Water Quality Associated with Hydraulic Fracturing in Shale Formations

Presented by Dave Yoxtheimer, P.G.

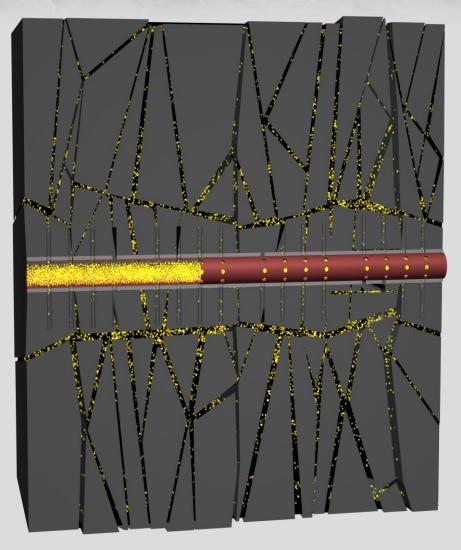
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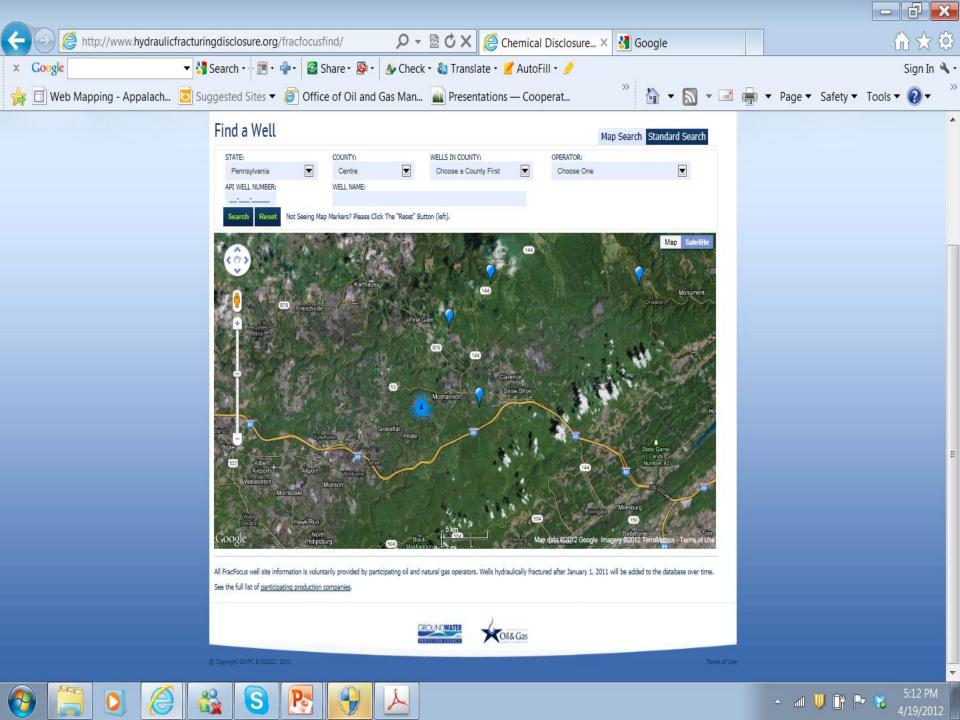
Fracturing Fluid Characteristics

Non-damaging

- Minimal leak-off
- High fluid efficiency
- No scaling
- Minimal skin effect
- Adequate scale and Fe control
- Sufficient viscosity to carry proppant
- Brine tolerant friction reducer (for reuse)
- Rapid clean-up
- Develop extensive fracture network
- Cost-effective
- Shale fracturing options:
 - Slickwater
 - Liquified propane
 - Carbon dioxide
 - Nitrogen/foam







Hydraulic Fracturing Fluid Product Component Information Disclosure

8/25/2011
Pennsylvania
Centre
37-027-61661
Williams
Resource Recovery 3-2H
-78.056658
41.020439
NAD83
Gas
8,517
5,663,806

To look up information on what chemicals are being used at a well site go to www.fracfocus.org

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Ingredient Concentration in Additive	Maximum Ingredient Concentration in HF Fluid (% by mass)**	Comments
Water	ARM - Moshannon Creek SR53	Carrier/Base Fluid	Water		100.00%	86.8502%	
Sand- Silica Sand	Halliburton	Proppant	Crystalline Silica Quartz	14808-60-7	100.00%	12.9850%	
LP-65	Halliburton	Scale Inhibitor	Ammonium Chloride	12125-02-9	10.00%	0.0034%	
WG-36 Gelling Agent	Halliburton	Gel					
			Guar Gum	9000-30-0	100.00%	0.0024%	
BE-9M	Halliburton	Biocide					
			Tributyl Tetradecyl Phosphonium Chloride	81741-28-8	10.00%	0.0026%	
			Methanol	67-56-1	30.00%	0.0079%	
FR-66	Halliburton	Friction Reducer	Hydrotreated Petroleum Distillate	64742-47-8	30.00%	0.0187%	
SP Breaker	Halliburton	Breaker	Sodium Persulfate	7775-27-1	100.00%	0.0014%	
HCI	Halliburton	Acid	Hydrochloric Acid	7647-01-0	30.00%	0.1111%	
GBW-30 Breaker	Halliburton	Breaker					
			Carbohydrates	Trade Ingredient	95.00%	0.0013%	
			Hemicellulase Enzyme	9012-54-8	15.00%	0.0002%	
BA-40L	Halliburton	Buffer	Potassium Carbonate	584-08-7	60.00%	0.0158%	
			rotassium Carbonate	004-00-7	00.0076	0.010076	

* Total Water Volume sources may include fresh water, produced water, and/or recycled water

** Information is based on the maximum potential for concentration and thus the total may be over 100%

All component information listed was obtained from the supplier's Material Safety Data Sheets (MSDS). As such, the Operator is not responsible for inaccurate and/or incomplete information. Any questions regarding the content of the MSDS should be directed to the supplier who provided it. The Occupational Safety and Health Administration's (OSHA) regulations govern the criteria for the disclosure of this information. Please note that Federal Law protects "proprietary", "trade secret", and "confidential business information" and the criteria for how this information is reported

Marcellus Shale Fracturing Fluids

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)**	Maximum Ingredient Concentration in HF Fluid (% by mass)**
35% HCL	Weatherford	Cleans Perforation	HCL	7647-01-0	35.00%	0.04410%
WFR-61LA	Weatherford	Friction Reducer	Sodium Chloride	7647-14-5	10.00%	0.00320%
	Weatherford	Friction Reducer	Ammonium Chloride	12125-02-9	7.00%	0.00230%
WFR-61LA	Weatherford	Friction Reducer	Petroleum Distillates	64742-48-8	40.00%	0.01290%
WFR-61LA	Weatherford	Friction Reducer	Alcohols, C-12-16, Ethoxylated	68551-12-2	7.00%	0.00230%
WAI-251 LC	Weatherford	Protects Casing	Tar Bases, Quinoline Derivs, Benzyl	72480-70-7	13.00%	0.00020%
WAI-251 LC	Weatherford	Protects Casing	Ethoxylated Nonylphenol	68412-54-4	10.00%	0.00010%
WAI-251 LC	Weatherford	Protects Casing	Cinnamaldhyde	104-55-2	10.00%	0.00010%
WAI-251 LC	Weatherford	Protects Casing	Ethylene Glycol	107-21-1	60.00%	0.00080%
WAI-251 LC	Weatherford	Protects Casing	2-Butoxyethanol	111-76-2	7.00%	0.00010%
WAI-251 LC	Weatherford	Protects Casing	Isopropyl Alcohol	67-63-0	7.00%	0.00010%
WAI-251 LC	Weatherford	Protects Casing	Triethyl Phosphate	78-40-0	7.00%	0.00010%
WAI-251 LC	Weatherford	Protects Casing	N. N-Dimethyloxazolidine	68-12-2	40.00%	0.00050%
WIC-641L	Weatherford	Prevents Precipitation	Citric Acid	77-92-9	70.00%	0.00520%
MX588-2	Multi-Chem	Scale Inhibitor	MX588-2	NA	0.00%	0.01900%
BMC B-8520	Multi-Chem	Antibacterial Agent	4,4-Dimethyloxazolidine	51200-87-4	78.00%	0.01350%
BMC B-8520	Multi-Chem	Antibacterial Agent	3,4,4-Trimethyloxazolodine	75873-43-7	5.00%	0.00090%
BMC B-8520	Multi-Chem	Antibacterial Agent	2-Amino-2-methyl-1-propanol	124-68-5	1.00%	0.00020%
BMC B-8520	Multi-Chem	Antibacterial Agent	Formaldehyde Amine	56652-26-7	0.50%	0.00010%
BMC B-8650	Multi-Chem	Antibacterial Agent	Glutaraldehyde	111-30-8	50.00%	0.00380%
BMC B-8650	Multi-Chem	Antibacterial Agent	Methanol	67-56-1	0.50%	0.00004%
Water	Operator	Carrier	Water	7732-18-5	100.00%	93.81300%
Sand	Weatherford	Fracture Proppant	Crystalline Silica	14808-60-7	100.00%	5.95600%

Bakken Shale Fracturing Fluids

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)**	Maximum Ingredient Concentration in HF Fluid (% by mass)**
Fresh Water	Operator				100.00%	88.75428*
SAND - COMMON BROWN	Halliburton	Proppant	Crystalline silica, quartz	14808-60-7	100.00%	4.17860%
CERAMIC PROP	Halliburton	Proppant	Crystalline silica, cristobalite	14464-46-1	30.00%	2.03744%
			Mullite	1302-93-8	100.00%	6.79145%
			Silica, amorphous - fumed	7631-86-9	30.00%	2.03744%
MO-67	Halliburton	pH Control Additive	Sodium hydroxide	1310-73-2	30.00%	0.00954%
CL-31 CROSSLINKER	Halliburton	Crosslinker	Potassium hydroxide	1310-58-3	5.00%	0.00047%
			Potassium metaborate	13709-94-9	60.00%	0.00566%
CL-22UCw	Halliburton	Crosslinker	Modified alkane	Confidential Business Information	60.00%	0.01453%
LoSurf-300D	Halliburton	Non-ionic Surfactant	1,2,4 Trimethylbenzene	95-63-6	1.00%	0.00084%
			Ethanol	64-17-5	60.00%	0.05061%
			Heavy aromatic petroleum naphtha	64742-94-5	30.00%	0.02531%
			Naphthalene	91-20-3	5.00%	0.00422%
			Poly(oxy-1,2-ethanediyl), alpha-(4-nonylphenyl)-omega-hydroxy-, branched	127087-87-0	5.00%	0.00422%
FR-66	Halliburton	Friction Reducer	Hydrotreated light petroleum distillate	64742-47-8	30.00%	0.00981%
WG-38 GELLING AGENT	Halliburton	Gelling Agent	Guar gum	9000-30-0	100.00%	0.08359%
OPTIFLO-III DELAYED RELEASE BREAKER	Halliburton	Breaker	Ammonium persulfate	7727-54-0	100.00%	0.00746%
			Crystalline silica, quartz	14808-60-7	30.00%	0.00224%
OptiKleen-WF™	Halliburton	Concentrate	Sodium perborate tetrahydrate	10486-00-7	100.00%	0.00209%

Marcellus Flowback Range of Water Quality

Parameter

Total dissolved solids: Chloride: Sodium: VOCs (primarily BTEX): Radium 226: Barium: Strontium:

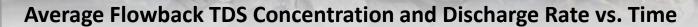
Concentration Range

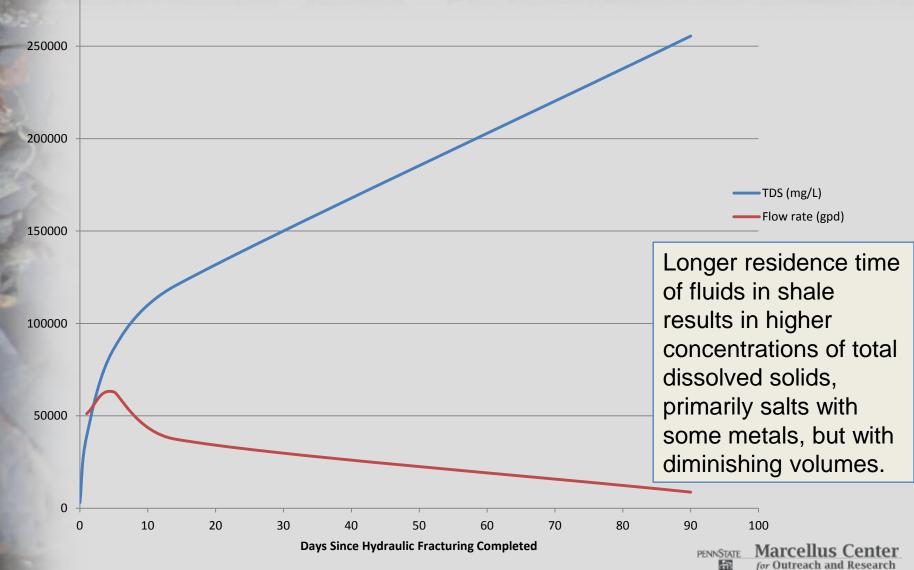
10,000 - >300,000 mg/L 5,000 - >150,000 mg/L 2,500 - >75,000 ND - 2 mg/L 100 pCi/L - 16,000 pCi/L 2,000 - 5,000 mg/L 1,000 - 7,000 mg/L



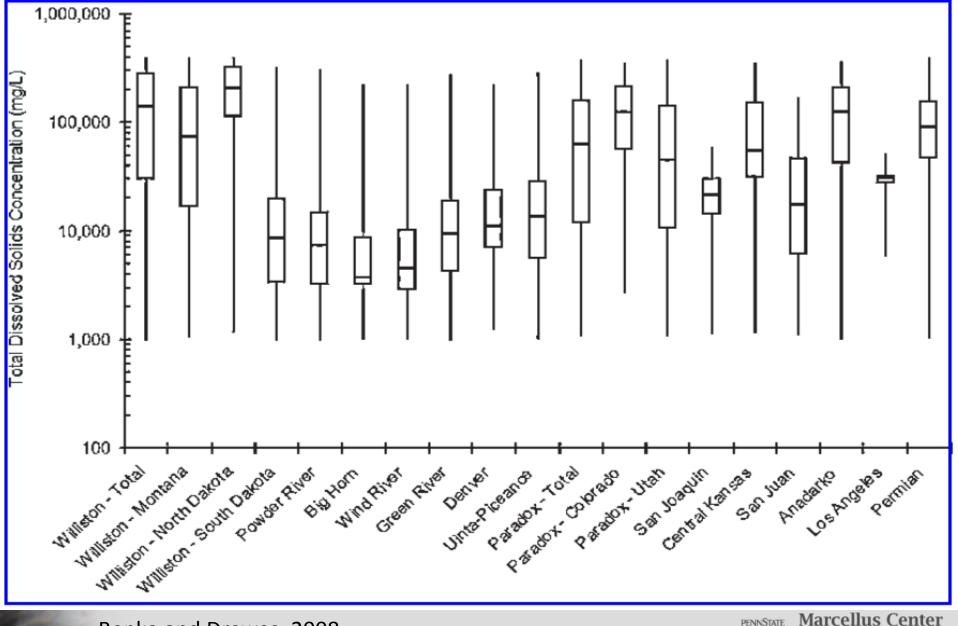
Flowback Water Quality Trends

300000





TDS Variability in Western Basins

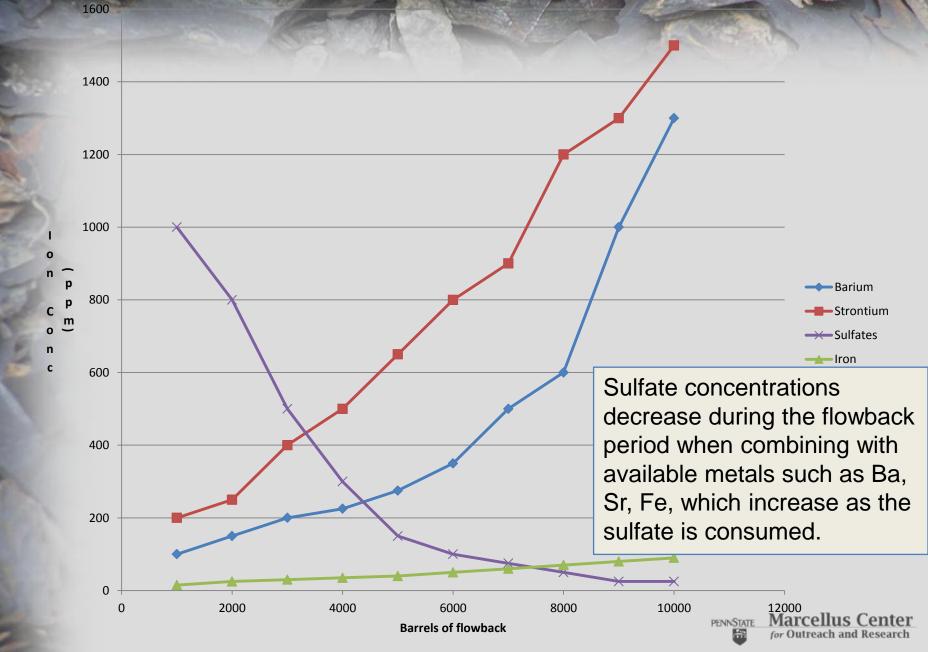


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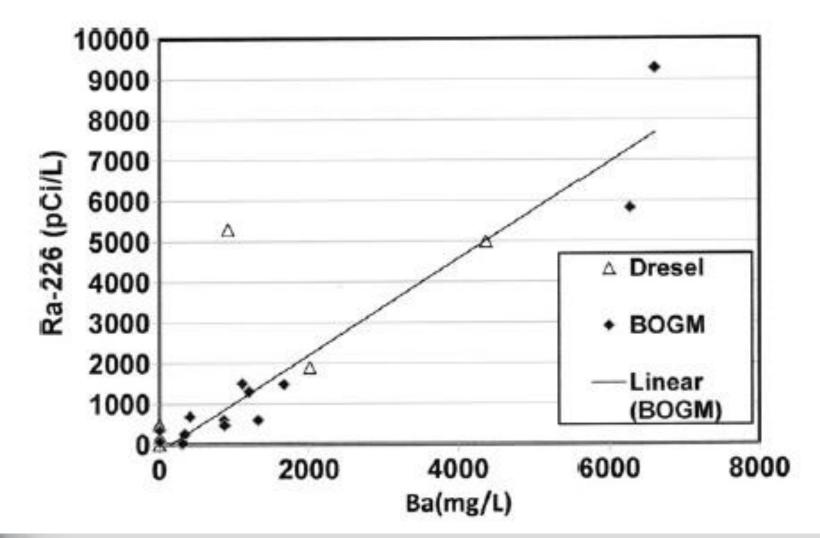
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Flowback Scaling Agent Levels

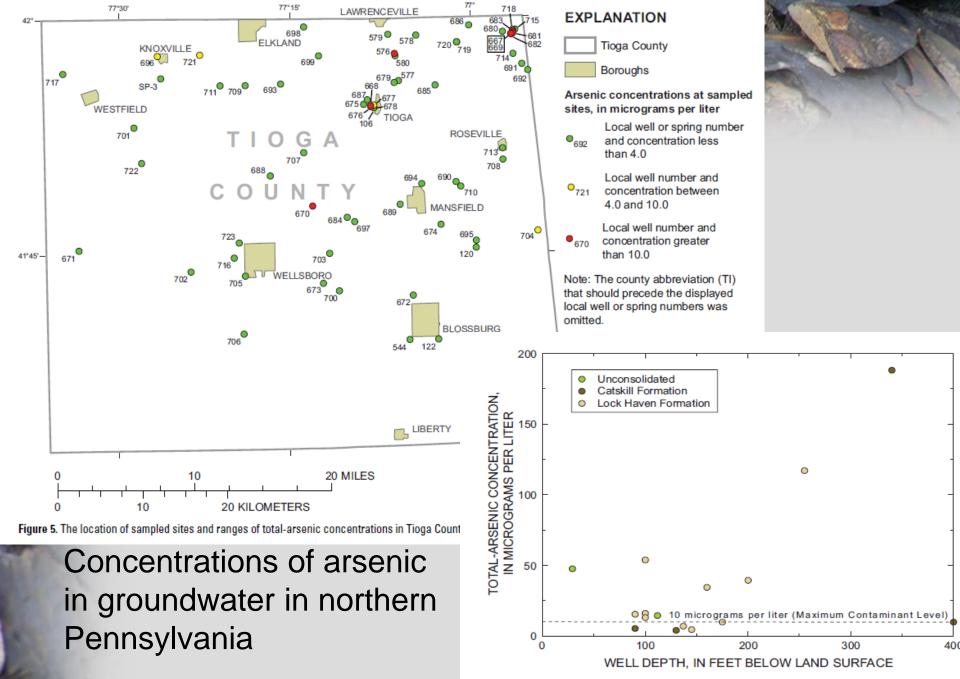


Correlation of Radium-226 with Barium (Marcellus Example)



Haluszczak, L.O., et al. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. Appl. Geochem. (2012)

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Low, D.J., and Galeone, D.G., 2007, : U.S. Geological Survey Open-File Report 2006-1376,

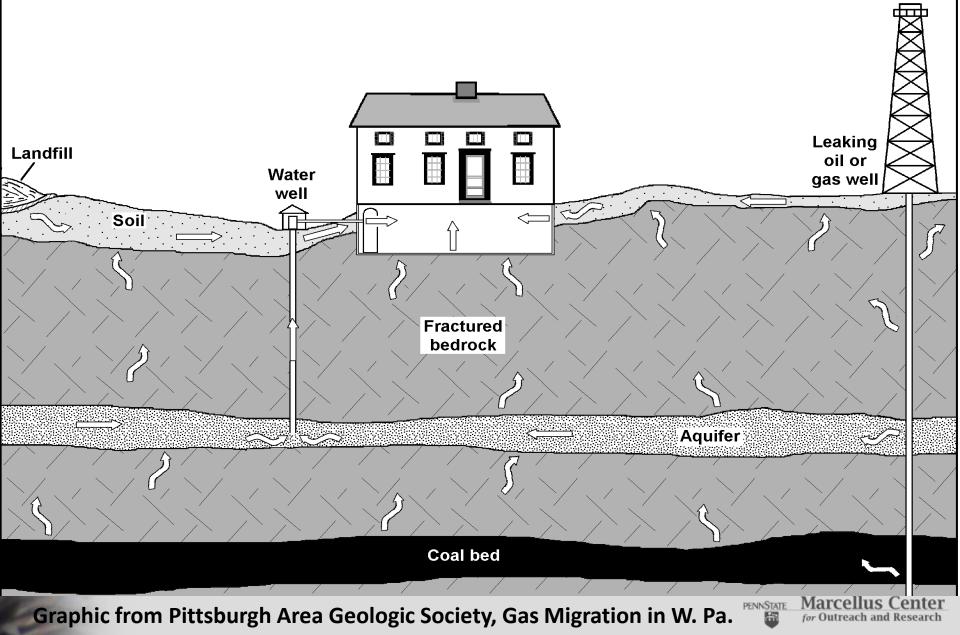
Figure 6. Distribution of total-arsenic concentration and well depth by geologic units, northern-tier counties of Pennsylvania.

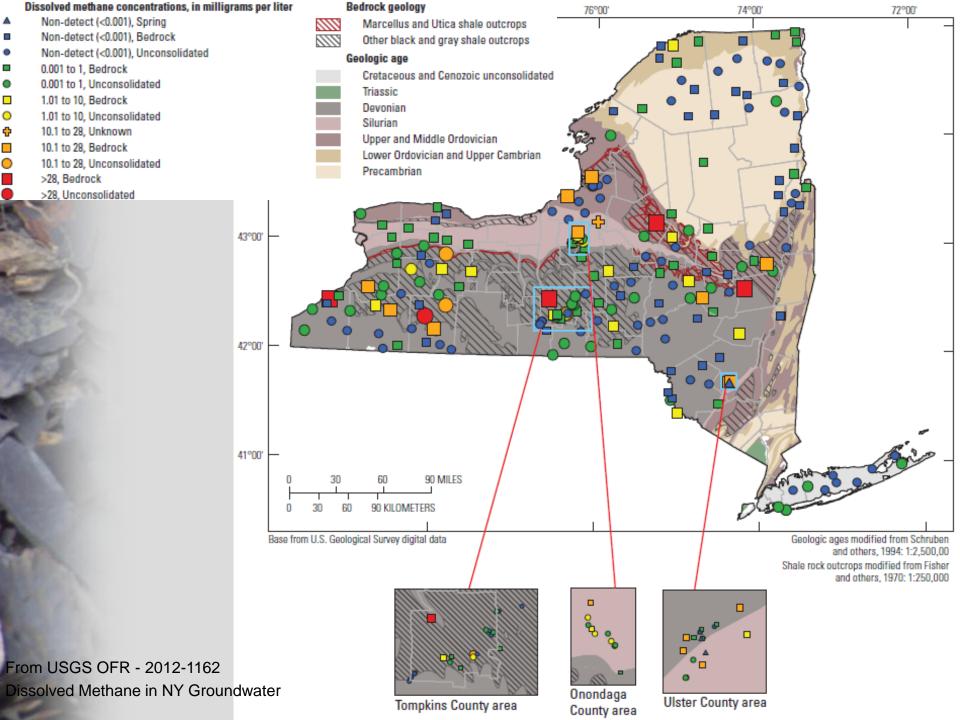
Gas Happens!

Photograph by Matthew Conheady (www.nyfalls.com)

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Sources of Methane in Groundwater

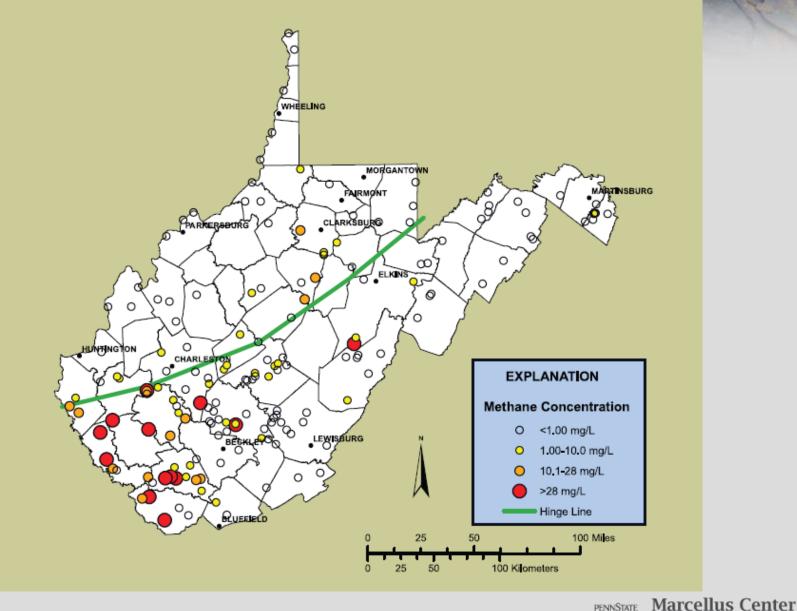




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Non- detect 75 14 2 3 7 9 3 113	<1.0 45 19 8 5 6 4 0	1.0-10.0 5 10 1 1 1 0 0	10.1-28.0 3 7 2 3 0 0	>28.0 1 3 0 1 0 0	Number of wells 129 53 13 13 13 14	Percent of wells 54 22 5 5 5 5 6
14 2 3 7 9 3	19 8 5 6 4	10 1 1 1 0	7 2 3 0	3 0 1 0	53 13 13	22 5 5
2 3 7 9 3	8 5 6 4	1 1 1 0	3 0	0 1 0	13 13	5 5
3 7 9 3	5 6 4	1 1 0	3 0	1	13	5
7 9 3	б 4	1 0	0	0		
9	4	0			14	6
3		_	0	0		v
	0	0		v	13	5
113		-	1	0	4	2
	87	18	16	5	239	
47	36	8	7	2		100
	No 150				1	-
		47 36	47 36 8 	47 36 8 7 	47 36 8 7 2 Non-detect - 113 samples (47 percent) 30 150 170 190 2	47 36 8 7 2

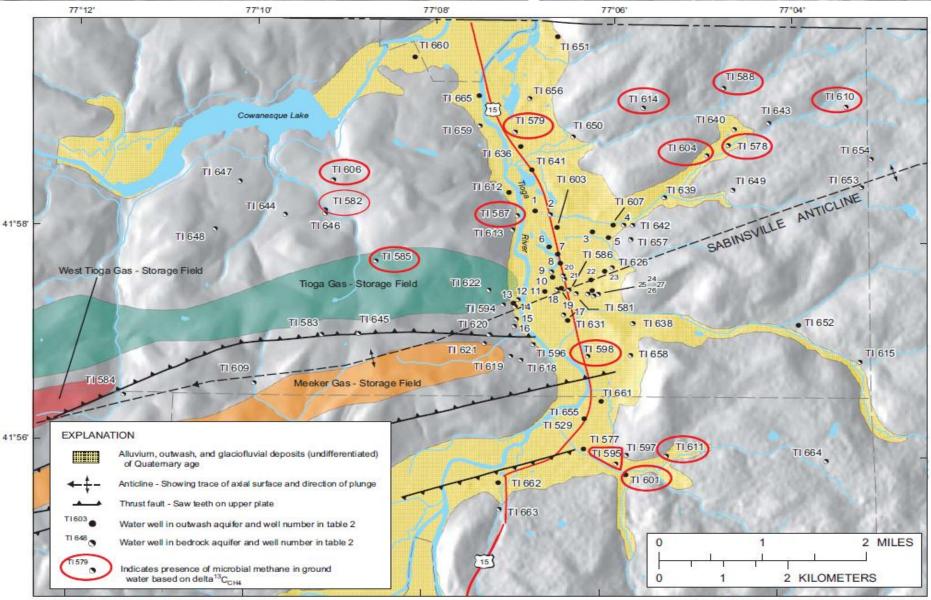
Methane in WV Groundwater



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USGS Fact sheet 2006_3011-Methane in WV groundwater

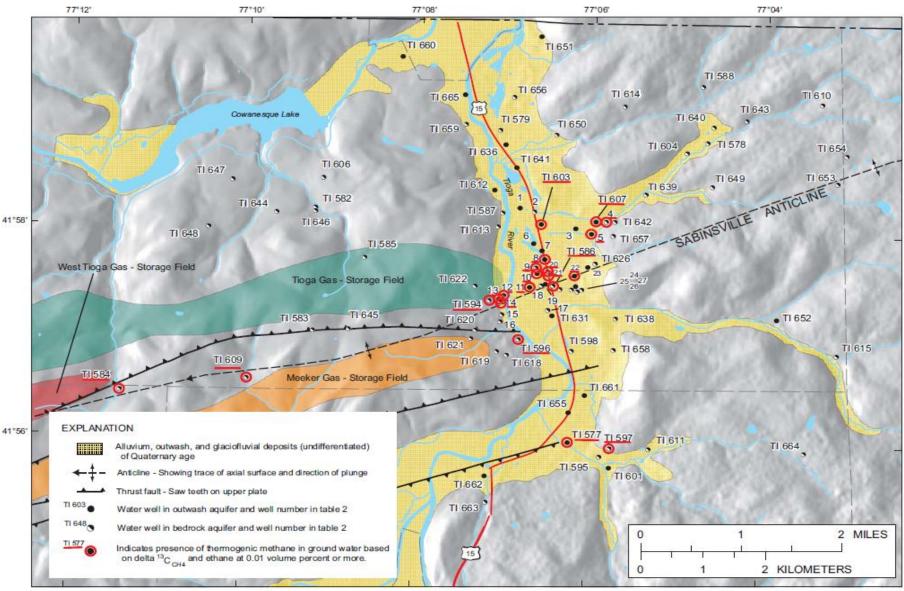
Distribution of Biogenic Methane



Surficial deposits from Commonwealth of Pennsylvania, 1989 Streams from U.S. Geological Survey, 2000 Township boundary and U.S. Routes from Commonwealth of Pennsylvania, 2006 Shaded relief prepared from U.S. Geological Survey National Elevation Dataset, 2004 Base from U.S. Department of Commerce digital data, 1993, 1:100,000 Albers Equal-Area Conic projection: Standard Parallels 29*30' N and 45*30' N, Central Meridian 77*45' W, Latitude of Origin 23*00' N

U.S.G.S. SIR 2007-5085

Distribution of Thermogenic Methane

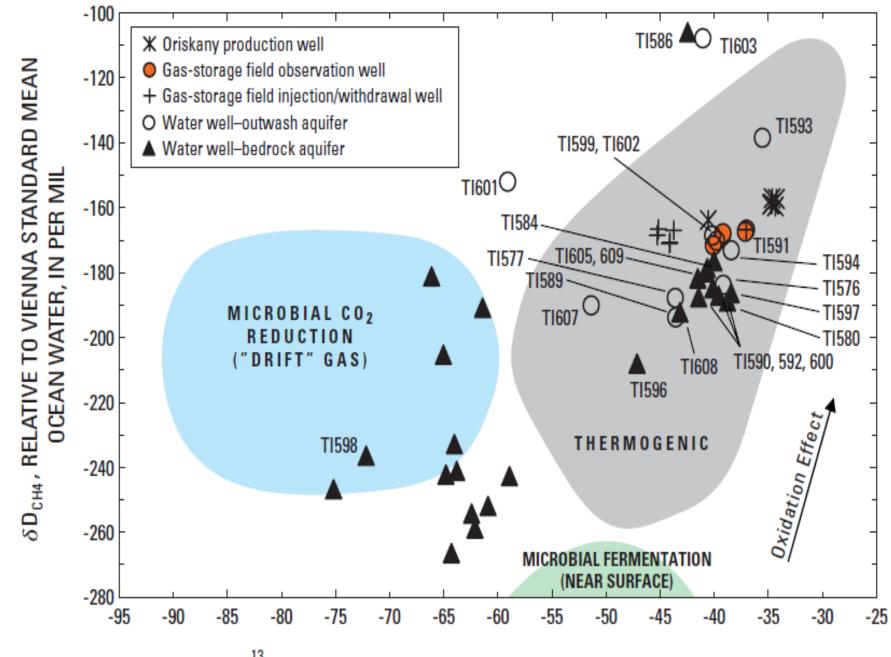


Surficial deposits from Commonwealth of Pennsylvania, 1989 Streams from U.S. Geological Survey, 2000 Township boundary and U.S. Routes from Commonwealth of Pennsylvania, 2006 Shaded relief prepared from U.S. Geological Survey National Elevation Dataset, 2004 Base from U.S. Department of Commerce digital data, 1993,

1:100,000 Albers Equal-Area Conic projection: Standard Parallels 29"30' N and 45"30' N,

Central Meridian 77°45' W, Latitude of Origin 23°00' N

U.S.G.S. SIR 2007-5085



U.S.G.S. SIR 2007-5085 $\delta^{13}C_{CH4}$, RELATIVE TO VIENNA PEEDEE BELEMNITE, IN PER MIL

Study of Groundwater Quality Before and After Drilling

- PSU Researchers received funding from *The Center for Rural PA* to collect pre- and postdrilling water sample from private wells
- Collected and analyzed nearly 230 samples within 1,000 feet and within 1 mile of Marcellus wells
- No significant before/after changes in water quality
 - ~40% of wells fail at least one drinking water standard and background methane found in ~24% of the wells.

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 Recommends sufficient setbacks from private wells and pre-drilling water sampling

Groundwater Quality in PA

Table 1. Water quality parameters measured in Phase 1 water wells in comparison to Pennsylvania drinking water standards and to typical concentrations in Pennsylvania water wells and Marcellus wastewaters. All concentrations are reported in units of mg/L except pH.

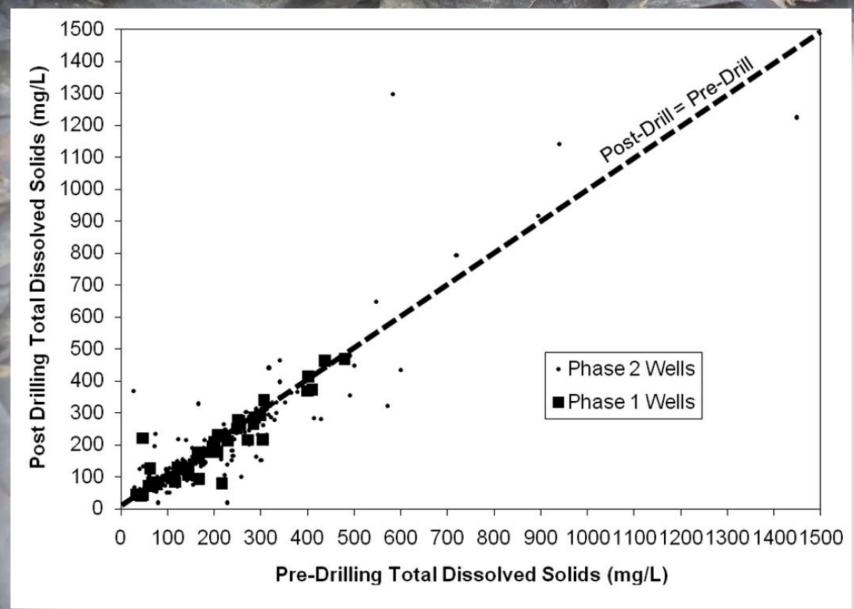
Parameter	Drinking Water Standard ¹	Approximate Median Concentration in Typical Pennsylvania Groundwater ²	Approximate Median Concentration in Typical Marcellus Wastewater ³
pH	6.5 to 8.5	7.50	6.60
Total Dissolved Solids	< 500	163.0	67,300
Total Suspended Solids	-	1.0	99.0
Barium	< 2.0	0.070	686
Iron	< 0.30	0.20	39
Manganese	< 0.05	0.01	2.63
Sodium	-	6.87	18,000
Hardness	-	86.1	17,700
Strontium	-	0.26	1,080
Chloride	< 250	5.3	41,850
Sulfate	< 250	18.0	2.4 to 106
Nitrate-Nitrogen	< 10	0.50	0.1 to 1.2
Bromide	-	0.016	445
Dissolved Organic Carbon	-	<1.0	62.8
Dissolved Methane		No data available	No data available
Oil & Grease	-	<5.0	6.3

¹ Pennsylvania Department of Environmental Protection, 2006. ² Pennsylvania State University, 2011; Davis et al., 2004; and Thurman, 1985. ³ Hayes, 2009.

The Impact of Marcellus Gas Drilling on Rural Drinking Water Supplies, Center for Rural PA, October 2011



Private Well TDS Pre- and Post-Drilling



The Impact of Marcellus Gas Drilling on Rural Drinking Water Supplies, Center for Rural PA, October 2011



Water Quality Protection Measures

- Geologic characterization to determine depth of aquifer and shallower gas-bearing sandstones
- Installation of casing with adequate grout to ensure groundwater is isolated and hydrocarbons sealed off
 Geophysical borehole log surveys to characterize gas-bearing zones and cement seal integrity
- Conduct pre-drilling groundwater sampling on private wells to verify baseline groundwater quality
- Characterizing methane found in water wells
 - Isotopic characterization of methane in water wells vs. in gas wells

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- Comparing ratio of methane and C2+ hydrocarbons
- Where stray gas is problematic well needs to be remediated or abandoned
- Careful fluids storage and handling at surface

Groundwater and Well Pad Protections

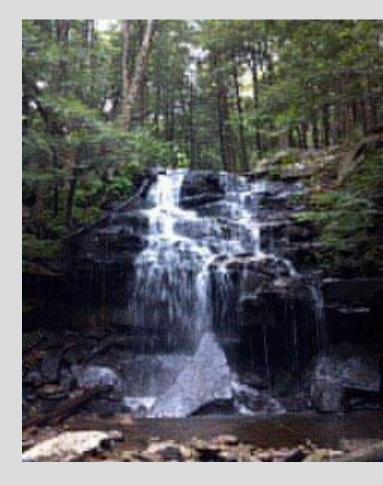


The End

Questions??

Thank you!!

David Yoxtheimer, P.G. Extension Associate PSU MCOR 320 EES Building University Park, PA 16802 814-865-1587 (office) day122@psu.edu www.marcellus.psu.edu



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