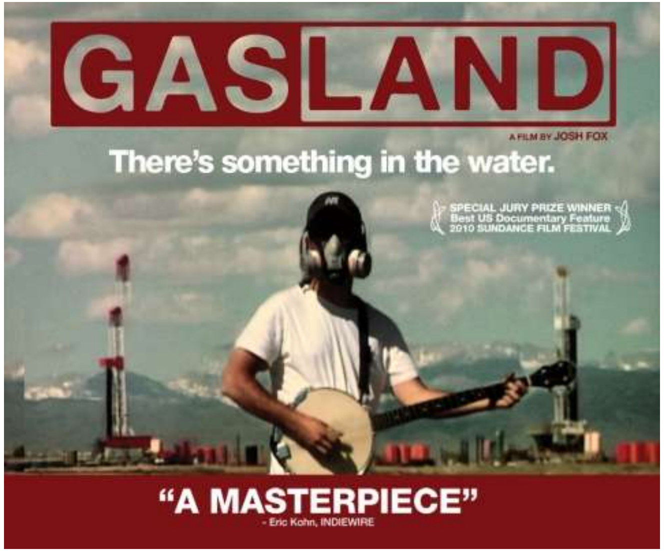
Characterize groundwater quality in area engaged in unconventional drilling

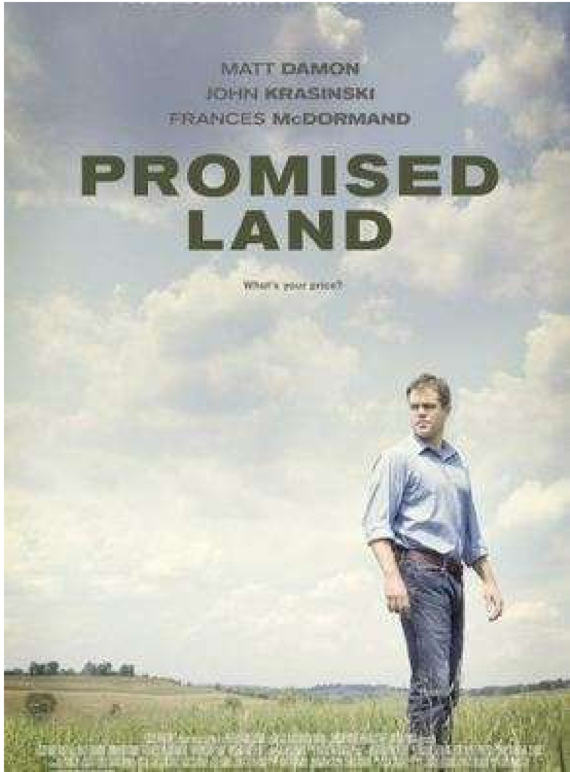
Zacariah L. Hildenbrand, Ph.D.

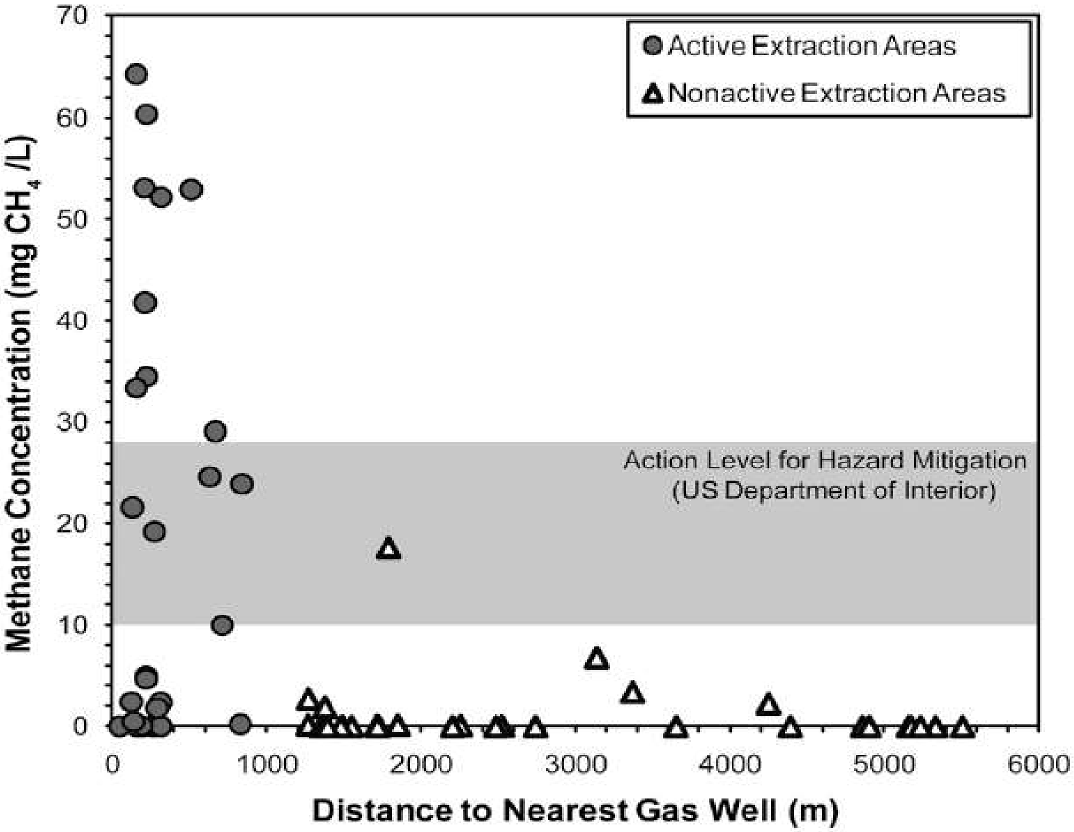
Inform Environmental, LLC, Dallas, TX 75227

The University of Texas at Arlington, Arlington, TX 76019

Lots of opinion but is there any data?







Elevated levels of methane

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.

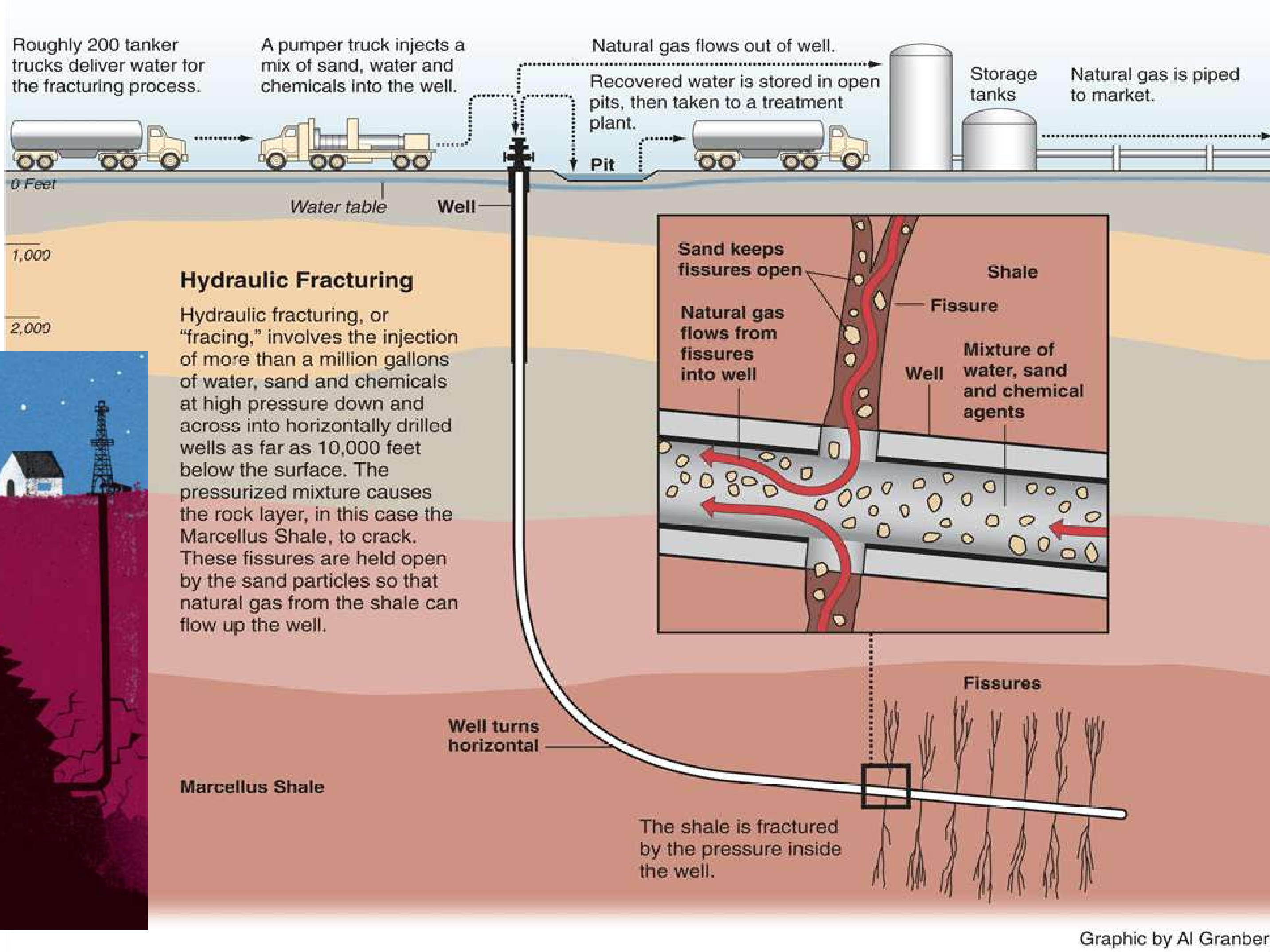
What is unconventional drilling?

Hydraulic Fracturing

Shale Acidization

Underground Injection Wells (Waste disposal)

What is Hydraulic Fracturing?



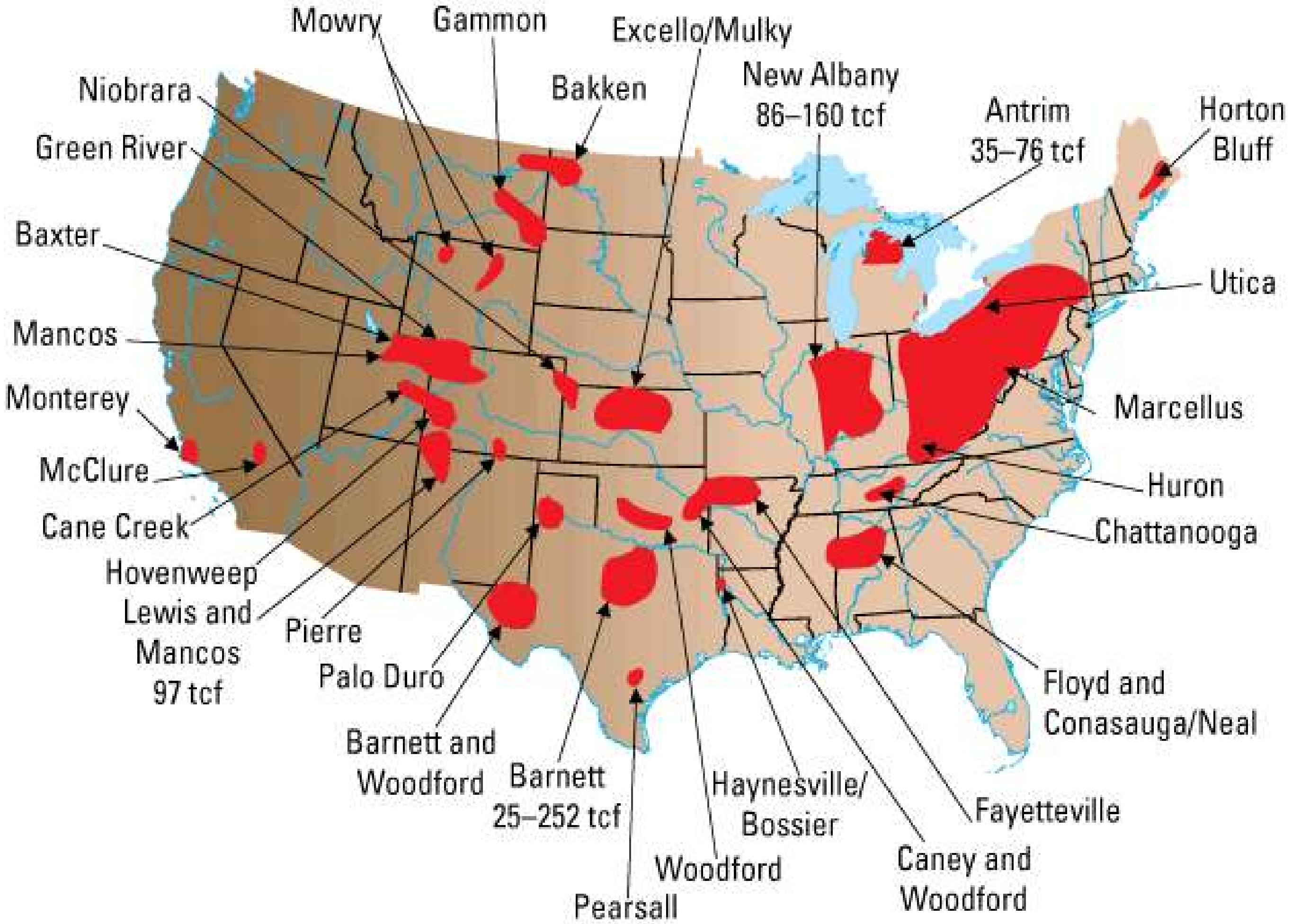
What is unconventional drilling?

Hydraulic Fracturing

Shale Acidization

Underground Injection Wells (Waste disposal)

Where is this occurring?



Shale Gas Basins
Devonian/Mississippian Shale Fairway
Horn River
Montney
Colorado Group
Gammon
Bakken
Mowry
Antrim
Utica
Horton
Bluff
Utica
Green River
Baxter
Mancos
Niobrara
Excello/Mulky
New Albany
Marcellus
Ohio
McClure
Cane Creek
Gothic
Pierre
Hovenweep
Monterey
Woodford
Fayetteville
Chattanooga
Palo Duro
Lewis
Mancos
Barnett/
Woodford
Floyd/
Conasauga/
Neal
Haynesville/
Bossier
Barnett
Eagle Ford

Environmental Concerns

Earthquakes

Cleburne, Irving, Azle, Dallas, OK, AR, Japan

USGS has evidence that underground waste injection can cause small scale earthquakes

Surface water contamination

Waste pits, fluid spills, pipeline leaks

Groundwater contamination

Waste pits, faulty casings

Is there a hydrologic connection to deep fractures?

Environmental Concerns

Earthquakes

Cleburne, Irving, Azle, Dallas, OK,AR, Japan

USGS has evidence that underground waste injection can cause small scale earthquakes

Surface water contamination

Waste pits, fluid spills, pipeline leaks

Groundwater contamination

Waste pits, faulty casings

Is there a hydrologic connection to deep fractures?

Composition of Fracturing fluid

Water (up to 99%, 3-5 million gallons per well)

Chemical additives (up to 2%)*

Biocides, surfactants, gelling agents, emulsifiers, corrosion inhibitors, BTEX compounds (benzene, toluene, ethylbenzene, xylene)

*Exact recipe is proprietary to each company although information is available at www.fracfocus.org

Proppants (sand and/or ceramics)

Large quantities of HCl (shale acidization)

Fate of fracturing fluids?

10-30% of flowback water is recovered

Flowback water is contaminated

Total Dissolved Solids (TDS), chlorides, Naturally Occurring Radioactive Material (NORM), chemical additives

Flowback can be:

Placed in containment pits, treated at wastewater plants, stored in underground injection wells or recycled (many new technologies are emerging)

Experimental Approach

Baseline measurements are incredibly valuable in assessing the anthropogenic effects of unconventional drilling

Scheduled monitoring can identify changes/fluctuations in groundwater quality

Advanced analytical tools are available to detect the occurrence of contamination events that may be directly or indirectly attributed to unconventional drilling activity

During a contamination event, environmental forensics can be used to identify the exact source

Basic Water Quality

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

Shimadzu Center for Advanced Analytical Chemistry

$8.5 Million dollar analytical facility

-Method development for the detection and quantification of multiple analytes

-Highly sensitive detection thresholds and screening applications allow for data to be collected rapidly, accurately and cost-effectively

More data equates to more informed decisions

Developed Methodologies

Gas-Chromatography Mass-Spectrometry (GC-MS)

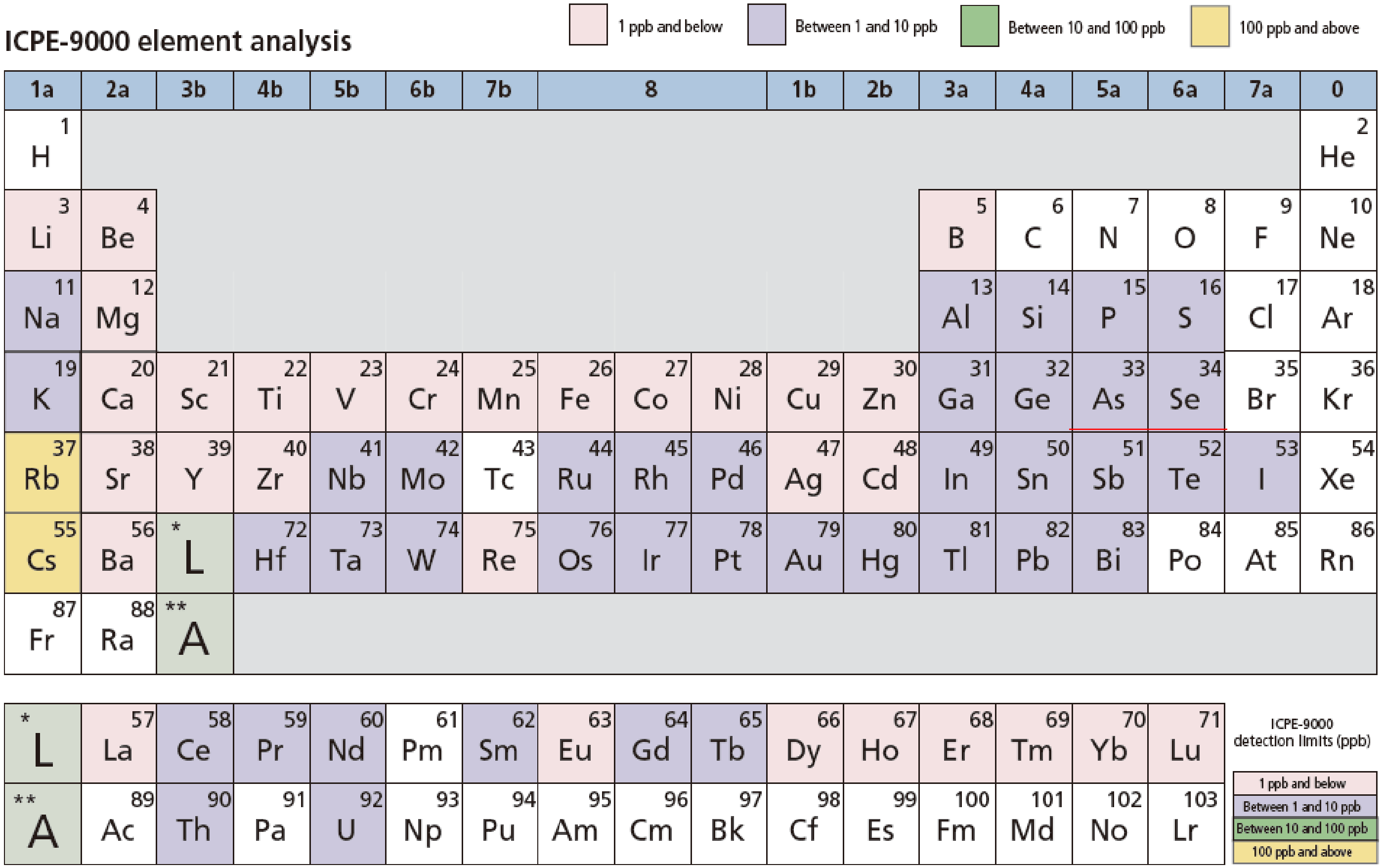
Methanol
Ethanol
n-propanol
Isopropanol
n-Butanol
2-Ethylhexanol
2-Butoxy Ethanol
Propargyl Alcohol
Benzene
Toluene
Phenol

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
Pthalic Anhydride
Bisphenol A

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Quantification of 70+ minerals and metals



Developed Methodologies

Quantification of Total Organic Carbon (TOC), Inorganic Carbon (IC)

Detection of petroleum hydrocarbons, volatile organics

Subsequent characterization with GC-MS, HS-GC-FID

Quantification of Total Nitrogen (TN)

Method to assess the relative effect of agriculture on groundwater quality

Quantification of major water ions

Fluoride, chloride, carbonate, sulfate, boron, bicarbonate

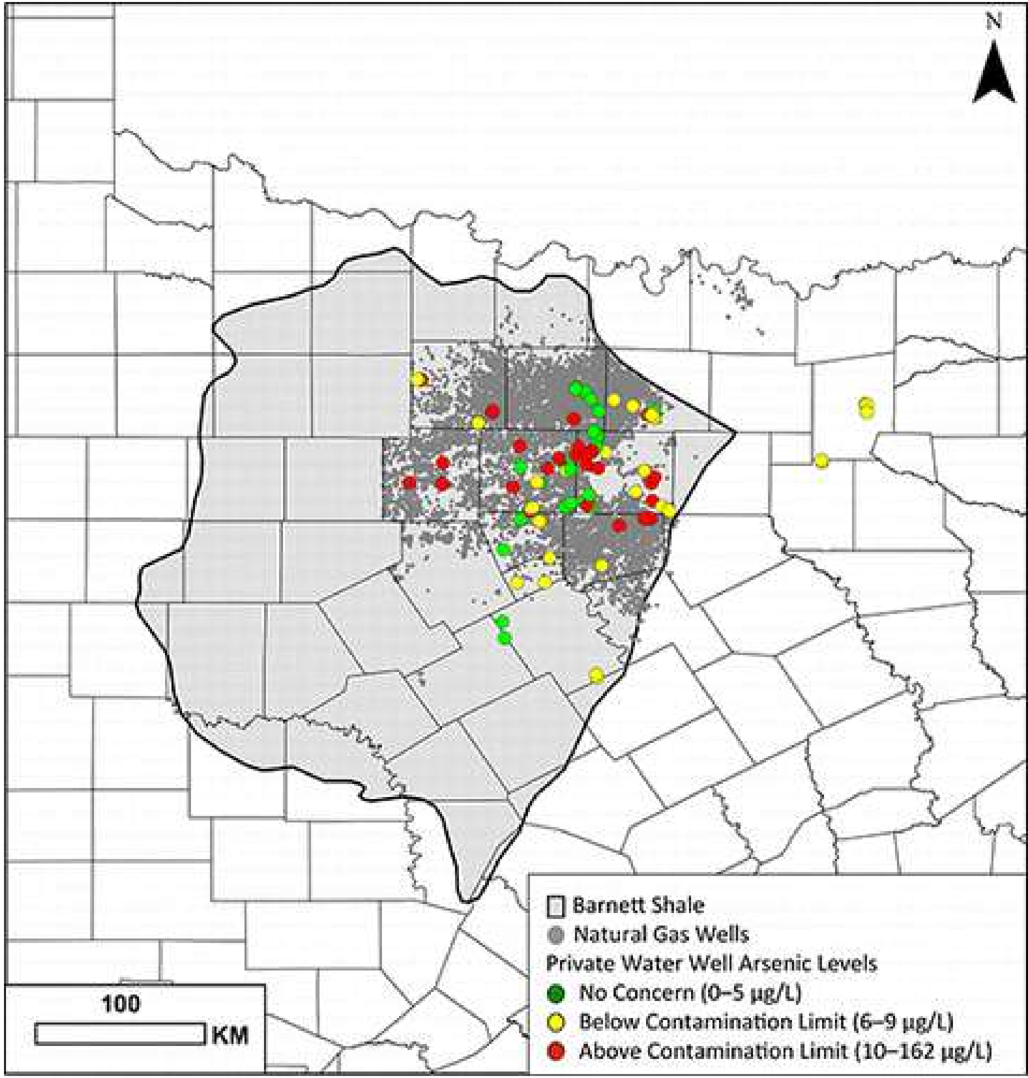
Elevated Levels of Arsenic

29 of the 91 samples collected with active extraction areas contained elevated levels of arsenic (>10 µg/L)

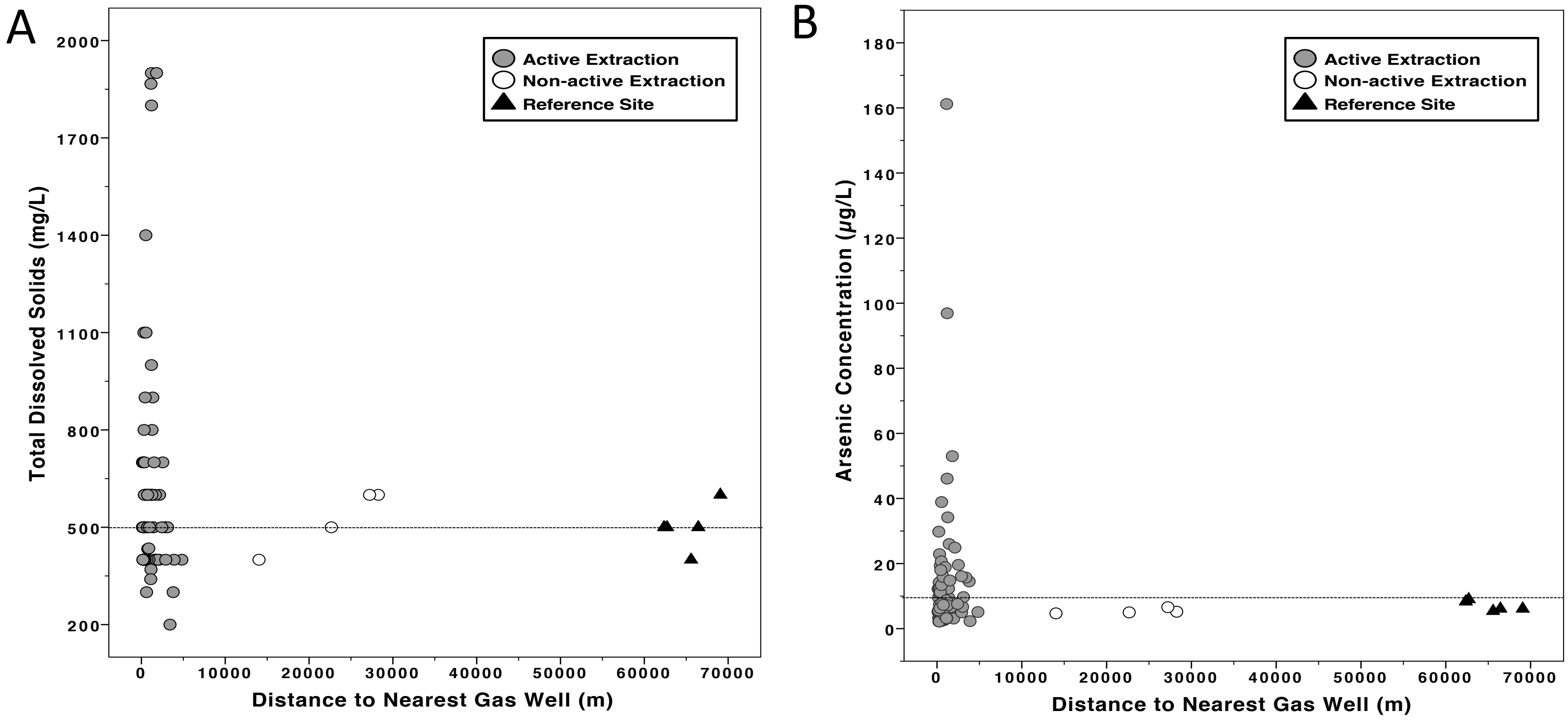
Highest concentration that was detected was 161 µg/L

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

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

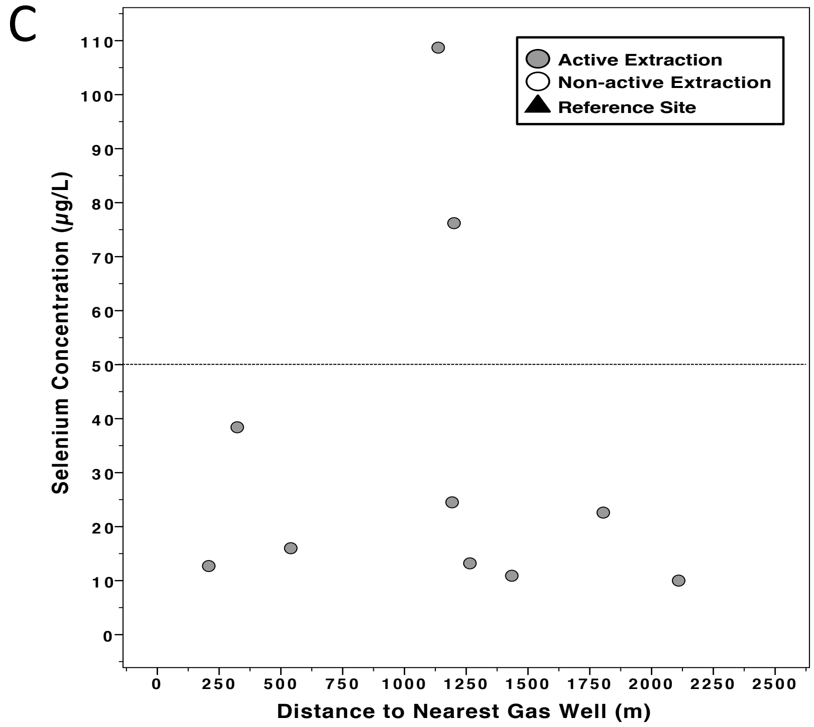


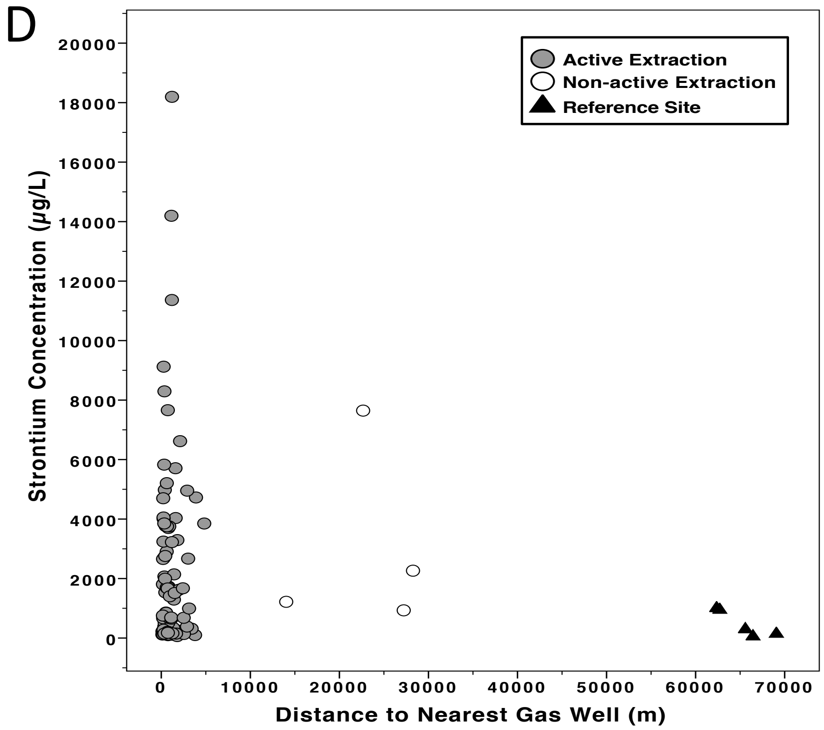
Geospatial analysis of TDS and Arsenic



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

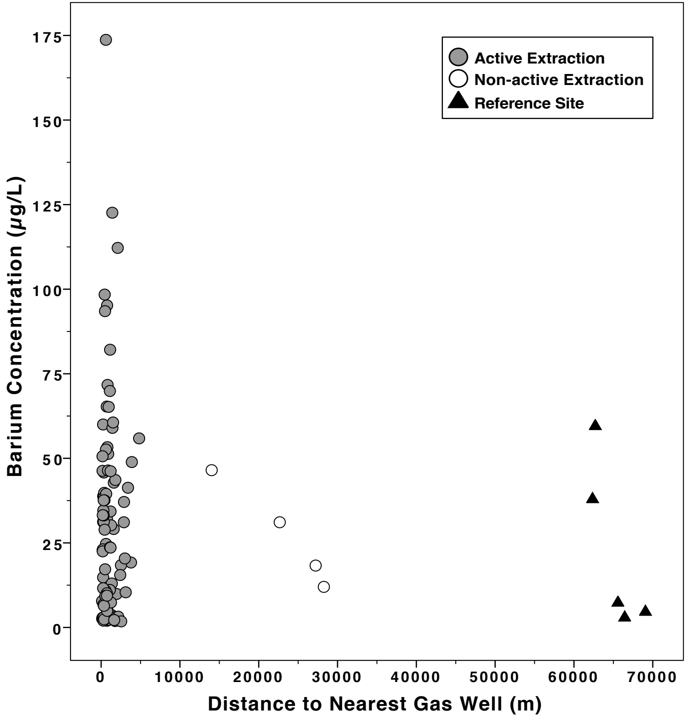
Geospatial analysis of Selenium and Strontium





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

Geospatial analysis of Barium



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

Comparison to historical data

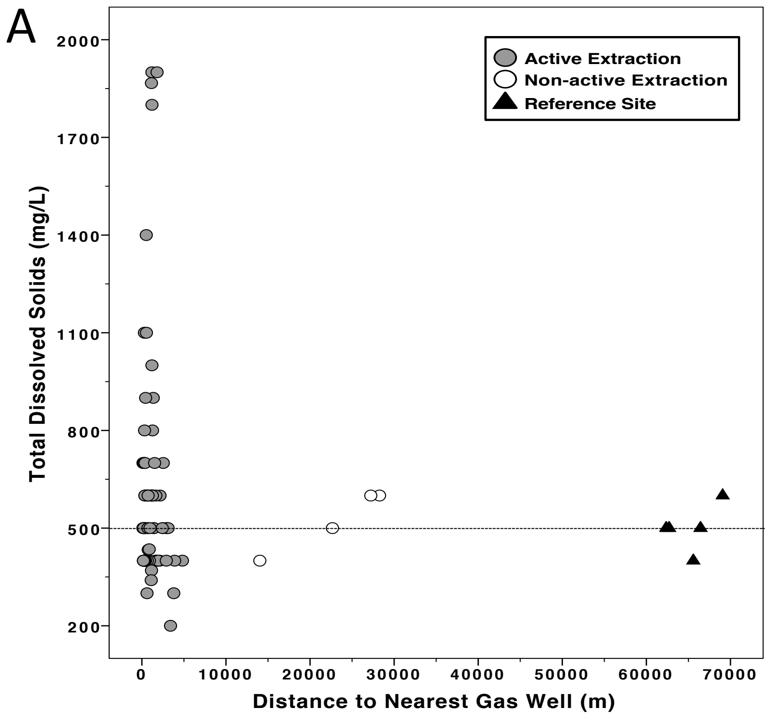
	Historical Data (1989-99)				Active Extraction Area Wells (N = 91)				Non-active and Reference Area Wells (N = 9)			
	N	Range	Mean ± Std Error	% ≥ MCL	N	Range	Mean ± Std Error	% ≥ MCL	N	Range	Mean ± Std Error	% ≥ MCL
TDS	344	129–3302	670.3 ± 21.5	61	91	200–1900	585.1 ± 35.1*	54.9	9	400–600	500 ± 31.6	77.8
Arsenic	241	1–10	2.8 ± 0.1	0	90	2.2–161.2	12.6 ± 2.2*	32.2	9	4.7–9.0	6.9 ± 0.7*	0
Selenium	329	0.1–50	3.9 ± 0.2	0.3	10	10–108.7	33.3 ± 10.5*	20	–	–	–	–
Strontium	99	20–16700	1028.9 ± 213.7	N/A†	90	66.2–18195	2319.8 ± 330.1*	N/A†	9	52.4–7646.2	1610 ± 787.1	N/A†
Barium	357	0.1–382	57.2 ± 2.9	0	90	1.8–173.7	32.3 ± 3.3*	0	9	2.9–60	22.4 ± 11.3*	0
Methanol	–	–	–	N/A	24	1.3–329	33.6 ± 13.3	N/A	5	1.2–62.9	27.4 ± 13.7	N/A
Ethanol	–	–	–	N/A	8	1–10.6	4.5 ± 1.2	N/A	4	2.3–11.3	6.8 ± 2.4	N/A

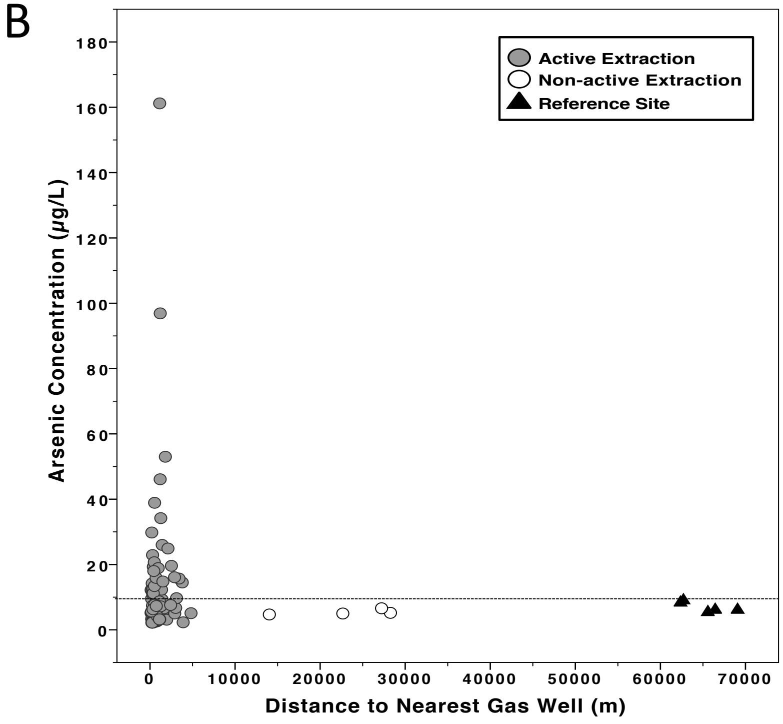
Historical data for the counties sampled in this study were obtained online at www.TWDB.state.TX.us/groundwater/
Maximum Contaminant Limits (MCL) obtained from the Environmental Protection Agency's (EPA) National Primary Drinking Water Regulations, 2009
TDS MCL = 500 mg/L, Arsenic MCL = 10 μg/L, Selenium MCL = 50 μg/L, Barium MCL = 2000 μg/L, N/A indicates no MCL has been established
† EPA recommends stable strontium values in drinking water do not exceed 4,000 μg/L

1

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

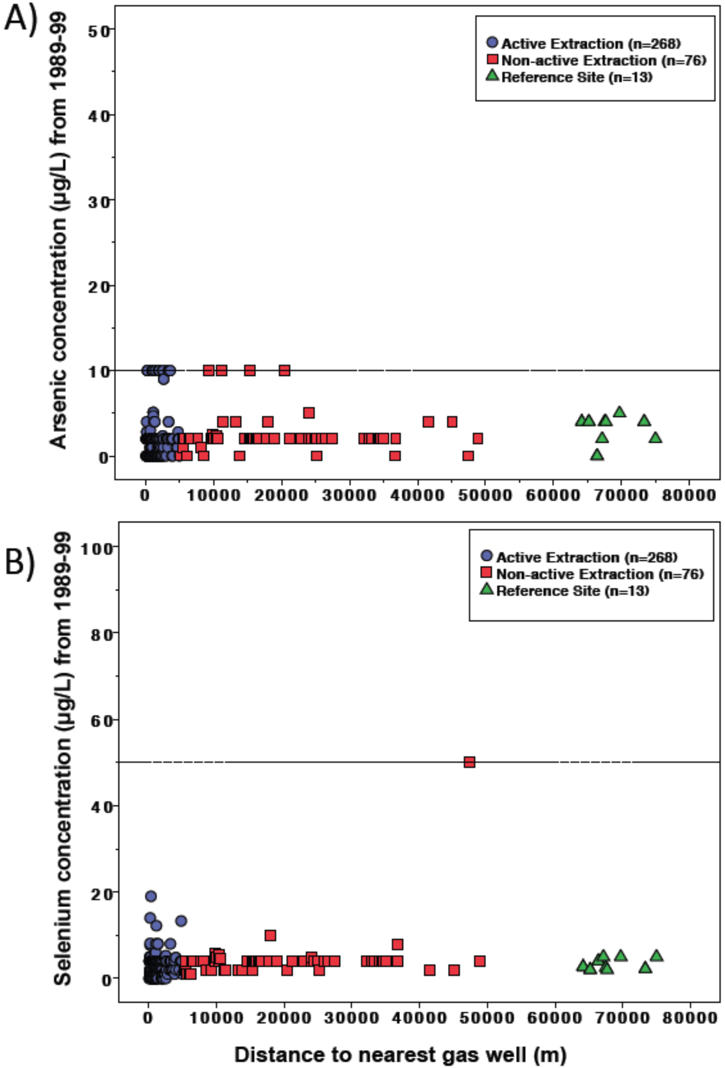
Geospatial analysis of TDS and Arsenic

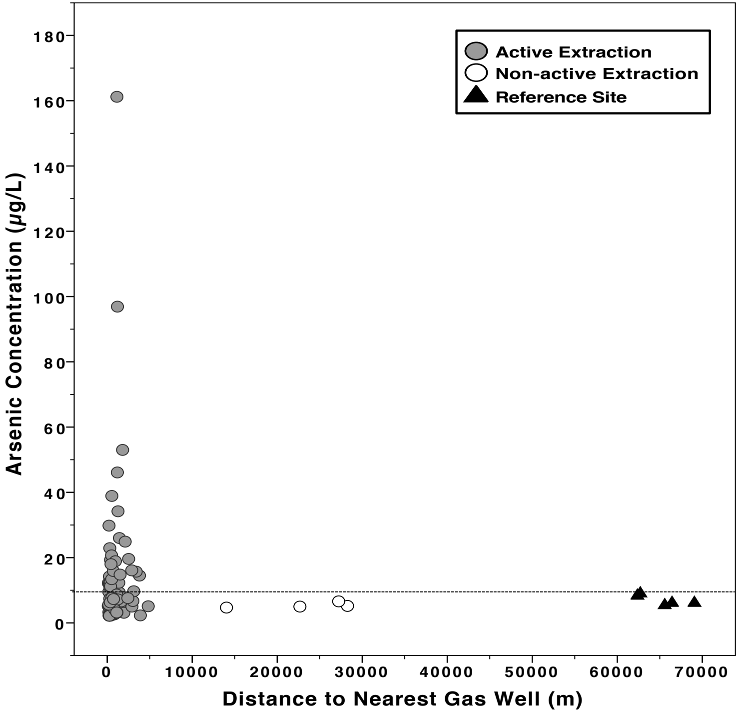




Fontenot, B. E., et al. *Environ. Sci. Tech.* **2013,** *47,* 10032-10040.

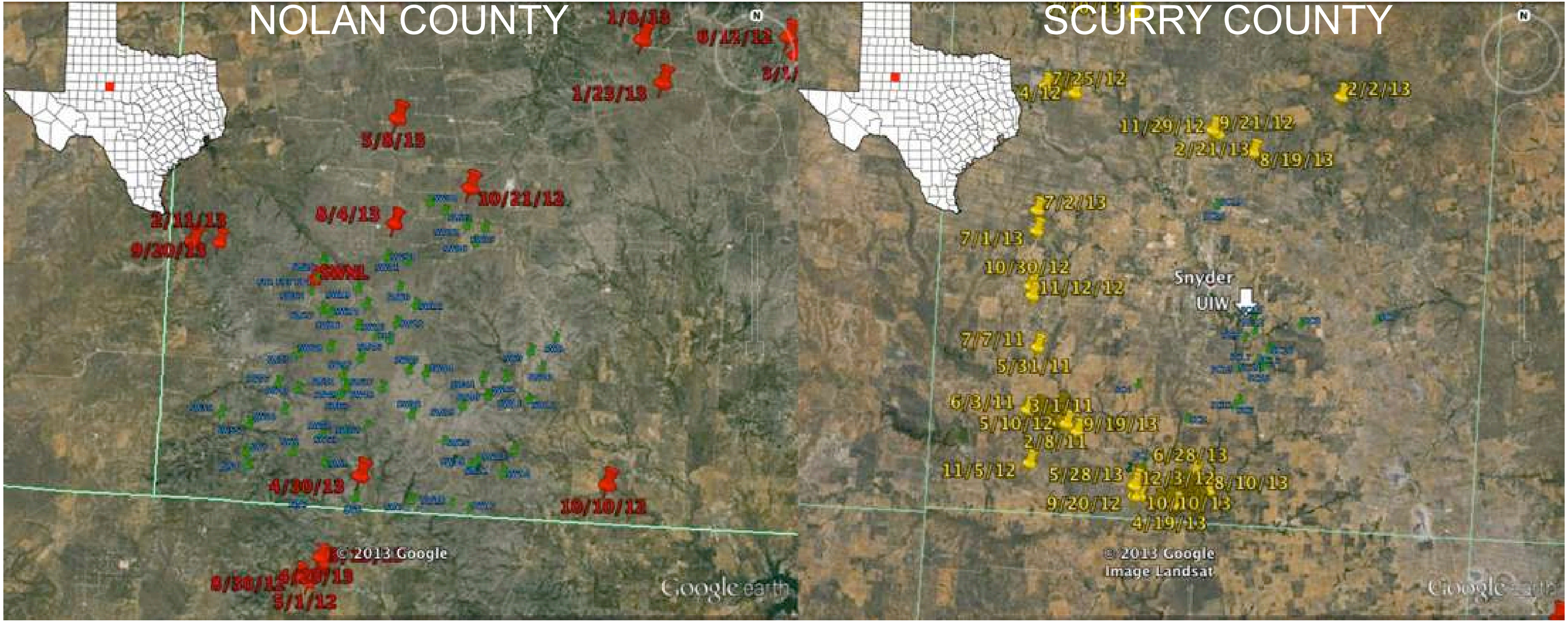
Comparison to historical data





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

Time-lapse analyses in the Cline Shale



60+ samples collected before, during and after unconventional drilling in Nolan county (left), and 50 samples collected in Scurry county (right)

Future Directions

Expand our reach into other shale formations

Across the United States, Canada and Europe

Become more involved into other components of the unconventional drilling process and other industrial processes

Use our advanced analytical capabilities to characterize a wide range of environmental events/catastrophes

Develop new technology and best management practices for instances of drilling-related contamination events

Remediation, recycling, appropriate waste disposal