Energy Opportunity, Environmental Issues and Monitoring

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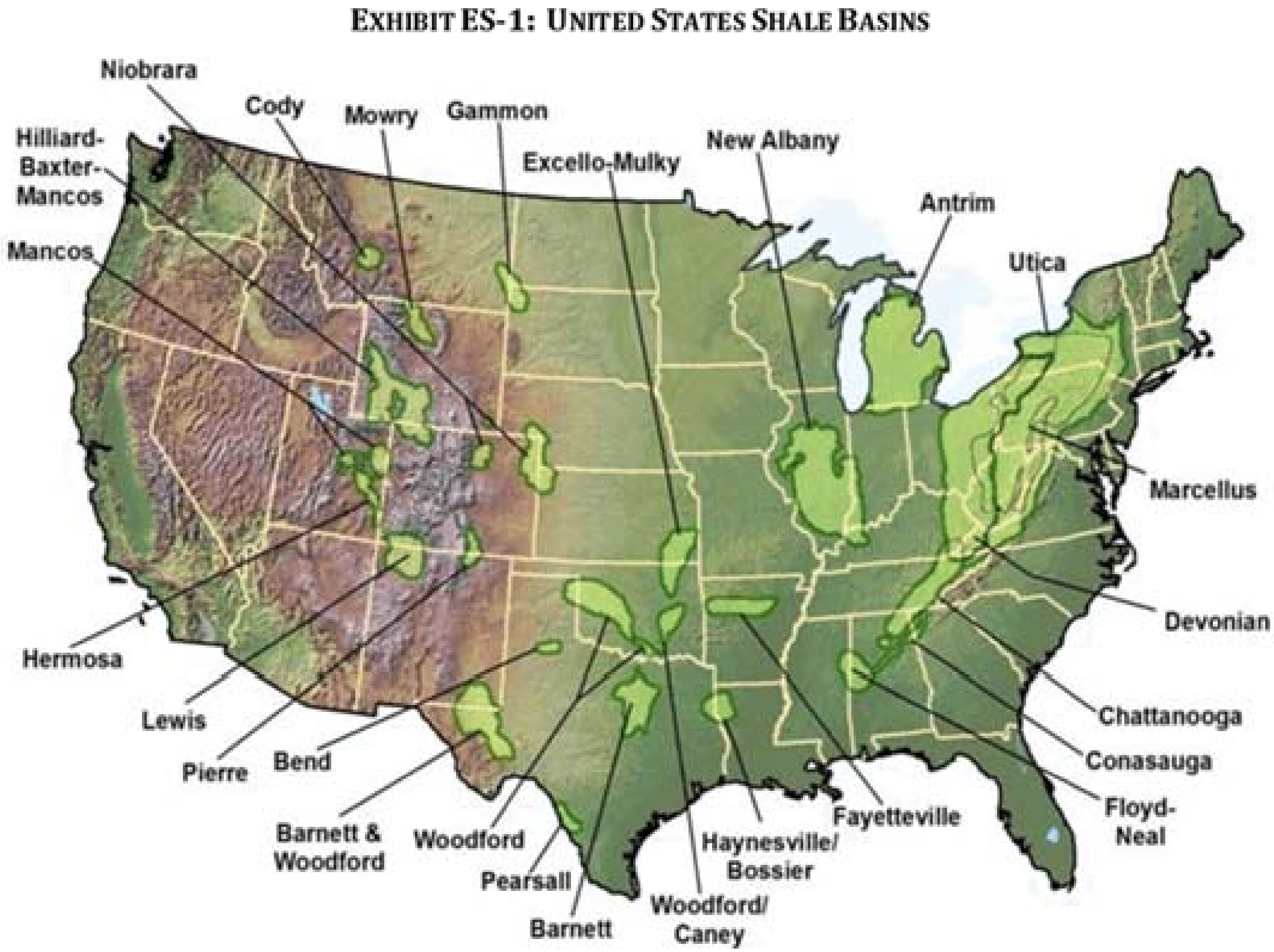
Do Not Drink This Water!

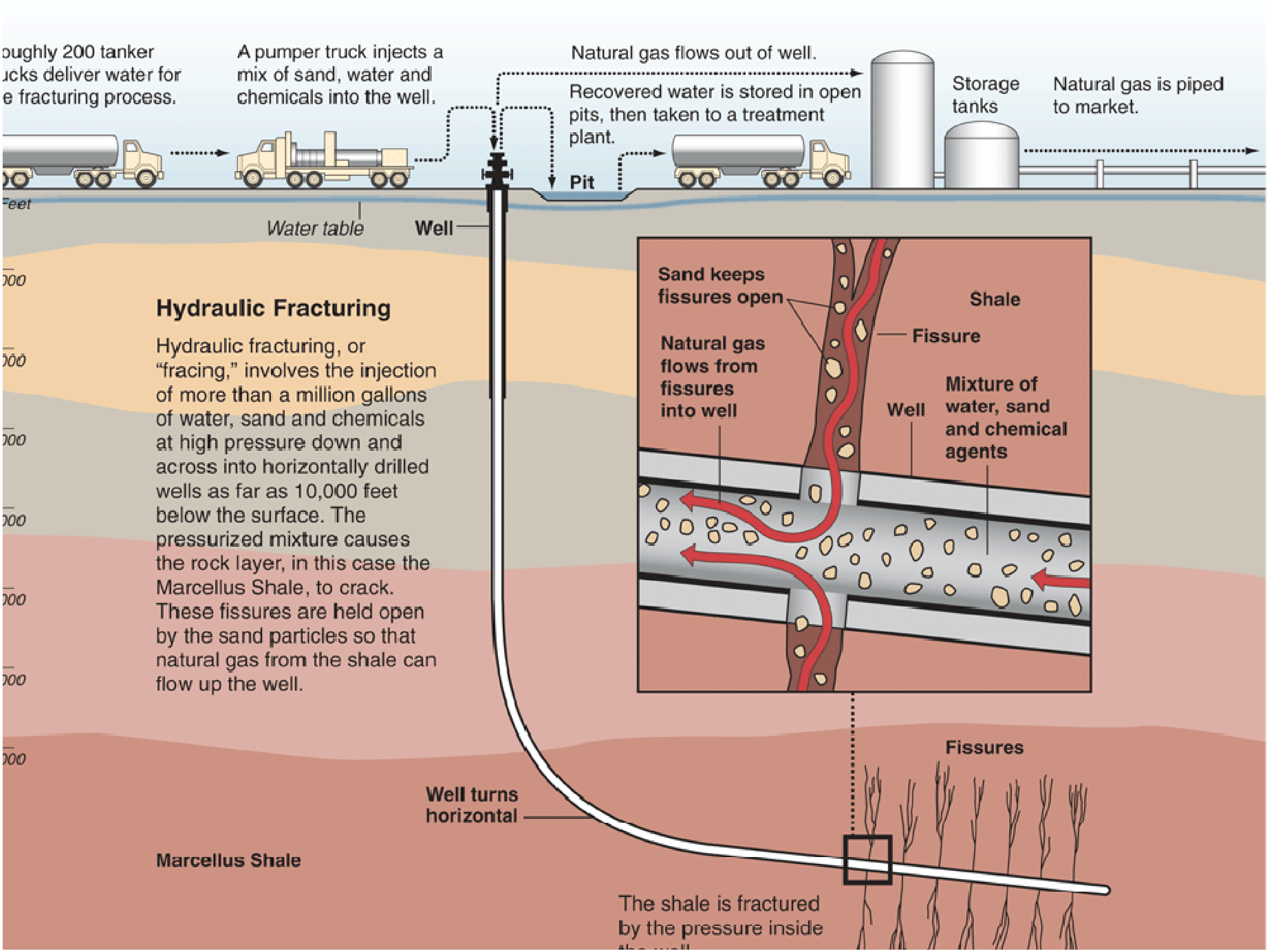
Shale Gas

- **Introduction to the technology**
  - **Horizontal Drilling**
  - **Hydraulic Fracturing**
- **Environmental Issues**
  - **Water Resources**
  - **Chemical Exposures – Water, Air, Waste & Radioactivity**
  - **Safety Culture**
- **Monitoring: Value of Measurement/Testing**

“Gas Equivalent of Two Saudi Arabias!”

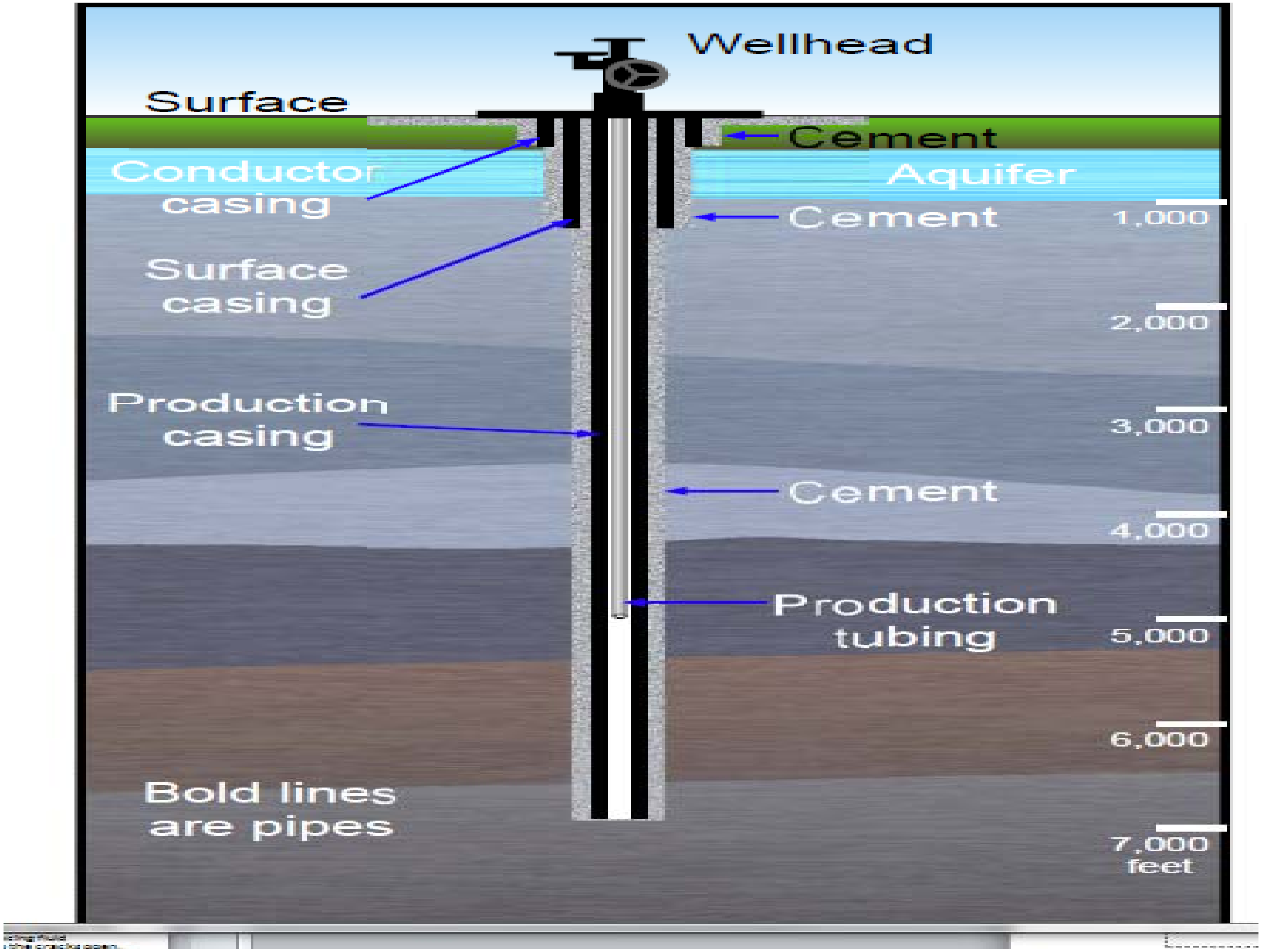


Rig Operation



oughly 200 tanker
ucks deliver water for
e fracturing process.
A pumper truck injects a mix of sand, water and chemicals into the well.
Natural gas flows out of well.
Recovered water is stored in open pits, then taken to a treatment plant.
Pit
Storage tanks
Natural gas is piped to market.
Water table
Well
Hydraulic Fracturing
Hydraulic fracturing, or "fracing," involves the injection of more than a million gallons of water, sand and chemicals at high pressure down and across into horizontally drilled wells as far as 10,000 feet below the surface. The pressurized mixture causes the rock layer, in this case the Marcellus Shale, to crack. These fissures are held open by the sand particles so that natural gas from the shale can flow up the well.
Sand keeps fissures open
Shale
Fissure
Natural gas flows from fissures into well
Well
Mixture of water, sand and chemical agents
Fissures
Well turns horizontal
Marcellus Shale
The shale is fractured by the pressure inside

Basic Well Structure



NATURALLY OCCURRING SUBSTANCES THAT MAY BE FOUND IN HYDROCARBON-CONTAINING FORMATIONS

Type of Contaminant	Example(s)
Formation fluid	Brine[a]
Gases	Natural gas[b] (e.g., methane, ethane), carbon dioxide, hydrogen sulfide, nitrogen, helium
Trace elements	Mercury, lead, arsenic[c]
Naturally occurring radioactive material	Radium, thorium, uranium[c]
Organic material	Organic acids, polycyclic aromatic hydrocarbons, volatile and semi-volatile organic compounds

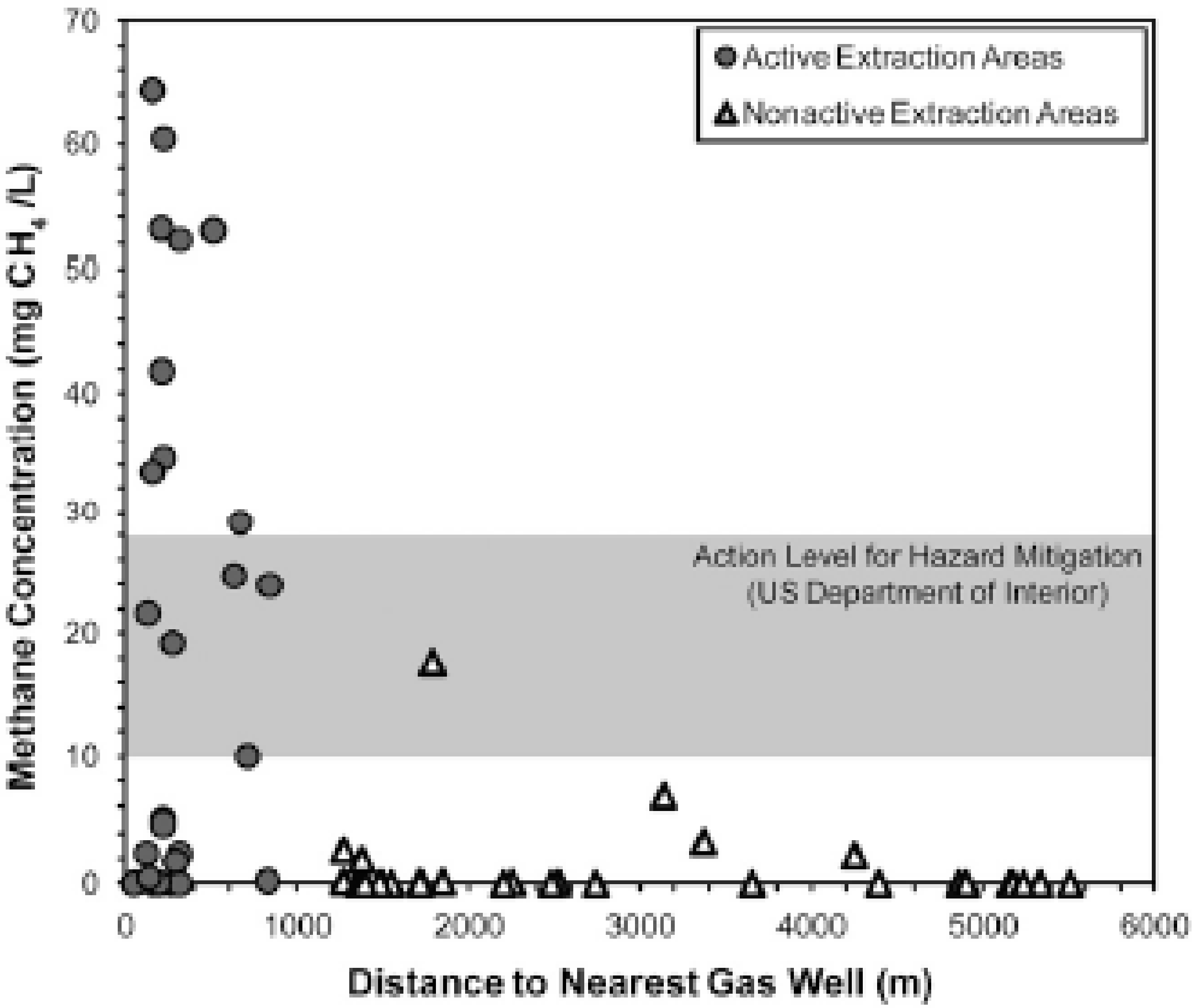
Chemical Used in Hydraulic Fracturing

Table 1. Chemical Components Appearing Most Often in Hydraulic Fracturing Products Used Between 2005 and 2009	
Chemical Component	No. of Products Containing Chemical
Methanol (Methyl alcohol)	342
Isopropanol (Isopropyl alcohol, Propan-2-ol)	274
Crystalline silica - quartz (SiO2)	207
Ethylene glycol monobutyl ether (2-butoxyethanol)	126
Ethylene glycol (1,2-ethanediol)	119
Hydrotreated light petroleum distillates	89
Sodium hydroxide (Caustic soda)	80

AN EXAMPLE OF THE VOLUMETRIC COMPOSITION OF HYDRAULIC FRACTURING FLUID

Component	Example Compound(s)	Purpose	Percent Composition (by Volume)	Volume Chemical (Gallons)a
Water		Deliver proppant	90	2,700,000
Proppant	Silica, quartz sand	Keep fractures open to allow gas flow out	9.51	285,300
Acid	Hydrochloric acid	Dissolve minerals, initiate cracks in the rock	0.123	3,690
Friction reducer	Polyacrylamide, mineral oil	Minimize friction between fluid and the pipe	0.088	2,640
Surfactant	Isopropanol	Increase the viscosity of the fluid	0.085	2,550
Potassium chloride		Create a brine carrier fluid	0.06	1,800
Gelling agent	Guar gum, hydroxyethyl cellulose	Thickens the fluid to suspend the proppant	0.056	1,680
Scale inhibitor	Ethylene glycol	Prevent scale deposits in the pipe	0.043	1,290
pH agent	Sodium or potassium carbonate	Maintain the effectiveness of other components	0.011	330
Breaker	Ammonium persulfate	Allow delayed breakdown of the gel	0.01	300
Crosslinker	Borate salts	Maintain fluid viscosity as temperature increases	0.007	210
Iron control	Citric acid	Prevent precipitation of metal oxides	0.004	120
Corrosion inhibitor	N,N-dimethyl formamide	Prevent pipe corrosion	0.002	60
Biocide	Glutaraldehyde	Eliminate bacteria	0.001	30

Methane in Well Water



Shortcomings from the Duke Study—Lockhaven

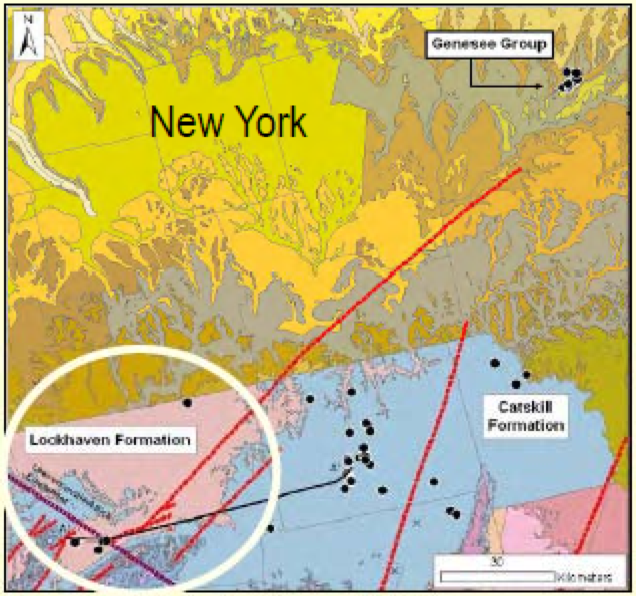
- **Study conclusion: A trend of high methane concentrations in "active" water wells and low concentrations in "nonactive" wells**

Table 1. Mean values ± standard deviation **of methane concentrations (as milligrams of CH_4 L^{-1}) and carbon isotope composition in methane in shallow groundwater $\delta^{13}C$-CH_4 sorted by aquifers and proximity to gas wells (active vs. nonactive)**

Water source, *n*	milligrams CH_4 L^{-1}	$\delta^{13}C$-CH_4, ‰
Active Lockhaver, 7	50.4 ± 36.1	−40.7 ± 6.7

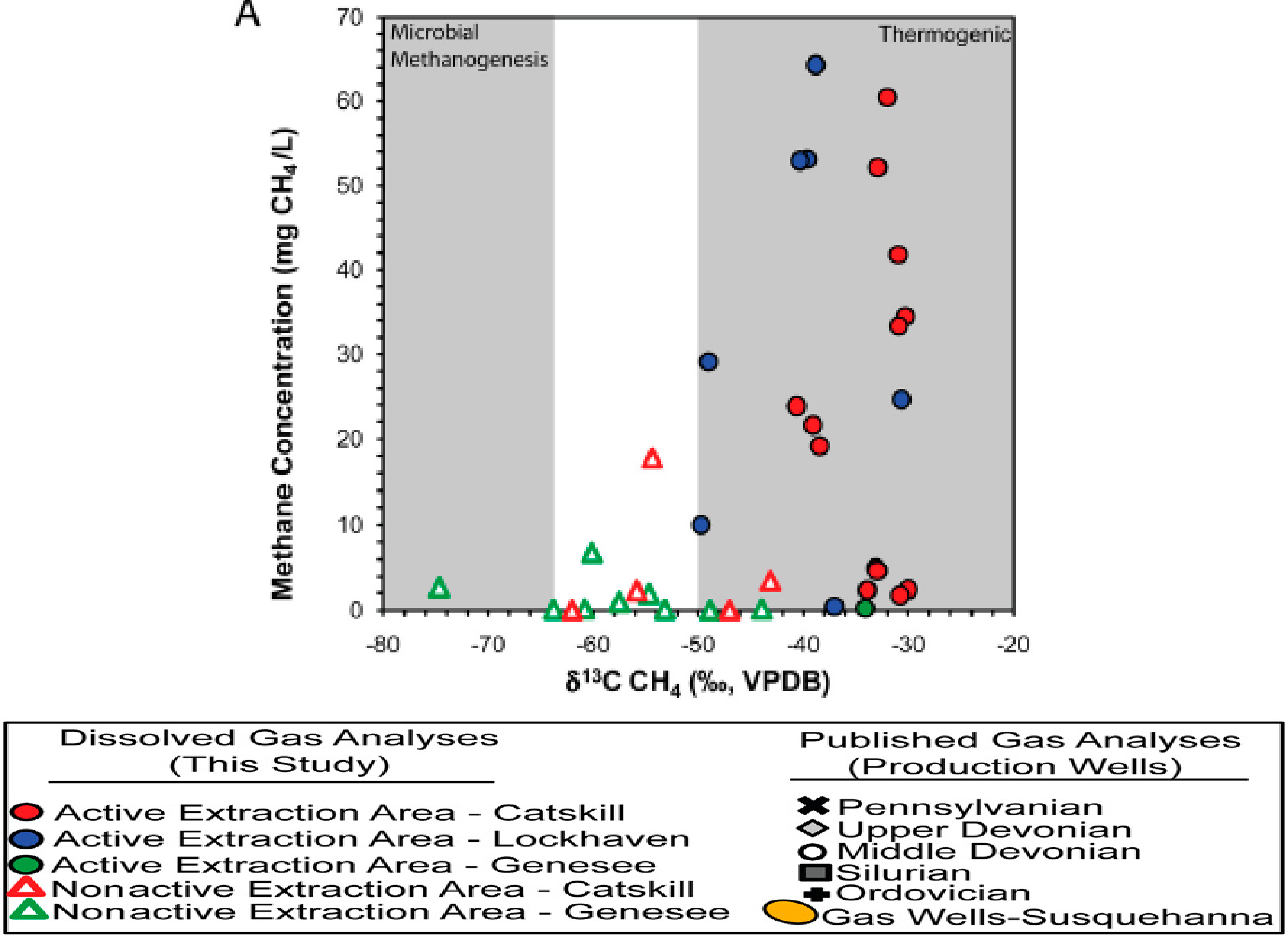
No nonactive wells were sampled.

Sample Locations

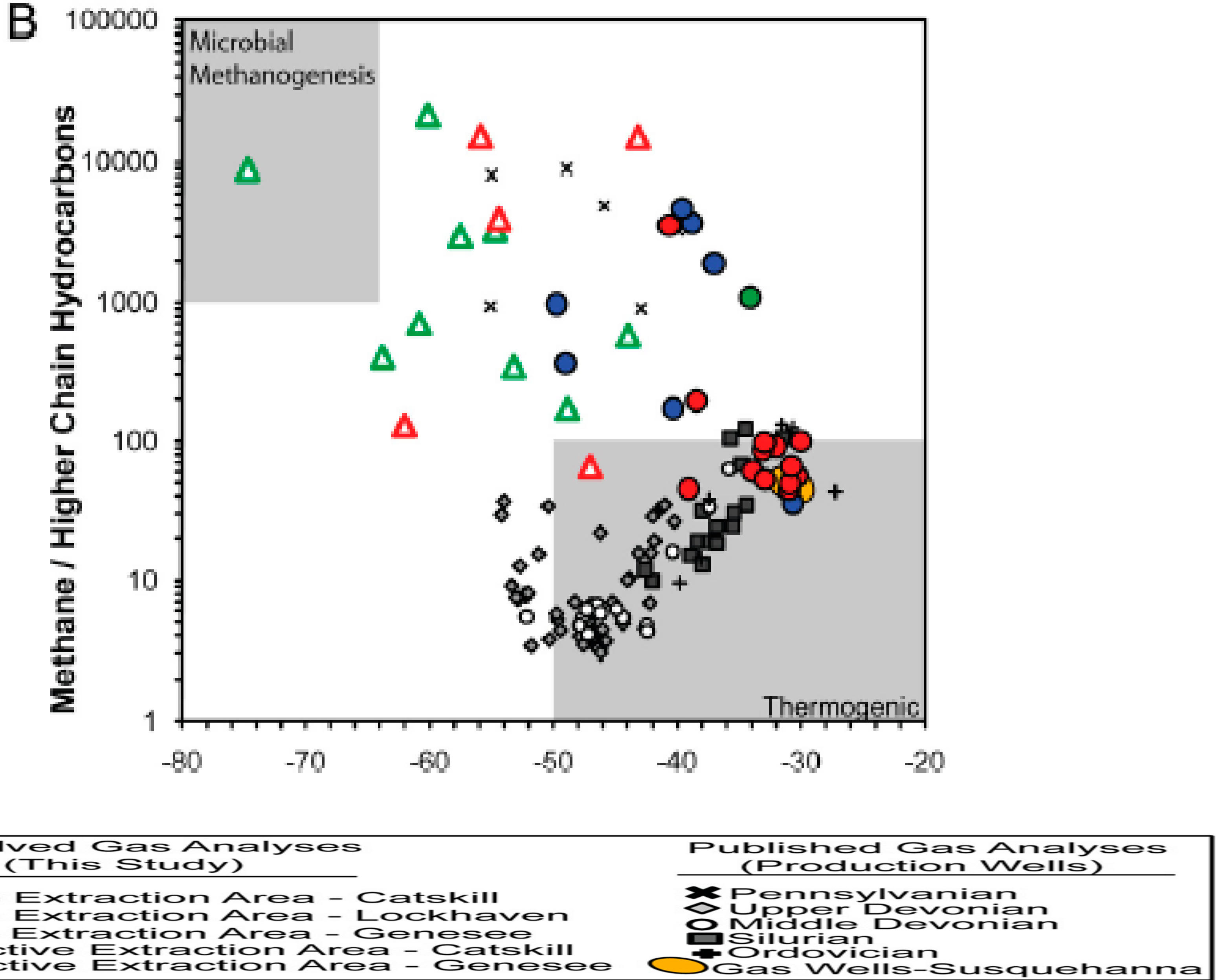


Source: The Duke Study. Osborne et al. (2011)

Methanogenesis vs Thermogenesis

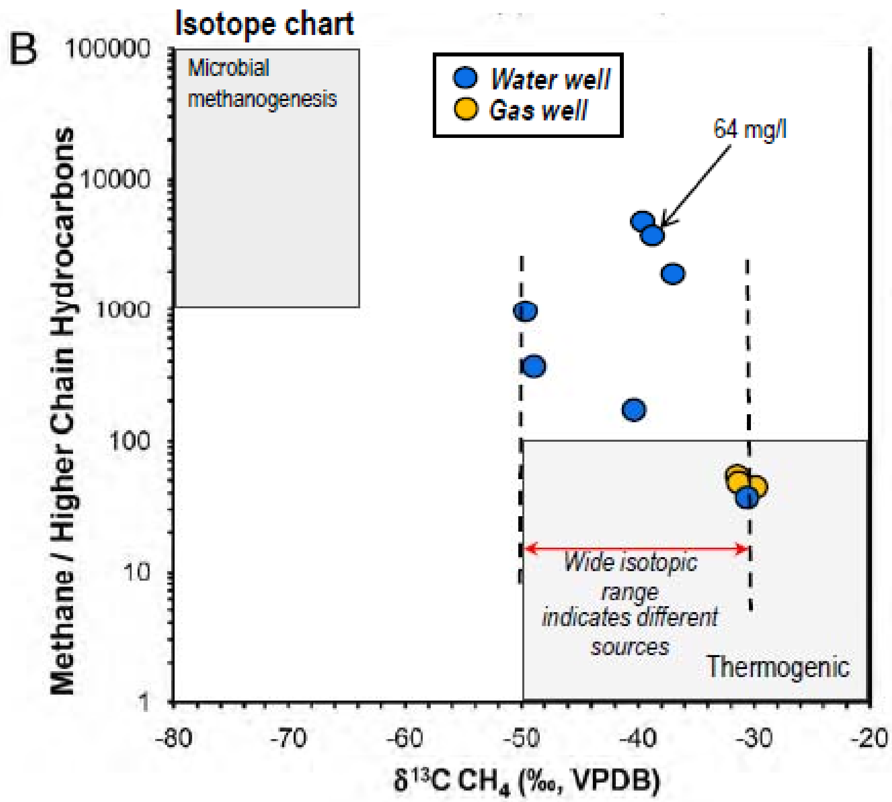


Methanogenesis vs Thermogenesis



Shortcomings from the Duke Study—Lockhaven

- Study conclusion: The thermogenic gas in the water wells is consistent with middle devonian [Marcellus]



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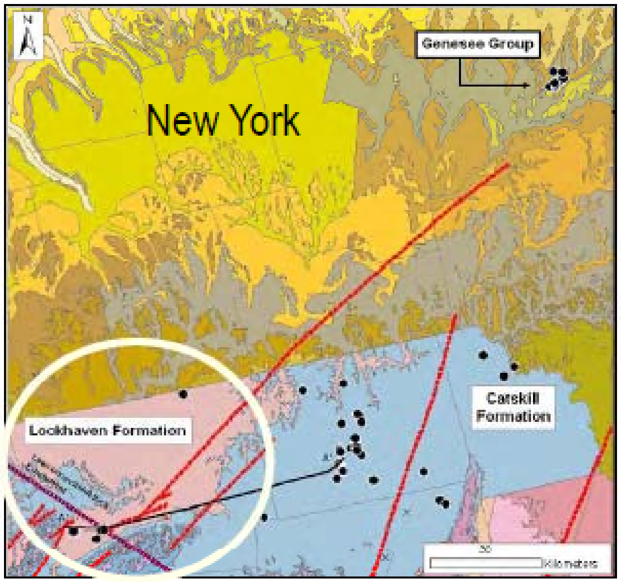

Source: The Duke Study. Osborne et al. (2011)

Comparison of Major Anions and Isotopes In Drinking-Water Wells

	Active		Nonactive	
	Lockhaven formation $N = 8$	Catskill formation $N = 25$	Catskill formation $N = 22$	Genesee group $N = 12$
Alkalinity as HCO_3^-,				
mg L^{-1}	285 ± 36	157 ± 56	127 ± 53	158 ± 56
mM	[4.7 ± 0.6]	[2.6 ± 0.9]	[2.1 ± 0.9]	[2.6 ± 0.9]
Sodium, mg L^{-1}	87 ± 22	23 ± 30	17 ± 25	29 ± 23
Chloride, mg L^{-1}	25 ± 17	11 ± 12	17 ± 40	9 ± 19
Calcium, mg L^{-1}	22 ± 12	31 ± 13	27 ± 9	26 ± 5
Boron, µg L^{-1}	412 ± 156	93 ± 167	42 ± 93	200 ± 130
$\delta^{11}B$ ‰	27 ± 4	22 ± 6	23 ± 6	26 ± 6
^{226}Ra, pCi L^{-1}	0.24 ± 0.2	0.16 ± 0.15	0.17 ± 0.14	0.2 ± 0.15
$\delta^{2}H$, ‰, VSMOW	−66 ± 5	−64 ± 3	−68 ± 6	−76 ± 5
$\delta^{18}O$, ‰, VSMOW	−10 ± 1	−10 ± 0.5	−11 ± 1	−12 ± 1

Monitoring

Key Points

- Using analytical $ wisely to get right balance of tests – type and frequency
- Designing a monitoring program to anticipate emerging environmental regs!
- Ensuring any data passes scrutiny
- Providing legally defense reports.

Program Management Considerations

- **Consistent analytical methods and reporting throughout the the complete cycle of well**
  - **Suitable for all matrices (frac fluid, flowback water, produced water, GW, SW, DW)**
  - **Allows for direct comparison of results through out the life of the well**
  - **Maintain consistent reportling limit and DL**

Components of Quality Program

- **Quality Assurance Project Plan (QAPP)**
- **Quality Control – specific compounds of analytical process that collectively ensures test conformance to set standard limits**
- **Matrix specific QC limits based on validation of QC elements (LCS, Blanks, MS/MSD, calibration verification, MDL verification)**
- **Control limits for each QC item – report the 95% (2 sigma) outcome on client reports.**

Takes Aways!

- Poor casing completion including cementing can allow methane migration into water
- No frac fluids in drinking water have been reported
- Frac fluids, produced water and flow back waters pose analytical challenges
- Technically sound and legally defensible monitoring programs are needed

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Questions & Answers