USGS Toxics Program Research Project

Geochemical and Microbiological Indicators of Oil and Gas Wastewater Releases

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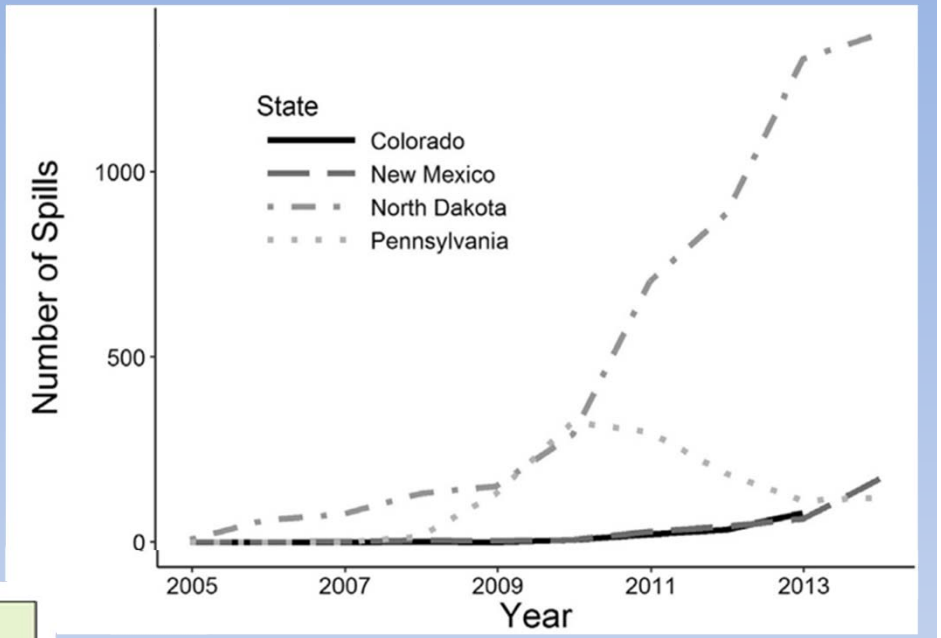
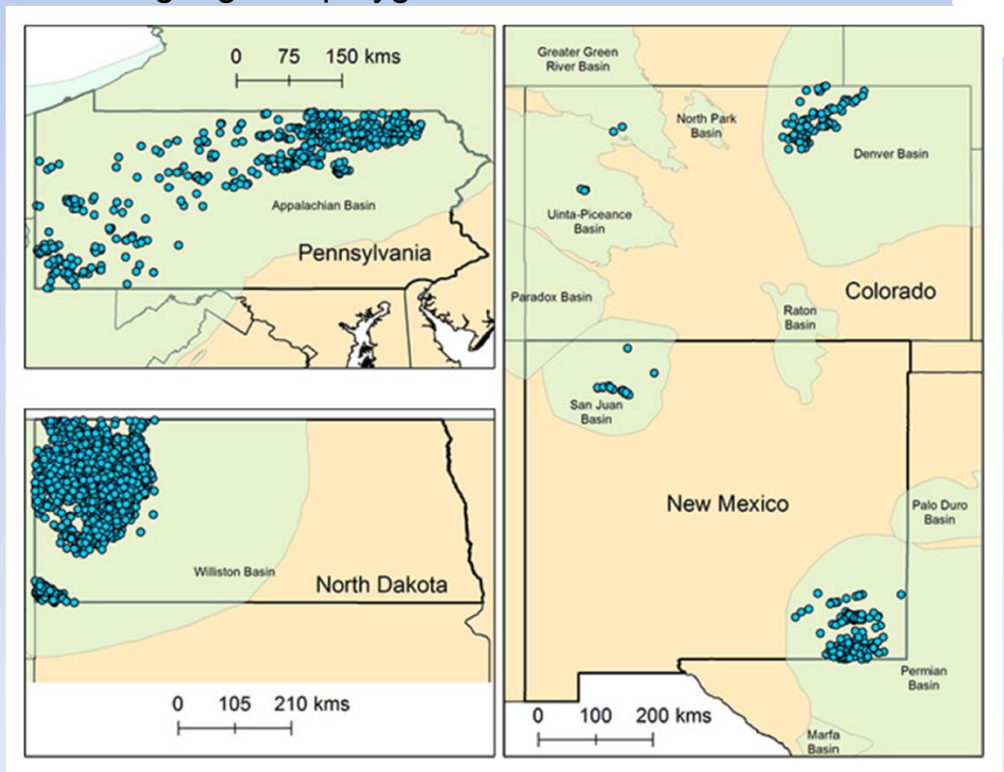
Mark A. Engle (U.S. Geological Survey, El Paso, TX)
Douglas B. Kent (U.S. Geological Survey, Menlo Park, CA)

Spills from Oil and Gas (OG) Production



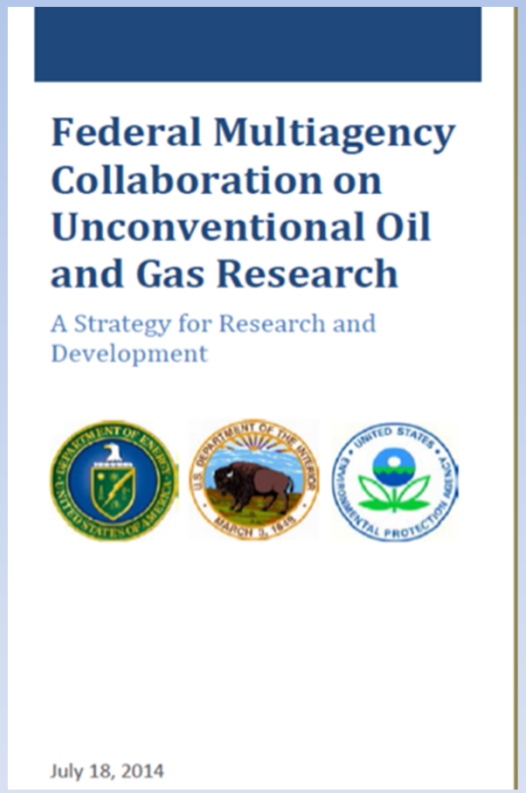
Distribution of spills attributed to UOG wells by state. Light green polygons indicate shale basins.



- 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.

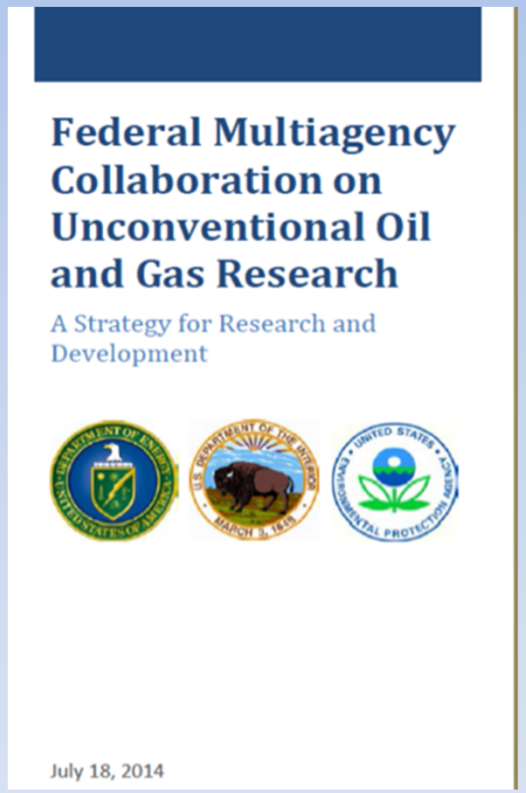
Maloney et al. 2017 STOTEN

Federal Multiagency Collaboration on Unconventional Oil and Gas (UOG)



- 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.

Federal Multiagency Collaboration on Unconventional Oil and Gas (UOG)



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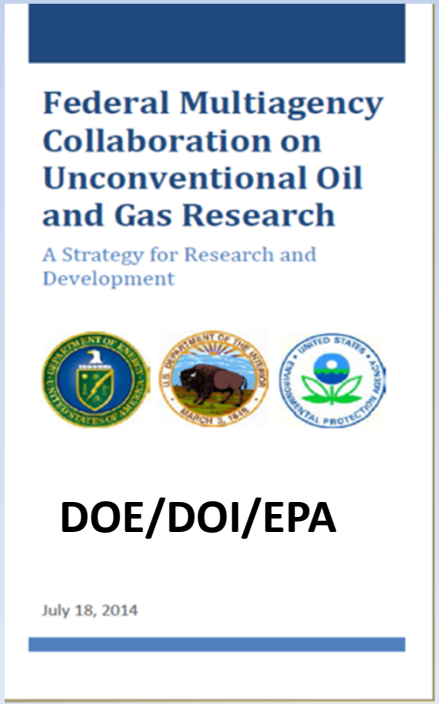
    and was

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

Toxics Program UOG Wastes Project Overall Goals

- To understand potential impacts of UOG-generated **wastewaters** and **solids** on water-resources and environmental health.
- To determine what are the potential contaminant-associated threats to humans, wildlife, and ecosystems?



Identified outstanding research needs by the Agencies:

- Understanding potential impacts on water quality and availability over the entire cycle of UOG operations
- Understanding the composition of UOG hydraulic fracturing fluids and/or wastewaters and potential risk
- And understanding the environmental pathways that could lead to exposures to toxic chemicals during extraction and waste management activities.

They identified 13 research areas of highest priority importance including:

- 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

Stakeholders

- Federal and state agencies in charge of resource protection
- Spill responders
- Remediation companies
- Land owners (e.g., Tribes, private land owners, and water users)
- Farmers and ranchers
- Recreational land users (e.g., fisherman, hunters)
- Water utilities
- Energy producers


http://blog.farmsreach.com/in-solidarity-farmers-against-fracking/

wo samples of well water from his neighborhood in Dimock, PA. He says the water was


Road spreading of Brine (Scientific American)


Photo: Skytruth

Core Project Team PIs

Isabelle Cozzarelli, Reston Biogeochemical Processes in Groundwater Laboratory
Biogeochemical processes, focusing on electron donors, electron acceptors and metabolites

Denise Akob & Adam Mumford, Reston Microbiology Lab
Microbial processes, biodegradation potentials, microbes as tracers

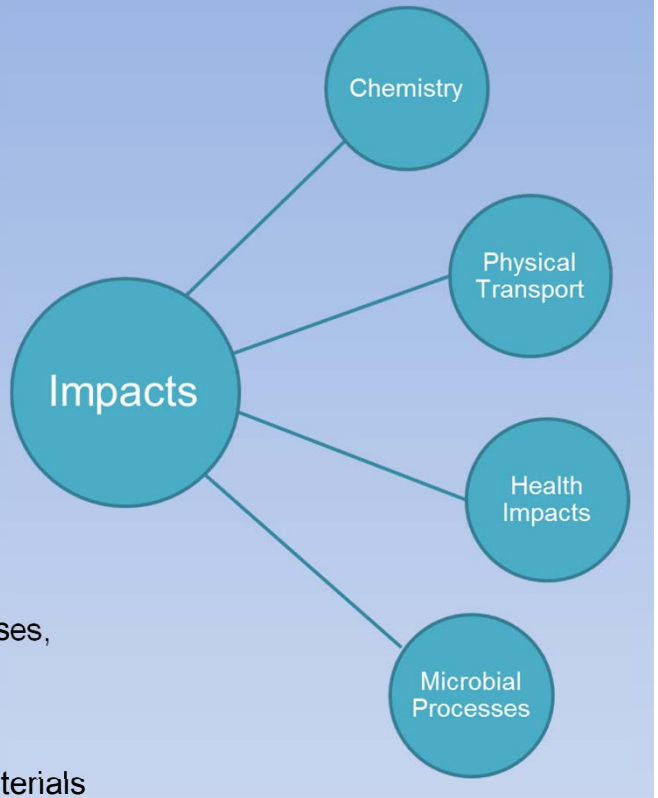
Bill Orem, Energy Environmental Labs
Semi-volatile and nonvolatile organics, source identification

Karl Haase, Groundwater Dating Lab
VOCs, hydrocarbons, and noble gases at trace levels to better characterize releases, air quality, and secondary impacts from UOG activities

Doug Kent, Solute Partitioning at Mineral-Water Interfaces
Inorganic elements and their chemical forms in UOG waste and contaminated materials

Katie Skalak, Geomorphic Controls on Contaminant Transport
Fine sediment and particle associated contaminant transport, radionuclides

Mark Engle, Energy Resources
Geochemical characterization of produced waters and isotopic tools



Collaborative project between USGS researchers, Universities, and other Federal Agency Partners

USGS Energy Life Cycle Project

Goal:

To understand the potential impacts of activities associated with the life cycle of energy development on water resources and environmental health, including the potential contaminant-associated threats and effects to humans, wildlife, and ecosystems.

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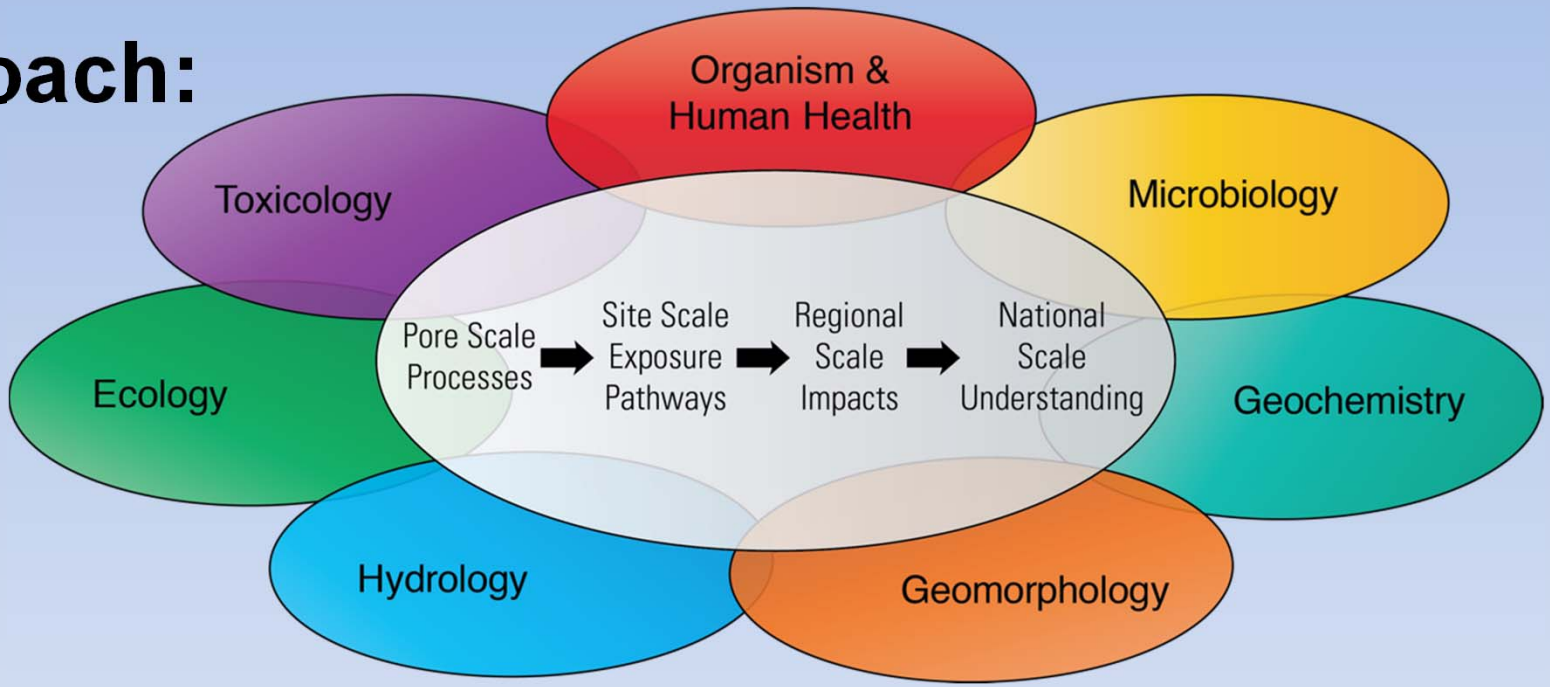
Approach:



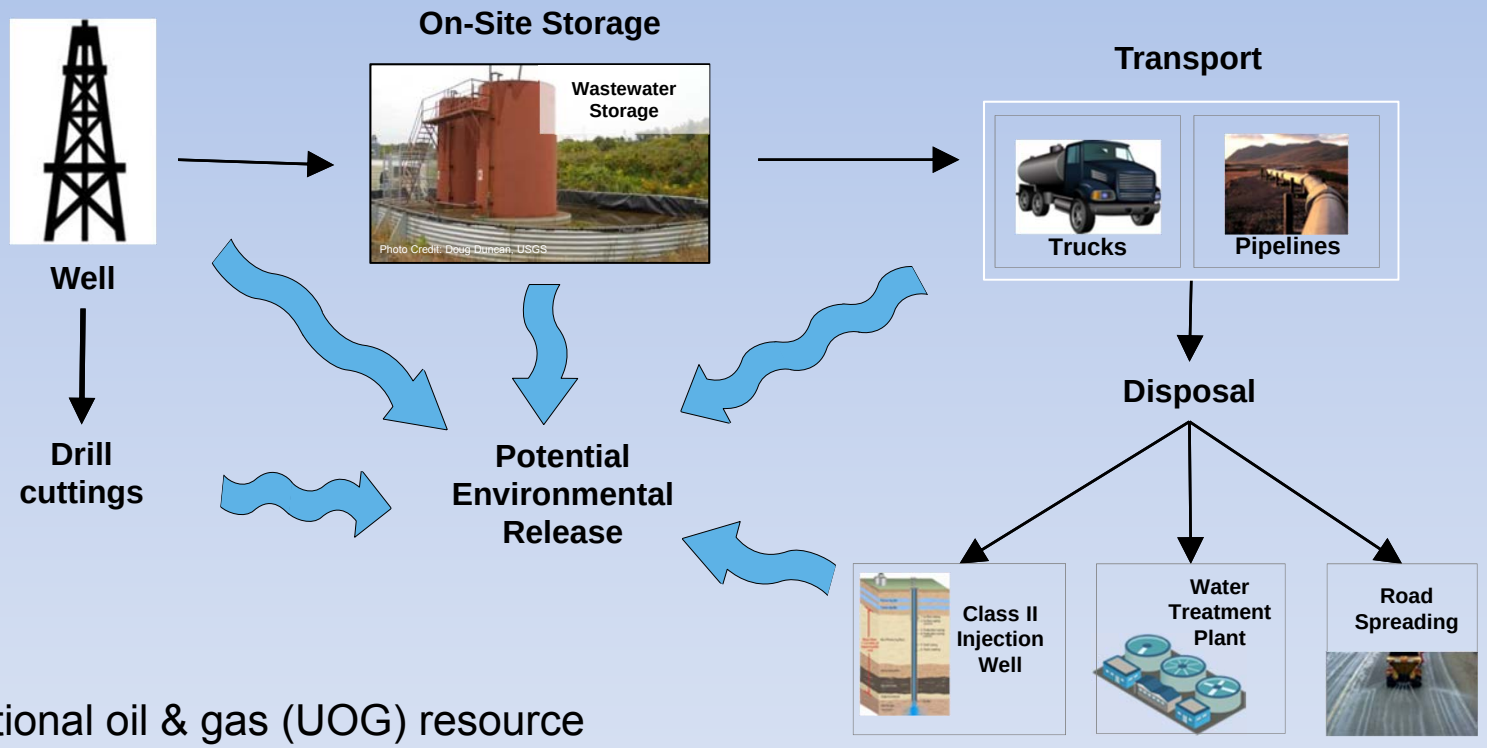
Collaborative project between USGS researchers, universities, and State and Federal Agency Partners







Prioritized Environmental Pathways



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

Current Research Efforts

Pore Scale ⟹ Site Scale ⟹ Regional Scale ⟹

National Scale Understanding

Marcellus Region

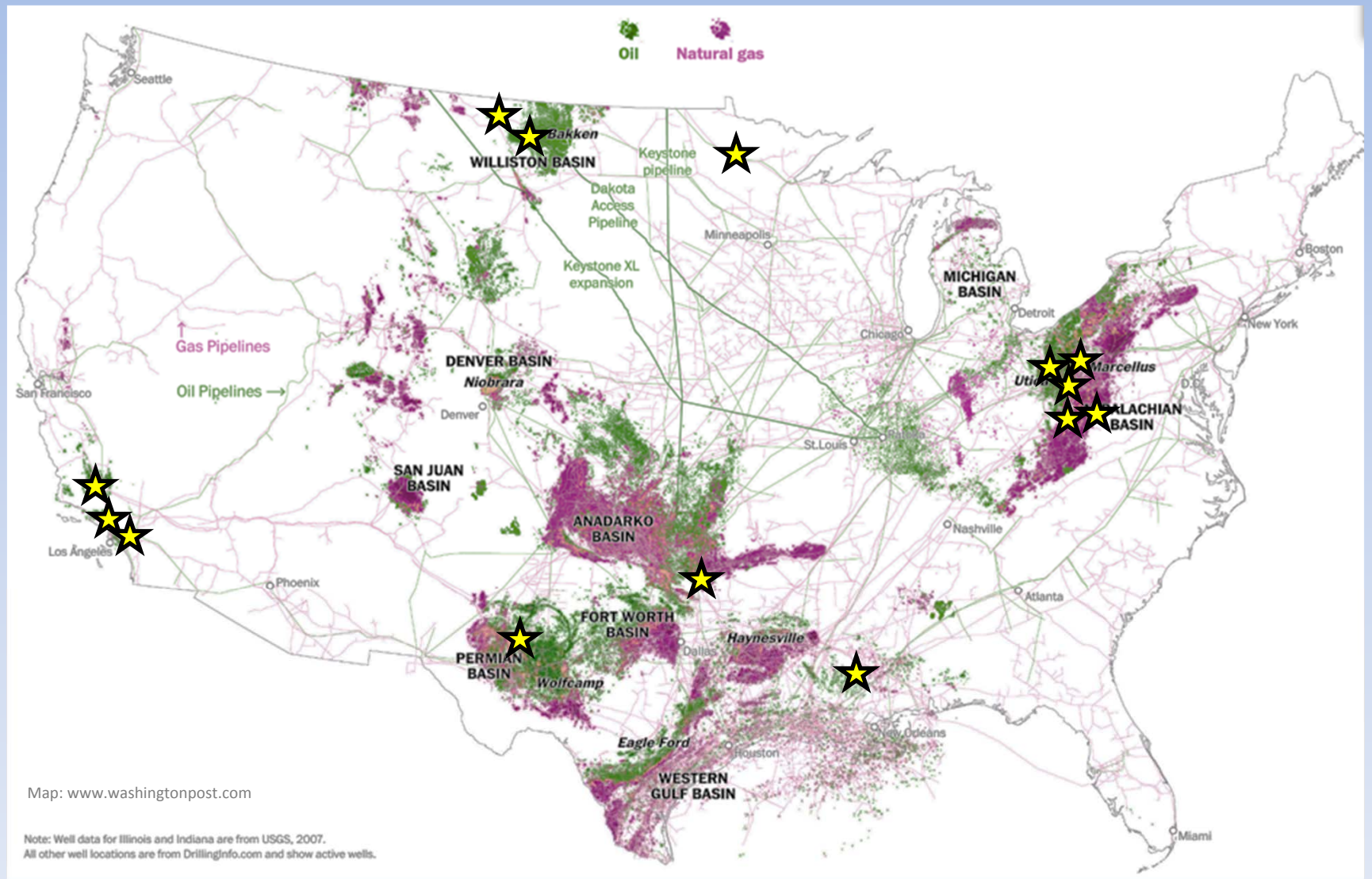
1. Characterizing source materials from existing wells and active production sites
2. Assessing watershed-scale UOG development impacts on low order streams and watersheds
3. Evaluating impacts of activities at Class II wastewater injection facilities

Williston Basin

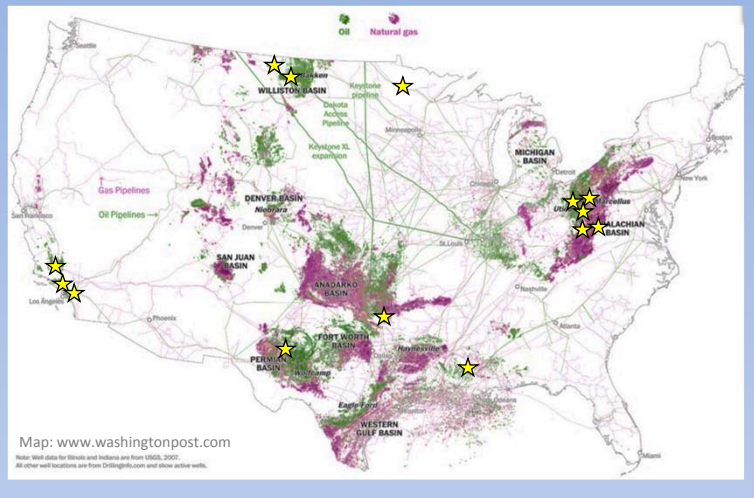
4. Studying historical (Montana) and recent (North Dakota) leaks and spills of brine wastewaters in the Williston Basin.

1. **Permian Basin**
   Studying wastewater and oil dumps on BLM lands (New Mexico).

Current Research Efforts



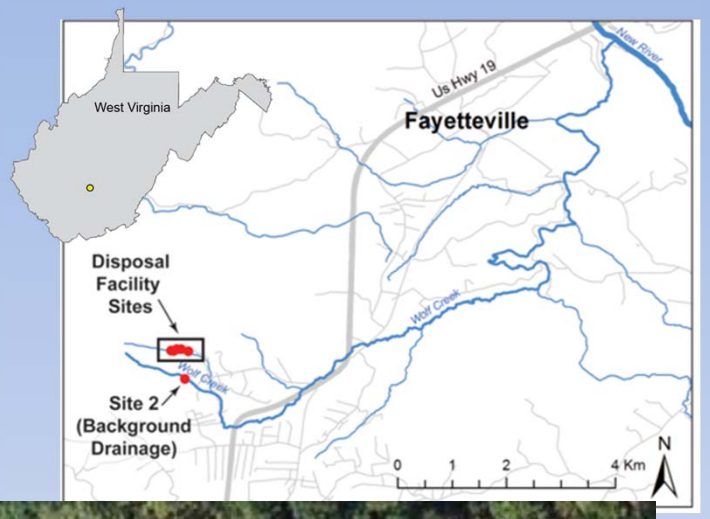
Current Research Efforts



1. Characterizing source materials from existing wells and active production sites
2. Assessing watershed-scale oil and gas development impacts on low order 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)
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.
7. Studying wastewater and oil dumps on Bureau of Land Management lands in New Mexico (Permian Basin).
8. Bemidji crude oil natural attenuation research site (Minnesota)

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.

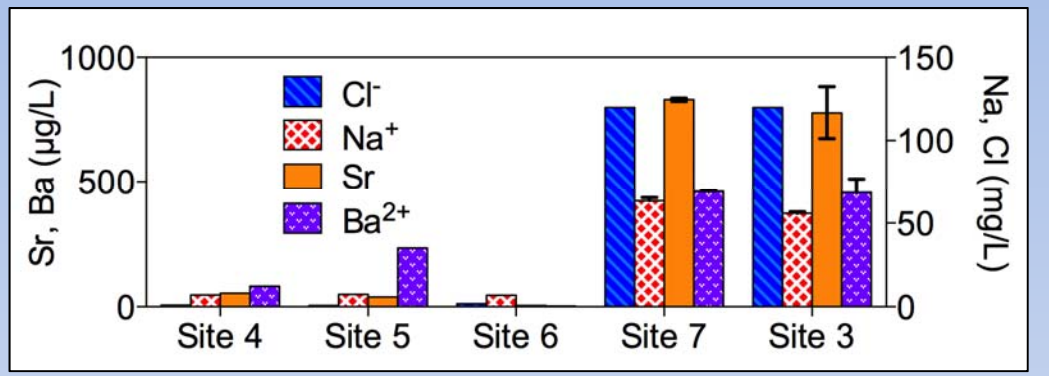


4 publications

Major observations in following slides

Elevated inorganic and organic signatures of OG in downstream creek waters

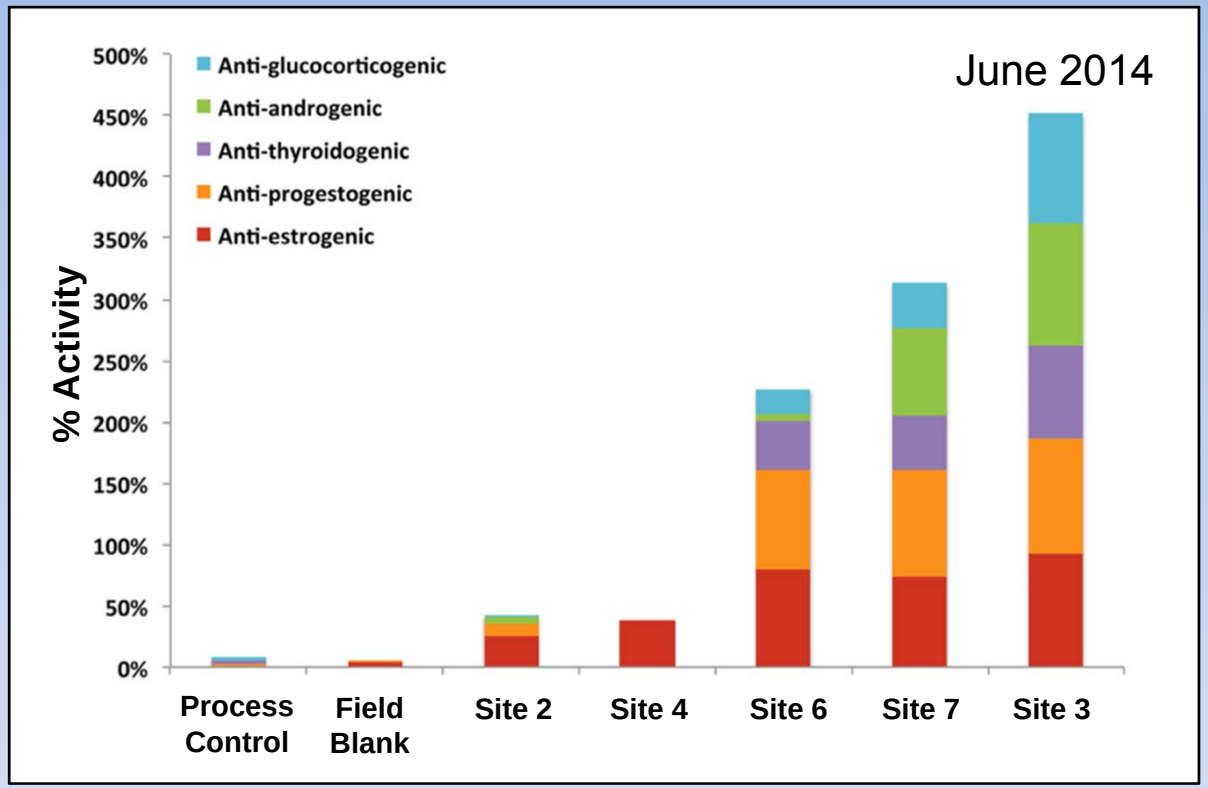
- Elevated Na^+, Cl^-, Ca^{2+}, Li^+, Ba^{2+}, and Sr at sites 7 and 3 is consistent with impacts from shale gas wastewater.



- Organic compounds (10-50 µg/L range) found below the former impoundment ponds but not upstream at the background site.
  - Numerous hydrocarbons and alcohols detected
    - **1-(2-butoxyethoxy) Ethanol**—used as a corrosion inhibitor and antifreeze
    - **bis(2-ethylhexyl) Hexanedioic acid ester** –a plasticizer used in manufacture of PVC and could be leached from pipes
    - **1,1-dioxide tetrahydro-Thiophene**—thiophenes are often found associated with coal extracts and shale formation waters
  - Organic signatures are consistent with shale gas produced waters.

From Akob et al. 2017 ES&T; Orem et al. 2017 App Geo

Combined Surface Water Antagonist Activities

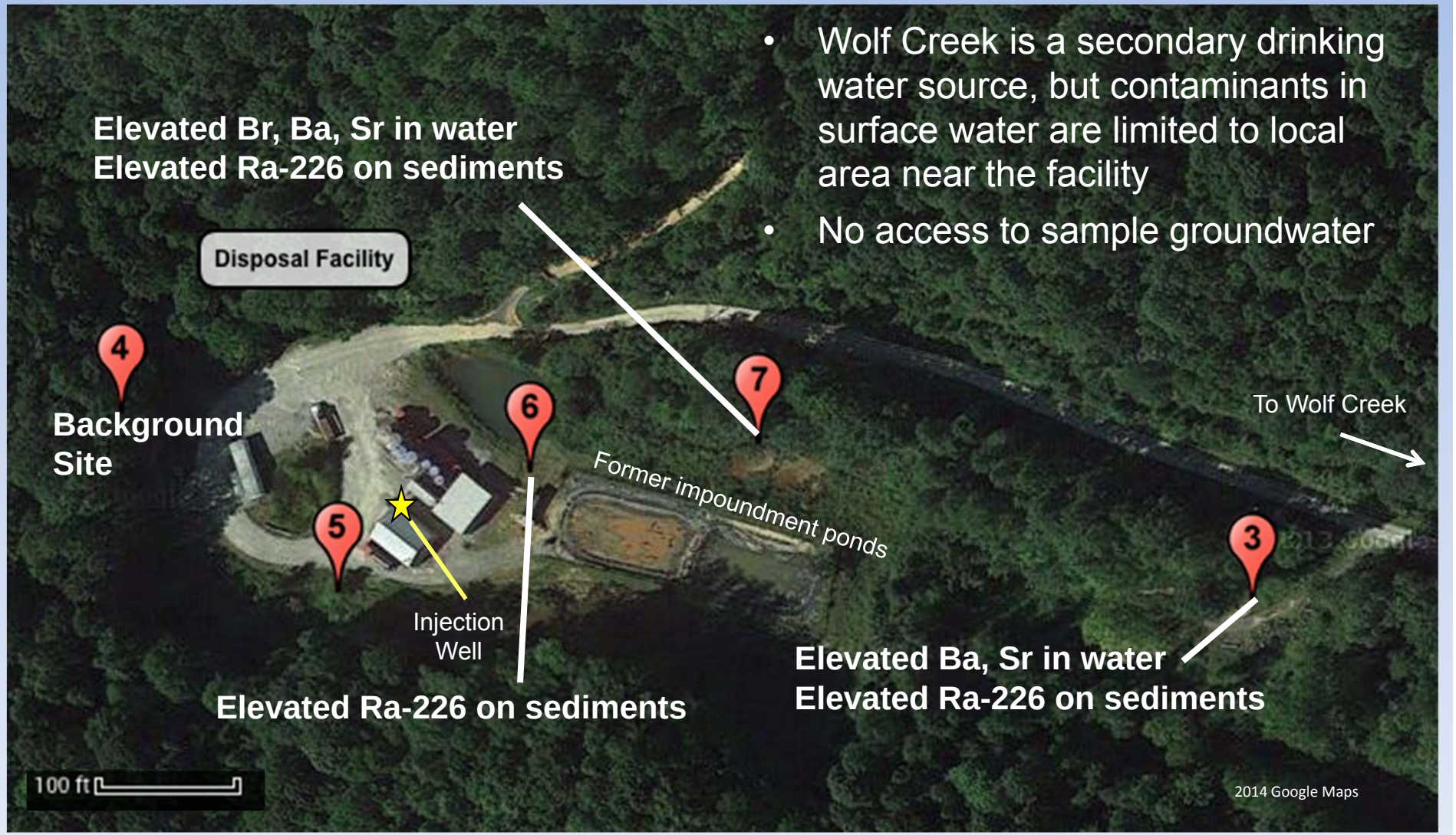


- Hormone receptor assays show endocrine disrupting activity with concentrated solutions of waters from sites 7 and 3.
- **Evidence for potential impacts on human and aquatic health.**

  --> reproductive and/or developmental

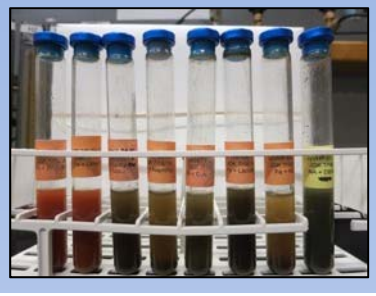
Kassotis et al. 2016 Sci. Tot. Environ.

Produced water signal is also reflected in the creek sediments

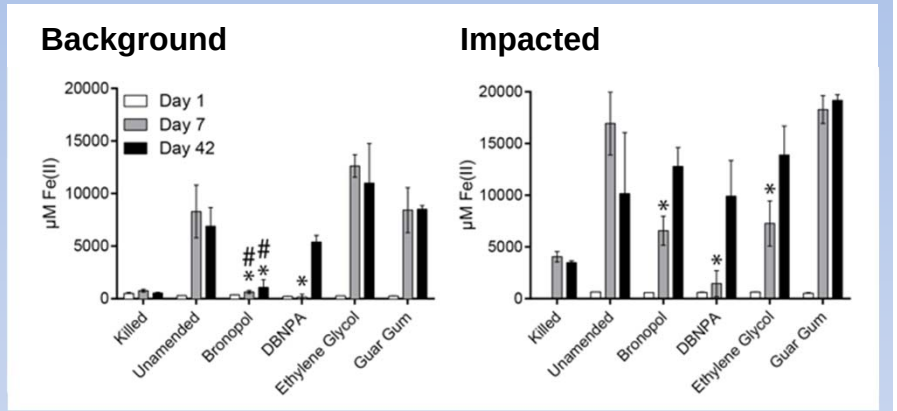


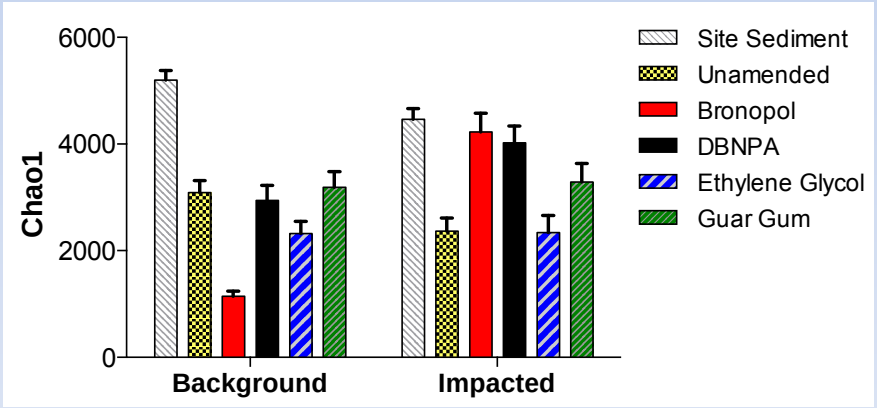
- Wolf Creek is a secondary drinking water source, but contaminants in surface water are limited to local area near the facility
- No access to sample groundwater

Impacts of hydraulic fracturing fluid (HFF) chemicals on microbial community structure and function



- Microbial processes play a key role in contaminant fate and transport.
- Cultivation studies with common hydraulic fracturing fluid additives showed:
  - Loss of iron-reducing functionality in the presence of commonly used HF biocides
  - Evidence of alterations to microbial communities





an index of microbial diversity

From Mumford et al., 2018 App Env Micro

Brine Leaks and Spills:
North Dakota Wastewater Pipeline Spill

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.XSZ26pjX.dpuf

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journal homepage: 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 [a,*], K.J. Skalak [a], D.B. Kent [b], M.A. Engle [c], A. Benthem [a], A.C. Mumford [a], K. Haase [a], A. Farag [d], D. Harper [d], S.C. Nagel [e], L.R. Iwanowicz [f], W.H. Orem [c], D.M. Akob [a], J.B. Jaeschke [a], J. Galloway [g], M. Kohler [b], D.L. Stoliker [b], G.D. Jolly [a]

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[b] U.S. Geological Survey, National Research Program, Menlo Park, CA 94025, USA
[c] U.S. Geological Survey, Eastern Energy Resources Science Center, Reston, VA 20192, USA
[d] U.S. Geological Survey, Columbia Environmental Research Center, Jackson Field Research Station, Jackson, WY 83001, USA
[e] Department of Obstetrics, Gynecology and Women's Health, University of Missouri, Columbia, MO 65211, USA
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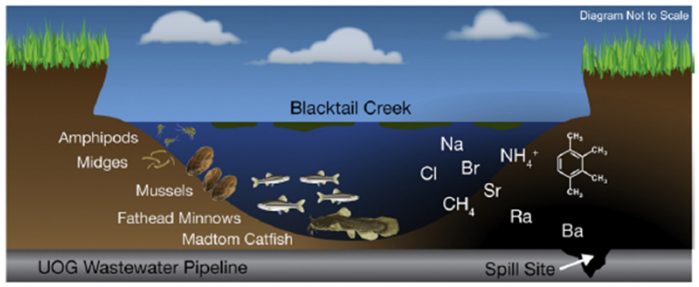
[g] U.S. Geological Survey, North Dakota Water Science Center, Bismarck, ND 58503, USA

Open Access Publication with All Data Available

HIGHLIGHTS

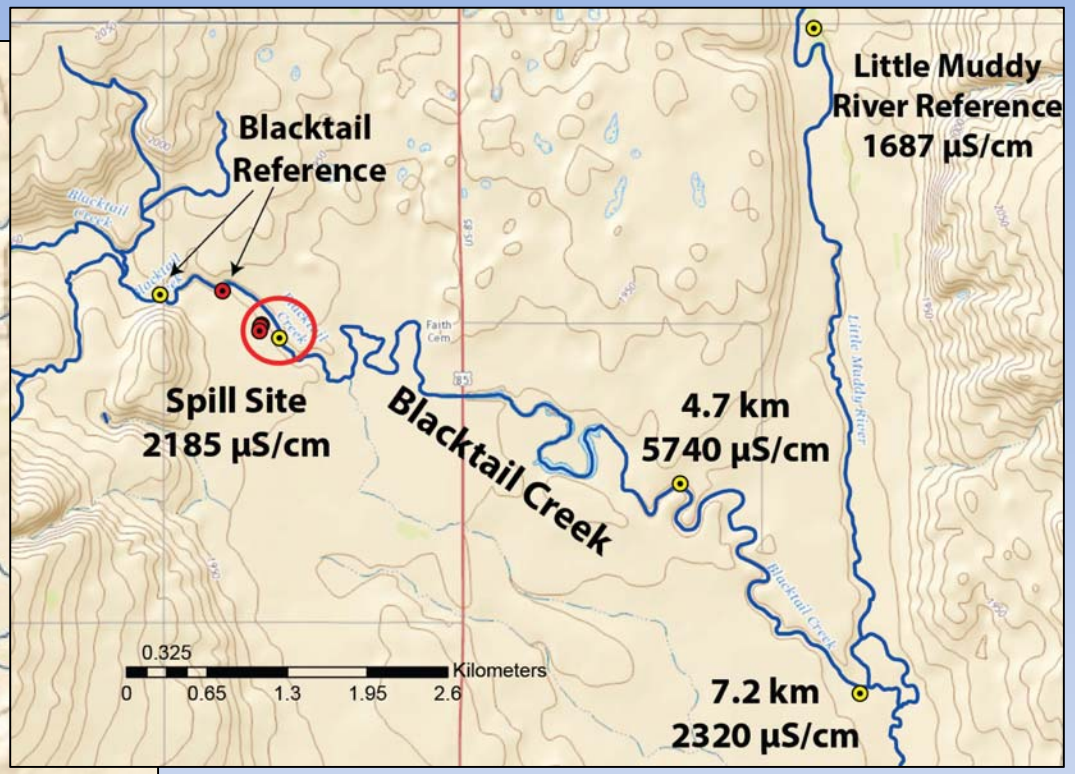
- UOG wastewater (>11 million liters) spilled into Blacktail Creek, ND in January 2015.
- Elevated Na, Cl, Br, Sr, B, Li, NH_4, and hydrocarbons were detected in creek waters.
- Geochemical baseline deviations persist months after remediation efforts started.
- B and Sr concentrations, and Ra activities were up to 15 times background in sediment downstream.
- Biological impacts include reduced fish survival and estrogenic inhibition downstream.

GRAPHICAL ABSTRACT



Major observations in following slides

1 publication; others in prep.



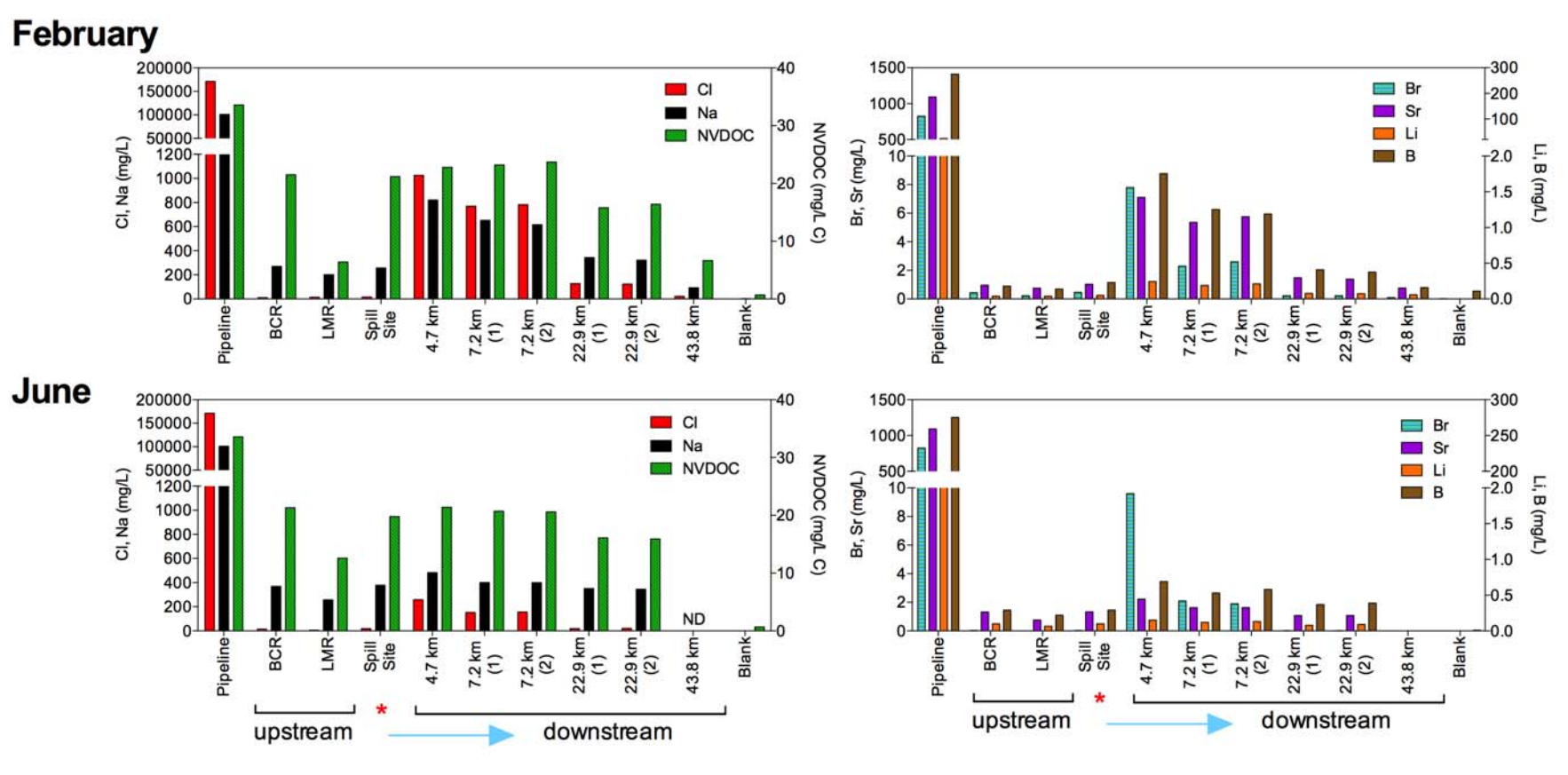
- We have completed 4 rounds of sampling, including sediment, water, and biota, February and June 2015, June 2016, June 2017.
- Samples were collected upstream and downstream from the spill along a 22-km reach

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.

Cozzarelli et al., 2017, STOTEN

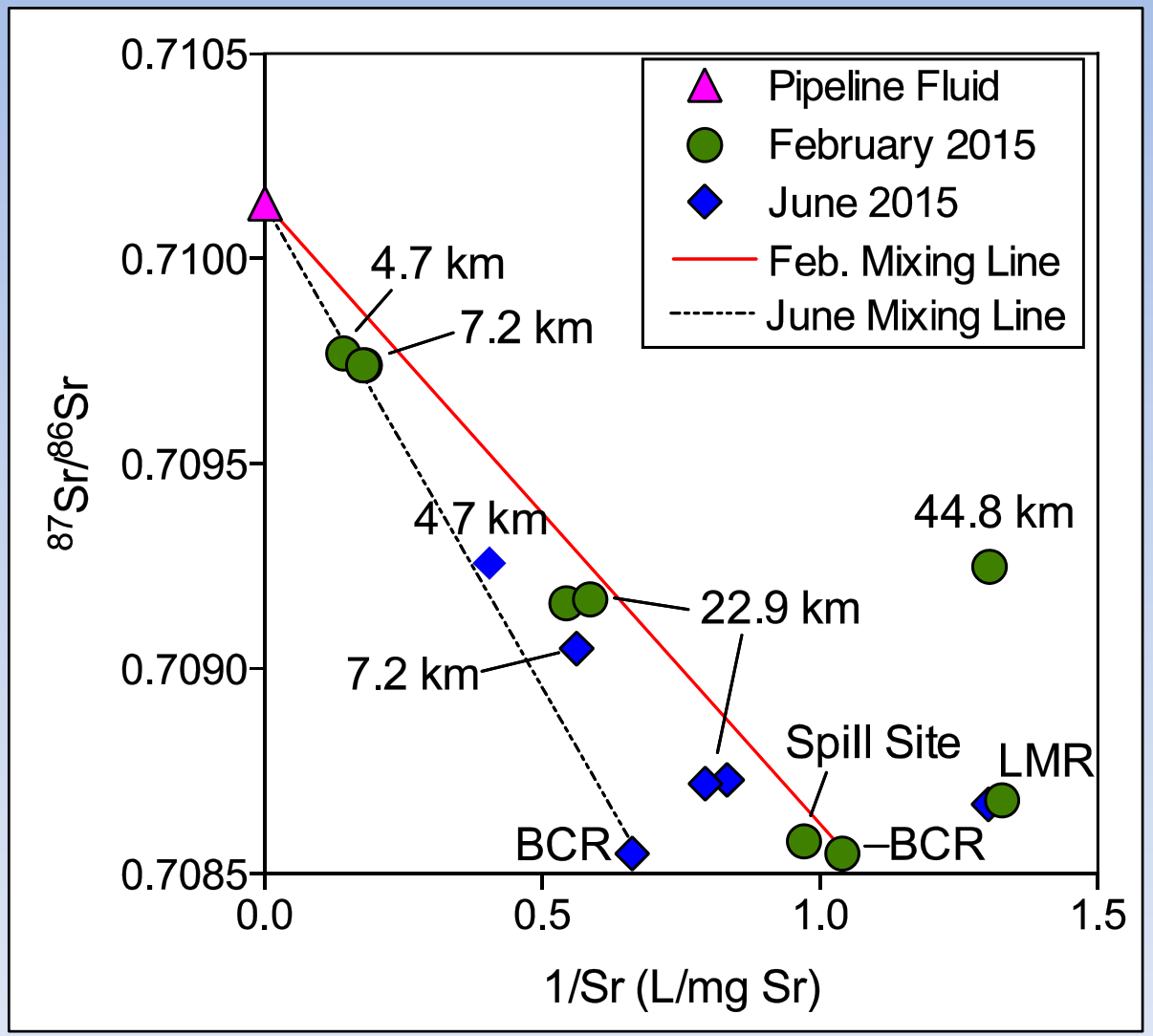
Water Geochemistry



- Pipeline sample had very high concentrations of Na, Cl, Br, Sr, Li, B
- Active remediation at the “Spill Site” diverted contaminated water and removed sediment
- DOC was >20 mg/L, both upstream and downstream from the spill, complicating the identification of organic fingerprints of the wastewater.

Cozzarelli et al., 2017, STOTEN

$^{87}Sr/^{86}Sr$ –sensitive tracer of OG wastewater

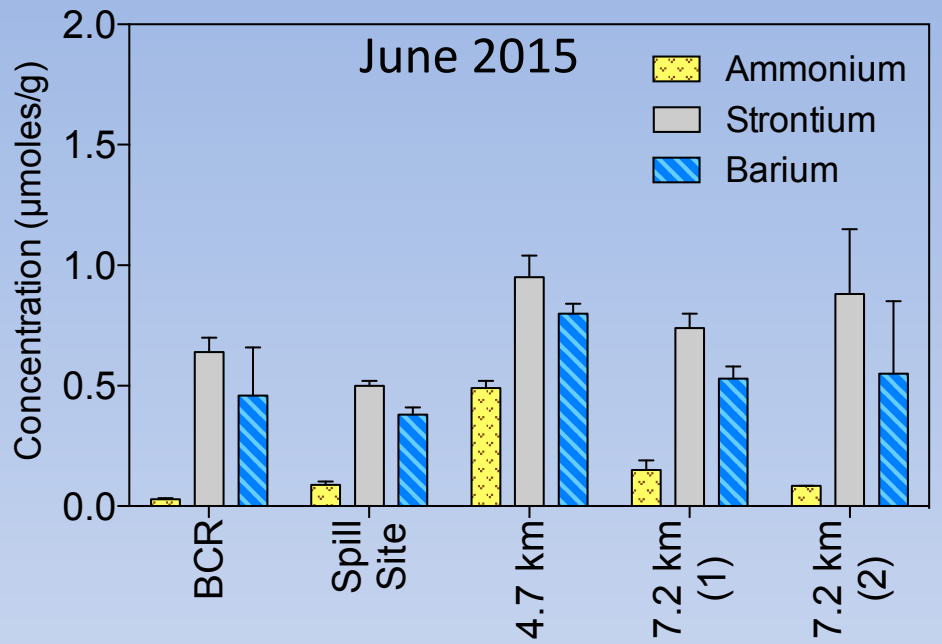


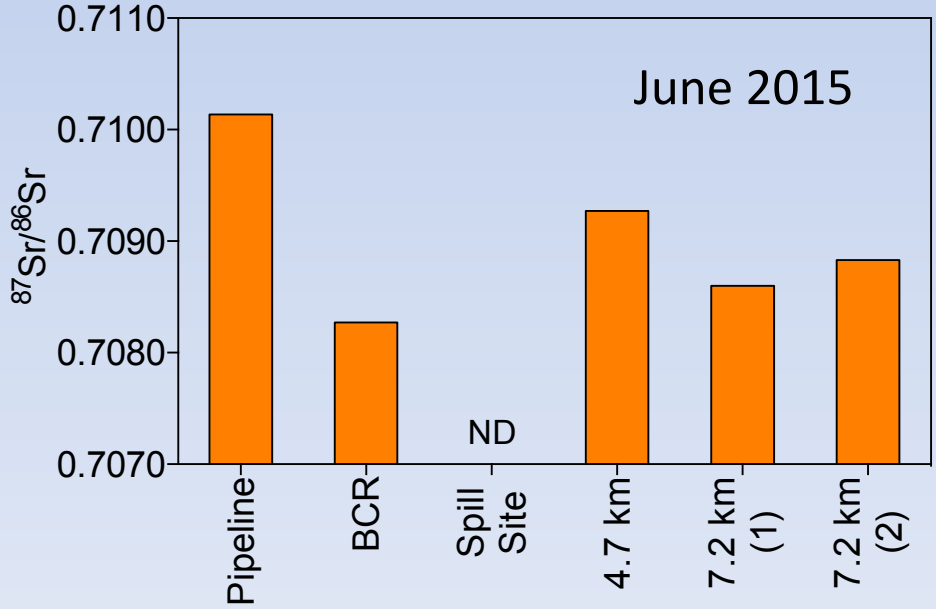
- Pipeline sample has distinct radiogenic signature
- Mixing between background and pipeline Sr composition evident along Blacktail Creek
- Pipeline contribution evident at 22.9 km downstream, 0.01% in June 2015

Cozzarelli et al., 2017, STOTEN

Contaminants are transported with sediment

Sediment-bound NH_4, Ba, Sr, elevated downstream



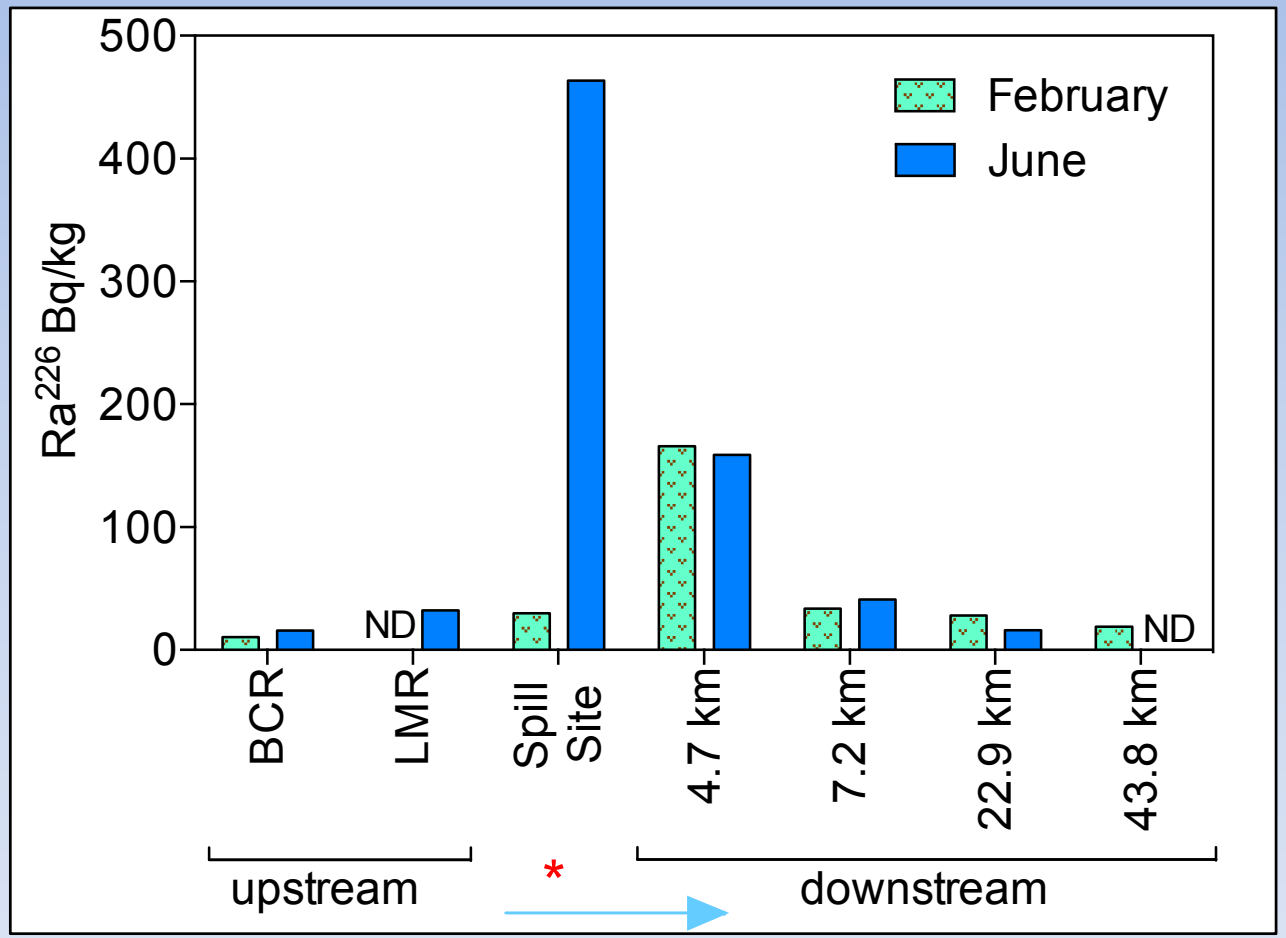


Sr in downstream sediments retains radiogenic signature reflecting pipeline contribution.

Ra^{226} was 29 times background activity, 464 Bq/kg.

Cozzarelli et al., 2017, STOTEN

Radium^{226} is retained and persists in river sediment



*EPA MCLs for total radium (226 plus 228) is 5 pCi/L (185 Bq/kg)

- Ra^{226} was 29 times background activity - 464 Bq/kg.
- Lauer *et al.*, 2016 reported total Ra= 553−4684 Bq/kg in stream sediments
- Ra^{226}/U^{238} activity ratios >> 1 at the spill site (June 2015) and the 4.7km and 7.2 km suggest pipeline source of Ra

In situ study of survival of early life stage Fathead Minnows —June 2015

- Fish In-situ Exposure Experiment
  → 96 hour caged bioassay with fathead minnows.
- Most notably, survival of fathead minnows after 96 h:
  - 88.6% and 94.7% at BCR and LMR
  - 2.5% at 7.2 km downstream
- Mortality of two native Madtom catfish observed at 7.2 km

- Cause of fish mortality? Measured elevated NH_4
- Reduced temperatures and increased Cl and HCO_3 concentrations suggests pulsed upwelling of groundwater into the stream at the time that mortalities were observed.

Data by Faag and Harper

Key Findings

- The river downstream from the spill had elevated UOG waste indicators including hydrocarbons and Cl, Br, Li, B, Ba and Sr, and $^{87}Sr/^{86}Sr$ ratios.
- Barium and radium accumulate in the river bed sediments. Radium is significantly above the EPA action level for radium 226, which should not exceed 185 Bq/kg.
- Potential health effects were indicated by fish bioassays in which fish experienced mortality, and human health impact indicators include modest endocrine disrupting activity (not shown) observed downstream from the spill.
- Episodic increases in NH_4 appeared to be high enough to be toxic to aquatic life. Potential groundwater inputs into the stream were indicated.
- Partitioning of chemicals onto the sediment limits movement of wastewater components downstream but could provide a long-term source to aquatic organisms. Ex: Ba and Ra uptake by snails.
- Future work will focus on potential groundwater pathways and sources to the stream, using geophysical surveys and geochemical measurements.

Update

- Water sampling in 2016 did not show any wastewater indicators in the river.
- Focus in 2016 was on geomorphic assessment to look at sediment as vehicle for contaminant transport. How far might Radium-226 be transported?

In 2016, we sampled the floodplain (longer-term storage). Ra was found on the lower floodplain at site 4.7km.

Radium did not infiltrate below the surface layer of soils at this site.

Future work will focus on potential groundwater pathways and sources to the stream, using geophysical surveys and geochemical measurements.

Next Steps: Additional work connecting compounds that persist in the environment with specific biological exposures and responses (combining chemistry, toxicology, and epidemiology).

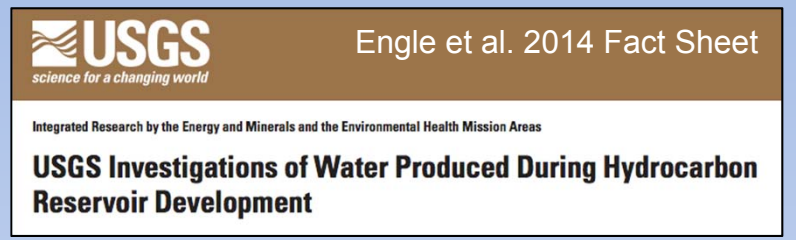
Questions?

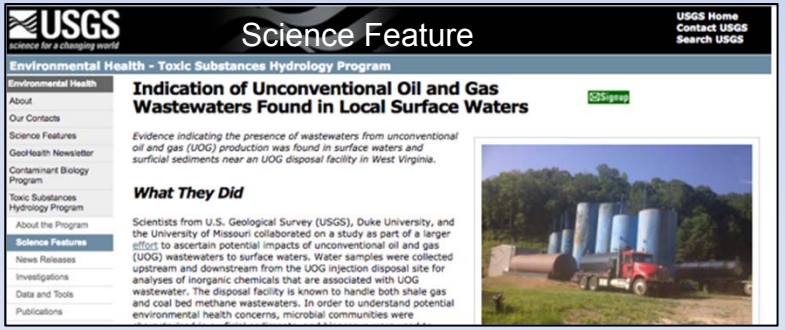
Isabelle Cozzarelli, icozzare@usgs.gov

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

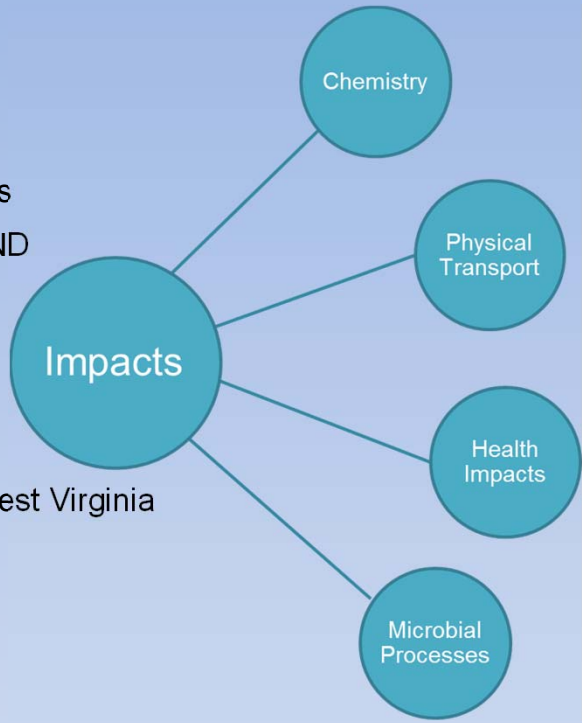
Other Technical Products of Value to Stakeholders

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).





Collaborators: Internal and External



USGS

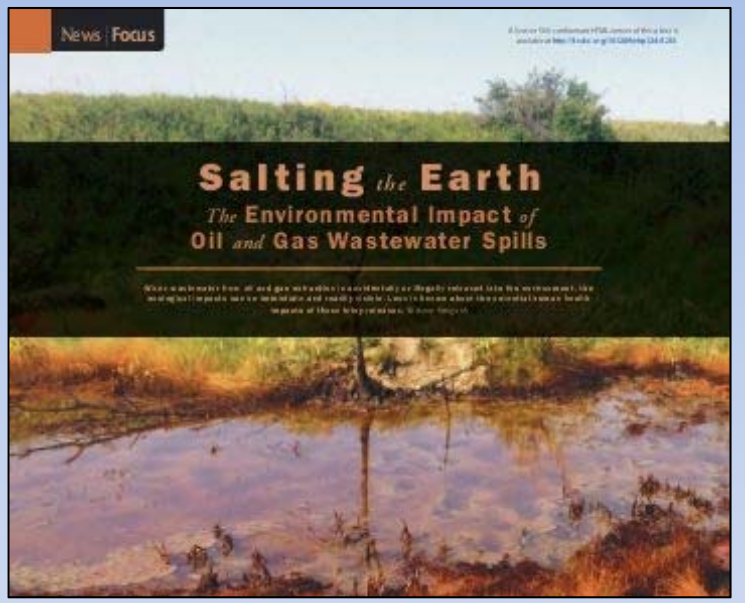
- Eastern Energy Resources Science Center: produced water chemistry, B/Sr isotopes
- MT and ND Water Science Centers (WSC): hydrology and water quality in MT and ND
- OR and NJ WSC and Northern Rocky Mountain SC (NOROCK)**:** impact of wastes on amphibian populations in Prairie Potholes
- Columbia Environmental 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

Communication with Stakeholders

- Products have received significant attention in the scientific literature and the news:
  - Over 150 citations since 2014
  - Over 50 mentions in news articles
  - Research highlighted in *Environmental Health Perspectives* article “Salting the Earth: The Environmental Impact of Oil and Gas Wastewater Spills” (Konkel, 2016)
  - Interview by Public Radio and highlighted on PRI’s Living Earth Program, 2015
  - Three interviews for Energy Wire (2015, 2016)
- Attended many stakeholder meetings and workshops, e.g., EPA, AAAS, NAS, HEI, and DOI workshops and conferences.



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.
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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.
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