissolved	2.72	18.59	WW-L
	-31.08	-172.7	NA		53.5	2036	6	6	1/21/2009	Free	7.02	41.07	WW-E
	-36.83	-216	-38.21		61.8	47545	6	6	10/6/2010	Free	1.53	4.92	WW-E
	-36.51	-206.7	-37.7		51.1	5110	6	6	11/7/2010	Dissolved	20.86	66.94	WW-E
	-31.03	-173.1	-34.8		54.5	1310	7	7	1/8/2009	Free	20.49	66.51	WW-A
	-30.66	-178.7	-34.82		55.2	1554	8	8	1/12/2009	Free	14.61	58.47	WW-B
	-30.98	-173.6	-34.61		49.6	-	8	9	11/20/2010	Dissolved	17.68	63.01	WW-J
	-38.35	-199.8	-35.99		277	-	9	10	11/9/2010	Dissolved	6.38	38.8	WW-K
	-34.71	-194.6	NA		5223	-	10	11	10/6/2010	Free	13.99	57.45	WW-P
	-35.5	-195	NA		5338	-	10	11	6/16/2010	Free	1.49	4.27	WW-P
	-45.83	-276.8	NA		109	-	11	12	6/16/2010	Free	1.36	2.13	WW-O
	-46.83	-280.8	NA		52.8	31079	12	13	8/18/2010	Free	1.52	4.66	WW-Q
	-45.72	-274.3	-41.81		50.5	1683	12	13	11/10/2010	Dissolved	53.64	89.37	WW-Q
	-45.4	-225.4	NA		6667	-	13	14	2/15/2010	Free	1.36	2	WW-M
	-45.84	-223.9	NA		--	-	13	15	8/24/2010	Free	1.36	2.1	WW-M
	-34.38	-199.9	NA		2789	-	14	15	6/16/2010 8/16/2010	Free	1.38	2.51	WW-R

PA DEP (Pennsylvania Department of Environmental Protection); CEC (Civil and Environmental Consultants, Inc.)

Table S4 (Continued) Isotopic and Molecular Data (all isotopic data in ‰)

					Ratio	Ratio	Water Well 2013			Conc. Est	Molar %	Water Well
	$\delta^{13}C-CH_4$	$\delta^{2}H-CH_4$	$\delta^{13}C-C_2H_6$	$\delta^{2}H-C_2H_6$	C1:C2	C1:C3		Date	Gas	mg/L	C1	
Geomark (Split Samples)	-33.5	-170	-35.4		59.9	-	1	11/13/2010	Dissolved	11.81	53.28	WW-H
	-33.1	-172	-34.3		55.4	-	2	11/9/2010	Dissolved	31.38	76.43	WW-I
	-32.7	-160	-35.4		76.3	8245	3	11/2/2010	Dissolved	40.46	82.45	WW-G
	-38.2	-193	-37.3		56.5	-	6	11/7/2010	Dissolved	2.11	12.43	WW-E
	-39.2	-187	-35.9		248	-	10	11/5/2010	Dissolved	1.71	7.44	WW-K
	-46.4	-254	-41.9		55.8	-	13	11/10/2010	Dissolved	2.09	12.28	WW-Q
							2012			**Actual**		
US EPA	-36.8	-202.4	-31.58	-177	112.7	121725	HW-1	1/25/2012	Dissolved	12	48.69	WW-F
	-29.36	-160.5	-28.83	-169	82.5	-	HW-2	1/25/2012	Dissolved	18	56.36	WW-J
	-29.3	-160.6	-28.6	-166	83.1	-	HW-2 (Dup)	1/25/2012	Dissolved	13	57.06	WW-J
	-24.98	-121.8	-31.2	-187	122.6	24400	HW-4	1/24/2012	Dissolved	1.7	9.76	WW-B
	-33	-162.9	NA	NA	318.1	-	HW-5	1/26/2012	Dissolved	2	8.24	WW-K
	-31.07	-169	-34.43	-195	88	9650	HW-6	1/26/2012	Dissolved	23	65.62	WW-G
	-36.58	-209.9	-35.9	-189	69.9	17880	HW-8a	1/25/2012	Dissolved	9.2	53.64	WW-E
	-35.9	-196.7	-35.33	-204	95.3	4356	HW-12	1/26/2012	Dissolved	52	94.06	WW-R/Q
	-26.58	-140.3	-26.6	-157	208.5	-	HW-14	1/26/2012	Dissolved	3.8	18.74	WW-C
	-31.54	-167.8	-32.9	-169	126.9	13609	HW-17	1/27/2012	Dissolved	3.3	14.97	WW-L
	-53.8	-165	NA	NA	N/A	-	HW-24	1/27/2012	Dissolved	0.7	3.11	
	-35.2	-193	NA	NA	5870.6	-	HW-60	3/5/2012	Dissolved	21	69.86	WW-P

US EPA – United States Environmental Protection Agency; GEOMARK – GeoMark Research, Ltd.

Table S4 (Continued) Isotopic and Molecular Data

(all isotopic data in ‰)

Annular Space Gas						
Well	$\delta^{13}C_1$	δDC_1	$\delta^{13}C_2$	C1:C2	C1:C3	Location
GW-1	-31.0	-173.1	-34.7	55.8	1674	18 cm casing
	-31.7	-183.2		49.9	1341	18 cm casing
GW-3	-31.2	-173.9	-34.6	52.1	1771	51 cm casing
	-31.6	-175.3	-35.0	50.9	1416	34 cm casing
GW-6	-30.0	-171.1		39.8	860	18 cm casing
Production Gas						
1V	-28.7	-157	-35.3	45.8	1317	
2H	-29.7	-160	-35.6	47.1	1414	
4H	-29.0	-160	-35.2	43.3	1097	
5H	-29.5	-161	-35.3	45.8	1354	
GW-1	-29.9	-161.1	-35.9	45.9	1394	11 cm casing
GW-1	-29.96	-161.1	-35.9	46.2	1338	Pipeline
N/R	-27.6	-157.9				GW-2?

Table S5 C1:C2 ratios after successful or partially successful remediation actions (all isotopic data in ‰)

			Ratio	Water Well		Conc (est)	Molar %	Molar %	Water Well
$\delta^{13}C-CH_4$	$\delta^{2}H-CH_4$	$\delta^{13}C-C_2H_6$	C1:C2		Date	mg/L	C1	C2	
Remediation Successful									
-30.66	-178.7	-34.82	55.2	8	1/12/2009	14.61	58.47	1.06	WW-B
-24.98	-121.8	-31.2	122.6	HW-4	1/24/2012	1.7	9.76	0.08	WW-B
-31.24	-174.1	NA	57.2	4	1/21/2009	1.52	4.74	0.083	WW-F
-36.8	-202.4	-31.58	112.7	HW-1	1/25/2012	12	48.69	0.432	WW-F
Migration > One Year After Completion									
-30.98	-173.6	-34.61	49.6	9	11/20/2010	17.68	63.01	1.27	WW-J
-29.36	-160.5	-28.83	82.5	HW-2	1/25/2012	18	56.36	0.683	WW-J
Migration > One Year After Completion									
-38.35	-199.8	-35.99	277	10	11/9/2010	6.38	38.8	0.14	WW-K
-39.2	-187	-35.9	248	10(split)	11/5/2010	1.71	7.44	0.03	WW-K
-33	-162.9	NA	318.1	HW-5	1/26/2012	2	8.24	0.026	WW-K
Both Samples After Remediation									
-32.85	-175.4	-32.99	109	5	11/9/2010	2.72	18.59	0.17	WW-L
-31.54	-167.8	-32.9	126.9	HW-17	1/27/2012	3.3	14.97	0.118	WW-L
Remediation Partially Successful									
-31.24	-174.4	-34.77	72.6	3	11/12/2010	41.82	83.46	1.15	WW-G
-32.7	-160	-35.4	76.3	3(split)	11/2/2010	40.46	82.45	1.08	WW-G
-31.07	-169	-34.43	88	HW-6	1/26/2012	23	65.62	0.746	WW-G

Table S5 (Continued) C1:C2 ratios after unsuccessful remediation actions, naturally occurring methane or late migrating methane (all isotopic data in ‰)

			Ratio	Water Well		Conc (est)	Molar %	Molar %	Water Well
$\delta^{13}C-CH_4$	$\delta^{2}H-CH_4$	$\delta^{13}C-C_2H_6$	C1:C2		Date	mg/L	C1	C2	
Remediation Unsuccessful									
-31.24	-174.4	-34.77	72.6	3	11/12/2010	41.82	83.46	1.15	WW-G
-32.7	-160	-35.4	76.3	3(split)	11/2/2010	40.46	82.45	1.08	WW-G
-31.07	-169	-34.43	88	HW-6	1/26/2012	23	65.62	0.746	WW-G
-32.04	-170.3	NA	63.4	1	1/18/2009	1.39	2.6	0.041	WW-H
-33.2	-186.9	-34.69	59.2	1	10/6/2010	28.78	74.58	1.26	WW-H
-32.04	-178.7	-35.21	52.8	1	11/13/2010	24.99	71.23	1.35	WW-H
-33.5	-170	-35.4	59.9	1(split)	11/13/2010	11.81	53.28	0.89	WW-H
-30.53	-176.8	-34.46	44.2	2	10/6/2010	7.54	42.77	0.968	WW-I
-31.51	-182.3	-35	50	2	11/9/2010	36.12	79.98	1.6	WW-I
-33.1	-172	-34.3	55.4	2(split)	11/9/2010	31.38	76.43	1.38	WW-I
Naturally Occurring Methane									
-34.71	-194.6	NA	5223	11	10/6/2010	13.99	57.45	0.011	WW-P
-35.5	-195	NA	5338	11	6/16/2010	1.49	4.27	0.0008	WW-P
-35.2	-193	NA	5871	HW-60	3/5/2012	21	69.86	0.012	WW-P
Late (Second) Migrating Methane, About Two Years After Completion									
-46.83	-280.8	NA	52.8	13	8/18/2010	1.52	4.66	0.088	WW-Q
-45.72	-274.3	-41.81	50.5	13	11/10/2010	53.64	89.37	1.77	WW-Q
-46.4	-254	-41.9	55.8	13(split)	11/10/2010	2.09	12.28	0.22	WW-Q
-35.9	-196.7	-35.33	95.3	HW-12	1/26/2012	52	94.06	0.987	WW-R/Q

Table S6 MGL Isotope Data by Depth for Marcellus Gas Wells Bradford County and Isotope Classification of Dimock Area Water Wells

Isotopes	Mean	Median	# of Data Points				Dimock Water Well Samples					
	(‰)	(‰)		Std. Dev.	90% C.I.	95% C.I.	2009		2010		2012	
0–1000 feet												
$d^{13}C_1$	−43.53	−44.90	71	6.84	1.34	1.59			WW-M C1:C2-6667	WW-O		
$d^{13}C_2$	−40.95	−41.10	63	2.56	0.53	0.63				WW-Q		
dDC_1	−226.88	−232.50	40	39.85	10.36	12.35						
0–2000 feet												
$d^{13}C_1$	−41.93	−42.40	161	6.76	0.88	1.04						
$d^{13}C_2$	−40.38	−40.50	144	2.58	0.35	0.42						
dDC_1	−226.60	−223.50	98	37.02	6.15	7.33						
1000–3000 feet												
$d^{13}C_1$	−41.60	−41.70	157	5.66	0.74	0.89			WW-E		WW-E	
$d^{13}C_2$	−40.13	−40.00	139	2.54	0.35	0.42						
dDC_1	−228.91	−223.00	93	33.93	5.79	6.9						
2000–5000 feet												
$d^{13}C_1$	−37.97	−36.60	269	4.85	0.49	0.58			WW-H	WW-I	WW-F	WW-P C1:C2-5700
$d^{13}C_2$	−39.60	−39.90	240	2.69	0.29	0.34			WW-J	WW-K	WW-Q/R	
dDC_1	−195.80	−180.00	163	36.55	4.71	5.61			WW-P C1:C2-5300	WW-R C1:C2-2800		
4000–5000 feet												
$d^{13}C_1$	−35.94	−35.90	143	3.56	0.49	0.58	WW-A	WW-B	WW-L	WW-G		
$d^{13}C_2$	−39.19	−39.85	132	2.69	0.38	0.46	WW-E	WW-F				
dDC_1	−180.28	−173.00	95	27.93	4.71	5.62	WW-H					
>5000 feet												
$d^{13}C_1$	−32.46	−32.80	1844	3.84	0.15	0.18					WW-G	WW-L
$d^{13}C_2$	−38.30	−38.90	1811	3.21	0.12	0.15						
dDC_1	−163.41	−162.00	1706	8.54	0.34	0.4						
							Microbial Oxidation				WW-B	WW-C
											WW-J	WW-K

Table S7 MGL Isotope Data by Formation for Marcellus Gas Wells Bradford County and Isotope Classification of Dimock Area Water Wells

Isotopes	Mean	Median	# of Data Points				Dimock Water Well Samples					
	(‰)	(‰)		Std. Dev.	90% C.I.	95% C.I.	2009		2010		2012	
Catskill/Lockhaven Formation												
$d^{13}C_1$	−42.12	−42.50	238	6.29	0.67	0.8			WW-M C1:C2-6667	WW-O		
$d^{13}C_2$	−40.25	−40.40	215	2.77	0.31	0.37				WW-Q		
dDC_1	−229.00	−232.00	129	35.78	5.18	6.18						
Brallier Formation												
$d^{13}C_1$	−37.19	−36.30	101	4.27	0.7	0.83			WW-E	WW-K	WW-E	WW-F
$d^{13}C_2$	−38.58	−39.30	87	2.98	0.52	0.63			WW-P C1:C2-5300	WW-R C1:C2-2800	WW-P C1:C2-5700	WW-Q/R
dDC_1	−208.08	−199.00	65	33.86	6.91	8.23						
Geneseo Shale												
$d^{13}C_1$	−34.59	−35.20	38	3.33	0.89	1.06	WW-B		WW-H	WW-I		
$d^{13}C_2$	−38.29	−38.40	37	2.84	0.77	0.91						
dDC_1	−180.42	−174.50	24	22.18	7.45	8.87						
Tully Limestone												
$d^{13}C_1$	−34.10	−34.20	51	5.3	1.22	1.45	WW-A	WW-E	WW-G	WW-J		
$d^{13}C_2$	−38.28	−39.30	42	2.91	0.74	0.88	WW-F	WW-H	WW-L			
dDC_1	−173.82	−164.00	33	20.78	5.95	7.09						
Hamilton Group												
$d^{13}C_1$	−33.33	−33.95	254	3.44	0.36	0.42					WW-G	WW-L
$d^{13}C_2$	−37.82	−38.60	245	3.42	0.36	0.43						
dDC_1	−167.88	−165.00	214	10.54	1.18	1.41						
Marcellus Formation												
$d^{13}C_1$	−32.37	−32.70	1592	3.75	0.15	0.18						
$d^{13}C_2$	−38.48	−39.10	1569	3.15	0.13	0.16						
dDC_1	−162.34	−162.00	1502	5.69								
							Microbial Oxidation				WW-B	WW-C
											WW-J	WW-K

Table S8 Operator / PA DEP LEL Measurements (% volume, balance normal air)

WW	Pre-drill	1/20/09	1/21/09	1/22/09	1/23/09	1/24/09	1/25/09	1/26/09	1/27/09	1/28/09	1/29/09	1/30/09	1/31/09	2/2/09	2/3/09	2/4/09
GW-1																
A					**12**	**13**	**13**	**21**	**0**	**10**	**19**	**0**	**5**	**10**	**3**	**1**
A				**60**				***2.5***	***2***		***0.5***				***1***	***2***
B	**0**				**50**	**100**		**100**	**100**	**131**				**85**	**55**	**30**
B		***55***	***19***	***10***				***40***	***22***		***39***				***20***	***18***
C	**0**				**45**	**0**		**100**	**0**	**0**	**100**			**8**	**62**	**3**
C				***40***				***17***	***0***						***20***	***5***
GW-2																
E		***55***	***50***					***19***	***23***		***17***				***21***	***12***
GW-3,-3a,-3b																
F					**20**	**20**	**16**	**19**	**23**	**52**	**33**	**27**	**54**	**65**	**20**	**41**
F		***0.8***	***10***	***10***					***12***		***10***				***4.5***	***4.5***
G					**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
G		***0***		***0***					***0***		***0***				***10***	
H					**10?**	**100**	**63**	**35**	**13**	**50**	**32**			**100**	**100**	**80**
H		***2.5***		***5***				***4.5***	***2.4***		***6***				***20***	***12***
I	**0**				**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**

Pre-drill samples, 12 wells all 0%; WW-B & -C, Post-Frack on 10/15 & 11/10/08 less than 1%, just prior to squeeze of GW-1 10/22-28/08 (venting?) WW-G & -I have separator devices installed on systems. Operator: 1/23/09-Readings taken prior to venting GW-1 & GW-3a?; 1/27/09-Readings taken before shut-in of GW-1. The significant differences between the operator/DEP values suggest that LEL measurements should be used only as a screening tool.

The lower explosive limit (LEL) and upper explosive limit (UEL) define the range of concentrations where flammable gases or vapors are explosive when mixed with air. Methane at 5% is at the lower explosive limit, and 15% is the upper explosive limit. Methane is often measured in the range of 0-100 percent of the LEL. Combustion is inhibited at methane concentration less than 5% due to the lack of sufficient fuel. Oxygen is deficient at methane levels greater than 15% in air, so combustion cannot be sustained. Methane levels above 15 percent are also dangerous because high concentrations can quickly dilute to explosive or flammable levels. Asphyxiation can occur at higher methane concentrations.