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Hydraulic Fracturing Flowback Water Chemical Composition Research

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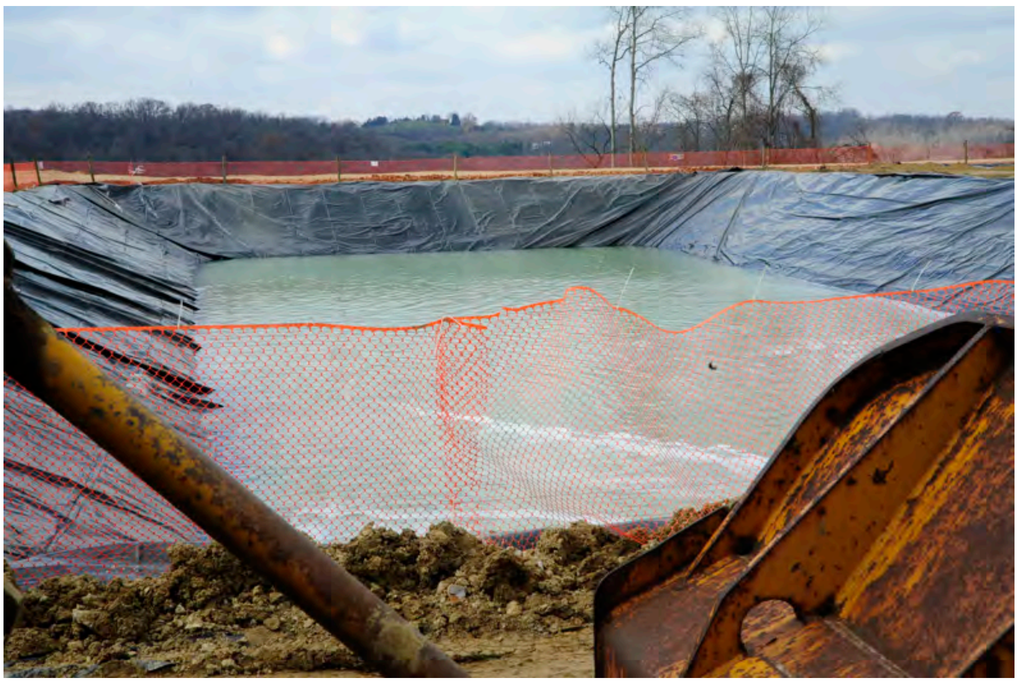

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Introduction:

The following articles have been selected from the available published information on the chemical composition of hydraulic fracturing flowback water, which is the fluid that flows back to the surface from an unconventional well after it has been drilled. Principle findings and the significance of each study are summarized below each source, listed chronologically by publishing date.

Articles:

1. **Hayes, Thomas and Marcellus Shale Coalition. "Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas." (2009) Web. Accessed June 2015.**
   http://energyindepth.org/wp-content/uploads/marcellus/2012/11/MSCommission-Report.pdf

   This early 2009 report summarizes the typical chemicals and other materials found in flowback water. Generally, flowback water contains varying concentrations of salts, heavy metals, oils, greases, and volatile (easily separable and able to evaporate) and semi-volatile soluble organics, which are characteristic of the zone of shale that has been drilled. It also contains friction reducing polymers, corrosion inhibitors, scale inhibitors, and biocides, which ease the drilling process and reduce potential operation problems. This flowback characterization study was executed under a Quality Assurance Project Plan (QAPP) and a Field Sampling and Analysis Plan (FSAP), and data were collected from 16 well sites in PA and three in WV. The results assert that the salt content of the flowback water (mostly chloride), as well as the concentration of total dissolved solids (TDS), greatly increased from 221 mg/L - 27,800 mg/L up to 90 days after drilling. Such results therefore recommend using chloride analyses to monitor and track the environmental fate of flowback water in further studies, as well as further exploring geographic parameters, well depth etc. Conclusions drawn from this study include that flowback water composition is very similar to the water used in conventional drilling. Also, levels of volatile and semi-volatile organics were low enough to be considered unnecessary for future flowback and sampling analyses. These analyses would be impractical to employ as primary tracing techniques for flowback water in the environment.

2. **Blauch, Matt. "Shale Frac Sequential Flowback Analyses and Reuse Implications, March 30, 2011."** ***Environmental Protection Agency*****. Web. Accessed June 2015. PDF.**
   http://www2.epa.gov/sites/production/files/documents/11_Blauch_-_Analyses_Reuse_508.pdf

   This 2011 presentation also discusses an early analysis of flowback water from Marcellus shale drilling. It presents both a recommendation for the recycling of flowback for further hydraulic fracturing and potential explanations for the high levels of salinity observed in the results. Results from 25 sequential flowback studies from Jefferson, Susquehanna, Armstrong and Fayette Counties in PA were assessed, and several significant trends in the chemical composition of the flowback water were found. First, there was a high positive correlation between total dissolved solids (TDS) and chlorides, with TDS levels ranging from 200 mg/L - 145,000 mg/L. This means that as chloride levels increased, so did TDS levels. These values increased with time after drilling along with an increased volume of flowback water. Similarly, concentrations of barium were low immediately after drilling but increased with time. Also, the study found that the calcium content of the water increased geographically from west to east, and also found a high brine content in the mid-region of the state. Potential mechanisms for this highly saline characteristic include: dissolution of autochthonous salt (the salt found originally in the shale), dissolution of allochthonous salt (salt originating from another source), the encroachment of basal brines, the movement of hypersaline connate fluids (fluids trapped in the pores of sedimentary rocks), or combinations of the above mechanisms. In order for flowback water to be recycled for further drilling, treatment to remove detrimental or toxic components should be employed and further researched.

3. Haluszczak, Lara O., et al. "Geochemical Evaluation of Flowback Brine from Marcellus Gas Wells in Pennsylvania, USA." ***Applied Geochemistry*** **28 (2013): 55-61.Web. Accessed June 2015.**
http://catskillcitizens.org/learnmore/Fracking-Flowback-Brine.pdf

This 2013 study encompasses a meta-analysis of the chemical materials found in flowback water, and concurs with the above studies that general concentrations of inorganic constituents increase with time after drilling. This trend was determined by analyzing concentrations of chloride (Cl), bromide (Br), sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), strontium (Sr), barium (Ba), radium (Ra), iron (Fe), manganese (Mn) and total dissolved solids (TDS). These levels are also characteristic of water used during conventional drilling, with some elements at levels 5 – 10 times higher than seawater, and the authors stipulate that the highly saline content of the water can be attributed to the dissolution of salts and minerals in the rock, combined with the drilling fluid additives. Data were collected from 40 conventional oil and gas wells in PA, two unconventional wells in PA, 22 flowback water studies collected by the Pennsylvania Department of Environmental Protection (PA DEP), and eight flowback water samples from a Gas Technology Institute study of unconventional gas drilling. The chloride concentration in these last samples increased from 82 mg/L – 98,000 mg/L in the first 14 days after drilling. This study finally asserts that levels of radium, a naturally-occurring radioactive material, and barium concentrations found in these waters, are many hundreds of times higher than Environmental Protection Agency (EPA) maximum contaminant levels (MCL) for drinking water regulation. These analyses prompt further research into safe-handling techniques of such highly saline and toxic waters for the protection of environmental and human health.

4. Capo, Rosemary C., et al. "The Strontium Isotopic Evolution of Marcellus Formation Produced Waters, Southwestern Pennsylvania." ***International Journal of Coal Geology*** **126 (2014):57-63. Web. Accessed June 2015.**
http://www.researchgate.net/publication/259510424_The_strontium_isotopic_evolution_of_Marcellus_Formation_produced_waters_southwestern_Pennsylvania

This 2014 study of flowback water composition also focused on the high total dissolved solids (TDS) concentration of water produced from drilling in the Middle Devonian Marcellus Formation. In particular, concentrations of strontium were analyzed along with the isotopic ratio of $^{87}Sr/^{86}Sr$ from four wells in southeastern PA, up to 27 months after drilling. Strontium is a signature, or fingerprint chemical, in shale gas extraction and flowback water because it is detectable 85-100% of the time. Over the course of this study, strontium concentrations increased from 330 mg/L – 2,698 mg/L and plateaued in the first year after drilling, whereas the isotopic ratio of $^{87}Sr/^{86}Sr$ gradually rose even after two years. Potential sources of strontium and other chemicals found in flowback water include: injected liquids dissolving the water-soluble materials in the fractured shale, freed brines from pores of organic matter in the shale, strontium found in the water trapped deep within the fractures, and water that migrated into the fractured zone from adjacent shale. Continuing to develop sensitive strontium tracing techniques could aid the development of safe, environmentally-responsible long-term storage plans for flowback water.

5. **Warner, NR, et al. "New Tracers Identify Hydraulic Fracturing Fluids and Accidental Releases from Oil and Gas Operations." *Environmental science & technology* 48.21 (2014): 12552-60. Web. Accessed June 2015.**
http://pubs.acs.org/doi/full/10.1021/es5032135

This 2014 study presents a novel approach to tracing fracturing fluid in the environment by using elemental and isotopic ratios and signatures. In particular, boron to chloride (B/Cl), lithium to chloride (Li/Cl) and the different compositions of particular isotopes ($\delta^{11}B$ and $\delta^{7}Li$) were employed to find that hydraulic fracturing flowback water in 39 samples was distinguishable from conventional produced waters. Samples from a brine treatment facility and a spill site in WV were also analyzed using these isotopic tracing techniques and found to be successful indicators by using the isotopic ratios to distinguish the fracturing flowback liquid from the surrounding water and other materials. The boron and lithium enrichment in the flowback water originates also from within the shale itself, either from the brine trapped in the shale or mobilized from the elements found on subsurface clay particles. These trends, as well as the elevated salinity and dissolved organic matter consistent with other studies, increase over time after the fracturing occurs. Further research is recommended on the relation of the isotopes to the organic matter found within the shale.

6. **Harkness, Jennifer S., et al. "Iodide, Bromide, and Ammonium in Hydraulic Fracturing and Oil and Gas Wastewaters: Environmental Implications." *Environmental science & technology* (2015) Web. Accessed June 2015**
http://sites.nicholas.duke.edu/avnervengosh/files/2011/08/es504654n_iodide-and-ammonium.pdf

This 2015 study from a prominent team of unconventional gas development impact researchers at Duke University presents new results on high concentrations of certain chemical constituents of flowback water that have not been as commonly seen in the literature- iodide (I^-) and ammonium (NH_4^+). Flowback water samples were collected from the discharged effluent of three brine treatment facilities in PA and a spill site in WV. Iodide was found at levels up to 28 mg/L and ammonium levels ranged from 12 mg/L – 106 mg/L. The presence of ammonia in particular in streams is toxic to aquatic life as it is not conducive to an oxygenated environment. Additionally, halides (iodide, bromide, chloride) have the potential to react with disinfectants like chlorine in drinking water treatment processes to form carcinogenic byproducts. Conclusions assert that flowback water is discharged into the environment from brine treatment facilities that have too limited of a restriction on total dissolved solids (TDS) outputs, and employ insufficient techniques to remove halide and ammonium concentrations. Further study into human and aquatic health impacts of these particular components of flowback water is recommended.

7. Lester, Yaal, et al. "Characterization of Hydraulic Fracturing Flowback Water in Colorado: Implications for Water Treatment." ***Science of the Total Environment*** **512 (2015): 637-44. Web. Accessed June 2015.**
http://www.researchgate.net/publication/272077832_Characterization_of_hydraulic_fracturing_flowback_water_in_Colorado_Implications_for_water_treatment

This 2015 study pertains to an analysis of flowback water in Colorado's Denver-Julesburg Basin, as opposed to in the Marcellus region of PA and WV. However, the chemical constituents found were similar to waste water in PA and WV, and proposed management and cleaning solutions are applicable regardless of hydraulic fracturing location. The total dissolved solids (TDS) concentration was found at 22,500 mg/L with chloride making up over half of that concentration, a trend comparable to Marcellus flowback water studies. Results also included a high concentration of dissolved organic carbon (DOC) at 590 mgC/L, and found within this organic matter high levels of acetic acid, an additive to the drilling fluids. Potential solutions for the management of the flowback water include recycling it for further hydraulic fracturing, reuse for crop irrigation, livestock watering etc. and a reverse osmosis desalination technique to reduce the high TDS content. General chemical composition of flowback is therefore similar in these two regions, with specific concentrations ranging more from the type of shale that is being drilled.

8. Ziemkiewicz, Paul F, et al. "Evolution of Water Chemistry during Marcellus Shale Gas Development: A Case Study in West Virginia." ***Chemosphere*** **134 (2015):224-31. Web. Accessed June 2015.**
http://www.researchgate.net/publication/276067054_Evolution_of_water_chemistry_during_Marcellus_Shale_gas_development_A_case_study_in_West_Virginia

This recent 2015 case study of water resource impacts, including flowback water from four sites in West Virginia, found results consistent with the published literature. After analyzing the organic, inorganic and radioactive constituents of flowback water, this study also concludes that the primary composition of the water comes from materials in the shale itself as opposed to the additives in the drilling fluid. Results found that the salt content was dominated by sodium (Na) and chloride (Cl), and elevated concentrations of magnesium (Mg), calcium (Ca), barium (Ba) and strontium (Sr) were also found and make up the total dissolved solids (TDS) values which ranged over time from 8,840 mg/L – 154,000 mg/L. This study also found that concentrations of the metals lead (Pb), selenium (Se), aluminum (Al), manganese (Mn), iron (Fe), and the normally occurring radioactive material radium (Ra) exceeded the EPA's maximum contaminant levels. Results also confirm that strontium and barium are excellent fingerprint signatures for flowback water specifically, whereas elevated levels of salts and TDS could be due to other contamination events from industry or from low flow events. A general recommendation for increasing the reusability and recycling of the flowback water for further drilling is made, and for further research into the best and safest ways to store this water.

Conclusion:

Since 2009, when Marcellus Shale gas development and hydraulic fracturing started in force in Pennsylvania, a large quantity of literature on potential impacts of unconventional drilling on local rivers and streams was generated. Research into what exactly made up the chemical composition of this flowback water took off. A selection of these studies are presented above and several general conclusions can be made:

i) First, very high concentrations of salts (mostly chloride and bromide) are found in flowback and this;
ii) Elevates TDS values, which is a bulk parameter that includes all dissolved inorganic materials.
iii) High concentrations of metals, particularly barium and strontium, in the water make them signature or fingerprint chemicals for tracing flowback in the environment.
iv) Concentrations of all chemicals detected in the water increase over time after drilling and with the volume of water that is produced.
v) The origin of the materials in flowback is uniquely characteristic of the zone of shale that is drilled.
vi) Newer methods and novel tracing techniques including strontium isotopes, boron and lithium ratios, and ammonium and iodide analysis have been published in the last year.
vii) Further research is prompted to determine the safest and most efficient method of treating flowback water before release back into the environment.
viii) Finally, these studies recommend recycling the flowback water for further drilling as a general practice.