



INDICATOR PARAMETERS

- Pre-drill Baseline Groundwater Surveys
- Post-drill Groundwater Monitoring
- Gas Analysis

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COMMON GROUNDWATER BASELINE PARAMETERS

The parameters listed below are commonly used. *Many of these parameters are not always useful:*

- Field Screening: pH, Temperature, Specific Conductivity, DO, Redox
- General Water Quality: Alkalinity, TDS, TSS, Hardness, Turbidity, MBAS, TOC
- Anions: Chloride, Sulfate, Bromide, Nitrates (as Nitrogen)
- Total and/or Dissolved Metals: As, Ba, Ca, Cr, Fe, K, Pb, Mg, Mn, Na, Se, Sr
- Organics: BTEX, Dissolved Light Gases (C₁-C₃), glycols
 - ¹³δC and ²δH isotopes of Methane: Headspace or if dissolved methane exceeds a threshold value (1 to 20 mg/L, State-dependent)
 - ¹³δC isotopes of Ethane, Propane+
- Radioactivity (less frequently)
 - Gross alpha, gross beta
 - Ra-226, Ra-228 may be more accurate measurements



OVERVIEW: COMPOSITION OF HYDRAULIC FRACTURING FLUIDS

- fracfocus.com has volume information and detailed composition of hydraulic fracturing fluids for most wells
- In general, additives are <1% total volume
- *What parameters should be used as indicators of potential impact to groundwater from hydraulic fracturing activities, flowback/produced water?*

INDICATOR PARAMETER SELECTION FOR POTENTIAL IMPACT TO GROUNDWATER FROM HYDRAULIC FRACTURING FLOWBACK/PRODUCED WATER

- Criteria for selection of indicator parameters
 - Relative abundance in flowback/produced water
 - Potential mobility in groundwater systems
 - Ability to identify and accurately quantify the parameter in produced water and groundwater using existing EPA and/or Standard Methods
- Identification of appropriate indicator parameters for assessment of potential impact to groundwater
 - Based on available data on produced water, TDS is significantly higher than any other parameter, chloride is the most abundant anion, sodium is the most abundant cation

GROUNDWATER, INFLUENT, FLOWBACK, PRODUCED WATER

Parameter	Units	Approximate Typical Pennsylvania Groundwater ¹	Influent ²		5 Day Flowback ²		Conventional Produced Water ³
		Median	Range	Median	Range	Median	Range
pH		7.5	6.7 - 7.4	7.2	5.8 - 7.2	6.2	5 - 8
TDS	mg/L	163	35 - 5,500	334	38,000 - 260,000	238,000	3,000 - 350,000
TOC	mg/L	<1	2 - 200	3.8	4 - 388	63	NA
O&G	mg/L	<5	19	31	<0.5 - 100	NA	3 - 100
Chloride	mg/L	5	4 - 3,000	42	26,000 - 148,000	42,000	
Sodium	mg/L	7	26 - 6,200	68	11,000 - 65,000	18,000	

¹ Pennsylvania State University, 2011 , <http://www.iogawv.com/Resources/Docs/Marcellus-drinking-water-2011.pdf>

² Hayes, http://www.epa.gov/hfstudy/12_Hayes_-_Marcellus_Flowback_Reuse_508.pdf

³ IPEC, 2004 GRI, 1994

Typical Produced Water TDS Levels (USGS):

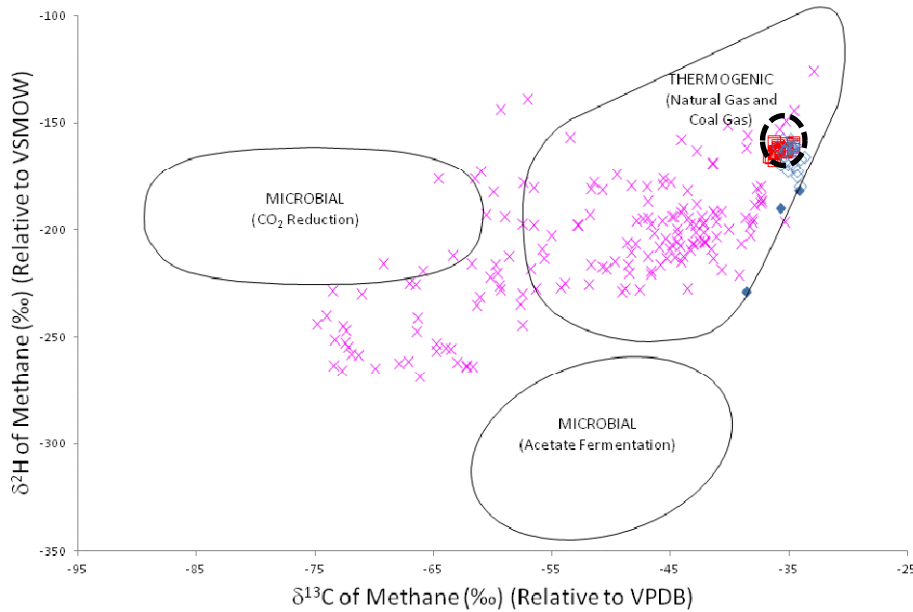
- Fayetteville Shale -25,000 mg/L
- Barnett Shale -60,000 mg/L
- Haynesville Shale -120,000 mg/L
- Permian Basin -140,000 mg/L
- Marcellus Shale -180,000 mg/L

Marcellus

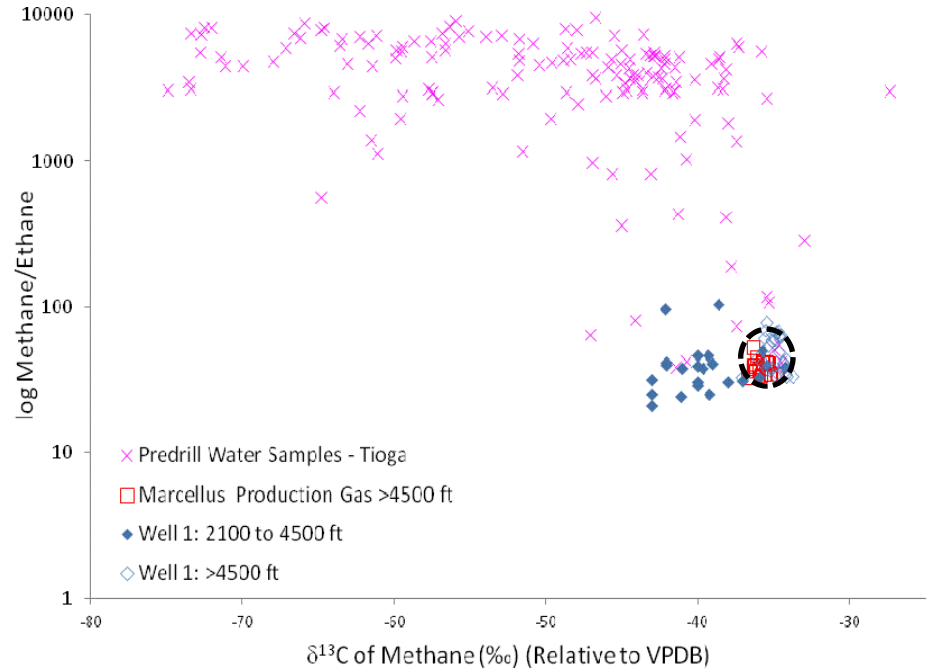
Siemens AG 2009

GAS CHARACTERIZATION

**Fingerprinting Isotopes:
 ^{13}C and ^2H of Methane**



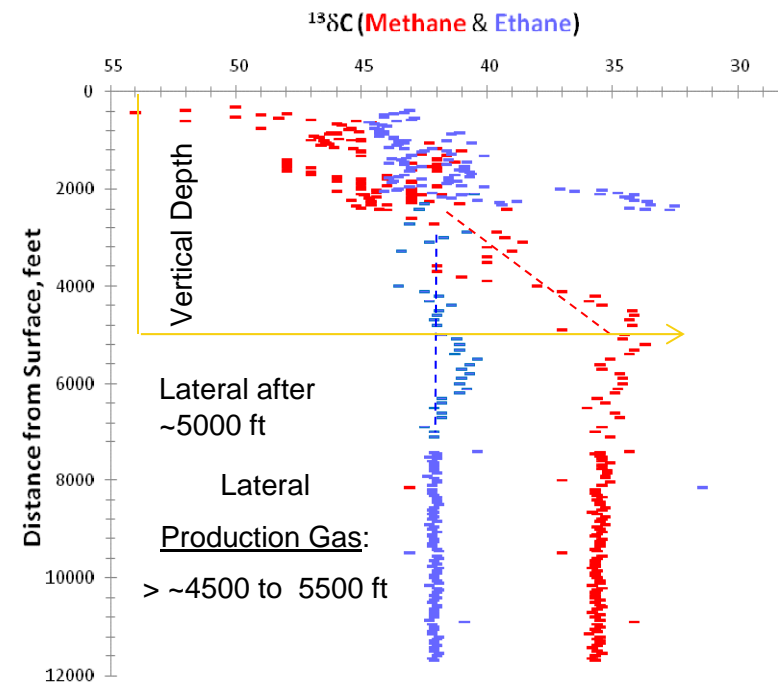
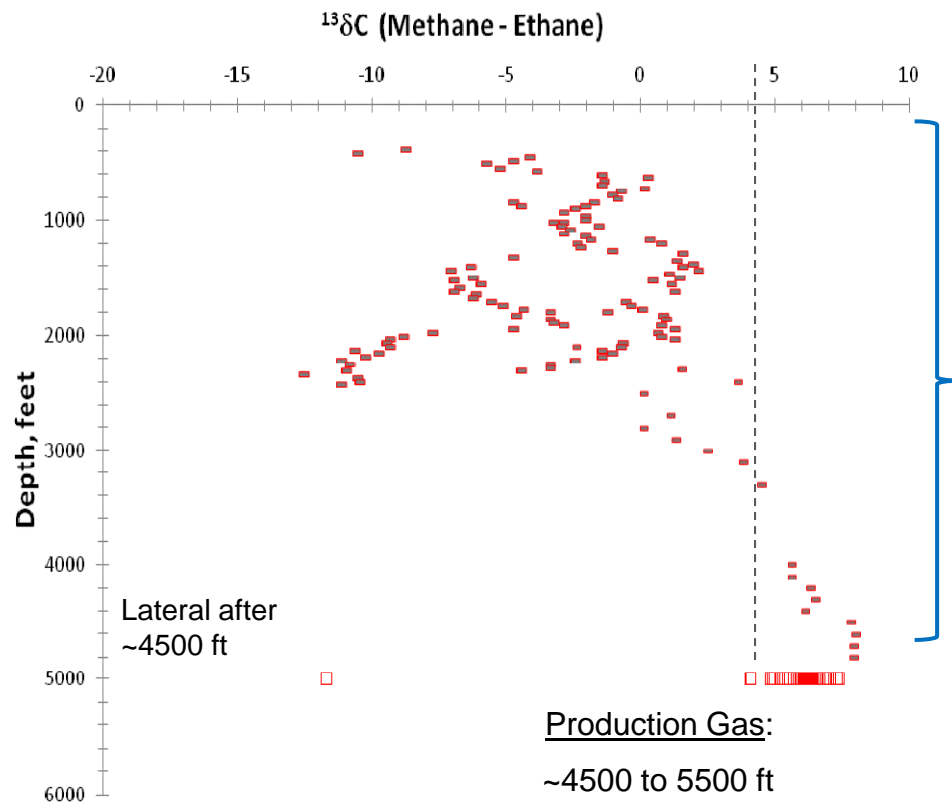
Methane to Ethane Ratio vs ^{13}C -Methane



- Lack of consensus on sampling method for casing headspace and dissolved gas
- Gas analyses and isotopic analyses should be carefully considered using multiple lines of evidence to determine potential gas migration source: Mud gas data, geological data, depth profile, area groundwater quality data are essential
- Conduct pre-drill baseline assessment of groundwater and water supply wells including isotopic analyses of headspace and dissolved gas (methane, ethane, propane+)
- Gas can be present in shallow groundwater and shallow to deep zones above shale prior to hydraulic stimulation operations

ISOTOPE REVERSAL - TIOGA: $^{13}\delta$ C-METHANE & $^{13}\delta$ C-ETHANE

- This correlation may not be applicable in the entire county
- Successful source identification requires multiple lines of evidence and a thorough understanding of site conditions



SUMMARY

■ Groundwater

If indicator parameters (TDS, chloride, sodium) are elevated above pre-drill and/or background conditions in groundwater at a given site or well, further evaluation may be warranted

- Note: Increases in TDS, chloride, and sodium do not always imply connection to deep production water from hydraulic stimulation. Changes in water well operations and water table fluctuations may introduce water from restricted flow zones with relatively high salinity and not from production water

■ Gas

Characterization of pre-drill groundwater and water supply wells, production gas, and shallow mud gas are helpful in gas migration investigations. Multiple lines of evidence are necessary for determination of gas composition and isotopic ratios of carbon and hydrogen (preferably methane, ethane, propane) with respect to depth, geologic strata, structure, etc. In areas where “wet” gas is produced, analysis for BTEX may be considered.

