Isotopic Fingerprints for Delineating the Environmental Effects of Hydraulic Fracturing Fluids

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Isotopic fingerprints for delineating the environmental effects of hydraulic fracturing fluids

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Abstract

Unconventional shale gas and tight sand exploration through hydraulic fracturing accounts for a large fraction of oil and gas production in the US and will soon be launched on a global scale. One of the complexities in evaluating the environmental impact of hydraulic fracturing and shale gas development is the legacy of conventional oil and gas exploration in the same areas. Data from the USGS produced water database coupled with new data generated from flowback and produced waters from several basins in the US reveal that the formation water is typically hypersaline and characterized by a Ca-chloride composition with high Br/Cl ratios that reflect different degrees of seawater evaporation and water-rock interactions. In many cases, the chemistry of effluents from unconventional and conventional wells is indistinguishable. In the Appalachian Basin, flowback from the Marcellus Shale has distinctive trace element (B/Cl, Li/Cl) and isotopic ($^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{7}Li$, $^{228}Ra/^{226}Ra$) fingerprints that are different from those in produced waters from conventional oil and gas wells. The integration of these geochemical and isotopic tracers could provide robust monitoring tools for evaluating the environmental effects and delineating the specific impact of unconventional oil and gas operations.

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Keywords: Hyraulic fracturing, shale gas, isotope tracers, water contamination

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1. Introduction

Production from unconventional natural gas reservoirs has expanded substantially through the use of horizontal drilling and high-volume hydraulic fracturing. These technological advances have opened vast new energy sources, such as low-permeability organic-rich shale formations and "tight-sand" reservoirs, altering the domestic energy landscape in the US.[1,2] The total production of natural gas has increased by more than 30% during the last decade, with unconventional shale gas and tight sand productions accounting for 34% and 24% respectively of the total natural gas production in the US (0.68 trillion m^3) in 2012.[3]

Future energy forecasts suggest that US unconventional natural gas production from shale formations will double by 2035 and constitute ~50% of the total domestic natural gas production.[4] Unconventional extraction (horizontal drilling and high volume hydraulic fracturing) for shale gas has already expanded in Canada, and will soon be launched on a global scale, with significant natural gas reservoirs in China, South America, northern and southern Africa, Europe, and Australia. The current global estimate of natural gas reserves in unconventional shale is approximately 716 trillion m^3 (2.53×10^{13} Mcf).[3,4]

One of the environmental risks for unconventional oil and gas development is the management, disposal, and frequent spills of oil and gas wastewater composed of flowback and produced waters.[5] While man-made chemical additives in hydraulic fracturing fluids have drawn most of the attention, the inorganic constituents in oil and gas wastewater also pose similarly serious environmental and human health risks. Recent findings have shown that the hydraulic fracturing fluids and produced waters contain high levels of bromide, iodide, and ammonium[6], radium[7,8], and toxic elements (e.g., barium[9]). Produced waters from conventional oil and gas wells contain similar levels of contaminants[6], and in many basins in the US shale gas and tight sand explorations are conducted in areas with a long legacy of conventional oil and gas exploration. Furthermore, the difference between "unconventional" and "conventional" exploration in many areas is becoming insignificant given new methodologies of enhanced oil and gas extraction even from vertical oil and gas wells and the use of similar chemicals for oil and gas extraction.

2. The geochemistry of formation brines

Based on the USGS produced water database[10] and data generated at Duke University, the geochemistry of flowback and produced waters from unconventional and conventional oil and gas wells have been compiled. The chloride distribution in unconventional flowback and produced waters from different oil and gas basins in the US varies widely, from 50,000 mg/L to 300,000 mg/L (Fig. 1). A comparison of the TDS in unconventional wells relative to conventional wells in the Appalachian Basin shows a similar range, although the mean TDS values of unconventional wells are typically lower (Fig. 2 ; $p<0.0001$), reflecting the dilution by hydraulic fracturing injection fluids. Likewise, the geochemistry of fluids extracted from unconventional and conventional oil and gas wells is similar, and is characterized by Ca-chloride composition, high Br/Cl and low Na/Cl (relative to modern seawater), that reflects different degrees of seawater evaporation and water-rock modification.[7,9,11,12,13] Variations in Cl^-, Br^-, I^-, NH_4^+, $\delta^{18}O$, and δ^2H indicate that the original brines were diluted by meteoric water.[6] One of the environmental risks for unconventional oil and gas development is the management, disposal, and the frequent spills of oil and gas wastewater composed of flowback and produced waters.[5] The ability to delineate and identify the differential environmental effects of unconventional oil and gas exploration based on major geochemistry alone is therefore limited and presents a major challenge for regulators and monitoring programs.

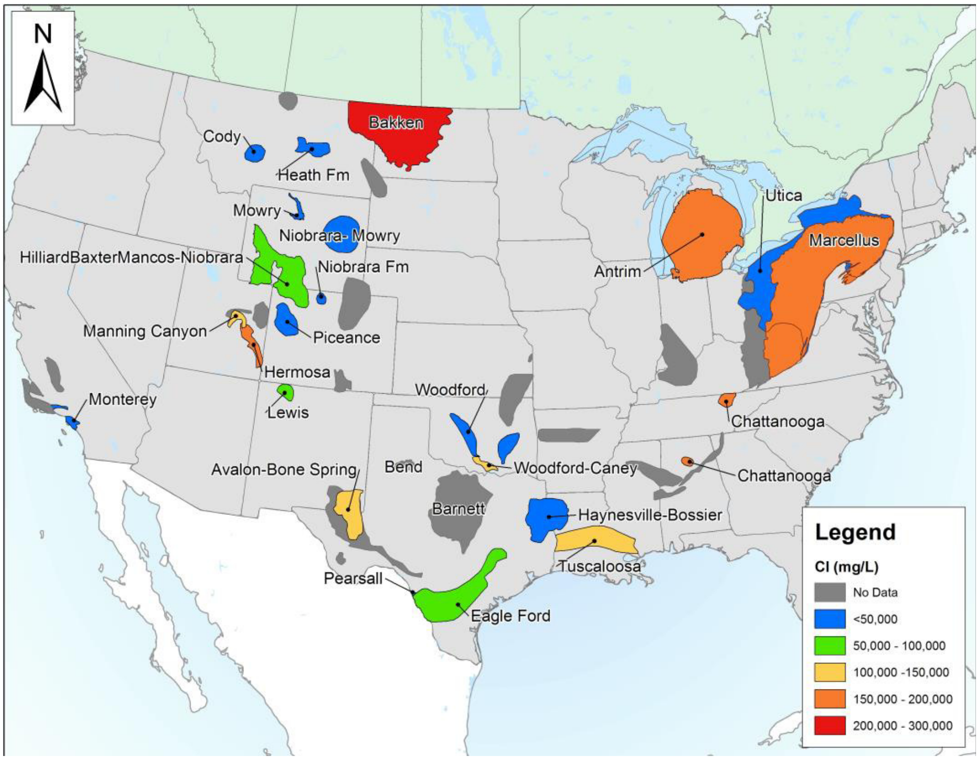

Figure 1. The distribution and salinity of fluids from the U.S. shale gas plays. The color of each basin corresponds to the salinity (chloride content) of flowback and produced waters from unconventional oil and gas wells in the basin. Data from USGS produced water database.[10]

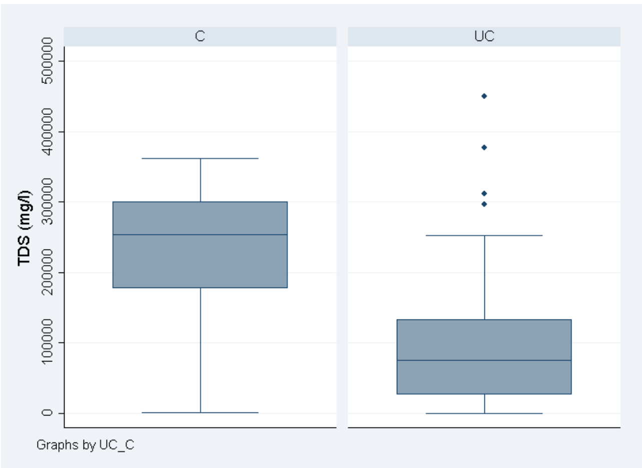

Figure 2. A comparison of the TDS of produced waters from conventional (C) and unconventional wells in the Appalachian basin.

3. The isotopic fingerprints of boron, lithium, strontium, and radium in hydraulic fracturing fluids from the Marcellus Shale

Previous research has shown that injection of typically low-saline water as part of hydraulic fracturing results in desorption of boron and lithium from the shale formation. The mobilization of relatively depleted ^{11}B and ^{7}Li from exchange sites on clay minerals results in low $\delta^{11}B$ (25-33‰) and $\delta^{7}Li$ (<10‰) in flowback water from the Marcellus Formation relative to produced waters from conventional oil and gas wells in the Appalachian Basin (38-52‰ and 10-24‰, respectively).[14] In addition, formation brines from the Middle Devonian Marcellus Formation have different $^{87}Sr/^{86}Sr$ ratios (~0.712) relative to conventional produced waters from the Upper Devonian (0.716-0.722), but overlap with the $^{87}Sr/^{86}Sr$ ratios in conventional oil and gas wells from the Lower Devonian formations (0.710-0.712).[12,15] Finally, the relative uranium enrichment in the Marcellus Shale relative to the higher abundance of ^{232}Th in permeable rocks such as sandstone results in lower $^{228}Ra/^{226}Ra$ activity ratios in flowback and produced waters from the unconventional Marcellus Shale (<0.3) relative to produced waters from conventional oil and gas in the Appalachian Basin (~1).[7,8]

4. Tracing the sources of contaminants in the environment

The high frequency of spills associated with high-density shale gas drilling[5] as well as the disposal of oil and gas wastewater from both conventional and unconventional oil and gas wells[6,8] requires a robust methodology for the distinguishing of unconventional from conventional sources. Fig. 3 presents a flow chart that illustrates the use of the multiple geochemical and isotopic tracers for delineating the sources of contamination from oil and gas effluents in Marcellus Shale in developing areas. Preliminary results from studying a spill in Tyler County, West Virginia show that the saline water (TDS~18,000 mg/L) has distinct geochemistry (e.g., high Br/Cl), $\delta^{11}B$ (~26‰), and $\delta^{7}Li$ fingerprints,[14] which mimic the composition of flowback waters from the Marcellus Shale. This analysis provides a direct and compelling indication for the source of contamination from the nearby shale gas well.

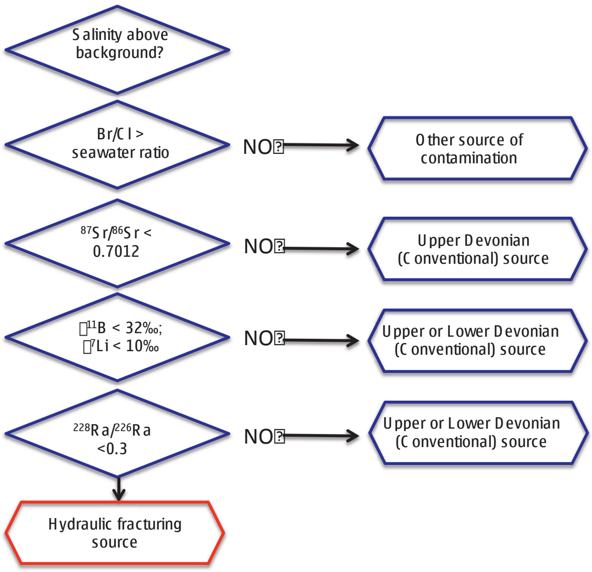

Figure 3. Diagnostic flowchart for identification of contaminated water based on integration of geochemical and isotopic tracers.

5. Acknowledgements

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6. References

1. Kargbo DM, Wilhelm RG, Campbell DJ. Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environ. Sci. Tech.* 2010; **44**: 5679-5684.
2. Kerr RA. Natural Gas From Shale Bursts Onto the Scene. Science 2010; **328**:1624-1626.
3. USEIA. *Annual Energy Outlook 2014*. U.S. Department of Energy 2014.
4. Boyer C, Clark B, Jochen V, Lewis R, Miller CK. Shale Gas: A Global Resource. *Oilfield Rev.* 2011**;** **23**: 28-39.
5. Vengosh A, Jackson RB, Warner NR, Darrah TH, Knodash AJ. A Critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and Hydraulic Fracturing in the United States. *Environ. Sci. Tech. 2014;* **48**:8334-8348.
6. Harkness J, Dwyer G, Warner NR, Parker K, Mitch W, Vengosh A. Iodide, Bromide, and Ammonium in Hydraulic Fracturing and Oil and Gas Wastewaters: Environmental Implications. *Environ. Sci. Tech.* 2015; **49**:1955–1963.
7. Rowan EL, Engle MA, Kraemer TF, Schroeder KT, Hammack RW, Doughten MW. Geochemical and isotopic evolution of water produced from Middle Devonian Marcellus shale gas wells, Appalachian basin, Pennsylvania. *AAPG Bull.,* 2015; **99**:181-206.
8. Warner NR, Christie CA, Jackson RB, Vengosh A. Impacts of shale gas wastewater disposal on water quality in western Pennsylvania. *Environ. Sci Tech.* 2013; **47**:11849–11857.
9. Barbot E, Vidic NS, Gregory KB, Vidic RD. Spatial and Temporal Correlation of Water Quality Parameters of Produced Waters from Devonian-Age Shale following Hydraulic Fracturing. *Environ. Sci. Technol.* 2013; ***47***:2562-2569.
10. USGS Produced water database (http://www.usgs.gov/science/cite-view.php?cite=1259).
11. Haluszczak LO, Rose AW, Kump LR. Geochemical evaluation of flowback brine from Marcellus gas wells in Pennsylvania, USA. *Appl. Geochem*. 2013; **28**: 55−61.
12. Warner NR, Jackson RB, Darrah TH, Osborn SG, Down A, Zhao K, White A, Vengosh A.Geochemical evidence for possible natural migration of Marcellus formation brine to shallow aquifers in Pennsylvania. *PNAS* 2012; **109**:11961–11966.
13. Engle MA. and Rowan E L. Geochemical evolution of produced waters from hydraulic fracturing of the Marcellus Shale, northern Appalachian Basin: A multivariate compositional data analysis approach. Int. J. Coal Geol. 2013 (in press).
14. Warner NR, Darrah TH, Jackson RB, Millot R, Kloppman W, Vengosh A. New Tracers identify hydraulic fracturing fluids and accidental release from oil and gas operations. *Environ. Sci Tech.* 2014;**48**:12552-12560.
15. Chapman EC, Capo RC, Stewart BW, Kirby CS, Hammack RW, Schroeder KT, Edenborn HM. Geochemical and strontium isotope characterization of produced waters from Marcellus shale natural gas extraction. *Environ. Sci Tech* 2012; **46:** 3545−3553.