



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

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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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## Federal Multiagency Collaboration on Unconventional Oil and Gas Research

A Strategy for Research and Development

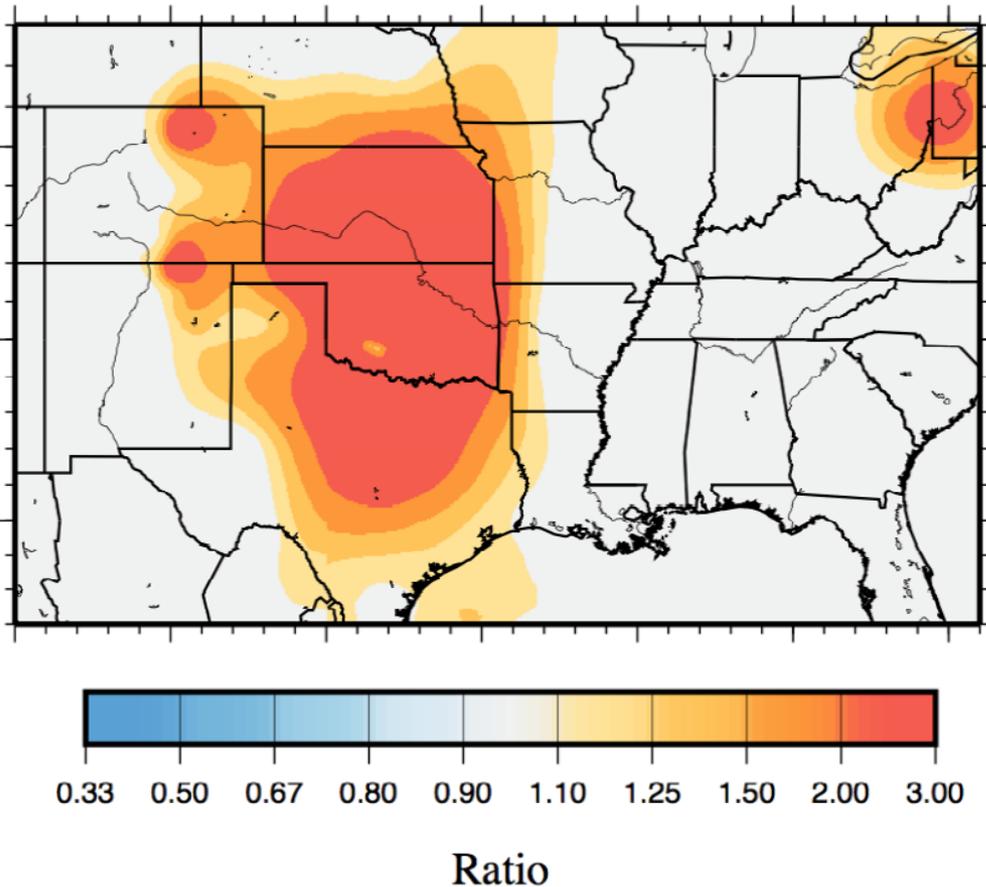


July 18, 2014

→ 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.

**HEI**

**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

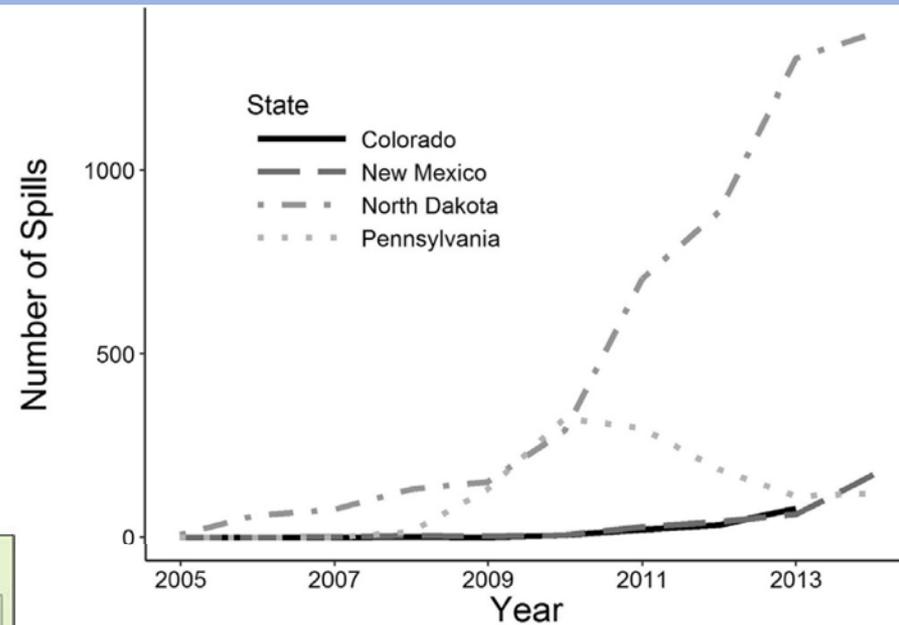
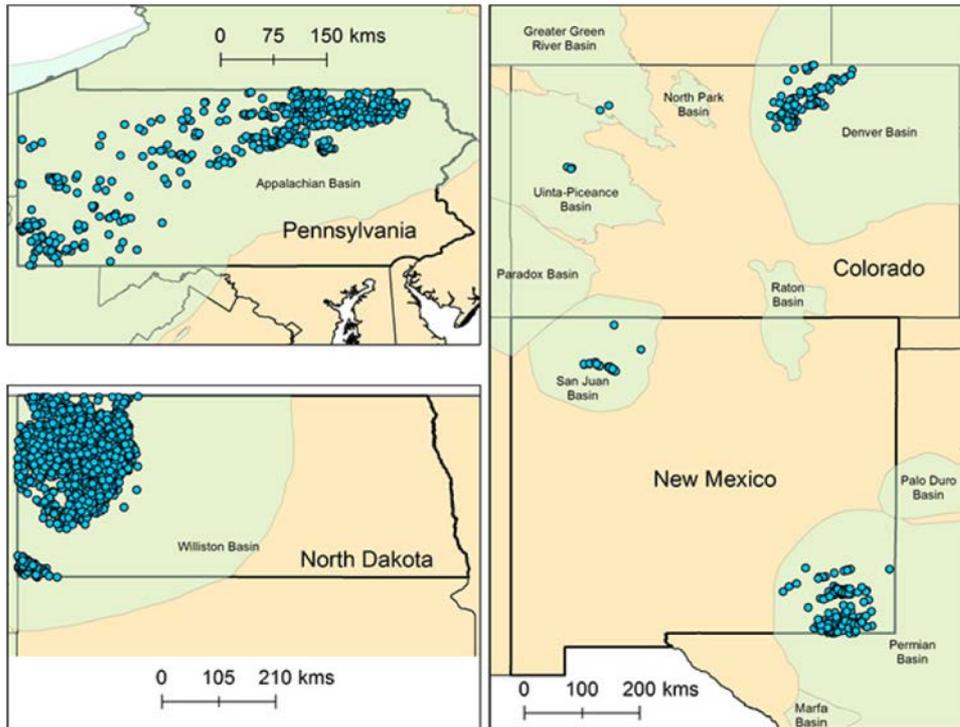
Patterson *et al.*, 2017, assessed spill data from 2005 to 2014 at 31,481 UOG wells in Colorado, New Mexico, North Dakota, and Pennsylvania.

- 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

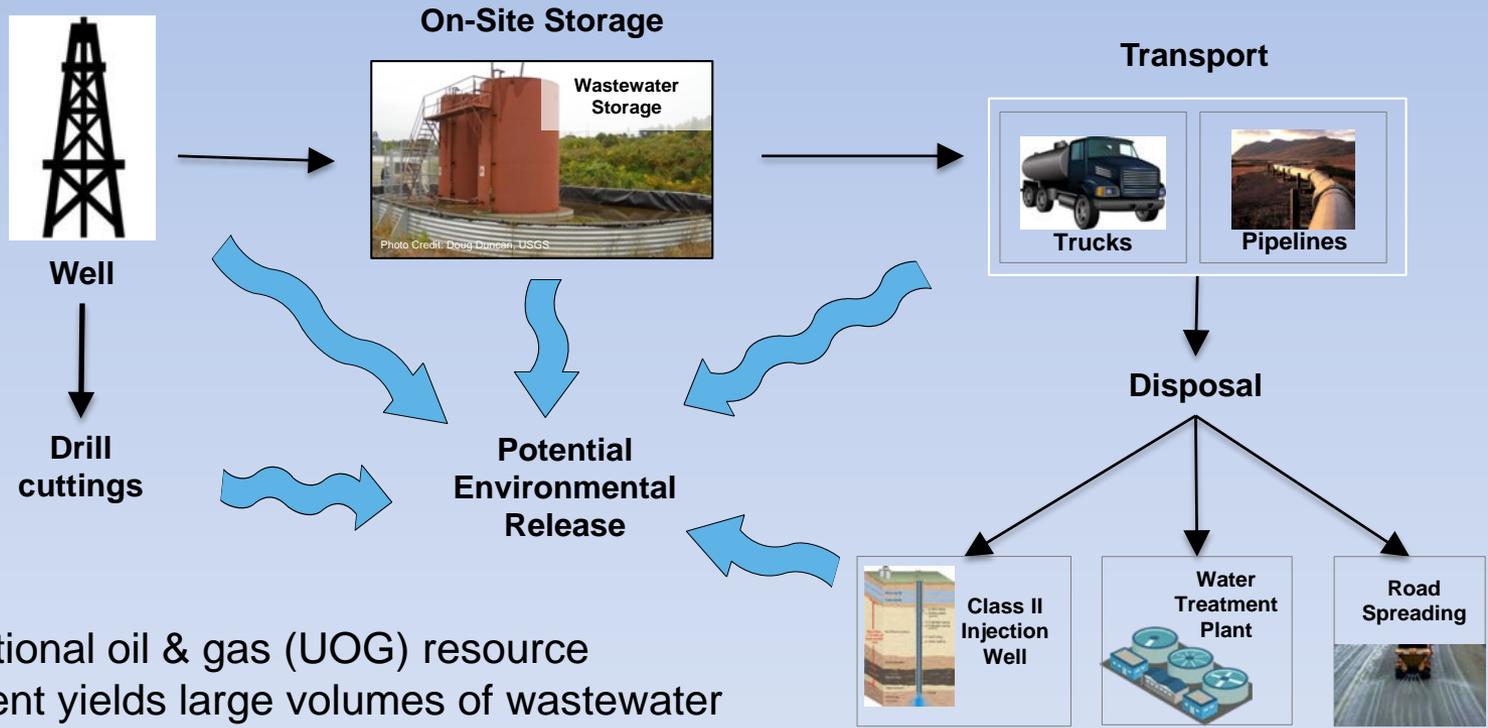
Distribution of spills attributed to UOG wells by state. Light green polygons indicate shale basins.



- 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

<https://toxics.usgs.gov/investigations/uog/>

# Questions Driving our Research

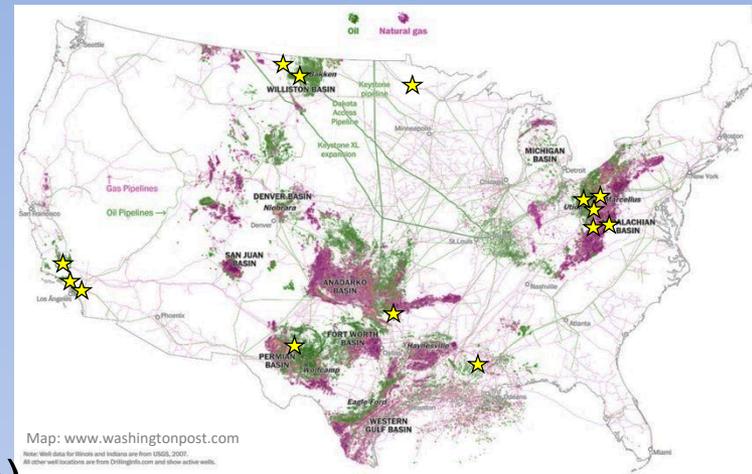
What is the composition of oil and gas associated materials, the potential pathways to the environment, the mode-of-action and the effects, if any, on receptor organisms from exposure to these materials?

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?

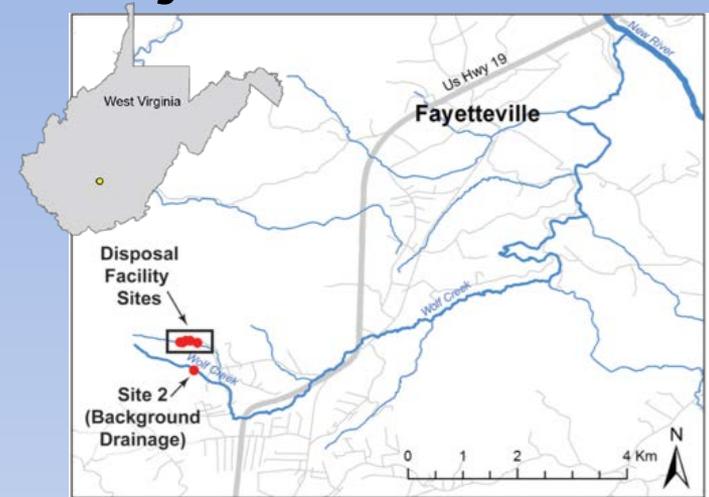
# Current Research Projects

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.



# Impacts of a Class II Wastewater Injection Facility

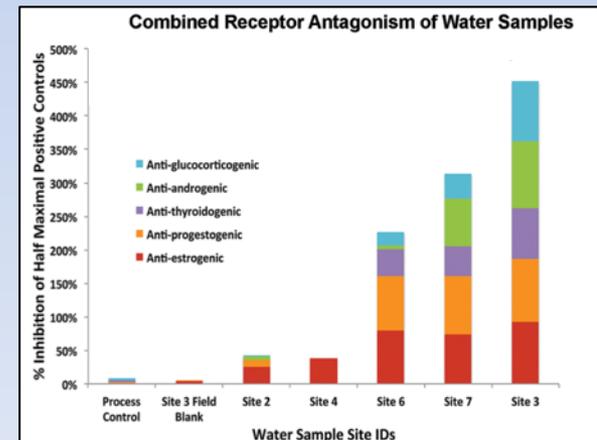
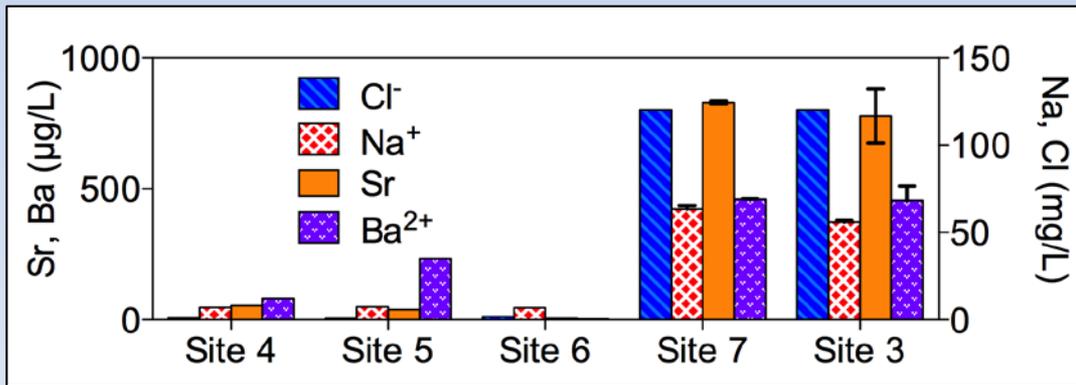
- Key findings:

- 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

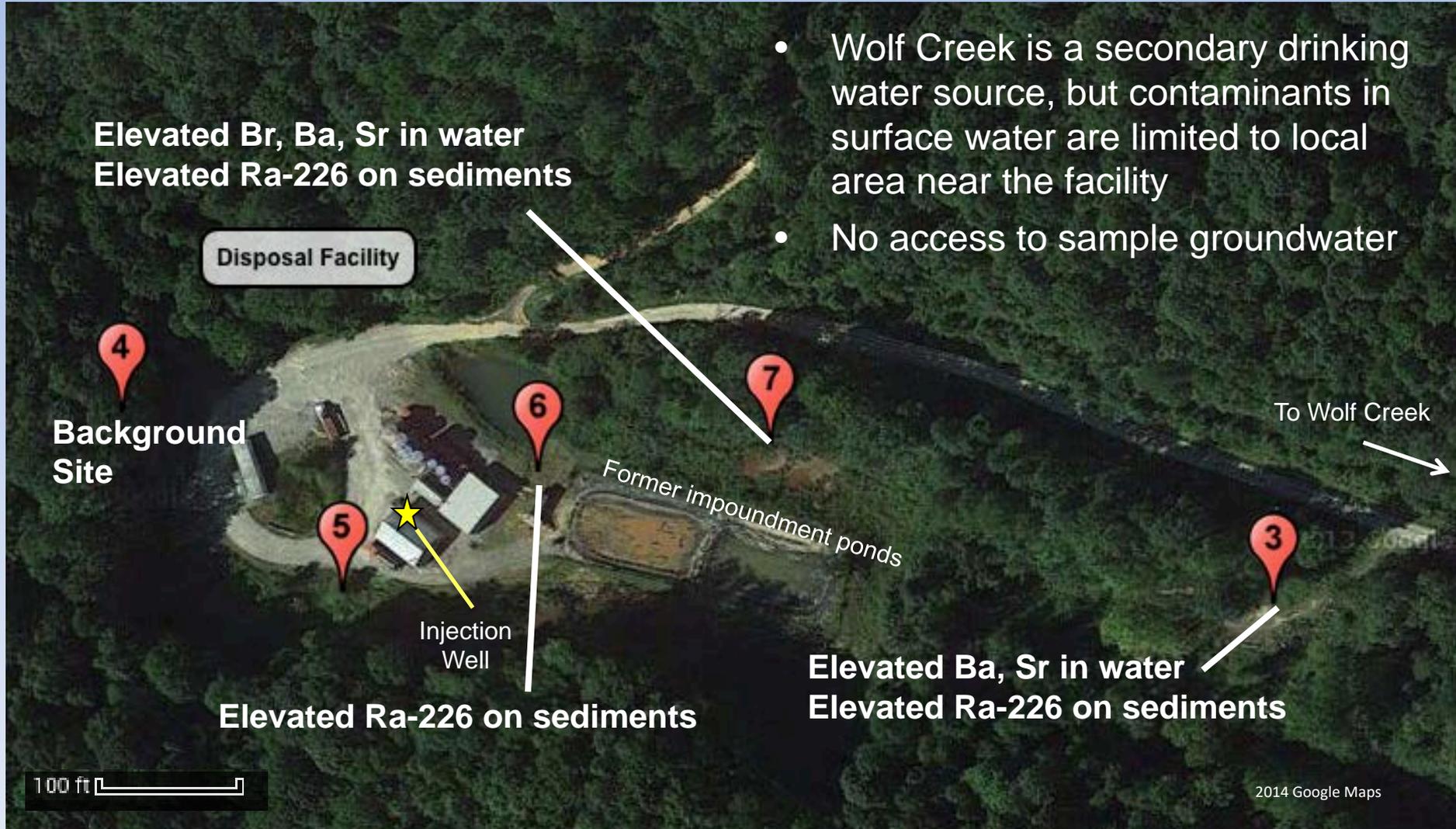
- Although the health of aquatic organisms was not assessed our results showed the potential for adverse biological effects due to:

- 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



- Wolf Creek is a secondary drinking water source, but contaminants in surface water are limited to local area near the facility
- No access to sample groundwater

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

Contents lists available at ScienceDirect

Science of the Total Environment 2017

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

ELSEVIER

Short Communication

Shifts in microbial community structure and function in surface waters impacted by unconventional oil and gas wastewater revealed by metagenomics

N.L. Fahrenfeld <sup>a,\*</sup>, Hannah Delos Reyes <sup>a</sup>, Alessia Eramo <sup>a</sup>, Denise M. Akob <sup>b</sup>, Adam C. Mumford <sup>b</sup>, Isabelle M. Cozzarelli <sup>b</sup>

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ELSEVIER

Organic geochemistry and toxicology of a stream impacted by unconventional oil and gas wastewater disposal operations

William Orem <sup>a,\*</sup>, Matthew Varonka <sup>a</sup>, Lynn Crosby <sup>a,c,1</sup>, Karl Haase <sup>a</sup>, Keith Loftin <sup>b</sup>, Michelle Hladik <sup>c</sup>, Denise M. Akob <sup>a</sup>, Calin Tatu <sup>d</sup>, Adam Mumford <sup>a</sup>, Jeanne Jaeschke <sup>a</sup>, Anne Bates <sup>a</sup>, Tiffani Schell <sup>a</sup>, Isabelle Cozzarelli <sup>a</sup>

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Environmental Science & Technology 2016

pubs.acs.org/est

Wastewater Disposal from Unconventional Oil and Gas Development Degrades Stream Quality at a West Virginia Injection Facility

Denise M. Akob <sup>a,\*</sup>, Adam C. Mumford <sup>†</sup>, William Orem <sup>‡</sup>, Mark A. Engle <sup>‡</sup>, J. Grace Klings <sup>†,1</sup>, Douglas B. Kent <sup>§</sup>, and Isabelle M. Cozzarelli <sup>†</sup>

Science of the Total Environment 2016

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

ELSEVIER

Endocrine disrupting activities of surface water associated with a West Virginia oil and gas industry wastewater disposal site

Christopher D. Kassotis <sup>a</sup>, Luke R. Iwanowicz <sup>b</sup>, Denise M. Akob <sup>c</sup>, Isabelle M. Cozzarelli <sup>c</sup>, Adam C. Mumford <sup>c</sup>, William H. Orem <sup>d</sup>, Susan C. Nagel <sup>e,\*</sup>

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)

ELSEVIER

Science of the Total Environment

Open Access Publication with All Data Available

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>

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<sup>e</sup> Department of Obstetrics, Gynecology and Women's Health, University of Missouri, Columbia, MO 65211, USA  
<sup>f</sup> U.S. Geological Survey, Leetown Science Center, Kearneysville, WV 25430, USA  
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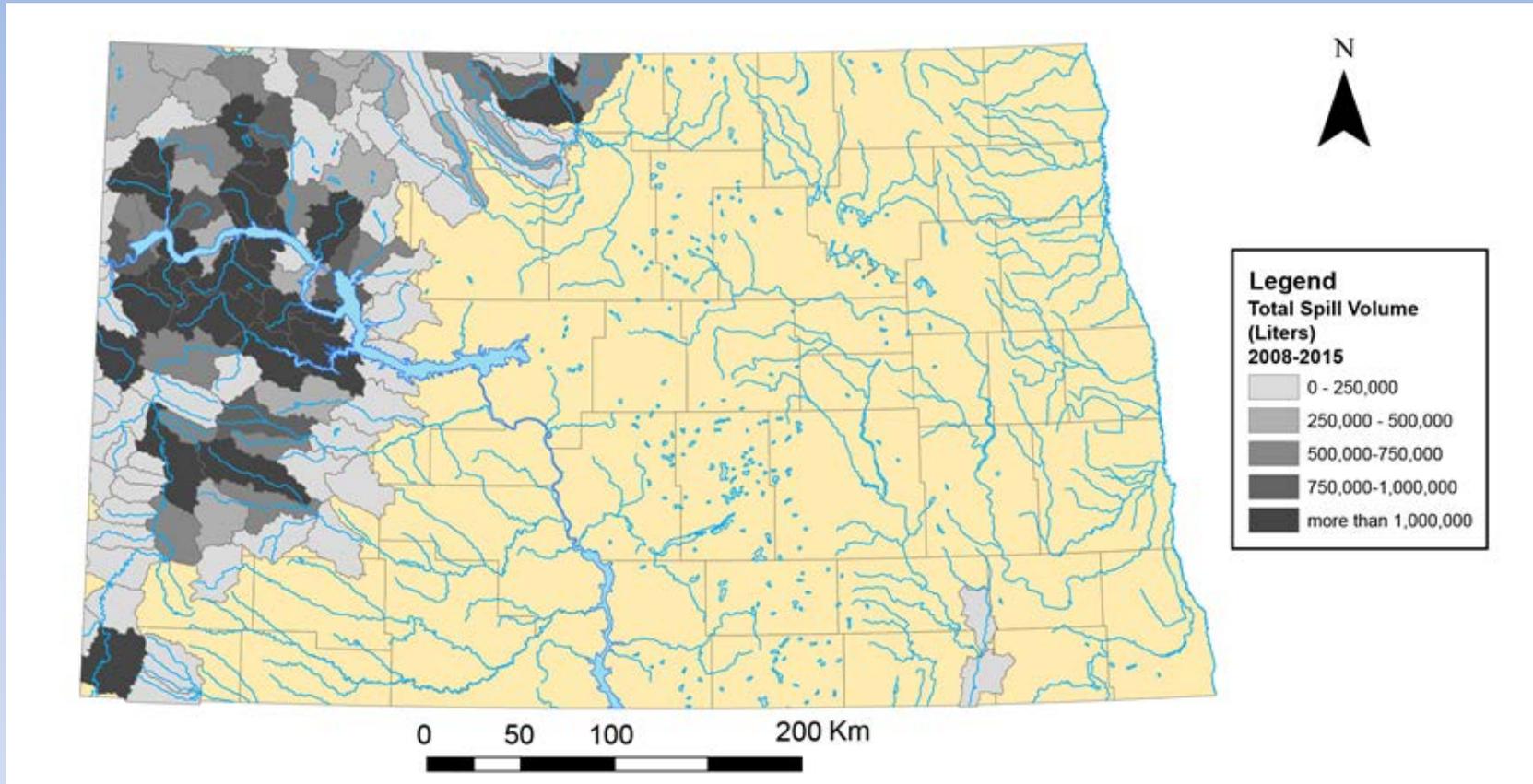
**HIGHLIGHTS**

- UOG wastewater (> 11 million liters) spilled into Blacktail Creek, ND in January 2015.
- Elevated Na, Cl, Br, Sr, B, Li, NH<sub>4</sub><sup>+</sup> 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**

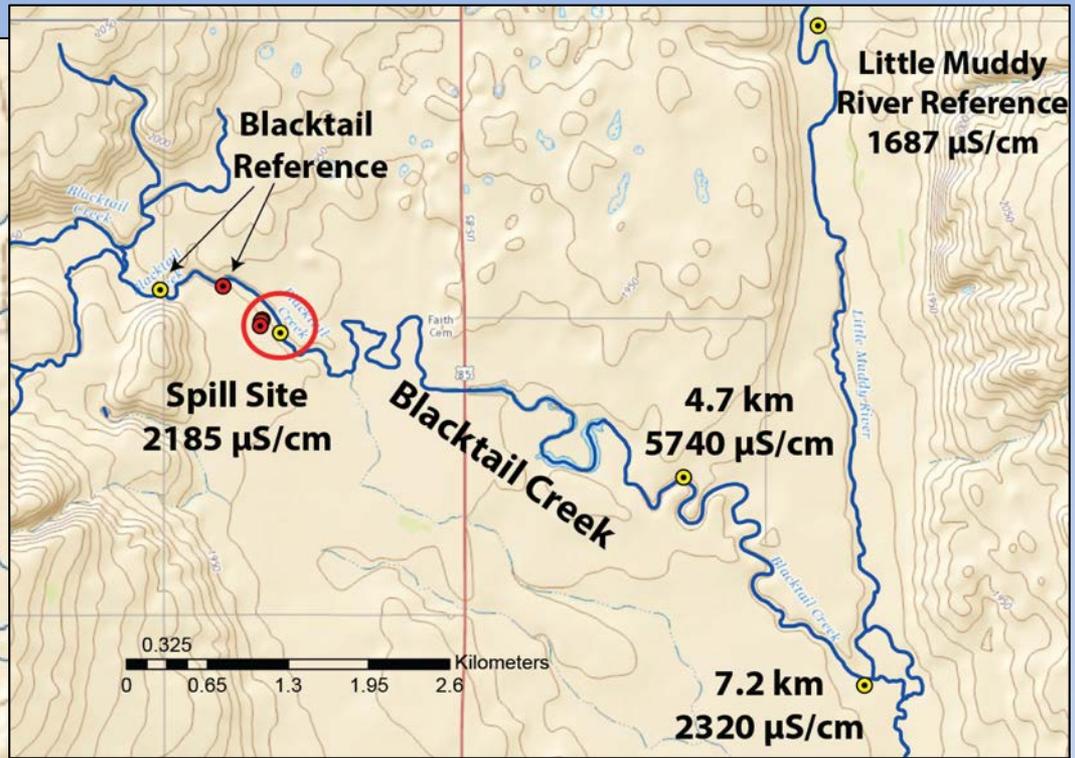
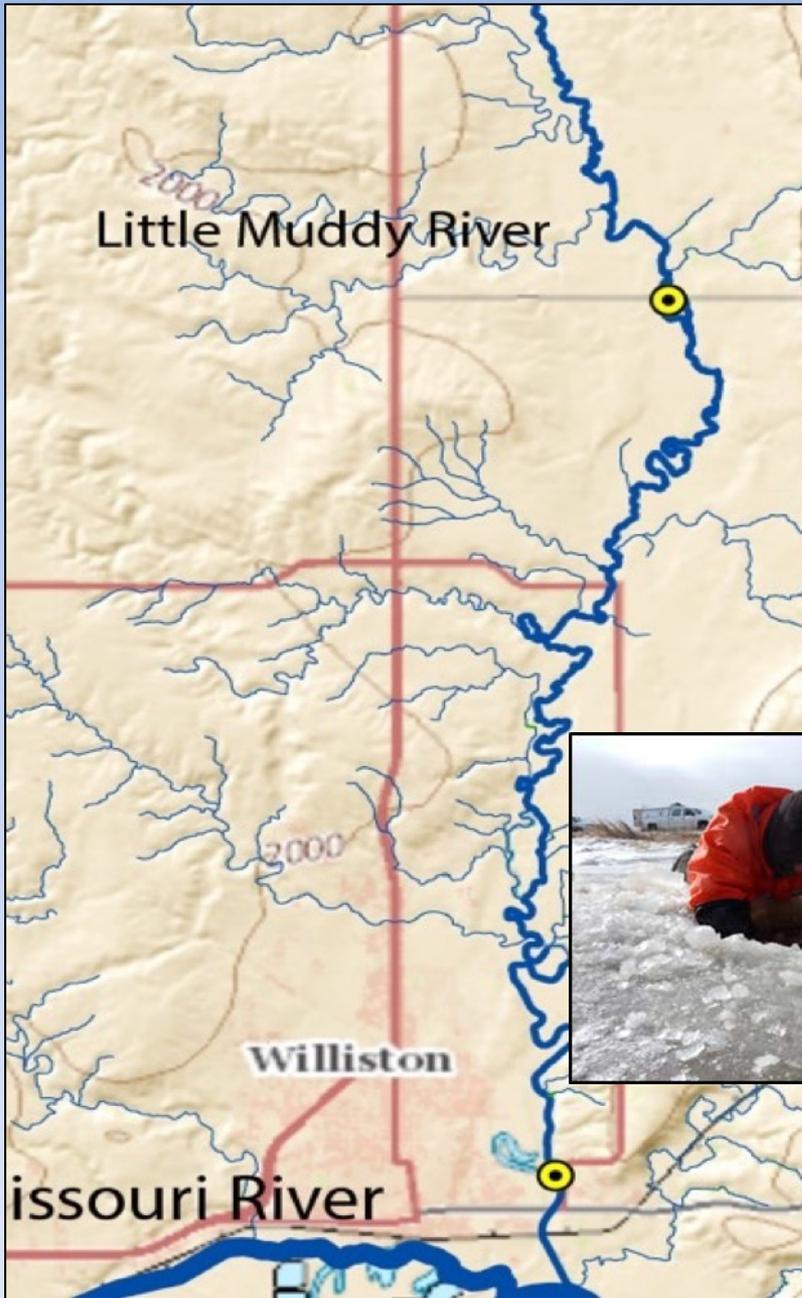
11 million liters of wastewater spilled

# 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

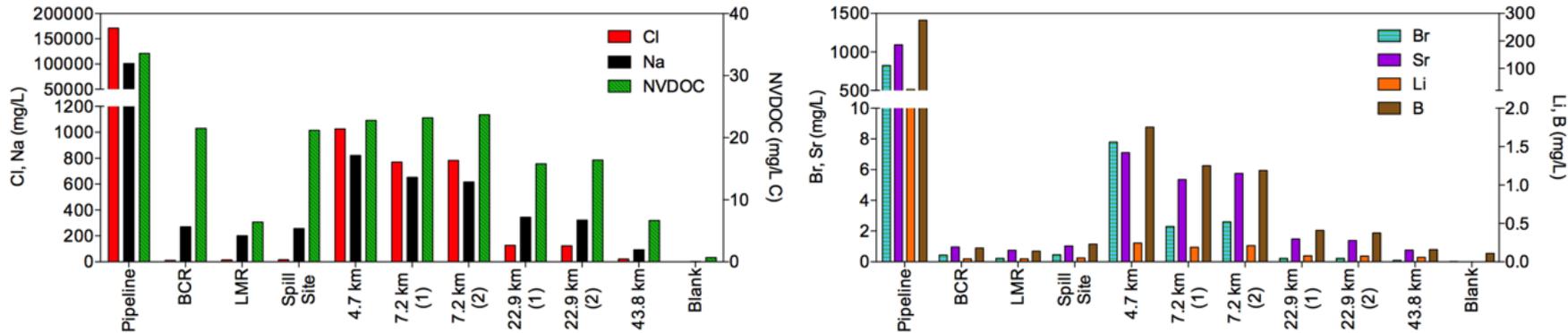
# Volatile and Semi-Volatile Hydrocarbons

## 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

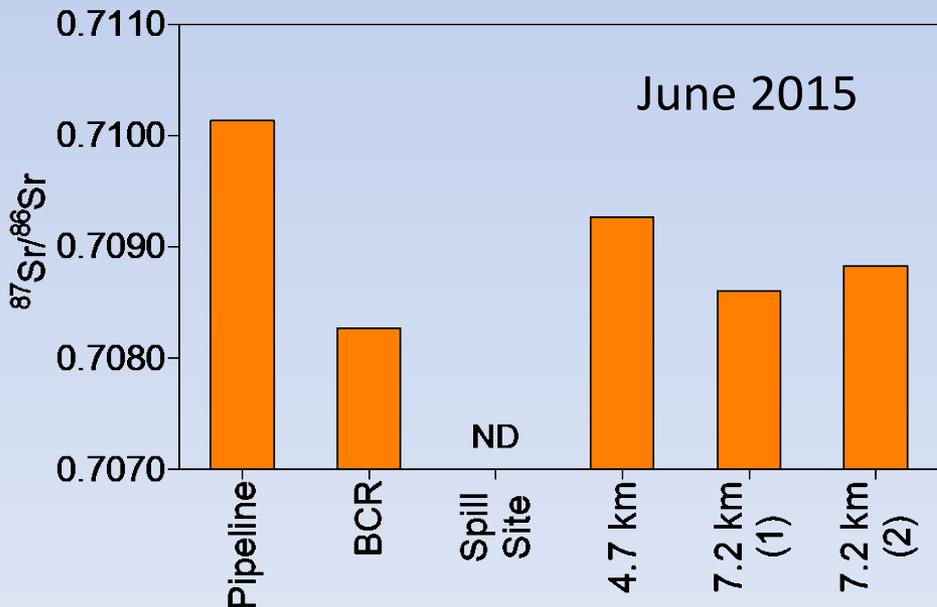
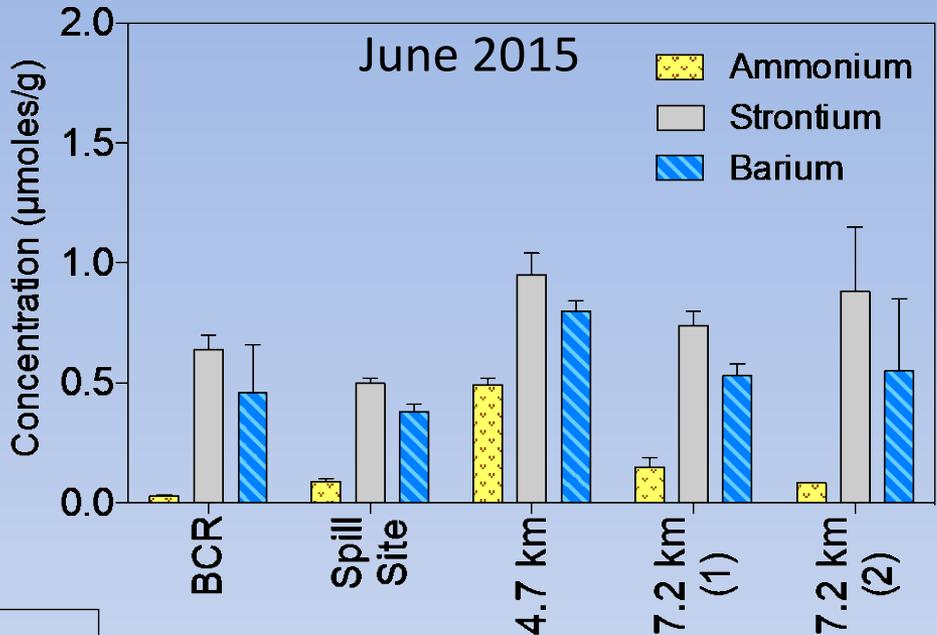
February



- 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



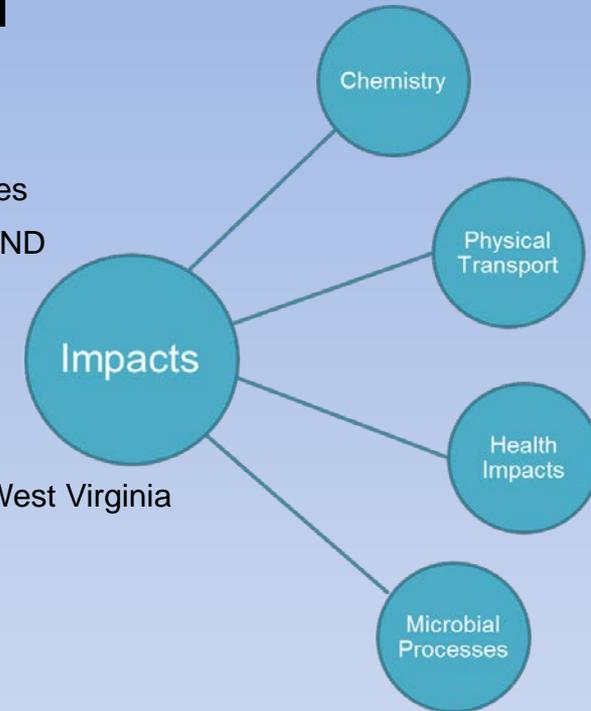
# Collaborators: Internal and External

## 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>.
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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.
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# Other Technical Products of Value to Stakeholders

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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).
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