Case Study:
The Barnett Shale of North Texas U.S.A.

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LANDOWNERS!

2011: Lots of opinions, any data?

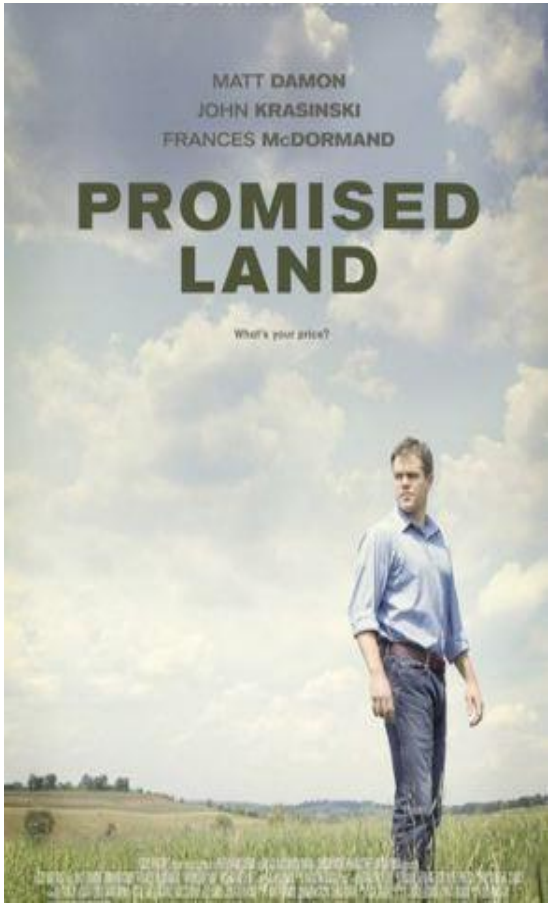
TALISMAN ENERGY

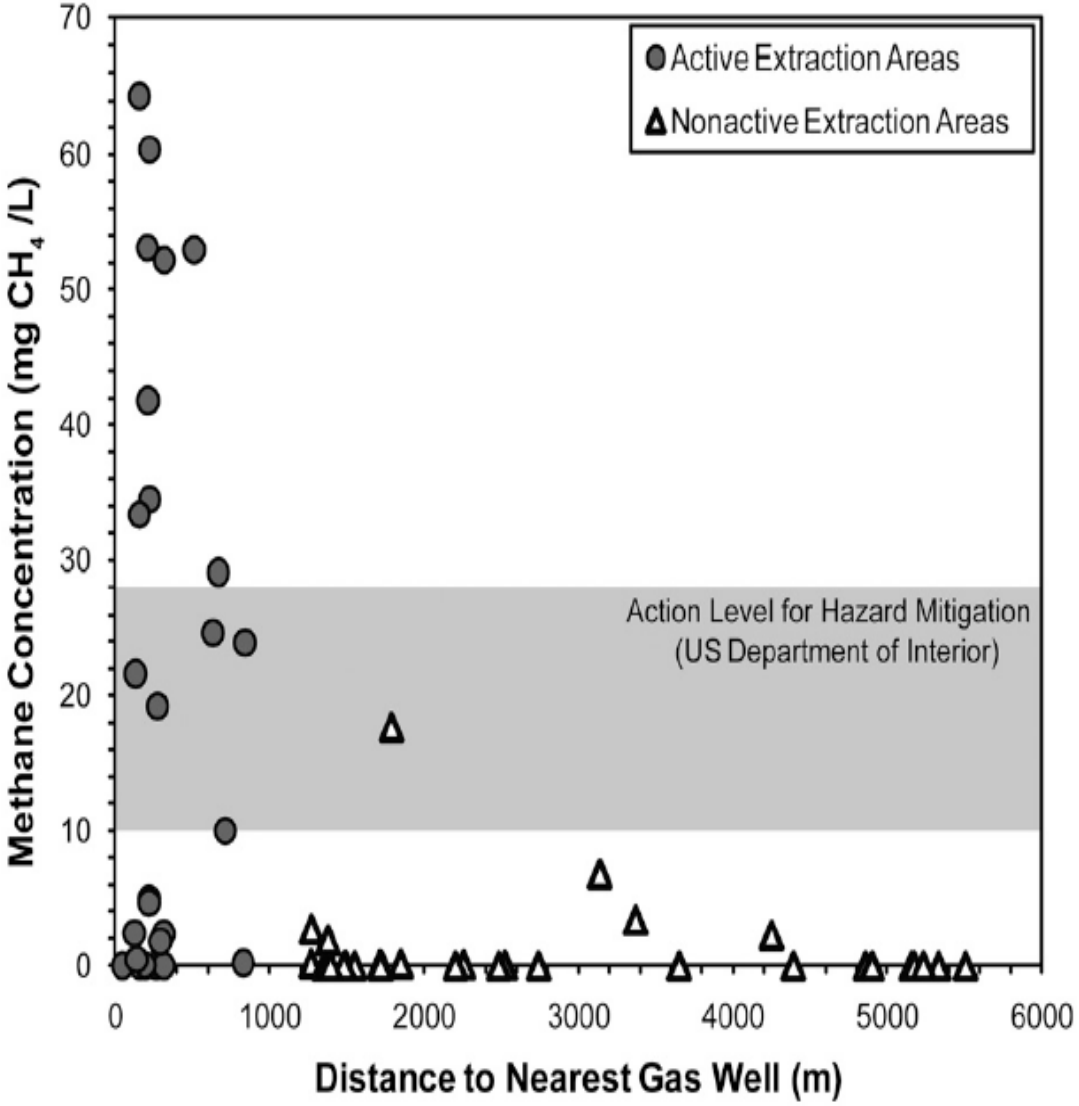
Good Neighbor Program Coloring Book

featuring "Talisman Terry the Fracosaurus"

FRACK NATION

Clean Energy®





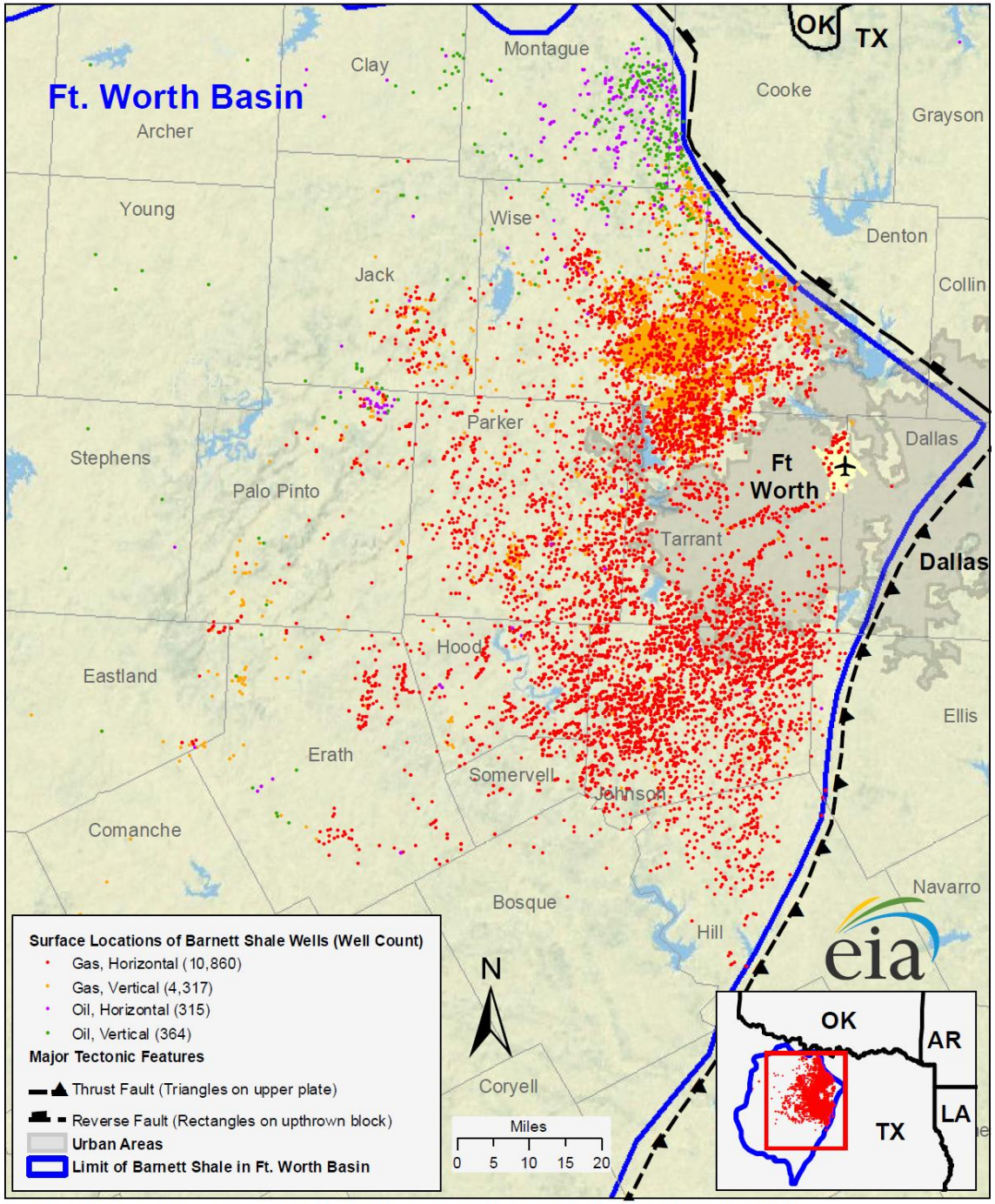
Elevated levels of methane; Marcellus shale, PA

Geospatial relationship between methane concentration and distance to neighboring gas well

Evidence of deep thermogenic methane contamination

Osborn, S. G., et al. *Proc. Natl. Acad. Sci.* **2011,** *108,* 8172-8176.

The Barnett Shale



Source: US Energy Information Administration based on data from HPDI, USGS, Pollastro et al (2007)
Updated: May 31, 2011

5000 mi^2
17 counties

1986 – 1st hydraulic frac

2002-2012 – most productive shale gas in the U.S.

Jan. 2013 – 4.56 bcf/day, which was 6.8% of U.S. natural gas


spring 2012, Arlington TX

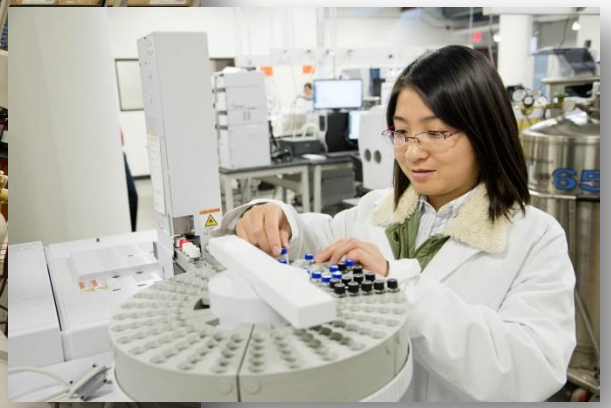
Ideal Experimental Approach

Baseline measurements for anthropogenic effects

Scheduled monitoring for changes/fluctuations over time

Targeted and untargeted analytical methods

Environmental forensics for sourcing



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ADVANCED ANALYTICAL CHEMISTRY

Analytical Methodologies

- On-site water quality tests

- Total Organic Carbon/Total Nitrogen
- Gas Chromatography (Targeted and untargeted)
- Headspace – GC (Targeted and untargeted)
- ICP-OES Metals (Qualitative/Quantitative)
- ICP-MS Metals (Arsenic and Selenium)
- Ion Chromatography (Inorganic and Organic)

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CHEMISTRY

Basic Water Quality

Wells purged at well head until pH and temperature stable, then samples collected and water quality measured.

- pH
- Total Dissolved Solids (TDS)
- Salinity
- Conductance
- Temperature
- Dissolved Oxygen (DO)
- Oxidation Reduction Potential (ORP)

Gas Chromatography – Mass Spectrometry Method and QC

- Ethyl acetate extraction

- Enhanced sensitivity GC-MS (electron ionization)
- SIM/Scan for Targeted/Untargeted
- Rxi-5ms, standard
- T program, 40 – 300 ^{0}C, 13 minute run

Quality Control

- Triplicate analysis of samples
- Multi-level quality control spiked standards
- Blanks
- Secondary instruments and secondary laboratories

Gas Chromatography Targets

Methanol
Ethanol
n-propanol
Isopropanol
n-Butanol
2-Ethylhexanol
2-Butoxy Ethanol
Propargyl Alcohol
Benzene
Toluene
Phenol
Benzylchloride
Ethylbenzene
0-, m-, & p-Xylenes

1,2,4-Trimethyl Benzene
1,3,5-Trimethyl Benzene
Isopropyl Benzene
d-Limonene
Naphthalene
1-Methyl Naphthalene
2-Methyl Naphthalene
1-Naphthol
2-Naphthol
Ethylene Glycol
Polyethylene Glycol
Propylene Glycol
Dipropylene Glycol Monomethyl Ether

PEG 200
Glycerol
Acetophenone
Dimethylformamide
Glutaraldehyde
Acetaldehyde
Di(2-Ethylhexyl) Phthalate
Phthalic Anhydride
Bisphenol A
Dichloromethane

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ICP-OES Method

- Acidified (2% HNO_3) and filtered water

- Qual/Semi-Quant/Quant method
  - Up to 60 metals; UD relevant
  - Matrix effects
  - 5 min per sample, triplicate
  - Standard addition, 3 points, multi-element std.

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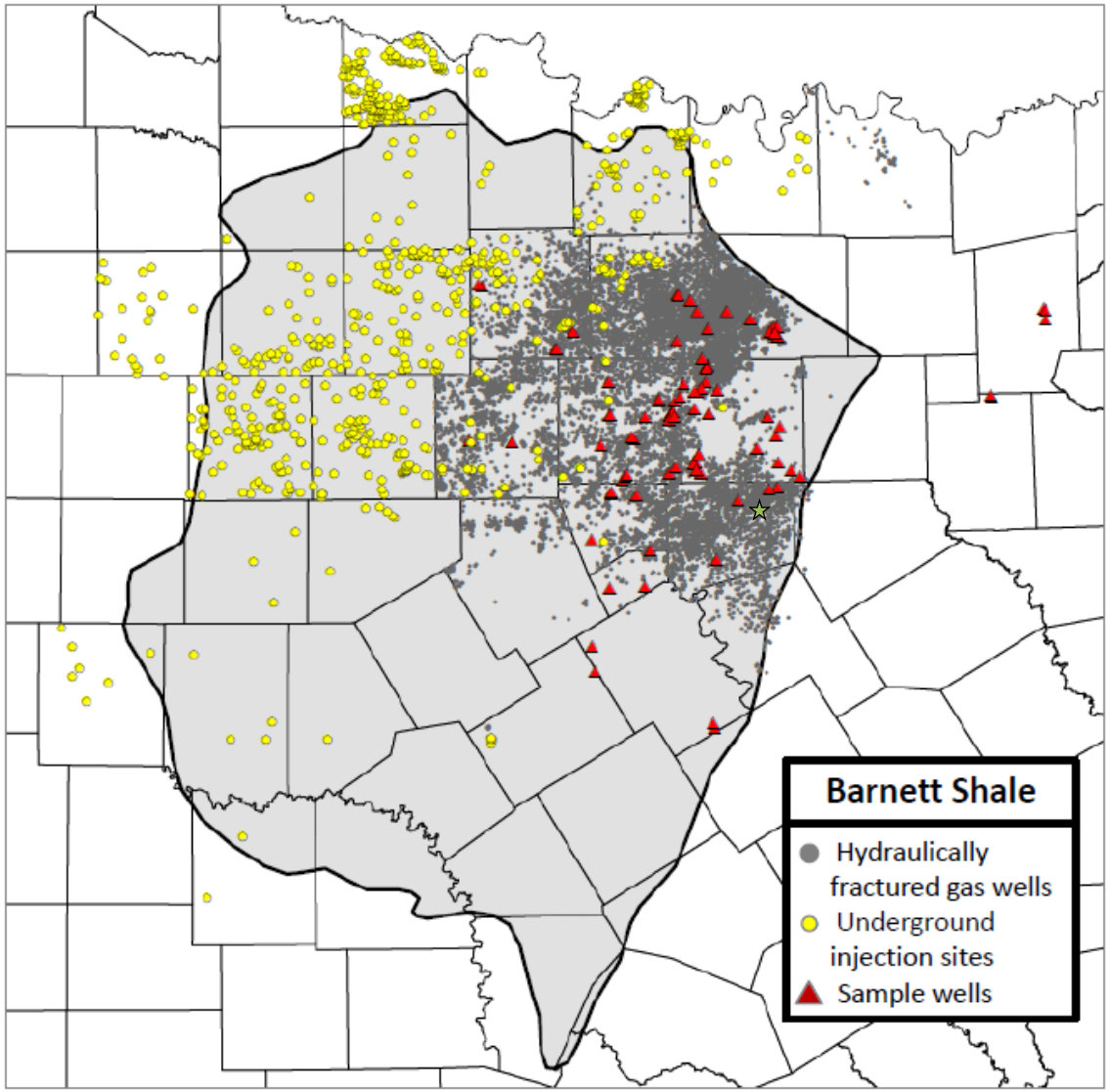
Sampling Map



- **91 Active wells**
  - water well < 3 km of gas well
- **9 reference wells**
  - In shale, > 20 km from gas well
  - Outside shale, ≈ 60 km from gas well

Fontenot et al. *Environ. Sci. Technol.* **2013,** *47,* 10032–10040.

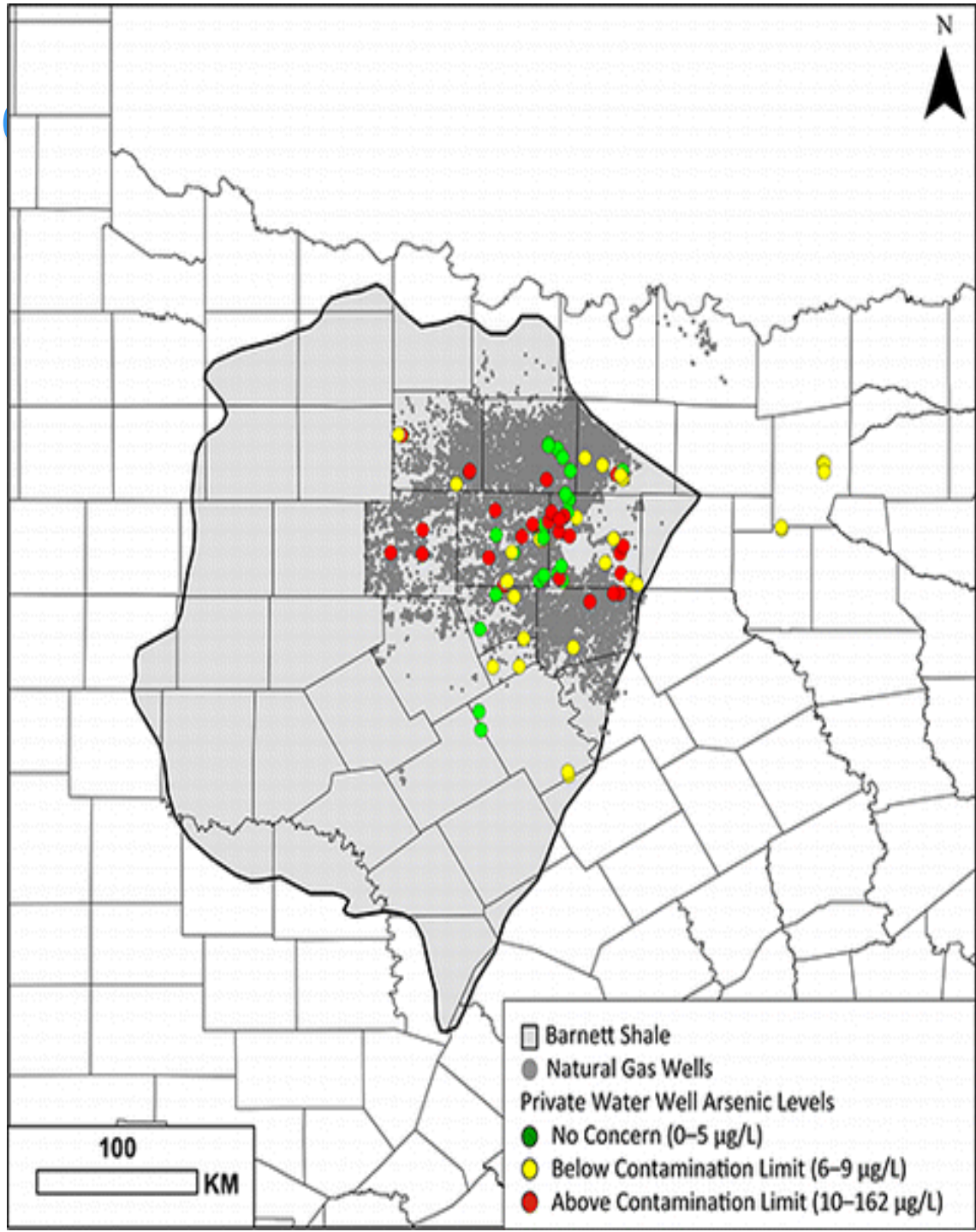
Does Unconventional Drilling Affect Private Well Water Quality in the Barnett Shale?

Elevated Levels of Arsenic

29 of the 91 samples in active extraction areas contained arsenic >10 µg/L

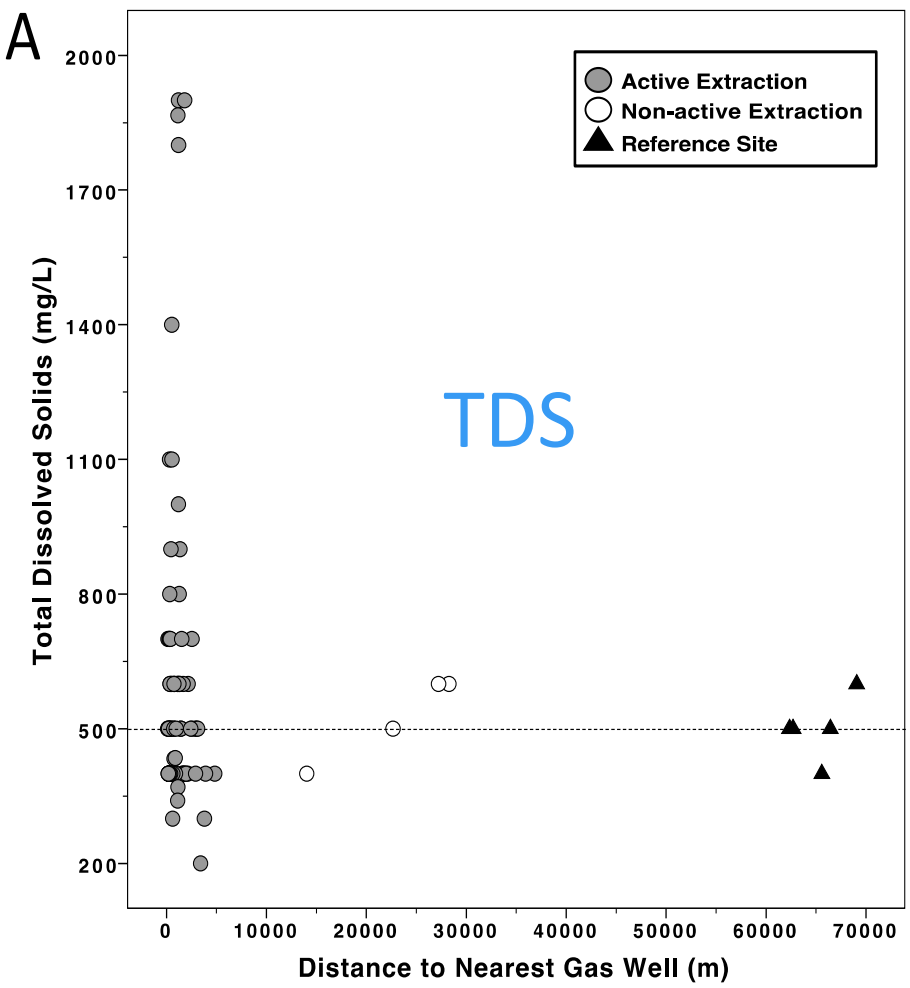
Highest concentration that was detected was 161 µg/L

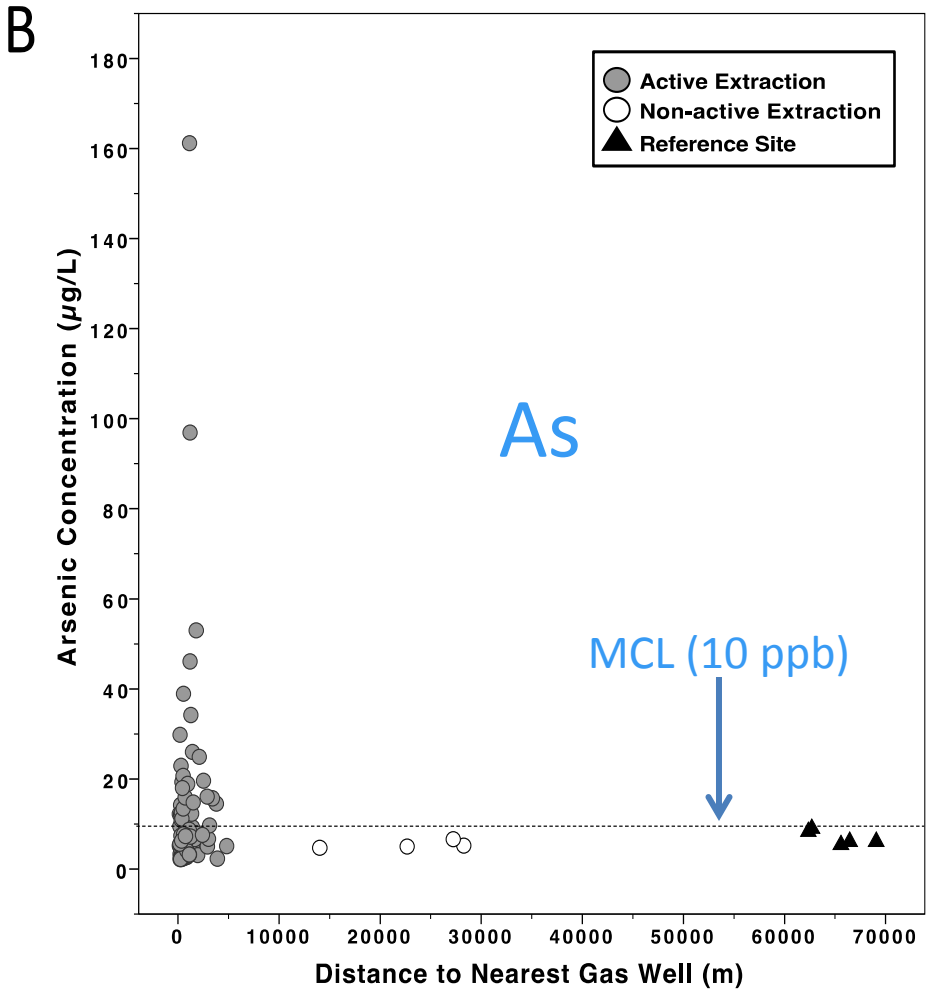
Arsenic was not found to be elevated in any of the reference sites



Fontenot et al. *Environ. Sci.Tech.* **2013,** *47,* 10032-10040.

Geospatial analysis of TDS and Arsenic





Fontenot, B. E., et al. *Environ. Sci. Tech.* **2013,** *47,* 10032-10040.

Explanations for Arsenic

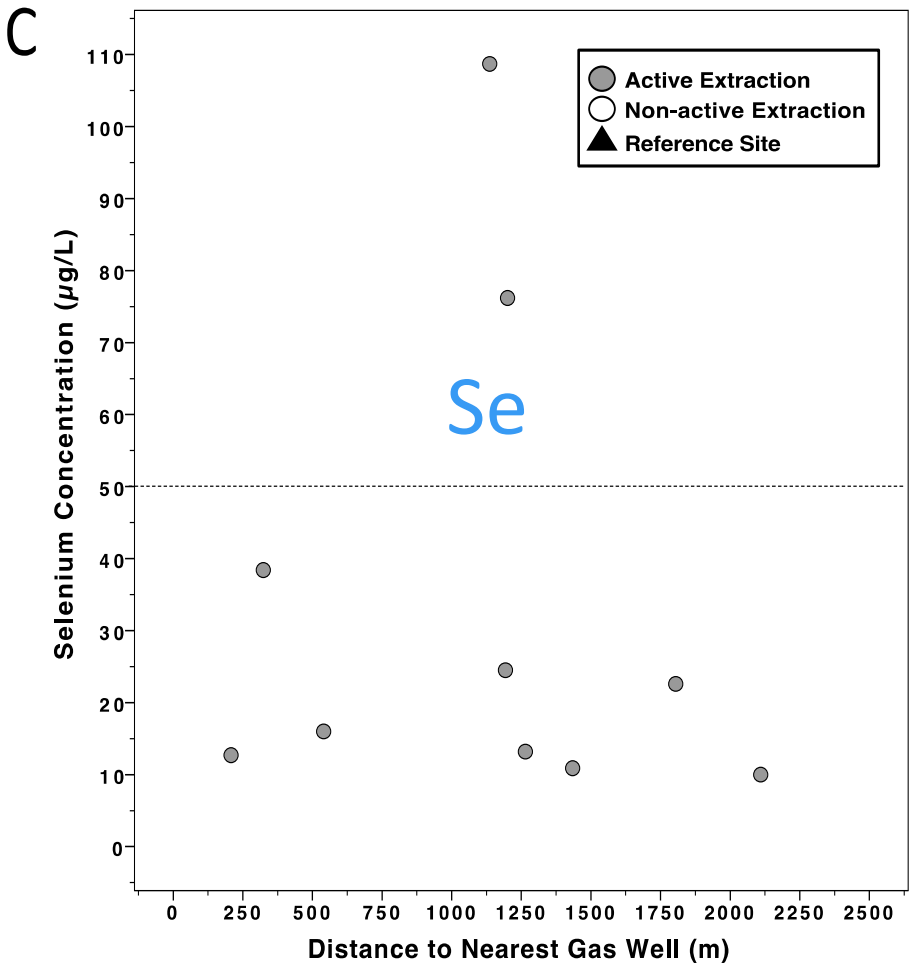
Instances of arsenic contamination are highest near hydraulic fracturing sites and in shallower water wells

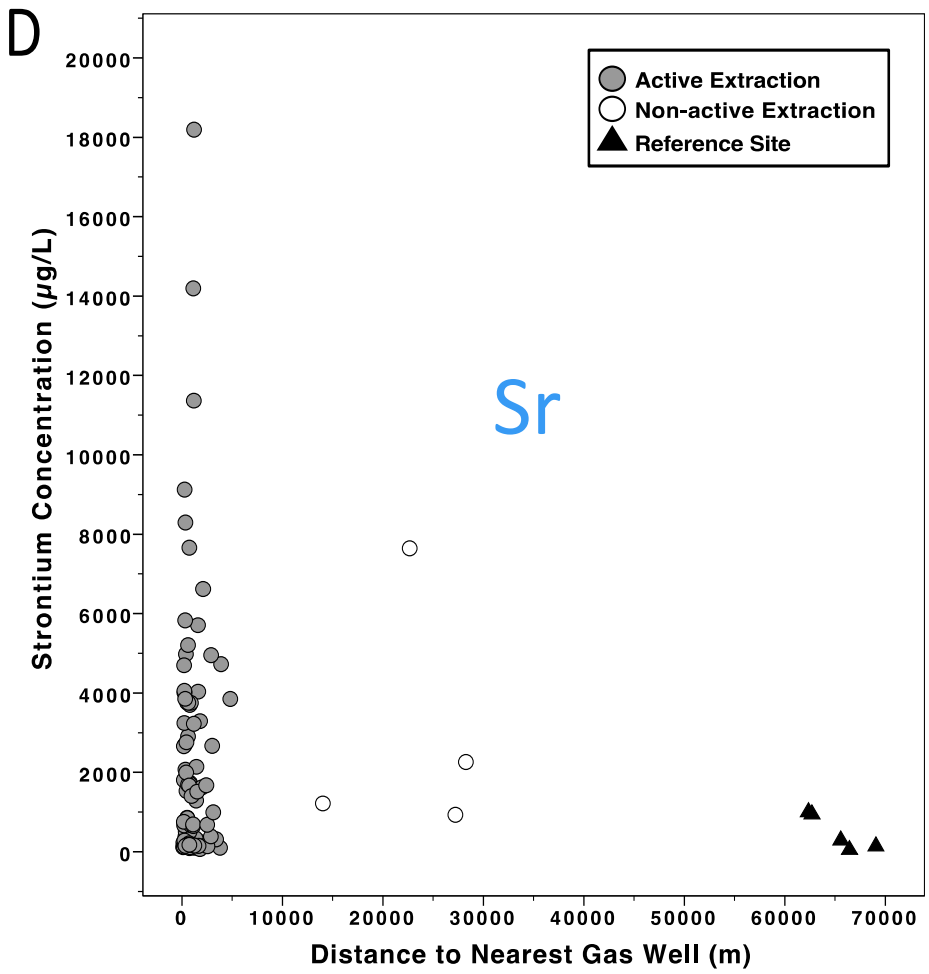
- Direct contamination not likely (e.g., flowback spills or faulty casing)
- Indirect causes
  - Scale/rust in wells – Increased pH and vibrations
  - Lowered water table – Shallow wells shallower

➢More data needed

Time-lapse analysis before, during and after drilling

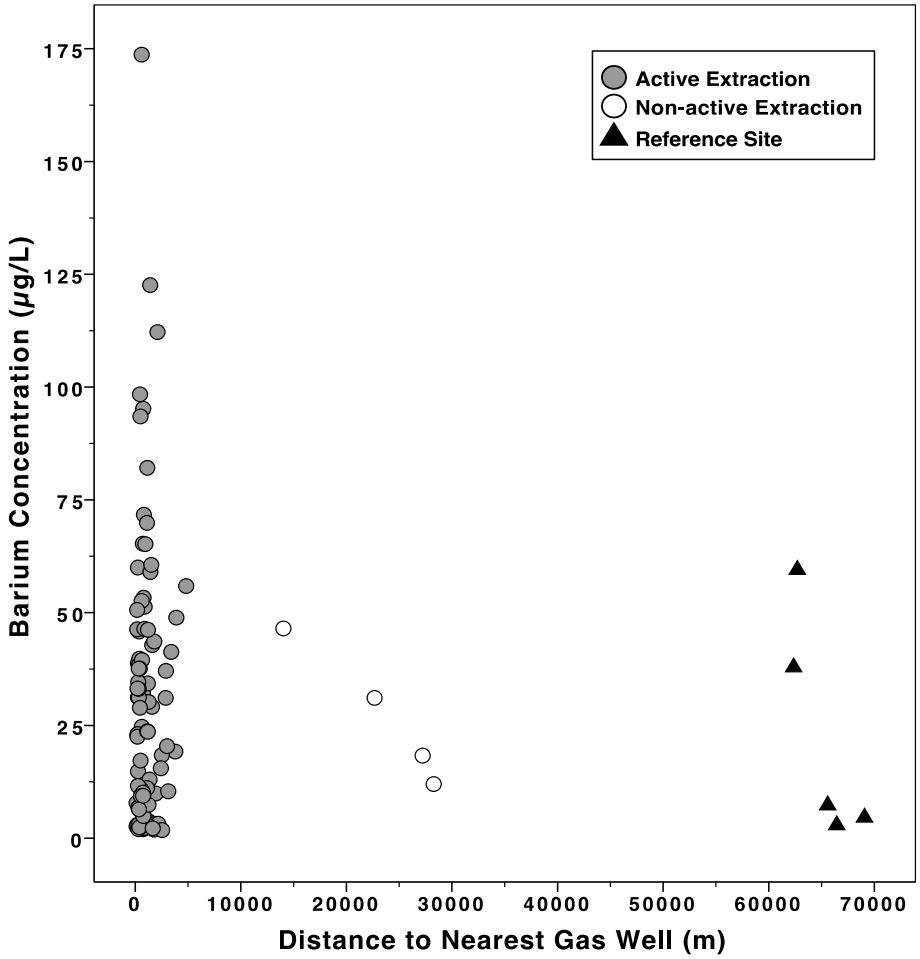
Selenium and Strontium





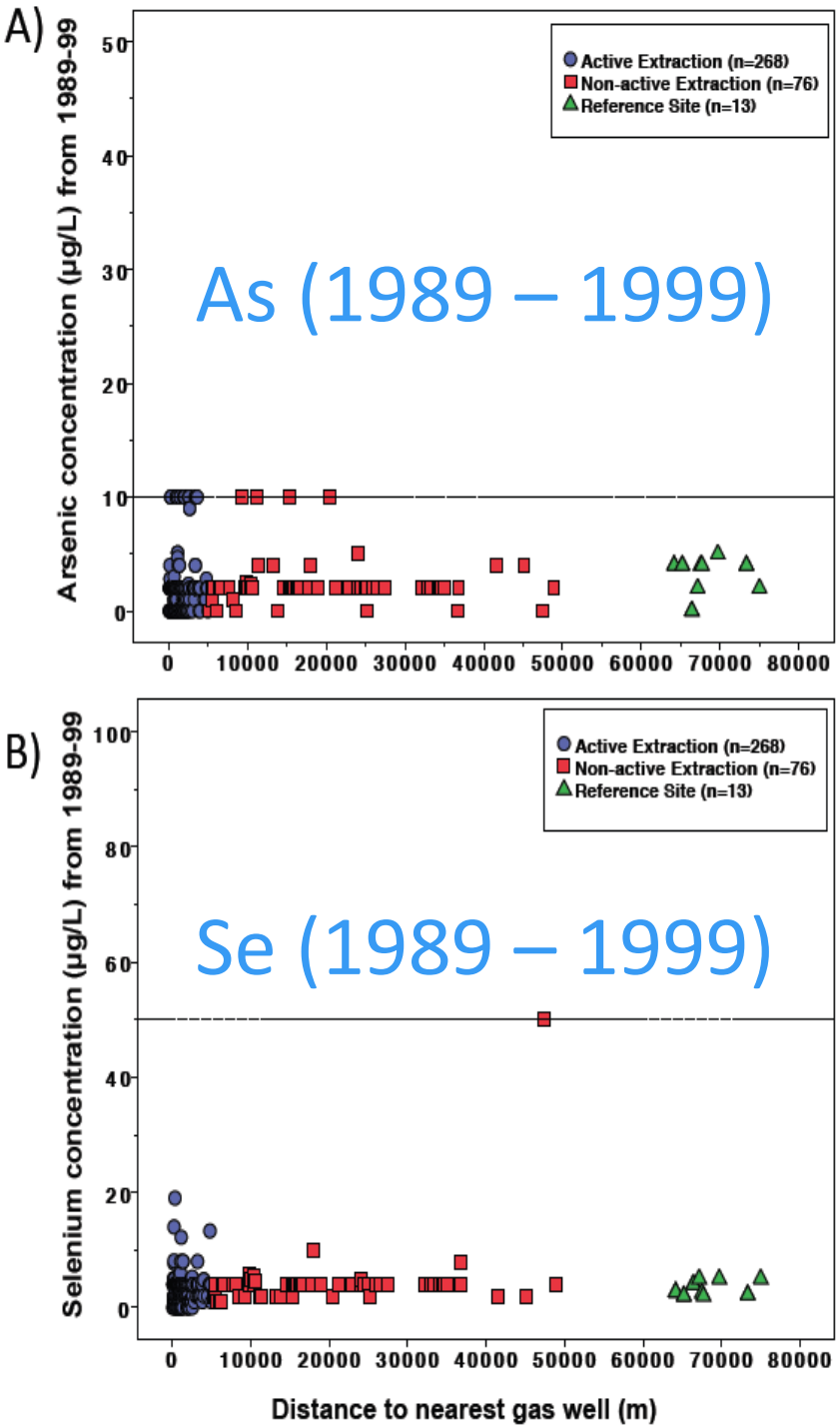
Fontenot, B. E., et al. *Environ. Sci. Tech.* **2013,** *47,* 10032-10040.

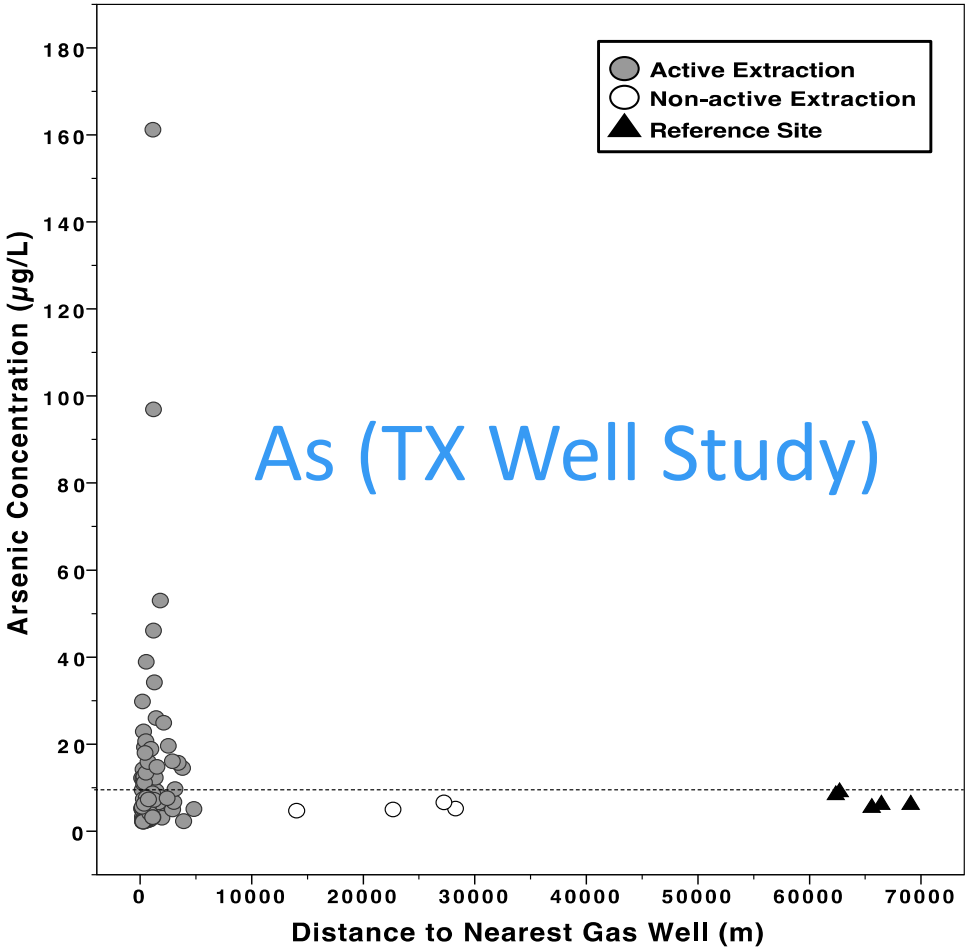
Barium



Fontenot, B. E., et al. *Environ. Sci. Tech.* **2013,** *47,* 10032-10040.

Comparison to historical data

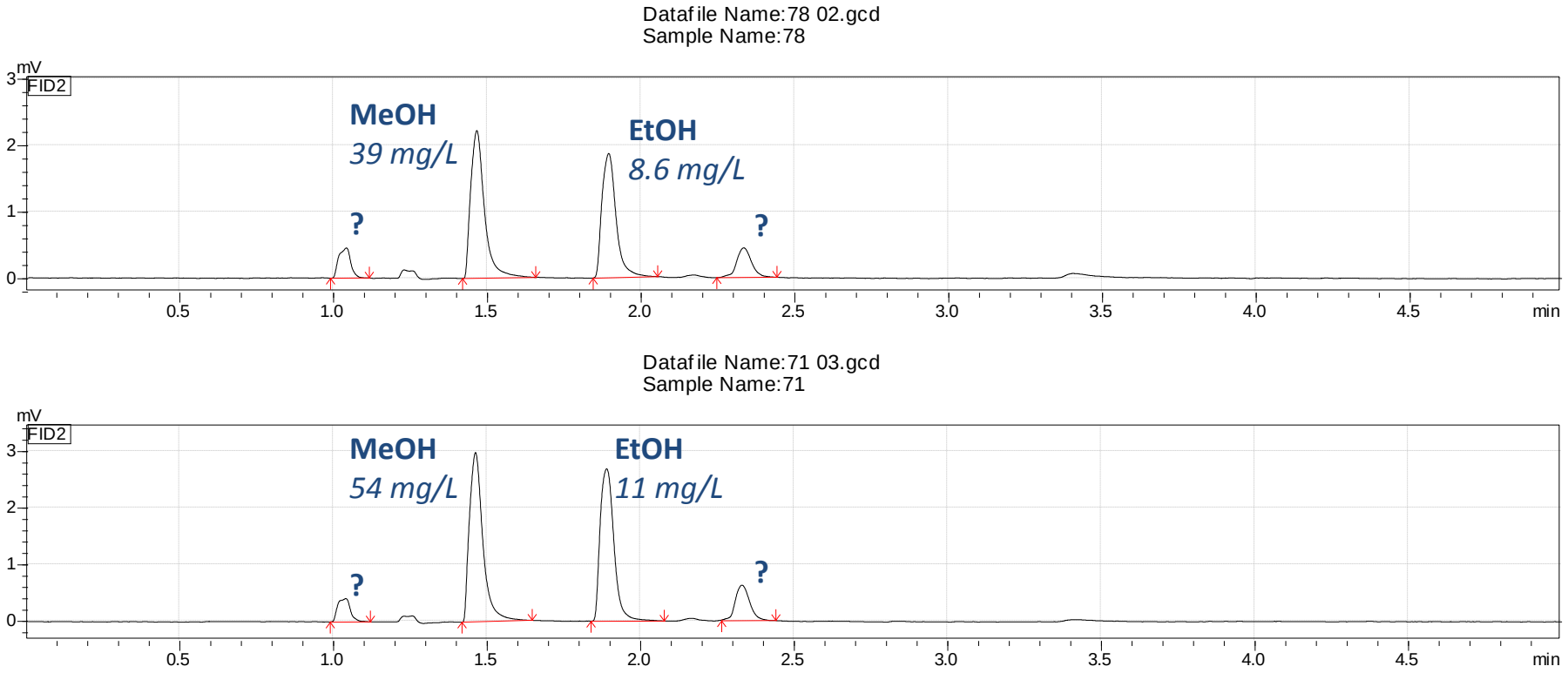




Fontenot, B. E., et al. *Environ. Sci. Tech.* **2014,** 48, 3597-3599

Significant Methanol and Ethanol

29 out of 91 wells had detectable MeOH and EtOH (range 1 – 329 mg/L)



Sourcing elevated alcohols difficult (anticorrosive vs. microbial metabolism vs. other industrial waste) – Not correlated with distance to nearest well.

Ideal Experimental Approach

Baseline measurements for anthropogenic effects

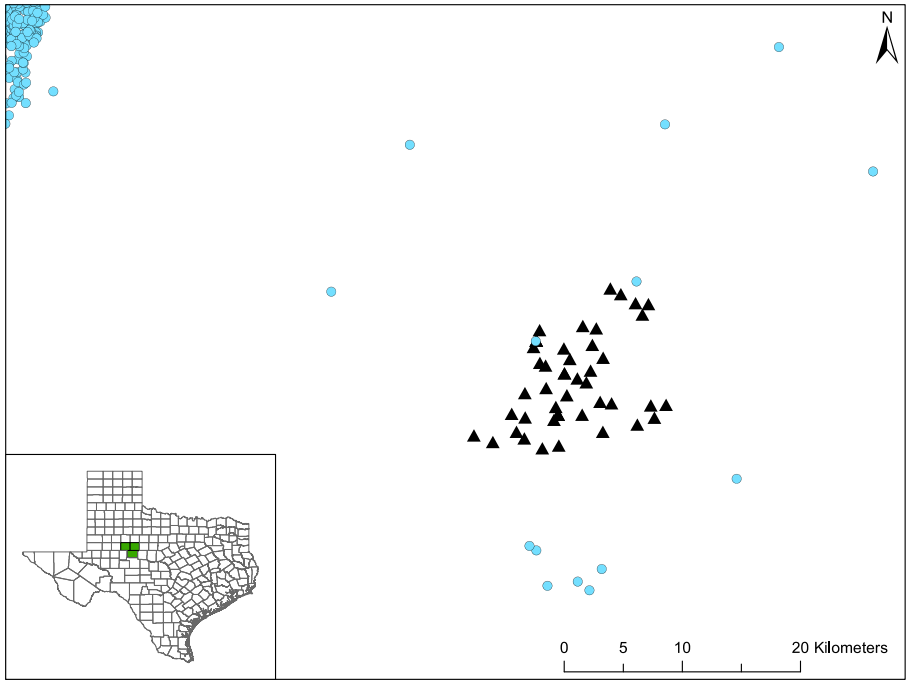
Scheduled monitoring for changes/fluctuations over time

✓ Targeted and untargeted analytical methods

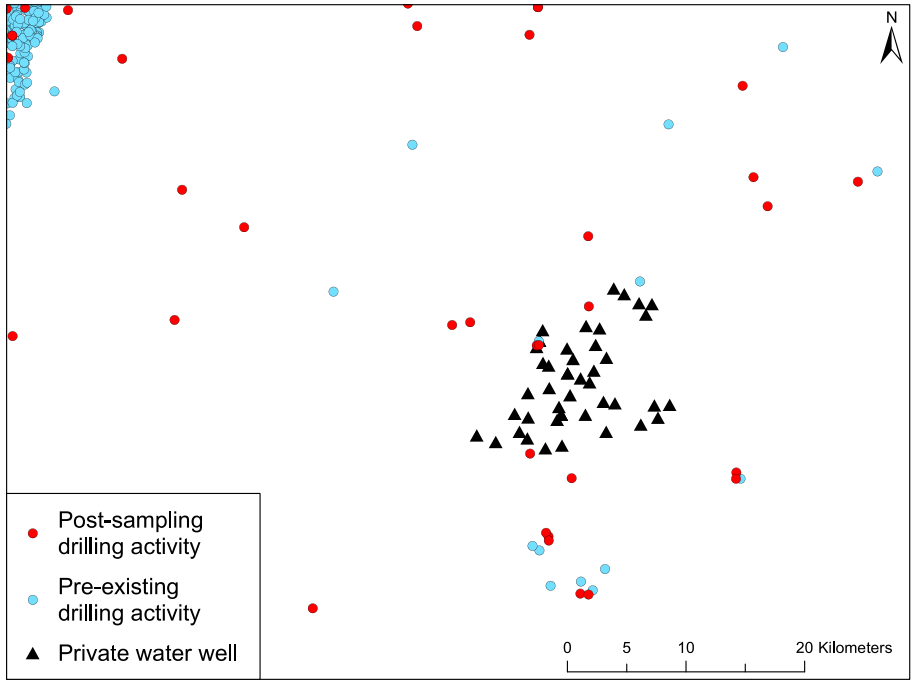
Environmental forensics for sourcing

Time-Lapse Analysis in the Cline Shale

Dec. 2012

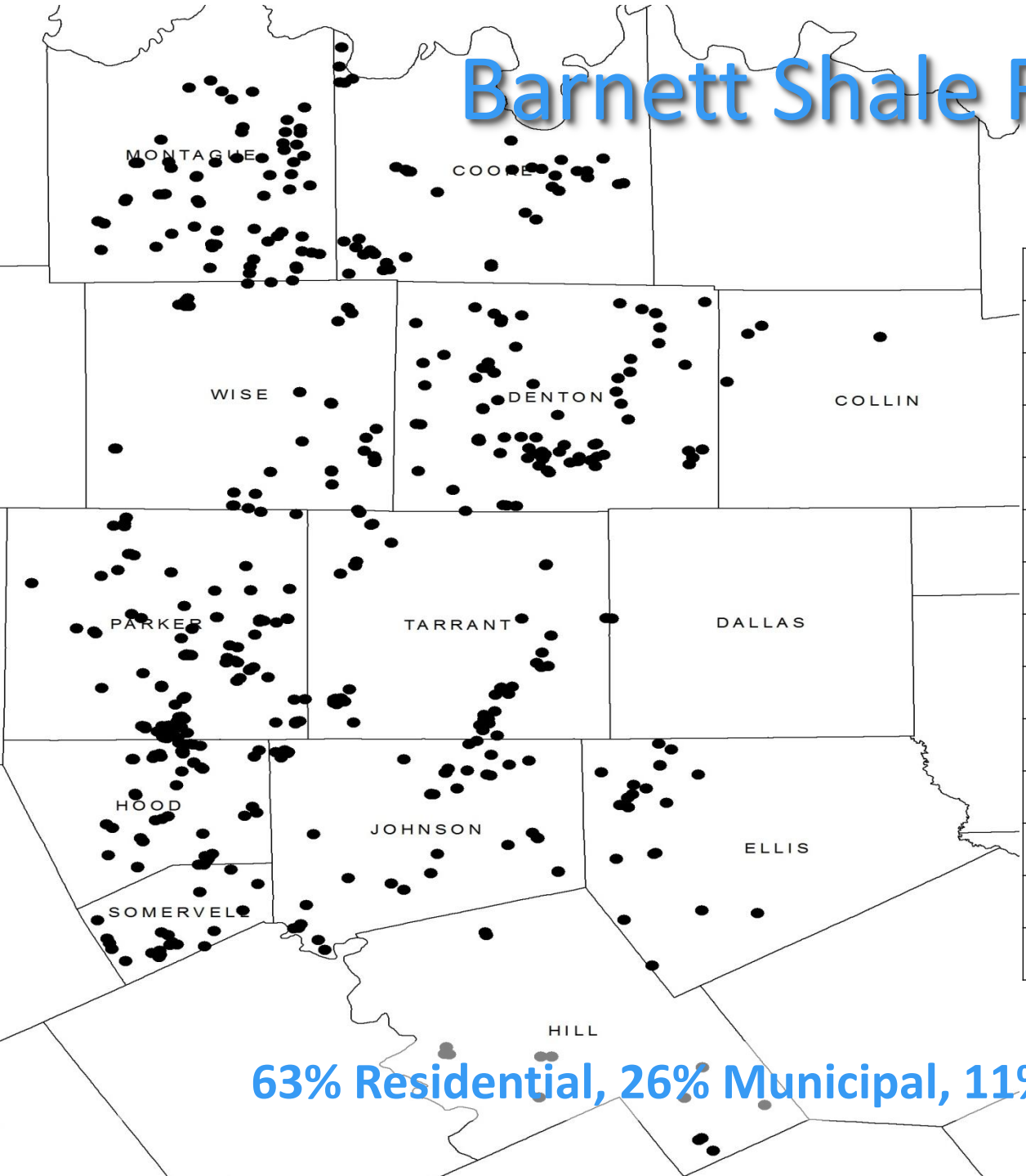


Summer, 2014



40+ water wells sampled before, during, and after unconventional drilling in Nolan county

Barnett Shale Rd. 2



550 samples

County	#
Collin	4
Cooke	40
Dallas	1
Denton	82
Ellis	25
Hill	14
Hood	60
Johnson	43
Montague	66
Parker	108
Somervell	19
Tarrant	47
Wise	41

63% Residential, 26% Municipal, 11% Agricultural

Future Directions

Expand our reach into other shale formations

Across the United States, South America, Canada, and Europe

Expand our environmental analysis tool kit

Advance tailored analytical capabilities to characterize a wide range of environmental events/catastrophes

Develop new technology and best management practices for unconventional drilling

Remediation, recycling, appropriate waste disposal

C.L.E.A.R.

Collaborative Laboratories for Environmental Analysis and Remediation

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Thank You for Your Attention!

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