Technical Workshop on Case Studies to Assess Potential Impacts of Hydraulic Fracturing on Drinking Water Resources
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Surface Water and Stray Gas Shallow Aquifer Contamination

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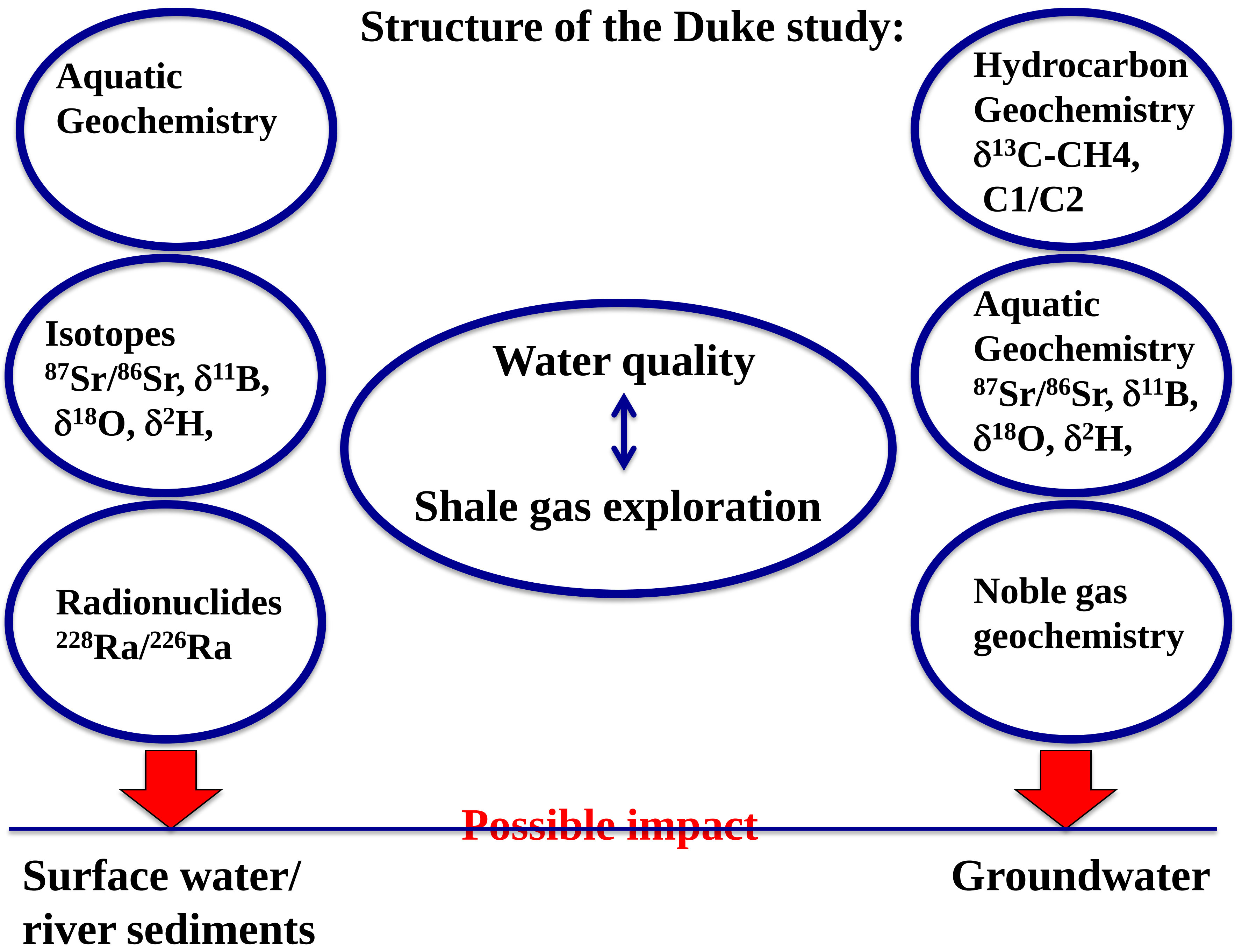
The approach of the Duke study:

- Conduct field-base studies in areas associated with shale gas development; search for temporal and spatial water-quality variations;
- Evaluate the geochemistry of groundwater from the associated aquifers; define the major geochemical features that characterize groundwater and surface water prior to shale gas development.
- Link possible water contamination to changes in water chemistry using multiple geochemical and isotopic tracers as proxies for sources and mechanisms of water contamination (using a single constitute in water as an evidence for, or lack of contamination, is misleading!).
- Integrate advanced geochemical and isotopic tools with hydrogeology.
- Evaluate the solid-phase (aquifer rocks, river sediments) and possible impact on water quality by using laboratory experiments).

Research conducted as part of the Duke study:

1. Since 2010 sampling over 600 shallow private wells in PA, NY, WV, AK, NC, TX;
2. Sampling produce/flowback waters from the Marcellus Shale and conventional oil and gas wells from PA and NY;
3. Sampling over 100 surface waters in PA and river sediments downstream from waste waters disposal sites;
3. Analysis of methane geochemistry in private wells – concentrations, ratios (ethane/methane), isotopes ($\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$)
4. Analysis of the chemistry (major and trace elements) and isotopes ($^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$-DIC)
5. Measurements of naturally occurring radium (^{226}Ra, ^{228}Ra) radionuclides;
6. Measurement of noble gases in groundwater.


Structure of the Duke study:
Aquatic Geochemistry
Hydrocarbon Geochemistry δ^{13}C-CH4, C1/C2
Isotopes ^{87}Sr/^{86}Sr, δ^{11}B, δ^{18}O, δ^{2}H,
Water quality
Shale gas exploration
Aquatic Geochemistry ^{87}Sr/^{86}Sr, δ^{11}B, δ^{18}O, δ^{2}H,
Radionuclides ^{228}Ra/^{226}Ra
Noble gas geochemistry
Possible impact
Surface water/ river sediments
Groundwater

Duke Study - Results

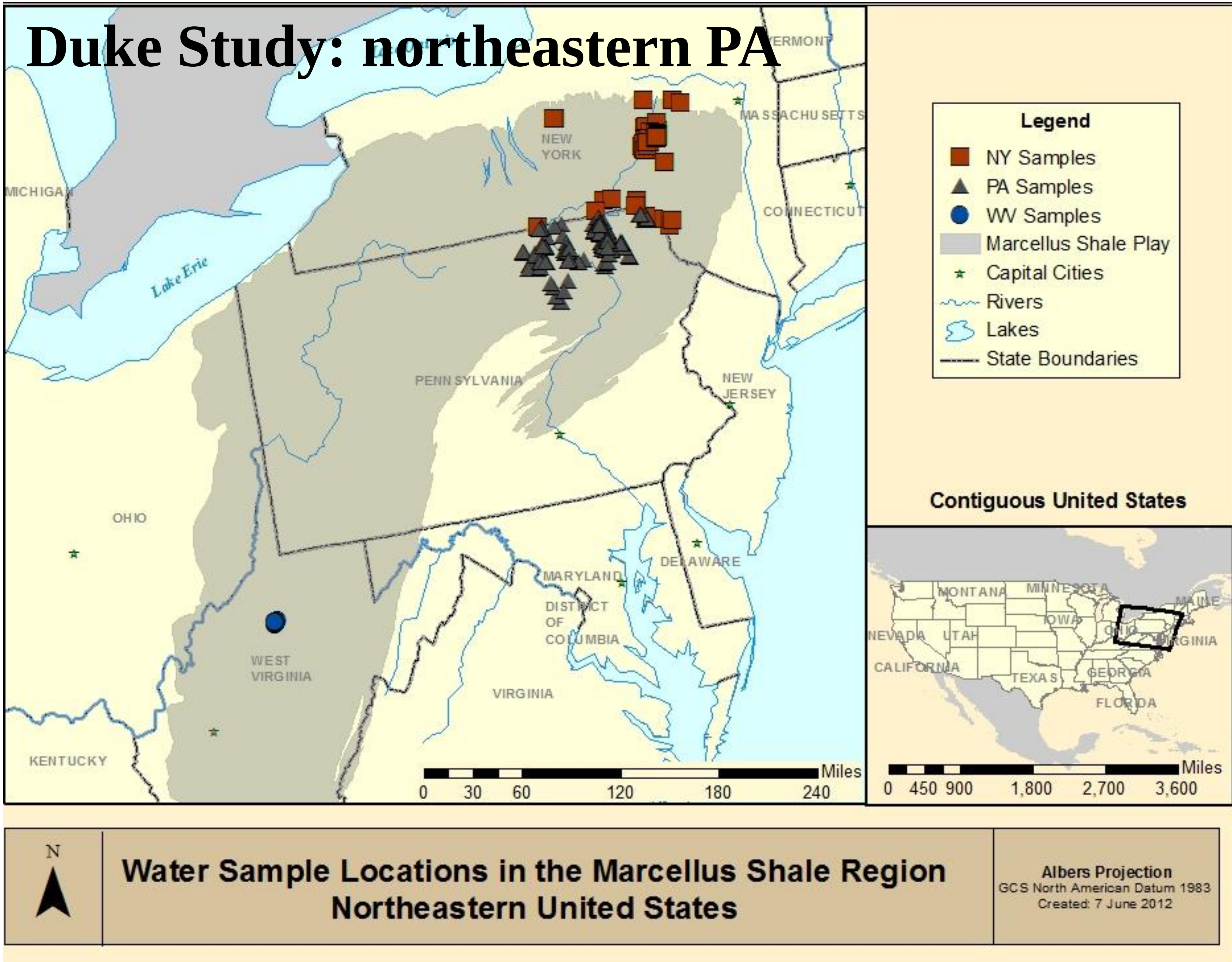
- Evidence for tray gas contamination in a subset of shallow wells near (<1 km) shale gas wells in northeastern PA (Osborn et al., 2011, Jackson et al., 2013).
- Evidence for natural flow of saline groundwater to shallow aquifers in in northeastern PA; indication to hydraulic connectivity to deep geological formations, but no indication to water contamination (Warner et al., 2012).
- Lack of stray gas and water contamination of shallow groundwater in Arkansas (Warner et al., 2013).
- Evidence for surface water contamination downstream from shale gas wastewater disposal site in western PA; accumulation of radium in river sediments (Warner et al., in review).

The debate on stray gas contamination

No risk:
Methane is ubiquitous in groundwater, with higher concentrations observed in valleys vs. upland; methane concentrations are best correlated to topographic and hydrogeologic features, rather than shale-gas extraction (Molofsky et al., 2013).

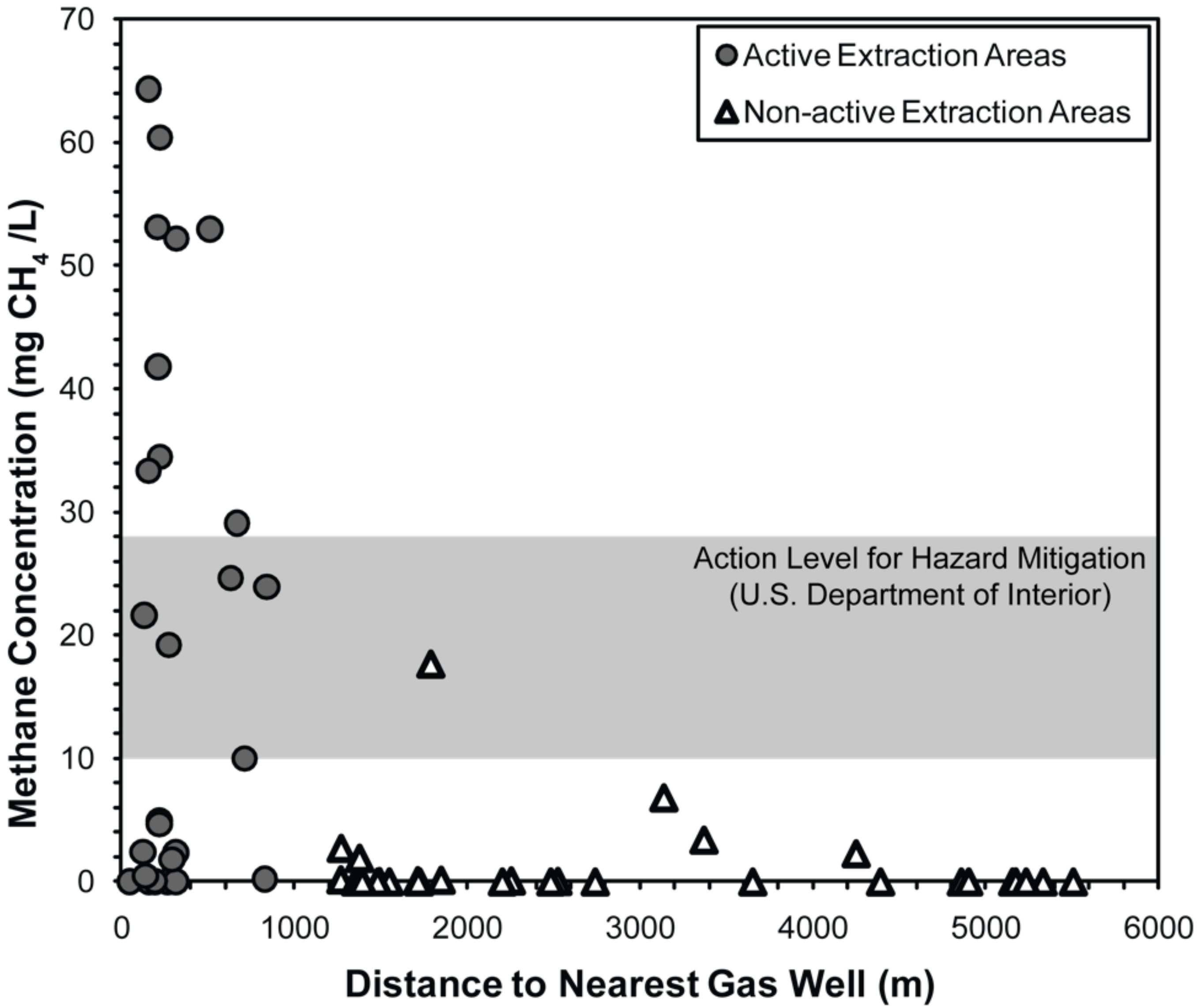
High risk in a subset of wells near shale gas sites :
Evidence for stray gas contamination in a subset of wells less than a km from shale gas sites in northeastern PA (Osborn et al., 2011; Jackson et al., 2013; Darrah et al., 2012).

Duke Study: northeastern PA



Definition of active versus non-active wells:

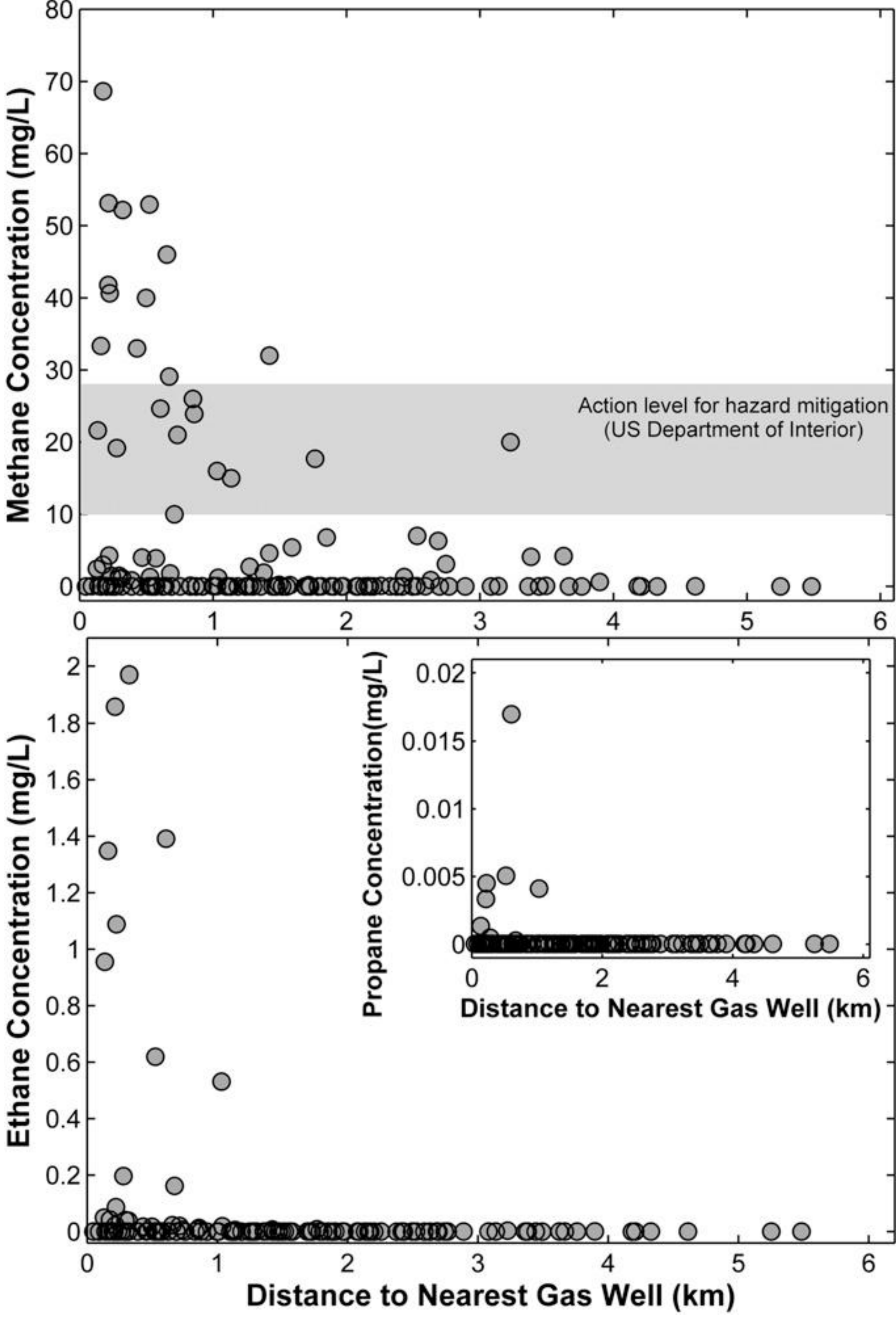
Private wells located <1km from a shale gas had typically higher methane



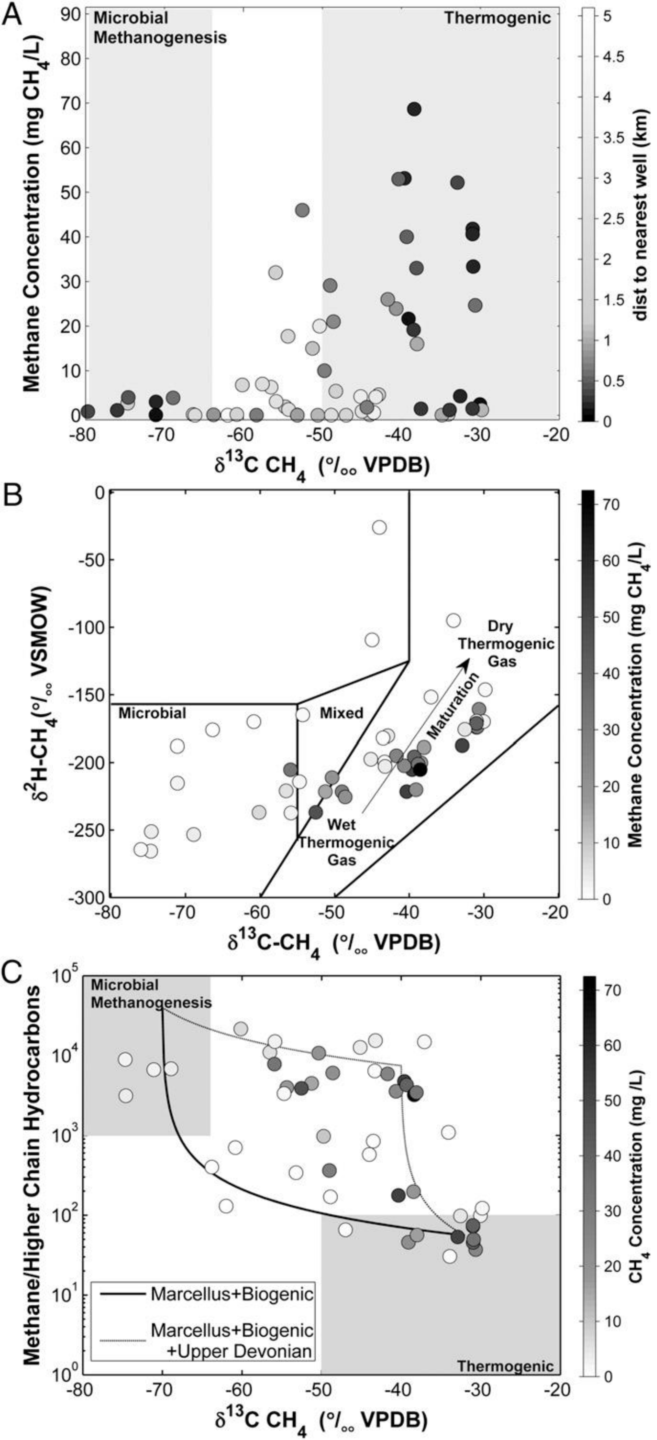
(Osborn et al., 2011; *PNAS*, 108,8172-8176)

Reinforcement of the data:

Presence of ethane and propane in wells <1 km from nearest gas well → must be derived from thermogenic source that occurs in shale gas wells (no ethane and propane in biological gas)



(Jackson et al., 2013; *PNAS*, June 2013)

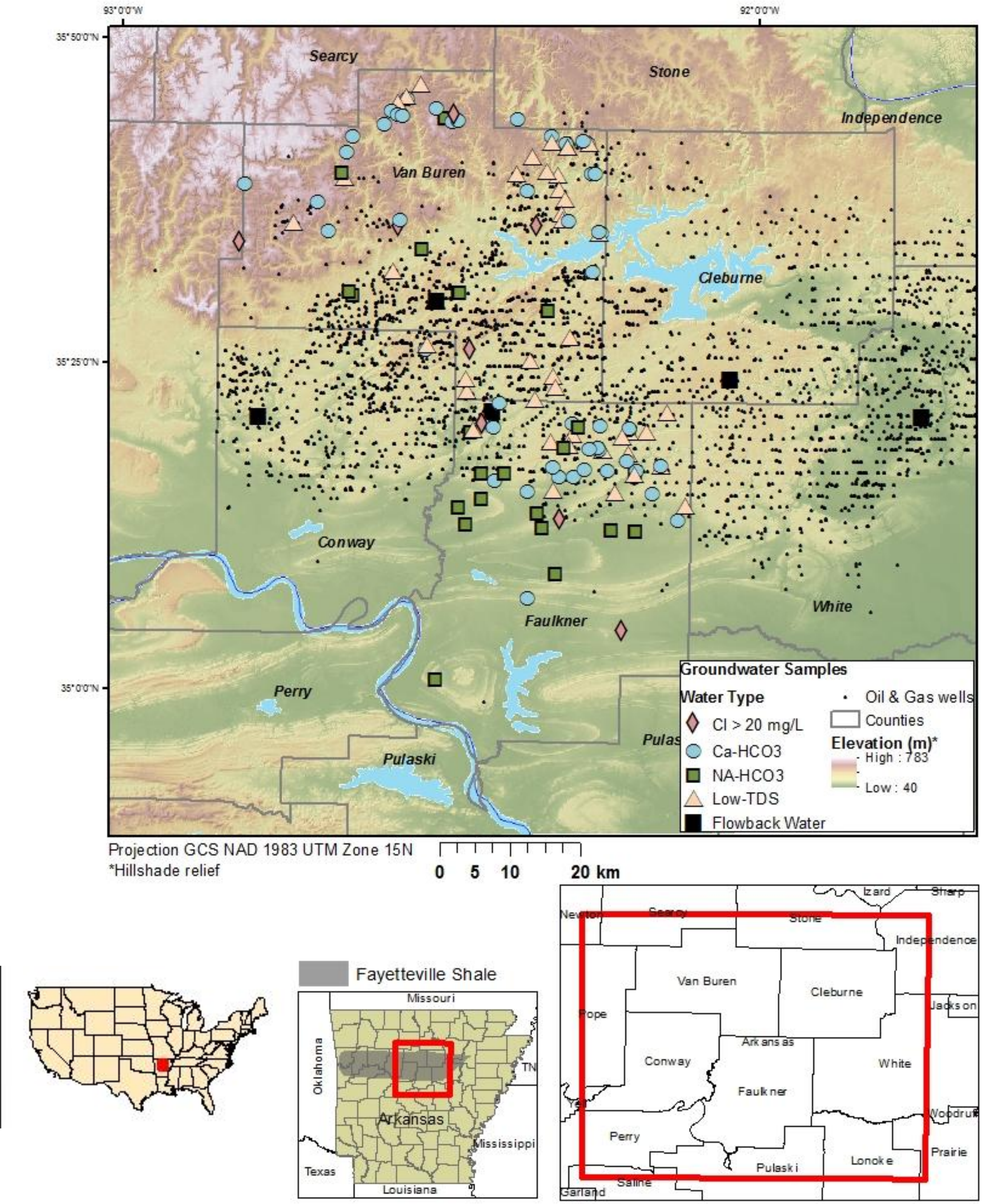


Methane sources?

Closer to shale gas wells → higher methane → higher $\delta^{13}C_{CH4}$ → lower CH_4/HC ratios

A distinction between a natural background methane flow and direct stray gas contamination

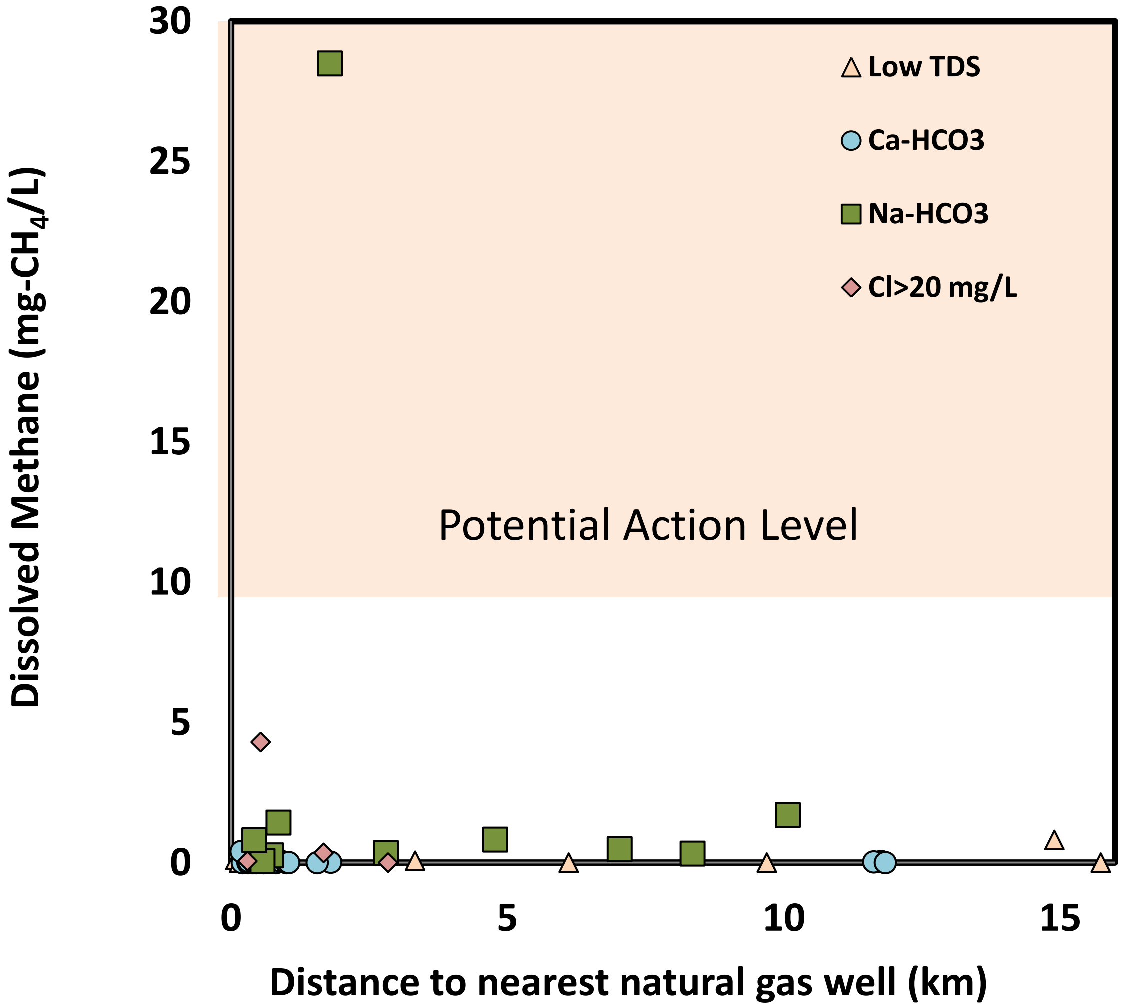
(Jackson et al., 2013; *PNAS*, June 2013)



GROUNDWATER IN FAYETTEVILLE SHALE NORTH-CENTRAL ARKANSAS

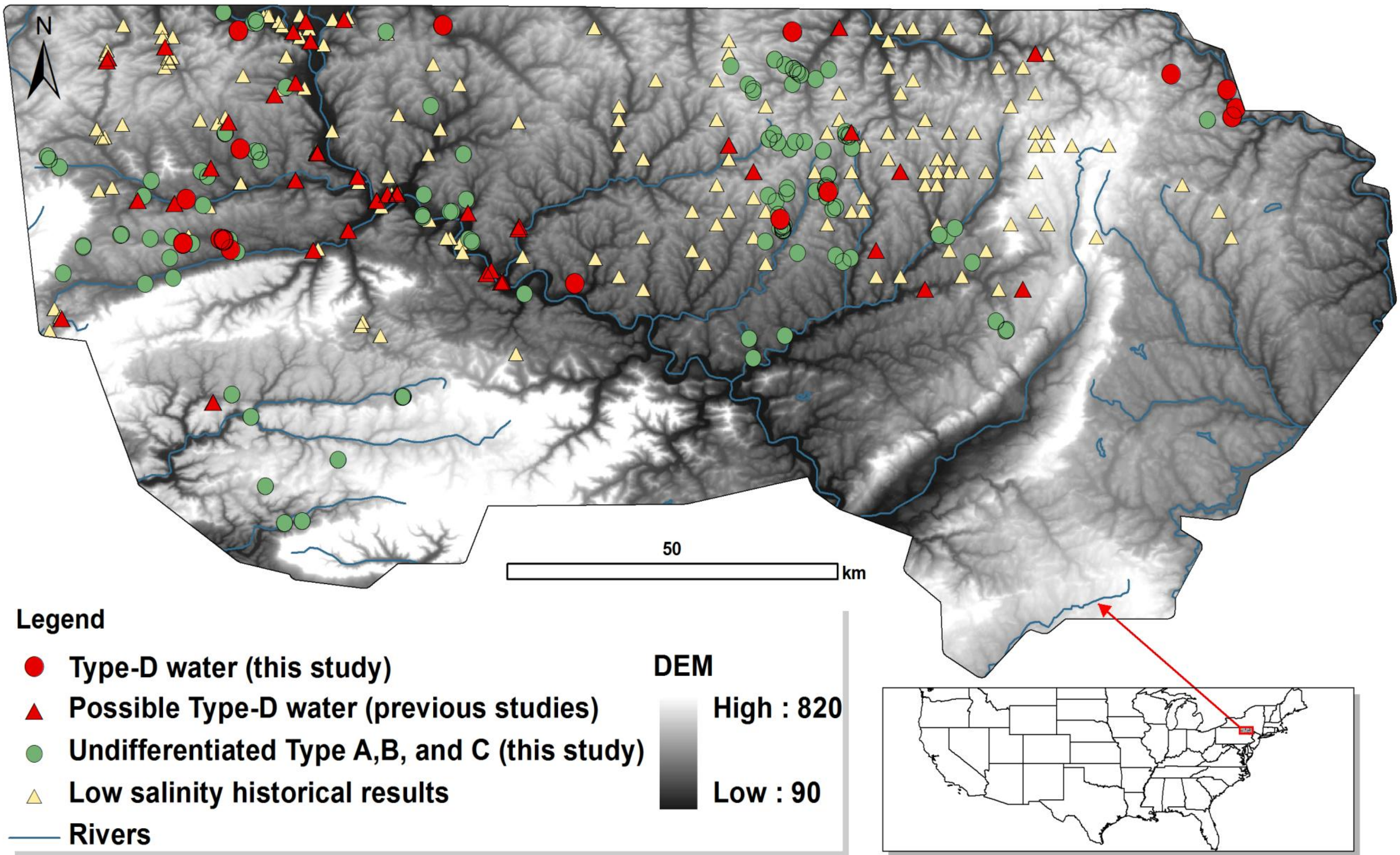
Warner et *al., (2013); Applied Geochemistry*, May 2013

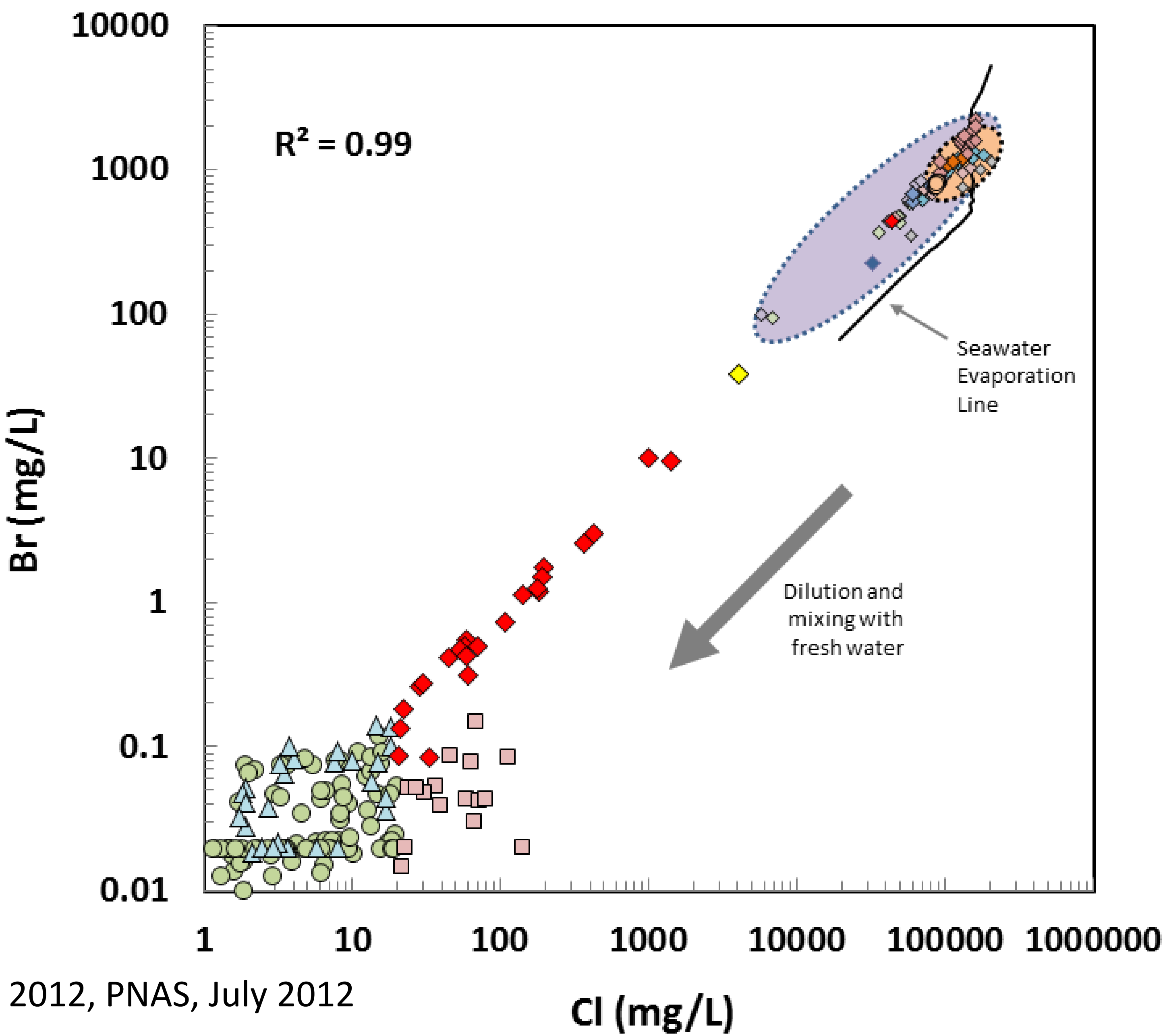
No evidence for stay gas contamination in Arkansas



Warner et *al*., *(2013); Applied Geochemistry*, May 2013

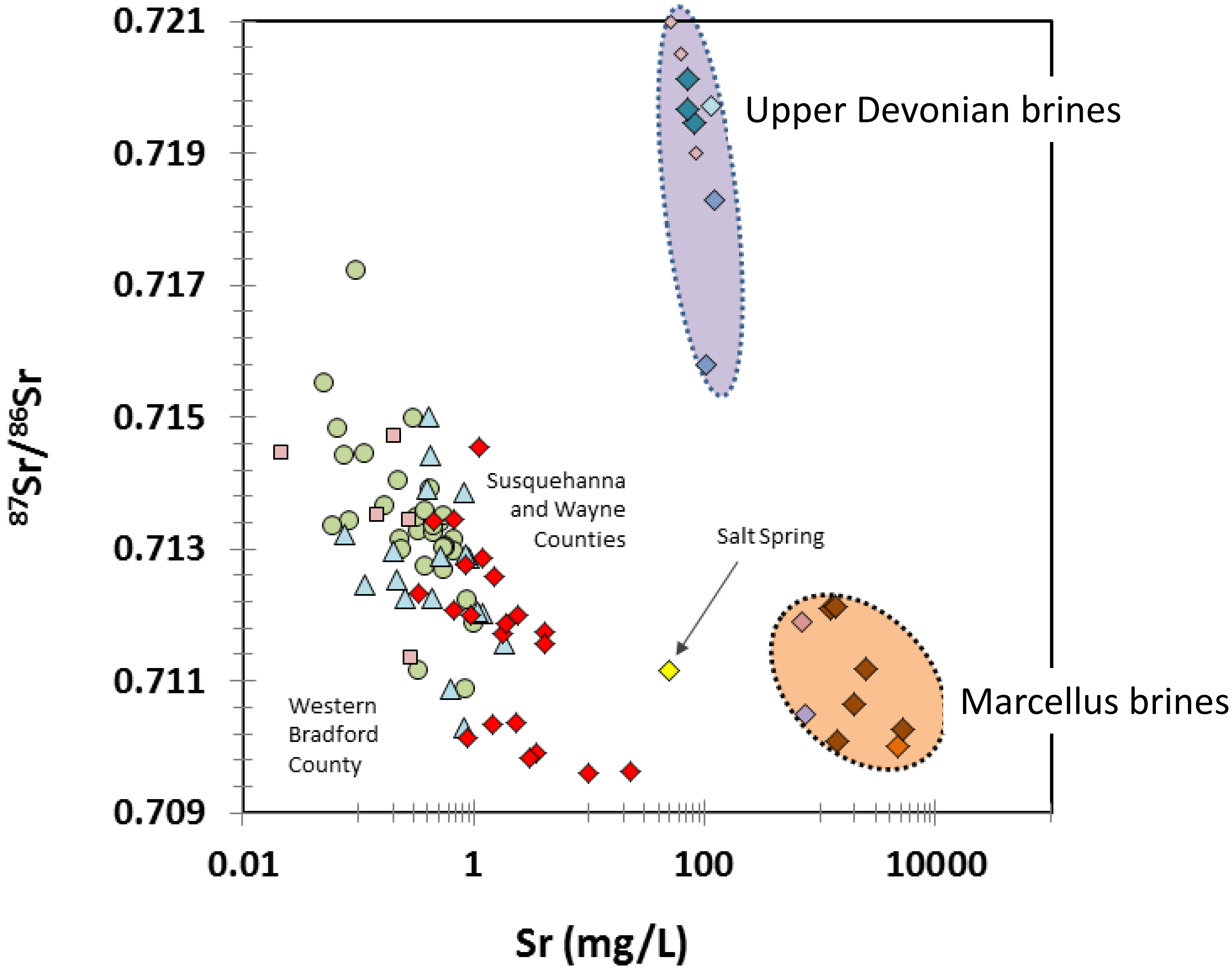
Occurrence of saline groundwater enriched in barium in shallow aquifers





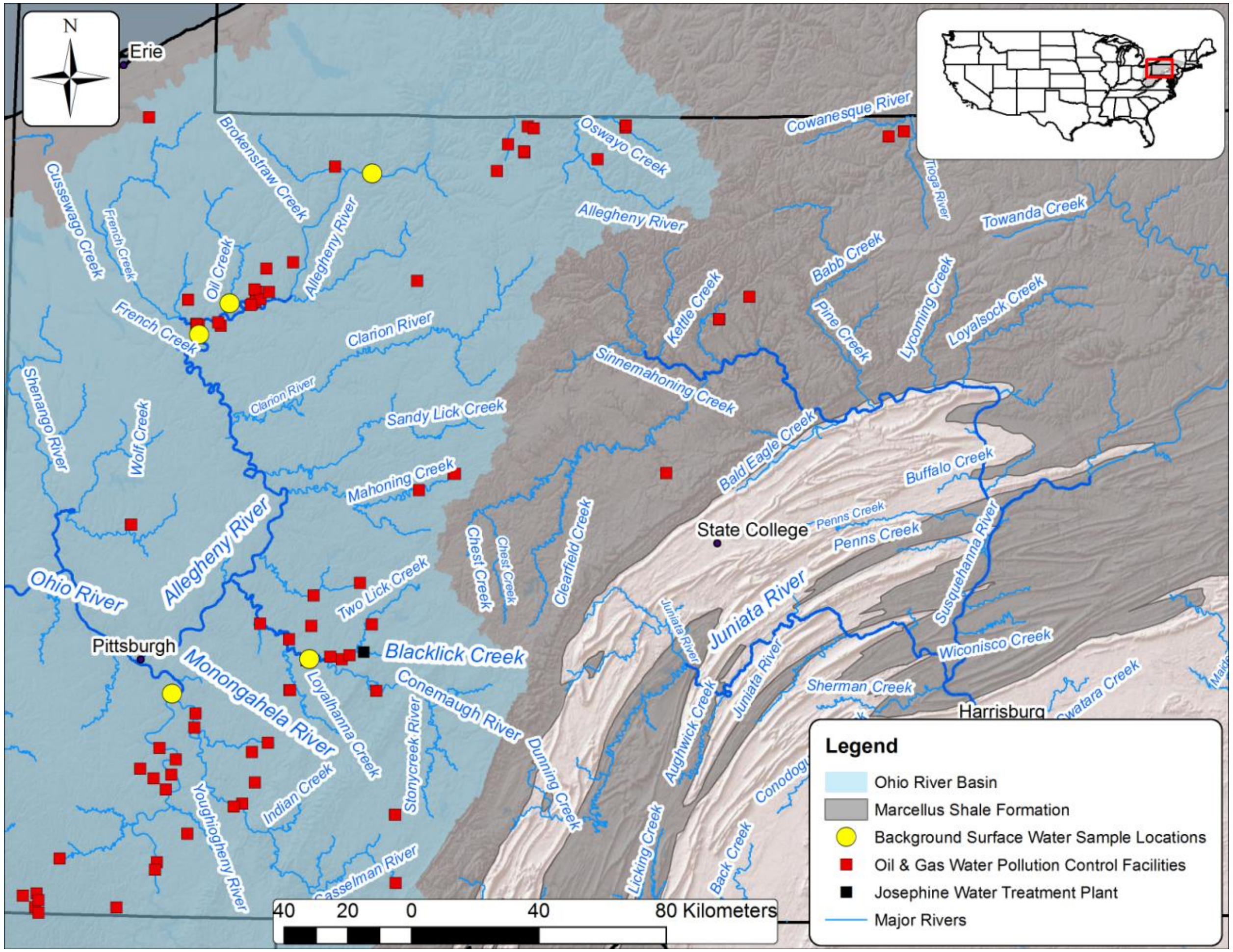
Warner et al., 2012, PNAS, July 2012

Geochemical and isotopic evidence for mixing with Marcellus brines



Warner et al., 2012, PNAS, July 2012

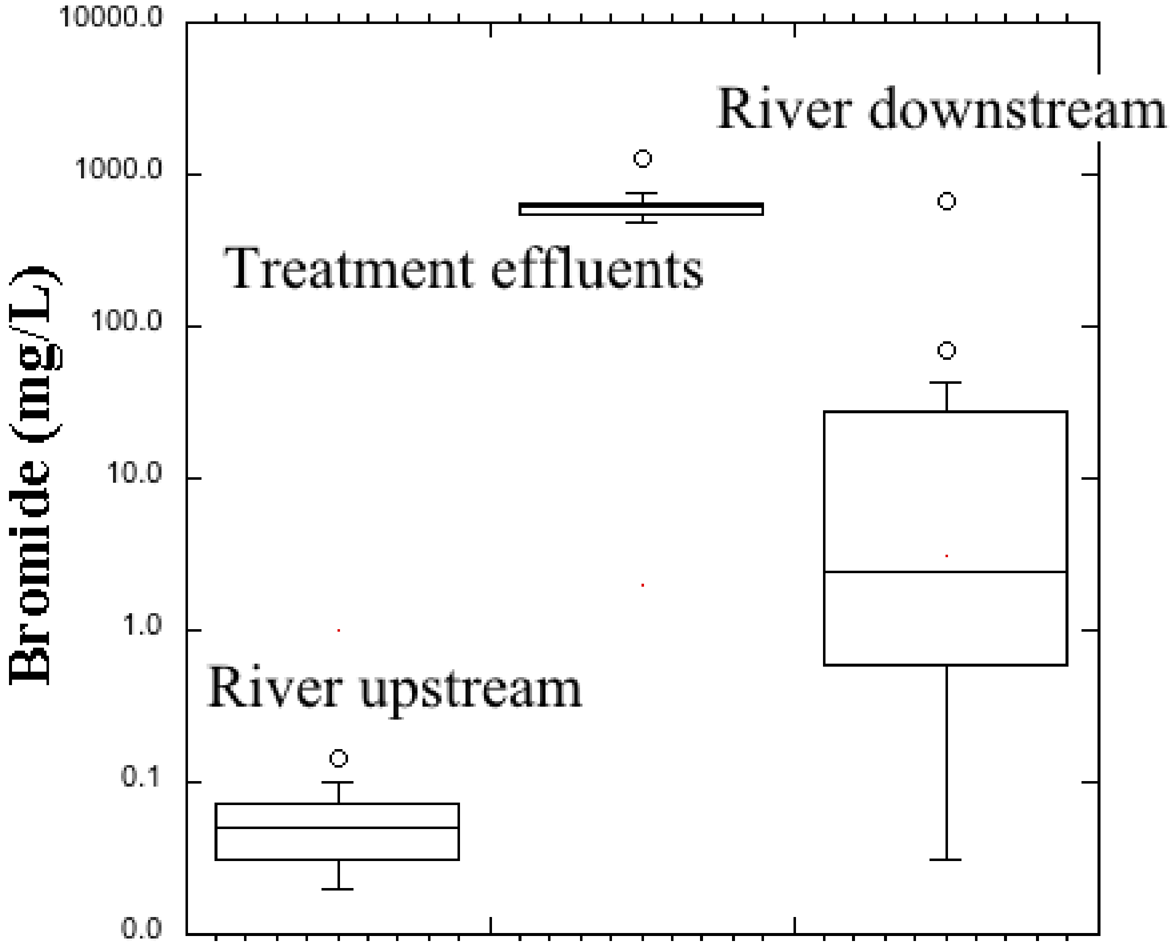
Disposal of wastewater from shale gas development



Warner et al., 2013, ES&T (in review)

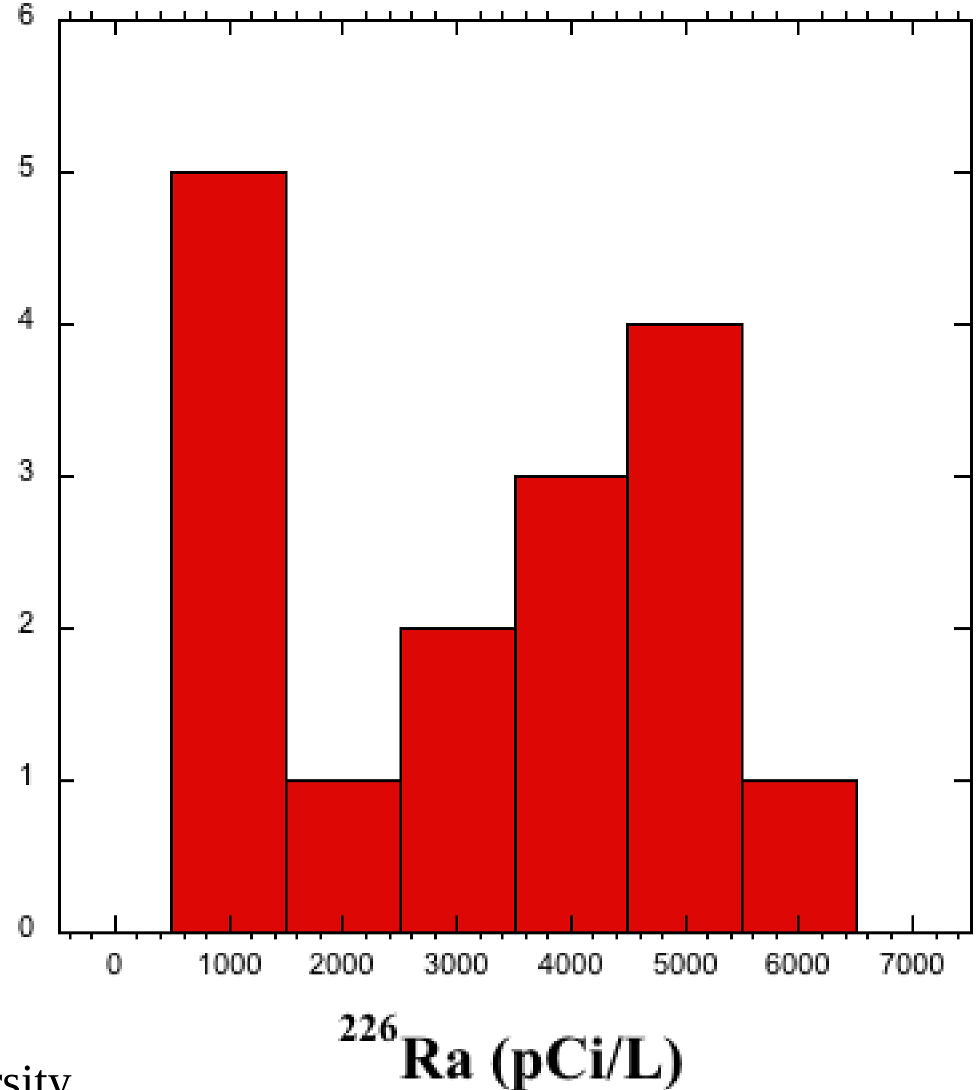
Josephine Brine Treatment Facility

Brine treatment has no effect on halogens



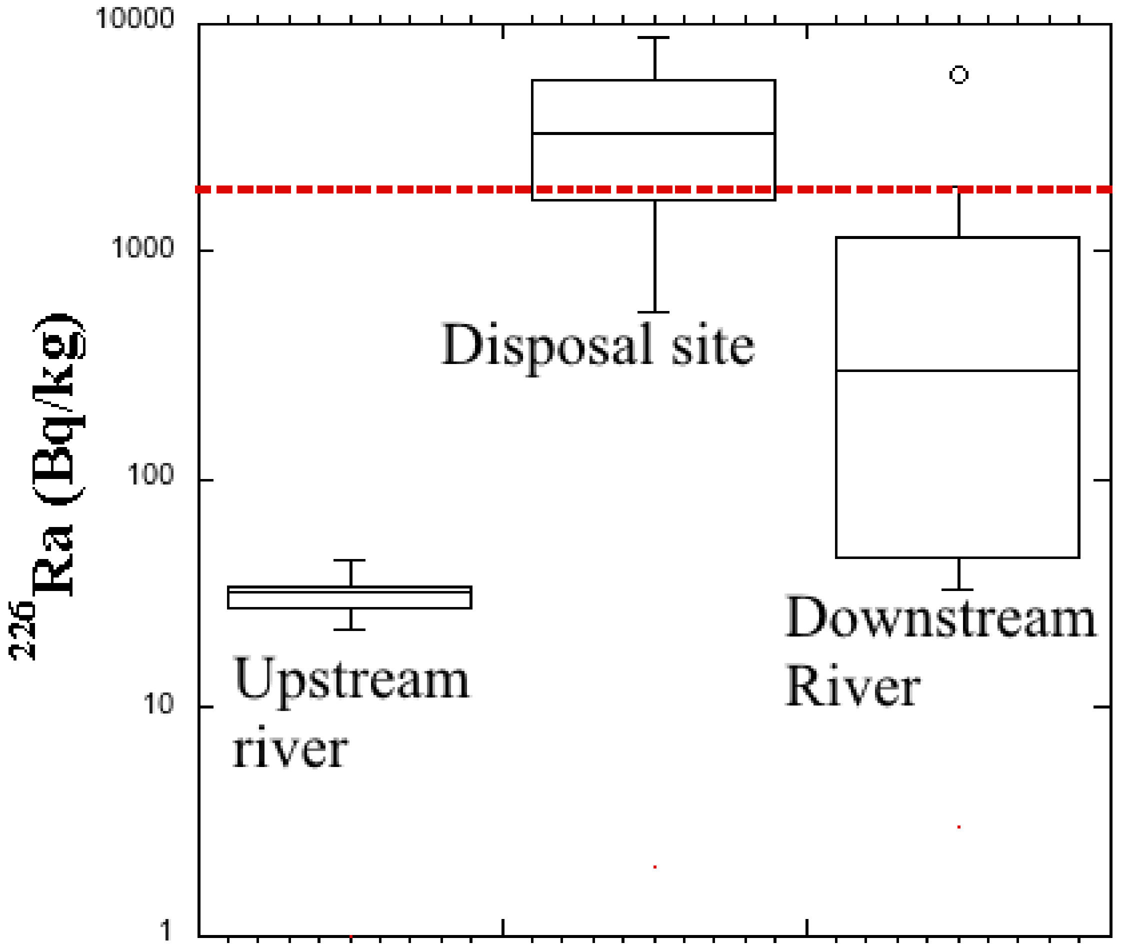
Warner et al., 2013, ES&T (in review)

Radium occurrence in flowback and produced waters from the Marcellus Shale



Source: Duke University

A long-term legacy of radioactivity accumulation in river sediments associated with a disposal site (Josephine, PA)



Radiation threshold (requires a licensed radioactive waste disposal facility)

Warner et al., 2013, ES&T (in review)

Conclusions:

• Evidence for methane contamination in shallow drinking water wells in some locations in northeastern Appalachian Basin (PA) but not in Fayetteville Basin (AK).

•No evidence has shown, so far, for direct groundwater contamination from produced/flowback water; yet we show evidence for hydraulic connectivity between the Marcellus and shallow aquifers in PA.

• Disposal of produced water from gas exploration directly into surface water poses a significant risks to water resources and long-term radioactivity hazard. A zero-discharge policy is recommended.

• Sustainable and long-term shale gas developments will need to accommodate the environmental issues associated with shale gas drilling and hydro-fracturing.

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For more information:

http://sites.nicholas.duke.edu/avnervengosh/

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