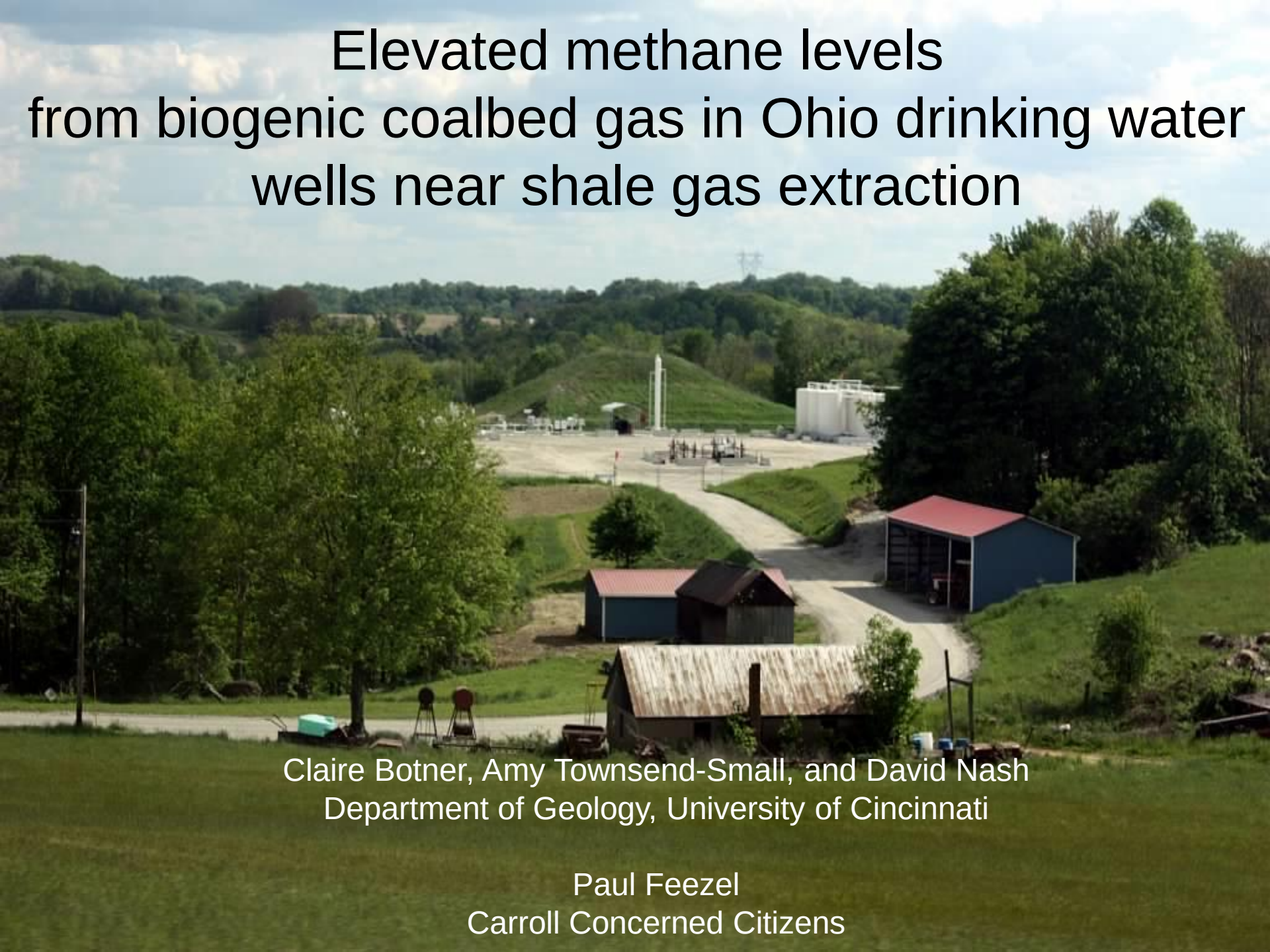
Elevated methane levels from biogenic coalbed gas in Ohio drinking water wells near shale gas extraction



Claire Botner, Amy Townsend-Small, and David Nash
Department of Geology, University of Cincinnati

Paul Feezel
Carroll Concerned Citizens

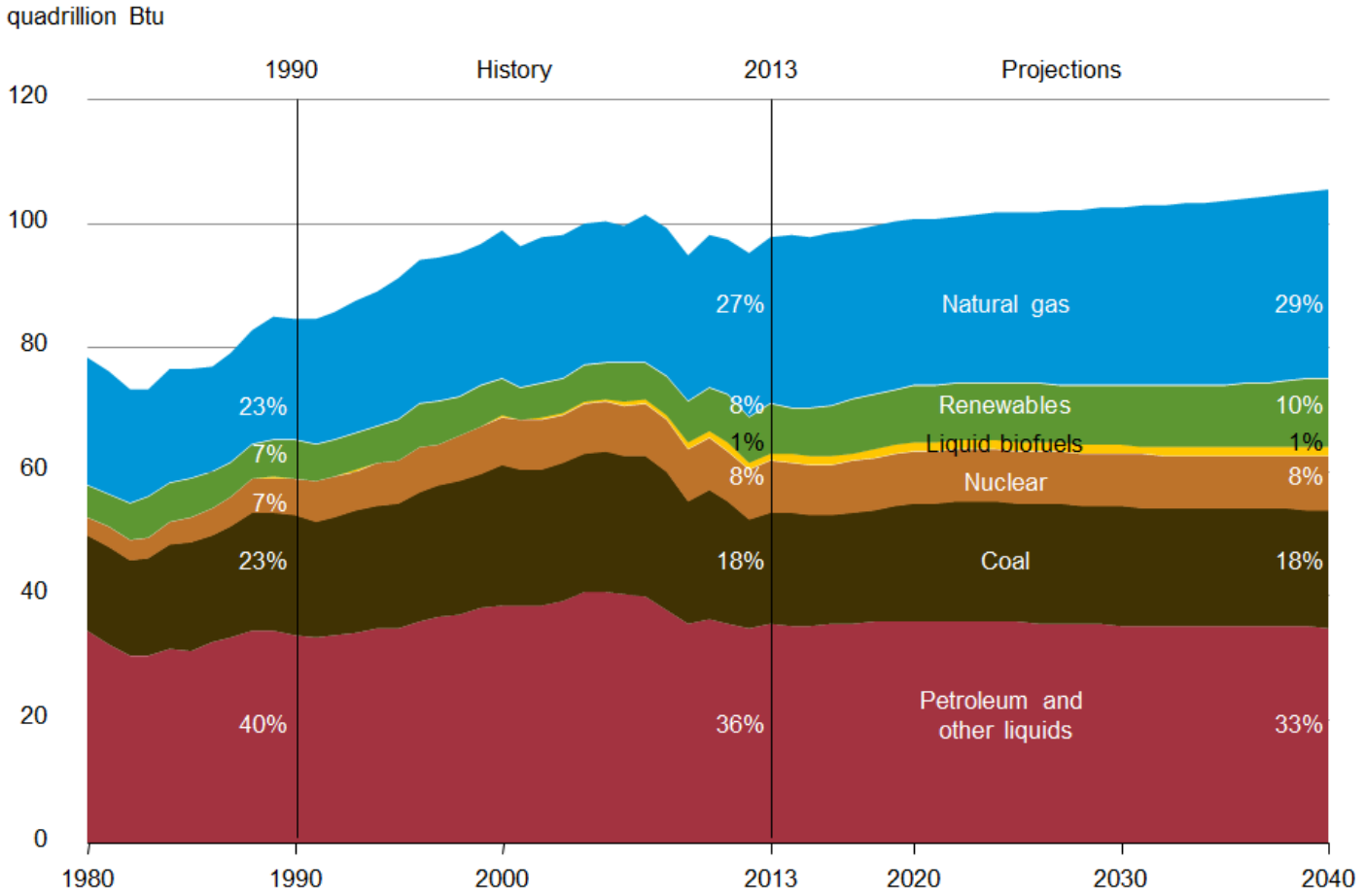
Natural Gas

- Recent glut in natural gas production in U.S.
- Is natural gas a bridge between traditional fossil fuel sources and renewable energy?
- Primary component is methane (CH_4) – a greenhouse gas 34x more powerful than CO_2

warriorpublications.wordpress.com

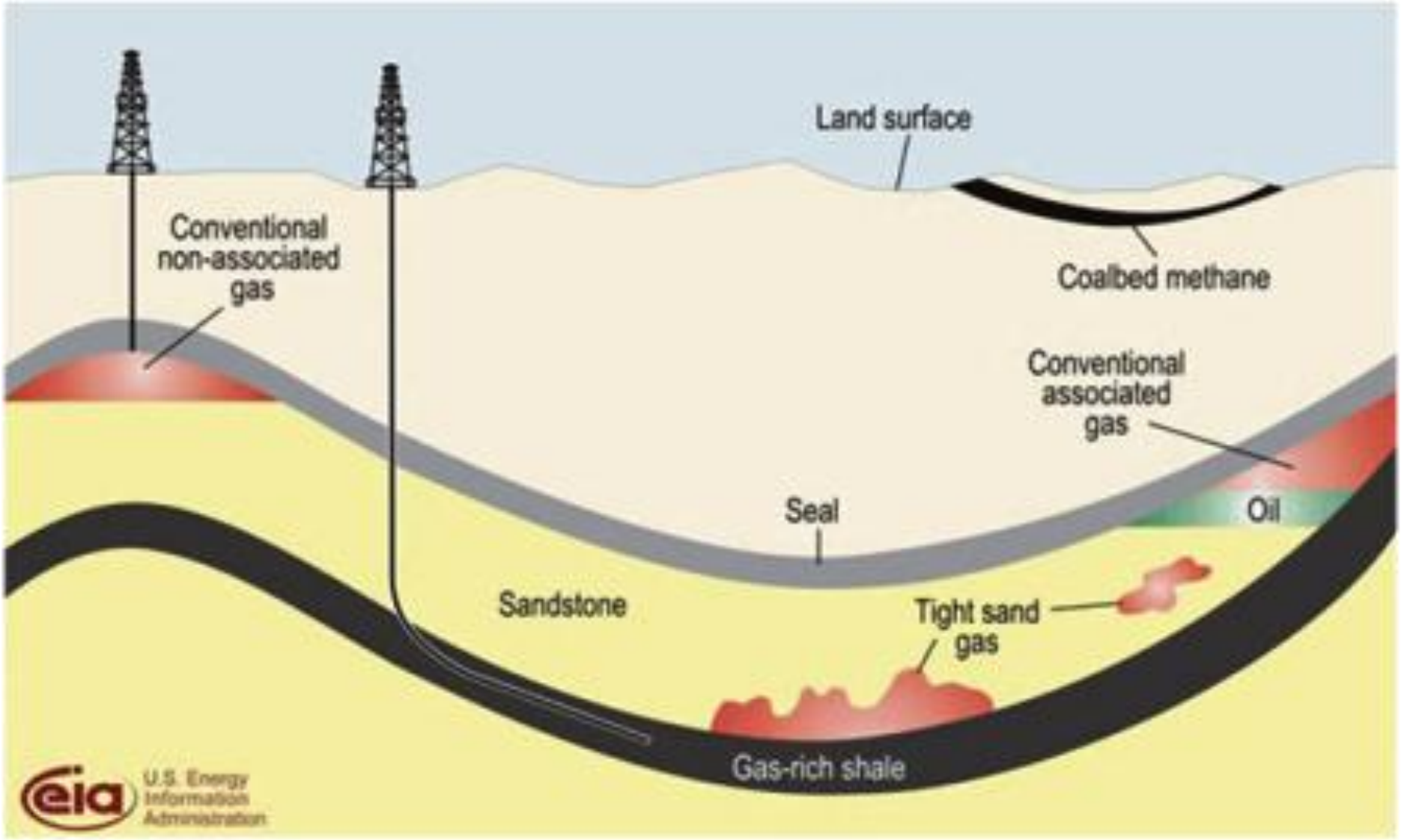
Coal/Oil-To-Gas Transition

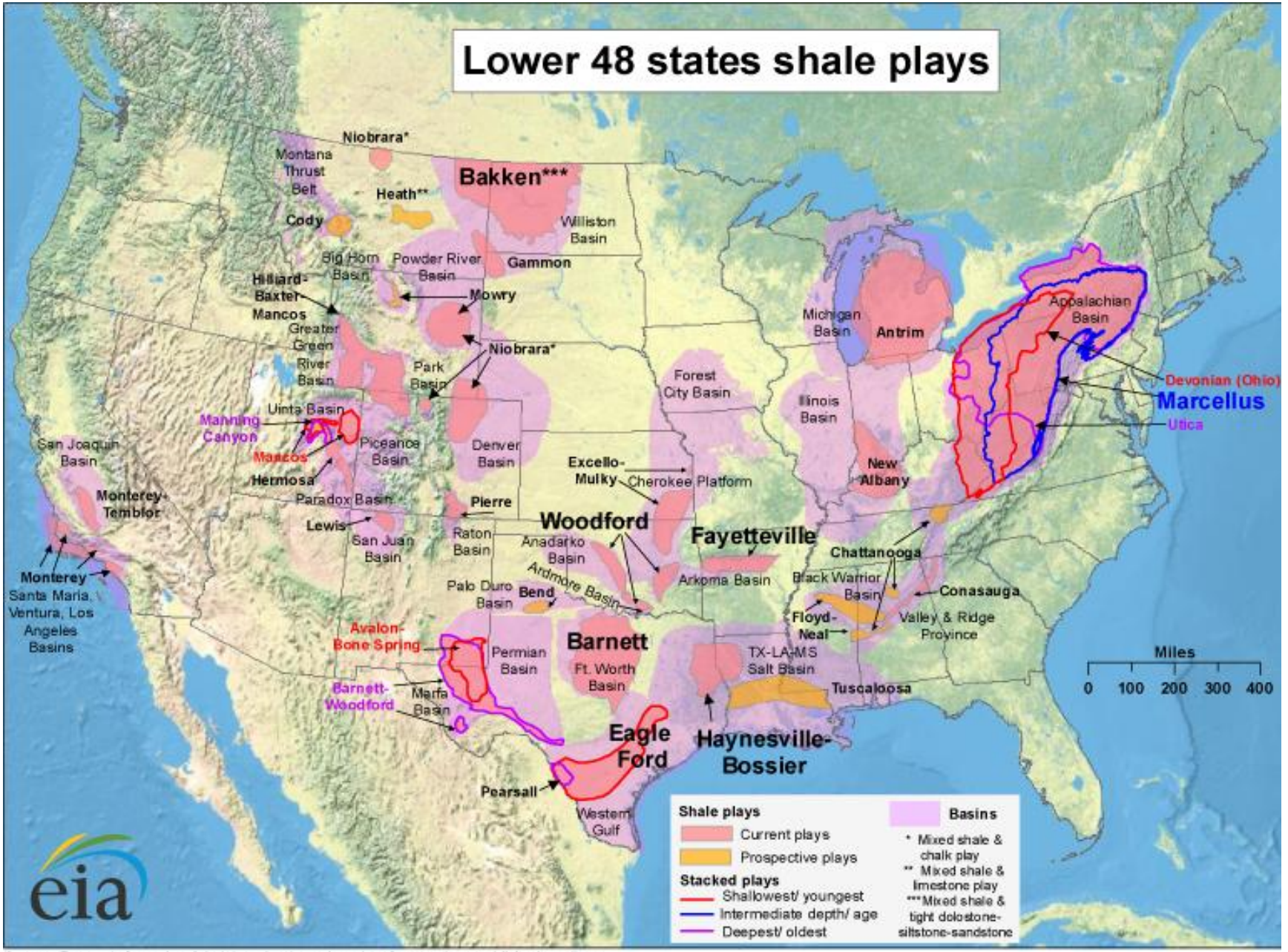
Figure 18. Primary energy consumption by fuel in the Reference case, 1980-2040



United States Energy Information Administration

Conventional vs. Unconventional Drilling





Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

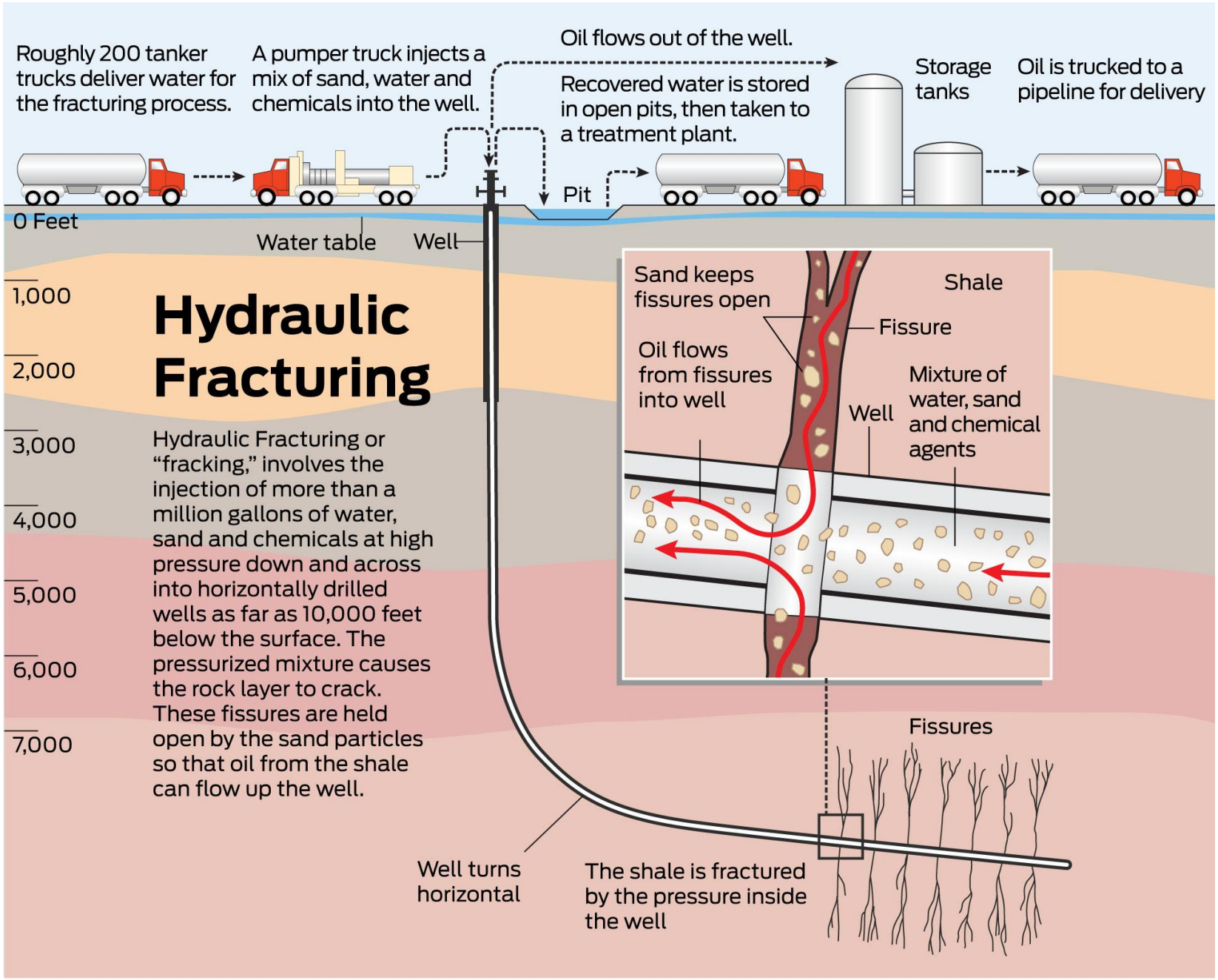
How Fracking Works

1. Vertical drilling ~3 km + horizontal drilling up to 1 km

1. Detonation of explosives in well after drilling

1. A mix of water, sand, and chemicals are pumped at very high pressure into the well to release gas from fissures

Photo credit: Casey White



Source: goodyearlake.org

FRANK VACULIN ● AVALANCHE JOURNAL

Potential Pathways of NG Contamination

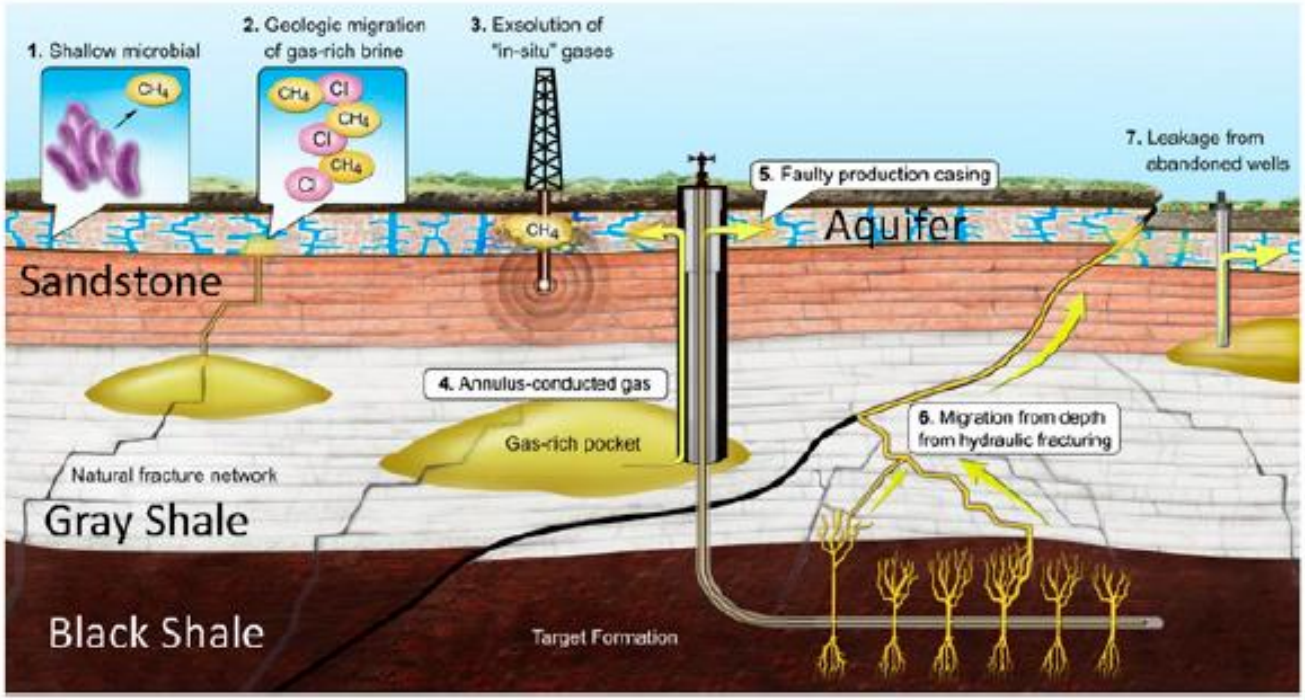


Fig. 1. A diagram of seven scenarios that may account for the presence of elevated hydrocarbon gas levels in shallow aquifers (see discussion in text). The figure is a conceptualized stratigraphic section and is not drawn to scale. Additional scenarios (e.g., coal bed methane and natural-gas pipelines leaking into aquifers) are unlikely in our specific study areas (Figs. S2 and S3).

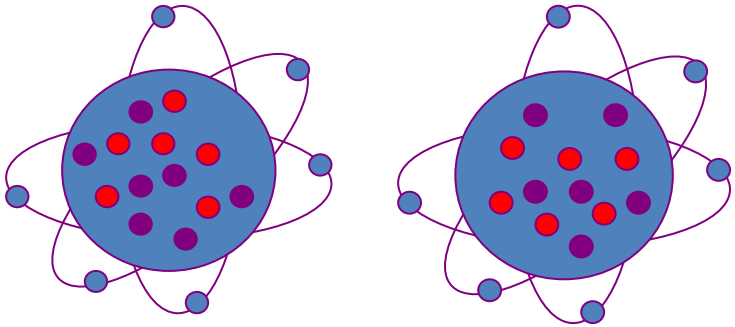
Darrah et al., 2014

Methane: Where can you find it?

- Natural gas: ~95% CH_4
- Two main forms of CH_4
  - **Thermogenic** (created from intense heat and pressure of organic matter deep in the Earth; i.e. **natural gas**, oil)
  - **Biological** (created from microbial methanogensis; i.e. landfills, ruminant animals, wetlands, rice paddy agriculture)
    - Acetate fermentation
    - Carbonate Reduction

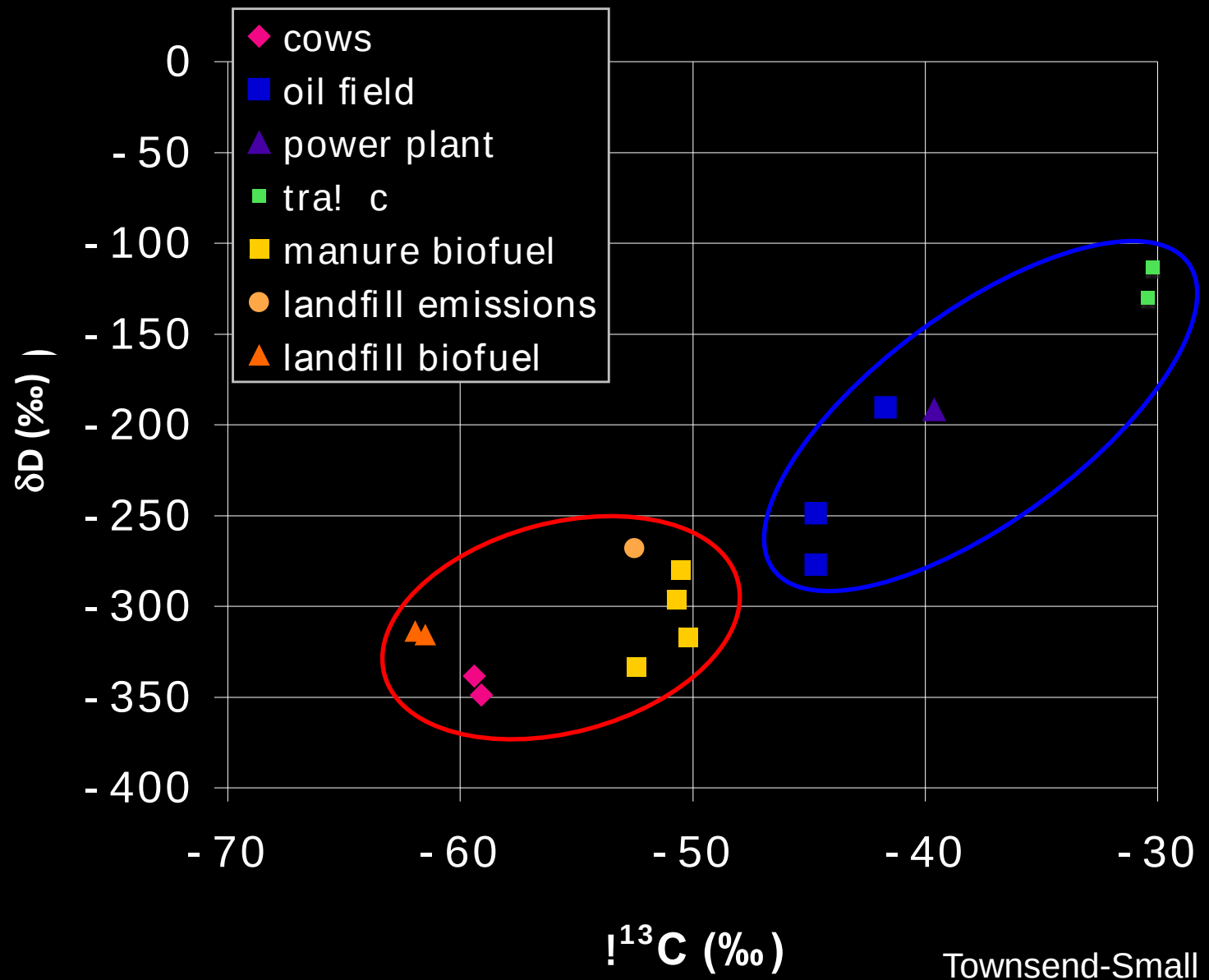
Stable Isotope Primer

- Isotope: Atom of a specific element that differs in the number of neutrons in the nucleus
- Isotopes with an extra neutron have the same chemistry but are slightly heavier than other atoms of the same element
- Stable isotopes of methane:
- Hydrogen
  - Hydrogen-1 (99.98% of all H atoms)
  - Hydrogen-2 (deuterium or D) (0.01%)
- Carbon
  - Carbon-12 (98.9%)
  - Carbon-13 (1.1%)



Carbon-13 Carbon-12

C and H stable isotopes of CH_4



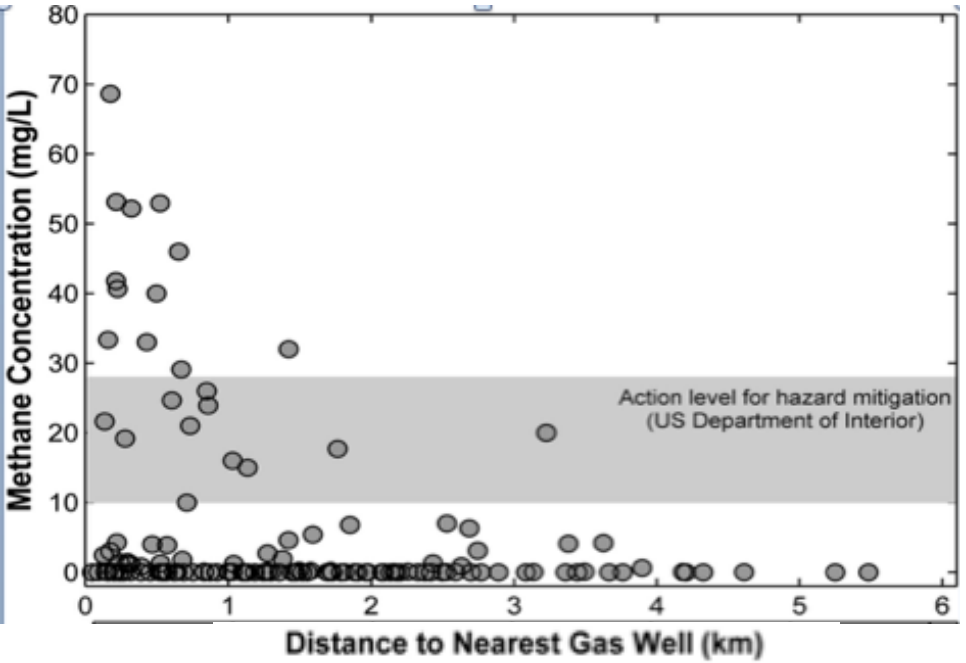
Townsend-Small et al., 2012

What is the problem?

- Is hydraulic fracturing contributing to methane found in groundwater resources of the Utica Shale?

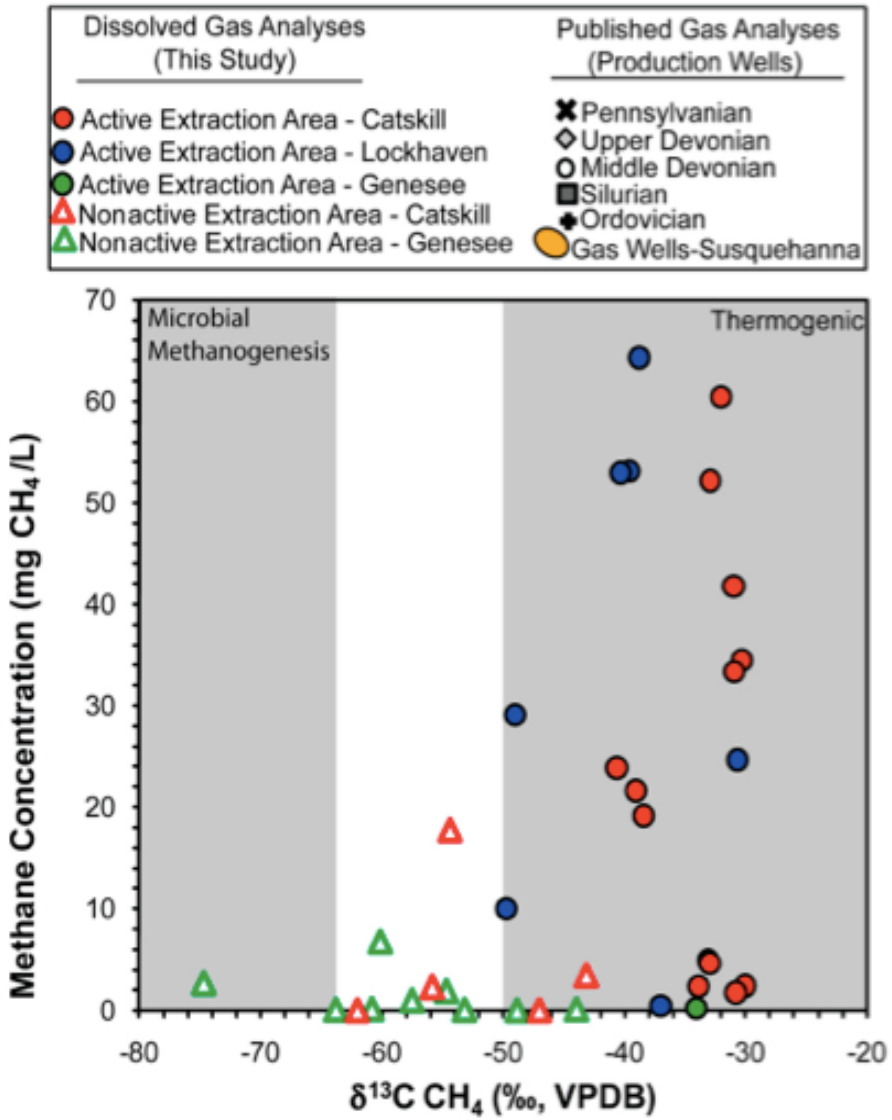
- Previous studies (Osborn *et al.,* 2011; Jackson *et al*., 2013) found that natural gas was present in groundwater resources after the onset of fracking in the Marcellus Shale
  - Utilization of stable carbon isotope analysis

- Our study aims to measure methane and its sources in groundwater before, during, and after the onset of fracking



Jackson et al., 2013

Osborn et al., 2011



Fracking and water resources

- Each well takes several million gallons of water to "frack"
  - Additives
    - Sand
    - Acids
    - Biocides
    - Salts
    - Antifreeze
    - Corrosion inhibitors
  - Some specific chemicals are proprietary and drillers need not disclose their formulas, although many do voluntarily

Fracking and water resources

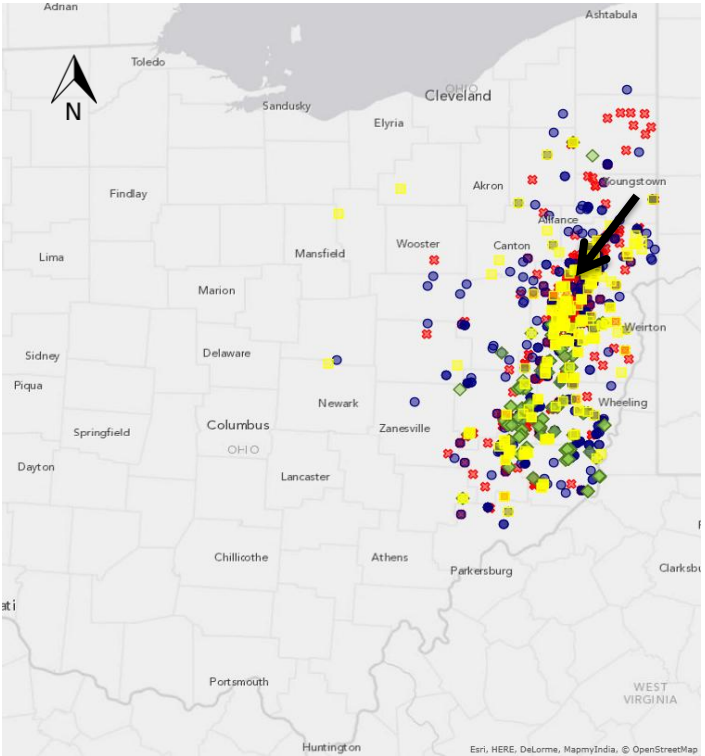
- After fracturing, water is returned to the surface with additional solutes from interactions with the shales
  - Salts
  - Methane
  - Hydrocarbons (benzene, etc.)
  - Radioactive materials
- Disposal or reuse

youtube.com

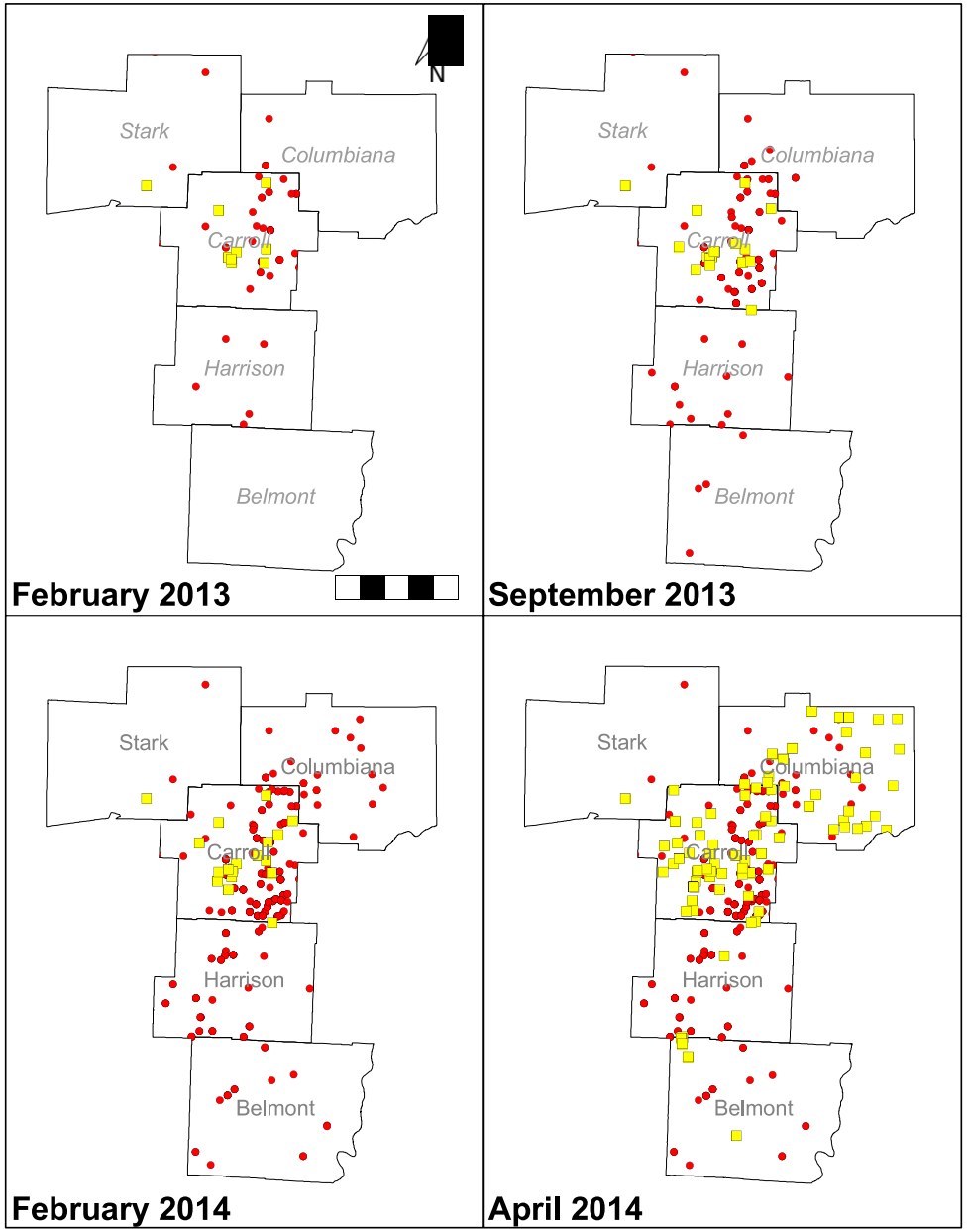
Highly viewed YouTube video showing drinking water with high levels of methane

Study Area

- Permitted
- Drilling
- Drilled
- Producing



14-Month Time-Series of Active Gas Wells and Sampled Groundwater Wells in Eastern OH



Legend

- Water Well
- Active Gas Well

Methods

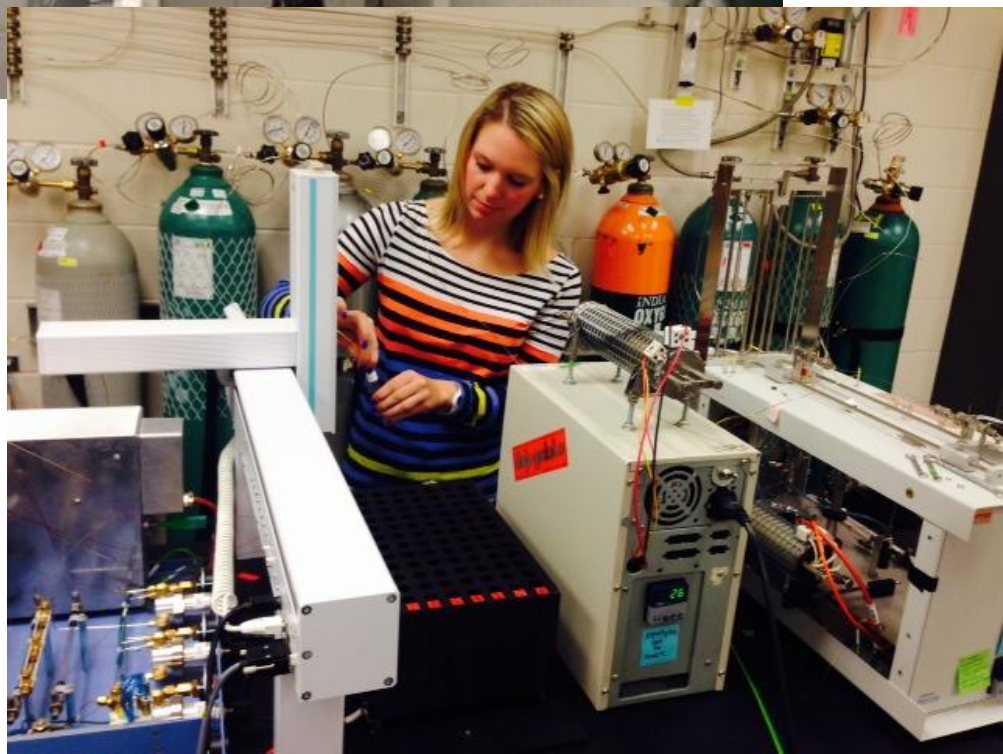
- Teamed with Carroll Concerned Citizens to recruit participants
- Private groundwater well sampling in Carroll County, Ohio and surrounding area
  - 23 wells sampled from 2012 to Feb. 2015 three to four times a year
    - 191 samples total
  - Larger campaign in May 2014

What was measured?

- CH_4 Concentration
- Stable isotope composition of methane
  - $\delta^{13}C$ and δD
- pH and Conductivity
  - Indicators of fracking fluid contamination
- $\Delta^{14}C$ analysis

University of Cincinnati's Stable Isotope Facility

Carbon and hydrogen isotope analysis performed with an isotope ratio mass spectrometer



Dr. Amy Townsend-Small
Department of Geology
University of Cincinnati
PO Box 210013
Cincinnati, OH 45221-0013

500 Geology/Physics Bldg.
Phone: (513) 556-3763
Fax: (513) 556-6931

Date: May 22, 2014
Participant names: John Doe
Address: 100 Main Street Carrollton, OH 44615

Water Sampling Test Results

Introduction: The following data were gathered during a research project investigating impact of hydraulic fracturing ("fracking") on groundwater resources in Carroll County, Ohio. These results will not be associated with your name, address or well location on any scientific publications, nor will your personal information be shared with anyone else. Questions? Contact Dr. Townsend-Small.

Sampling Date	Type	Electrical conductivity (microsiemens per centimeter)	pH	Temp. (°C)	Total dissolved organic carbon (milligrams per liter)	Total dissolved nitrogen (milligrams per liter)	Dissolved methane (milligrams per liter)	Carbon isotopic composition of methane ($\delta^{13}C$; ‰)	Benzene, toluene, ethylbenzene, and xylene (BTEX) (micrograms per liter)
3/8/2014	G/W	753	NM	12.8	0.7	0.3	4.123	-66.5	NM
5/25/2014	G/W	863	8.24	16.9	0.4	0.3	18.610	NM	NM

NM = not measured

Explanation of Results

Type: GW = groundwater; SW = surface water (probably collected at a stream near your house)

Electrical conductivity: This is a measurement of the total amount of dissolved salts in your water. Most groundwater in this area has conductivity between 100 and 500 mS/cm. Measurements in the 1000 to 10,000 uS/cm range may indicate salty brine water is present.

pH: The acidity of your water. A pH value of 7 indicates neutral acidity. Most wells in this area have a pH of between 6 and 8.5. A lower pH may indicate the presence of additional acid.

Total dissolved organic carbon: This indicates the abundance of organic carbon molecules in water. Most unpolluted waters have values between 0.5 and 10 mg/L.

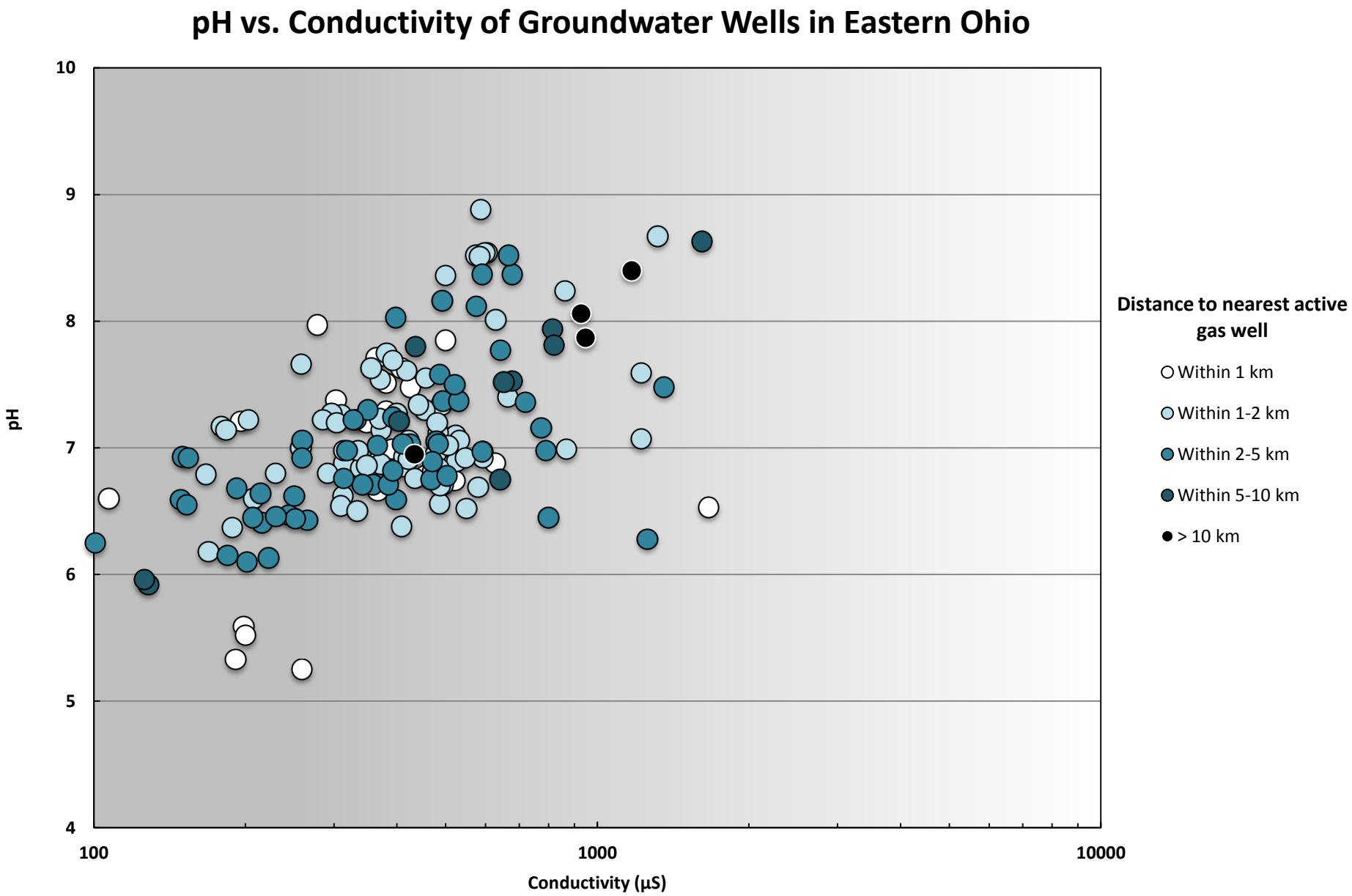
Total dissolved nitrogen: The total amount of dissolved nitrogen in your water. This could be derived from natural materials in soil, from fertilizer, or from human or animal waste. Most unpolluted waters have values between 0.05 and 0.7. Higher values may indicate the presence of fertilizer or wastewater.

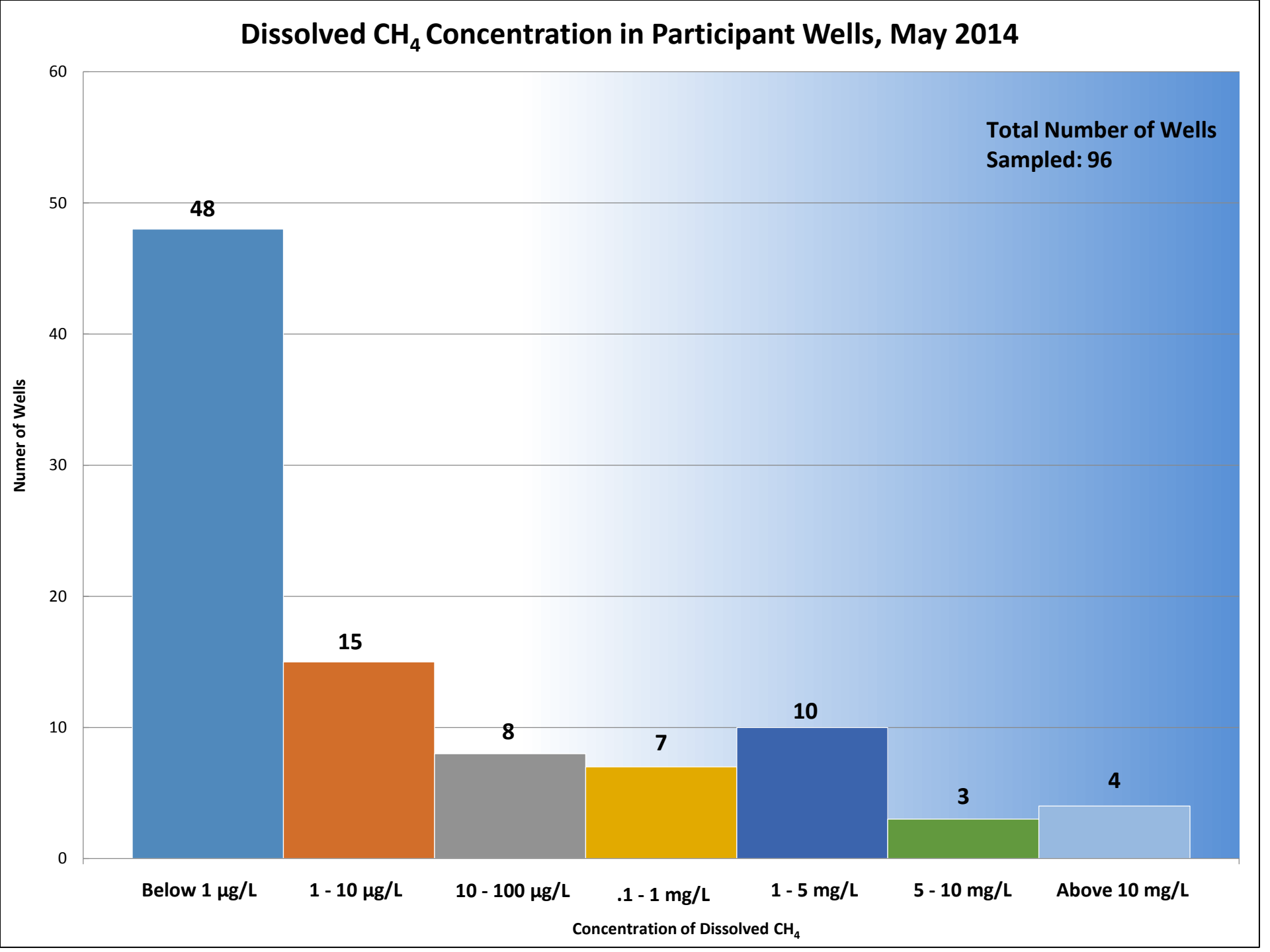
Dissolved methane: Methane is the primary component of natural gas, and is also naturally produced by harmless microbes living in oxygen-free environments, such as at the bottom of lakes or in mud. The presence of methane in groundwater is normal. Methane levels over 10 mg/L may indicate the presence of natural gas, but this can be confirmed with stable isotope analysis.

Carbon isotopic composition of methane: This is a way to determine the source of methane. Methane derived from natural gas has a value between -45 and -30‰. Methane from naturally occurring microbes has a value between -70 and -50‰. We are currently analyzing a backlog of samples for carbon isotopes so more data are forthcoming.

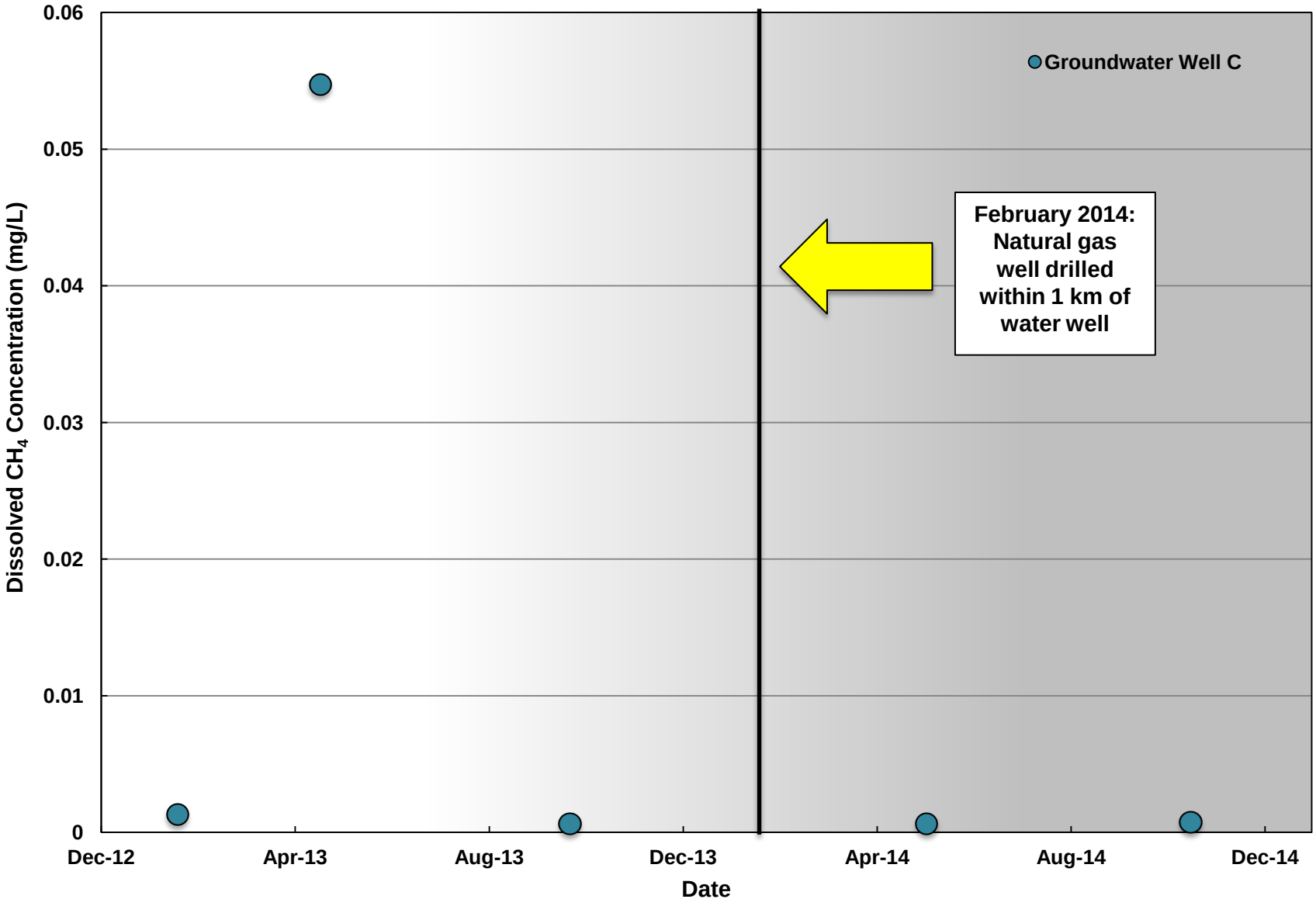
Benzene, toluene, ethylbenzene, and xylene: This suite of chemicals (sometimes referred to as BTEX) represents the carcinogenic component of natural gas. Any BTEX chemical present in your water represents a health hazard. We are currently seeking more funding for further analyses of these chemicals.

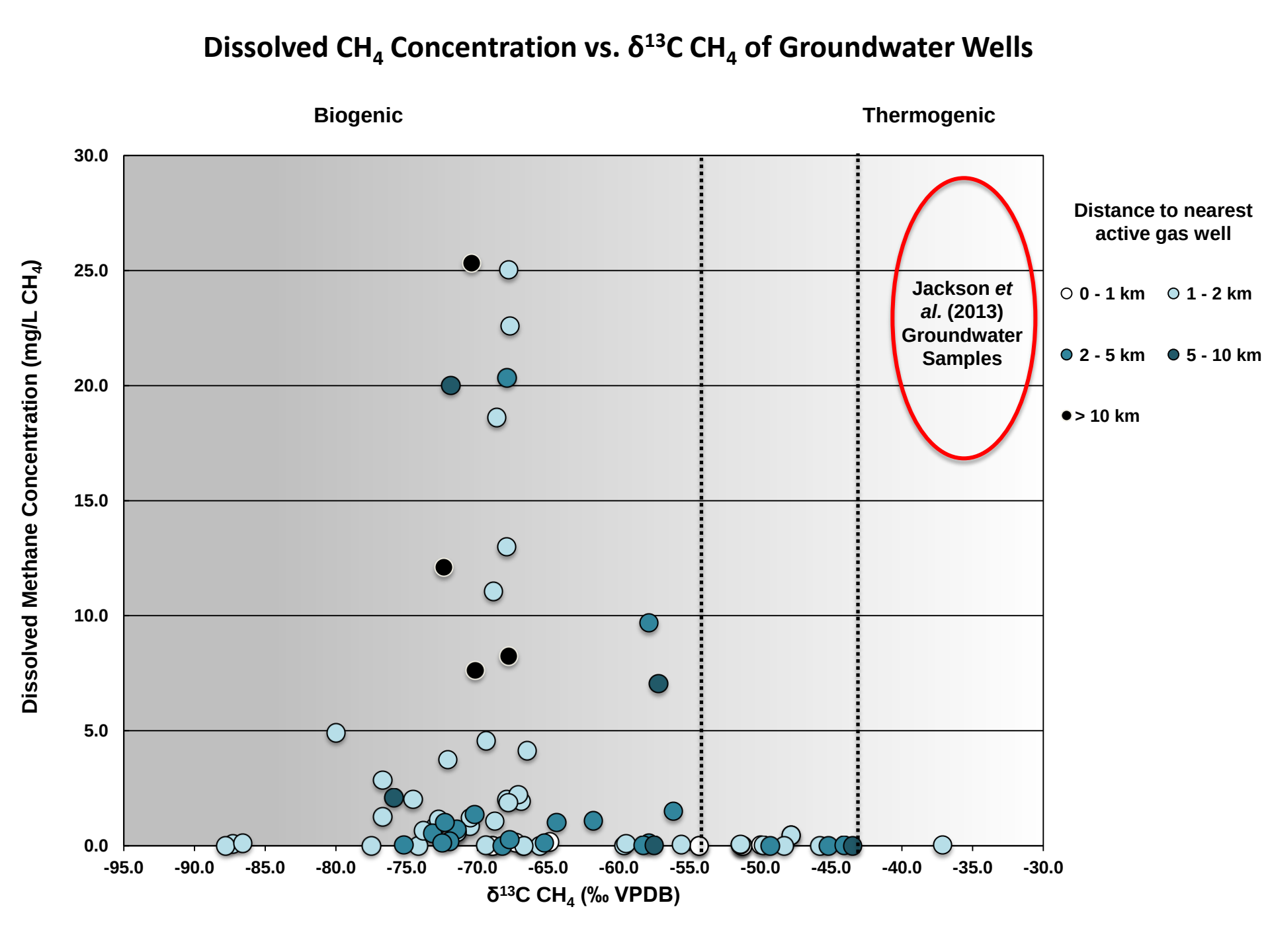
Results


pH vs. Conductivity of Groundwater Wells in Eastern Ohio
10
9
8
7
6
5
4
pH
100
1000
10000
Conductivity (µS)
Distance to nearest active gas well
Within 1 km
Within 1-2 km
Within 2-5 km
Within 5-10 km
> 10 km

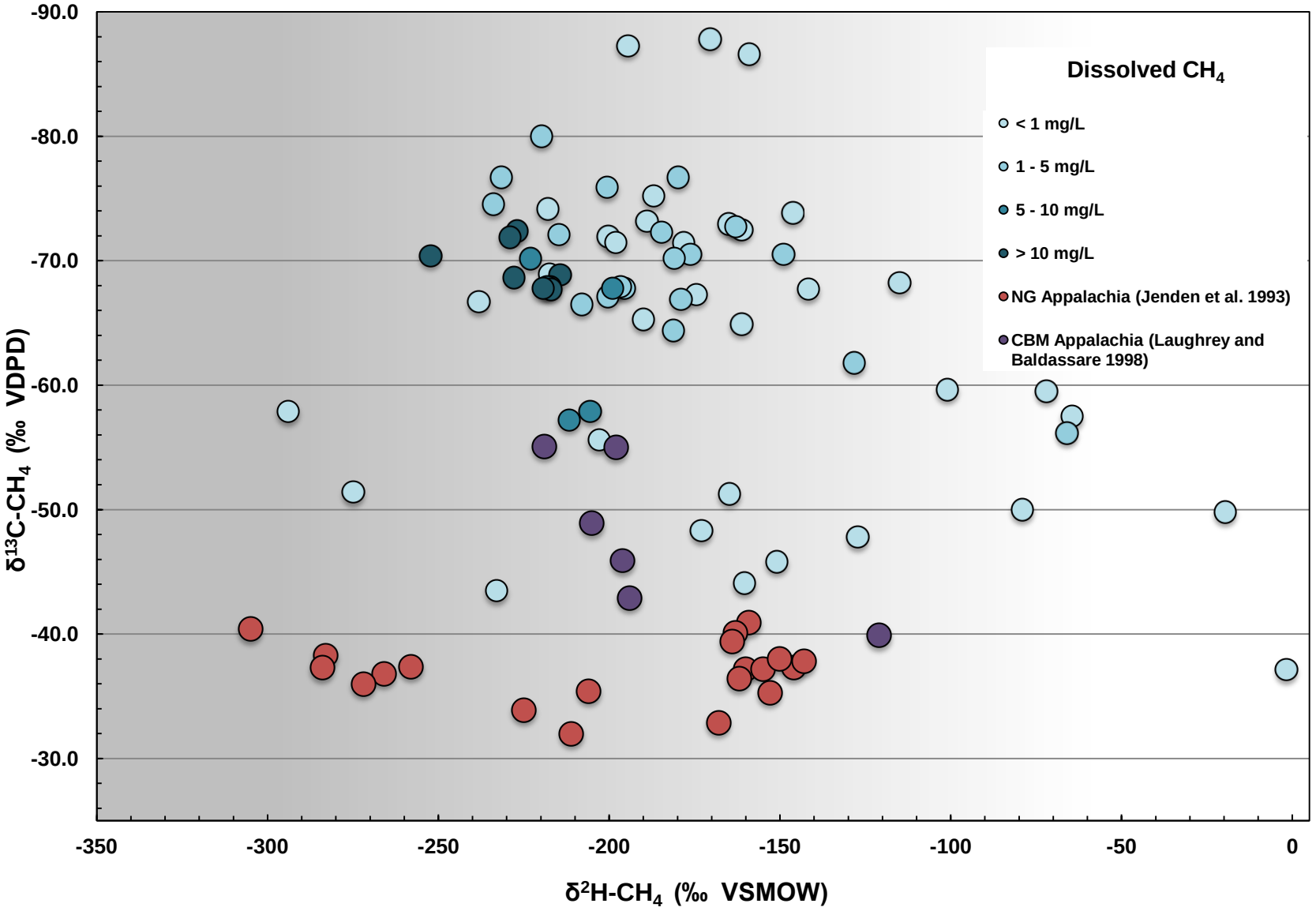

Dissolved CH4 Concentration in Participant Wells, May 2014
Total Number of Wells Sampled: 96
Numer of Wells
60
50
40
30
20
10
0
48
15
8
7
10
3
4
Below 1 µg/L
1 - 10 µg/L
10 - 100 µg/L
.1 - 1 mg/L
1 - 5 mg/L
5 - 10 mg/L
Above 10 mg/L
Concentration of Dissolved CH4

Time Series of CH_4 Levels in Groundwater Well "C"



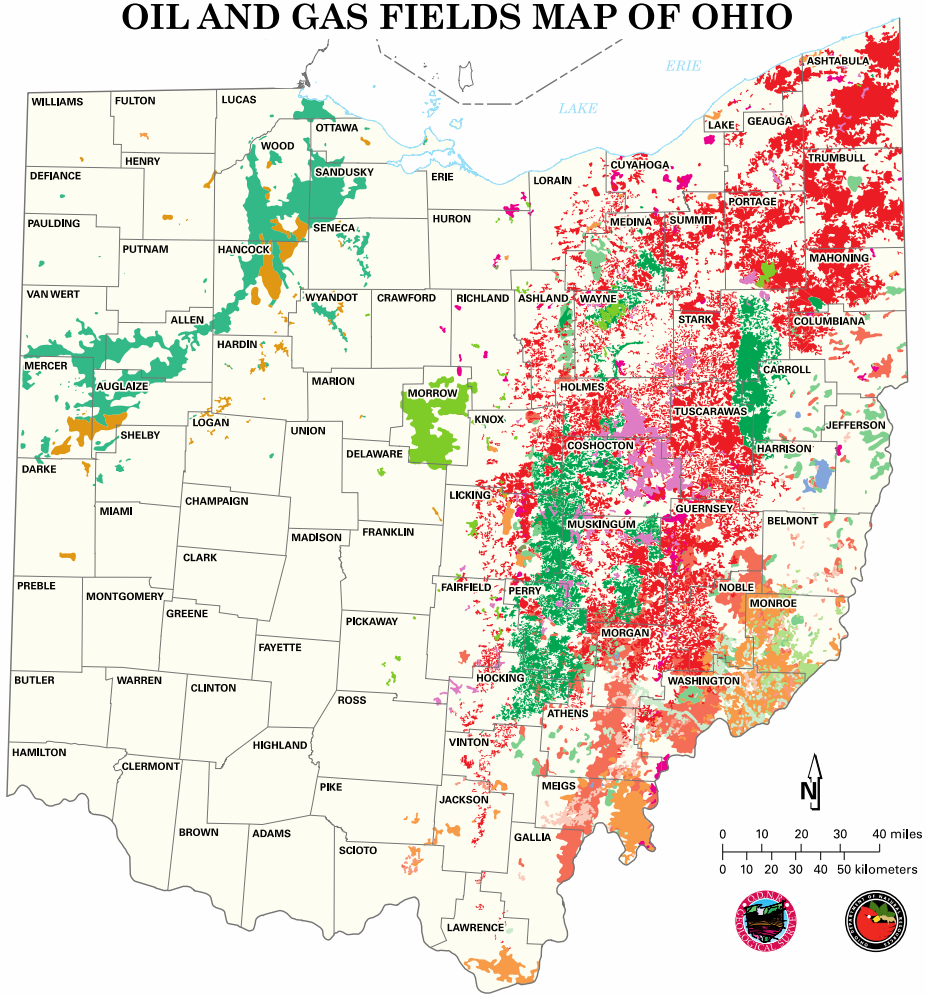

Dissolved CH4 Concentration vs. δ13C CH4 of Groundwater Wells
Biogenic
Thermogenic
Dissolved Methane Concentration (mg/L CH4)
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-95.0
-90.0
-85.0
-80.0
-75.0
-70.0
-65.0
-60.0
-55.0
-50.0
-45.0
-40.0
-35.0
-30.0
δ13C CH4 (‰ VPDB)
Jackson et al. (2013) Groundwater Samples
Distance to nearest active gas well
0 - 1 km
1 - 2 km
2 - 5 km
5 - 10 km
> 10 km

$\delta^{13}C\text{-}CH_4$ vs. $\delta^{2}H\text{-}CH_4$ of Groundwater Samples and Previously Reported Appalachian Natural Gases



STATE OF OHIO • DEPARTMENT OF NATURAL RESOURCES • DIVISION OF GEOLOGICAL SURVEY

OIL AND GAS FIELDS MAP OF OHIO



EXPLANATION

OIL FIELD | GAS FIELD | COALBED METHANE

PRODUCING HORIZON(S) GROUPED BY STRATIGRAPHIC INTERVAL

- Pennsylvanian undifferentiated sandstones and coals
- Mississippian undifferentiated sandstones and Maxville Limestone
- Devonian Berea Sandstone and Cussewago Sandstone
- Devonian Ohio Shale and siltstones
- Silurian-Devonian "Big Lime" interval
- Silurian "Clinton/Medina" sandstone and "Packer Shell"
- Ordovician fractured shale, Trenton Limestone, Black River Group, and Wells Creek Formation
- Cambrian-Ordovician Knox Dolomite

Recommended citation: Ohio Division of Geological Survey, 2004, Oil and gas fields map of Ohio: Ohio Department of Natural Resources, Division of Geological Survey Map PG-1, generalized page-size version with text, 2 p., scale 1:2,000,000. [Updated 2014.]

odnr.gov

Radiocarbon Primer

- Sun → ^{14}N to ^{14}C → $^{14}CO_2$ → Plants → Animals

- "Modern" carbon: contains measureable ^{14}C
  - Positive $\Delta^{14}C$ values
  - Methane originating from bacteria

- "Dead" carbon: undetectable level
  - Reaching close to -1000 ‰
  - Coalbed CH_4

$\Delta^{14}C$ vs. $\delta^{13}C$ of various CH_4 sources

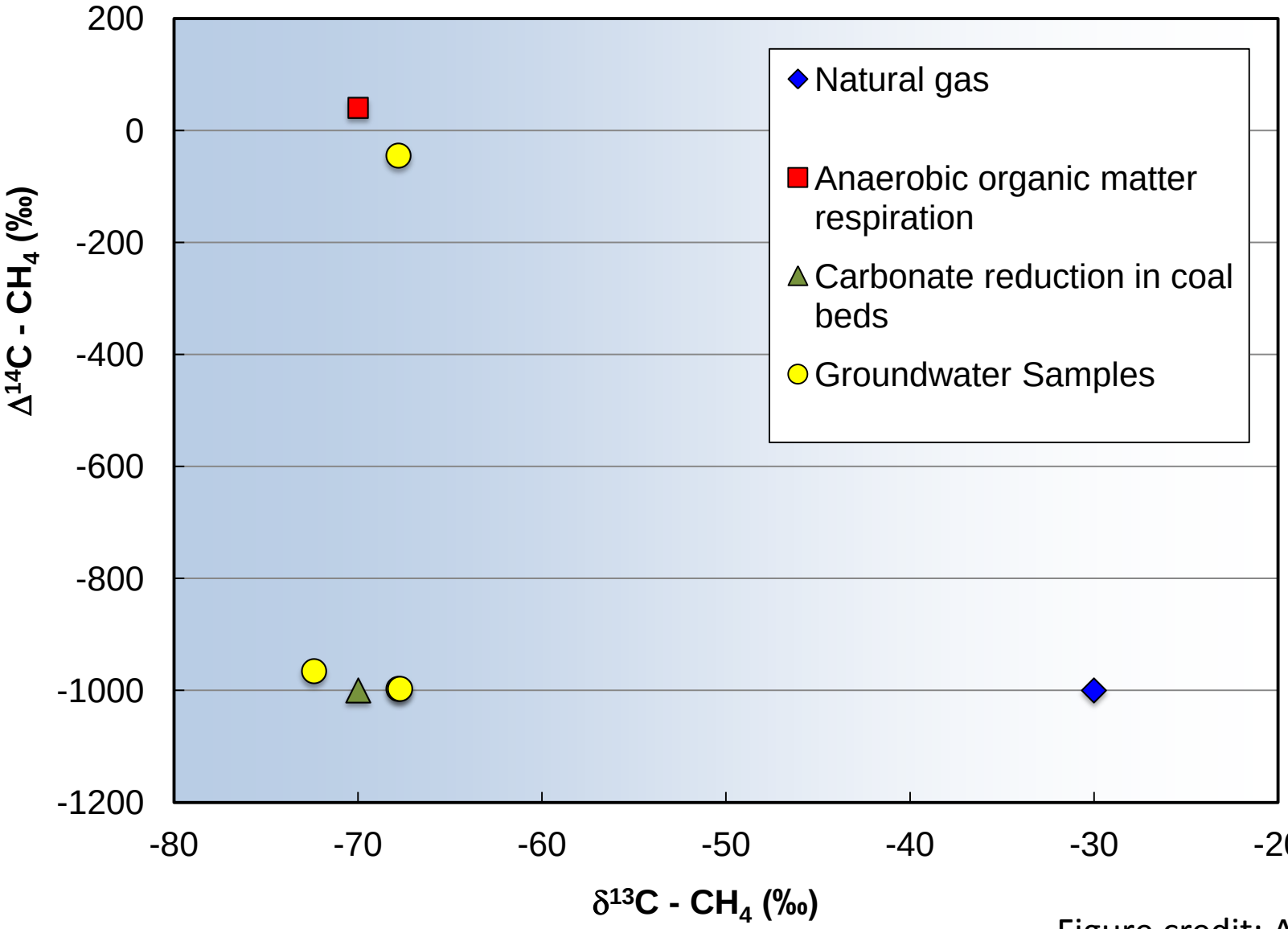


Figure credit: Amy Townsend-Small

Conclusions

- Some water wells contain very high levels of CH_4
  - Explosive range ~10 – 24 mg/L CH_4
- $\delta^{13}C$ values indicate that CH_4 found in groundwater has biological origins
- Groundwater contamination from fracking has happened, but it isn't the norm
- Normal pH and conductivity values show that fracking fluid is likely not present in sampled groundwater resources

Conclusions & Future Work

- $\Delta^{14}C$ analysis of four select wells indicates high levels of CH_4 can be attributed to biogenic coalbed gases in at least three of the wells

- Further characterization of coalbed gas in eastern Ohio groundwater

- Long-term monitoring necessary

Acknowledgements

- Dr. Amy Townsend-Small
- Dr. David Nash
- Paul Feezel, Carroll Concerned Citizens
- Kristine Jimenez
- Deer Creek Foundation
- Alice Weston Foundation

UNIVERSITY OF Cincinnati

CarrollConcernedCitizens.org

Questions?

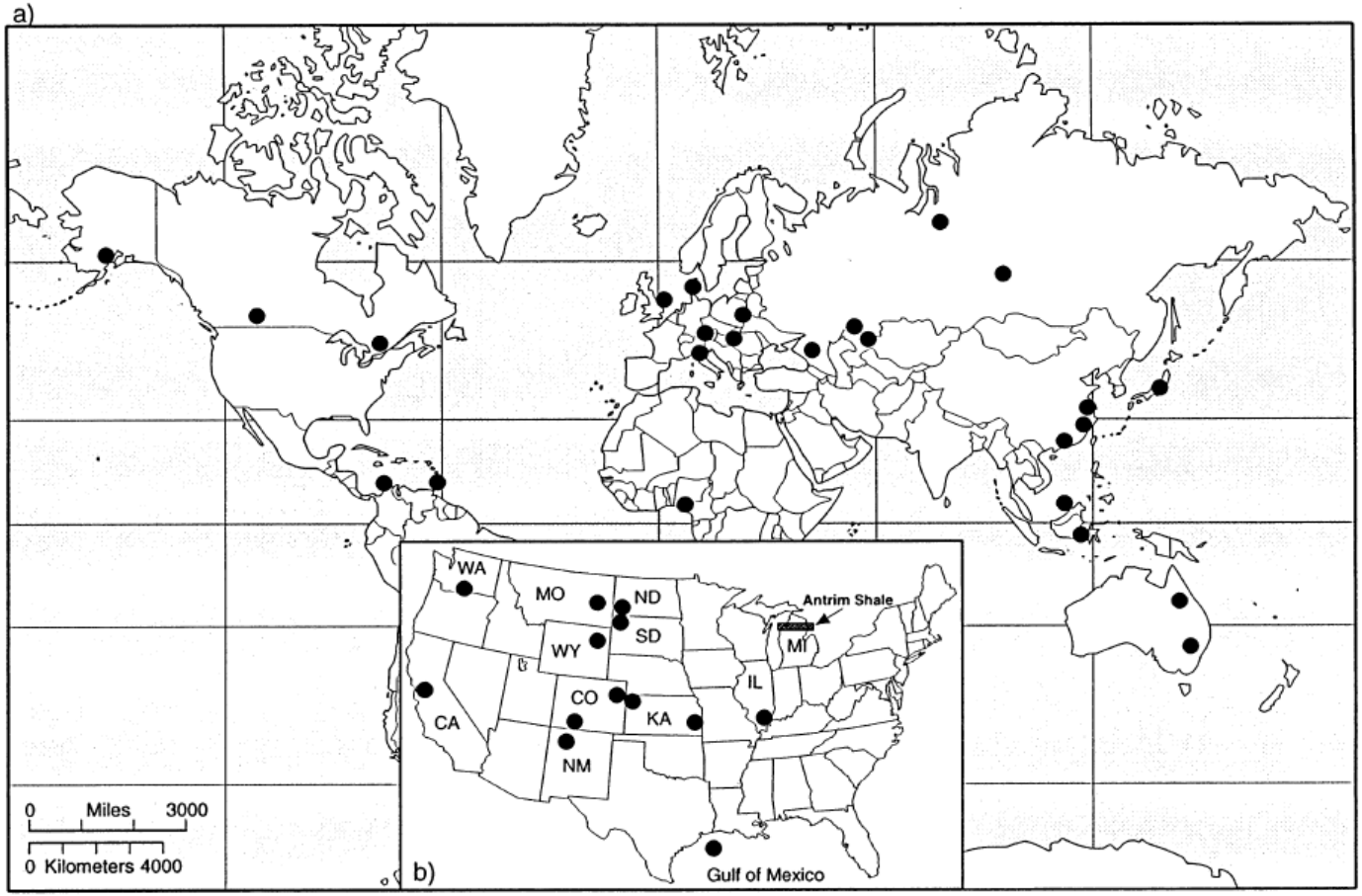


Fig. 1. Methane occurrences of known bacterial origin: (a) Worldwide and (b) United States (modified from Rice, 1993). Location, reservoir age, C + H isotope compositions and original source of data shown as solid circles are in Rice (1993). More recent biogenic methane occurrences are added; for coalbed methane from the San Juan Basin, New Mexico, U.S. (Scott et al., 1993), the Bowen and Sydney basins, Australia (Smith and Pallasser, 1996), and for the Antrim Shale (grey rectangle), Michigan, USA (Martini et al., 1996).

Martini *et al*. 1998