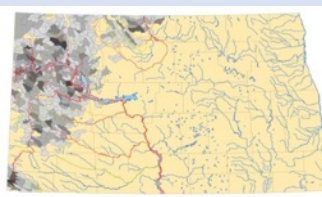




# USGS studies investigating chemical composition and environmental exposure pathways of unconventional oil and gas products and wastes

Isabelle M. Cozzarelli  
U.S. Geological Survey, Reston, VA

Health Effects Institute's Energy Research Program Planning Meeting  
July 11-12, 2018, Denver Colorado



# Federal Multiagency Collaboration on Unconventional Oil and Gas (UOG)

## Federal Multiagency Collaboration on Unconventional Oil and Gas Research

A Strategy for Research and Development



July 18, 2014

- Agencies: DOE, **DOI**, and EPA
- Outstanding research needs identified:
  - Understanding the potential impacts on water quality and availability over the entire life cycle of UOG operations
  - Understanding the composition of hydraulic fracturing fluids and/or wastewaters and potential risk
  - Understanding the environmental pathways that could lead to exposures to toxic chemicals during energy extraction and waste management activities.

USGS: non-regulatory science information agency

# Federal Multiagency Collaboration on Unconventional Oil and Gas (UOG)

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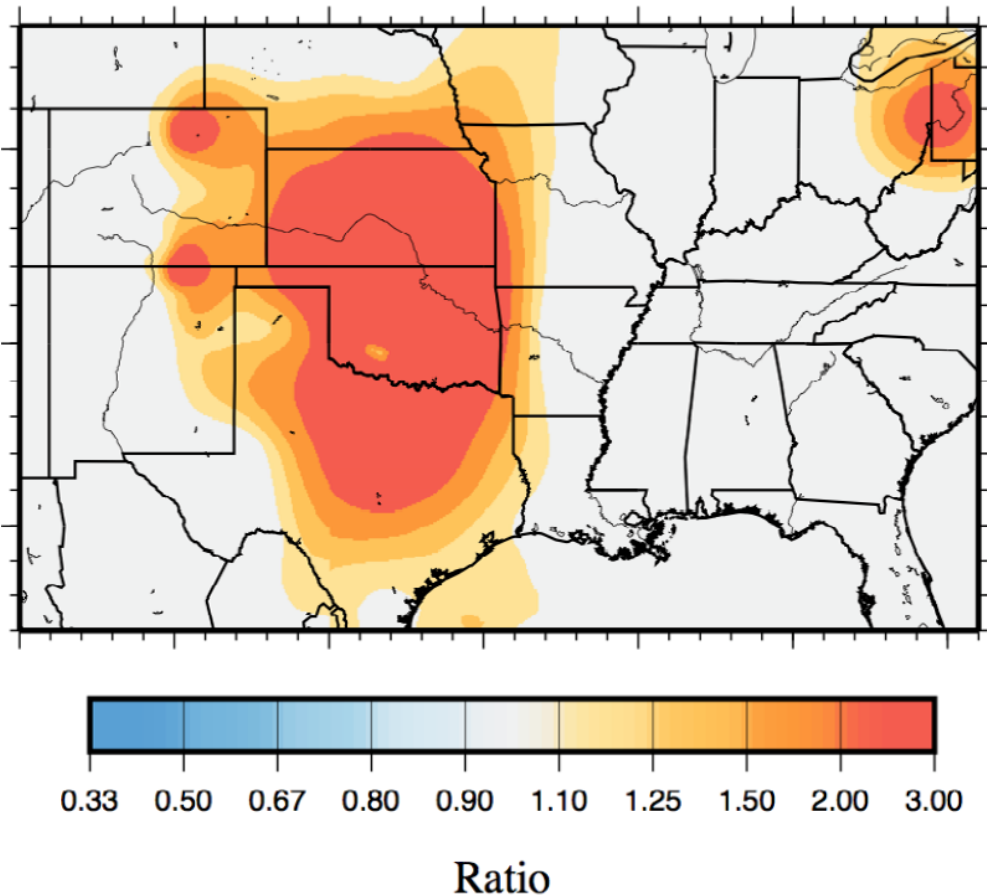


July 18, 2014

→ Research being conducted by  
USGS Energy & Minerals, Water, and  
Environmental Health Mission Areas

# USGS Hazards Mission Are: Induced Seismicity Science

## National Seismic Hazard Maps: Change



- One year forecast in regions of induced seismicity.
- Based on short term seismicity rates.
- Used to communicate risks to local populations.
- Forecasts made for 2016, 2017, and 2018.
- Goal: Prediction. Are there observable signals, surface or subsurface, prior to triggering. Prediction and mitigation can reduce stress on local populations.



HEALTH  
EFFECTS  
INSTITUTE

October 2015

**Strategic Research Agenda on the  
Potential Impacts of 21st Century  
Oil and Natural Gas Development  
in the Appalachian Region and  
Beyond**

HEI Special Scientific Committee on  
Unconventional Oil and Gas Development in  
the Appalachian Basin

USGS is conducting research in several of the research areas identified as highest priority in the Strategic Research Agenda:

- Identifying long-term and short-term trends in water quality in impacted areas
- Toxicity studies of UOG wastewater
- Ecological impacts due to landscape changes
- Evaluation of impacts of accidental releases of OG fluids and wastes
- Determination of potential impacts of OG waste disposal

# Product and wastewaters can be released throughout the energy life cycle

Patterson *et al.*, 2017, assessed spill data from 2005 to 2014 at 31,481 UOG wells in Colorado, New Mexico, North Dakota, and Pennsylvania.

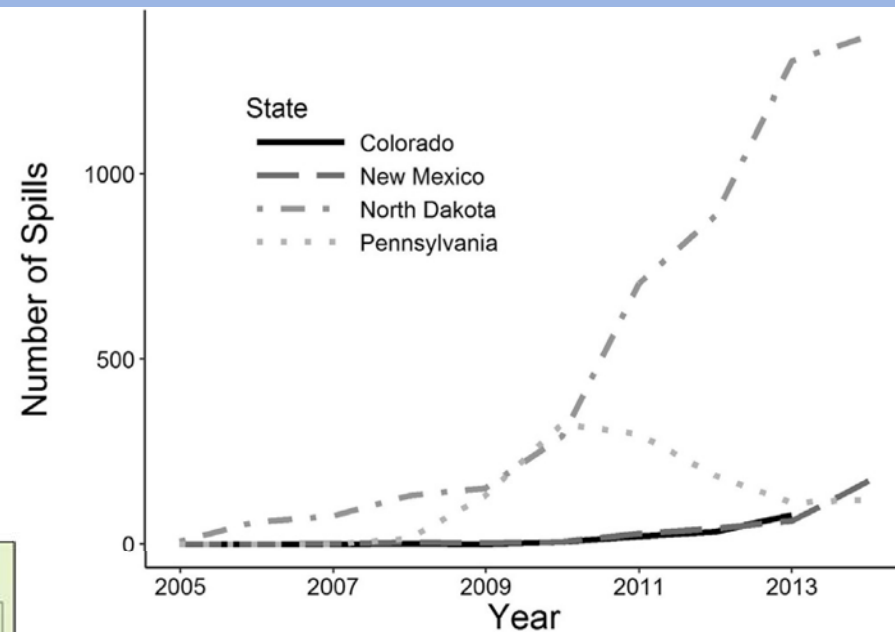
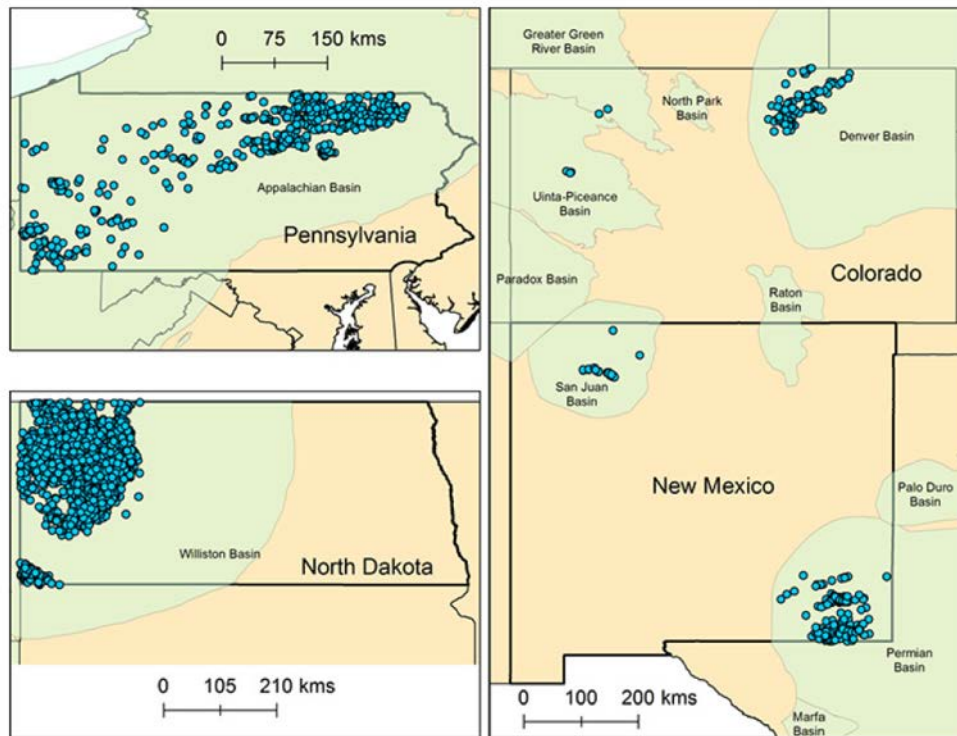
- They found 2–16% of wells reported a spill each year.
- The largest spills exceeded 100 m<sup>3</sup>
- 50% of spills were related to storage and moving fluids





# Spills from Oil and Gas (OG) Production

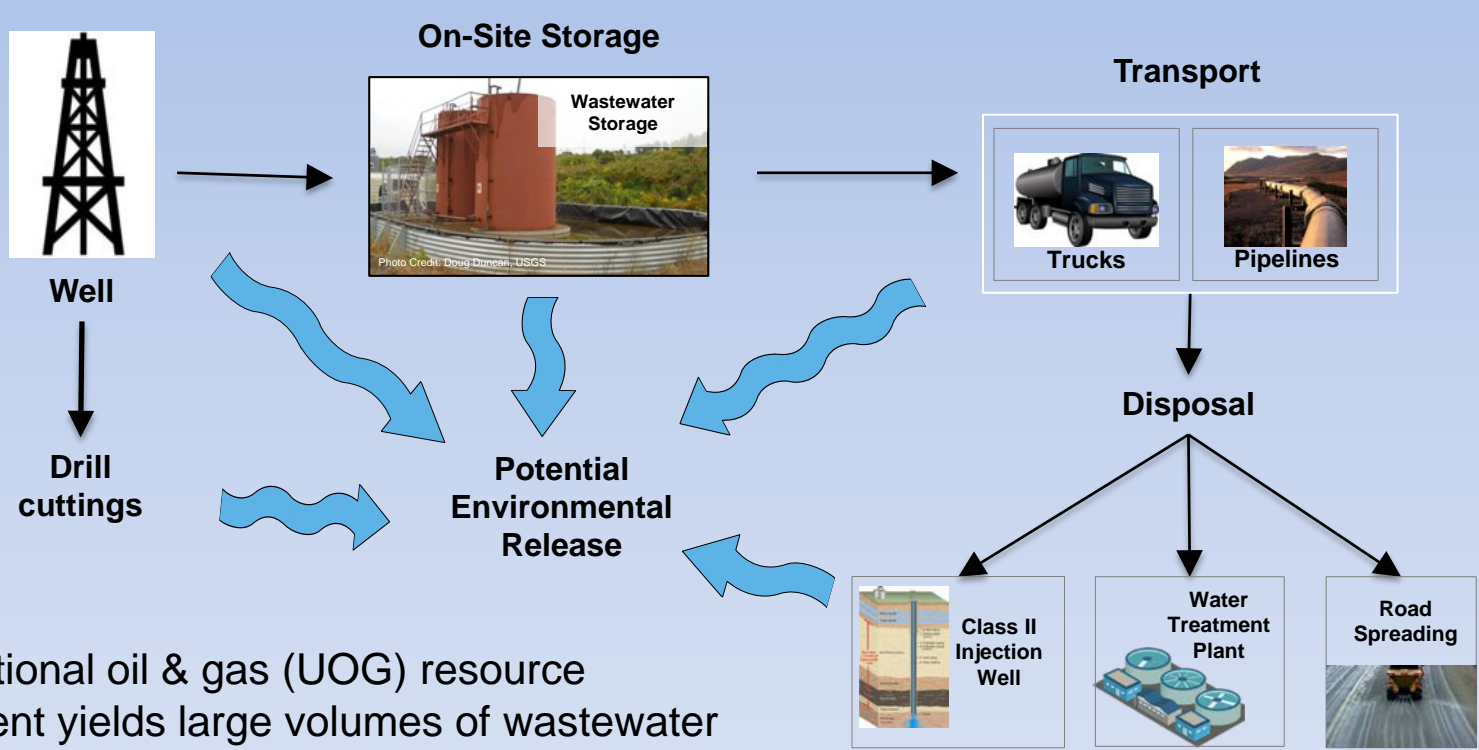
Distribution of spills attributed to UOG wells by state. Light green polygons indicate shale basins.



- The expansion in production activity has resulted in a similar expansion in unintentional releases into the environment.
- Unintentional releases are occurring across the Nation and affecting large geographical areas.
- This trend will likely continue into the future.



# Prioritized Environmental Pathways of UOG Wastewaters



- Unconventional oil & gas (UOG) resource development yields large volumes of wastewater (>2 million gallons per well).
- Wastewater has high TDS, organics, metals, radionuclides



# Questions Driving our Research

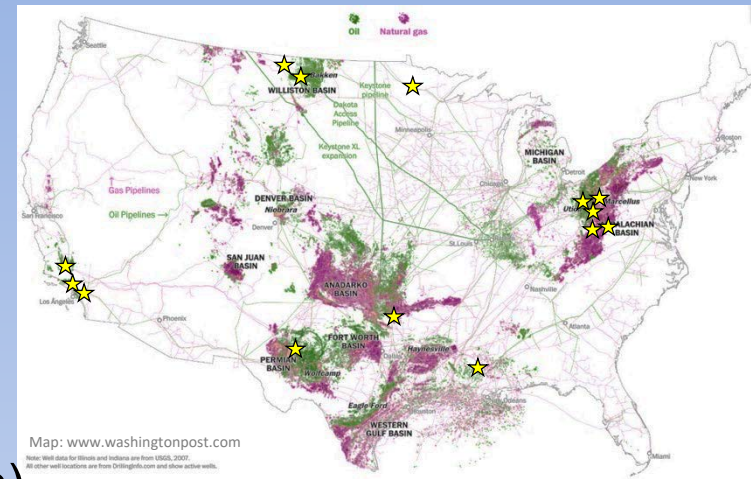
What is the composition of oil and gas associated materials, the potential pathways to the environment, the mode-of-action and the effects, if any, on receptor organisms from exposure to these materials?

When releases in a watershed occur, are there contaminant exposures and actual, not perceived, public health concerns throughout the watershed or underlying aquifers downstream or downgradient from the release?

Releases of energy-associated materials to the environment can occur at various time scales thereby altering biogeochemistry and potential health effects on fish and wildlife as well as contaminant exposures to humans. Is persistence related to actual health effects?

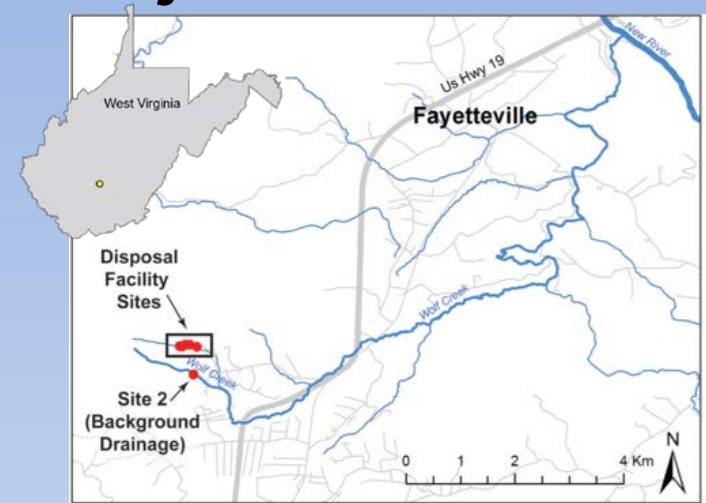
# Current Research Projects

1. Characterizing source materials from existing wells and active production sites.  
*USGS Produced Waters database*
2. Assessing watershed-scale oil and gas development impacts on high-value trout streams and watersheds (Marcellus Region)
3. \* Evaluating impacts of Class II wastewater injection facilities (West Virginia)
4. Regional study of the extent to which fluids from oil and gas development may be moving out of oil zones into protected groundwater zones. (San Joaquin Valley, California)
5. \* Studying historical (Montana) and recent (North Dakota) leaks and spills of brine wastewaters in the Williston Basin.
6. Determining the aquatic toxicity of major ions associated with oil and gas waters (Williston Basin).
7. Studying wastewater and oil dumps on Bureau of Land Management lands in New Mexico (Permian Basin).



# Impacts of a Class II Wastewater Injection Facility on WV Stream

**Objective:** Evaluate impacts of activities at an OG wastewater disposal facility on stream water and sediment biogeochemistry and endocrine disruption.

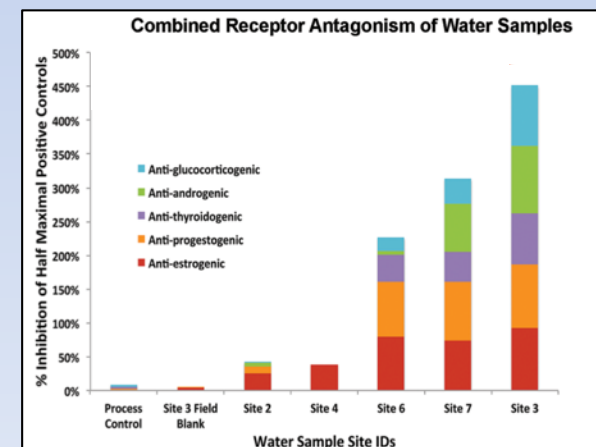
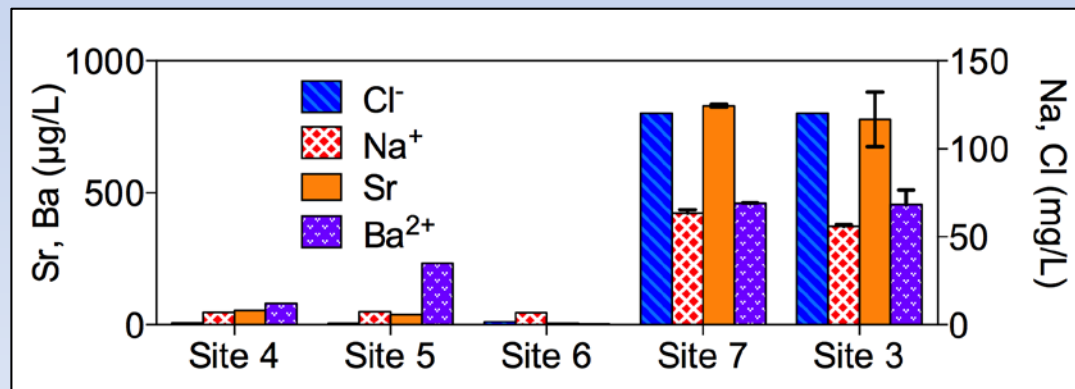
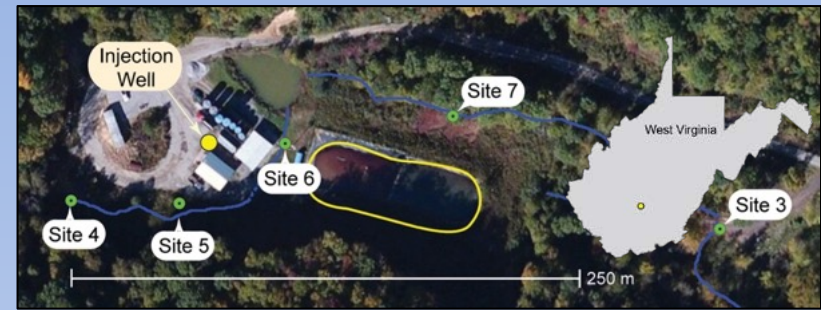


Major observations in following slides



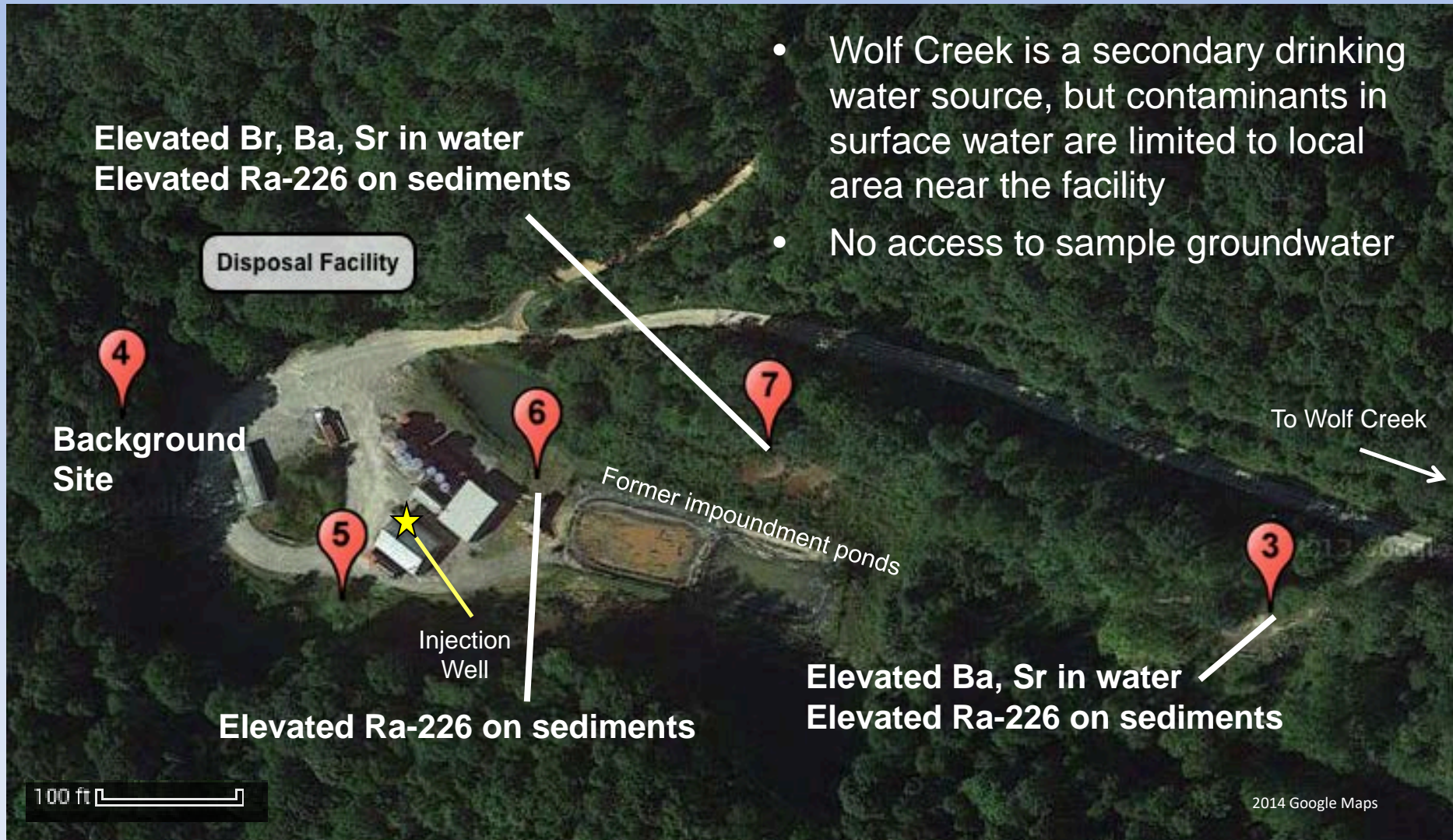
# Impacts of a Class II Wastewater Injection Facility

- Key findings:
  - Water and sediment samples collected downstream from the disposal facility are impacted by UOG waste contaminants.
    - Elevated Na, Cl, Ca, Li, Ba, and Sr concentrations in surface water at sites 7 and 3 are consistent with impacts from shale gas wastewater
  - Although the health of aquatic organisms was not assessed our results showed the potential for adverse biological effects due to:
    - Endocrine disrupting activity in surface waters; could have implications for reproductive and/or developmental health
    - Altered microbial communities and nutrient cycling in downstream sediments.



From Akob *et al.* 2016 *ES&T* and Kassotis *et al.*, 2016 *STOTEN*

# Produced water signal is also reflected in sediments





# Organic tracers of wastewater fluids and microbiological alterations of affected sediments



Relative abundance of antibiotic-resistance genes similar in background and downstream sediments

But, higher relative abundances of two genes encoding for multidrug resistance (*acrB* and *mexB*) found in sediments downstream

Higher relative abundance likely due to their function as efflux pumps to remove foreign chemicals as well as antibiotics from cells



Organic substances detected in surface water indicative of UOG wastewater:

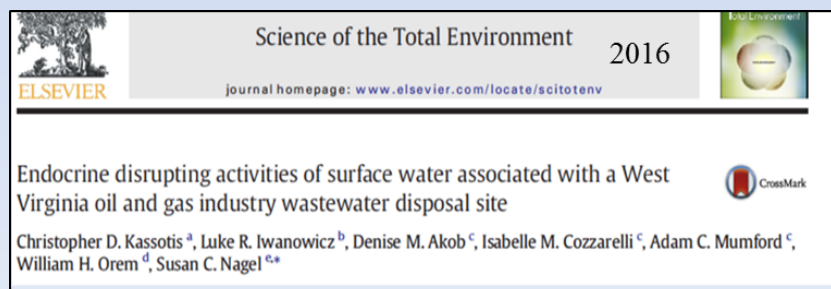
2-(2-butoxyethoxy)-ethanol

Tris (1-chloro-2-propyl)phosphate

$\alpha$ ,  $\alpha$ -dimethyl-benzenemethanol

3-ethyl-4-methyl-1H-pyrrole-2,5-dione

tetrahydro-thiophene-1,1-dioxide



# North Dakota Wastewater Pipeline Spill: Blacktail Creek

**Objective:** To identify and characterize the fate and transport of constituents released during a spill and evaluate the health impacts to wildlife and humans due to the spill.





Crews work to recover oil from Blacktail Creek north of Williston, N.D., on Sunday, Jan. 25, 2015, after the pipeline leak. Photo courtesy of Environmental Protection Agency. See more at: <http://oilpatchdispatch.areavoices.com/tag/environment/#sthash.XS226pX.dpuf>


Science of the Total Environment 579 (2017) 1781–1793

Contents lists available at ScienceDirect

**Science of the Total Environment**

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)



## Environmental signatures and effects of an oil and gas wastewater spill in the Williston Basin, North Dakota

I.M. Cozzarelli<sup>a,\*</sup>, K.J. Skalak<sup>a</sup>, D.B. Kent<sup>b</sup>, M.A. Engle<sup>c</sup>, A. Benthem<sup>a</sup>, A.C. Mumford<sup>a</sup>, K. Haase<sup>a</sup>, A. Farag<sup>d</sup>, D. Harper<sup>d</sup>, S.C. Nagel<sup>e</sup>, L.R. Iwanowicz<sup>f</sup>, W.H. Orem<sup>c</sup>, D.M. Akob<sup>a</sup>, J.B. Jaeschke<sup>a</sup>, J. Galloway<sup>g</sup>, M. Kohler<sup>b</sup>, D.L. Stoliker<sup>b</sup>, G.D. Jolly<sup>a</sup>

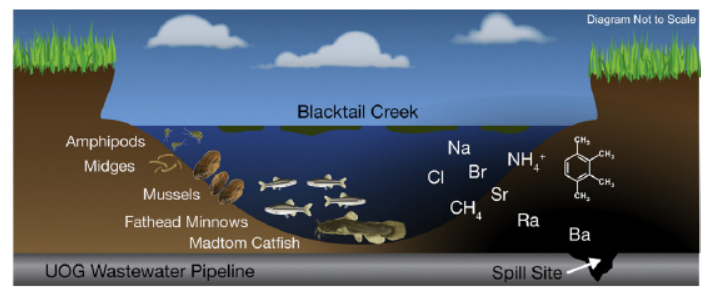
<sup>a</sup> U.S. Geological Survey, National Research Program, Reston, VA 20192, USA  
<sup>b</sup> U.S. Geological Survey, National Research Program, Menlo Park, CA 94025, USA  
<sup>c</sup> U.S. Geological Survey, Eastern Energy Resources Science Center, Reston, VA 20192, USA  
<sup>d</sup> U.S. Geological Survey, Columbia Environmental Research Center, Jackson Field Research Station, Jackson, WY 83001, USA  
<sup>e</sup> Department of Obstetrics, Gynecology and Women's Health, University of Missouri, Columbia, MO 65212, USA  
<sup>f</sup> U.S. Geological Survey, Leetown Science Center, Kearneysville, WV 25430, USA  
<sup>g</sup> U.S. Geological Survey, North Dakota Water Science Center, Bismarck, ND 58503, USA

## Open Access Publication with All Data Available

### HIGHLIGHTS

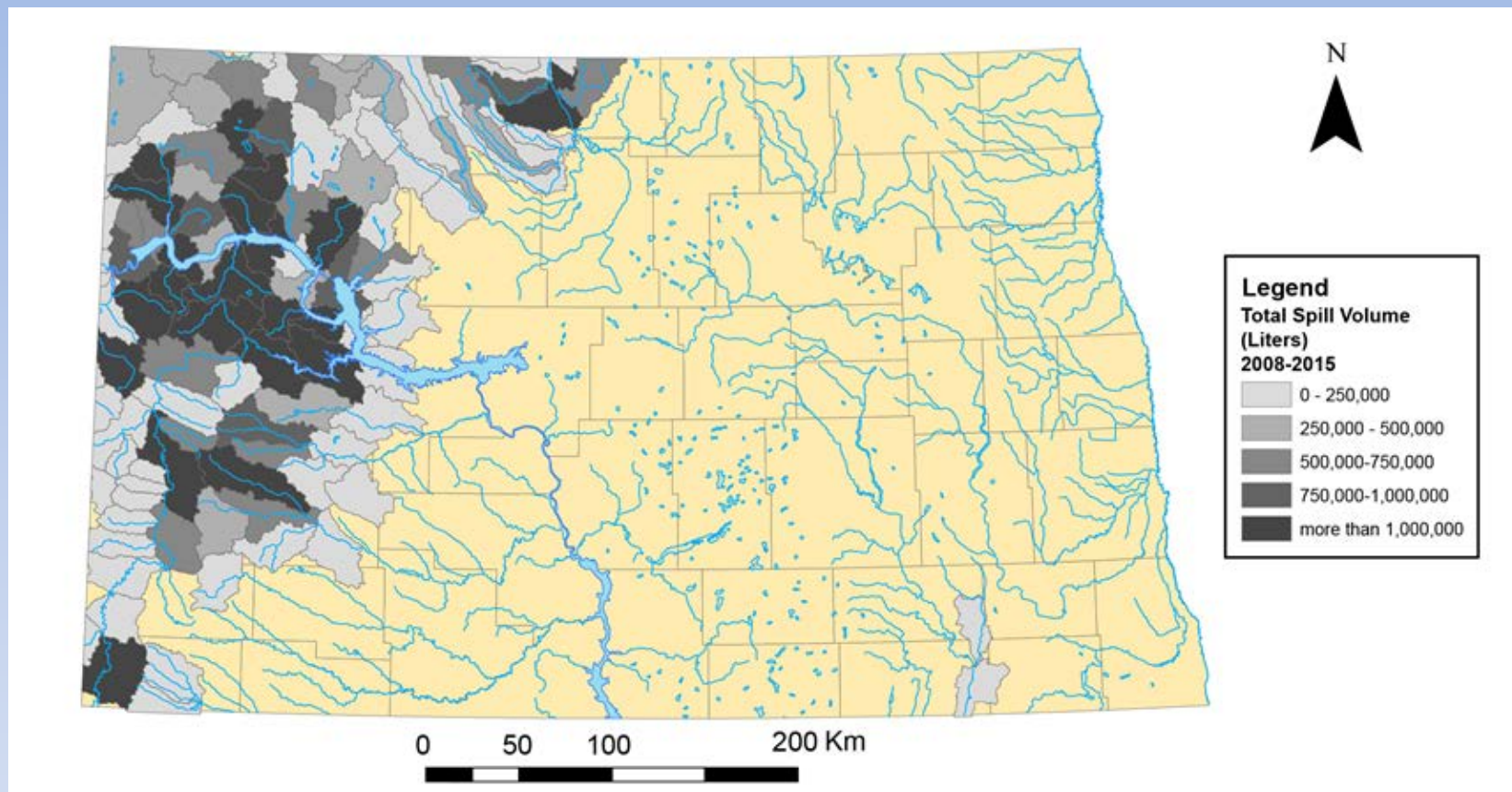
- UOG wastewater (> 11 million liters) spilled into Blacktail Creek, ND in January 2015.
- Elevated Na, Cl, Br, Sr, B, Li, NH<sub>4</sub>, and hydrocarbons were detected in creek waters.
- Geochemical baseline deviations persist months after remediation efforts started.
- B and Sr concentrations, and Ra activities were up to 15 times background in sediment downstream.
- Biological impacts include reduced fish survival and estrogenic inhibition downstream.

### GRAPHICAL ABSTRACT



11 million liters of wastewater spilled

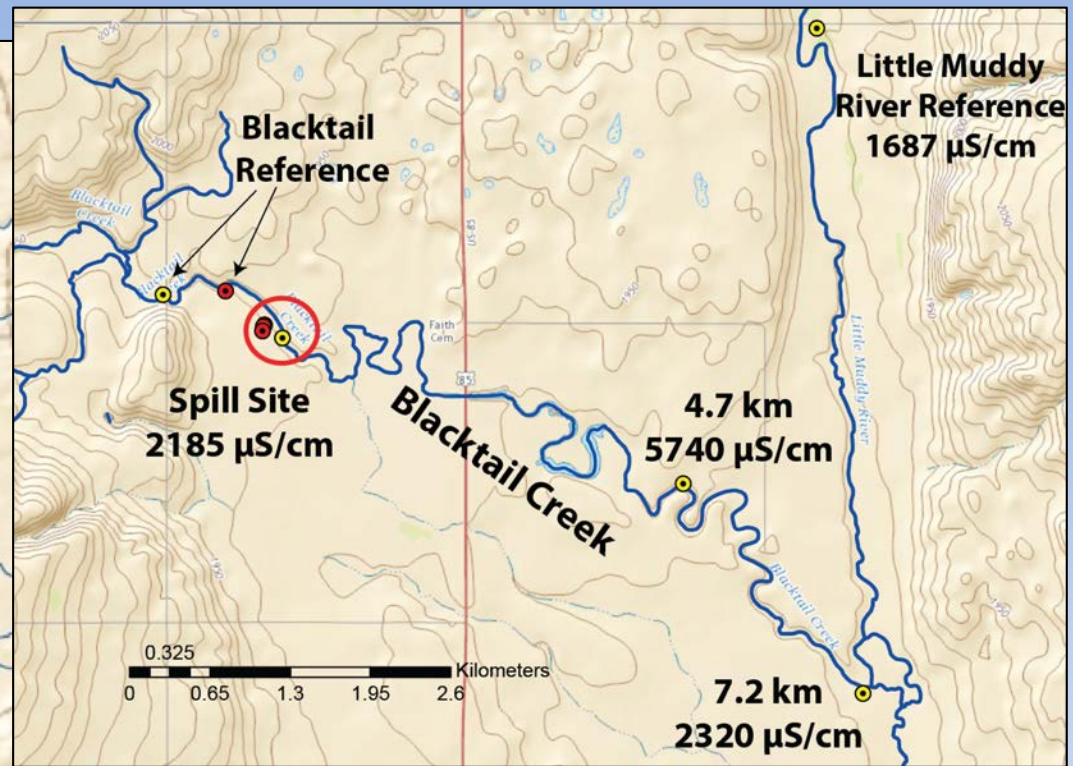
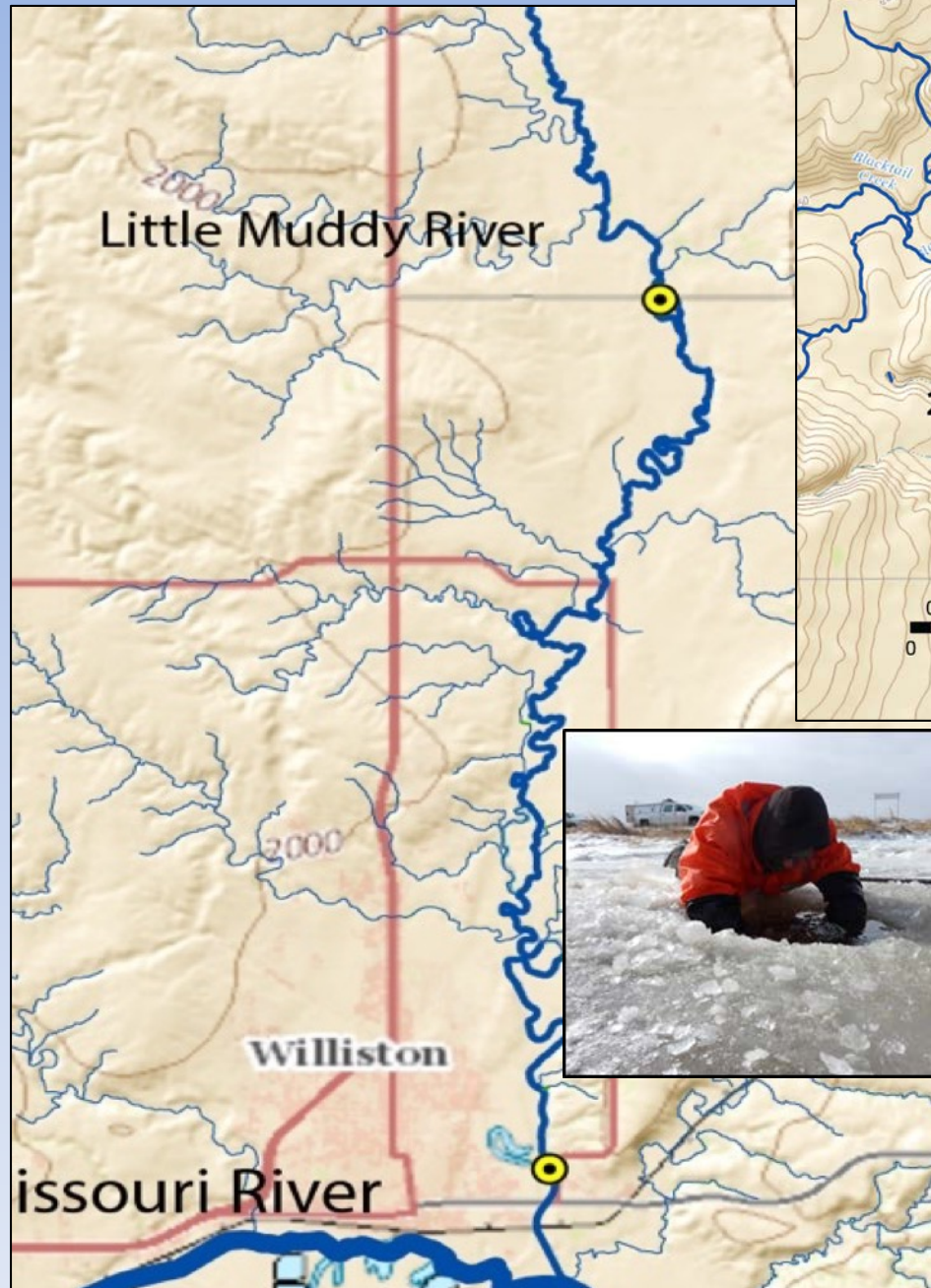
# North Dakota Dept of Health Data



- Between 2008 and 2015 there were 8,424 spills that included:
  - 4,548,782 gallons of oil
  - 13,997,959 gallons of brine
  - 1,755,532 gallons of "other" fluids

Our goal is ultimately to look at the cumulative effects of these spills





- We have completed 4 rounds of sampling, including sediment, water, and biota, February and June 2015, June 2016, June 2017.
- Samples were collected upstream and downstream from the spill along a 22-km reach

# Volatile and Semi-Volatile Hydrocarbons

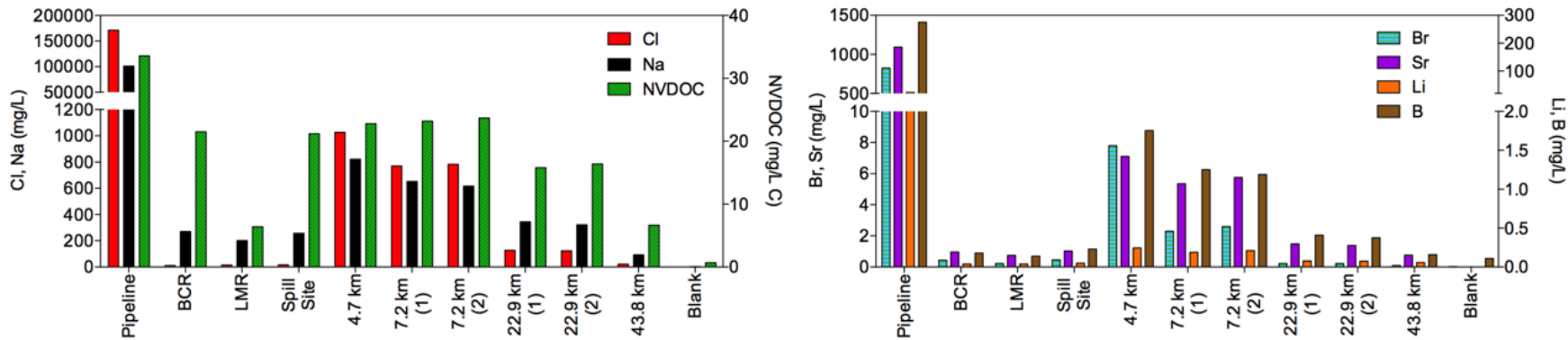
## February 2015

- Hydrocarbons –
  - 1,3,5- trimethylbenzene
  - 1,2,3,4- tetramethylbenzene
  - 1- methynaphthalene
  - Numerous di-and tri-methylnaphthalenes
- Detected in downstream unfiltered samples, but not filtered samples, indicating these compounds might be associated with suspended particulates. In June 2015 these compounds were not detected.
- Light hydrocarbons ( $C_1$ - $C_6$ ) showed distinct thermogenic hydrocarbon signature.
- This signature was still present in June 2015 at 7.2 km downstream.



# Water Geochemistry

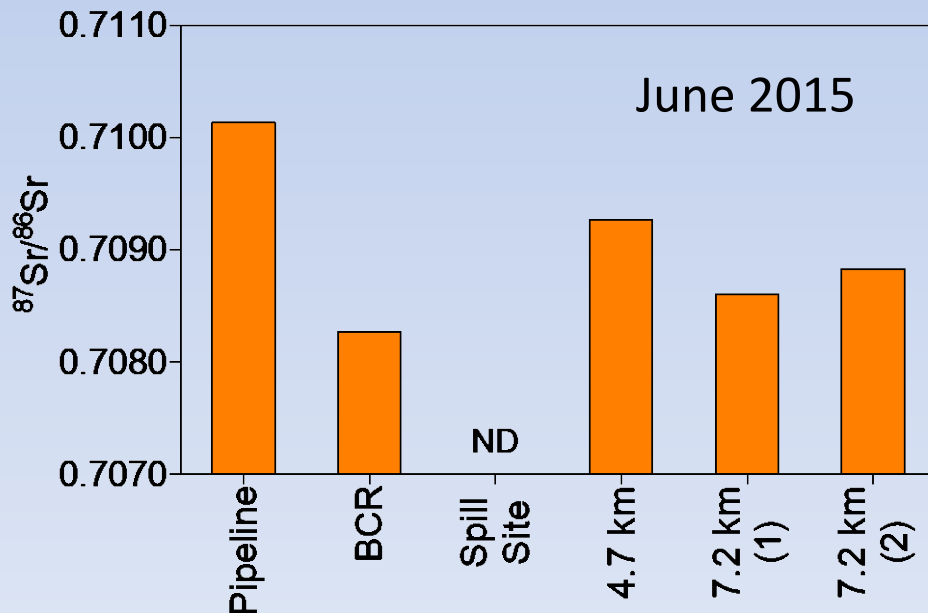
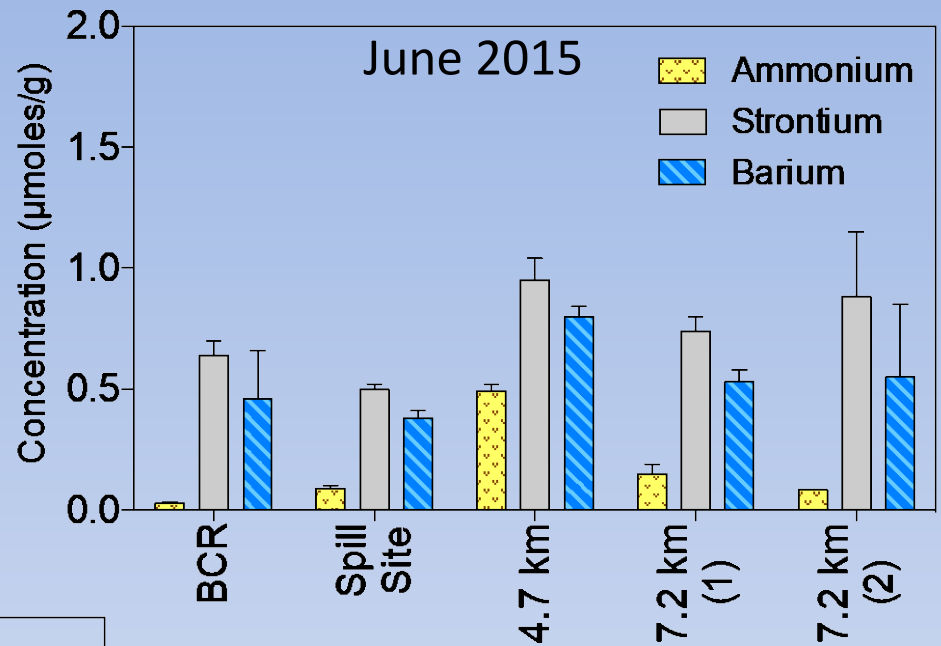
February



- Pipeline sample had very high concentrations of Na, Cl, Br, Sr, Li, B
- The Sr had a distinct radiogenic signature making it a good tracer and useful in mixing models
- Slight signal of pipeline contribution was still evident at 22.9 km downstream, representing 0.01% mass, in June 2015

# Some contaminants are transported with sediment

Sediment-bound  
 $\text{NH}_4$ , Ba, Sr,  
elevated  
downstream



Sr in downstream sediments retains radiogenic signature reflecting pipeline.

*$\text{Ra}^{226}$  was 29 times background activity, 464 Bq/kg in stream sediments.*

*$\text{Ra}^{226}$  was found in surface soils of floodplain in 2016.*

# Key Findings

- Surface waters downstream from spills had elevated UOG waste indicators including hydrocarbons, alcohols, Cl, Br, Li, B, Ba, Sr, and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Distance of transport and temporal persistence is site specific. Potential human exposures through drinking water/recreation.
- Barium and radium accumulate in the river bed sediments and in flood plain soils. Radium is significantly above the EPA action level for radium 226, which should not exceed 185 Bq/kg. Potential direct contact exposures or aeolian transport could result in inhalation exposures.
- Potential aquatic health effects indicated by fish bioassays in which fish experienced mortality at the Blacktail site, and human health impact indicators include modest endocrine disrupting activity observed downstream from multiple spill sites.
- Partitioning of chemicals onto sediment limits movement of wastewater components downstream but could provide a long-term source to aquatic organisms. Ex: Ba and Ra uptake by snails. Potential food web exposures.
- Reactions can cause the potential exposure routes to change over time, i.e. contaminants partition from liquid to solid phase.



# Future Directions

- Advance the tools we have developed at specific sites to investigate alterations in the environment caused by oil and gas activities, at the site, regional and national scales. Improve understanding of how exposure pathways can change over temporal scales.
- Consider both conventional and unconventional development and overlapping exposures (historical and recent).
- Advance non-invasive and cost-effective monitoring tools for both water quality and biological effects.
- Relate chemical disturbances and persistence to any biological effects in a mechanistic way, combining chemistry, toxicology, and epidemiology.

## Questions?

icozzare@usgs.gov



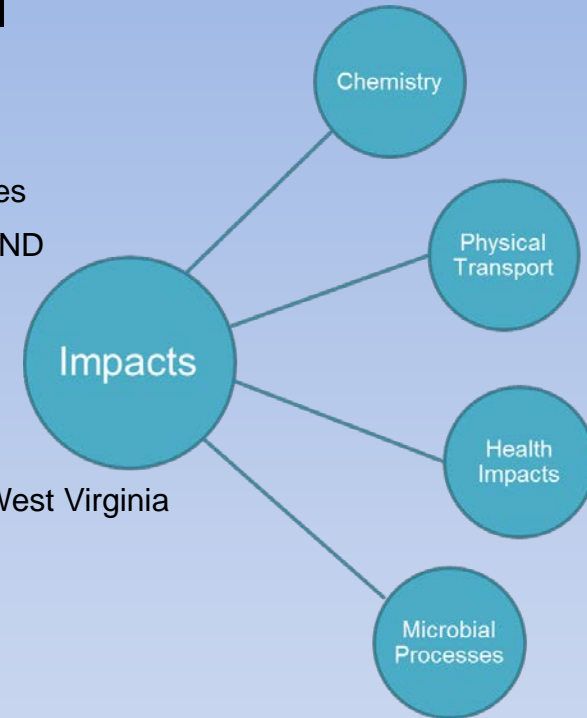
# Collaborators: Internal and External

## USGS

- Eastern Energy Resources Science Center: produced water chemistry, B/Sr isotopes
- MT and ND Water Science Centers (WSC): hydrology and water quality in MT and ND
- OR and NJ WSC and Northern Rocky Mountain SC (NOROCK): impact of wastes on amphibian populations in Prairie Potholes
- Columbia Environmental Research Center (CERC): biological toxicity of sediments/waters, fish health
- WV WSC: hydrology and history of contamination at wastewater disposal wells in West Virginia
- PA WSC: groundwater quality in areas of UOG development
- CA WSC: disinfection byproducts, COGG project
- WI WSC: watershed risks of UOG development
- Leetown Science Center: endocrine disruption from sediment and water exposures, macro-invertebrate response to UOG development
- Branch of Geophysics, Office of Groundwater: geophysical tools, groundwater-surface water interactions

## External

- West Virginia University, The Ohio State University, DOE National Energy Technology Laboratory (NETL): Marcellus Shale Energy and Environment Laboratory (MSEEL project)
- Rutgers University: microbial diversity and function; antibiotic resistance
- University of Missouri: endocrine disruption from sediment and water exposures
- Pennsylvania Dept. of Conservation and Natural Resources and Susquehanna River Basin Commission: watershed impacts of UOG development
- Appalachian State University: watershed risks of UOG development





# Peer-Reviewed Scientific Products

1. Fahrenfeld, N.L., H. Delos Reyes, A. Eramo, D. M. Akob, I.M. Cozzarelli, and A. Mumford. 2017. Shifts in microbial community structure and function in surface waters impacted by unconventional oil and gas wastewaters revealed by metagenomics, *Science of the Total Environment*, available online 27 December 2016, <http://dx.doi.org/10.1016/j.scitotenv.2016.12.079>.
2. Cozzarelli, I.M., Skalak, K.J., Kent, D.B., Engle, M.A., Benthem, A., Mumford, A.C., Haase, K., Farag, A., Harper, D., Nagel, S.C., Iwanowicz, L.R., Orem, W.H., Akob, D.M., Jaeschke, J.B., Galloway, J., Kohler, M., Stoliker, D.L., and Jolly, G.D., 2017, Environmental signatures and effects of an oil and gas wastewater spill in the Williston Basin, North Dakota: *Science of the Total Environment*, v. 579, p. 1781-1793.
3. Ouyang, B., D. M. Akob, D. S. Dunlap, and D. Renock. 2017. Microbially mediated barite dissolution in anoxic brines. *Applied Geochemistry*, 76: 51-59, <http://dx.doi.org/10.1016/j.apgeochem.2016.11.008>.
4. Akob, D.M., Mumford, A.C., Orem, W.H., Engle, M.A., Klinges, J.G., Kent, D.B., and Cozzarelli, I.M., 2016, Wastewater disposal from unconventional oil and gas development degrades stream quality at a West Virginia injection facility: *Environmental Science and Technology*, v. 50, no. 11, p. 5517-5525, doi:10.1021/acs.est.6b00428.
5. Kassotis, C.D., Iwanowicz, L.R., Akob, D.M., Cozzarelli, I.M., Mumford, A.C., Orem, W.H., and Nagel, S.C., 2016, Endocrine disrupting activities of surface water associated with a West Virginia oil and gas Industry wastewater disposal site: *Science of the Total Environment*, v. 557-558, p. 901-910, doi:10.1016/j.scitotenv.2016.03.113.
6. Kent, D.B., Blondes, M.S., Cozzarelli, I.M., Geboy, N., LeBlanc, D.R., Ng, G.-H., Repert, D., and Smith, R.L., 2016, Sewage disposal, petroleum spills, eutrophic lakes, and wastewater from oil and gas production--Potential drivers of arsenic mobilization in the sub-surface, in Bhattacharya, P., and others, eds., *Arsenic Research and Global Sustainability--Proceedings of the Sixth International Congress on Arsenic in the Environment (As2016)*, Stockholm, Sweden, June 19-23, 2016: London, CRC Press (Taylor and Francis Group), p. 25-26, ISBN:9781138029415.
7. McMahon, P.B., Kulongoski, J.T., Wright, M.T., Land, M.T., Landon, M.K., Cozzarelli, I.M., Vengosh, A., and Aiken, G.R., 2016, Preliminary results from exploratory sampling of wells for the California oil, gas, and groundwater program, 2014–15: USGS Open-File Report 2016-1100, 8 p.
8. Akob, D.M., Cozzarelli, I.M., Dunlap, D.S., Rowan, E.L., and Lorah, M.M., 2015, Organic and inorganic composition and microbiology of produced waters from Pennsylvania shale gas wells: *Applied Geochemistry*, v. 60, p. 116-125, doi:10.1016/j.apgeochem.2015.04.011.
9. Lester, Y., Ferrer, I., Thurman, E.M., Sitterley, K.A., Korak, J.A., Aiken, G., and Linden, K.G., 2015, Characterization of hydraulic fracturing flowback water in Colorado--Implications for water treatment: *Science of the Total Environment*, v. 512-513, p. 637-644, doi:10.1016/j.scitotenv.2015.01.043.
10. Williams, J.H., Risser, D.W., and Dodge, C.M., 2015, Geohydrologic and water-quality characterization of a fractured-bedrock test hole in an area of Marcellus shale gas development, Tioga County, Pennsylvania: Pennsylvania Geological Survey 4th ser., Open-File Miscellaneous Investigations OFMI 15–24.0 (plus supplemental information in a ZIP file).
11. Hladik, M.L., Focazio, M.J., and Engle, M., 2014, Discharges of produced waters from oil and gas extraction via wastewater treatment plants are sources of disinfection by-products to receiving streams: *Science of the Total Environment*, v. 466-467, p. 1085-1083, doi:10.1016/j.scitotenv.2013.08.008.
12. Engle, M.A., Cozzarelli, I.M., and Smith, B.D., 2014, USGS investigations of water produced during hydrocarbon reservoir development: U.S. Geological Survey Fact Sheet 2014-3104, 4 p. (Fact Sheet).
13. Orem, W., Tatu, C., Varonka, M., Lerch, H., Bates, A., Engle, M., Crosby, L., and McIntosh, J., 2014, Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale: *International Journal of Coal Geology*, v. 126, p. 20-31, doi:10.1016/j.coal.2014.01.003.
14. Skalak, K.J., Engle, M.A., Rowan, E.L., Jolly, G.D., Conko, K.M., Benthem, A.J., and Kraemer, T.F., 2014, Surface disposal of produced waters in western and southwestern Pennsylvania--Potential for accumulation of alkali-earth elements in sediments: *International Journal of Coal Geology*, v. 126, p. 162-170, doi:10.1016/j.coal.2013.12.001.
15. Risser, D.W., Williams, J.H., Hand, K.L., Behr, R.-A., and Markowski, A.K., 2013, Geohydrologic and water-quality characterization of a fractured-bedrock test hole in an area of Marcellus Shale gas development, Bradford County, Pennsylvania: Pennsylvania Geological Survey 4th ser., Open-File Report OFMI 13-01.1 (4 appendices).

# Other Technical Products of Value to Stakeholders

1. Akob, D.M., and Lee, K.E., 2016, Indication of unconventional oil and gas wastewaters found in local surface waters: U.S. Geological Survey, access date 09/01/2016 (Science Feature).
2. Demas, A., Focazio, M., and Akob, D., 2016, Evidence of unconventional oil and gas wastewater found in surface waters near underground injection site: U.S. Geological Survey News Release, 05/09/2016 (Press Release).
3. Akob, D.M., Cozzarelli, I.M., and Lee, K.E., 2015, Microbiology and chemistry of waters produced from hydraulic fracking--A case study: U.S. Geological Survey, access date 2015/10/16 (Science Feature).
4. Campbell, J., and Akob, D., 2015, The chemistry of waters that follow from fracking--A case study: U.S. Geological Survey News Release, 05/11/2015 (Press Release).
5. Campbell, J., and Cozzarelli, I., 2015, Natural breakdown of petroleum underground can lace arsenic into groundwater: U.S. Geological Survey News Release, 01/26/2015 (Press Release).
6. Cozzarelli, I.M., Akob, D.M., Morganwalp, D.W., and Lee, K.E., 2015, Fate and effects of wastes from unconventional oil and gas development: U.S. Geological Survey, access date 05/15/2015 (Website).
7. Engle, M.A., Cozzarelli, I.M., and Smith, B.D., 2014, USGS investigations of water produced during hydrocarbon reservoir development: U.S. Geological Survey Fact Sheet 2014-3104, 4 p. (Fact Sheet).
8. Focazio, M., and Demas, A., 2013, Disinfection of energy wastewater can lead to toxic byproducts: U.S. Geological Survey Technical Announcement, 09/04/2013 (Technical Announcement).
9. Hladik, M.L., Focazio, M.J., and Buxton, H.T., 2013, Disinfection byproducts from treatment of produced waters: U.S. Geological Survey, access date 10/20/2016 (Press Release).

