

Hydraulic Fracturing Bulk Characteristics Determination and Analysis

A Research Thesis

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Abstract

The goal of this research is to begin to characterize the chemical composition of residual fracturing and flowback fluids being produced by hydraulic fracturing of Marcellus Shale in our region. During the summer of 2012, fracturing and flowback fluid samples were collected from three wells in Pennsylvania. Samples were shipped to OSU for determination of conductivity, total dissolved solids, dissolved oxygen, and pH. Further chemical analysis was conducted to determine concentrations of select anions, cations, carbon, and nitrogen species. Most analyte species increased in concentration dramatically in the days immediately following fracturing and gradually plateaued during the subsequent 82 days of flowback. Data was compared to that published in recent years and to the Ohio Environmental Protection Agency's maximum contaminant levels (MCLs) and secondary maximum contaminant levels (SMCLs). Every constituent measured for which the EPA has set an MCL or SMCL—including the actinide uranium and the trace metals strontium and arsenic—was present at concentrations significantly higher than that constituent's respective MCL or SMCL. Furthermore, total dissolved solids, barium, calcium, chloride, iron, magnesium, sodium, and strontium concentration magnitudes and trends were consistent with the limited existing data available, providing confidence that our data accurately represents the chemical characteristics of fluids produced from hydraulically fracturing Marcellus Shale. Better characterization of fracturing and flowback fluids will help shed light on appropriate treatment technologies and impacts these fluids might have if accidentally released to the environment.

Acknowledgements

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Chapter 1: Introduction

The role natural gas plays in meeting global energy demands has shifted dramatically in recent years. While this versatile, readily transportable fuel has long been used for residential and commercial heating, steam production, and thermoelectric power; increasing demands for cleaner alternative energy sources has put the spotlight on natural gas as a major means of electricity production in the coming decades [1]. By comparison, natural gas combustion produces half of the carbon dioxide emissions and lower pollutant loads (including carbon monoxide, nitrates, sulfates, and mercury) for an equivalent amount of electric power generation relative to coal—which has long remained the dominant fuel source for electricity production [ibid]. As a result, many countries are moving to rely more heavily on natural gas as a fuel source. China, for instance, has set a goal to double the portion of their total energy produced from natural gas between 2010 and 2020 [ibid].

There are three primary characteristics that make natural gas an attractive energy source in the U.S., they include: (1) a well-developed infrastructure; (2) a reliable, abundant, and easily transportable natural gas supply; and (3) a delivery system less subject to interruption compared to imported fossil fuel [1]. New technologies, including directional drilling and hydraulic fracturing, are providing the petroleum industry the capability to meet growing demands by tapping vast natural gas reserves from organic-rich shales. This has in turn made shale gas the fastest-growing source of natural gas and the largest projected contributor to growth in natural gas production in the U.S. and many other nations for the next 25 years [ibid]. Two expansive shale gas plays in our region, the Marcellus and Utica Shales, have brought hydraulic fracturing drilling operations to eastern Ohio [3]. Given the depth of published information on the environmental impacts of these new technologies, there remains public concern surrounding such

activities contaminating drinking water resources [ibid]. Public concerns stem from the management of fluids involved in the hydraulic fracturing and well completion process.

Large amounts of water are used to retrieve the natural gas of organic-rich shales, which is entrapped in pore spaces or adsorbed into the organic material and minerals of the formation rock. Shale is a sedimentary rock that is both the source and reservoir for the natural gas, which is typically about 90 percent methane but also may contain other hydrocarbons, carbon dioxide, nitrogen, and hydrogen sulfide [1]. To release the gas, rock fissures are engineered by hydraulic fracturing techniques [ibid]. The first step in this process is the drilling of a vertical borehole to the shale layer to be exploited and then gradually turning the drill bit so that the borehole is continued horizontally through the 50-300 ft thick shale layer, typically for 1,500 to more than 6,000 ft from the vertical well bore [2]. Next, an explosive gun is detonated along the horizontal borehole to perforate a protective casing in contact with the shale [ibid]. An aqueous fracturing fluid is then delivered into the borehole at a rate sufficient to raise the pressure within well above the fracture pressure of the formation rock. The stress induced by the pressure creates hairline-width fissures that connect the pore spaces to one another and to the borehole and increase shale permeability, thereby allowing gas to flow out of the shale's pores and into the well so that it can be collected [1]. Once the fracturing process is complete, fluid pumping pressure is relieved and the fracturing fluid is allowed to return to the surface so that the well can be put into production and natural gas allowed to flow out of the shale and into the well [ibid].

About 10 to 40 percent of the fracturing fluid volume returns to the surface as "flowback," a process that can take anywhere from a week to several months to complete [1]. There is growing concern about the management and disposal of flowback water, including environmental and public health impacts associated with accidental releases of flowback water

into the environment [ibid]. Options available for treatment of residual hydraulic fracturing fluids are limited by high capital and operating costs and thus the most widely used option for the management of flowback water is deep-well injection [2].

A typical fracturing procedure in the Marcellus Shale uses 7,000 to 18,000 cubic meters of fracturing fluid, or on the order of five million gallons [ibid]. Fracture fluid is a mixture of water, propping agents, and chemical modifiers (Table 1.1). Fluorocarbons, naphthalene, butanol, formaldehyde, pesticides, and numerous other chemicals that are either carcinogenic or associated with numerous health problems or environmental consequences have been reported to be added to hydrofracture fluids [5].

Not all of the chemicals added to fracturing fluids are known as specific chemical formulations of fracturing fluids are often proprietary. Moreover, these fluids are excluded from regulation by the U.S. Environmental Protection Agency's (US EPA) Resource Conservation and Recovery Act (CERCLA) and Safe Drinking Water Act. Intensified concerns by the public have prompted some companies to develop more environmentally friendly hydraulic fracturing fluid formulas. For example, some companies have reportedly stopped using certain chemicals that cause reproductive problems in animals [5]. While this may produce an optimistic outlook on current hydraulic fracturing operations, replacements for discontinued chemicals have yet to be identified.

While in the well, because hydraulic fracturing fluid is in close contact with the shale formation, minerals and organic constituents present in the formation are allowed to dissolve into the fracturing water. Thus, in addition to chemical modifiers intentionally introduced into the fracturing fluid, a variety of compounds and elements that are naturally present in deep geological formations—including a large number of organic compounds, salts, heavy metals, and

radionuclides—are inadvertently added to the fracturing water and are brought to the surface in the flowback fluid [2].

The development of treatment infrastructure currently lags far behind the fast-paced exploration and extraction of Marcellus shale gas activities [4]. Systematic and independent data on flowback water quality should be collected before or concurrent with drilling operations in a region. Such baseline data would improve environmental safety, scientific knowledge, and public confidence and could clarify the existence and extent of problems and help identify the mechanisms behind them [ibid]. Understanding the bulk characteristics of fluids used to hydraulically fracture the Marcellus Shale is key to developing effective policies governing hydraulic fracturing (e.g. mandates for requiring surveyance of residual radioactivity before it is allowed to leave the well site, etc.), adequately reviewing the thousands of current and future permit applications, extracting natural gas in an environmentally sound manner, knowing the implications of groundwater contamination with hydraulic fracturing residuals, and effectively treating and/or disposing of spent fracturing fluids.

The goal of this research is to characterize the chemical composition of residual fracturing and flowback fluids being produced by hydraulic fracturing Marcellus Shale in our region and which are being disposed of by deep well injection in Ohio. This research project is only a very small chunk of a much larger-scale nationwide study the Department of Energy is conducting on the safety of hydraulic fracturing. The constituents that were investigated include basic water quality parameters, major cations, bulk organic content, total organic carbon, ammonium, and various anions. This fluid characterization allows for recommendations regarding potential risks, environmental impacts, health hazards, disposal methods, and directions for further research regarding residual hydraulic fracturing fluids to be made.

**Table 1.1: Typical Chemical Modifiers Added to Hydrofracture Fluids
(Data compiled from sources 1, 4, and 5)**

Constituent	Purpose	Example
Acid	Removes drilling mud near the wellbore and initiates cracks in the rock.	Hydrochloric or muriatic acid
Biocide	Inhibits growth of organisms that could produce gases (e.g. hydrogen sulfide) that could contaminate the methane gas.	Gluteraldehyde; 2-Bromo-2-nitro-1,2-propanediol
Breaker	Reduces hydrofracture fluid viscosity in order to release propping agent into fractures and enhance recovery of the hydrofracture fluid.	Peroxydisulfates
Buffer / pH-Adjusting Agent	Controls the pH of the solution in order to maximize the effectiveness of other additives.	Sodium or potassium carbonate; acetic acid
Clay Stabilizer / Control	Prevents swelling and migration of formation clays which could block pore spaces and reduce shale permeability.	Salts (e.g., tetramethyl ammonium chloride)
Corrosion Inhibitor	Reduces rust formation on wellbore steel pipe casing	Methanol; n,n-dimethyl formamide
Friction Reducer	Allows hydrofracture fluid to be injected at higher rates and pressures by minimizing friction between the fluid and the wellbore pipe casing.	Sodium acrylate-acrylamide copolymer; polyacrylamide (PAM); petroleum distillates
Gelling Agent	Increases hydrofracture fluid viscosity, allowing the fluid to carry more propping agent into the fractures.	Guar gum; petroleum distillate
Iron Control	Prevents the precipitation of carbonates and sulfates (calcium carbonate, calcium sulfate, barium sulfate) which could reduce shale permeability.	Ammonium chloride; ethylene glycol; polyacrylate; citric acid
Propping Agent	Lodges in fractures to ensure that they remain open when pressure is relieved.	Sand (sintered bauxite; zirconium oxide; ceramic beads)
Scale Inhibitor	Controls the precipitation of carbonates and sulfates in wellbore pipe casing and shale fractures.	Ethylene glycol
Solvent	Used to increase the solubility of contact surfaces or to prevent break emulsions.	Various aromatic hydrocarbons
Surfactant	Reduces interfacial tension between the fluid and formation materials, thereby aiding fluid recovery.	Methanol; isopropanol; ethoxylated alcohol

Chapter 2: Site Information

Three wells fractured on June 4, 2012 in the Marcellus Shale region using hydraulic fracturing techniques were sampled between June 4 and August 25, 2012 by personnel from the Department of Energy's National Energy Technology Laboratory (Pittsburgh, PA) from a site located in Carmichaels, Greene County, Pennsylvania (Figure 2.1). The privately operated site is comprised of one well pad with three communicating, horizontally fractured wells. All three wells were successively fractured with a mixture of recycled and freshwater-derived fracking fluid within 23 hours of each other (Table 2.1). The samples taken included the raw fracturing fluid and flowback fluid from the 82 days following the fracturing process during which time fracturing fluid flowed back up the borehole.

Table 2.1: Individual Well Details [9]

Well Name and Number	Relative Order of Fracturing	Vertical Depth of Well (feet)	Volume of Fluid Used to Fracture (gal)	Days of Flowback	Borehole Longitude	Borehole Latitude
Mohr A #3MH	1	8,250	3,156,426	7	-80.055719	39.869428
Mohr A #2MH	2	8,300	4,223,563	82	-80.055750	39.869461
Mohr A #1MH	3	8,220	8,446,621	82	-80.055781	39.869490



Figure 2.1: Aerial photograph of well pad in Charmichaels, PA from which samples were received.

Chapter 3: Experimental Methodology

3.1: Sample Processing

Samples were shipped overnight and arrived in sterile 500 mL or 1 L Nalgene bottles filled to capacity and stored on ice. The samples were logged upon receipt, stored at 4°C, and processed within 24 hours. A visual inspection was made and the fluids were noted as viscous and in varying shades of yellow. Color intensity ranged from clear to opaque, pale to dark yellow, and with the exception of small fractions of green, brown, or black sand, contained no solids. 300 mL of each sample was passed through a 1.2 µm glass fiber filter using a sterile vacuum apparatus to remove organic matter and large particles that could clog and damage sensitive instrumentation and then preserved.

3.2: Water Quality Parameter Testing

Conductivity, DO, and pH probes were cleaned using instruction booklets included with the instrumentation, rinsed with Millipore water, and calibrated with new standard solutions. The probes were then used to measure conductivity, total dissolved solids, dissolved oxygen, and pH on the raw, unprocessed fluids. Alkalinity was measured on the raw samples using a Hach alkalinity test kit. To ensure accuracy of the Hach test, the test kit was performed on a standard made by dissolving 529.1 mg Na_2CO_3 in 1 L Millipore water to make a solution equivalent of 499.64 (~500) mg/L calcium carbonate. The standard was serially diluted several times and the test was repeated to ensure accuracy on the entire range of alkalinity concentrations measured on fracturing and flowback samples.

3.3: Analytical Measurements

Analytical techniques used to characterize fracturing and flowback fluids are summarized in table 3.1 below.

Table 3.1: Analytical Techniques Used

Method	Analytes Measured
Conductivity probe	Conductivity and TDS
DO probe	Dissolved oxygen
pH probe	pH
Hach alkalinity test kit	Alkalinity
Colorimetry using phenol-hypochlorite with nitroprusside catalyst	Ammonium
Total carbon analyzer	Dissolved carbon and dissolved organic carbon
Total nitrogen measuring unit	Total nitrogen
Multi-parameter colorimeter configurator	Total phosphorus
Ion chromatography	Cl, Br, NO ₂ , NO ₃ , SO ₄
Inductively coupled plasma atomic emission spectrophotometry	Al, As, Ba, Ca, Fe, K, Mg, Na, S, Si, Sr, U

Ammonium was measured on the processed samples that had been further filtered using a Fast Flow & Low Binding Millipore 0.22 μm filter unit (Millex, Inc.). Ammonium was measured colorimetrically using phenol-hypochlorite with nitroprusside catalyst and comparing the results to a standard curve. A standard ammonium solution was made by dissolving 1.3374 g ammonium chloride in 500 mL Millipore water and then diluted with 99 mL Millipore water for every 1 mL standard solution to make a stock solution of 500 μM ammonium. 0.3750 g sodium nitroprusside was dissolved in 500 mL Millipore water and stored in a glass bottle wrapped in aluminum foil to prevent the introduction of light to the solution and stored at 4°C. This solution was stable for up to one month and then discarded and a new nitroprusside solution was made. A

phenol solution was made by dissolving 4 g of 99% pure phenol that was melted to a volume of 3.78 mL and dissolved in 500 mL Millipore water and stored in a glass jar in the fume hood. The test was run several times on samples that were serially diluted over a small range of concentrations, with each subsequent test performed using a set of dilutions beyond the previous test until test results fell within the range of the standard curve. Each time the test was performed, a citrate reagent was prepared immediately before use by dissolving 7.5 g trisodium citrate and 0.4010 g sodium hydroxide into 500 mL Millipore water. In 2 mL eppendorf tubes, 0.5 mL of diluted sample, blank, or standard was added to the tube followed by 0.25 mL phenol solution, 0.25 mL nitroprusside solution, and 0.5 mL citrate/hypochlorite mixture. These tubes were covered in foil and placed in a cabinet with the door closed to let sit in the dark for one hour and then read on the spectrophotometer at 630 nm. The results were compared to a standard curve that was created using a blank and ammonium standards serially diluted to 25, 50, 100, 150, 200, 250 and 350 μM . After 5 test runs, it was finally determined that a 1:25 dilution produced results that fell within the range of the standard curve for every sample measured.

Dissolved carbon and dissolved organic carbon were measured on processed samples using a TOC-V CSN total carbon analyzer (Shimadzu, Inc.). Total nitrogen was measured on a TNM-1 total nitrogen analyzer (Shimadzu, Inc.). Total phosphorus was measured on the processed samples using method 8190 on a DR-800 Multi-parameter Colorimeter Configurator and compared to a standard that was made by dissolving 1.4329 mg potassium phosphate monobasic (KH_2PO_4) into 500 mL Millipore water to make a solution of 2 mg/L PO_4^{-3} .

A literature review was conducted to determine other constituents expected to be present in detectable concentrations and their expected concentration ranges. A standard solution of the anions Cl^- , Br^- , NO_2^- , NO_3^- , and SO_4^{-2} was made and those constituents were subsequently

measured on an ICS-2100 ion chromatography system (Dionex, Inc.) and that standard solution on samples that had further been filtered using a 0.22 μm filter unit (Millex, Inc.). A second standard solution was made for the cations Al^{+3} , As^{+3} , Ba^{+2} , Ca^{+2} , $\text{Fe}^{+2/+3}$, K^{+1} , Mg^{+2} , Na^{+1} , $\text{S}^{+4/+6}$, Si^{+2} , Sr^{+2} , and $\text{U}^{+6/+5/+4/+3}$ and was used to measure the samples using a Vista AX CCD Simultaneous ICP-AES inductively coupled plasma atomic emission spectrometer (Varian, Inc.) on samples that had been filtered using a 0.22 μm filter (Millex, Inc.) and then mixed with 5% nitric acid. All ion species were summed for each sample and compared to that sample's measured TDS to determine whether or not species present in significant concentrations had been omitted from analysis. For reference purposes, flowback samples were compared with Chapman et al. (2012) and Barbot et al. (2013) [10, 11].

Results were also compared to *Geohydrology and Water Quality in Northern Portage County, Ohio, In Relation to Deep-Well Brine Injection*, a 1991 Water-Resources Investigative Report by Sandra M. Eberts of the U.S. Geological Survey [12]. Data was obtained on the wells studied in Eberts' report by visiting the Ohio Department of Natural Resources and communicating with them via email thereafter to continue to gather additional data.

3.4: Trend Analysis

For reference purposes, flowback samples were compared with Chapman et al. (2012) and Barbot et al. (2013) [10, 11]. Temporal concentrations distributions were constructed of major analytes of interest. Plots of analyte average concentration values and respective ranges were constructed to graphically compare each well to each other, the EPA's MCLs and SMCLs, and to the published data. Single factor ANOVA tests were completed for select species to determine statistical variance between wells. Concentration plots were constructed comparing two analytes of interest to gauge analytes' concentration interdependencies on each other.

Chapter 4: Results and Discussion

A summary of the results of this study are tabulated below. Dissolved oxygen measurements are omitted from analysis because they were taken well after sampling had taken place. It is important to note that every constituent for which the United States EPA has set an MCL or SMCL is present in concentrations far in excess of its respective MCLs or SMCL with the exception of nitrate and nitrite, both of which were below the detection limit.

Table 4.1: Data Summary and Comparison to US EPA’s MCLs and SMCLs

Constituent	Flowback Fluid Concentration Range (mg/L)	Mean Flowback Fluid Concentration (mg/L)	Detection Limit (mg/L)	MCL or SMCL (mg/L) [13]
Al	UD-8.5	2.05	0.01	—
As	UD-2.2	0.80	0.01	0.01
Ba	270-15,500	1,979	20	2
Br	125-939	511	100	—
Ca	500-12,200	4,818	2	—
Cl	14,740-92,020	48,588	2,000	250
Fe	UD-73.6	16.9	0.2	0.3
K	52-516	222	1	—
Mg	44-1,188	473	1	—
Na	96-30,500	10,631	1	20 ¹

¹ A non-enforceable health based value of 20 mg/L Na is recommended for individuals on a sodium restricted diet [13].

P	1.1-8.8	3.47	0.01	—
S	1-1,155	82.8	0.5	—
Si	1-1,016	109	1	—
Sr	411-2,368	1,111	20	4 ²
U	UD-9.4	5	1	0.03
NO ₂	UD	UD	100	1
NO ₃	UD	UD	100	10
NH ₄	72-154	104	25	30
SO ₄	3-7,057	1,083	10	250
TDS	25,600-155,380	79,324	—	500
TC	100-562	228	50	—
TOC	65-562	173	50	—
TN	76-149	98	50	—
Alkalinity ³	140-440	309	20	—
Conductivity	41.1-176.4 mS/cm	111	—	—
pH	5.95-7.10	6.40	—	<7.0 or >10.5

² A non-enforceable health advisory level of 4 mg/L Sr has been implemented for drinking water [13].

³ Alkalinity units are in mg/L CaCO₃.

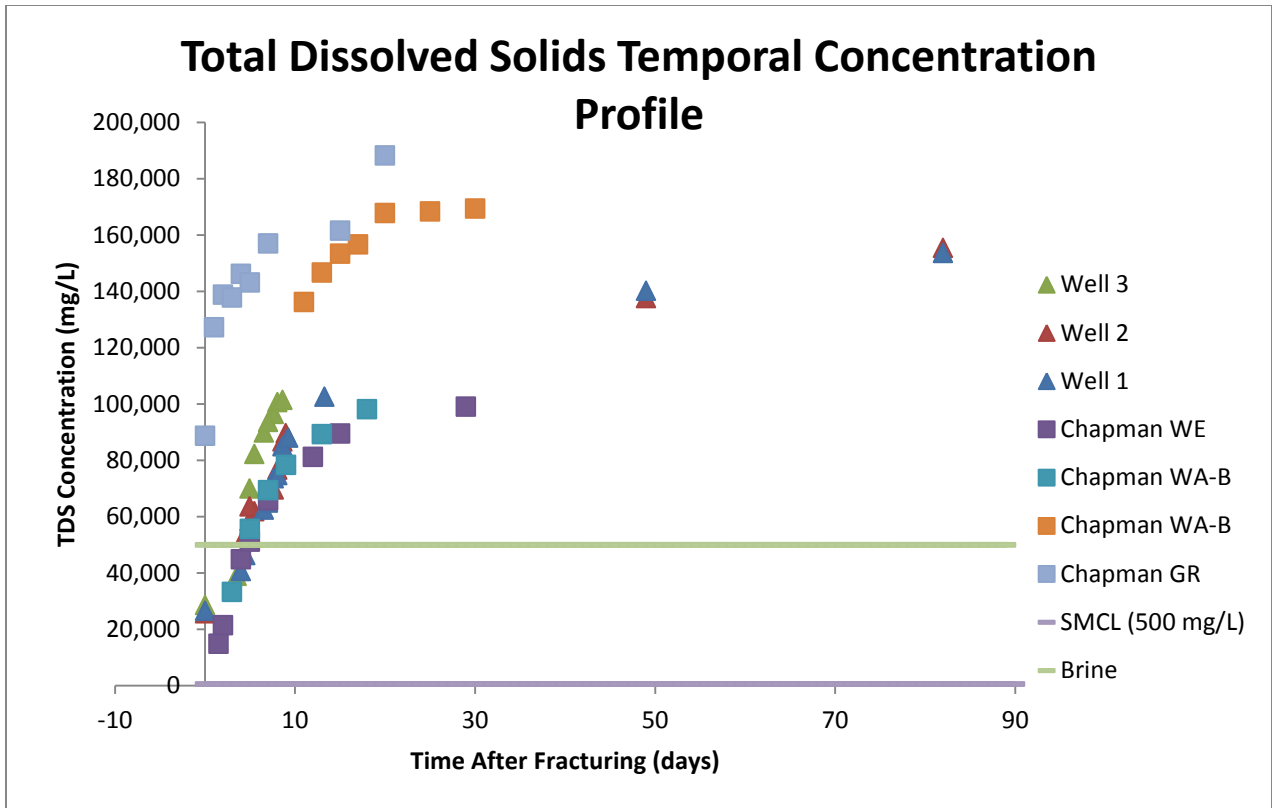


Figure 4.1: Total Dissolved Solids Temporal Concentration Profile

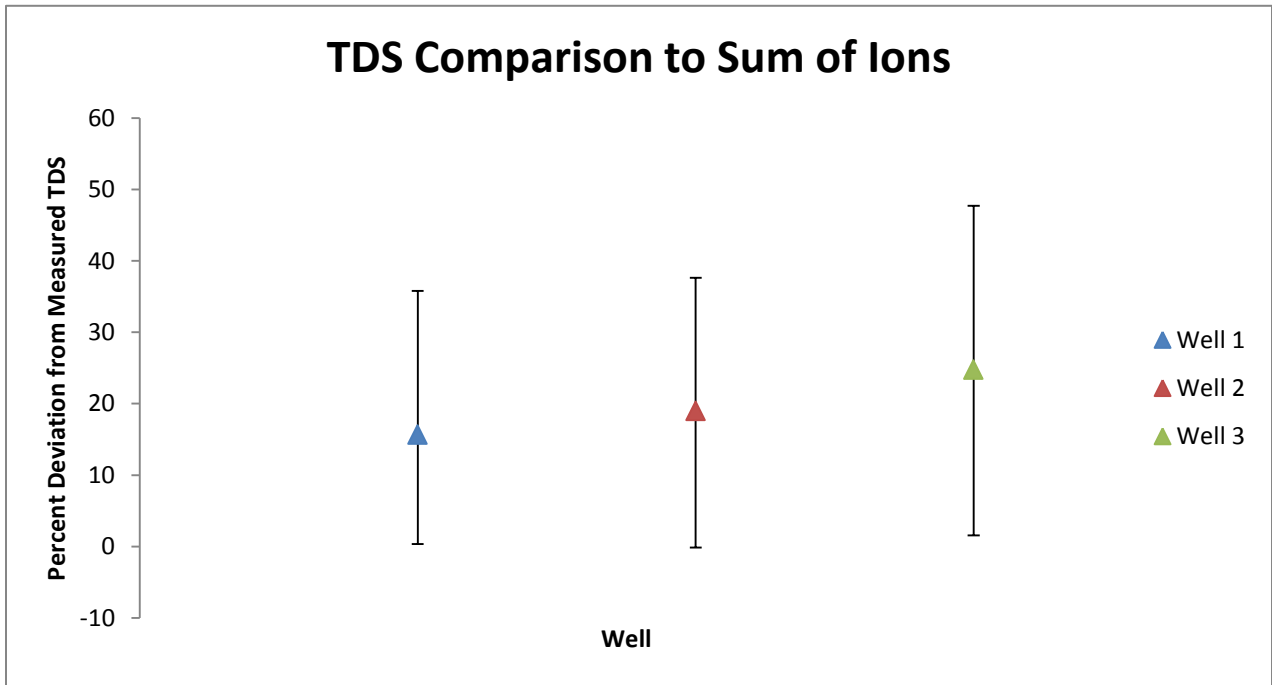


Figure 4.2: Total Dissolved Solids Comparison to Sum of Ions

The total dissolved solids of each well increased substantially the longer the fluid remained in the well, indicating the dissolution of minerals naturally present in the formation rock into the fluid. The dissolution of minerals in such large amounts resulted in brine waters with TDS concentrations as high as 155,380 mg/L. The typical TDS range of raw wastewater that is treated at municipal wastewater treatment plants across the country is between 250 and 850 mg/L [14]. Even the sample with the lowest TDS measured—25,600 mg/L—is far in excess of typical wastewater. This demonstrates the difficulty surrounding the disposal of residual hydraulic fracturing fluids as most wastewater treatment plants simply aren't designed to treat waters as concentrated in pollutants as is found in the samples measured in this study. Furthermore, all three wells follow the same trend of increasing in concentration very rapidly at first and gradually leveling out—a trend followed by all four wells studied by Chapman et al. (2012) and the three studied by Barbot et al. (2013). Lastly, our data has virtually the same TDS concentration ranges as four of the seven wells from those studies.

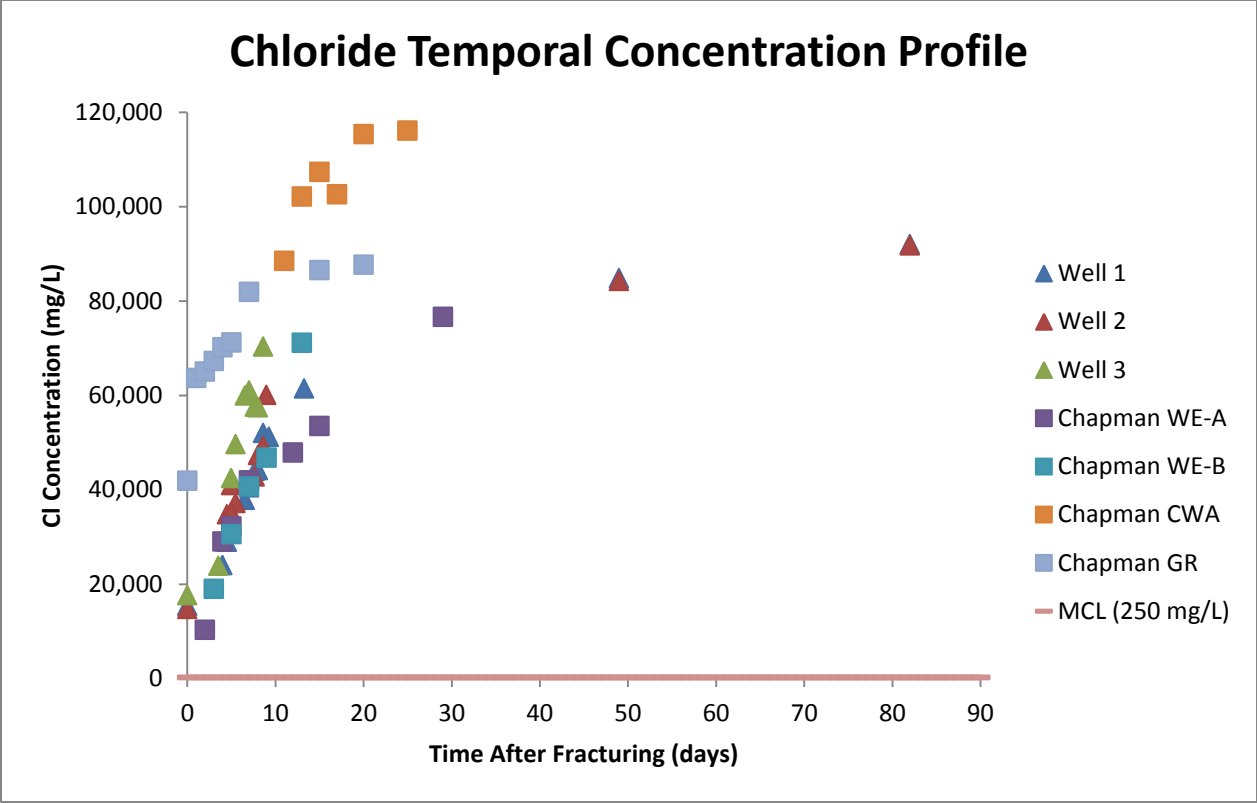


Figure 4.3: Chloride Temporal Concentration Profile

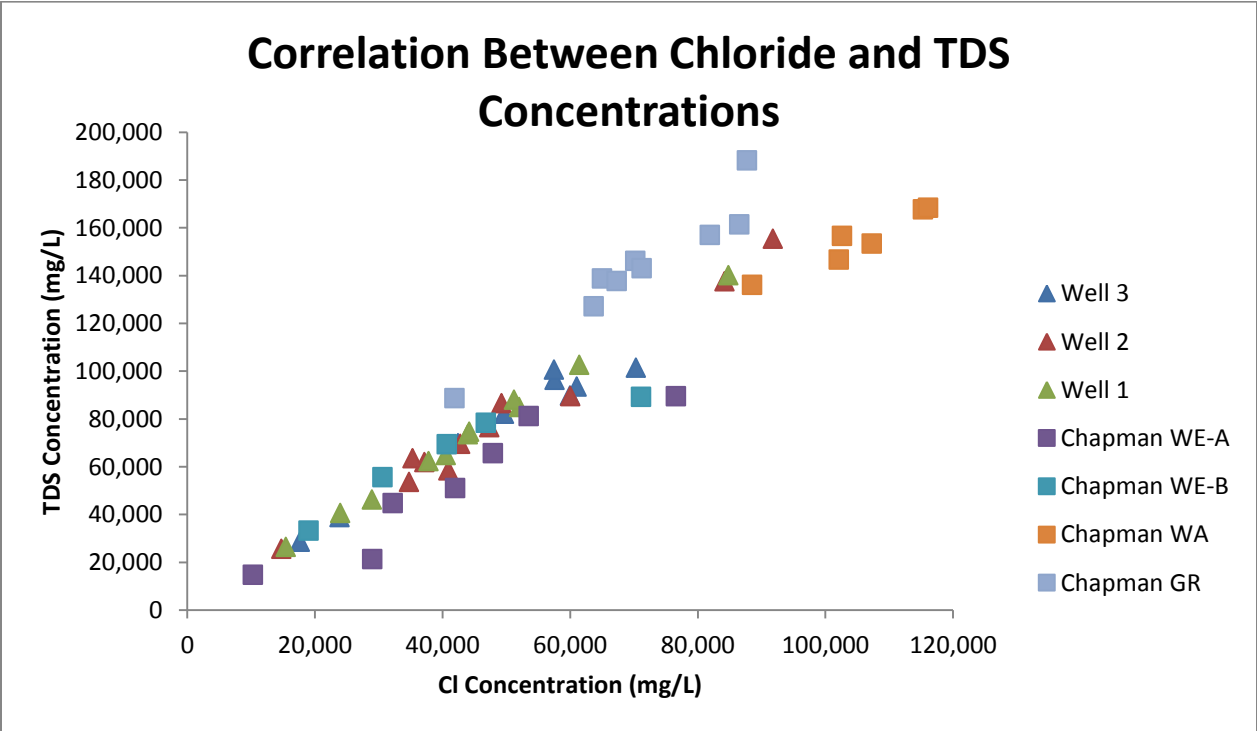


Figure 4.4: Correlation Between Chloride and TDS Concentrations

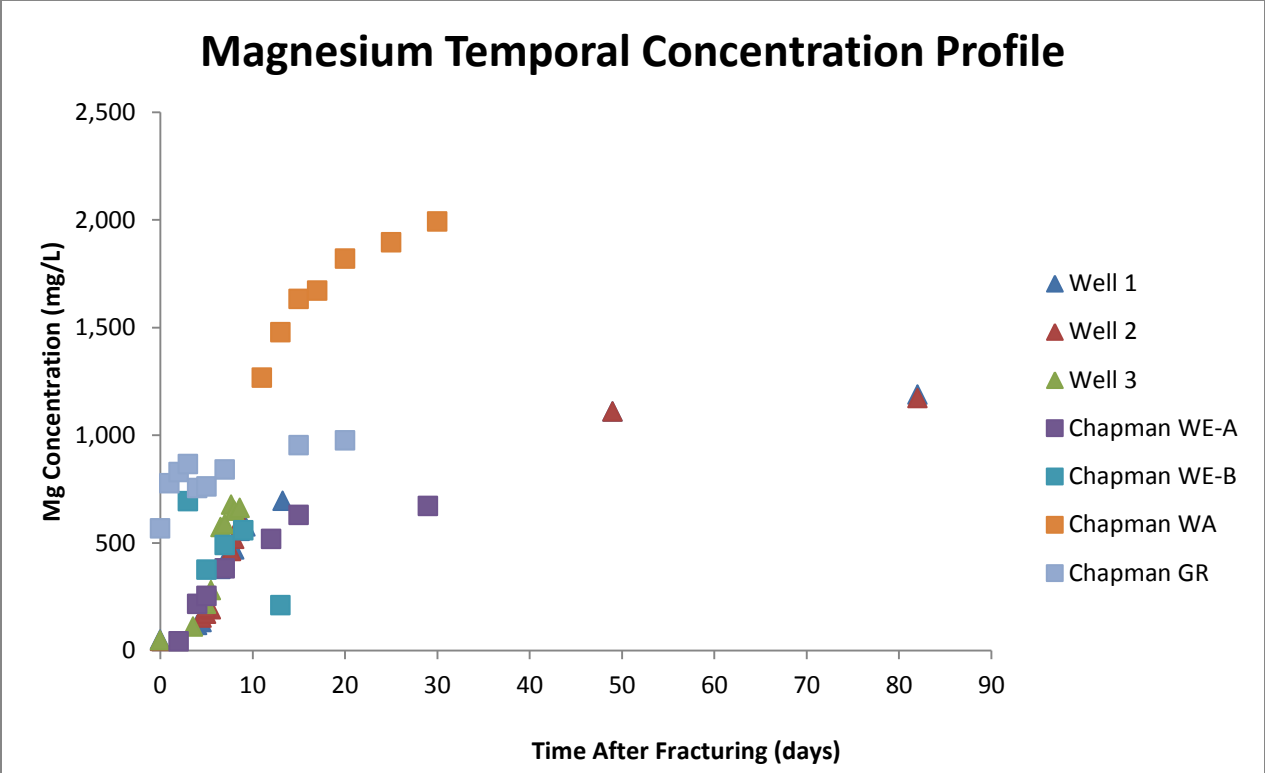


Figure 4.6: Magnesium Temporal Concentration Profile

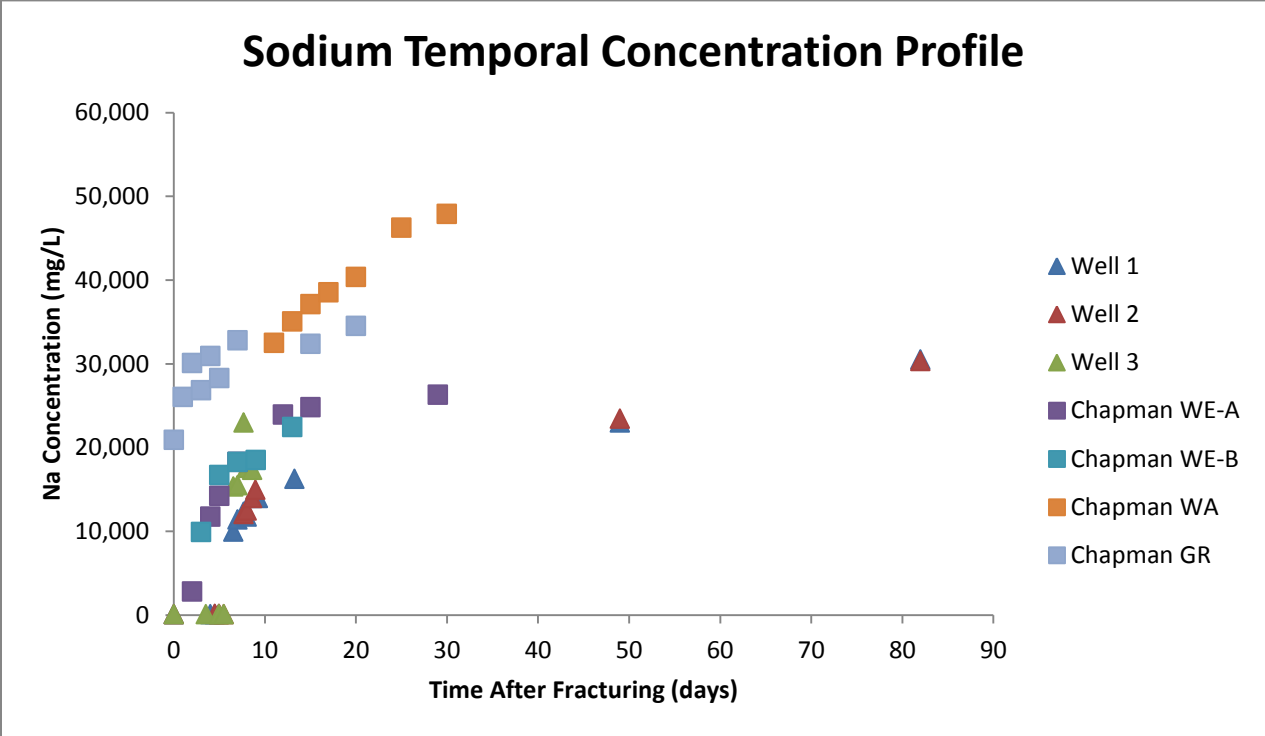


Figure 4.7: Sodium Temporal Concentration Profile

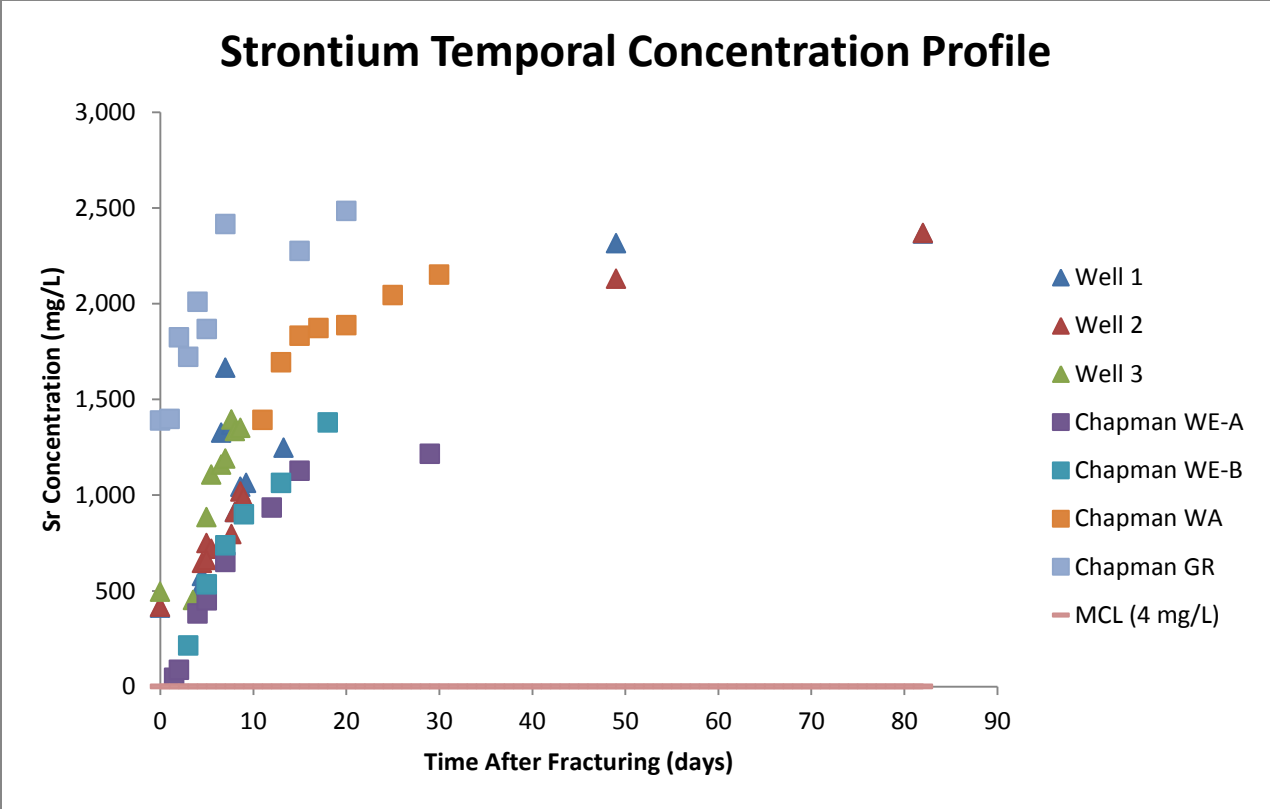


Figure 4.8: Strontium Temporal Concentration Profile

The cation salts calcium, magnesium, sodium, and strontium all had very similar trends. Like TDS and chloride, they increase very rapidly at first and eventually level off as the fracturing water remained in the well over several months. Moreover, all four elements fall within the concentration ranges of the data tabulated in Chapman et al. (2012) and Barbot et al. (2013). At up to almost 600 times the MCL, strontium is present in many of the samples in extremely high concentrations that could be cause for concern if the fluids are not properly treated of isolated.

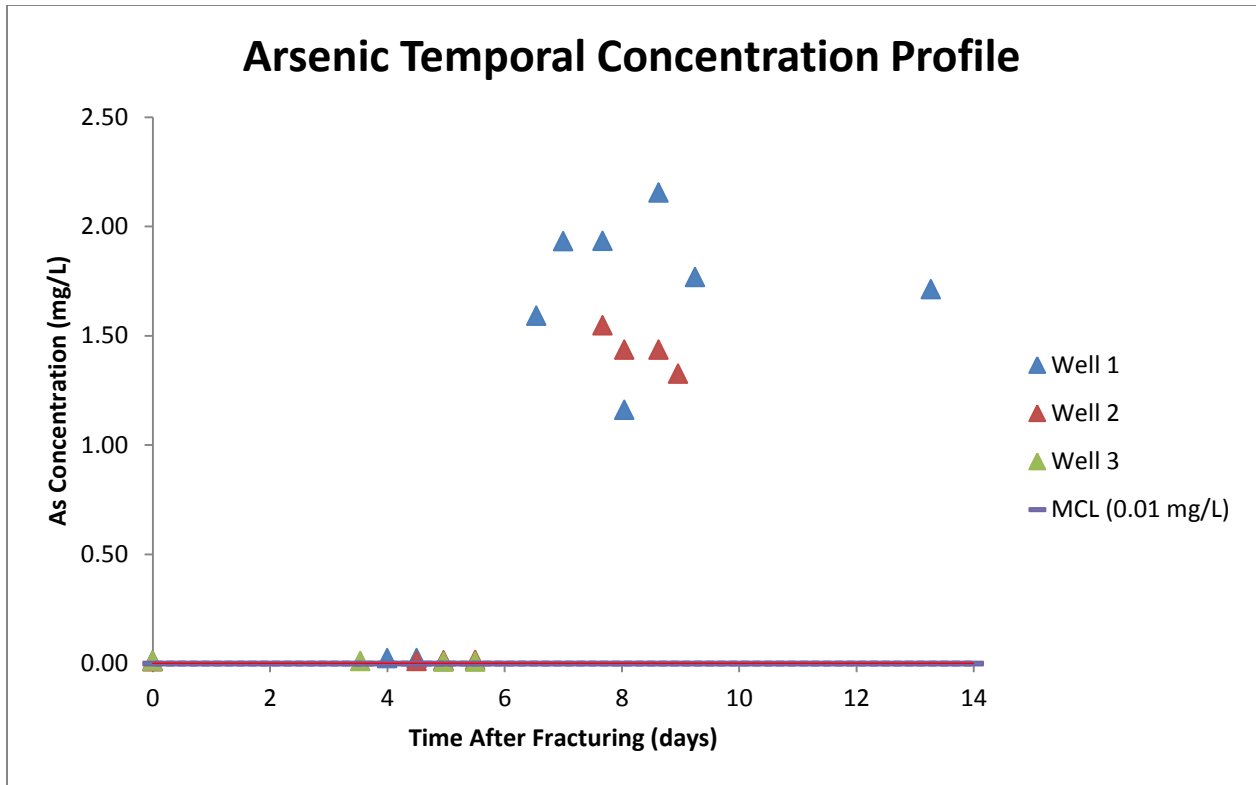


Figure 4.9: Arsenic Temporal Concentration Profile

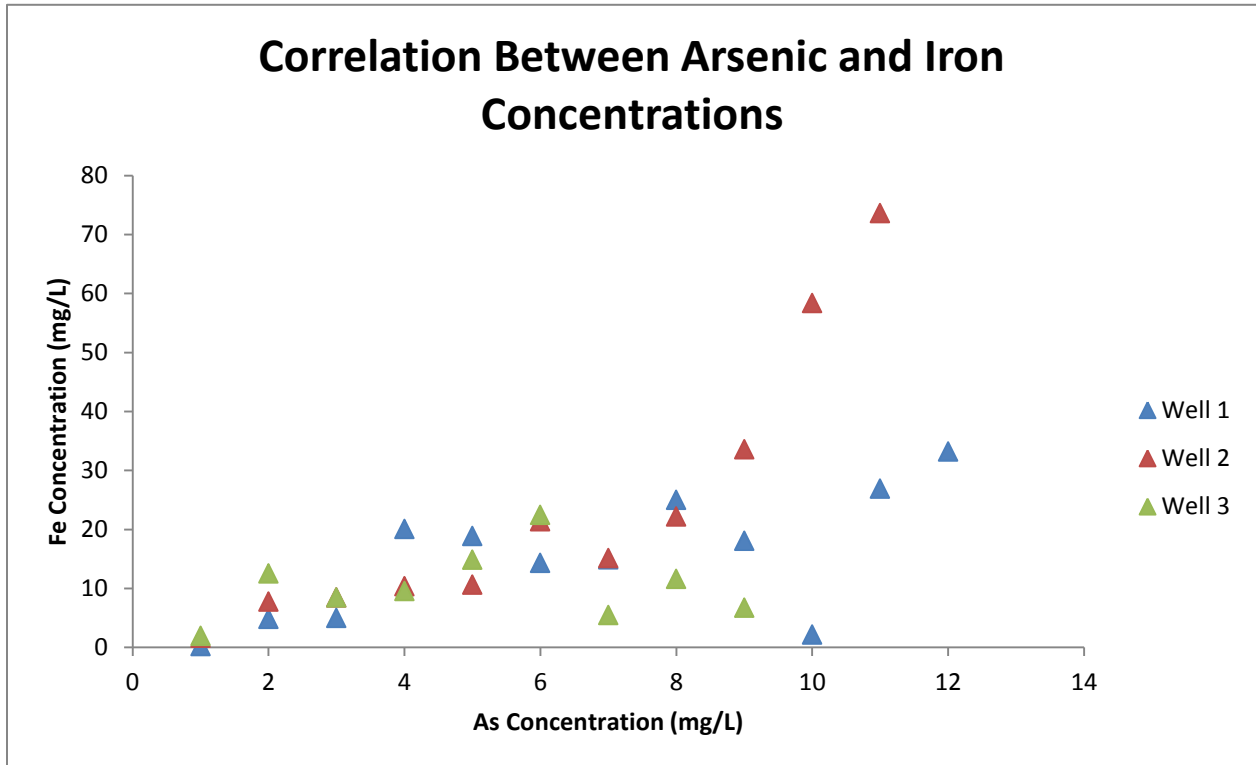


Figure 4.10: Correlation Between Arsenic and Iron Concentrations

A strong trend of the arsenic concentration of the three wells is difficult to establish. Samples taken both within the first few days of flowback and after several months fell below our detection limit of 0.01 mg/L, while peak concentrations of up to 2.15 mg/L occurred during the second week of flowback. In aqueous environment the inorganic arsenic species arsenite (As(III)) and arsenate (As(V)) are the most abundant species, but the mobility of these species is influenced by a complex interaction of factors including the pH of the water, the redox potential, and the presence of adsorbents such as oxides and hydroxides of Fe(III) (refer to Figure 4.10), Al(III), Mn(III/IV), humic substances, and clay minerals [15]. However, as many arsenic compounds are toxic and cause acute and chronic poisoning and because concentrations in flowback samples reached up to 2.15 mg/L, the dissolution of arsenic into residual hydraulic fracturing fluids could be cause for concern if these fluids are not either properly treated or isolated from communities and ecosystems.

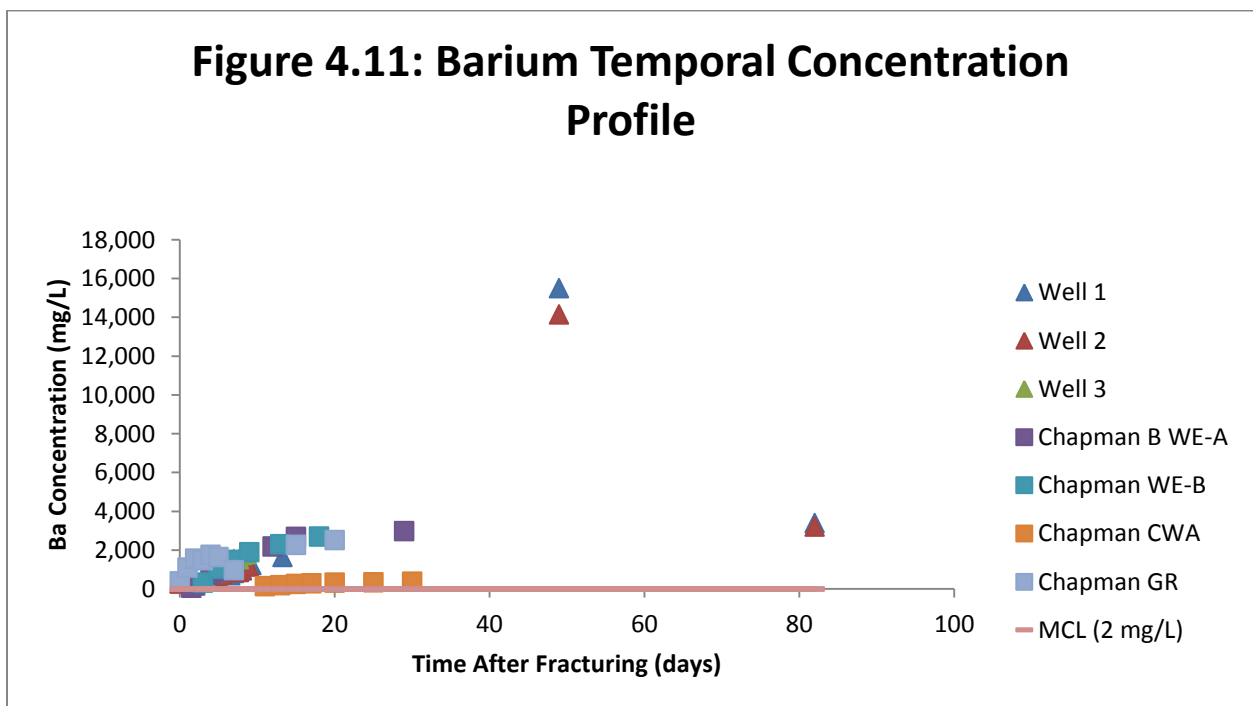


Figure 4.11: Barium Temporal Concentration Profile

Barium exhibited a trend of increasing in concentration the longer the fluids remained in the well. The concentrations present in samples studied are almost exactly on par with those of Chapman et al. (2012)'s study with the exception of the samples from wells 1 and 2 taken on day 49 of flowback, leading to suspicions that those samples are possible outliers and may have either been contaminated or encountered an error during ICP measurement. This is even more apparent by considering figure 4.9 below and noticing that, if omitted, the maximum concentration of wells 1 and 2 would be about 3,300 mg/L and within the range of Chapman et al. (2012)'s data rather than almost 16,000 mg/L maximum they reach because of the data points on day 49 of flowback. Furthermore, the mean value of wells 1 and 2 would be 1,107 and 1,058 mg/L, respectively, versus means of 278-1,630 mg/L for Chapman et al. (2012)'s data. The two data points of interest lay within the range of Barbot's data, however, and may very well be legitimate representations of the barium concentration in the wells' flowback water at that time.

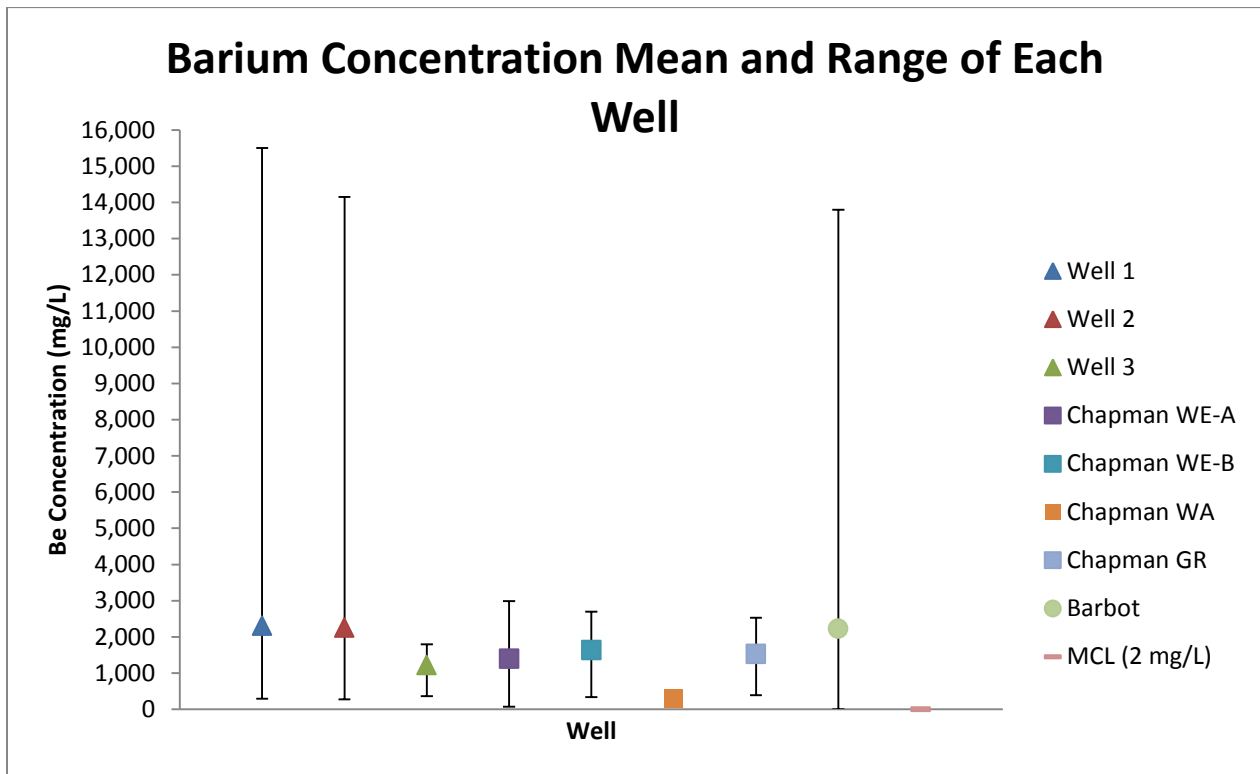


Figure 4.12: Barium Concentration Mean and Range of Each Well

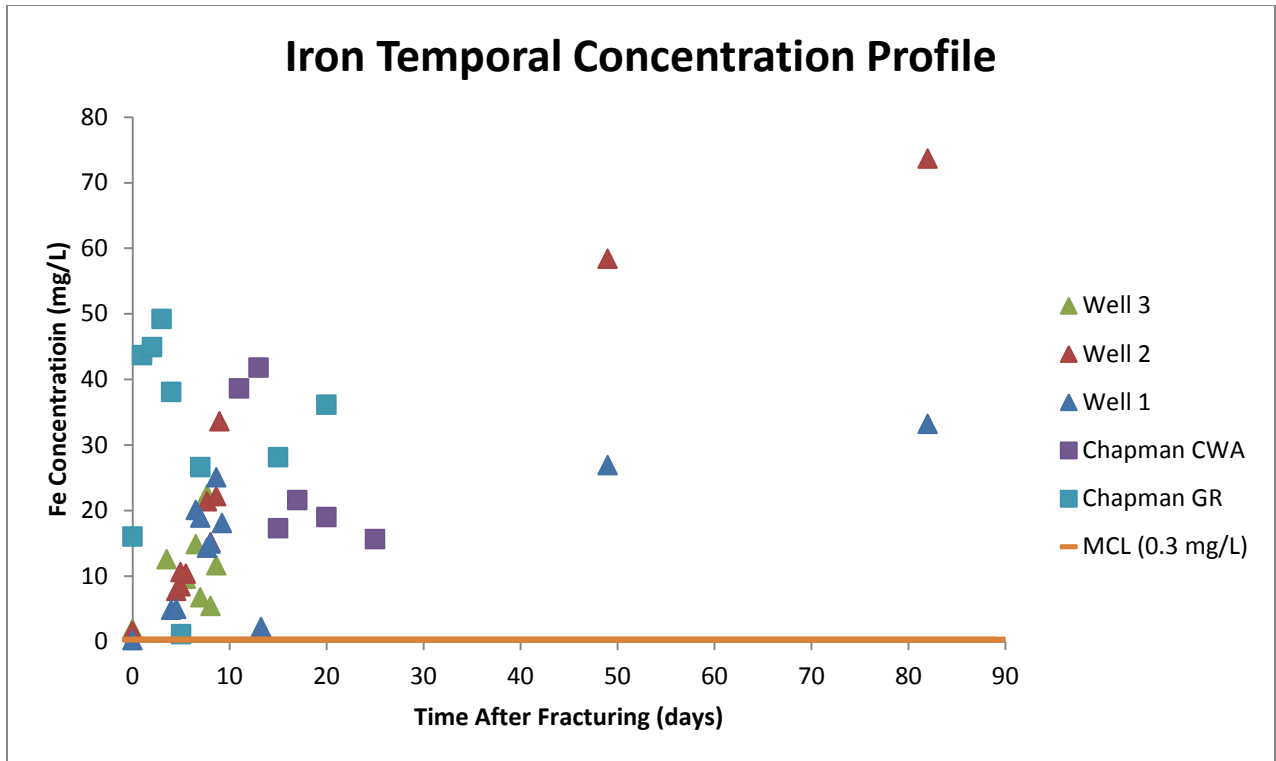


Figure 4.13: Iron Temporal Concentration Profile

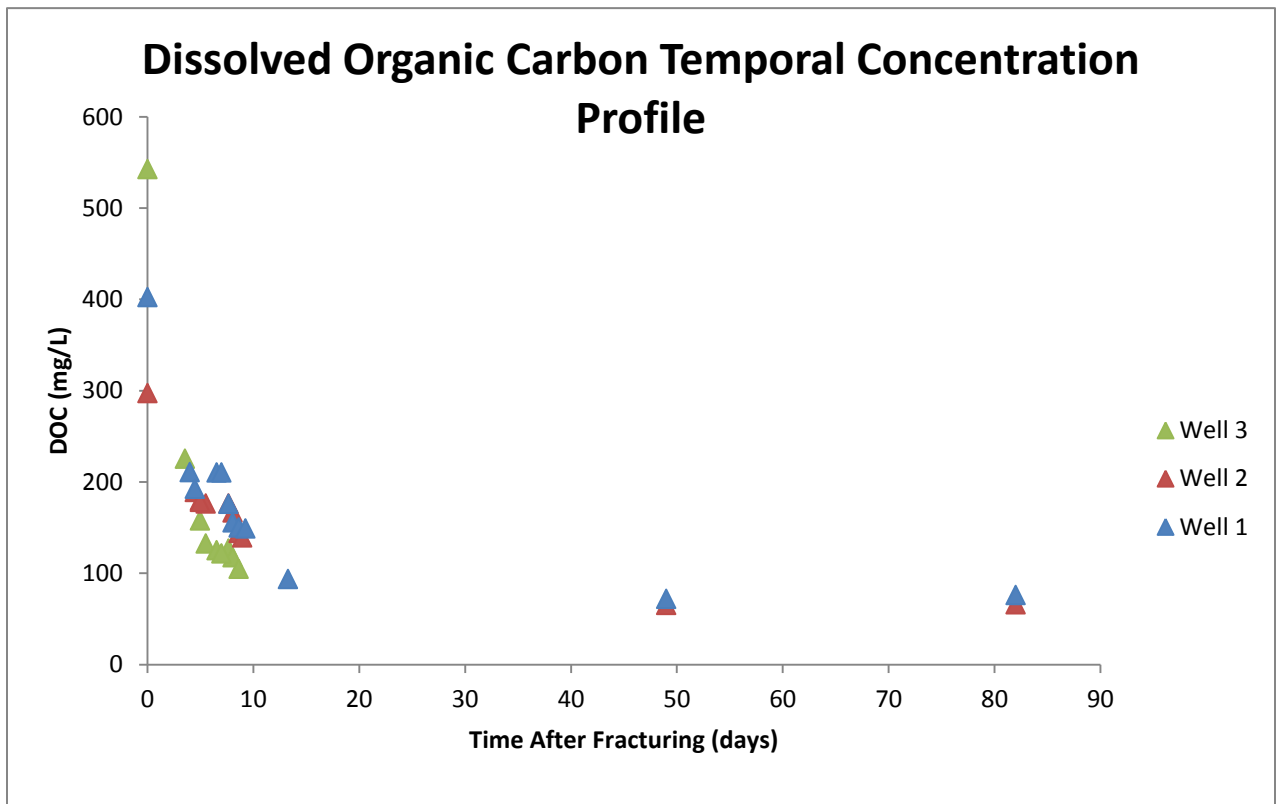


Figure 4.14: Dissolved Organic Carbon Temporal Concentration Profile

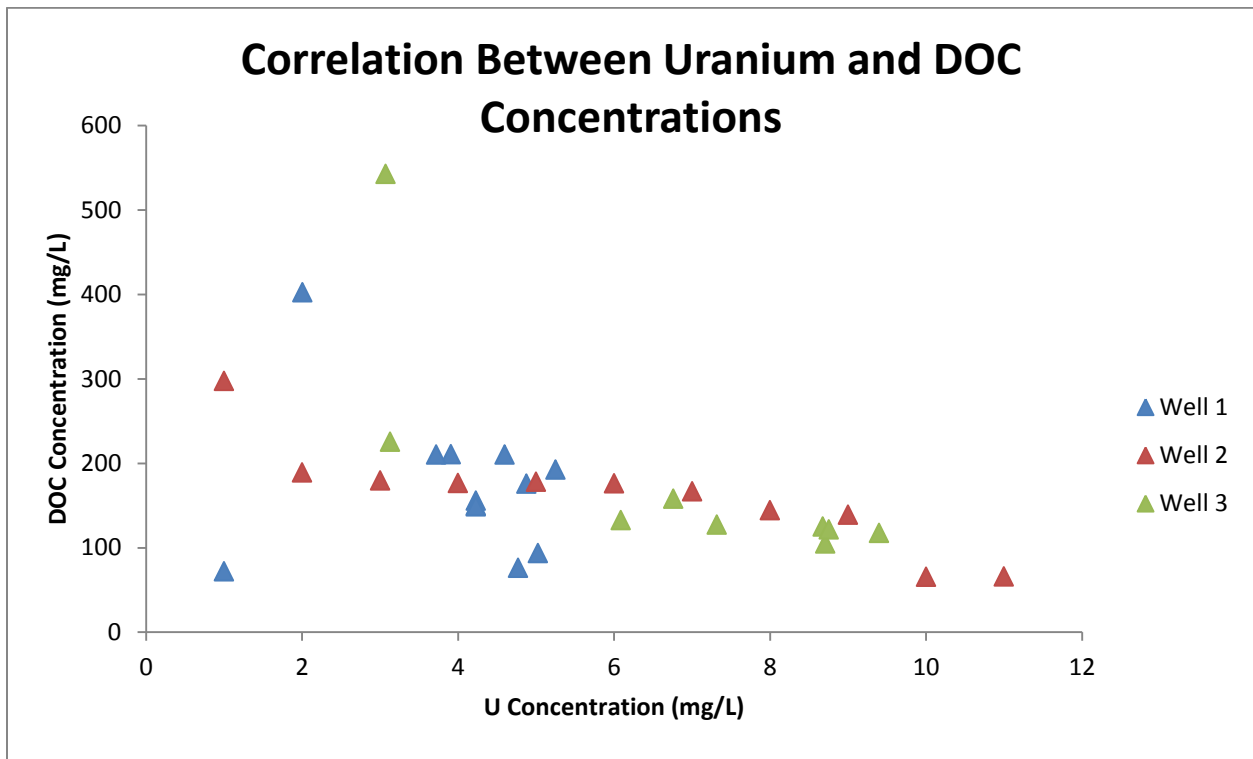


Figure 4.15: Correlation Between Uranium and DOC Concentrations

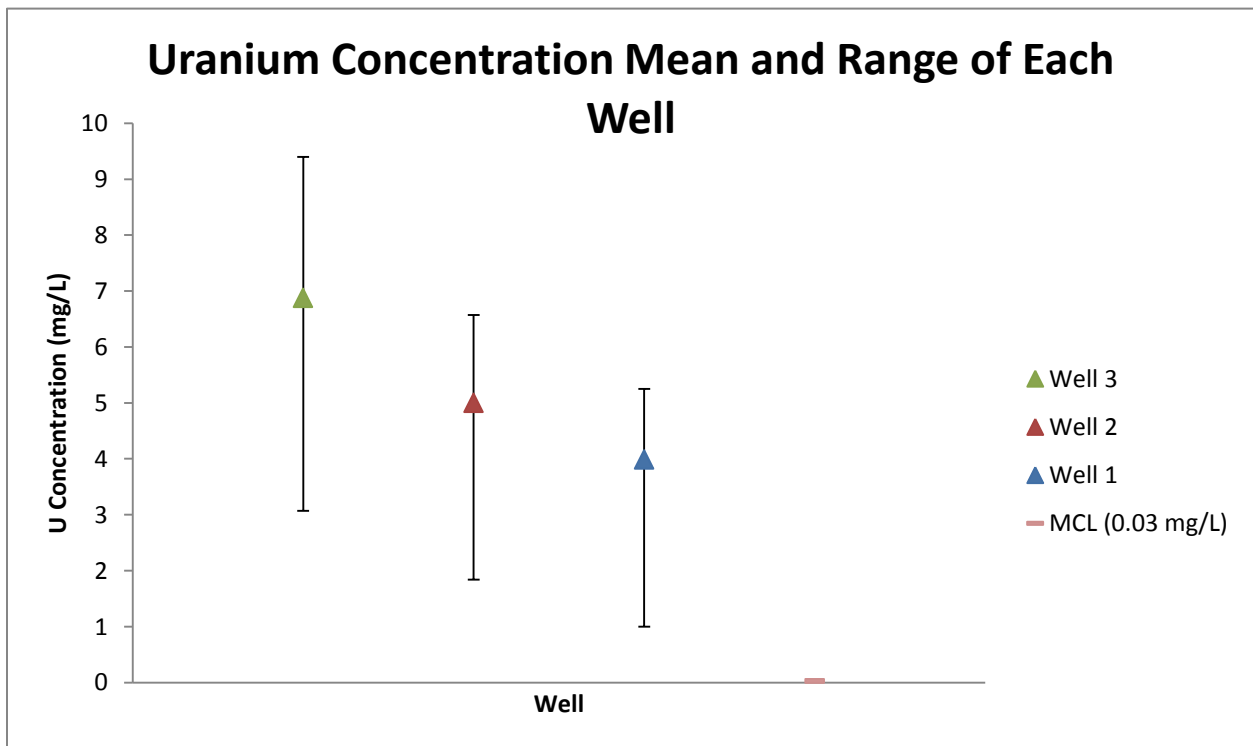


Figure 4.16: Uranium Concentration Mean and Range of Each Well

There is an abrupt initial spike in uranium concentrations from the raw fracturing water through the first several days of flowback, suggesting that, like many other elements studied, uranium naturally present in the formation rock is dissolving into the fracturing fluids. Furthermore, it has been shown that Devonian-age shales, such as the Marcellus Shale from which these flowback waters were produced, contain naturally occurring radioactive metals such as uranium [5]; and in fact, Ohio Devonian Shale contains uranium concentrations of between 10 and 40 ppm [16]. Interestingly, uranium concentrations in the flowback water decrease with each subsequently fractured well, even while recycled flowback waters from the preceding fractured well were used to fracture the wells 1 and 2. This trend, coupled with the fact that iron concentrations increase with each subsequently fractured well, suggests that enzymatic U(VI) reduction in the subsurface is possible, which reduces soluble U(VI) to insoluble U(IV) nanoparticles known as uraninite and concurrently reduces insoluble Fe(III) to soluble Fe(II). It was demonstrated by Anderson et al. (2003) that U(VI)-reducing microorganisms have the potential to immobilize uranium in situ, which is exactly what we see here [17]. This gradual decrease of soluble uranium concentrations is not the result of a pH change as the pH of waters produced from each well followed no particular trend and fluctuated relatively sporadically. The uranium and iron trends are coincident to a gradual reduction in dissolved organic carbon in each well, suggesting the utilization of organic carbon as an electron donor and hence, food source for the microbial populations inhabiting the wells.

While uraninite can still be mobile in subsurface waters and thus could still pose health and environmental risks, this is not of significant concern as U(IV) products of microbial U(VI) reduction aggregate into larger U(IV) precipitates which are highly insoluble and which cannot pass through filter media in the event that these fluids were ever to be treated rather than

disposed of by well injection [17]. Thus, even if the initial products of U(VI) reduction are tiny hazardous uraninite crystals, processes such as agglomeration and/or adsorption onto sediments remove them from the flowback water and allow them to remain deep in the formation rock [ibid]. Thus, results of the study show that, while hydraulic fracturing does generate the potential to release toxic soluble uranium from the formation rock into the flowback water, abiotic or biotically mediated reduction processes might subsequently remove it during later stages of flowback. However, these concentrations are still far above current MCLs and are therefore cause for concern.

Conclusions

The total dissolved solids of every well sampled, including those included in Chapman's paper, increased substantially the longer the water remained in the well. Well 2, for instance, increased nearly 4-fold during the first 8 days of flowback and over 6-fold by day 82. This illustrates the extent to which minerals in the formation rock—many of which are radioactive and/or toxic—dissolve into the fracturing water and are brought up to the surface as the water flows back up the borehole. Even the sample with the lowest TDS measured—25,600 mg/L—is more than 30 times as concentrated in dissolved material than even the most concentrated wastewater. Furthermore, every constituent measured for which an MCL or SMCL exists far exceeded that constituent's respective MCL or SMCL concentrations (oftentimes by several orders of magnitude) with the exception of nitrate and nitrite. This demonstrates the difficulty surrounding the treatment of residual hydraulic fracturing fluids and the importance of successfully isolating them from people and the environment.

The data of this research agrees with that of Chapman et al. (2012) and Barbot (2013), both in magnitude and trend, providing confidence that we have successfully characterized residual flowback fluids resulting from hydraulically fracturing Marcellus Shale in our region. While hydraulic fracturing does generate the potential to release toxic soluble uranium from the formation rock into the flowback water, abiotic or biotically mediated reduction processes might subsequently remove it during later stages of flowback. However, these concentrations are still far above current MCLs and are therefore cause for concern.

Little is currently known on how accidental release of the highly saline flowback fluids, which also contain organic compounds from fracking chemicals and the formation, might impact water resources and ecosystems. Further research is needed, which should focus on how to safely

and economically treat and/or dispose of these residual fluids given the species that are present and their respective concentrations. Furthermore, efforts should be made to understand both the microbial processes that take place in these fluids—particularly those that show promise of removing soluble uranium and other toxic compounds from solution—and the organic chemicals present and which could pose a threat to human and ecological health and wellbeing.

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