

DISSERTATION

CHARACTERIZATION AND TREATMENT OF WATER FOR UNCONVENTIONAL OIL
WELLS WITH TEMPORAL VARIABILITY AND FRACTURING FLUID TYPE

Submitted by

Seongyun Kim

Department of Civil and Environmental Engineering

In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

Fall 2017

Doctoral Committee:

Adviser: Pinar Omur-Ozbek

Kenneth Carlson

Kimberly Catton

Gregory Dooley

Copyright by Seongyun Kim 2017

All Rights Reserved

ABSTRACT

CHARACTERIZATION AND TREATMENT OF WATER FOR UNCONVENTIONAL OIL WELLS WITH TEMPORAL VARIABILITY AND FRACTURING FLUID TYPE

Flowback/produced water from unconventional oil and gas wells cannot be optimized without an understanding of water quality which need to be treated for reuse, the factors to be considered include the temporal variability and different frac fluid types used for hydraulic fracturing. Produced water treatment for reuse is becoming a critical factor for water management surrounding unconventional oil and gas industry.

For this research flowback/produced water samples were collected over 200 days from two wells in the Wattenberg Field, located in northeast Colorado. One of the frac fluids had an initial pH greater than 10 and had a guar-based gel. The other frac fluid included a non-guar polysaccharide based polymer and an initial pH less than 6. Total dissolved solids (TDS) and total organic carbon (TOC) analyses were conducted as an indicator for presence of organic and inorganic solids, and the data was compared with key ions (barium, calcium, chloride, magnesium, sodium, strontium, boron and iron) with the different frac fluid types. High values of the coefficient of determinant (over 0.85) were observed between TDS and the key ions, showing that significant positive correlations between two. Despite the significant initial pH differences, the concentrations of calcium, chloride, sodium and strontium were statistically equivalent between the two frac fluids. A mass balance approach was applied to evaluate the quantity of mass of injected additives that was recovered over the 200-day period. Zirconium, potassium and aluminum were selected due

either to the lack of contribution from the formation (Zr, Al) or the conservative (non-reactive) nature of the ion (K). Recoveries of these ions ranged from 3 % to 33 % after 200 days, and notable differences were observed between frac fluids. The fraction of cross-linking chemical (Zr) recovered was significantly less for the residue-free polysaccharide-based fluid than the derivatized guar-based fluid. It is hypothesized that the polysaccharide-based Zr cross-linked gel is broken down more completely than the guar-based gel, releasing the Zr metal with subsequent precipitation in the formation.

Another study conducted for this dissertation involved the analysis and treatment of produced water samples from three wells that were fractured with different fracturing fluid types over 63 days. TOC analysis showed significantly higher organics composition in produced water from wells fractured by the gel and hybrid fluid (943-1,730 mg/L) compared to the well fractured by the slickwater (222-440 mg/L). TDS levels increased with time, varying from roughly 18,000 mg/L to 30,000 mg/L between 1 to 63 days at each well. Liquid chromatography–mass spectrometry (LC-MS) was applied to characterize the organic matters and similar mass spectra were observed from each well with no temporal trend. Chemical equilibrium modeling was used to predict the precipitation of metals from produced water mixed with groundwater. Chemical coagulation was successfully performed for reducing the turbidity from produced water samples at each well.

LC-MS was performed to study the compositions of frac fluid prepared with fresh water (FWA) only and frac fluid prepared with recycled water (RWA) mixed with fresh water. Ethylene oxide and propylated glycol functional units were observed from both FWA and RWA samples. Qualitative analysis from FWA and RWA was performed through Agilent qualitative analysis software B.06.00 based on the exact mass of the chemical compound. Van Krevelen diagram

proved FWA and RWA show highly saturated and low degree of oxidation of organic compounds. Kendrick mass defect (KMD) from ethylene oxide was below 0.1 while KMD analysis from propylated glycol were close to 1. FWA showed 32.3 average carbon number and 9.8 double bond equivalent and RWA showed 31.5 average carbon number and 9.5 double bond equivalent.

For the last phase of this research, produced water samples were treated by electrocoagulation (EC), ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO) in series. Total dissolved solids (TDS), total organic carbon (TOC), dissolved organic carbon (DOC), BTEX, total petroleum hydrocarbons (TPH), turbidity, propylene glycol, ethylene glycol and ethylene glycol monobutyl ether were measured after each treatment. Gas chromatography–mass spectrometry (GC-MS) with solid phase extraction (SPE) method was applied to detect propylene glycol (PG), ethylene glycol (EG) and ethylene glycol monobutyl ether (EGME) in the samples. EGME was not detected in any produced water samples. PG concentration was between 0.07ug/ml to 5.39ug/ml and EG ranged from 0.07 ug/ml to 5.52ug/ml. GAC removed both PG and EG for acceptable drinking water criteria. EC was effective at removing both turbidity (85%) and TPH (80%) and most of turbidity and 90% of TPH were removed after UF. This study confirmed that almost 95% of BTEX, TOC, and DOC in produced water samples were removed by GAC. GAC contributed approximately 15% of TDS removal while RO removed 90% of TDS (2550mg/L) which is still high for reuse for various purposes.

TABLE OF CONTENTS

ABSTRACT.....	ii
1. Introduction.....	1
2. Literature Review.....	4
2.1 Unconventional oil and gas development	4
2.2 Environmental impacts.....	7
2.2.1 Water consumption and quality related issues and concerns.....	9
2.2.2 Air quality related issues and concerns.....	10
2.2.3 Land related issues and concerns.....	11
2.2.4 Public concern.....	11
2.2.5 Produced water with high salinity.....	12
2.2.6 Produced water with organic carbon.....	13
2.2.7 Discharging chemicals in surface waters	13
2.3 Produced water quality.....	14
2.3.1 Flowback water characterization	15
2.3.2 Produced water characterization	15
2.3.2.1 Inorganic compounds/minerals.....	17
2.3.2.2 Additive chemical in oil and gas productions.....	18
2.3.2.3 Clay stabilizer	18
2.3.2.4 Friction reducer.....	19
2.3.2.5 Breaker.....	19
2.3.2.6 Surfactant.....	20
2.3.2.7 Biocides	20
2.3.2.8 Gelling agents	20
2.3.2.9 Cross-linkers.....	20
2.4 Method for reuse of produced water	21
2.5 Method of analysis organic compounds for produced water	24
3. Research Hypothesis and Objectives	26
3.1 Reserch hypothesis	26
3.2 Research objectives	26

4. Temporal Analysis of Flowback and Produced Water Composition from SHALE Oil and Gas Operations: Impact of Frac Fluid Characteristics	30
4.1 Introduction	30
4.2 Materials and methods	32
4.2.1 Composition of frac fluid.....	32
4.2.2 Sample collection.....	33
4.2.3 Analytical methods	34
4.3 Results and discussions	34
4.3.1 Impacts of temporal variation on flowback water quality	34
4.3.2 Different frac fluid trends in flowback/produced water	42
4.3.3 Mass balance and recovery	47
4.4 Conclusion.....	51
5. Investigating the Influence of Hydraulic Fracturing Fluid Type and Well Age on Produced Water Quality: Chemical Composition and Treatment and Reuse Challenges/Options	53
5.1 Introduction	53
5.2 Material and methods	57
5.2.1 Well characteristics	57
5.2.2 Sample collections	61
5.2.3 Analytical methods	62
5.2.4 Jar testing to determine optimum dose	63
5.2.5 LC-MS method	64
5.2.6 Chemical equilibrium modeling	64
5.3 Results and discussion.....	66
5.3.1 Produced water characterization	66
5.3.2 Chemical coagulation jar testing.....	75
5.3.3 LC-MS analysis for comparison between gel frac fluid well and slickwater frac fluid well with temporal variability	78
5.3.4 Ion speciation in selected produced water samples	84
5.3.5 Blended water modeling	86
5.4 Conclusions	89
6. Characterization of Organic Matter in Water from Oil and Gas Wells Hydraulically Fractured with Recycled Water	91
6.1 Introduction	91
6.2 Material and methods	93
6.2.1 Composition of fracturing fluid and sample preparations.	93

6.2.2	Liquid chromatography mass spectrometry analysis.....	95
6.3	Results and discussion.....	96
6.3.1	Spectrum interpretation.....	96
6.3.2	Identification of organic compounds	104
6.3.3	Organic compounds characterization trends from FWA and RWA	105
6.4	Conclusions	113
7.	Organic and inorganics from flowback and produced water from shale gas operation: treatment and identification of glycols using gas chromatography-mass spectrometry	115
7.1	Introduction	115
7.2	Materials and methods	119
7.2.1	Sample collection, location and storage.....	119
7.2.2	Treatment process and sample collection	119
7.2.2.1	Electrocoagulation	120
7.2.2.2	Ultrafiltration	120
7.2.2.3	Granular activated carbon process.....	120
7.2.2.4	Reverse osmosis	121
7.2.3	GC-MS method.....	122
7.2.3.1	Sample preparation	122
7.2.3.2	Gas chromatography-mass spectrometry analysis.....	122
7.2.3.3	Calibration curve	123
7.2.3.4	Quality control	125
7.2.3.5	1,3-propanedial signal in samples without IS spiking.....	125
7.2.4	Water quality analysis.....	125
7.2.5	Statistical analysis.....	126
7.3	Results and discussion.....	126
7.3.1	Water quality parameters in the raw flowback water	126
7.3.2	Total dissolved solids.....	127
7.3.3	Total petroleum hydrocarbon.....	129
7.3.4	Turbidity	130
7.3.5	Total organic carbon and dissolved organic carbon	131
7.3.6	Propylene glycol and ethylene glycol	134
7.3.7	Benzene, toluene, ethylbenzene and xylene	137
7.4	Conclusion.....	139
8.	Conclusion	140
9.	References	142

Appendix A: detailed characterization dataset	158
Appendix B: Detailed flowback/produced water characteristics.....	162
Appendix C: Detailed information of GC-MS results for PG and EG analysis described in Chapter 7.....	167

1. Introduction

Energy demand is estimated to increase at an annual rate of 0.2 % from 2010 through 2035, and electricity demand will grow by 0.8 % per year (AEO, 2012). The successful expansion of hydraulic fracturing in the unconventional formations is expected to meet the fastest growing energy demand. As a result of recent advances in hydraulic fracturing and horizontal drilling, the unconventional natural gas production increased 10 fold between 2001 and 2011 (Gregory, et al, 2011; Dammal, et al, 2011).

Although the permeability of shale formations is lower than the permeability of the conventional formation and need stimulation to produce oil and gas efficiently, recent advances in the hydraulic fracturing and horizontal drilling have allowed to extract oil and natural gas economically from unconventional formations (Arthur, et al, 2010; Rahm, 2011; Suarez, 2012). In addition, utilization of shale gas generates less carbon emission compared to coal, it is easy to transport and has widespread accessibility (Gregory, et al, 2011; Jaramillo, et al, 2007). Even though statewide estimates of water withdrawal for hydraulic fracturing to be less than 0.1% of total water usage in Colorado (COGCC, 2012), water volume consumption, water quality and sourcing of useful water resources can be a significant concern as the fracturing process requires a significant amount of water. Water demand for hydraulic fracturing is approximately between 2-5 million gallons (Suarez, 2012; Goodwin and Douglas, 2012; Hickenbottom, 2013; Lee, et al, 2011).

The water demands for drilling and hydraulic fracturing are different depending on the geological formation of permeability, depth, compressibility and porosity (US.EPA, 2004). The characteristic of flowback/produced water may be affected by geological formation with temporal

and spatial variation (Barbot, et al., 2013), fracturing fluid composition, the wellbore length and also ratio of recycled water used.

After hydraulic fracturing, between 5 to 60 percent of the fluid mixture flow back to the surface as flowback or produced water as the pressure is released (Suarez, 2012; Rahm and Riha, 2012; USDOE, 2009a; USDOE, 2009b; Clark, et al, 2012). Flowback/produced water bring any remaining chemical additives and naturally occurring materials, including organic compounds, from the geological formation and the oil and gas in gets in contact with (Hickenbottom, et al, 2013; Rahm and Riha, 2012; Clark, et al, 2012; Veil, et al, 2004; Soeder and Kappel, 2009).

Recycling of flowback and produced water for beneficial use is being pursued in many parts of the country and this trend is expected to minimize concerns related to hydraulic fracturing and regional water scarcity. The characteristics of produced water from oil and gas reservoirs and the possible treatment options for waters have been studied and published (Andrew, et al, 2009; Ahmadun, et al, 2009; Sirivedhin and Dallbauman, 2004). Many oil and gas production companies utilize the produced water by mixing it with fresh water (USDOE, 2009a; USDOE, 2009b; Lutz, et al, 2013; Jenner and Lamadrid, 2013; Spellman, 2012). Most organic compounds remained in produced water even if treated by conventional wastewater treatment processes (Hickenbottom, et al, 2013). In addition, Carter et al. (2013) reported that the mass spectra of produced water sample between inflow and effluent from centralized water treatment facility were almost identical in spectra from using liquid chromatography-mass spectrum (LC-MS) analysis (Carter, et al, 2013). Since characteristics of flowback /produced water can be affected by geological formation, the analysis of flowback/produced water is difficult for the organic compounds.

This Ph.D. work focused on characterizing and treatment of the flowback and produced water samples from unconventional hydraulic fracturing operations to understand the inorganic

and organic composition of the studied samples for temporal and fracturing fluid variations. This document contains eight chapters: The literature review for overview of shale oil and gas operations is presented in Chapter 2 and the research hypothesis and objectives is summarized in Chapter 3.

Chapter 4 and Chapter 5 provide analysis of inorganic and organic constituents in flowback/produced with temporal variation and different fracturing fluid types. Chapter 6 illustrates an in-depth analysis of organic compounds in mixed recycled water with frac fluid and fresh water with frac fluid samples by applying LC-MS. In Chapter 7 the results from water treatment processes were presented for the produced water samples and water quality parameters after each treatment were compared. GC-MS with SPE were used for measuring glycols in produced water samples.

2. Literature Review

2.1 Unconventional oil and gas development

Natural gas and oil were exploited from conventional and unconventional reservoir in geological formations. While oil and gas in conventional reservoirs can flow readily, oil and gas in unconventional reservoir is relatively hard to flow because of low permeability in rocks. Hydraulic fracturing technic have been used for about more than 50 years. However, hydraulic fracturing technic have been advanced in recent years. Advancement technic, hydraulic fracturing and horizontal drilling, have led to development oil and gas production in unconventional production. Figure 2.1. shows the schematic diagram of conventional and unconventional oil and gas reservoir.

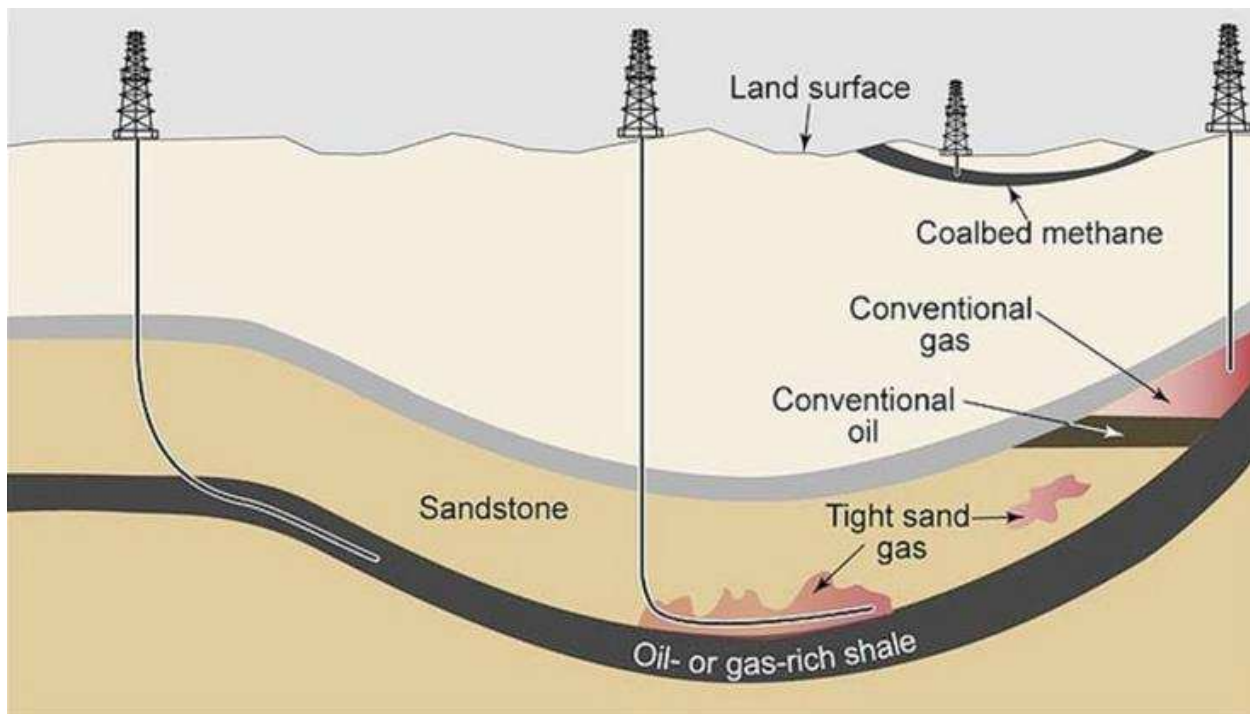


Figure 2.1. Conventional and unconventional oil and gas production (GNS, 2012).

The development of unconventional oil and gas is expected to meet today's industrialization and regarded as important energy supply to meet an increasing fraction of the energy demand and has spurred an interest in its potential in other parts of the world (GNS, 2012). Energy demand is estimated to increase at an annual rate of 0.2 % from 2010 through 2035, and electricity demand will grow by 0.8 % per year (AEO, 2012).

In the U.S, the technically recoverable reserves of shale gas are greater than 1,452 trillion cubic feet (USEIA, 2013), a supply that could potentially power this country for up to 100 years. The successful expansion of hydraulic fracturing for extracting oil and gas from shale formations has allowed the U.S. to almost double its oil production in last ten years. In addition, the advances in hydraulic fracturing and horizontal drilling have led to unconventional natural gas production increasing 10 fold between 2001 and 2011 (Gregory, et al, 2011; Dammal, et al, 2011).

Figure 2.2 shows the various unconventional current and prospective shale plays are distributed through the U.S. The major shale plays in U.S are Bakken, Eagle ford, Permian, Marcellus and Anadarko-Woodford. The major seven shale plays consist of more than 80 percent of recent production and 88 percent of projection of cumulative production through 2014.

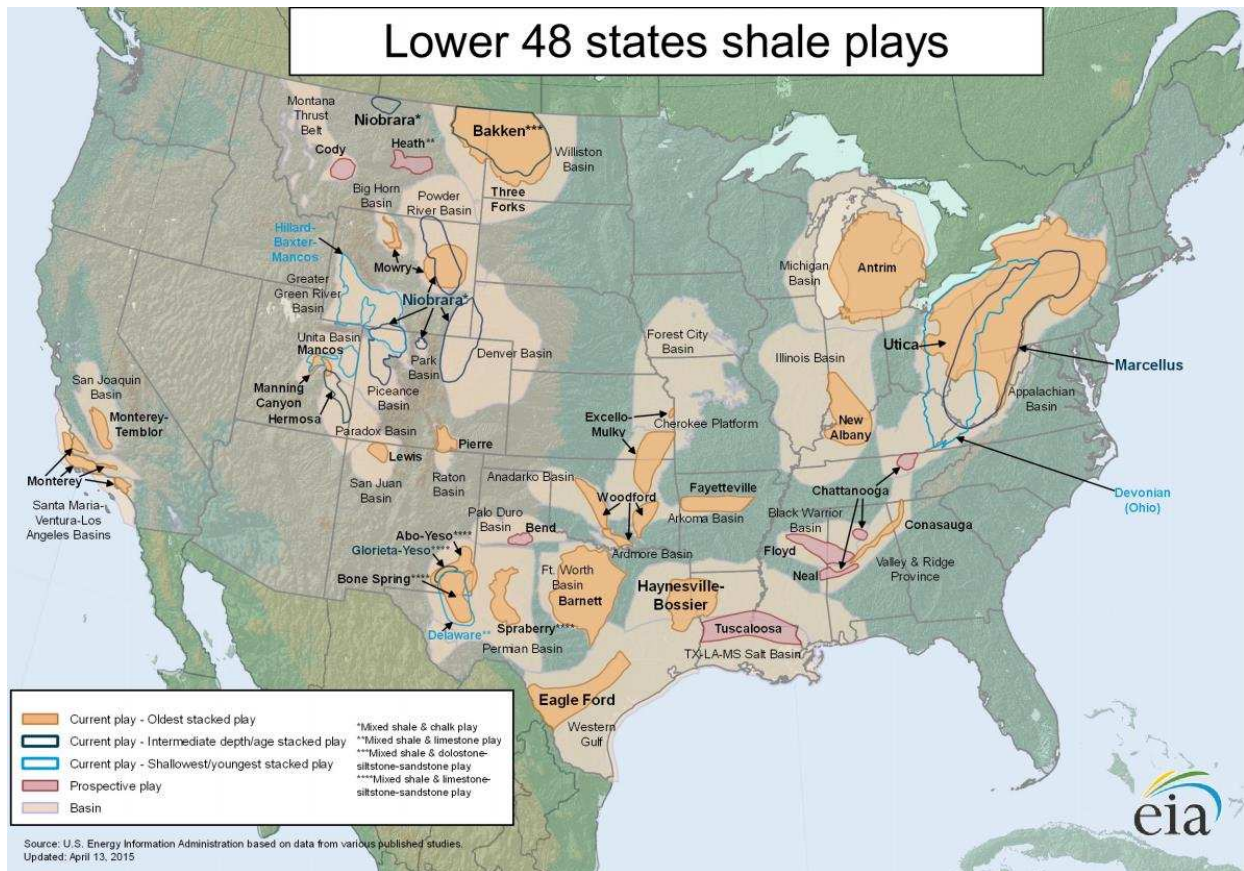


Figure 2.2. Location of shale plays in U.S (USEIA, 2015).

Natural gas consisted of 27% of energy consumption in the U.S and is estimated to continue to make up roughly one third of U.S energy supply until 2040 (AEO, 2013). The increase of natural gas until 2040 is due to the results of development of shale gas. Figure2.3 shows shale gas is mostly supporter to natural gas growth in U.S. The prediction of shale gas development up to almost half of total U.S. natural gas production in 2035 which are almost more than shale gas production in 2010.

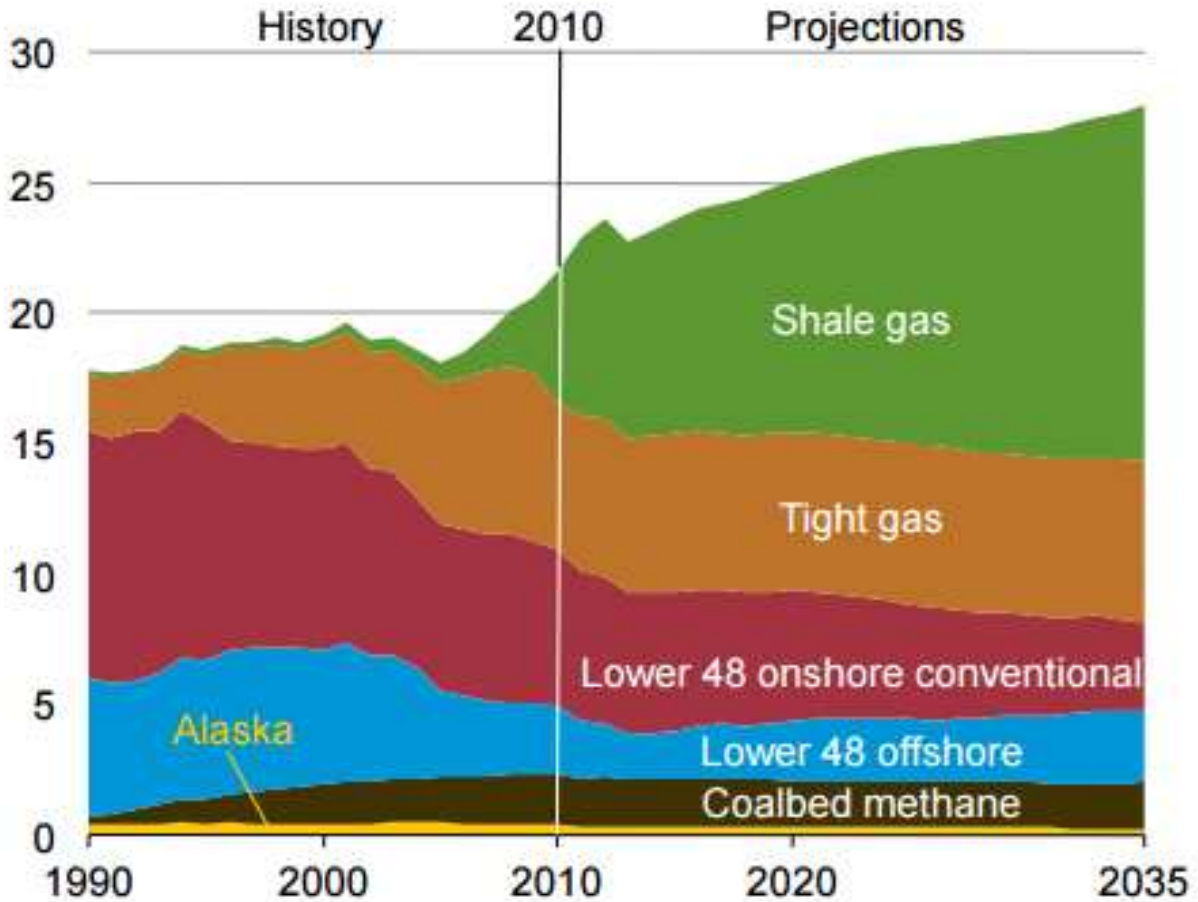


Figure 2.3. Natural gas prediction in U.S by 2035 (AEO, 2012).

2.2 Environmental impacts

The primary advantages of utilization of natural gas are its widespread accessibility, easy transport and relative to coal, clean combustion (Gregory, et al, 2011; Jaramillo, et al, 2007). Since utilization of shale gas releases much less carbon emissions compared to coal and there is an existing and expanding national pipeline system, it is expected that natural gas extracted from shale formations will be an important fuel well into the future (Gregory, et al, 2011; Jaramillo, et al, 2007).

However, the hydraulic fracturing process, used to enable economical production from low permeability unconventional reservoirs such as shale oil and shale gas formations, can place increased pressure on the use of finite natural resources such as fresh water, raising social concerns in the community. The development of unconventional oil and gas has caused issues which are summarized in Figure 2.4: water, air, land and community issues.

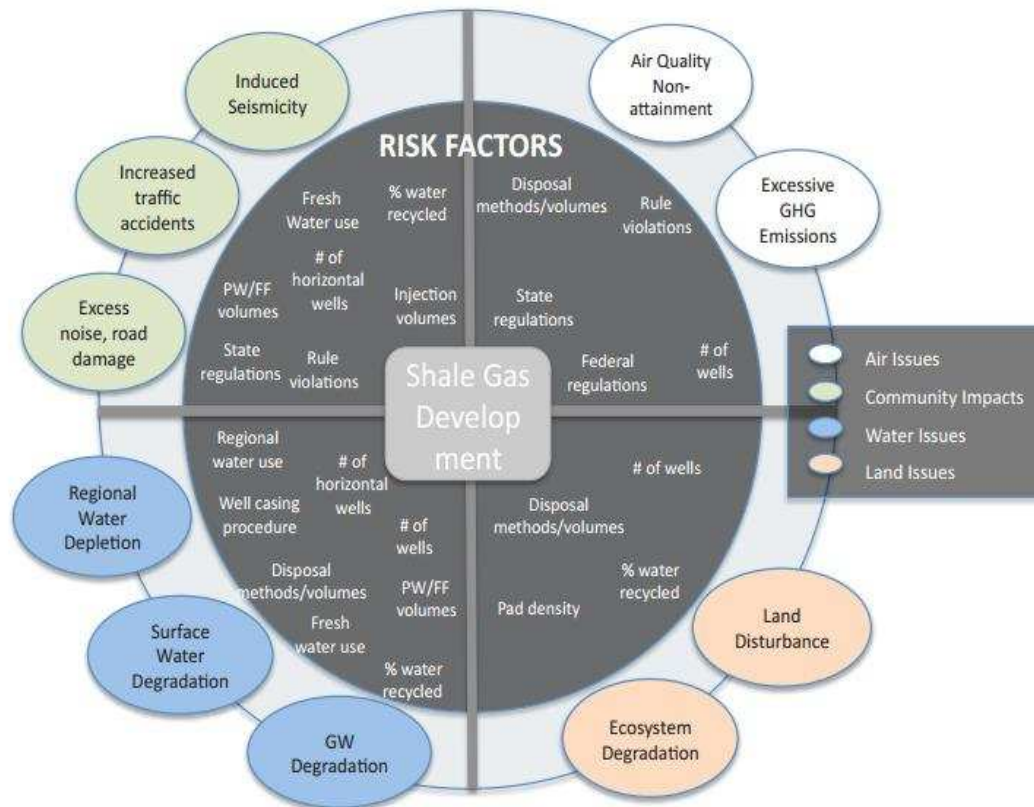


Figure 2.4. The summarized possible factors from development of unconventional oil and gas (Carlson, 2013).

2.2.1 Water consumption and quality related issues and concerns

The volume of water consumed, the risk to the environment of returned water and the disposal of the wastewater continue to be significant concerns. Water demand for hydraulically fracturing a single well can range from approximately between 2-8 million gallons of water (Suarez, 2012; Goodwin and Douglas, 2012; Hickenbottom, et al, 2013; Lee, et al, 2011; Nicot and Scanlon, 2012; Rahm and Riha, 2012; Stephenson, et al, 2011). Statewide estimates of water withdrawal for hydraulic fracturing has been estimated to be less than 0.1% of total water usage in Colorado (COGCC, 2015).

The required water volume for hydraulic fracturing a well depends on the length of the horizontal lateral in addition to geological formation, depth, compressibility and porosity (Kargbo, et al, 2010). The characteristics of the flowback/produced water will be affected by the geological formation with temporal and spatial variation (Barbot, et al, 2013), but other factors include the fracturing fluid composition, the wellbore length and also the ratio of recycled water used.

After hydraulic fracturing, between 5 and 60 percent of the fluid mixture to the surface to the as flowback or produced water in the first 6 months as the pressure is released (Suarez, 2012; Rahm and Riha, 2012; USDOE, 2009a; USDOE, 2009b; Clark, et al, 2012). Flowback/produced water may contain unaltered chemical additives and organic compounds indigenous to the formation (e.g. hydrocarbons, benzene, etc.), but also organic compounds that have broken down through either reaction with the formation rock or the high temperatures associated with the producing regions or both (Hickenbottom, et al, 2013; Rahm and Riha, 2012; Clark, et al, 2012; Veil, et al, 2004; Soeder and Kappel, 2009; Lutz, et al, 2013; Kargbo, et al, 2010).

There are also possibility of accidental leaking oil, gas, fracturing chemical that can affect groundwater or surface water quality. In September 2013, Colorado suffered from a devastating

flood by record rainfall, which resulted in facing the threat of contaminated waters from the leaking oil and gas. The accumulated rainfall continues increasing through 7 days, and corresponding AEPs (annual exceedance probabilities) are less than 1/1000, but they remain below the 95% confidence limit for the 1/1000 AEP for all durations up to 4 days (NOAA, 2013). Therefore, the rainfall in Colorado 2013 might be called a return period of 1000 year. According to the COGCC report, a total of about 37,380 gallons of leaking oil have been released in Colorado resulted from the catastrophic flooding and brought over 2 billion dollars in property damage (HUFFPOST, 2013).



Figure 2.5. Oil and water storage tanks toppled by flood in Weld County, Colorado (UUFFPOST, 2013).

2.2.2 Air quality related issues and concerns

Most of people focused on water issues, air issues are also most severe problem from shale gas development. Shale gas development can lead to leakages of methane, carbon dioxide which can cause climate change. Level of methane and greenhouse gas can be a trace of shale gas

development (Howarth and Santoro; 2011). In addition, increased truck traffic that transport flowback water, oil and gas can cause increasing emissions of pollutant. However, emission of greenhouse gas from unconventional oil and gas wells are controversial (O'Sullivan and Paltsev; 2012) and direct and indirect methane emission is not fully figured out (SOW, 2012). The carbon dioxide emission are lowered by changing from using coal to gas in electricity generation since the gas turbine power plant can accomplish effectively compared to coal fired power plant. Substituting oil and gas from unconventional wells for coal can lower the overall air issues.

2.2.3 Land related issues and concerns

Another important environmental impacts is the land that will have both land effect and local effect. The land issues from shale gas development means not only a single well but also regional and cumulative effects. The unconventional oil and gas development require considerable infrastructure that consists of staging areas, well pads, roads and pipelines. The square mile can occupy about 16 wells and normal size town can deal with up to 1500 wells in a Marcellus formation (SOW, 2012). Land impacts may also consider the negative effects on land uses such as tourism and agriculture, the damage of wildlife habitat. Large number of fish were killed September 2009 in Pennsylvania and it might result from the inflow of the wastewater of produced water or flowback water from unconventional wells (Soeaghan and Greenwire, 2011).

2.2.4 Public concern

Until now, public concern from unconventional oil and gas development have not been surveyed well. Although unconventional oil and gas development give use various economical profit, it also brings adversely effect on air quality and water problem that cause public concern recently. Public concern comprises safety issues associated with truck traffic, health issues, and psychosocial impacts such as stress from noise to both communities and individuals. More than

300 trucks are needed for carrying fresh water and more than 180 trucks are required for carrying flowback or produced water to wastewater treatment (SHALESHORK, 2012). Health issues is affected by many factors, comprising of environmental effect such as water quality and air issues, socio-economic and cultural effects.

2.2.5 Produced water with high salinity

EPA considers water with high level of TDS would make drinking water unpalatable because water with high concentration of TDS might transfer toxicity, affecting organisms in aquatic system (USEPA, 2012).

Salinity is considered as one of the main factors in produced water that would have negative effect on the environment and human resources. Discharging water with high salinity can have a negative effect on buildings, roads, fences, and railways (Lubczenko, 2004). Salinity can impact productivity of crops, contaminate the freshwater, and make streams toxic (Allen and Robinson, 1993). High level of TDS in produced water would carry out toxic materials such as metals and organic compounds or could be beneficial as nutrients for plants (Weber-Scannell, et al, 2007).

Sodium Adsorption Ratio (SAR) equation used to determine whether produced water is acceptable for reuse in irrigation process. SAR is ratio of sodium value to the square root of the average for calcium and magnesium, as follows:

$$SAR = \frac{[Na^{2+}]}{\sqrt{\frac{([Ca^{2+}] + [Mg^{2+}])}{2}}}$$

A value higher than 6 for SAR for irrigation water would cause increasing susceptibility to erosion and reduced soil permeability (Horner, et al, 2011). Discharging produced water with high salinity would create a scaling problem, forming in the tubing, vessels, and treatment equipment during drilling, production process and treatment. Additional cost is needed for removing scales.

In short, high levels of TDS in produced water is considered as one of main issues in oil and gas industry due to the various negative impacts on human and environment.

2.2.6 Produced water with organic carbon

Soluble hydrocarbons in produced water are defined as simple aliphatic, aromatic hydrocarbons, fatty acids, and naphthenic acids. Oils in water are presented as the dispersed oil, soluble hydrocarbons, and soluble organic compounds. Many technologies are developed to separate organic compounds from produced water in oil and gas field. Treatment process would be selected based on diameter of the oil droplets. The droplets' size would be varied from 0.5 to 200 microns in diameter (Stewart, 2011). Additional chemical compounds would be needed to make droplets for removing hydrocarbons in produced water by making droplets in produced water (Bansal and Caudle, 1998).

Some dissolved hydrocarbons are needed for production process in oil and gas. Benzene, toluene, ethylbenzene and xylene are applied to polish stage of granular activated carbon (Doyle and Brown, 2000). Discharging produced water with high organic compounds have toxic effects on both onshore and offshore oil fields) and the biological oxygen demand will rise in near discharging area (Veil, et al, 2004).

2.2.7 Discharging chemicals in surface waters

Various chemicals in produced water would cause the pollution in rivers or streams if produced waters were discharged without proper treatment processes. There are many toxic chemicals used for hydraulic fracturing for various factors such as biocides, corrosion inhibitors and reverse emulsion breakers Veil, et al, 2004). Fracturing additives for biocides are very toxic and harmful for living organisms (Allen and Robinson, 1993).

Produced water from oil and gas contains heavy metals that may cause operational problems for production in oil and gas field (Bansal and Caudle, 1998). Type and concentration of heavy metals in produced water depend on field and most of heavy metals detected are barium, iron, manganese, lead and zinc (Veil, et al, 2004). When these metals enter the surface without proper treatment processes, environmental problems would occur such as iron staining (Veil, et al, 2004) and human health problems were reported by heavy metals (Duruibe, et al, 2007).

2.3 Produced water quality

The flowback/produced water recovered from fracturing operations during the completion of the well may vary greatly in character depending on the fracture fluid composition, location of the wells due to different formations (spatial variation), the time the water is collected after well completion (temporal variation), and the wellbore length.

After hydraulic fracturing, between 5 and 60 percent of the fluid mixture to the surface to the as flowback or produced water in the first 6 months as the pressure is released (Suarez, 2012; Rahm and Riha, 2012; USDOE, 2009a; USDOE, 2009b; Clark, et al, 2012).

Flowback/produced water may contain unaltered chemical additives and organic compounds indigenous to the formation (e.g. hydrocarbons, benzene, etc.), but also organic compounds that have broken down through either reaction with the formation rock or the high temperatures associated with the producing regions or both (Hickenbottom, et al, 2013; Rahm and Riha, 2012; Clark, et al, 2012; Veil, et al, 2004; Soeder and Kappel, 2009; Lutz, et al, 2013; Kargbo, 2010). Understanding of characterization of flowback/produced water is an indispensable for reusing the flowback/produced water for fracturing.

2.3.1 Flowback water characterization

Injected chemical fluid for hydraulic fracturing and geological formation are considered as main factors can affect flowback water quality. Flowback water is recovered earlier than produced water and comprised of injected chemical for hydraulic fracturing. Flowback water includes injected chemical additives, inorganics, organics, total dissolved solids and clays. A great part of flowback is recovered first week (after flowback water begin) and the rest of flowback occurs until a month. Flowback is recovered between 20 to 40% of input water for hydraulic fracturing until about a month (US. Marcellus, 2011.). Table 2.1 shows flowback water quality in Colorado.

Table 2.1. Average of flowback water quality during 1-30 days after flowback began in Colorado.

Water Quality Parameter	Flowback Water
pH	7.28
TDS (mg/L)	9660.23
Aluminum(mg/L)	2.75
Barium(mg/L)	2.81
Boron(mg/L)	12.28
Calcium(mg/L)	132.97
Iron(mg/L)	39.07
Magnesium(mg/L)	18.74
Potassium(mg/L)	47.36
Sodium(mg/L)	3908.97
Strontium(mg/L)	14.25
Chloride(mg/L)	5695.28
Sulfate(mg/L)	254.38
Bicarbonate(mg/L)	1018.23
Silicon(mg/L)	42.26
Zirconium(mg/L)	34.86

2.3.2 Produced water characterization

Produced water is recovered water in the unconventional wells and move to the surface from under formation for the whole lifespan of wells. Produced water tend to have higher levels of TDS because of contact time of geological formations (Barbot, et al, 2013).

Table 2.2. Produced water quality (Fakhru'l-Razi, et al, 2009; Tibbetts, et al, 1992).

Water Quality Parameter	Values	Metals/ Heavy metals	Values (mg/L)
Ammonical nitrogen (mg/L)	10–300	Arsenic	<0.005–0.3
Base/neutrals (mg/L)	<140	Aluminum	310–410
Bicarbonate (mg/L)	77–3990	Barium	1.3–650
Chloride (mg/L)	80–200,000	Beryllium	<0.001-0.004
COD (mg/L)	1220	Boron	5–95
Density (kg/m ³)	1014–1140	Cadmium	<0.005–0.2
Higher acids (mg/L)	<1–63	Calcium	13–25800
pH	4.3–10	Chromium	0.02–1.1
Phenols (mg/L)	0.009–23	Copper	<0.002–1.5
Sulfate (mg/L)	<2–1650	Iron	<0.1–100
Sulfite (mg/L)	10	Lead	0.002–8.8
Surface Tension (dynes/cm)	43–78	Lithium	3–50
Total non-volatile oil and grease by GLC/MS base (g/L)	275	Magnesium	8–6000
TOC (mg/L)	0–1500	Manganese	<0.004–175
Total oil (IR; mg/L)	2–565	Mercury	<0.001–0.002
Total polar (mg/L)	9.7–600	Potassium	24–4300
TSS (mg/L)	1.2–1000	Silver	<0.001–0.15
VFA's (volatile fatty acids) (mg/L)		Sodium	132–97000
Volatile (BTX; mg/L)		Strontium	0.02–1000
		Titanium	
		Zinc	

Produced water characteristics are dependent on geological formation, contact time with the formation, and type of fracture additives. Produced water characteristics are summarized in Table 2.2. Produced water characteristics depend on formation minerals (in dissolved form), crude

oil constituents, fracturing additives, production solids (bacteria, corrosion products, metal scales and solids by formation) and gases (only in the dissolved status)(Hansen, 1994).

Crude oil is a mixture of hydrocarbons containing benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenanthrene, dibenzothiophene, phenols and polyaromatic hydrocarbons. It is not possible for all hydrocarbons to dissolve in produced water due to their polarity (Ekins, et al, 2007).

The solubility of oil in produced water varies with type of oil, amount of produced water, and age of wells (Stephenson, 1992). The solubility of cyclic compounds (BTEX) in produced water is relatively high (Ekins, et al, 2007).

2.3.2.1 Inorganic compounds/minerals

Dissolved inorganic compounds include anions, cations, radioactive materials and heavy metals (Fakhru'l-Razi, et al, 2009).

Main cations in produced water are sodium, magnesium, calcium, potassium, barium, strontium and iron and main anions in produced water are chloride, sulfate, carbonate and bicarbonate. Cation and anions in produced water would affect the buffering capacity, salinity and scaling potential (Hansen, 1994).

One of the main characteristics in produced water is salinity that is affected by main cations and anions including sodium, chloride, calcium, potassium, and magnesium. The level of salinity in produced water varies from approximately 1,000 to 350,000 mg/L (Bostick and Luo, 2001; McCormack, et al, 2001). The level of heavy metals in produced water are depending on the geological formation and well age (Stephenson, 1992). Cadmium, chromium, copper, mercury, nickel, silver and zinc would be included in produced water and presented as a trace (Hansen, 1994).

2.3.2.2 Additive chemical in oil and gas productions

Fracturing fluid are made of a wide range of chemicals, a proppant (typically sand) and carrier fluids (typically water). A variety of chemicals are used in fracturing additives for various uses including biocides, breakers, cross-linkers, gels, friction reducers, corrosion inhibitors and pH adjusting. Fracturing fluid should be carefully designed considering the various geological formation properties before hydraulic fracturing.

Fracturing additives can be divided into the gel fluid and slickwater fluid. While the gel fluid contains a high concentration of gel polymer that is able to be cross-linking for increasing the viscosity during hydraulic fracturing process, slickwater fluid utilizes a low level of polymer or no polymer and applies lower proppant concentration (Zuh, 2012).

Most of hydraulic fracturing processes occurred with gel fluid and high concentration of proppants before hydraulic fracturing started in the Barnett Shale in 1997. Gel fluid have been proved that it is more effective in deep, wet and high temperature reservoirs while slickwater fluid would be more effective in shallower, dryer and low temperature reservoirs (Zuh, 2012).

2.3.2.3 Clay stabilizer

When fresh water contacts formation clay and shale formation, it will swell. KCI typically uses for minimizing clay swelling via cation exchange. Effective temperature is between 50°F and 400°F and typical concentrations of KCI are between 2 to 7 wt% at the base fluid based on the clay characteristics in the geological formations (Gijtenbeek, et al, 2006). The capable of clay stabilization is highly varied by different salt type and brine concentration. KCI of 2% proved a marginal effect on swelling clay or shale from many capillary suction time test and flow test (Kaufman, et al, 2008).

2.3.2.4 Friction reducer

Friction reducer can lower friction and increase injection rates while fracturing additives flows in a pipeline. Its general properties are large polymers, varying degrees and losing some of effectiveness for prolonged agitation (Sharp and Adrian, 2004). Three main factors for evaluating friction reducer's effectiveness are the friction reduction, the leaking off control and the viscosity. Cationic friction reducer type can be used in hydraulic fracturing process, but it is significantly more expensive than the anionic types. Gelling agent can reduce friction in some degree compared to slick fluid. Using synthetic anionic polymers is good options for hydraulic fracturing in tight formation. Polyacrylamid-based polymers in slickwater fluid is recently most commonly used as the friction reducers (Kaufman, et al, 2008).

2.3.2.5 Breaker

Chemical breakers in hydraulic fracturing degrade molecular weight of polymer gel that lowers viscosity of fluid and remove the residuals in facilitates, bringing fast recovery of polymer. Failed or ineffective breakers can lead to decreased productivity due to screenouts.

The most often used for breakers are oxidizing agents such as peroxides and persulfate which produce “free radicals” to degrade polymer chains. A study for activity of oxidative breakers in various temperature range presents that the persulfate breakers shows best performance at 180 °F and are applicable at 100 °F with concentration of between 5 to 10 pptg of water (Kaufman, et al, 2008).

Enzymes is also applied to fracturing additives for breakers. Enzymes play a role as a catalyst for degrading the gel. Enzyme breakers are not consumed and sensitive to temperature and pH during the breaking process.

2.3.2.6 Surfactant

Surfactants are generally used in hydraulic fracturing to increase the fluid recovery from the formation by reducing the surface tension. There main classification of surfactants from the hydrophilic group include anionic, cationic, non-ionic and zwitterionic. Anionic surfactants is applied for enhanced oil recovery (EOR) because of its low adsorption on sandstone. While cationic surfactants can be applied to carbonate rocks, it cannot be normally utilized on sandstone reservoirs due to its strong adsorption in sandstone. Zwitterionic surfactants are categorized into two active group including nonionic-anionic, nonionic-cationic, or anionic- cationic which are tolerant to the temperature and salinity.

2.3.2.7 Biocides

Biocides are critical chemical components for hydraulic fracturing additives to prevent bacterial growth in downhole equipment. Bacteria may cause the biofilm that can foul the well, make toxic hydrogen sulfide that can cause corrosion and decrease gas extraction.

2.3.2.8 Gelling agents

Gelling agents are used in small amounts to increase viscosity and sufficiently carry proppant into the geological formation. Guar gum and cellulose derivatives are most commonly used as gelling agents, While slickwater fluid usually contains relatively low concentration of gelling agents, gel fluids contains relatively larger concentration of gelling agents

2.3.2.9 Cross-linkers

Cross-linker is used for increasing molecular weight of gelling agent from linking polymer molecular to increase the viscosity. Boron is the most generally used but only activated at high pH. Zirconium and titanium are also commonly used and can be applied both low and high pH value.

Rest of fracturing additives include corrosion inhibitors, non-emulsifiers, scale inhibitors, paraffin inhibitors, and iron-controlling compounds which are typically in smaller concentrations.

Produced water quality will be affected by fracturing additives, particularly early flowback/produced water. Some of fracturing additives, which are not affected by the high pressure and temperature and not react in the formation, may stay in the same form that they were added.

2.4 Method for reuse of produced water

Water demand for hydraulically fracturing a single well can range from approximately between 2-8 million gallons of water (Suarez, 2012; Goodwin and Douglas, 2012; Hickenbottom, et al, 2013; Lee, et al, 2011; Nicot and Scanlon, 2012; Stephenson, et al, 2011).

After hydraulic fracturing, between 5 and 60 percent of the fluid mixture to the surface to the as flowback or produced water in the first 6 months as the pressure is released (Rahm, 2011; Stephenson, et al, 2011; Barbot, et al, 2013; USDOE, 2009 a; USDOE, 2009b). Flowback/produced water may contain unaltered chemical additives and organic compounds indigenous to the formation (e.g. hydrocarbons, benzene, etc.), but also organic compounds that have broken down through either reaction with the formation rock or the high temperatures associated with the producing regions or both (Goodwin and Douglas, 2012; Rahm and Riha, 2012; Clark, et al, 2012; Veil, et al, 2004; Soeder and Kappel, 2009; Lutz, et al, 2013; Kargbo, et al, 2010).

Reusing the flowback/produced water for fracturing additional wells is a good approach to managing the wastewater and efforts are being made to expand this practice across the country. Several studies have identified the characteristics of produced water from oil and gas reservoirs and the possible treatment options for waters but none have looked at the characteristics of organic

matter that has been used at least twice (i.e. flowback from a well that was fractured with recycled water) (Andrew, et al, 2005; Ahmadun, et al, 2009; Sirivedhin and Dallbauman, 2004). Recently, reusing produced water in Pennsylvania has risen up to approximately 90 % in 2011 from approximately 5% in 2008, leading to closed to 30% of lessening an average distance of truck traveling for wastewater from shale gas wells (Rahm, et al, 2013). One of the treatment for produced water is the mixing produced water with freshwater.

Normal wastewater treatment process includes coagulation/flocculation, filtration, and disinfection. Additional processes are required for recycling of produced water. Some of the inorganic (calcium, barium and strontium) in produced water or flowback water are regarded as major concern owing to high level of scaling potential for reused for hydraulic fracturing (Gregory, et al, 2011). In addition, BaSO_4 , SrSO_4 and CaCO_3 are also considered as major concerns (Vidic, et al, 2013).

Figure 2.6 shows examples of diagram of produced water treatment process. Mantell (2011) suggests the strategies of water treatment via several shale gas basins in U.S. Mantell (2011) mentions that most crucial factors are produced water quantity, water quality and rate of production for produced water treatment.

Total dissolved solids (TDS) is one of the important parameter for produced water treatment. TDS concentration can vary by well ages and spatial variability. TDS concentration in shale is from 50,000 ppm to 140,000 ppm in Barnett, higher than 120,000 ppm in Marcellus and 15,000 ppm in Fayetteville (Mantell, 2010). TDS concentration is tend to increase by well ages (Barbot, et al, 2013).

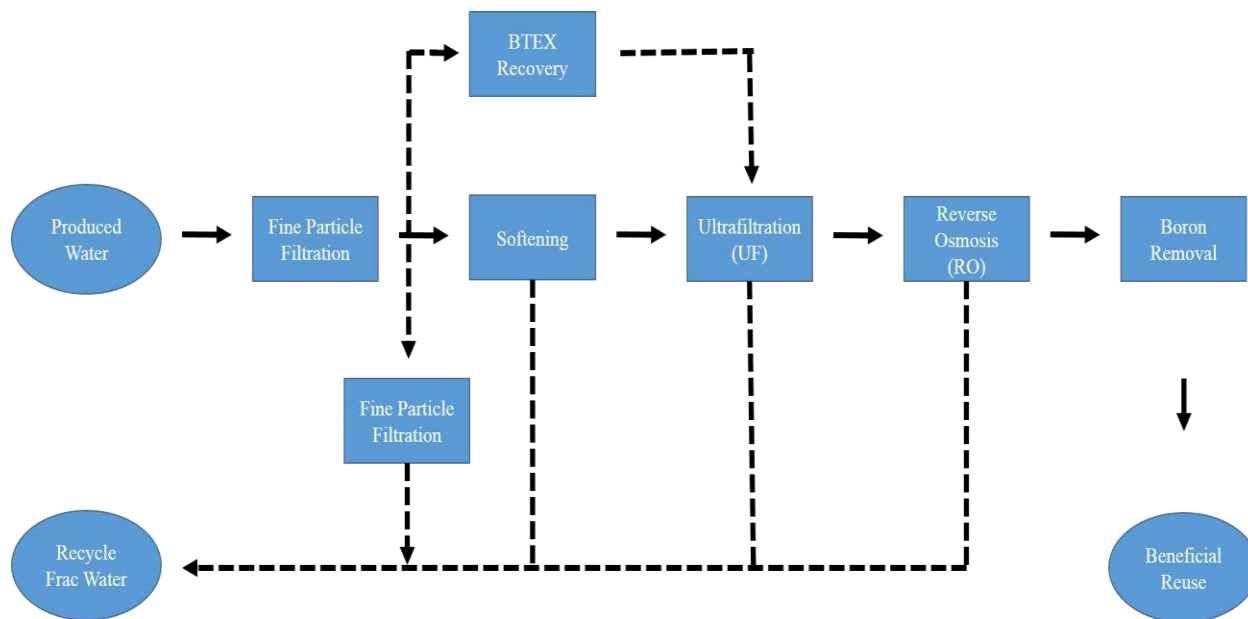


Figure 2.6. Example diagram of produced water treatment process.

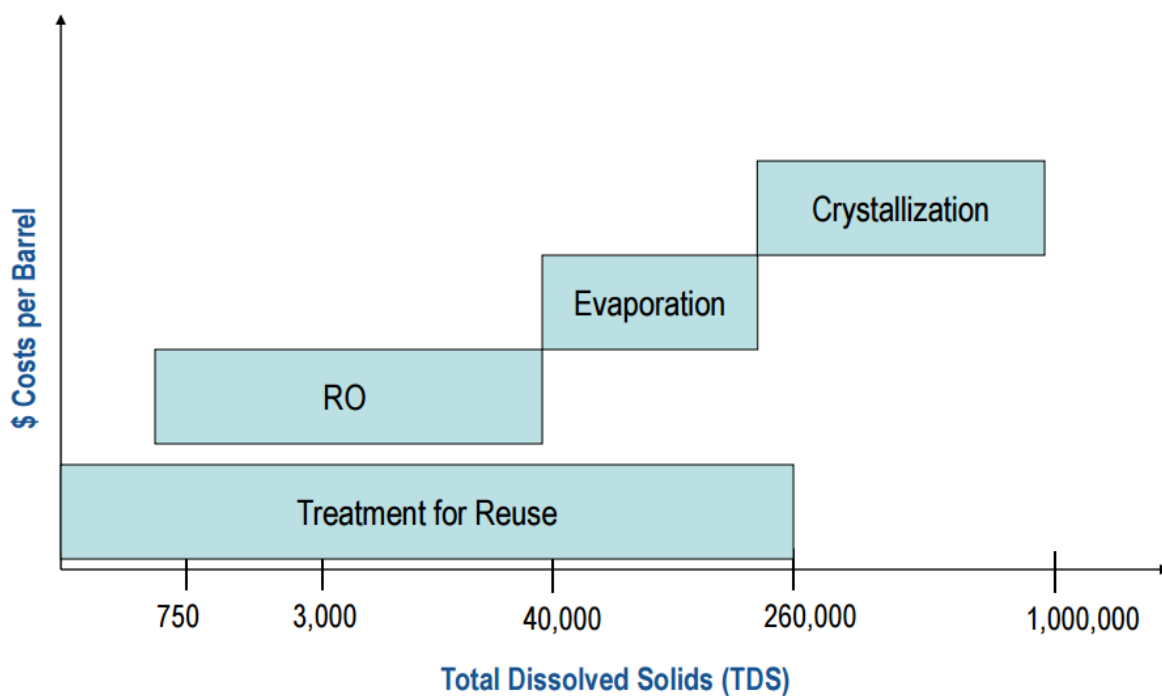


Figure 2.7. Range of applicability versus cost with total dissolved solids (Kimball, 2010).

The cost for produced water treatment can varies based on the water quality and targeted water uses. Figure 2.7 shows the range of applicability versus cost with various level of TDS.

There are several studies focused on treatment and reuse of flowback water (Esmaelirad, et al, 2015; Rosenblum, et al, 2016). High TDS water can be difficult to treat with wastewater treatment processes such as biological treatment, ultrafiltration and forward osmosis (Lester, et al, 2014; Lefebvre, et al, 2004; Altaee and Hilal, 2014). Coagulation is widely utilized for both domestic and industrial wastewater treatment because it is very efficient in removing suspended and colloidal particles. Flowback/produced water has similar water quality characteristics to industrial wastewater such as high TDS and TSS, and hence coagulation is applied for its treatment (Esmaelirad, et al, 2015; Rosenblum, et al, 2016). Activated carbon is the most often used as an adsorbent for treatment of drinking water, municipal and industrial wastewater because of its capability of adsorbing organic contaminants and its reasonable costs (Zhang, et al, 2013). In addition, activated carbon process have also been proven to be useful to reduce the hydrocarbons from hypersaline salt waters (Karapanagiotic, 2007) and surfactants within flowback/produced water (Wu and Pendleton, 2001). The electrocoagulation, ultrafiltration, granulated activated carbon adsorption and reverse osmosis were performed to investigate how contaminants of interest in produced water were effectively removed especially total organic carbon and total dissolved solids for the purpose of an irrigation of switch grass and canola (Caschette, 2016).

2.5 Method of analysis organic compounds for produced water

A common practice for oil and gas production companies is to dilute the produced water by mixing with fresh water, either due to water quality concerns or lack of recycled water volumes (USDOE, 2009a; USDOE, 2009b; Jenner and Lamadrid, 2013; Spellman, 2012; Carter, et al, 2013). Treatment processes for recycling water are typically designed to remove particles and disinfect

the water and therefore much of the organic matter returned during flowback remains (Hickenbottom, et al, 2013). Carter et al . (2013) reported that the mass spectra of produced water samples between inflow and effluent from a centralized water treatment facility were almost identical in spectra using liquid chromatography-mass spectrum (LC-MS) analysis. Since characteristics of flowback /produced water can be affected by the geological formation, high temperatures and the presence of breakers, the analysis of flowback/produced water for specific organic compounds is difficult.

Due to presence of various chemicals introduced as fracturing additives, including toxic chemicals (e.g. 2-butoxyethanol, ethylene glycol, etc.) or biocides (e.g., glutaraldehyde), biological treatment is not a reasonable choice (Rogers, et al, 2015; Stringfellow, et al, 2014). High levels of total organic carbon (TOC) in flowback/produced water can negative impact on the membrane processes and make it difficult to use as a direct treatment option (Pandey, et al, 2012).

Rosenblum et al. (2016) investigated the chemical coagulants and powdered activated carbon to lower level of water quality parameters such as dissolved organic carbon, polyethylene glycols and total petroleum hydrocarbons from produced water in Colorado. Thurman et al. (2017) identified polypropylene glycols and polyethylene glycol carboxylates from flowback and produced water from hydraulic fracturing by using ultrahigh-performance liquid chromatography/quadrupole-time-of-flight mass spectrometry (Thurman, et al, 2017).

3. Research Hypothesis and Objectives

3.1 Reserch hypothesis

The research hypotheses are:

- I. Different frac fluid types can affect inorganic and organic constituents in flowback/produced water with respect to well ages.
- II. Different fracturing fluid types (gel and slickwater) can affect treatment of inorganic and organic constituents in flowback/produced water with coagulation-/flocculation jar testing in terms of well ages.
- III. Frac additives mixed with freshwater and recycled water from other fracturing operations may have different treatment efficiencies.

3.2 Research objectives

- I. Characterize the variation in organic and inorganic constituents in the flowback/produced water with respect to time and frac fluid composition.
 - Select two wells which are within 100 yard and fractured different frac fluid.
 - Collect flowback/produced water samples at 2 hour intervals from 0 to 1 day, at 6 hour intervals from 1 to 3 days, at 12 hour intervals from 3 to 5 days and at 24 hour intervals from 6 to 12 days. More samples were collected at 30 days, 70 days, 102 days, 145 days and 203 days.
 - Measure main inorganics and pH, TOC and TDS.
 - Calculate the charge balance to evaluate the inorganic result.

- Create inorganics and pH, TOC and TDS graph with temporal variability from two different wells.
 - Make the piper diagram to analyze the similarities and difference in the water chemistry.
 - Check the correlation between main inorganics and TDS by temporal variability.
 - Conduct statistical analysis between TDS and main inorganics from different frac fluid by using nonlinear regression model with dummy variable.
 - Check statistical analysis of water quality parameters in terms of temporal variability for flowback water from different frac fluid by using nonlinear regression model with dummy variable.
 - Calculate mass balance of zirconium and aluminum during 200 days.
- II. Identify the variability of produced water quality with well age and fracturing fluid type.
- Select three wells fractured slickwater, gel fluid and hybrid (using both slickwater and gel fluid) which are within 20 meters.
 - Collect sampling over 63-days period after flowback began from three wells.
 - Measure main inorganics, organics, pH, conductivity, and pH.
 - Create water quality parameters graph by temporal variability to compare three wells.
 - Conduct coagulation-flocculation jar testing by temporal variability from three wells and determine the variability in optimum dose.
 - Conduct by Liquid chromatography–mass spectrometry (LC-MS) for sample analysis from Well S and Well G at 4, 25, and 56 days.
 - Identify organic matter by using Agilent Technology Software linked to a library based on the exact mass of chemicals used for hydraulic fracturing between 2005 and 2009 in U.S.

- Simulate chemical equilibrium modeling to determine the forms in which ions actually exist in the solution by using OLI stream analyzer.
- III. Determine organic compound characteristics in recycled and fresh water mixed with frac additives that are not affected by the formation, only thermal and oxidative degradation.
- Analyze recycled water with frac additives (RWA) and fresh water with frac additives (FWA) by using Liquid chromatography–mass spectrometry (LC-MS).
 - Measure recycled water quality.
 - Compare mass spectrum and mass spectra of RWA and FWA.
 - Observe ethoxylated functional group and propylene oxide functional group from FWA and RWA.
 - Identify organic matter of FWA and RWA by using Agilent Technology Software linked to a library based on the exact mass of chemicals used for hydraulic fracturing between 2005 and 2009 in U.S and compare organic matter of FWA and RWA.
 - Make the van Krevelen diagrams to identify structure relationships.
 - Analyze the Kendrick mass defect analysis of ethylene oxide unit and propylated glycol.
 - Perform double bond equivalent (DBE) analysis versus carbon distribution.
 - Make categories of carbon content.
- IV. Organic characteristic of flowback/produced water will be much different after wastewater treatment processes
- Collect flowback/produced water samples.
 - Conduct electrocoagulation/ultrafiltration/granular activated carbon process and reverse osmosis process.

- Run gas chromatography–mass spectrometry (GC-MS) for raw flowback/produced water samples and after each wastewater treatment process to check ethylene glycol butyl ether, ethylene glycol and propylene glycol.
- Compare Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) before treatment and after treatment.
- Measure total dissolved solids (TDS), total organic carbon (TOC) and dissolved organic carbon (DOC) to compare before treatment and after treatment

4. Temporal Analysis of Flowback and Produced Water Composition from SHALE Oil and Gas Operations: Impact of Frac Fluid Characteristics¹

4.1 Introduction

Energy demand is estimated to increase at an annual rate of 0.2 % from 2010 through 2035, and electricity demand will grow by 0.8 % per year (AEO 2012). The successful development of the shale gas industry in the United States is expected to meet an increasing fraction of the energy demand and has spurred an interest in its potential in other parts of the world (GNS, 2012). In the U.S, the technically recoverable reserves of shale gas are greater than 1,452 trillion cubic feet (USEIA, 2013), a supply that could potentially power this country for up to 100 years.

The primary advantages of utilization of natural gas are its widespread accessibility, easy transport and relative to coal, clean combustion (Gregory, et al, 2011; Jaramillo, et al, 2007). However, the hydraulic fracturing process, used to enable economical production from low permeability unconventional reservoirs such as shale oil and shale gas formations, can place increased pressure on the use of finite natural resources such as fresh water, raising social concerns in the community. Even though statewide estimates of water withdrawal for hydraulic fracturing has been estimated to be less than 0.1% of total water usage in Colorado (COGCC, 2015), there have been local issues related to water sourcing and competition. Recycling of flowback and produced water for beneficial use is being pursued in many parts of the country and this trend is expected to minimize concerns related to hydraulic fracturing and regional water depletion.

¹ As Published to Journal of Petroleum Science and Engineering

Seongyun Kim^a, Pinar Omur-Ozbek^a, Ashwin Dhanasekara, Adam Prior^b, Ken Carlson^a

^a Department of Civil and Environmental Engineering, Colorado State University, Fort Collins, CO 80523-1372, USA

^b Noble Energy

The water demands for drilling and hydraulic fracturing are different depending on the formation depth, formation permeability, in-situ stress in the pay zone, in-situ stresses in the surrounding layers, reservoir pressure, formation porosity, formation compressibility, and the thickness of the reservoir (USDOE, 2004). In addition, fracturing fluid formulations may influence the volume of water required for a particular fracturing treatment. On average, water consumption to complete horizontal wells is between 2-5million gallons of water (Goodwin, et al, 2012; Hickenbottom, et al, 2013; Lee, et al, 2011; Nicot and Scanlon, 2012; Rahm, 2011; Stephenson, et al, 2011; Suarez, 2012).

The flowback/produced water recovered from fracturing operations during the completion of the well may vary greatly in character depending on location of the wells due to different formations (spatial variation), the time the water is collected after well completion (temporal variation) (Barbot, et al, 2013). The injected different frac fluid might also be expected to affect flowback/ produced water quality. However, there is no study investigating the flowback/produced water quality based on different frac fluid with temporal variation in Wattenberg field in Colorado. Reusing of flowback/produced water cannot be performed without understanding the water quality characterization. Flowback/produced water reusing varies based on factors, involving regulations, availability of injection, scale of development and accessibility of water treatment infrastructure (Rahm, et al, 2013).

The objective of this study was to characterize the variation in organic and inorganic constituents in the flowback/produced water with respect to time and frac fluid composition. To understand the temporal variation, the samples were collected for a 200-day period from two co-located wells that were completed using significantly different frac fluids.

The characteristics of produced water from conventional and unconventional oil and gas reservoirs and the possible treatment guidelines for produced water have been published (Andrew, et al, 2005; Fakhru'l-Razi, et al, 2009; Sirivedhin and Dallbauman, 2004). This study focused not on the produced water treatment but how the produced water quality changes with well age and two representative frac fluids.

4.2 Materials and methods

4.2.1 Composition of frac fluid

Oil and gas service companies have been working on developing the most the effective hydraulic frac fluid composition to achieve a higher conductivity of the proppant pack placed during the fracturing operation in order to increase the production rate of oil and gas wells. The well performance depends largely on how well the proppant is transported down the wellbore into the reservoir and how long the proppant remain suspended in the frac fluid (FFCF, 2000). The main considerations for the frac fluid are the fracture conductivity, proppant transport, and the mitigation of potential formation permeability damage that may be induced during frac operation (Dusterhoft, et al, 2009).

For this study, the flowback water quality characteristics from wells completed with two different frac fluids that are used in the Wattenberg field in northeastern Colorado are compared. The components of Frac Fluid A and Frac Fluid B are summarized in Table 4.1.

The main differences between the frac fluids are the use of either a residue-free polysaccharide or derivatized guar as gelling agents and the initial pH value. Zirconium (Zr) is used as the polymer cross-linker for both fluids. In addition, EDTA was only used in Frac Fluid B as an activator.

Table 4.1. Summary of frac fluid components (Frac Focus Chemical Disclosure Registry, 2013).

Component	Ingredients	
	Frac Fluid A(pH=5.0)	Frac Fluid B – High pH=10.2
Proppant	Crystalline silica, quartz	Crystalline silica, quartz
Friction Reducer	Hydrotreated light petroleum distillate	Hydrotreated light petroleum distillate
Crosslinker	Ammonium chloride	Ammonium chloride
	Zirconium, acetate lactate ammonium complex	Zirconium, acetate lactate ammonium complex
	Inorganic Salt	Glycerin, propanol
		Triethanolamine Zirconate
Additive	Ammonium salt	Ammonium salt
Breaker	Chlorous acid	Chlorous acid
	Sodium chloride	
	Ammonium persulfate	Sodium chloride
	Crystalline silica, quartz	
	Sodium persulfate	
Biocide	4,4Dimethyloxazolidine	4,4Dimethyloxazolidine
	3,4,4-Trimethyloxazolidine	3,4,4-Trimethyloxazolidine
	2-Amino-2-methyl-1-propanol	2-Amino-2-methyl-1-propanol
	Glutaraldehyde	Acetone, glutaraldehyde
Buffer	Acetic acid	Potassium carbonate
	Ammonium acetate	
Non-ionic Surfactant	1,2,4 Trimethylbenzene	Ethanol
	Ethanol	
	Aromatic petroleum naphtha	Methanol
	Naphthalene91-20-3	
	Poly(oxy-1,2-ethanediyl),alpha-(4-nonylphenyl)-omega-hydroxy	Terpenes and terpenoids
Gelling Agent	Residue-free polysaccharide	Guar gum derivative
Surfactant	Proprietary Component	-
	Isopropanol67-63-0	
	Terpenes and Terpenoids	
Activator	-	EDTA/Copper chelate
		Diethylenetriamine
Scale Inhibitor	-	Ethylene Glycol
		Substituted Carboxylate

4.2.2 Sample collection

The flowback/produced water samples were collected from two horizontal wells located in Northeast Colorado. The flowback water sampling began on March 21, 2013. Samples were

collected at 2 hour intervals from 0 to 1 day, at 6 hour intervals from 1 to 3 days, at 12 hour intervals from 3 to 5 days and at 24 hour intervals from 6 to 12 days. More samples were collected at 30 days, 70 days, 102 days, 145 days and 203 days from the Frac Fluid B well, and at 20 days, 70 days, 102 days, 146 days and 202 days for the Frac Fluid A well. The wells were on the same pad, located 100 yards apart at the same depth within 50 feet and therefore minimal formation variability was assumed.

4.2.3 Analytical methods

Sodium, calcium, magnesium, potassium, iron, zirconium, silicon, strontium, barium, boron, and aluminum were quantified using USEPA method 6010C (ICP-AES); chloride and sulfate were measured with USEPA Method 300 (IC); carbonate and bicarbonate were measured with USEPA Method 310. A Shimadzu TOC-VCSH analyzer with a detection limit of 5µg/L was used to measure the TOC concentrations in the flowback/produced water samples.

4.3 Results and discussions

4.3.1 Impacts of temporal variation on flowback water quality

A summary of pH from Frac Fluid A and B wells with well age is shown in Figure 4.1. The range of pH was between 6.62 and 7.94 with 7.22 of average from Frac Fluid A (initial pH=5) and between 6.06 and 7.65 with 7.13 of average from Frac Fluid B (initial pH=10). The pH value were fluctuated about until 30 days and were stable after 30 days to 200 days. The initial pH values in the flowback for Frac Fluid A and B were similar even though the fluid pH values were significantly different, indicating the influence of the formation on buffering and determining flowback ionic composition.

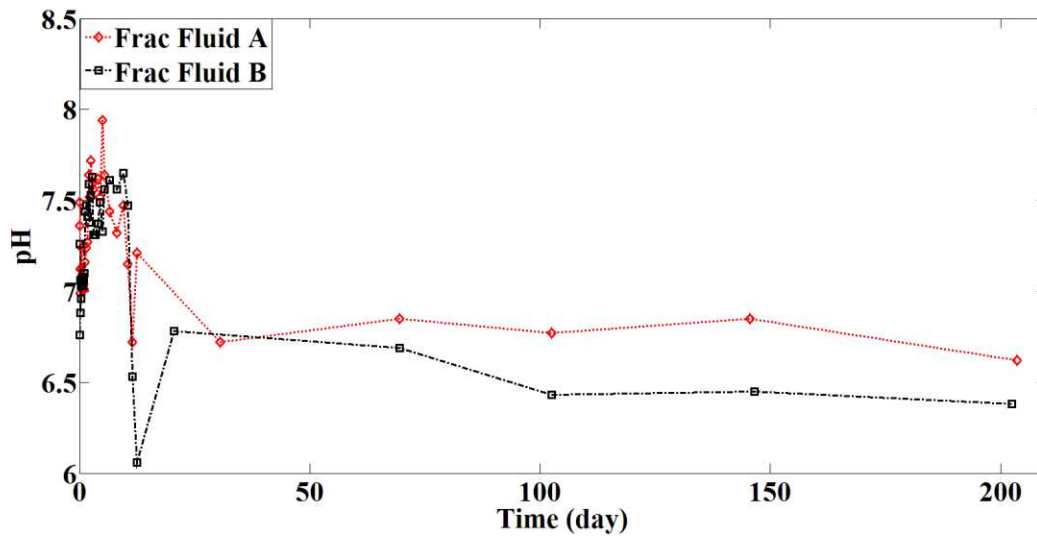


Figure 4.1. pH in flowback from both Frac Fluid A and B.

To evaluate the inorganic analytic results, charge balances were calculated with major elements (aluminum, calcium, magnesium, potassium, sodium, strontium, chloride, sulfate and bicarbonate) and the deviation from zero is shown in Figure 4.2. Charge balance means that sum of positive charge should equal the sum of negatives in aqueous solution. Charge balance is generally used to evaluate the validity and water quality analysis. In general, the anions and cations balanced within 5%, an acceptable result.

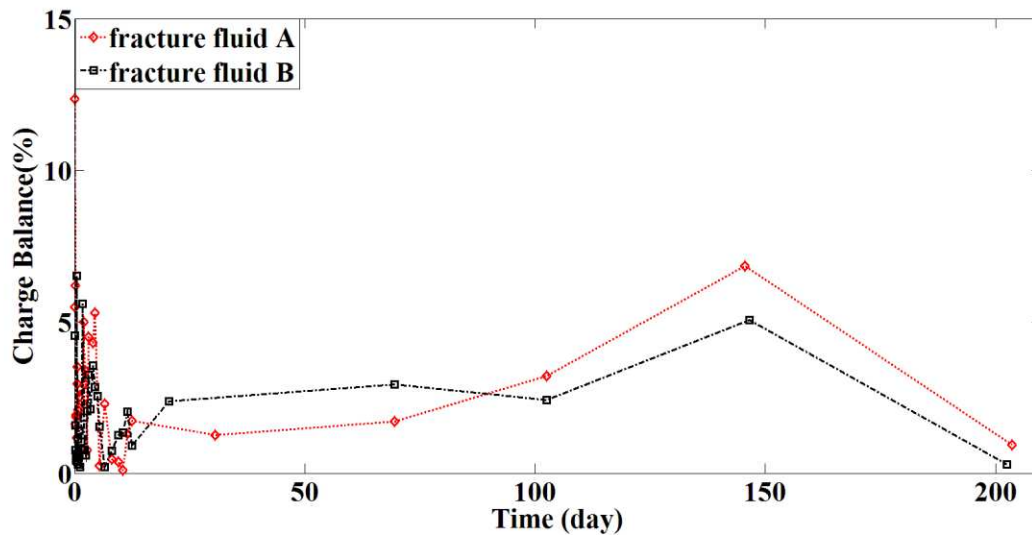
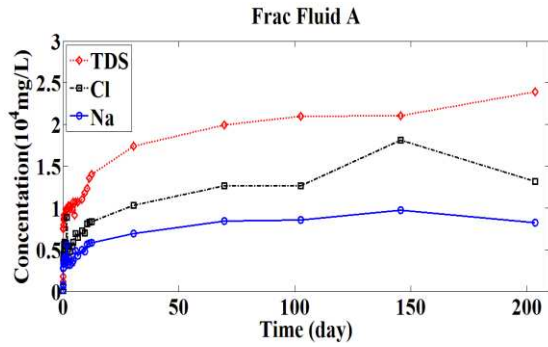


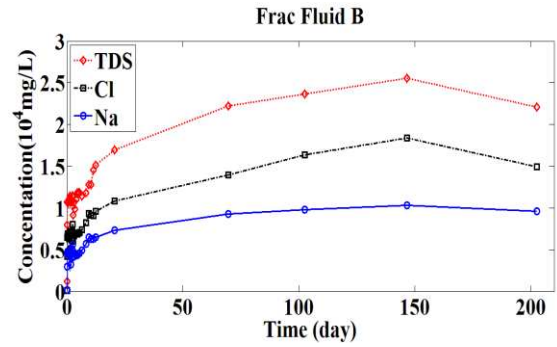
Figure 4.2. Charge balance in flowback from both Frac Fluid A and B.

Total dissolved solid (TDS) measurement is an easy and reliable way to predict aggregate water quality parameters and better manage the water quality in shale oil and shale gas produced water. A summary of the inorganic constituents in the two different frac fluids with temporal variation is shown in Figure 4.3 and Figure 4.4. The dominant inorganics in flowback/produced water were determined as chloride, sodium and calcium and all slightly increased until day 150, following a trend similar to TDS. Chloride, sodium and calcium concentration were stable or slightly decreased after 150 days. The concentrations of Cl, Na and Ca were similar in both fracture fluids. Barium and strontium were measured at lower levels and the concentrations increased with time similar to TDS, however, the levels of Ba and Sr were slightly higher in Frac Fluid B (high pH) flowback water. Sulfate and zirconium levels in both flowback waters decreased drastically after 30 days.

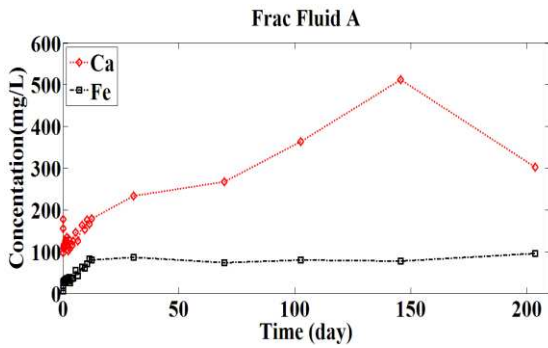
(a)



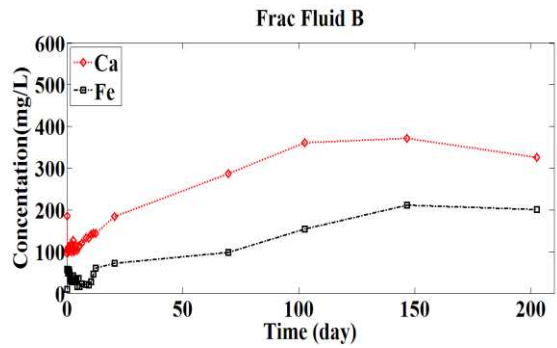
(b)



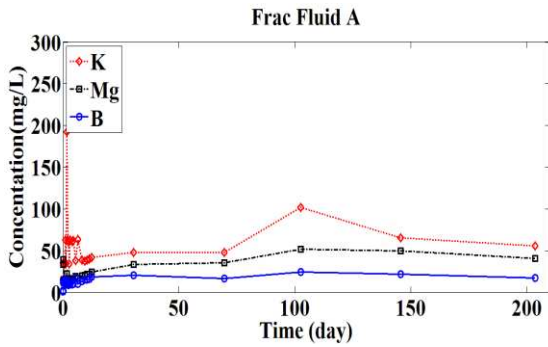
(c)



(d)



(e)



(f)

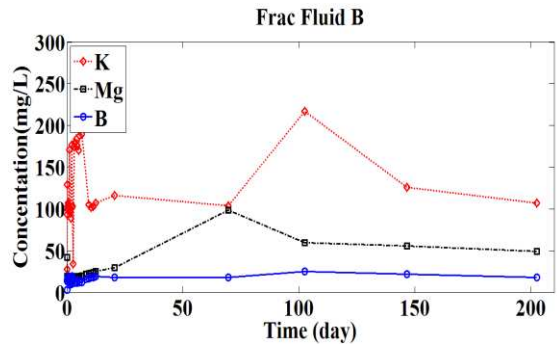
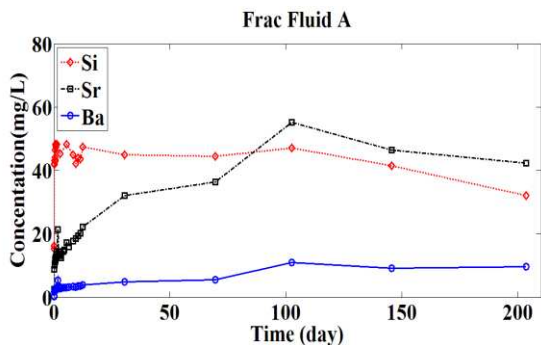


Figure 4.3. Concentration profiles for all inorganics for different frac fluid with time.

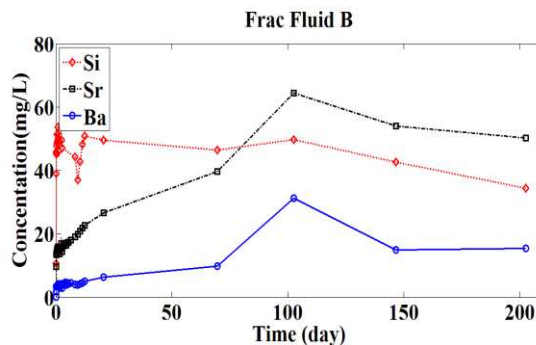
Decrease in sulfate concentrations may be attributed to its removal through precipitation and/or the low levels of sulfate in the formations. It is assumed that Zr is not coming from the formation and the decrease in concentration is due to washout from the well. Boron remained

stable in both frac fluid flowback waters throughout the analysis period and its presence is likely due to dissolution of the formation. The concentration of silicon for both frac fluids did not exhibit a trend indicating a chemical equilibrium had been reached.

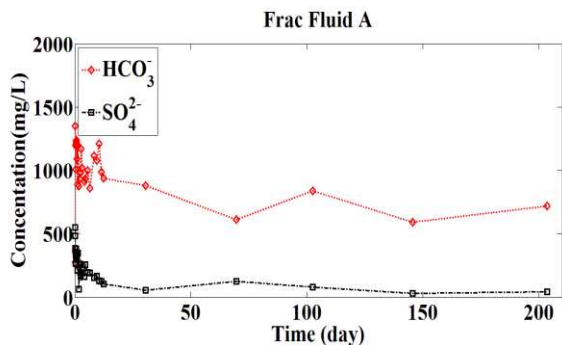
(a)



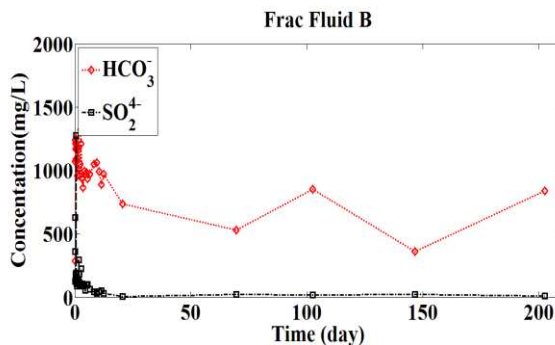
(b)



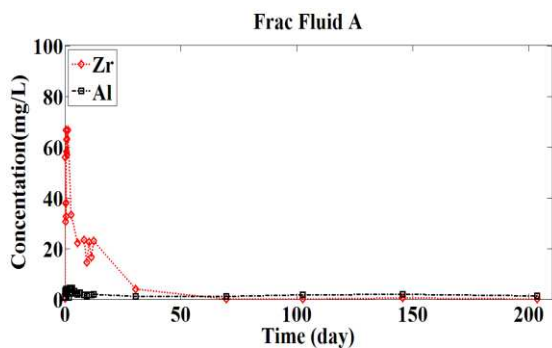
(c)



(d)



(e)



(f)

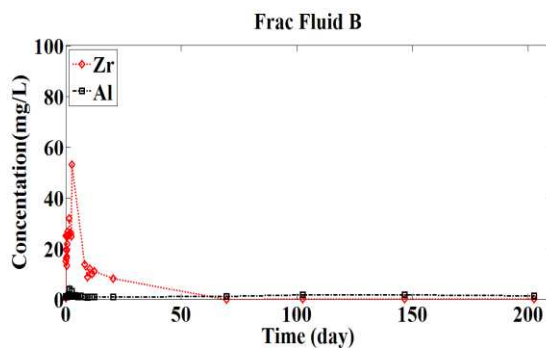


Figure 4.4. Concentration profile for all inorganics for different frac fluid with time.

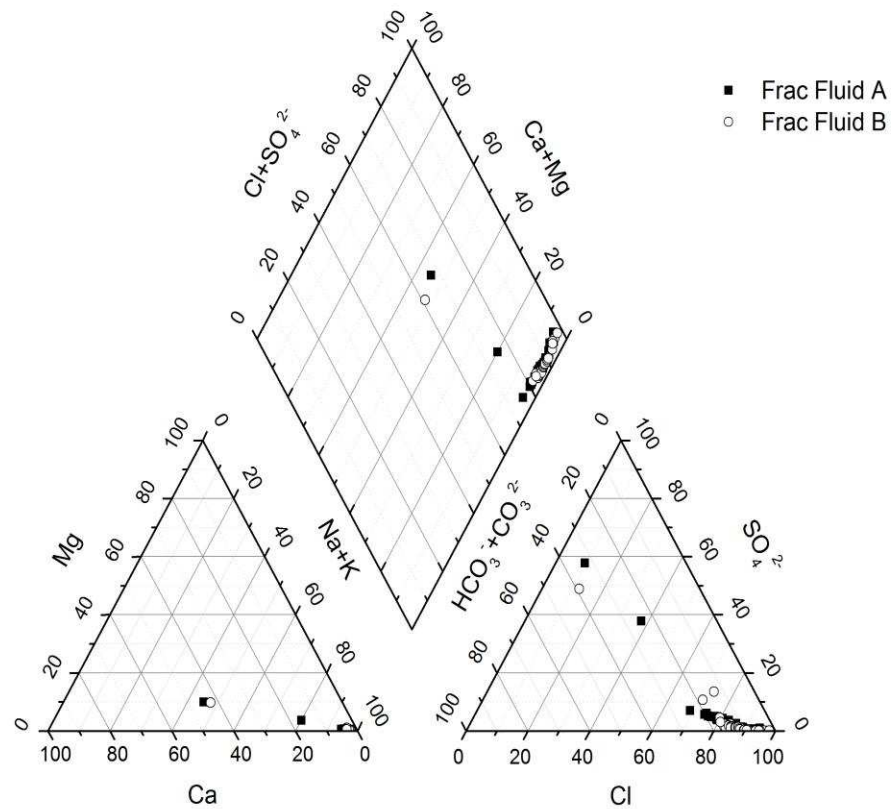


Figure 4.5. Piper diagram showing the produced water quality from Frac Fluid A and B. Ions are presented as percentages.

A piper diagram is commonly used to analyze the similarities and differences in the water chemistry and to sort them into chemical types (Chadha, 1999). Many studies have presented the application of the Piper diagram to explain the chemical process in water samples (Jalali, 2011; Parasanna, et al, 2011; Subba Rao, et al, 2012). The data from this study is presented as a Piper diagram Figure 4.5. Frac Fluid A and B show similar trends in terms of water types and it is evident that Na-Cl predominates in water samples from both Frac Fluid A and B, exhibiting highly saline water. In addition, Na-Cl ratio is higher in later flowback water than early flowback water.

Potassium and iron levels were much higher in the Frac Fluid B flowback water than the initially lower (pH 5.0) Frac Fluid A flowback water. Potassium was added with Frac Fluid B as part of the buffer package to achieve a pH of 10 whereas there was no addition of this element with Frac Fluid A.

The organic constituents in the frac fluids were measured as total organic carbon (TOC) and shown in Figure 4.6. TOC concentrations in both frac fluids fluctuated significantly before 30 days but stabilized at 2000 mg/L after this period and show similar concentrations for both flowback scenarios.

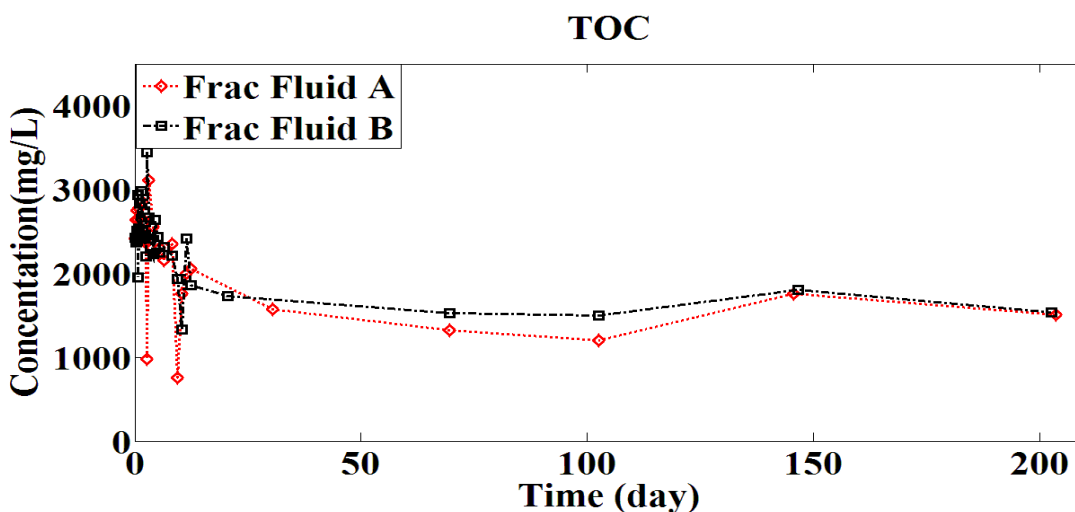


Figure 4.6. Total organic carbon (TOC) concentrations in flowback water.

The correlation of calcium, chloride, sodium, barium, magnesium, strontium, boron and iron with TDS was also studied. In flowback/produced water, salt layers in the formation containing these elements can dissolve and contribute to salinity in flowback and produced water. Correlations of the key ions (barium, calcium, chloride, magnesium, sodium, strontium, boron and iron) with TDS for the two flowback waters are shown in Figure 4.7 and Figure 4.8. To fit the trend line, a log-log graph was used and the analysis indicated that there is a significant positive

correlation between the key ions and TDS, with R^2 values greater than 0.85, except for boron and iron. The best correlation was obtained for sodium.

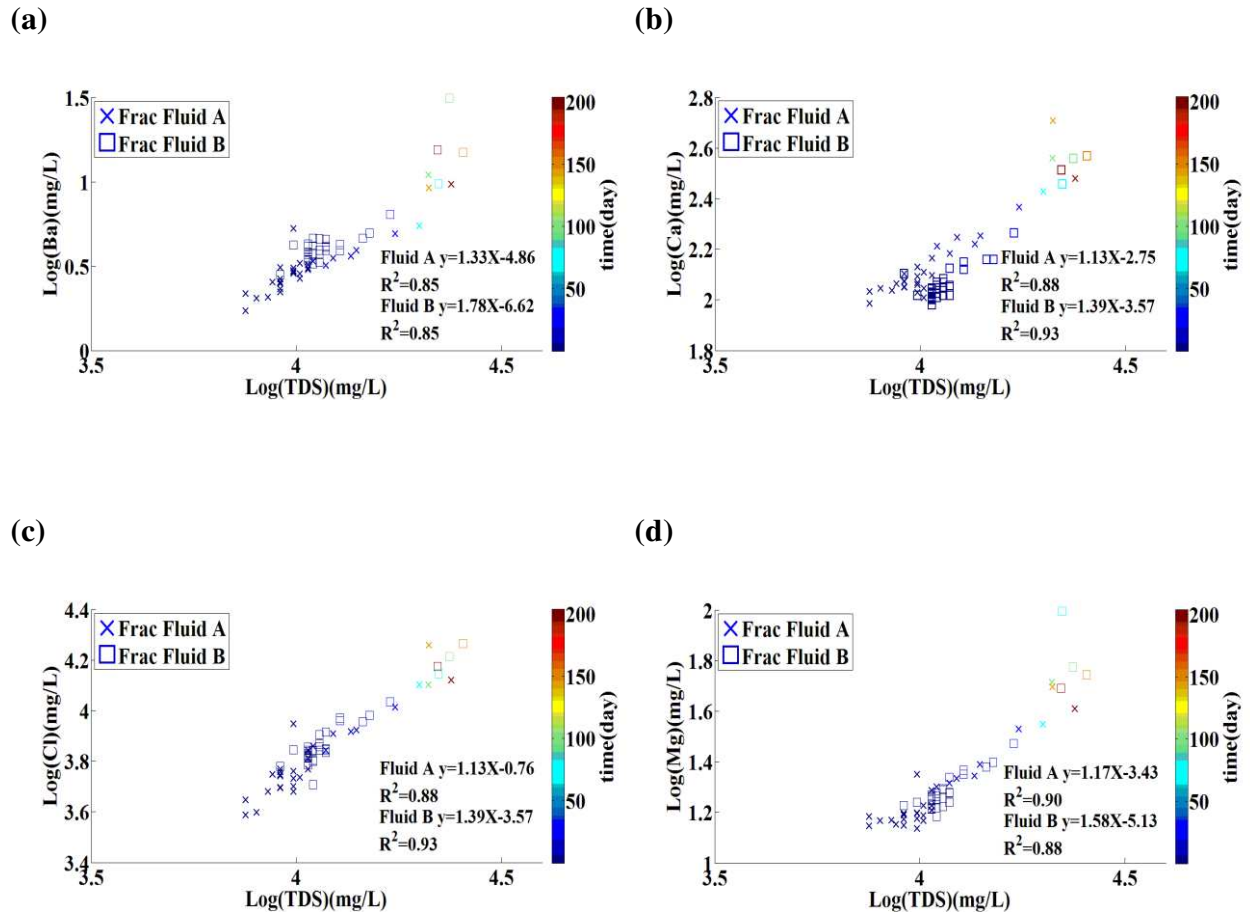


Figure 4.7. Correlation of major ions with TDS in the flowback/produced water.

The correlation results shown in Figure 4.7 and Figure 4.8 indicate that all of the ions are increasing with TDS and time and therefore are sourced from the formation itself. At least for the major ions shown here, there appears to be no depletion effect as frac fluid-based water is extracted.

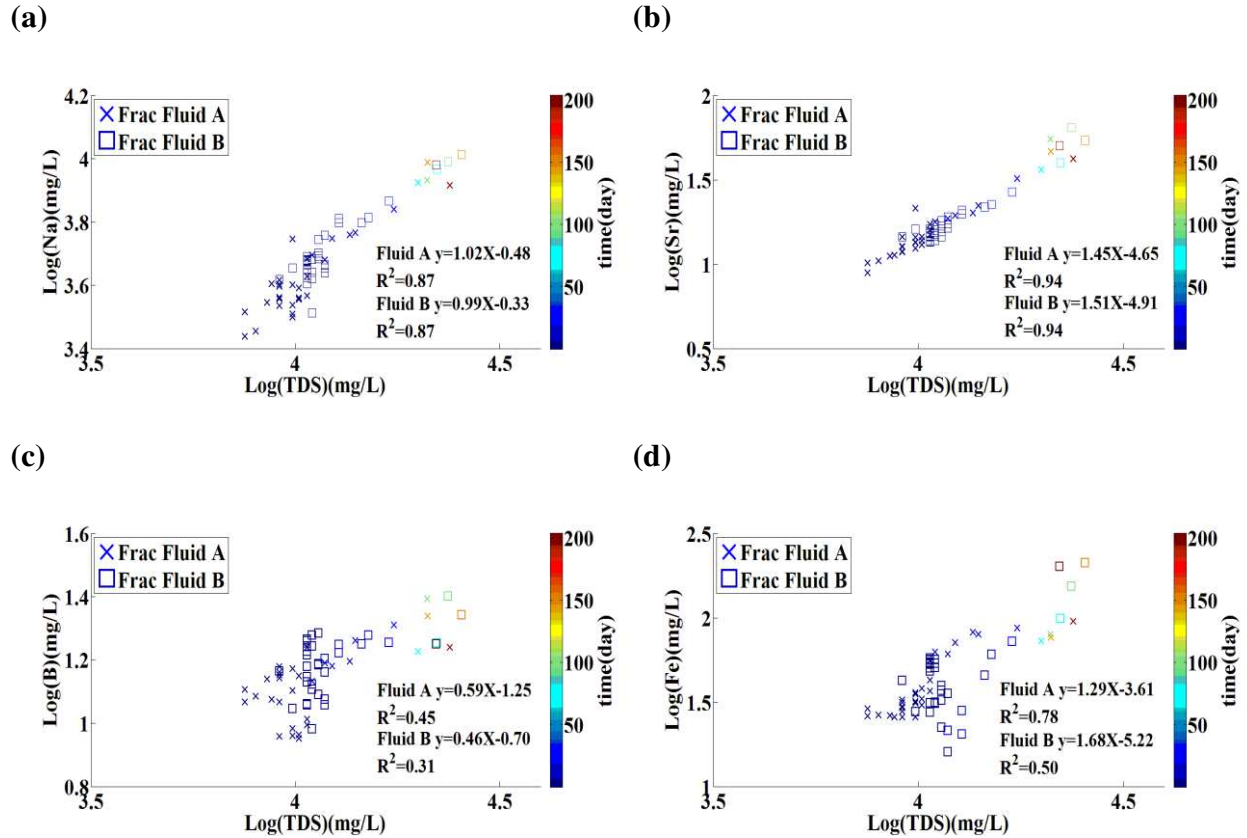


Figure 4.8. Correlation of major ions with TDS in the flowback/produced water.

4.3.2 Different frac fluid trends in flowback/produced water

It is difficult to estimate the flowback/produced water quality parameters since there are many variables that may affect the concentrations of the constituents. However, it is essential to analyze and predict the flowback/produced water quality for recycling purposes as it may be economically feasible to treat and use the water on-site. For this study, the wells were located very close to each other so the variability due to the geological formation was assumed to be insignificant. Hence, all major water quality parameters were assumed mainly affected by the temporal variation and the initial frac water composition. Since the flowback water quality changed significantly with well age, a nonlinear regression model was used to account for outliers and correct for failures of distribution normality (Eqn. 1).

$$Y = \alpha_1 X^{\alpha_2} \quad (1)$$

Where Y is the concentration of the selected constituent, X is TDS and α_1, α_2 are fitted parameters. A logarithmic approach is a common transformation for nonlinear equations and was selected for this trend analysis, resulting in Equations 2 and 3.

$$Y' = \log Y \quad (2)$$

$$X' = \log(TDS) \quad (3)$$

Simple linear regression modeling was then used leading to Equation 4.

$$\log(Y) = \alpha_1 + \alpha_2 \log(TDS) \quad (4)$$

In this model, dummy variable T was used, which was set to 0 if the water quality parameters come from Frac Fluid A, and T was 1 if the data come from Frac Fluid B. That is,

$$T = \begin{cases} 0, & \text{if data come from fracture fluid A} \\ 1, & \text{if data come from fracture fluid B} \end{cases} \quad (5)$$

By combining Equations (4) and (5), the following equation is obtained:

$$\log Y = \alpha_1 + \alpha_2 \log(TDS) + (\alpha_3 + \alpha_4 \log(TDS)) \times T \quad (6)$$

Where $\alpha_1, \alpha_2, \alpha_3$ and α_4 are the fitting coefficients and T is a dummy variable. Two different equations were acquired based on the different frac fluids:

$$\log(Y_A) = \alpha_1 + \alpha_2 \log(TDS_A) \quad (7)$$

$$\log(Y_B) = (\alpha_1 + \alpha_3) + (\alpha_2 + \alpha_4) \log(TDS_B) \quad (8)$$

The results obtained from the non-linear regression analyses are summarized in Table 4.2.

Table 4.2. Statistical and estimated coefficients for models of water quality parameters versus TDS obtained from equations (7) and (8).

	α_1	p-value	α_2	p-value	α_3	p-value	α_4	p-value	R^2
Barium	-4.854	<0.001	1.329	<0.001	-1.767	0.010	0.451	0.008	0.866
Calcium	-2.754	<0.001	1.215	<0.001	-0.812	0.068	0.172	0.114	0.906
Chloride	-0.761	0.004	1.132	<0.001	0.136	0.727	-0.028	0.770	0.907
Magnesium	-3.429	<0.001	1.165	<0.001	-1.596	0.002	0.388	0.002	0.895
Sodium	-0.480	0.074	1.021	<0.001	0.147	0.716	-0.031	0.758	0.879
Strontium	-4.649	<0.001	1.452	<0.001	-0.262	0.505	0.059	0.542	0.940

If p-value in bold is higher than 0.05, the constant α_i is not a significant constant.

The null hypothesis for the nonlinear regression model was that all coefficients α_i are equal to zero and the alternative hypothesis was that α_i is not zero. Coefficients α_1 , α_2 and α_3 , α_4 are fitting constants for Frac Fluids A and B independently. Constants α_3 , and α_4 indicate a statistically significant difference between fracture fluids A and B. Higher values obtained for the coefficients of determination indicate that the TDS is strongly correlated to the particular ion and shows that TDS may be used as an indicator of the levels of that particular ion in the flowback/produced water.

As can be observed from Table 4.2, except for barium and magnesium, p-values of α_3 and α_4 were determined to be higher than 0.05, meaning that the fitted parameters are not significant. Hence, α_3 and α_4 are taken as zero, which means there was no statistically significant difference of flowback/produced water quality between the two different frac fluids. However, for barium and magnesium this is not the case and hence the water quality has a different trend between Frac Fluids A and B. This might be due to different initial pH values that may have affected the release and precipitation of barium and magnesium.

P-values for α_3 and α_4 for sodium, chloride and strontium were relatively high, indicating similarity between Frac Fluids A and B. However, the p-value for α_1 for sodium was slightly higher than 0.05, meaning that the variability of sodium concentrations at the beginning of water extraction was relatively high. Calcium also exhibits a similar trend as sodium, chloride and strontium. However, the p-value for α_3 and α_4 were slightly higher than 0.05.

To check temporal variability for flowback water from different frac fluids, the same approach was applied by changing the X-value from log(TDS) to log(Time). The results are summarized in Table 4.3.

Table 4.3. Statistical and estimated coefficients for models of water quality parameters versus time.

	α_1	p-value	α_2	p-value	α_3	p-value	α_4	p-value	R^2
Aluminum	0.475	<0.001	-0.156	<0.001	-0.391	<0.001	0.172	<0.001	0.587
Barium	0.409	<0.001	0.213	<0.001	0.139	<0.001	0.015	0.667	0.753
Boron	1.085	<0.001	0.083	<0.001	0.087	0.002	-0.044	0.141	0.303
Bicarbonate	3.045	<0.001	-0.083	<0.001	0.005	0.772	-0.023	0.254	0.590
Calcium	2.063	<0.001	0.190	<0.001	-0.044	0.064	-0.007	0.787	0.786
Chloride	3.723	<0.001	0.181	<0.001	0.097	<0.001	-0.037	0.083	0.810
Iron	1.505	<0.001	0.218	<0.001	0.076	0.181	-0.089	0.139	0.363
Magnesium	1.188	<0.001	0.181	<0.001	0.043	0.118	0.016	0.574	0.733
Potassium	1.635	<0.001	0.078	0.024	0.414	<0.001	-0.029	0.547	0.659
Sodium	3.565	<0.001	0.161	<0.001	0.091	<0.001	-0.035	0.112	0.760
Strontium	1.101	<0.001	0.232	<0.001	0.066	0.003	-0.028	0.227	0.855
Sulfate	2.419	<0.001	-0.305	<0.001	-0.269	<0.001	-0.156	0.022	0.743
Silicon	1.653	<0.001	-0.012	0.172	0.030	0.026	-0.009	0.461	0.230
Zirconium	1.586	<0.001	-0.893	<0.001	-0.266	0.151	0.053	0.761	0.700
TOC	3.386	<0.001	-0.114	<0.001	0.008	0.770	0.034	0.255	0.424

If p-value in bold is higher than 0.05, the constant α_i is not significant constant.

P-value for α_3 and α_4 for aluminum was less than 0.05, meaning that there is a statistically significant difference between the Frac Fluids A and B with time.

Bicarbonate, calcium, iron, magnesium, zirconium and TOC exhibited a statistically identical behavior for the two different Frac Fluids A and B with time since all p-values for α_3 and α_4 were higher than 0.05. However, iron's p-value for α_3 and α_4 was just slightly higher than 0.05. P-values for α_3 for barium, boron, chloride, potassium, sodium, strontium, sulfate and silicon were less than 0.05. On the other hand, all p-values for α_4 were higher than 0.05. This could mean that

there is a different y-intercept between frac fluids with time, indicating there exists a different flowback water concentration between frac fluids during the early stages of flowback. However, aluminum, boron, bicarbonate, iron, potassium, silicon, and TOC cases show a comparatively low coefficient of determination (R^2), less than 0.7.

4.3.3 Mass balance and recovery

The water volume recovery is estimated to be about 20%-40% during the initial flowback period of 3-4 weeks suggesting that more than half of the frac fluid additives stay in the formation during this period (Bai, et al, 2013) and only between 5 and 60 percent of water flow back as flowback/produced water when the pressure is down (USDOE, 2009; Clark, et al, 2012; Rahm and Riha, 2012; Suarez, 2012). However, the frac fluid additive mass recovery varies based on geochemical formation characteristics and the fate of the compound relative to this. For the current study, a simple mass balance approach was applied to evaluate how much of selected additives were recovered in flowback water for the different frac fluids and compare these values to how much flowback water was recovered during the first 200 days.

Zirconium was selected since it is added to the fluid as a cross-linker and the concentrations at $t > 60$ days are less than 0.1 mg/L, indicating minimal contribution from the formation. Potassium was selected because it was a component in Frac Fluid B but not a significant additive with Frac Fluid A. Initially during flowback, the zirconium concentration was approximately 20 mg/L for Frac Fluid A (Figure 4.4 (e)) and 15mg/L for Frac Fluid B (Figure 4.4 (f)). The potassium concentration was relatively stable over time, approximately 200 mg/L for flowback water from the Frac Fluid B well and 100 mg/L from the Frac Fluid A well.

Mass balance calculations were made based on data obtained from fracfocus.org including water volume injected, identity of additives and a range of their concentrations. Table 4.4 shows a

summary of the data that was used for the zirconium, potassium and aluminum mass balances in this analysis. The concentrations shown Table 4.4 were obtained by measuring lab created frac fluid according to the methods described in 4.2.3

Table 4.4. Summary of frac fluid ingredients and mass concentration of both wells.

Well Name	Water input(liters)	Ingredients	Concentration(mg/l)	Input Mass(Kg)
Frac Fluid A	15.9x10 ⁶	Zr	83.4	1,328
		Al	26.8	426
Frac Fluid B	18.1x10 ⁶	Zr	30.6	554
		K	159.0	2,883

Results from the analysis include an estimation of the volume of flowback over time based on a water production model developed with 86 surrounding wells (Bai, et al, 2013). Using this Arps-equation based water production model (Arps, 1944), cumulative output water volume during 1-200 days was estimated to be 7.45x10⁶ liters and this is compared to input volumes of 15.9x10⁶ liters for Frac Fluid A and 18.1x10⁶ liters for Frac Fluid B (actual frac operation report). The estimated fraction of flowback water recovered during the first 200 days was 47% for the Frac Fluid A well and 41% for the Frac Fluid B well.

The time-based concentrations of Zr, K and Al were multiplied by the flowback water volume and compared to total mass of these elements added. The measured concentration values of frac fluid in the laboratory are provided in Figure 4.9

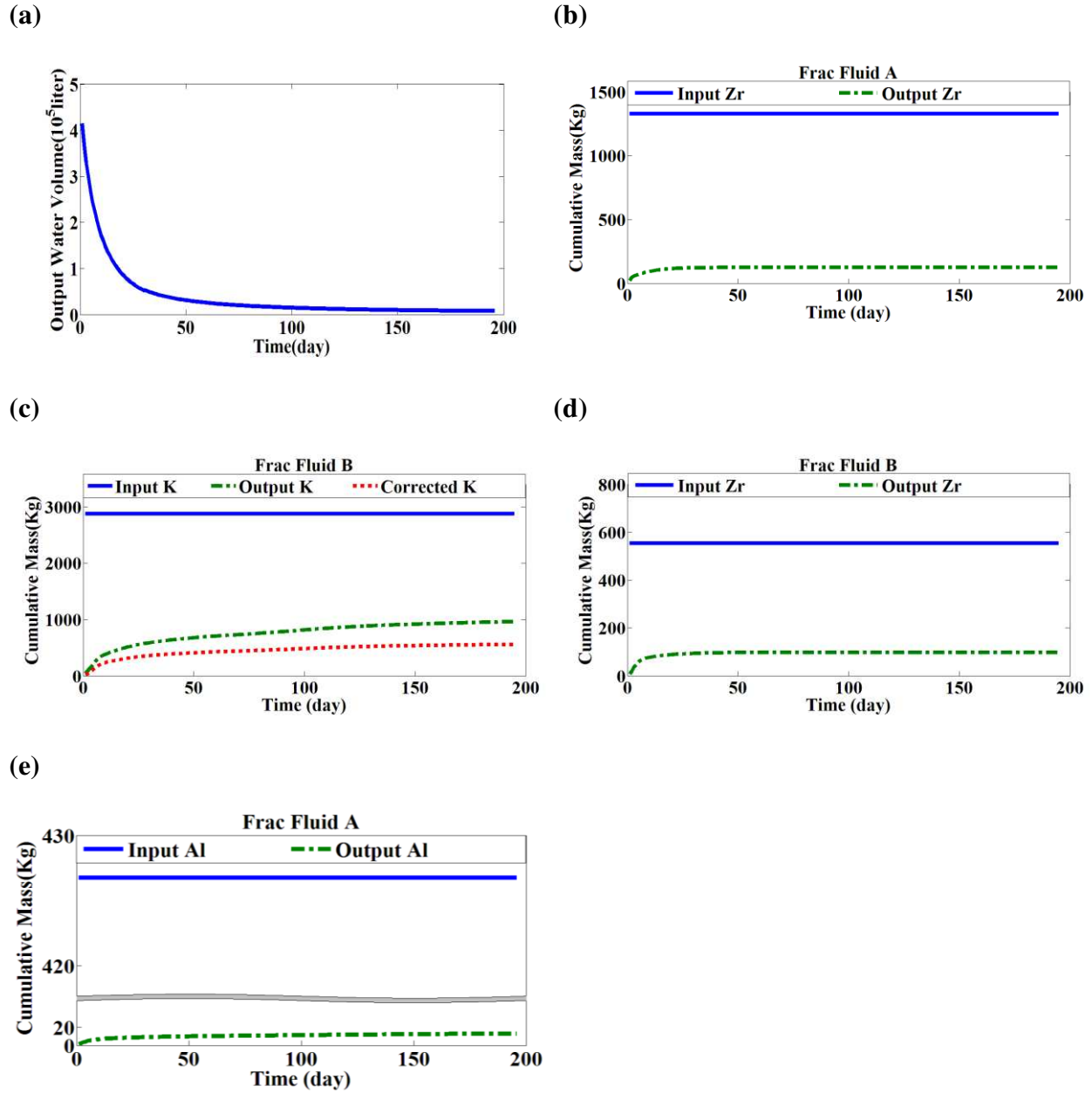


Figure 4.9. Flowback water volume (a) and cumulative mass (kg) for zirconium (b and d) ,potassium (c) and aluminum (e) with Frac Fluid A and B during 1-200 days.

For Frac Fluid A the zirconium input mass was about 1,328 kg and it is estimated that 9.3% was recovered in 200 days. These results contrast with Frac Fluid B for which recovery of 17.8% was estimated, almost twice the Frac Fluid A well. The greater recovery was not due to a higher

concentration in the produced water but the lower estimated input range of 554 kg for Frac Fluid B versus 1,328 kg for Frac Fluid A.

Potassium was only examined for the Frac Fluid B package since it is not added with Frac Fluid A. The input mass of potassium for this frac fluid was 2,888 kg. The estimated recovery was 33.7% for potassium in the flowback water assuming all of the element is from the injected fluid. If we assume that the background level of potassium from the formation is indicated by the mass results from Frac Fluid A, the corrected recovery would be 19.5%.

As shown in Table 4.3, the water recovery is 2 to 10 times the frac fluid additive recovery. It would be expected that K recovery would continue to increase as additional water is recovered since the concentration of this element was relatively constant, even after 200 days. However, for both frac fluid wells, the Zr decreased to very low levels (<0.1 mg/L) and therefore with approximately 45% of the water recovered, an insignificant mass of additional additive is expected to be recovered. The results indicate that use Frac Fluid A resulted in significantly less cross-linker Zr recovery than Frac Fluid B.

Zr and Al are both used as cross-linking metals for Frac Fluid A and in this role bind to the organic polymer increasing the viscosity of the solution. Zr is used in a similar manner for Frac Fluid B only in this case the polymer backbone is derivatized guar. It is hypothesized that the significantly lower recovery of both Zr and Al for Frac Fluid A is due to the more complete “break” of the gel in the formation resulting in release or mineralization of the metal ions leading to precipitation and minimal recovery with the flowback fluid. Oxidants are used as “breakers” for both frac fluids and the results could indicate a more complete oxidation of the polysaccharide-based gel (Frac Fluid A) than the derivatized guar gel (Frac Fluid B). If the cross-linking metal is released from the polymer structure, rapid hydrolysis reactions will occur resulting in insoluble Zr

and Al hydroxides and minimal recovery (Aja, et al,1996; Ekberg, et al, 2004). If the metals remain unbroken and complexed with dissolved organic compounds, recovery will be more complete although it is likely that more high molecular-weight polymers are remaining in the formation with Frac Fluid B than Frac Fluid A. Another difference of chemical additive is the EDTA, which is only used in Frac Fluid B. This chemical additives as the copper chelate might also affect recovery of Zr or Al. If using EDTA as a chelating agent, oil recovered can be increased through different recovery mechanisms, including different pH, different rocks and different reservoirs (Chen and Mohanty, 2013; Mahmoud and Abdelgawad, 2015). Using EDTA in Frac Fluid B might lead to increase recovery of Zr than Frac fluid A case in this study.

Table 4.3. Summary of recovery from mass balance and flowback production.

	Flowback Water Recovery (%)	WQ parameter	Frac fluid Additive Recovery (%)
Frac Fluid A	47%	Zirconium	9.3
		Aluminum	3.1
Frac Fluid B	41%	Zirconium	17.8
		Potassium	33.7
		Potassium (corrected)*	19.5

*Background concentration from Frac Fluid A well was subtracted

4.4 Conclusion

This work has shown that the main inorganics in flowback/produced water were observed to be chloride, calcium and sodium, each gradually increasing over the 200-day period in a similar manner to TDS. Correlation of the key ions (barium, calcium, chloride, magnesium, sodium,

strontium, boron and iron) with TDS for both Frac fluids indicated that there is a significant positive correlation between the key ions and TDS, except for boron and iron. Sodium showed the best correlation with TDS. A nonlinear regression model was selected to assess whether TDS is correlated to the main ions with the different frac fluids. Sodium, chloride, strontium and calcium indicated similarity between Frac Fluids A and B. However, barium and magnesium exhibited statistically different profiles between the frac fluids.

Temporal variability was also studied with the nonlinear regression model. Bicarbonate, calcium, iron, magnesium, zirconium and TOC show a statistically identical behavior for Frac Fluids A and B. Barium, boron, chloride, potassium, sodium, strontium, sulfate and silicon indicate that there are different flowback water concentrations between Frac Fluid A and B initially. Aluminum also does not exhibit statistically identical behavior between the two frac fluids.

A simple mass balance approach was applied to check frac fluid load recovery between the two conditions studied. In the Frac Fluid A case for zirconium, the recovery was 9.3% versus 17.8% for the Frac Fluid B cases. The higher recovery of the cross-linker element for the guar based fluid could indicate a lesser penetration of the gel relative to the cellulose-based polymer gel.

5. Investigating the Influence of Hydraulic Fracturing Fluid Type and Well Age on Produced Water Quality: Chemical Composition and Treatment and Reuse Challenges/Options²

5.1 Introduction

Oil and natural gas have played an integral role in the development of today's global industrial society and remain an important part of the current global energy portfolio. As more readily extracted conventional oil and gas resources are exhausted, technological improvements with directional drilling and hydraulic fracturing have allowed previously cost-prohibitive unconventional resources to become one of the largest and fastest growing sources of US domestic energy over the past five years (AEO, 2013).

Although unconventional oil and gas are among the least water-intense forms of energy currently utilized (Mielke, et al, 2010), water demand for hydraulic fracturing and the associated wastewater generation result in significant water management challenges. Each hydraulically fractured well requires roughly two to seven million gallons of water (Goodwin, et al, 2012; Hickenbottom, et al, 2013; Lee, et al, 2011; Nicot and Scanlon, 2012; Rahm, 2011; Stephenson, et al, 2011; Suarez, 2012), which is mixed with sand and chemical additives to form an engineered fluid that is injected under high pressure into the formation in order to create and prop open fractures (Lee, 2011; Spellman, 2013; USDOE, 2009).

Once a well has been hydraulically fractured, it is opened and fluid is allowed to return to the surface. Initially, a high flow rate of predominantly water, often referred to as "flowback," is

² As Submitted to Desalination and Water Treatment
Seongyun Kim^a, Pinar Omur-Ozbek^a, Brad Sick^a, Ken Carlson^a

^a Department of Civil and Environmental Engineering, Colorado State University, Fort Collins, CO 80523-1372, USA

returned to the surface. Within hours to weeks after the well is opened, the well begins producing a significant amount of oil and/or gas and is put into production. During the production phase, a mixed stream of oil and/or gas and water is generated, typically at a decreasing rate over the life of the well. Water separated from this mixed stream is typically referred to as “produced water,” and results in a constant generation of wastewater over the operating life of a well. The rate of wastewater production from a well is typically greatest when the well is initially opened and then sharply declines. As much as one-third of the overall 30-year projection of total produced water may be produced in the first 30 days after completion (Bai, et al, 2013).

Produced water management options depend on many factors, including availability of injection and disposal wells, availability of water treatment infrastructure, regulations, and overall pace and scale of development (Rahm, et al, 2013). Sourcing and hauling water for fracturing fluid and hauling and disposing of generated wastewater to and from well sites results in significant operating costs as well as a variety of social and environmental risks and impacts (Olmstead, 2013). In 2007, the vast majority of produced water in the US, 95.2% of the reported volume, was managed through injection (Clark and Veil, 2009). There are reports regarding the chemical and physical characteristics of produced water from conventional and unconventional oil and gas reservoirs and the possible treatment options for produced water (Andrew, et al, 2005; Fakhru'l-Razi, et al, 2009; Sirivedhin and Dallbauman, 2004). More recently, treatment and reuse (i.e., recycling) of produced water to counterbalance the freshwater demand for fracturing other wells is becoming a more integral part of produced water management to minimize total dissolved solids (TDS)(Jennifer and Lamadrid, 2013). This strategy has the potential to reduce the amount of overall wastewater that must be injected or treated to discharge standards, while also reducing water demand, public burden, environmental impacts, and overall cost of production.

The recycling process typically involves some extent of treatment and/or blending with freshwater in order to improve the quality of the produced water to the point that it can be effectively used as a fracturing fluid. Typical treatment objectives for reuse include removal of suspended solids and scale-forming components, and disinfection. High suspended solids and/or bacteria loads can foul the wellbore and/or formation fractures. Bacteria may also contribute to corrosion issues and hydrogen sulfide production. Concentrations of calcium, barium, and strontium are considered serious issues due to the high scaling potential when the produced water is reused for hydraulic fracturing (Gregory, et al, 2011). Major scaling concerns include BaSO_4 and, to a lesser extent, SrSO_4 and CaCO_3 (Vidic, et al, 2013).

An understanding of the quality and variability of produced water is crucial in designing effective water management strategies and treatment systems. It has been shown that the age of a well has a significant impact on produced water quality, particularly over the first few months of production (Barbot, et al, 2013). It is also expected that the type of fracturing fluid used to stimulate a well may have a significant impact on produced water quality.

Fracturing fluids can be separated into two main categories: gel and slickwater fluids. A gel fluid uses high concentrations of a polymer gelling agent, which often has the ability to be cross-linked for the purpose of greatly increasing the viscosity of the fracturing fluid. Slickwater fluids use low concentrations of viscosity-increasing polymer (typically defined as less than 20 lbs of polymer per 1,000 gal of fluid) or no polymer at all and typically use lower proppant concentrations (Zuh, 2013). The use of recycled produced water is more common with slickwater fluids because recycled water is more likely to contain components that interfere with cross-linked gel fracture additives (Montgomery, 2013).

This study analyzed data from produced water samples collected over a 63-day study period from three wells fractured with different fracturing fluids. Extensive water quality characterization was performed on each sample. Chemical coagulation jar testing was conducted to understand variability in chemical optimum dose due to type of fracturing fluid and well age. The studied wells were unconventional oil and gas wells located in the Wattenberg Field of the Denver-Julesburg Basin, located in northeastern Colorado. The system of formations targeted for production in this field is commonly referred to as the Niobrara Shale, an Upper Cretaceous hybrid shale/carbonate with production depths ranging from 6,000 to 9,000+ ft and an overall thickness of roughly 300 ft, with carbonate-rich targets for horizontal laterals that range from 10- to 25-ft thick (NETL, 2013). Many operators utilize both slickwater and gel hydraulic fracturing fluids in this field and wastewater management often involves a decision of whether or not to combine wastewater streams from wells fractured with different fluids or from wells of different ages. It is essential to understand whether the fracturing fluids behave differently and may be blended and treated together for possible reuse.

The objectives of this study were to: identify the variability of produced water quality with well age and fracturing fluid type; measure the relative and temporal difference in chemical optimum dose between the three studied wells; characterize organic compounds by liquid chromatography–mass spectrometry (LC-MS) present in different fracturing fluid types and well ages. Chemical equilibrium software was used to model the speciation of measured ions and to predict the precipitation of metal solids from blending produced water with a fresh groundwater source.

5.2 Material and methods

5.2.1 Well characteristics

The study involved field collection of 15 sets of produced water samples from three separate unconventional oil and gas wells located in Weld County, Colorado. Table 5.1 and Figure 5.1 provide information on the studied wells.

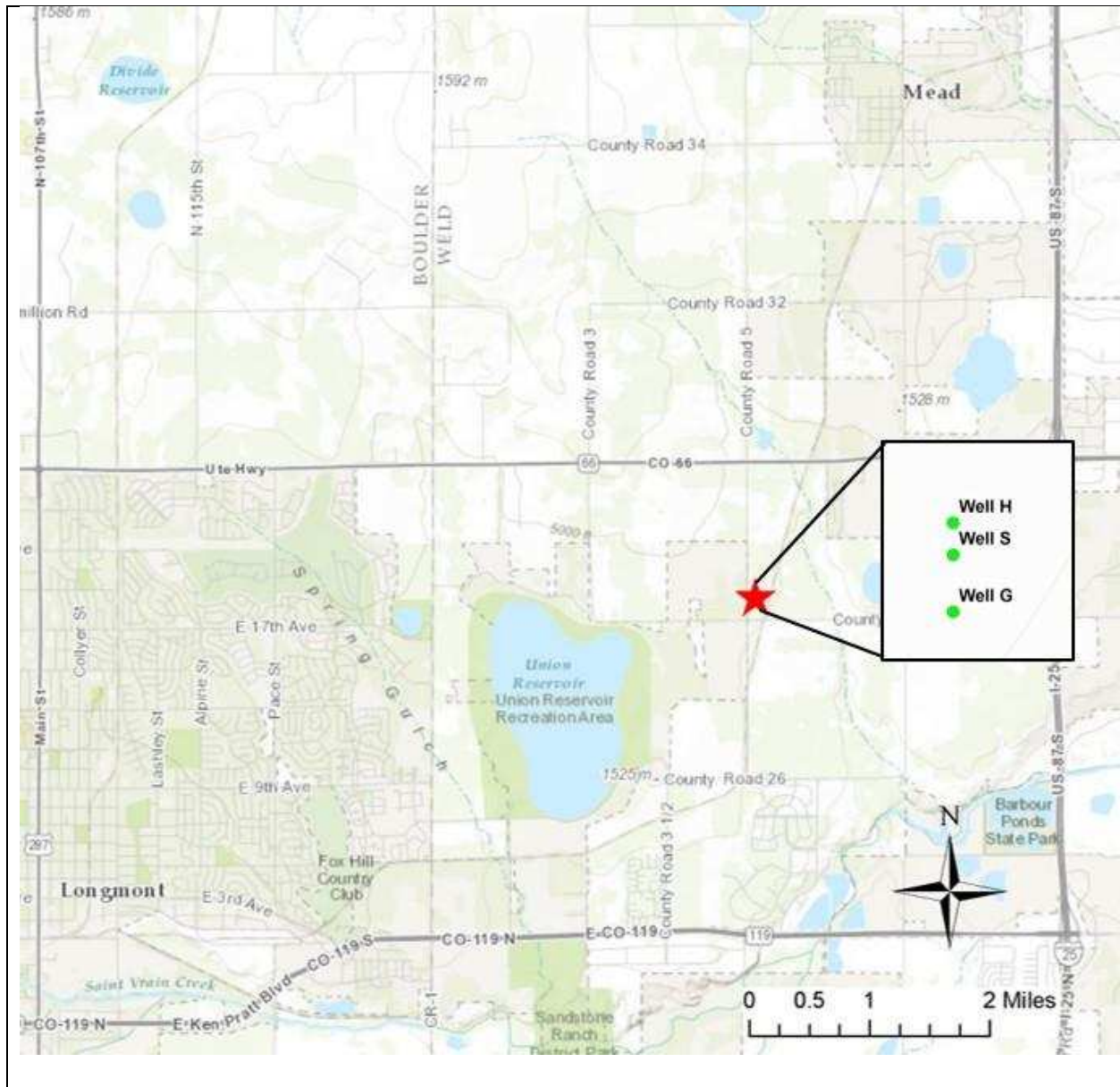


Figure 5.1. Map of the configuration of three unconventional oil and gas wells in located in Weld County, Colorado.

Table 5.1. Properties of studies wells.

Well Name	Job Start	Job End	Production start date	True Vertical Depth (feet)	Effective Lateral Length (feet)	Lateral Number of Stages	Input Water Volume (gal)	Fracture Fluid Type
Well S	10/21/2013	10/26/2013	11/25/13	7,064	4,367	28	3,986,430	Slickwater
Well G	11/4/2013	11/9/2013	11/26/13	7,193	4,561	29	4,115,076	Cross-linked gel
Well H	10/28/13	11/3/2013	11/25/13	7,132	4,502	28	4,344,942	Hybrid

*Effective Lateral Length: length from the top of the upper most perforation to the bottom of the deepest perforation.

*Lateral number of stages: number of stages in the total horizontal length.

The wells were located on the same centralized pad and targeted the same formation, but were stimulated with a different fracturing fluid package (Table 5.2 and Table 5.3). FracFocus.org (Frac Focus Chemical Disclosure Registry, 2013) the national hydraulic fracturing chemical registry, was used to identify the names and maximum concentrations of compounds used in each fracturing fluid package.

Table 5.2. FracFocus.org Frac Fluid compositions for well S.

Well S				
Purpose	Trade Name	Ingredients	Max Conc.(mg/L)	Approximate Chemical Formula
Acidizing	HCl, 10.1-15%	Hydrochloric Acid	1,218	HCl
Corrosion Inhibitor	CI-31	Formic Acid	9	CH ₂ O ₂
		Oxyalkylated Fatty Acid	4.5	[COH]
		Aromatic Aldehyde	4.5	C ₆ H ₅ CHO
		Quaternary Ammonium Compound	4.5	NR ₄
		Isopropanol	1.5	C ₃ H ₈ O
		Methanol	0.8	CH ₄ O
		Cyclic Alkanes	0.8	[CH]
		Organic Sulfur Compound	0.8	[CHS]
		Benzyl Chloride	0.2	C ₇ H ₇ Cl
Iron Control	Ferrotrol 300L	Citric Acid	10	C ₆ H ₈ O ₇
Paraffin inhibitor	Paras orb 5000,bag	Calcined Diatomaceous Earth	270	N/A
		White Mineral Oil	125	C ₍₁₅₋₄₀₎ H _x
		Proprietary Paraffin Inhibitor	104	N/A
		Silica, Crystalline-Quartz	21	Si
Biocide	Alpha452	Tetrakis(hydraxymethyl) Phosphonium Sulfate	167	C ₈ H ₂₄ O ₁₂ P ₂ S
Breaker	GBW-5	Ammonium persulphate	113	H ₈ N ₂ O ₈ S ₂
Clay Control	Clay care, tote	Choline Chloride	747	C ₅ H ₁₄ ClNO
Friction Reducer	MaxPerm-20A, bulk	Polyacetate	563	(C ₄ H ₆ O ₂) _n
		Petroleum Distillates	281	C ₍₉₋₁₆₎ H _x
		Sodium Chloride	47	NaCl
		Oxyalkated Alcohol	47	N/A
Surfactant	Flo-Back 40, tote	Amphoteric Surfactant	338	N/A
Non-emulsifier	NE-945W, 265gl tote	Glycerine	150	C ₃ H ₈ O ₃
		Oxyalkylated Alcohol	25	N/A
		Polyethylene Glycol	25	C _{2n} H _{4n} +2O _n +1

Table 5.3. FracFocus.org Frac Fluid Compositions for Well G.

Well G				
Purpose	Trade Name	Ingredients	Max Conc.(mg/L)	Approximate Chemical Formula
Breaker	High Perm CRB	Ammonium Persulphate	90	H ₈ N ₂ O ₈ S ₂
Breaker	Enzyme G HT-II	Water	379	H ₂ O
		Tryptone	19	[CHON]
		Yeast Extract	19	N/A
Buffer	BF-9L, 300 gal tote	Potassium Carbonate	315	KCO ₃
		Potassium Hydroxide	158	KOH
Cross linker	XLW-30AG,tote	Petroleum Distillates	382	C ₍₉₋₁₆₎ H _x
Cross linker	XLW-32	Methanol	164	CH ₄ O
		Boric Acid(H ₃ BO ₃)	82	H ₃ BO ₃
		Methyl Borate	82	C ₃ H ₉ BO ₃
Gelling Agent	GW-3LDF	Guar Gum	3,355	C ₆ H ₁₂ O ₆ /unit
		Paraffinic Petroleum Distillate	1,677	[CH]
		Petroleum Distillate	1,677	C ₍₉₋₁₆₎ H _x
		Isotridecanol, ethoxylated	280	[CHO]
		1-butoxy-2-propanol	280	C ₇ H ₁₆ O ₂
Biocide	Alpha452	Tetrakis(hydraxymethyl) Phosphonium Sulfate	145	C ₈ H ₂₄ O ₁₂ P ₂ S
Breaker	GBW-5	Ammonium persulphate	9	H ₈ N ₂ O ₈ S ₂
Clay Control	Clay care, tote	Choline Chloride	668	C ₅ H ₁₄ CINO
Friction Reducer	MaxPerm-20A, bulk	Polyacetate	30	(C ₄ H ₆ O ₂) _n
		Petroleum Distillates	15	C ₍₉₋₁₆₎ H _x
		Sodium Chloride	3	NaCl
		Oxyalkated Alcohol	3	N/A
Surfactant	Flo-Back 40, tote	Amphoteric Surfactant	287	N/A
Non-emulsifier	NE-945W, 265gl tote	Oxyalkated Alcohol	20	N/A

Well S was fractured with a slickwater fluid, the primary chemical additive of which was hydrochloric acid (HCl). Other unique components of the slickwater fluid, which constitute a total

maximum concentration of 556 mg/L, include acidizing, corrosion inhibitor, iron control, and paraffin inhibitor packages.

Well G was fractured with a cross-linked gel fluid, unique components of which include gelling agent, crosslinker, and breaker packages. The primary compounds that make up these packages, in terms of maximum possible concentration, are petroleum distillates (~41%) and guar gum (~37%), both of which are organic compounds that significantly modify the viscosity of the fracturing fluid as the well is stimulated. It should be noted that the slickwater fluid used in Well S did not contain these modifying components of the gel fluid and, as such, maintained a fairly consistent viscosity. The cross-linker package also includes boric acid, which makes the element boron unique to the cross-linked gel fluid.

Well H was fractured as a hybrid, using portions of both slickwater fluid and cross-linked gel fluid. For this well, each stage was stimulated by first injecting a slickwater fluid - ~40% of the total stage volume - followed by injection of a cross-linked gel fluid - ~60% of the total stage volume. The slickwater and cross-linked gel fluids used for Well H are the same as those used for Well S and Well G, respectively.

Both the slickwater and cross-linked gel fracturing fluids contained similar biocide, breaker, clay control, friction reducer, surfactant, and non-emulsifier packages. The primary components of these packages, in terms of maximum possible concentration, are the following organic compounds: choline chloride, polyacetate, petroleum distillates, and amphoteric surfactants.

5.2.2 Sample collections

Fifteen sampling events were conducted over a 63-day period. Sampling began immediately after the start of oil and gas production (referred to as day 0). The pre-production flowback period ranged from three days for Well H to seven days for Well S; no pre-production

flowback samples were collected as a part of this study. Samples were collected every three days for the first nine events; every five days for events 10 and 11; and every seven days for events 12 through 15.

All samples were collected from a dedicated production separator associated with each well. The only exception was the first sample collected from Well G, which was collected directly from the wellhead. Approximately five gallons of sample were collected from each well at each sampling event and allocated to appropriate containers. Volatile compounds analysis samples were collected in glass vials, headspace free. All other samples for water quality characterization were placed in 1L polyethylene bottles. All vials and bottles were immediately placed on ice and kept refrigerated until analyzed. All samples were analyzed within a week after sampling. The remaining samples from each collection, ~four gallons, were placed in five-gallon container and used for jar testing.

5.2.3 Analytical methods

Conductivity and pH were measured in the field and verified in the lab using probes (Hach CDC401 and Hach PHC10105, respectively). Field-collected pH and conductivity readings are presented in this study. Alkalinity was measured using standard method 2320B; total dissolved solids (TDS) and total suspended solids (TSS) were determined using Standard Method 2540 (APHA, 2012). Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured using a Shimadzu TOC-VCSH analyzer. Whatman 934-AH glass microfiber filters (1.5-um-equivalent pore size) were used for TDS, TSS, and DOC analyses. Turbidity was measured with a Hach 2100N turbidimeter, according to EPA Method 180.1. The ultraviolet (UV) absorbance was measured with a HACH DR/4000 spectrophotometer at 254 nm (referred to as UV254). Al, Ba, B, Ca, Fe, K, Mg, Na, Si, Sr, and Zr concentrations were determined using inductively coupled

plasma–atomic emission spectrometry (ICP-AES) after acid digestion of samples to pH below 2. Chloride was measured using a silver nitrate titration, according to EPA method 9253. Bromide was measured using an ion chromatograph, according to EPA method 300. Sulfate was measured using American Society for Testing and Materials (ASTM) method D516. Ammonia was measured using EPA method 350.1. Each sample collected from the production separators (i.e., 15 samples from each of the three wells) was analyzed for each of the listed parameters.

5.2.4 Jar testing to determine optimum dose

Coagulation-flocculation jar testing was conducted on each sample to determine the variability in optimum dose as a function of fracturing fluid and well age, following ASTM Method D2035-13 with a Phipps & Bird PB-900 programmable jar tester. The bench-scale jar testing was intended to identify relative differences in optimum dose, not to identify an optimum coagulation-based treatment process. As such, only one coagulant was tested and no flocculation aiding polymer was used.

Each well-mixed sample was divided into five square jars, each containing 1L of sample. A dose of concentrated aluminum chlorohydrate (ACH) solution was simultaneously added to each jar. The five doses used were as follows: 100, 150, 200, 250, and 300 mg/L as Al. These doses were adjusted if the optimum dose was found to be outside of this range. Immediately following the addition of chemical coagulant, rapid mixing was conducted at 120 revolutions per minute (rpm) for one minute, followed by flocculation mixing at 25 rpm for 20 minutes and a subsequent 15-minute settling period.

At the end of the setting period, a sample was collected from the sampling port built into each jar. Sample turbidity was immediately measured for each of the five sub-samples. Of the five doses tested, an optimum dose was selected as the lowest dose at which an increase to the next

dose resulted in less than 1.5% increase in net turbidity (NTU) removal. Additional water quality analyses were conducted on each optimum dose sample in order to measure treatment removals. These additional analyses included pH, UV254 absorbance, TOC, DOC, TSS, and TDS.

5.2.5 LC-MS method

Samples from three sampling events were further analyzed by LC-MS run under ESI mode. 20 mL of samples from Well S and Well G were collected in glass vials at 4, 25 and 56 days. C18 column was used for separation, the nebulizer pressure was set to 30 psig and the scan spectra were collected in the range m/z 50-1600. The carrier flow rate was 0.4 mL/min. 5 μ L of sample was injected and each run lasted 18 minutes at 30°C. The mobile phase A was 0.1% formic acid in water and B was 0.1% formic acid in acetonitrile. The mobile phase gradients during the run were 95 to 80% A for 1-8 minutes, 80 to 5% A for 8-17 minutes and 5 to 95% A for 17-18 minutes.

5.2.6 Chemical equilibrium modeling

Ion concentrations tested in the laboratory are reported as mg/L of the base ion, such as mg/L as Ca^{+2} . However, these ions do not necessarily exist in the raw solution as the base ion; instead, they exist as one or several species of ion complexes such as CaCO_3 or CaSO_4 . Multivalent metal ions can cause potential clogging problems during hydraulic fracturing and also during well production. Chemical equilibrium modeling can determine the form(s) in which ions actually exist in the solution; such speciation knowledge can help in understanding phenomena such as solids formation and scaling potential and support decisions regarding softening and other treatment options.

This study utilized OLI Stream Analyzer (OLI Systems, Cedar Knolls, NJ), a chemical equilibrium modeling software that provides thermodynamic equilibrium equations for the physical and chemical understanding of aqueous-phase systems (Dyer, et al., 2003), to determine

what form or forms the measured ions exist in the sample and the distribution of chemical species as both aqueous and solid species. The limitation and assumptions of OLA analyzer were summarized in Table 5.4. Speciation modeling was conducted on samples collected from Well H on Days 1, 19, and 63 to reflect temporal variation. Each system was modeled at the measured pH of the respective sample (~pH 7).

Table 5.4. Summary of limitation and assumption of using OLI analyzer for both aqueous phase and non-aqueous phase.

Aqueous phase	Non-aqueous phase
Water content>65%	The enhanced SRK equation of state was applied to determined Non-aqueous and vapor fugacity coefficient
Temperature: -50 to 300°C	Vapor critical of temperature, pressure, volume and acentric factor are correlated to find a Fugacity coefficient
Pressure:0 to 1500 Atm	
Ionic strength: 0 to 30	

Untreated produced water is sometimes blended with freshwater to dilute the produced so that it may be used for fracturing without treatment. This study also used OLI Stream Analyzer to model the expected precipitation of metal solids that would result from blending produced water from Well H with a freshwater source that reflects typical groundwater quality of Northeast Colorado. Water quality of a typical Northeastern Colorado groundwater was summarized in Table 5.5.

Table 5.5. Water quality of a typical Northeastern Colorado groundwater source.

Parameter	Concentration (mg/L)
pH	8.3
Alkalinity	305
Aluminum	0.44
Barium	0.01
Calcium	60.4
Iron	0.20
Magnesium	23.8
Potassium	4.15
Sodium	330
Strontium	1.51
Zinc	0.17
Bicarbonate	305
Chloride	35.3
Sulfate	429
Boron	2.11

5.3 Results and discussion

5.3.1 Produced water characterization

Temporal trends for pH, alkalinity, conductivity, and TOC are presented in Figure 5.2. The pH of all produced water samples was within 6.75-7.5, with a slightly decreasing temporal trend in pH observed at each well. The consistent pH readings among the three wells suggest that the type of fracturing fluid does not greatly influence the pH of the produced water. Alkalinity concentrations among the three wells at each time point were fairly consistent; the exception was the alkalinity concentration at Well S, which was significantly lower than the other two wells after Day 30. A slight downward temporal trend in alkalinity was observed for every well. Alkalinity concentrations were typically greater than 500 mg/L as CaCO_3 during the study period, suggesting a significant buffering capacity. Due to this high buffering capacity, a softening process using pH adjustment to precipitate metals could require a significant chemical demand. The temporal decrease in the alkalinity trend suggests a lesser buffering capacity in older samples, especially

from Well S, which was observed to have a more steeply declining trend compared to the other two wells.

Conductivity was fairly consistent among the three wells at each time point, with Well G generally having a slightly lower conductivity than the other two wells over the sampling period. Conductivity readings were strongly correlated with TDS concentrations. An upward temporal trend in conductivity was observed at each well, increasing from 25-35 mS/cm at Day 1 to approximately 51 mS/cm at Day 63.

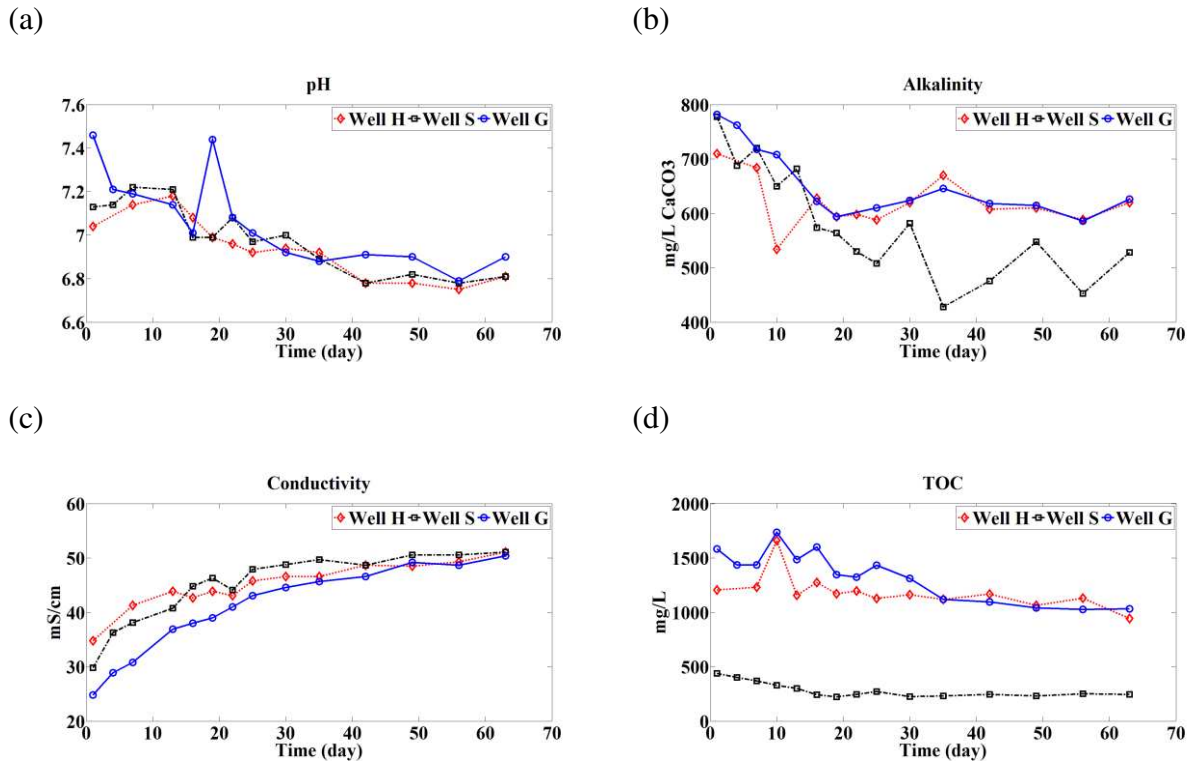


Figure 5.2. Temporal trends of pH (a), alkalinity (b), conductivity (c), and TOC (d) measurements. Day 0 corresponds to the first day that the wells were put online for production (3 to 7 days after the wells were opened).

The trends of measured inorganic ions of temporal variability and different fracturing type were shown in Figure 5.3 and Figure 5.4. TDS concentrations also increased over the course of the sampling period, from approximately 17,000 to 22,000 mg/L at Day 1 to approximately 34,000

mg/L at Day 63. Chloride and sodium made-up the primary inorganic constituent ions, followed by calcium and bicarbonate. Chloride, sodium, and the majority of the component metals and inorganic ions measured followed trends similar to TDS. Exceptions included bicarbonate, sulfate, and silicon which showed a slight decreasing temporal trend.

One way ANOVA was performed to check difference in water quality parameters from each well by flowback time. With a few exceptions, metals and inorganic ions concentrations were fairly consistent from well to well (i.e., did not seem to be impacted by fracture fluid type). One exception was that the concentrations of divalent cations (Ca (p-value=0.42), Mg (p-value=0.45) and Sr (p-value=0.62)) were significantly lower in Well G samples, compared to samples from the other two wells. The other exception was that boron concentrations were less in Well S samples compared to those from the other two wells. The lower concentration of boron in Well S is likely due to the absence of the borate-based cross-linker in the slickwater fracturing fluid. The low boron concentration at Well S may represent the introduction of boron from the formation. The boron concentration difference between Well S and other wells approves there are no communication of wells due to their proximity of wells.

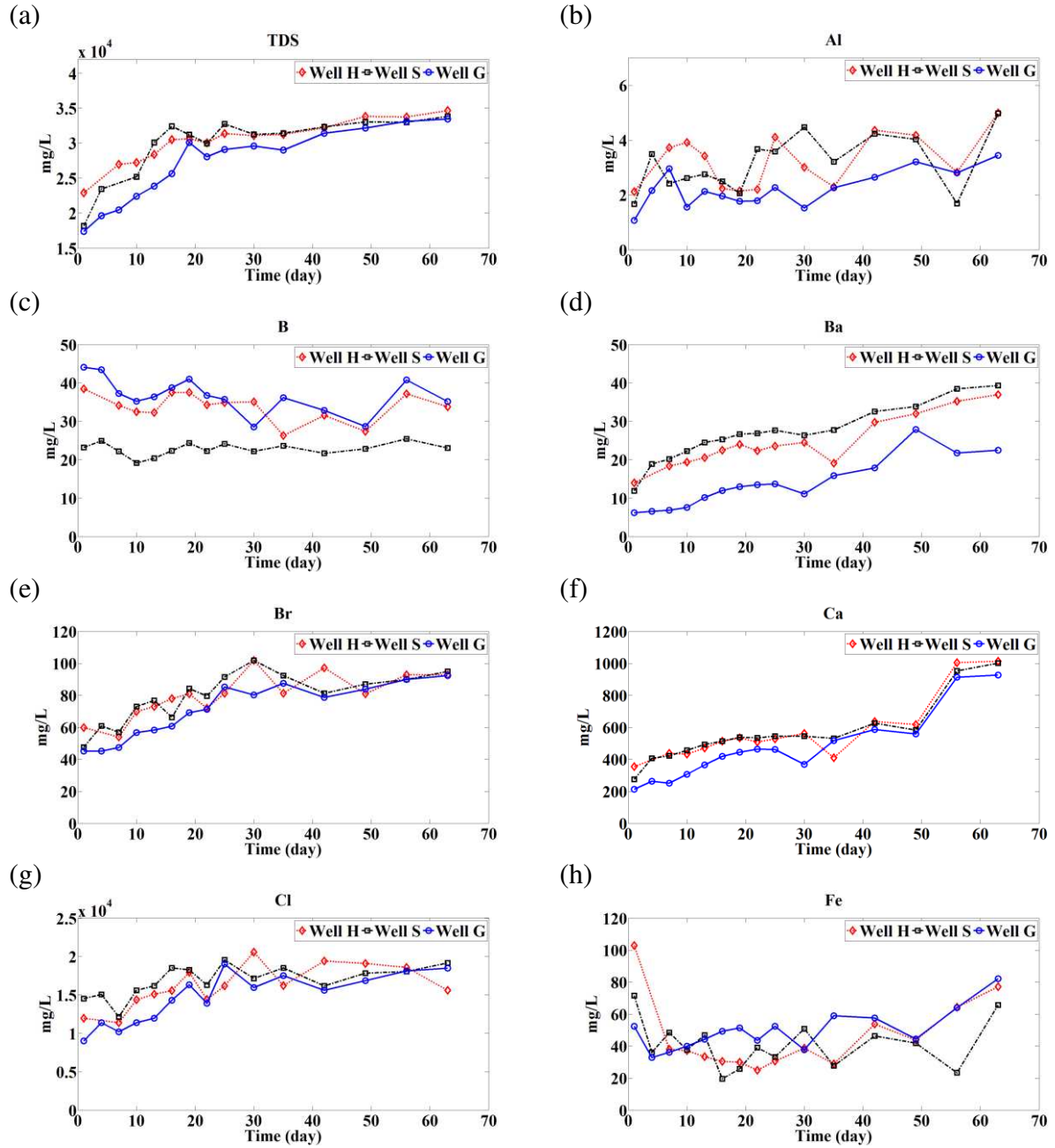


Figure 5.3. TDS, Al, B, Ba, Br, Ca, Cl, and Fe trends for Wells H, S, and G.

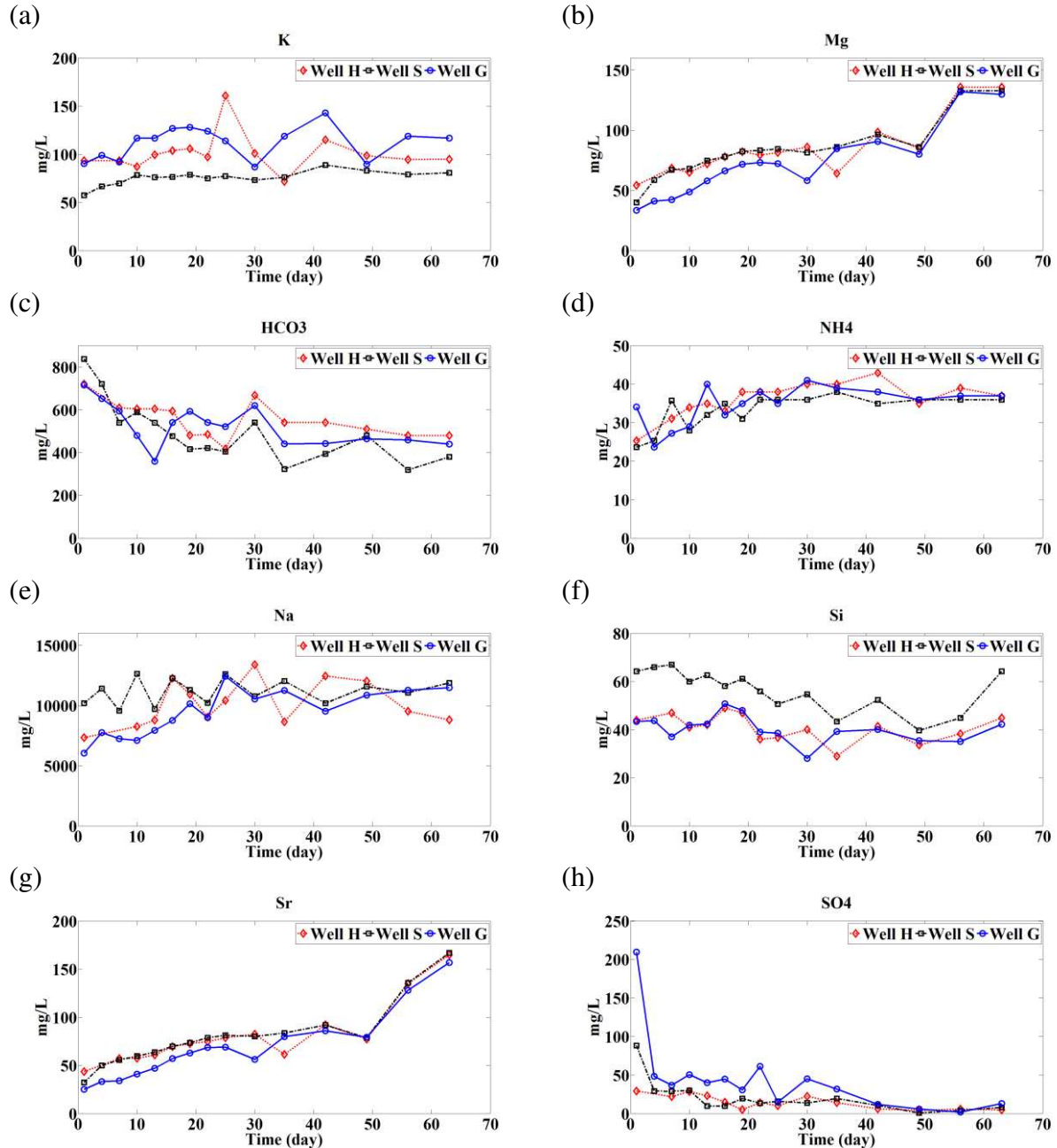


Figure 5. 4. K, Mg, HCO₃, NH₄, Na, Si, Sr, and SO₄ trends for Wells H, S, and G.

The rest of water quality parameters trends of three wells and age of wells were shown in Figure 5.5 and Figure 5.6.. No significant trends were observed for turbidity (p-value=0.86) or TSS (p-value=0.75). Turbidity readings ranged from 115 to 763 NTU, with average turbidity at each well ranging from 247 NTU at Well G, 295 NTU at well H to 262 NTU at Well S. TSS

readings ranged from 38 to 339 mg/L, with average TSS at each well ranging from 144 mg/L at Well S, 155 mg/L at well H to 148mg/L at Well G.

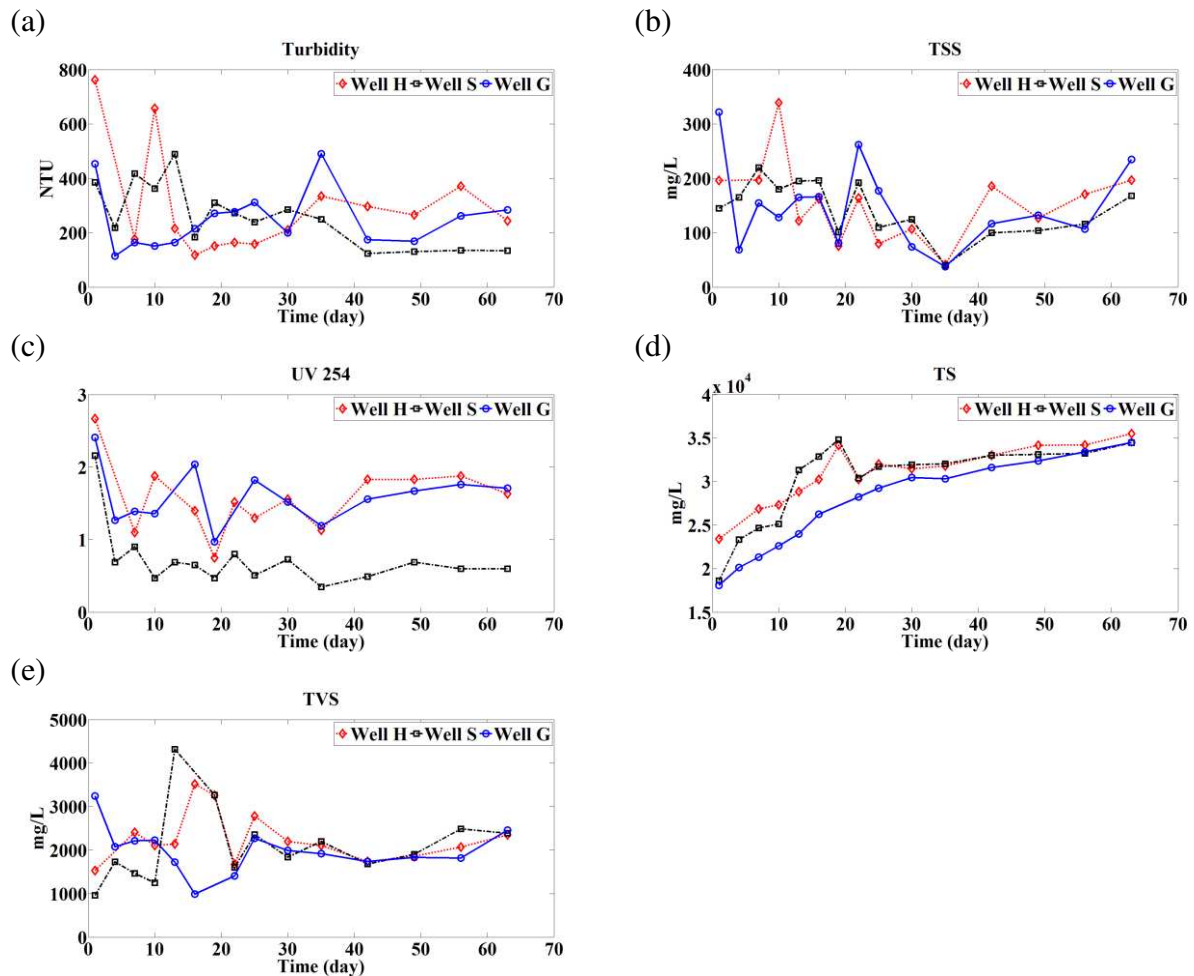


Figure 5.5. Turbidity, TSS, UV254, TS, and TVS trends for Wells H, S, and G.

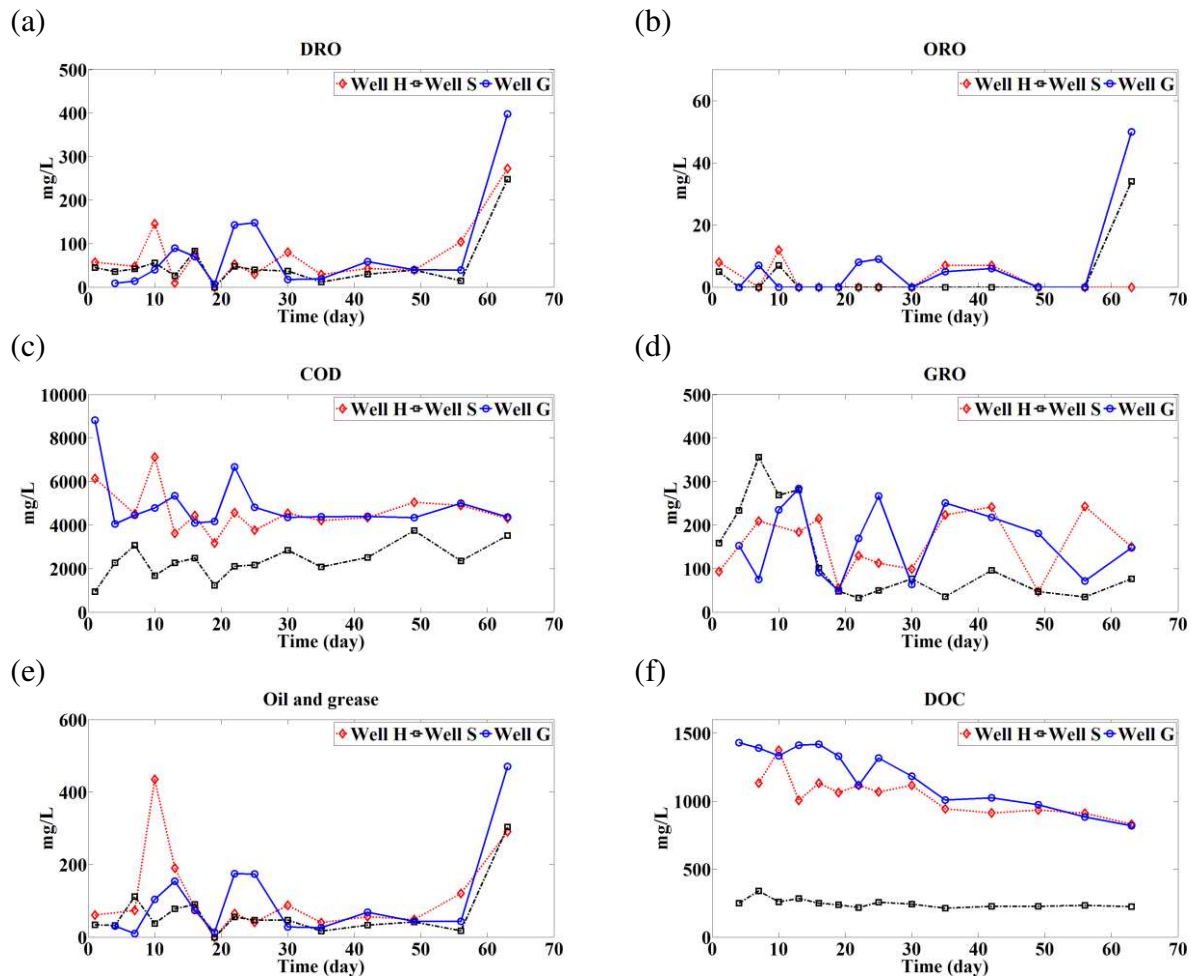


Figure 5.6. DRO, ORO, COD, GRO, Oil and Grease, and DOC trends for Wells H, S, and G.

TOC concentrations were significantly higher in samples from Well H and Well G than in samples from Well S. TOC concentrations in Well G were generally slightly higher than Well H over the first 30 days, at which point the TOC concentrations in these two wells converged. A slight downward temporal trend in TOC was observed for each well. DOC concentrations followed a similar trend to TOC for each well, with DOC concentrations generally falling between 80% and 100% of the associated TOC concentration, suggesting that greater than 80% of organic molecules present in each sample were smaller than 1.5 μm .

High TOC concentrations - 943 to 1,735 mg/L as C - in produced water from Wells H and G is likely a result of the organic additives specific to the gel fluids (predominantly petroleum distillates and guar gum). The lower TOC concentration in the produced water from Well S - 222 to 440 mg/L as C - is likely a result of organic fracturing additives common to both slickwater and cross-linked gel fluids, including choline chloride, polyacetate, petroleum distillates, and amphoteric surfactants. Petroleum hydrocarbons present in the formation may also contribute to the TOC concentrations in produced water; however, based on the difference in TOC concentrations between the wells fractured with slickwater and cross-link gel fluids, it appears that fracturing additives have a greater impact on TOC concentration than contributions from the formation.

The observed temporal increase in TDS and decrease in TOC in each produced water stream is likely due to the increased impact on water quality from the formation and decreased impact from fracturing fluid additives with time. Produced water samples collected during the first ten days of production had less contact time with the formation and typically are flowing back from the well at a higher rate than produced water collected later in the study. As such, the water quality of earlier produced water samples is more similar to the raw fracturing fluid; these samples exhibit higher concentrations of TOC and cross-linker-associated salts - in this case, boron - and lower concentrations of dissolved salts contributed by the formation. These trends, however, tend to stabilize as the well ages. The data presented here show that TOC and alkalinity concentrations became fairly stable at approximately 30 days after production. pH, conductivity, and the majority of the metals and ions that contribute to conductivity became more stable about 45 days after production.

The observed trend in TDS in this study is similar to other published data, with the difference being the magnitude of the stabilized TDS concentration, which can vary greatly from field to field. For example, TDS concentrations in Marcellus produced water has been observed to increase dramatically over the first roughly 30 days after the well is opened and then stabilize at values between roughly 60,000 and 140,000 mg/L (Barbot, et al, 2013).

Reported average TOC concentrations for Marcellus wells, which are typically fractured with slick water fluids (Vidic , et al, 2013), are generally less than 250 mg/L and are reported to decrease with time (Barbot, et al, 2013; Hayes, 2009). These published results are consistent with the TOC concentrations measured for slickwater fluids in this study.

Daily water production values are presented in Figure 5.7. The magnitude and general trend of daily water production does not differ greatly from well to well, with each well showing a gradual downward temporal trend. Between November 25, 2013 and January 30, 2014 study period, Well B produced at total of 9,915 bbl, Well D produced a total of 7,709 bbl, and Well G produced a total of 6,208 bbl.

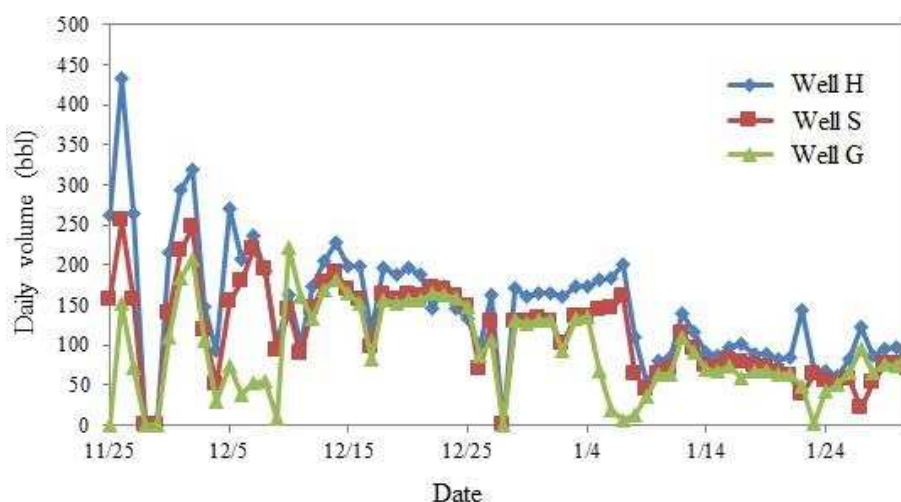


Figure 5.7. Daily water production.

5.3.2 Chemical coagulation jar testing

The optimum dose was selected out of each of the five tested doses. As shown Figure 5.8, this optimum dose was selected as the smallest dose where an increase in dose does not result in a significant increase in turbidity or UV254 removal.

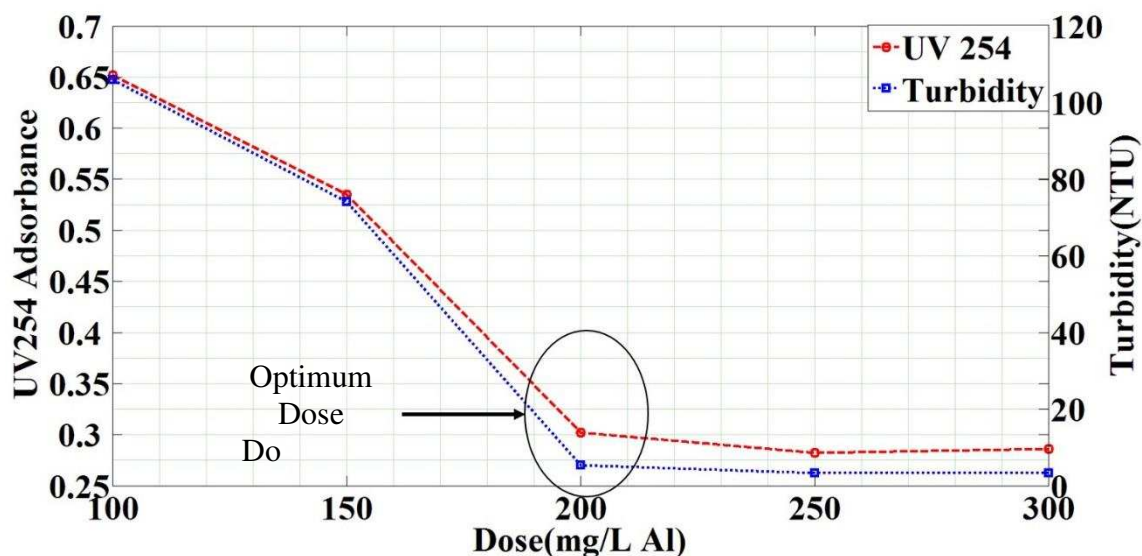


Figure 5.8. Selection of optimum dose based on turbidity and UV254.

The optimum coagulant dose determined for each five-point jar test is presented in Figure 5.9. The optimum dose for 1 day sample from Well G was found to be 800 mg/L - about three times the next highest dose. Figure 5.9 does not include the optimum dose for the Day 1 sample from Well G collected prior to connection of the well to the production separator. Because this sample was collected directly from the wellhead, prior to the start of production, this data point was not included in the dataset.

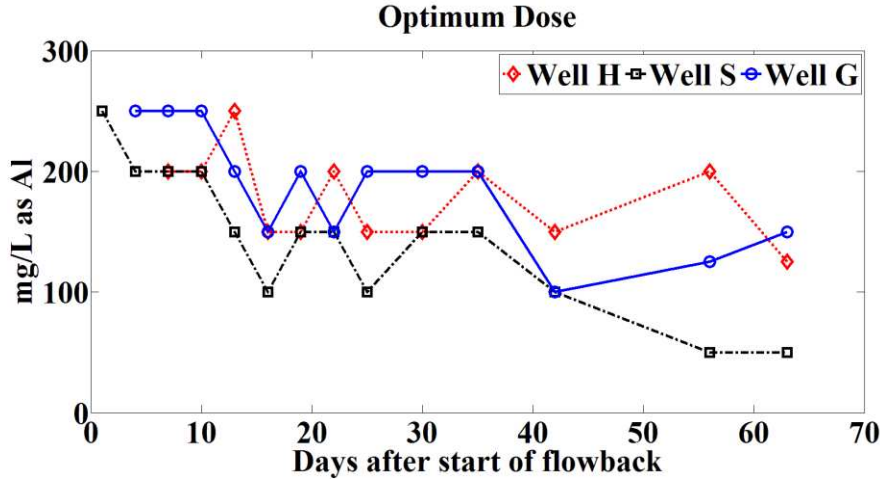


Figure 5.9. Temporal trends in optimum aluminum chlorohydrate coagulant dose.

Produced water samples for 56 days and 63 days from Well G, fractured with cross-linked gel fluid, had 300% to 400 % higher optimum dose than samples from Well S, fractured with slickwater fluid. The observed optimum dose of produced water samples from Well H generally measured between that of the other two wells, except after about 35 days, when the optimum dose of produced water from Well H measured slightly higher than that of produced water from Well G. The optimum dose of produced water from each well was observed to decrease with time. The average linear decrease ranged from 0.8 mg/L Al per day (Well H) to 2.7 mg/L Al per day (Well S).

Average removal of measured parameters following the optimal coagulant dose for all samples from given well tested is presented in Table 5.6. Organics removal, as suggested by average TOC and DOC removals, was generally less than 20% for each well. TOC removal was higher than DOC removal, suggesting that larger organic molecules are more effectively removed by the coagulation process. TSS removal ranged from 56% (Well G) to 74% (Well S), with average treated water TSS concentrations of 93 mg/L (Well G) to 29 mg/L (Well S). No significant

TDS removal was observed. Mean turbidity removal was 96% or more for samples from each well, resulting in an average turbidity of all treated samples measuring less than 10 NTU.

Organics removal results are consistent with other published literature. Cardoso et al.(2012) showed that dissolved organic material with a negative surface charge (e.g., humic acids and fulvic acids) can be removed via coagulation/flocculation and solid/liquid separation, but low-weight particles with no surface charge, such as carbohydrates, are not removed via coagulation/flocculation. Instead, biological processes must be used, or partial oxidation can be used to potentially generate negatively charged species from low-charged organic compounds to promote coagulation/flocculation.

Table 5.6. Average removal of selected constituents for 0 to 63 day produced water samples using chemical coagulation.

Parameter	Average Removal (%)		
	Well S	Well G	Well H
Turbidity (NTU)	97%	96%	97%
UV254 (Abs.)	80%	70%	67%
TOC (mg/L)	12%	18%	17%
DOC (mg/L)	6%	7%	8%
TSS (mg/L)	74%	56%	57%
TDS (mg/L)	1%	0%	1%

While the treatability testing performed in this study was not intended to identify specific chemical coagulant dosing requirements, the study provides valuable insight into the relative differences in treatability among produced waters from wells fractured with different fracturing

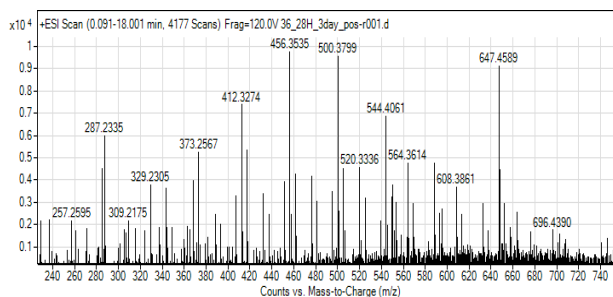
fluids as well as the relative changes in treatability with time. Similarly, measuring removal of parameters with each coagulation treatment was not conducted to identify an overall, optimized treatment process; instead, the data collected provides a general idea of what is and isn't removed from produced water via the chemical coagulation process. The results indicate that flowback from the slickwater wells (no cross-linked polymer added) is easier to treat and therefore the water will be more amenable to beneficial reuse. Operators are beginning to recycle flowback water for additional fracturing and are considering treating the water to discharge standards. The water quality and treatment data presented here will provide a basis for some of these decisions.

The higher optimum dose in produced waters from Well G and Well H, compared to Well S, suggests that some additive(s) specific to the cross-linked gel fluid make coagulation treatment more difficult. Yet, the difference in chemical optimum dose is not large enough to suggest these waste streams could not be blended and sent through a single treatment process.

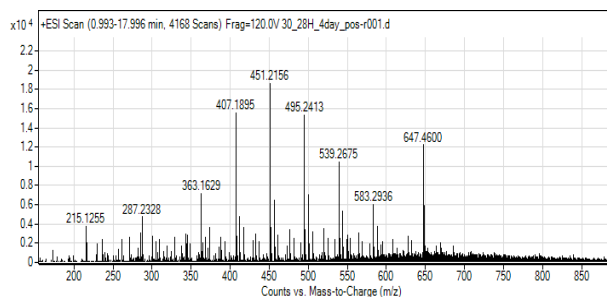
5.3.3 LC-MS analysis for comparison between gel frac fluid well and slickwater frac fluid well with temporal variability

Flowback water samples 4 days, 25 days and 56 days from Well G and Well S were analyzed by LC-MS and the Agilent mass hunter qualitative analysis. Figure 5.10 shows the mass spectra from the Well G of the 4 days (a), 25 days (c) and 56 days (e) and Well S of the 4 days (b), 25 days (d), 56 days (f) with relative abundances. Although there are different relative abundances of peaks for the same well age samples for Well G and Well S, similar organic compounds were detected at each well and there was no observed trend with time. The detected different organic compounds means there was communication between Well G and Well S due to the closed distance.

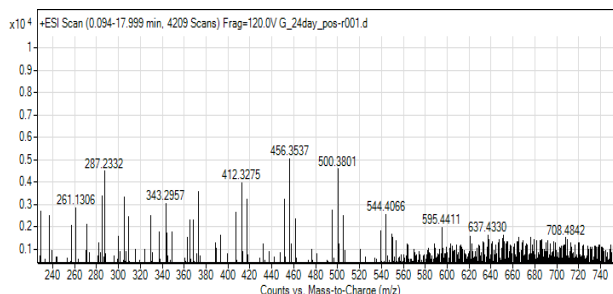
(a) Well G :4days



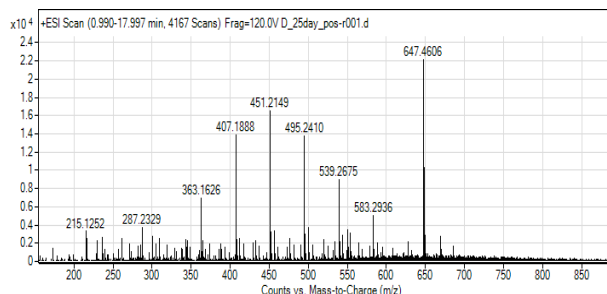
(b) Well S :4days



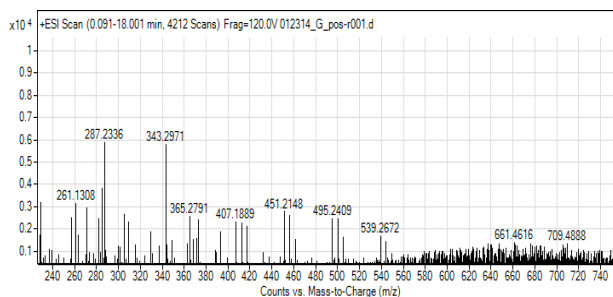
(c) Well G:25days



(d) Well S:25days



(e) Well G:56days



(f) Well S :56days

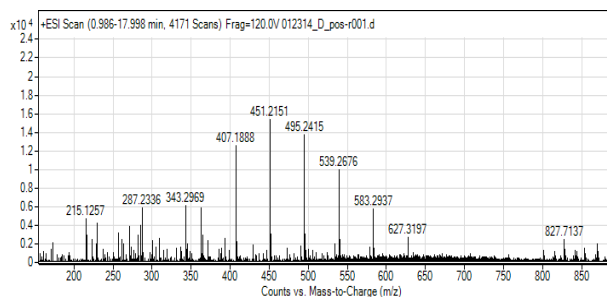


Figure 5.10. Mass spectra of detected organic constituents with relative abundance using LC/MS for Well G at (a) 4days (c) 25days (e) 56 days and Well S at (b) 4days (d) 25days (f) 56 days.

LC-MS data was further analyzed to identify the organic compounds in both gel and slick wells with temporal variability by using Agilent Technology Software linked to a library based on the exact mass of chemicals used for hydraulic fracturing between 2005 and 2009 in U.S (USHRC, 2011). Benzenecarboxylic acid, 1,1-dimethylethyl ester, cocamidopropyl betaine, dipropylene glycol, phthalic anhydride, polyethylene glycol and triethylene glycol were detected in both Well

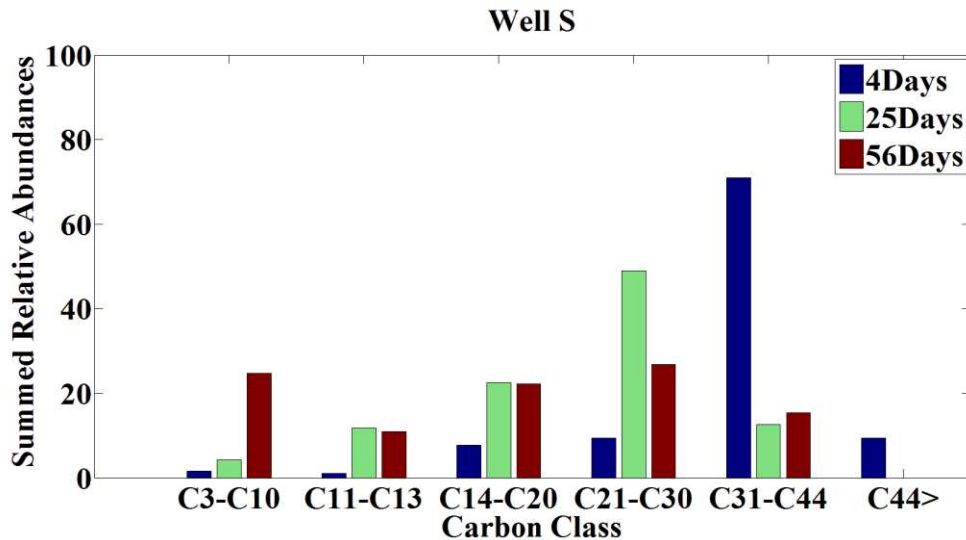
G and Well S. Some of the organic compounds were not detected in the early samples while others were not detected in the later samples indicating the presence or absence of degradation byproducts or compounds extracted from shale formation during fracturing. 1-methoxy-2-propanol, 3,4,4-trimethyloxazolidine, aldol, dodecylbenzenesulfonate isopropanolamine, ethoxylated octyl phenol, ethyl acetoacetate, methyl salicylate, n,n'-methylenebisacrylamide, methyl salicylate, n,n'-methylenebisacrylamide, polyethylene-polypropylene glycol, propanol, [2(2-methoxymethylethoxy) methylethoxyl] and triamcinolone were detected only in Well G, meaning that they are likely degradation products of the gel additives (see Table 5.7).

Table 5.7. Chemical found in flowback water for Well S and Well G with temporal variability.

	Well S			Well G		
	4 days	25 days	56 days	4 days	25 days	56 days
1-methoxy-2-propanol				X	X	
3,4,4-Trimethyloxazolidine						X
Adipic acid				X		
Aldol						X
Alkoxyated phenol formaldehyde resin			X			X
Benzenecarboperoxoic acid, 1,1-dimethylethyl ester	X	X	X	X	X	X
Butyl lactate				X		X
Cocaidopropyl betaine	X	X	X	X	X	X
Cyclohexanone						X
Di (2-ethylhexyl) phthalate	X	X	X	X		
Dipropylene glycol	X	X	X	X	X	X
Dipropylene glycol monomethyl ether (2-methoxymethylethoxy propanol)	X		X	X	X	X
Dodecylbenzenesulfonate isopropanolamine				X		
Ethoxylated octyl phenol				X		
Ethyl acetoacetate						X
Ethylene glycol monobutyl ether (2-butoxyethanol)		X	X	X	X	X
Methyl salicylate						X
n,n'-Methylenebisacrylamide						X
Phthalic anhydride	X	X	X	X	X	X
Polyethylene glycol	X	X	X	X	X	X
Polyethylene-polypropylene glycol					X	X
Propanol, [2(2-methoxy-methylethoxy) methylethoxyl]				X		
Triamcinolone					X	
Triethylene glycol	X	X	X	X	X	X

The distribution of constituents obtained from positive spectra and compared wells for temporal variability are presented in Figure 5.11. Organic carbon compound classes were sorted by different range groups. The class distribution of the carbon fraction showed similar trends for both Well G and Well S. The carbon classes from both wells indicate that early flowback water tends to have a higher number of carbon classes than later flowback water. The most abundant compounds in 4-day Well S sample were C31-C44, and C21-30 compounds were predominant in 25-day Well S whereas the compounds in 56-day Well S sample were evenly distributed except over C44. The 4-day Well G sample showed the highest concentrations in C31-C44, similar to Well S, and the 25-day Well G was dominant in the C31-C44 range.

(a)



(b)

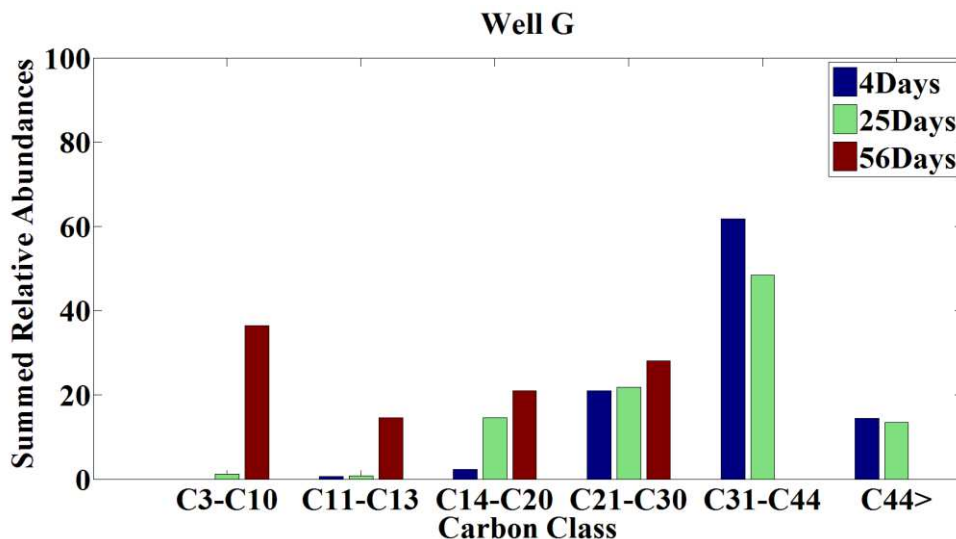


Figure 5.11. Comparison of carbon classes with relative abundances for temporal variability with different well fractured.

Early flowback water required more aluminum for better coagulation (Figure 5.9), indicating a higher organic matter optimum dose. To check how carbon classes distribution affect coagulation, linear regression analysis was performed. Since there are many range of carbon

classes, classes were grouped (C3-C30) to make two dimensional plot. The total abundance of C3-30 and C> 30 is 100. A relatively strong correlation was obtained ($R^2 > 0.8$ in both) as presented in Figure 5.12. As can be observed from the Figure 5.12, 20% of the abundance of compounds was from C3-30 and the remaining 80% was from C>30. The sample which are 20% of C3-C30 and 80% of C>30 was needed 200mg/L as Al and the sample which are 85% of C3-C30 and 15% of C>30 was needed 50mg/L as Al, confirming that organic matter with a higher number of carbons increases coagulation demand.

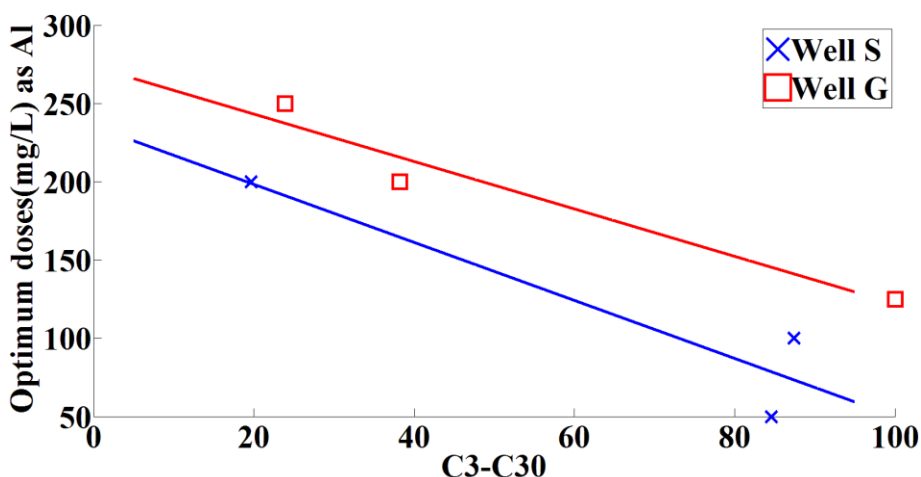


Figure 5.12. Optimum doses trend in summed carbon between 3 to 30 from Well S and Well G.

5.3.4 Ion speciation in selected produced water samples

The results of chemical speciation modeling for samples collected from Well H on Days 1, 19, and 63 are summarized in Table 5.8. Calcium carbonate (calcite) makes up the majority of the inorganic solids in each of the analyzed samples, followed by ferric hydroxide and barium sulfate. At the modeled pH (each near a pH of 7), magnesium, boron, zirconium, and strontium are only present in the aqueous phase; this finding is consistent with common softening processes, where it is known that magnesium will not start precipitating until the pH is raised to roughly 10, at which

point it will precipitate out as $\text{Mg}(\text{OH})_2$. While the solubility of barium sulfate is extremely low, the presence of the barium ion in all three samples suggests that each produced water sample is sulfate-deficient and that if sulfate was introduced into the system - by means of dilution with a freshwater source of a high sulfate concentration - barium sulfate could become a significant scaling concern. Trivalent cations such as aluminum and iron have a strong tendency to hydrolyze in a solution and to precipitate out as hydroxide complexes. It was found that all aluminum in the solution was present in the solid form of either $\text{NaAl}(\text{OH})_2\text{CO}_3$ or $\text{Al}(\text{OH})_3$, and all ferric ions were in the form of $\text{Fe}(\text{OH})_3$. These solid particles of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ are often small with a positive surface charge; therefore, they present as a colloidal suspension. As such, a coagulation treatment process may be required to remove these suspended solids from the solution in order to lower aluminum and iron concentrations to desired treatment levels.

Table 5.8. Modeled speciation on measured metals for well H.

Measure d Ion	Chemical Formula	1 day			19 days			63 days		
		Tota l	Aqueo us	Soli d	Tota l	Aqueo us	Soli d	Tota l	Aqueo us	Soli d
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Al	$Al(OH)_3$	-	-	-	-	-	-	14.4	-	14.5
	$NaAl(OH)_2CO_3$	11.3	-	11.3	11.5	-	11.5	-	-	-
Ca	Ca^{2+}	161. 1	161.1	-	379. 3	379.4	-	758. 7	758.9	-
	$CaCO_3$	477. 5	1.8	475. 8	383. 8	1.7	382. 1	631. 1	1.7	629. 5
	$CaH_2BO_3^+$	0.0	0.0	-	0.1	0.1	-	0.2	0.2	-
	$CaHCO_3^+$	6.5	6.5	-	7.1	7.1	-	5.7	5.7	-
	$CaSO_4$	0.2	0.2	-	0.0	0.0	-	0.1	0.1	-
Mg	Mg^{2+}	51.3	51.4	-	79.8	79.8	-	134. 4	134.4	-
	$MgCO_3$	0.1	0.1	-	0.1	0.1	-	0.1	0.1	-
	$MgHCO_3^+$	10.5	10.5	-	8.3	8.3	-	5.5	5.5	-
	$MgSO_4$	0.2	0.2	-	0.0	0.0	-	0.0	0.0	-
B	H_3BO_3	29.8	29.8	-	29.1	29.1	-	26.0	26.0	-
	$B(OH)_4^-$	0.4	0.4	-	0.4	0.4	-	0.4	0.4	-
	$NaB(OH)_4$	0.1	0.1	-	0.1	0.1	-	0.1	0.1	-
Zn	Zn^{2+}	0.4	0.4	-	0.0	0.0	-	0.6	0.6	-
	$ZnCl^+$	0.1	0.1	-	-	-	-	0.1	0.1	-
	$ZnHCO_3^+$	0.0	0.0	-	-	-	-	-	-	-
Ba	Ba_2^+	1.8	1.8	-	16.8	16.8	-	26.5	26.5	-
	$BaCl^+$	0.4	0.4	-	5.0	5.0	-	7.3	7.3	-
	$BaHCO_3^+$	0.0	0.0	-	0.2	0.2	-	0.1	0.1	-
	$BaSO_4$	20.2	-	20.2	5.3	-	5.3	7.8	-	7.8
Fe	$Fe(OH)_3$	197. 1	-	197. 1	57.4	-	57.4	147. 7	-	147. 7
Sr	Sr^{2+}	43.7	43.7	-	72.8	72.8	-	164. 9	165.0	-

5.3.5 Blended water modeling

Modeled concentrations of solid calcium carbonate, ferric hydroxide, aluminum hydroxide, and barium sulfate with blending ratios ranging from one part produced water to five parts fresh water (1:5) to one part produced water to 30 parts fresh water are presented in Figure 5.13. for each of the three samples modeled. A shaded area is also provided for each solid in Figure 5.13, which

represents the concentration of each solid due to simple dilution. The upper boundary of each shaded area is defined by the sample with the highest solid concentration, and the lower boundary of the shaded area is defined by the sample with the lowest solids concentration. This shaded area does not consider changes in solids concentrations due to the reestablishment of equilibrium resulting from blending. As shown in Figure 5.13, ferric hydroxide (Figure 5.13B) and barium sulfate (Figure 5.13D) follow the trend of simple dilution but the concentration of calcite (Figure 5.13A) and aluminum hydroxide (Figure 5.13C) remains relatively constant with an increase in the blend ratio. With larger ratios of freshwater mixed with produced water, the dissolved portion of calcium and aluminum tend to reproduce more solids, which compensate the effect of dilution and lead to the flatter curves shown in Figure 5.13A and Figure 5.13C.

As demonstrated by this analysis, the solid species present in the system will not necessarily be diluted as expected due to the redistribution of chemical species caused by changes in equilibrium. When produced water was blended with freshwater that typically is oversaturated in terms of carbonate, additional calcium carbonate solid is formed. Similarly, when sulfate-deficient produced water is blended with fresh water with a significant sulfate concentration, barium sulfate solids form. This generation of solid precipitate must be considered when developing a produced water management strategy that involves blended produced water with a fresh water source to achieve a blended water quality that can be used as a fracturing fluid.

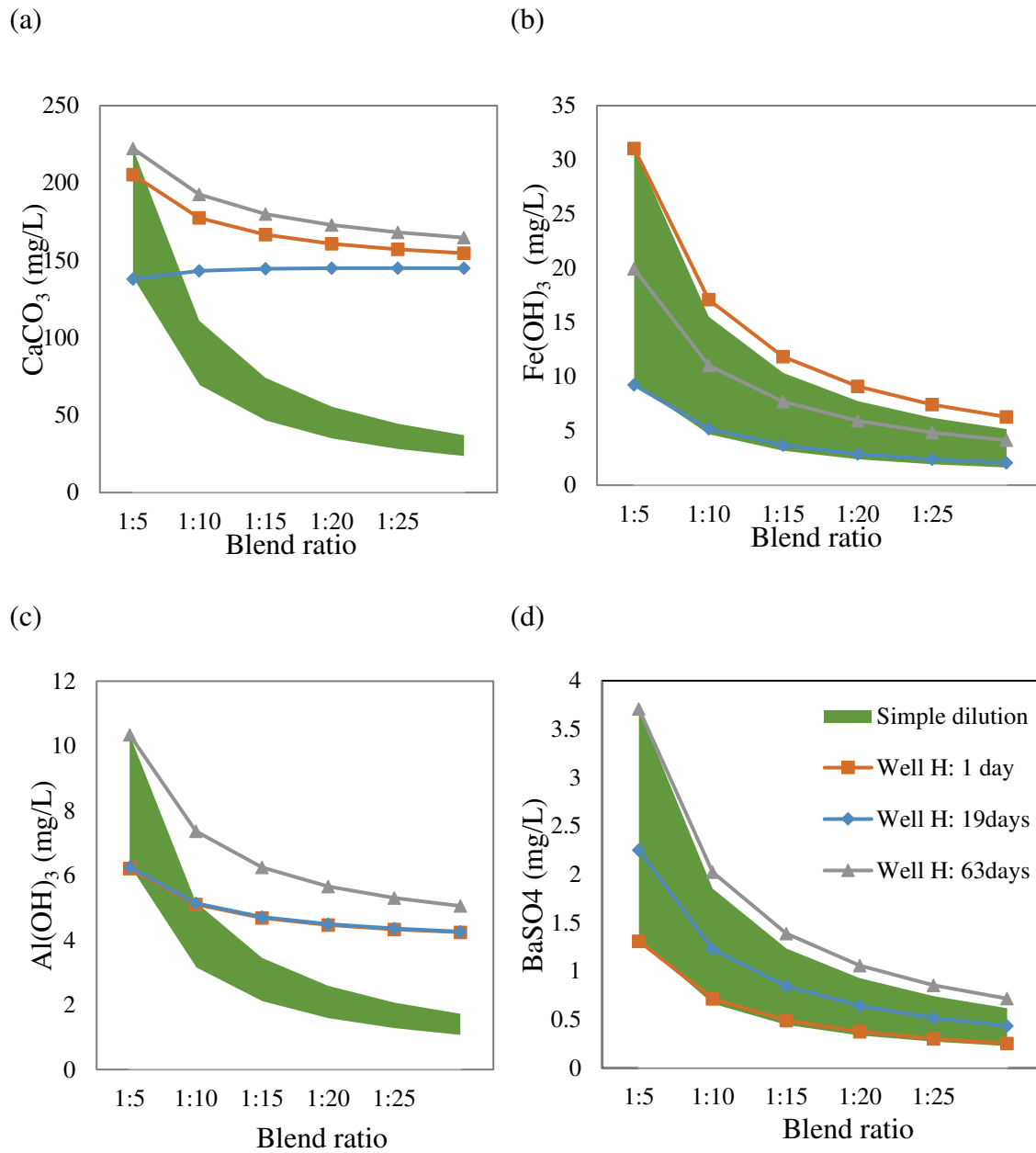


Figure 5.13. Modeled Blending of Well H samples collected at Days 1, 19, and 63.

5.4 Conclusions

The following conclusions are drawn from the result and discussion provided herein. These conclusions pertain only to the studied wells; further work is needed to determine if these conclusions hold true for a larger set of wells.

- Fracturing fluid additives have a significant impact on at least the first 63 days of produced water quality, particularly in regard to the effect additive packages specific to cross-linked gel fluids have on the organic makeup of produced water.
- Produced water from wells fractured with gel fluids have a significantly greater organic compound load (>1,000 mg/L) compared to produced water from wells fractured with slickwater fluids (approximately 200 to 400 mg/L).
- Fracturing fluid additives have a greater impact on TOC concentrations in produced water over the first 63 days of production than contributions from the formation.
- Chemical coagulation decreases TOC concentrations by roughly 20% for produced waters from wells fractured with both gel and slickwater fluids, independent of their difference in makeup.
- Chemical coagulation can successfully reduce the turbidity of produced waters from wells fractured with both slickwater and gel fluids immediately after the start of production.
- Chemical coagulant demand for produced waters from wells fractured with gel fluids is roughly 25 to 400 % higher than that for wells fractured with slickwater fluids, with the demand from each produced water type decreasing with the age of the well.

- Similar organic compounds are detected from wells of fractured with slick water fluid and fracture with gel fluids by using LC-MS and higher carbon group are needed more aluminum dose for coagulation process.
- Fracturing fluid additives have a large enough effect on the treatability of produced water that the impacts of different fracturing fluid types should be considered when blending produced water streams for water management and treatment.
- When produced water is blended with a fresh water source, solid species present in the system will not necessarily be diluted as expected due to the redistribution of chemical species caused by changes in equilibrium.

6. Characterization of Organic Matter in Water from Oil and Gas Wells Hydraulically Fractured with Recycled Water³

6.1 Introduction

The expansion of hydraulic fracturing for extracting oil and gas from shale formations has allowed the U.S. to almost double its oil production in the last ten years. In addition, the advances in hydraulic fracturing and horizontal drilling have led to unconventional natural gas production increasing 10 fold between 2001 and 2011 (Gregory, et al, 2011; Dammal, et al, 2011).

Since the permeability of shale formations is significantly lower than the permeability of conventional sandstone and carbonate formations, stimulation techniques have been developed to economically extract oil and natural gas economically. However, the supply is now exceeding demand and commodity prices have dropped significantly (Arthur et al.2010; Rahm 2011; Suarez 2012). Since utilization of natural gas releases less carbon emissions compared to coal and there is an existing and expanding national pipeline system, it is expected that natural gas extracted from shale formations will be an important fuel well into the future (Gregory, et al, 2011; Jaramillo, et al, 2007).

The volume of water consumed, the risk to the environment of returned water and the disposal of the wastewater continue to be significant concerns. Water demand for hydraulically fracturing a single well can range from approximately between 2-8 million gallons of water (Goodwin, et al, 2012; Hickenbottom, et al, 2013; Lee, et al, 2011; Nicot and Scanlon, 2012; Rahm, 2011; Stephenson, et al, 2011; Suarez, 2012). The required water volume for hydraulic fracturing

³ As Submitted to Journal of Natural Gas Science and Engineering
Seongyun Kim^a, Ken Carlson^a, Pinar Omur-Ozbek^a

^aDepartment of Civil and Environmental Engineering, Colorado State University, Fort Collins, CO 80523-1372, USA

a well depends on the length of the horizontal lateral in addition to the geological formation, depth, compressibility and porosity (USDOE, 2004). The characteristics of the flowback/produced water will be affected by the geological formation with temporal and spatial variation (Barbet, et al, 2013), but other factors include the fracturing fluid composition, the wellbore length and also the ratio of recycled water used.

After hydraulic fracturing, between 5 and 60 percent of the fluid mixture returns to the surface as flowback or produced water in the first 6 months (USDOE 2009a; USDOE 2009b; Clark , et al, 2012; Rahm and Riha, 2012 ; Suarez, 2012). Flowback/produced water may contain unaltered chemical additives and organic compounds indigenous to the formation (e.g. hydrocarbons, benzene, etc.), but also organic compounds that have broken down through either reaction with the formation rock, the high temperatures and pressures associated with the producing regions or reaction with oxidants that are used as viscosity breakers (Veil, et al, 2004; Soeder and Kappel, 2009; Karbo, et al, 2010; Clark, et al, 2012; Hickenbottom, et al, 2012; Rahm and Riha, 2012; Lutz, et al, 2013; NDRC, 2012).

Reusing the flowback/produced water for fracturing additional wells is a good approach to managing the wastewater and efforts are being made to expand this practice across the country. Several studies have identified the characteristics of produced water from oil and gas reservoirs and the possible treatment options for waters but none have looked at the characteristics of organic matter in water that has been used at least twice (i.e. flowback from a well that was fractured with recycled water)(Sirivedhin and Dallbauman, 2004; Adrew, et al, 2005; Fakhru'l-Razi, et al, 2009).

A common practice for oil and gas production companies is to dilute the produced water by mixing with fresh water, either due to water quality concerns or lack of recycled water volumes (USDOE, 2009a; USDOE, 2009b; Veil, 2010; Spellman, 2012; Jennifer and Lamadrid, 2013; Lutz,

et al, 2013). Treatment processes for recycling water are typically designed to remove particles and disinfect the water and therefore much of the organic matter returned during flowback remains (Hickerbottom, et al, 2012). Carter et al. (2013) reported that the mass spectra of produced water samples between inflow and effluent from a centralized water treatment facility were almost identical in spectra using liquid chromatography-mass spectrum (LC-MS) analysis. Since characteristics of flowback /produced water can be affected by the geological formation, high temperatures and the presence of breakers, the analysis of flowback/produced water for specific organic compounds is difficult.

The objective of this study was to determine organic compound characteristics in recycled and fresh water mixed with frac additives that are not affected by the formation, only thermal and oxidative degradation. Two samples were analyzed; recycled water with frac additives (RWA) and fresh water with frac additives (FWA), both subjected to post processing thermal conditions simulating a typical formation (120°C). Liquid chromatography-mass spectrum (LC-MS) with electrospray ionization (ESI) of positive mode was utilized for samples analysis.

6.2 Material and methods

6.2.1 Composition of fracturing fluid and sample preparations.

Fracturing fluid chemicals were provided by Halliburton, Inc. and testing was completed at their Brighton, CO labs. The chemical ingredients and concentrations are summarized in Table 6.1.

Table 6.1. Fracturing fluid design and ingredients.

Components	Chemical
Gelling Agent	Residue-free polysaccharide
Surfactant	-
Clay Stabilizer	Potassium chloride
Biocide	-
Buffer	Acetic acid
Breaker	Chlorous acid, sodium salt
Catalyst	Ammonium chloride
Crosslinker	Zirconium, acetate lactate oxo ammonium complexes
Crosslinker	Inorganic Salt

De-chlorinated tap water from Colorado State University (CSU) was used as the fresh water and recycled water was provided from a local produced water treatment facility. Recycled water quality is presented in Table 6.2.

Table 6.2. Recycled water characterization from treatment facility.

Parameter (mg/l)	Recycled Water
TDS	27,355
TOC	1,868
NH ₄	20
Br	79
Cl	16,520
SO ₄	290
HCO ₃	260
Al	1.3
Ba	1.0
B	10.1
Ca	31.2
Fe	1.5
K	351
Mg	10
Mn	<0.1
Na	9,764
Si	12.9
Sr	3.6
Cu	<0.1

1000mL of tap water from CSU and recycled water were measured. Samples were added to a blender and gel was mixed for 30 seconds. All other chemicals were added and mixed for 9 minutes. After all fracturing fluid ingredients were added and fully blended, samples were moved into stainless steel roller sleeves. To totally break down the fluid viscosity, the sleeves were moved into the temperature-controlled oven at 120°C and “rolled” for 5 hours. The samples were then moved into VOA bottles and stored at 0°C before analysis by LC-MS. The sample preparations are summarized in Figure 6.1.

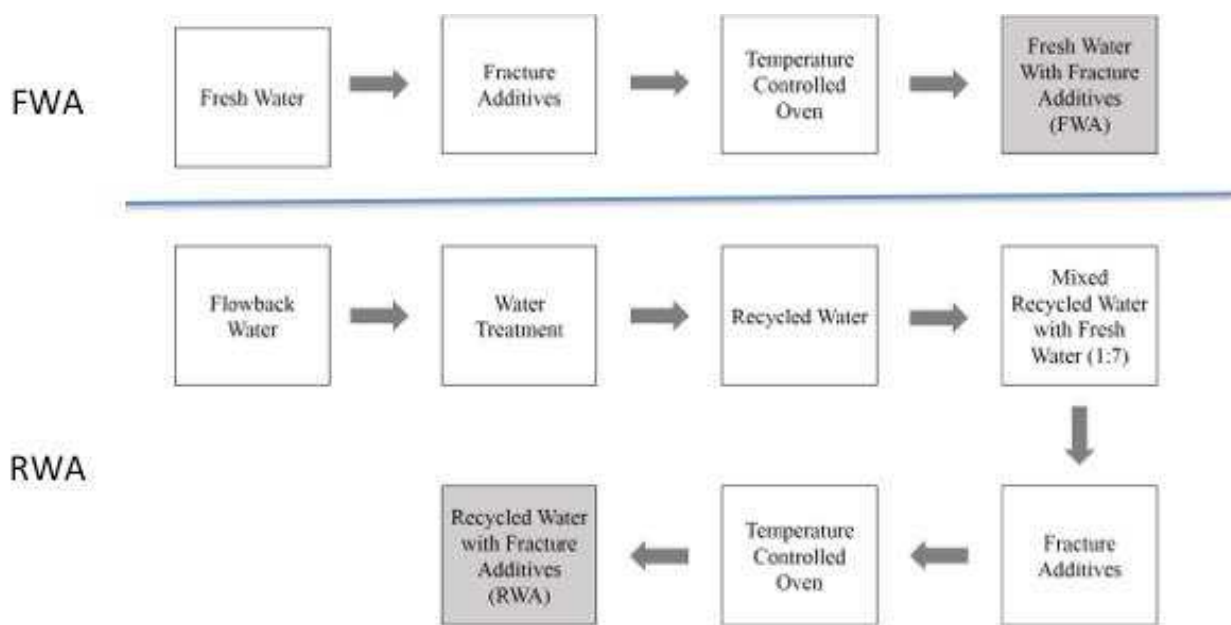


Figure 6. 1. Flow chart of sample preparation.

6.2.2 Liquid chromatography mass spectrometry analysis

Sample analysis was performed by using an Agilent 1290 series liquid chromatography (LC) instrument with Agilent 6530 quadrupole time of flight (QTOF) mass spectrometer equipped with electrospray ionization of positive mode. The analyses were conducted under the following conditions: gas temperature, 325°C ; gas flow, 12 L/ min; nebulizer pressure, 30 psig; sheath gas

temperature, 400 °C; sheath gas flow, 12 L/min; nozzle voltage, 500 V; fragmentor voltage, 120 V; skimmer voltage, 60 V; octopole RF peak, 750 V. The mobile phase is A: 0.1% formic acid in water and B: 0.1% formic acid in acetonitrile. The gradient is 95~80% A for 1-8 minutes, 80~5% A for 8~17 minutes and 5~95% A for 17~18 minutes. A C-18 column (2.1mm × 100mm, 2.7µm) was used and the carrier flow rate was 0.3ml/min through the column. 5µl is injected and samples run for 18 minutes at 30°C. Due to the unavailability of standard solutions, organic matter characterization was accomplished using the qualitative analysis software B.06.00.

6.3 Results and discussion

6.3.1 Spectrum interpretation

Figure 6.2 presents the LC-MS spectrum for RWA (red) and FWA (black). There are two zones of particular interest. More polar compounds are detected at earlier retention times and non-polar compounds are detected at later retention times in the spectrum. RWA has more abundance than FWA in the relatively polar zone at retention times between 5 and 11 minutes, referred to as the relatively more hydrophilic zone. FWA has higher peaks than RWA in the relatively non-polar zone at retention times between 11 and 16 minutes, referred to as the relatively more hydrophobic zone. The separated zones are based on retention times with different gradients in the mobile phase. The relatively more hydrophilic zone eluted at 85-55% formic acid in water and the relatively more hydrophobic zone eluted at 55-5% formic acid in water. This difference might be caused by RWA passing through the simulated formation temperature and breaker oxidation twice. Non-polar compounds might be broken down more easily than polar compounds under these conditions. In addition, since a relatively higher number of carbon chains tend to be detected at later retention times, FWA has a greater abundance of high-number carbon chains than RWA.

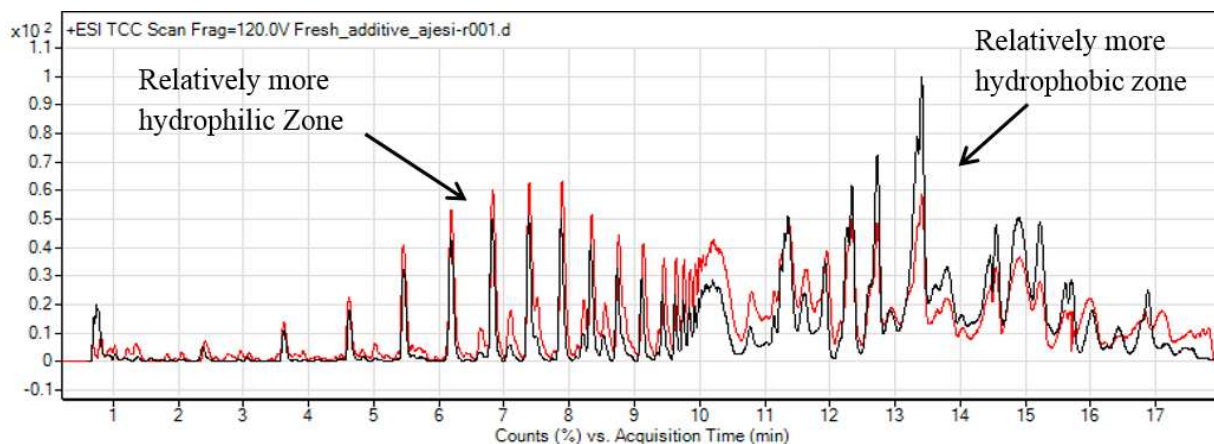
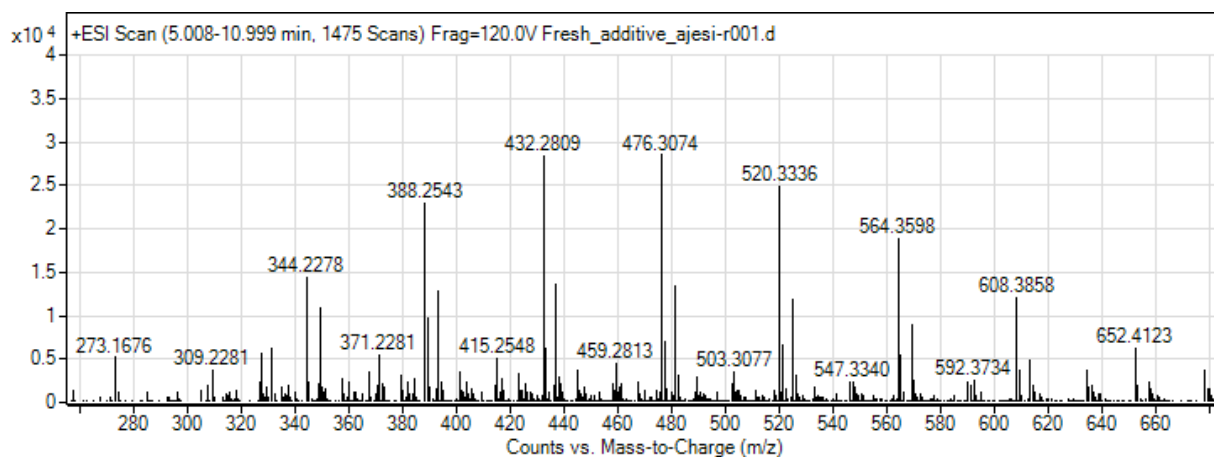


Figure 6.2. LC/MS chromatogram in Positive ion mode of RWA (recycled water with frac additives (red)) and FWA (fresh water with frac additives (black)).

Figure 6.3 shows the mass spectra of FWA (a) and RWA (b) in the relatively polar zone at retention times between 5 and 11 minutes. While there is a difference in the relative abundance of many of the peaks, the mass spectra of both FWA and RWA are almost the same. This seems to indicate that the compounds present in frac flowback when using fresh water and recycled water are the same but occur at greater concentrations when recycled water is used. Figure 6.4 shows the mass spectra of FWA (a) and RWA (b) in the relatively non-polar zone at retention times between 11 and 17 minutes. Figure 6.4 indicates that the greater high temperature processing of the RWA samples resulted in more breakdown of the higher molecular weight, non-polar compounds although it appears that the spectra are equivalent except for magnitude.

(a) FWA



(b) RWA

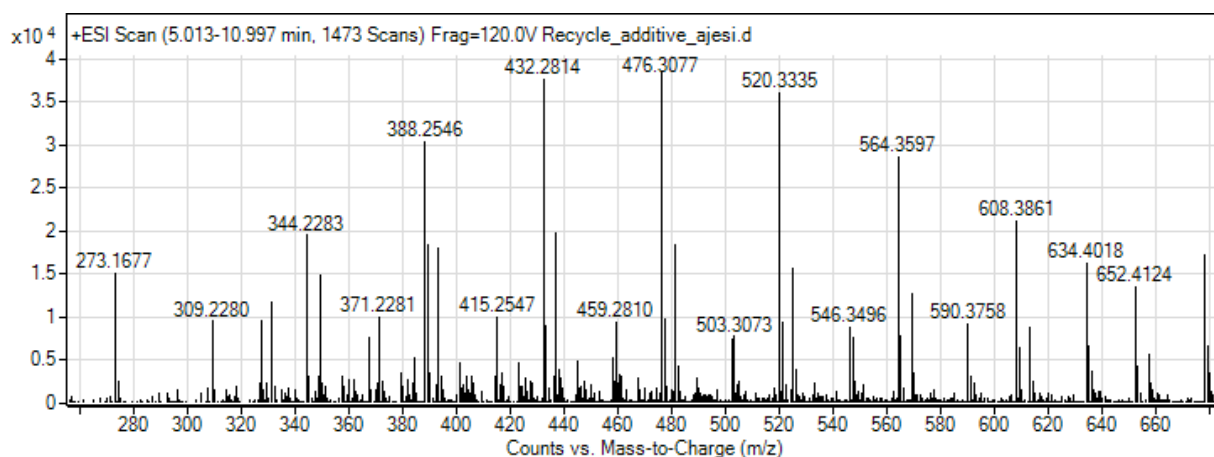
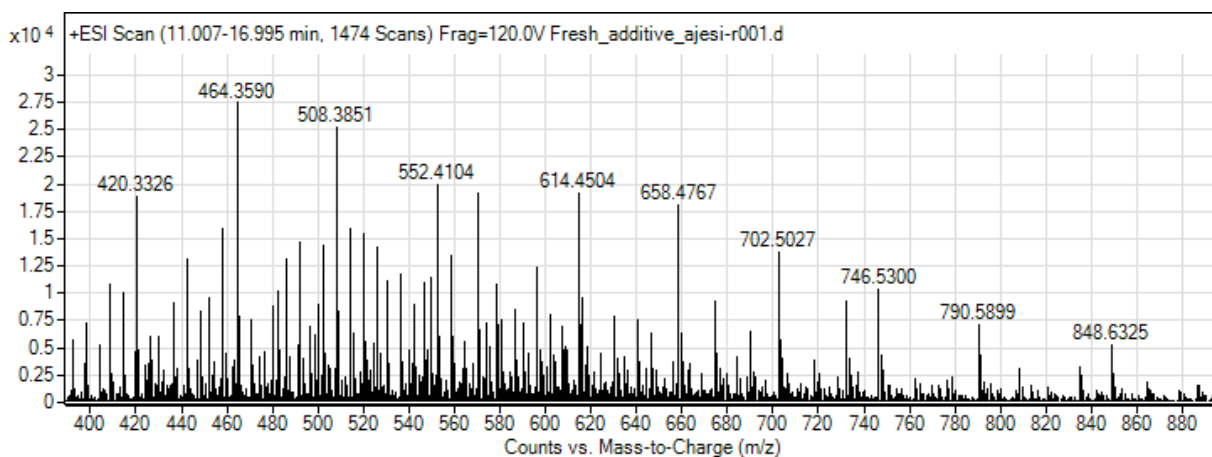


Figure 6.3. Mass spectra with relative abundance of (a) fresh water with frac additives and (b) recycled water with frac additives at relatively polar zone (retention time between 5 to 11 minutes).

(a) FWA



(b) RWA

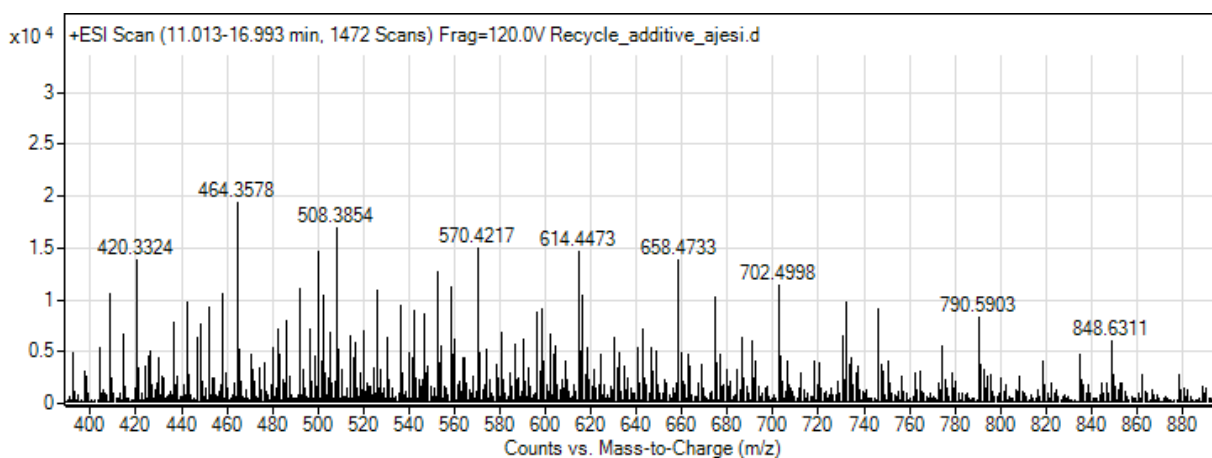


Figure 6.4. Mass spectra with relative abundance of (a) fresh water with frac additives and (b) recycled water with frac additives at relatively non polar zone (retention time between 11 to 17 minutes).

The peaks in the spectrum from both the hydrophilic and hydrophobic zones show an array of $\Delta m/z \cong 44.026$ (Table 6.3 and Table 6.4), suggesting that the peaks might be separated by an ethoxylated unit ($\text{CH}_2\text{-CH}_2\text{-O}$) (Chiron, et al, 2000; Gonzalez, et al, 2007; Petrovic, et al, 2001 ; Thurman, et al, 2014, Maciejczek, et al, 2010). Table 6.3 shows the mass differences with the first 10 peaks in the relatively more hydrophilic zone (between 5 and 11 minutes of retention times) for both RWA and FWA. Masses differed from 44.0256 to 44.272 with an average mass delta of

44.263, which is close to the exact mass of ethoxylated units (44.0262). According to Table 6.4, similar mass spectrum results were also observed for the relatively more hydrophobic zone between 11 to 17 minute retention time with the first 10 peaks distinguished from mass differences of $\Delta m/z \cong 44.026$ (mass differences ranged from 44.0245 to 44.0272 with an average mass of 44.0262). The hypothesis of the existence of ethoxylated units in samples from both zones is supported by the measured mass differences being almost identical to the mass of the ethoxylate functional group. Ethoxylated compounds are used for various functions during hydraulic fracturing including friction reduction, scale inhibition, gel sweep and breakers (Carter, et al, 2013).

Compounds that have a $\Delta m/z \cong 58.04$, were also observed but were not consecutive in the mass spectra. This result indicates another compound is observed in both samples and is likely to be propylene oxide compounds ($\text{CH}_3\text{-CH-CH}_2\text{-O}$) or propylated surfactant units. The measured mass differences from both samples are summarized in Table 6.5. The average of the measured mass differences are 58.0431 and 58.0425 from RWA and FWA and are close to the exact mass of propylate oxide functional group surfactant (58.041).

Propylene glycol, one of the most common ingredients in frac fluid, which is used as a friction reducer, biocide and scale inhibitor is produced from propylene oxide (Carter, et al, 2013). Propylene glycol may be transformed into a propylated oxide during the thermal processing that the samples were subjected to. Propylene oxide compounds can be carcinogenic and are used for clay stabilizers (Clapper and Watson, 1996).

Table 6.3. Mass differences of ethoxylate compounds from RWA and FWA in “Relatively more hydrophilic zone” between 5 to 11 minute retention times.

RWA			FWA		
Retention time	Measured mass(m/z)	Mass difference	Retention time	Measured mass(m/z)	Mass difference
5.461	344.2285	44.026	5.461	344.2284	44.026
6.192	388.2545	44.0272	6.186	388.2544	44.0265
6.829	432.2817	44.0262	6.818	432.2809	
7.39	476.3079	44.0263			
7.894	520.3342	44.0257	9.624	379.2511	44.0264
8.346	564.3599	44.0269	9.845	423.2775	
8.761	608.3868	44.0256			
9.14	652.4124	44.0261	9.75	401.2642	44.0265
9.457	696.4385		9.922	445.2907	
			8.21	416.7496	44.0263
6.655	634.4018	44.0263	8.825	460.7759	
7.105	678.4281	44.0263			
7.513	722.4544		7.378	476.3073	44.0259
			7.877	520.3332	44.0265
			8.329	564.3597	44.026
			8.739	608.3857	44.0265
			9.113	652.4122	44.0268
			9.433	696.439	
	Average	44.0263		Average	44.0263
	Standard Deviation	0.0004		Standard Deviation	0.0002

Table 6.4. Mass differences of ethoxylates compounds from RWA and FWA in relatively more hydrophobic zone between 11 to 17 retention times.

RWA			FWA		
Retention time	Measured mass(m/z)	Mass difference	Retention time	Measured mass(m/z)	Mass difference
11.309	364.2702	44.027	11.241	342.2256	44.0264
11.357	408.2972	44.026	11.303	386.252	
11.382	452.3232				
			11.35	408.2966	44.0262
13.426	420.3361	44.0268	11.373	452.3228	
13.408	464.3629	44.0228			
13.362	508.3857	44.0261			
15	526.3962	44.0272	13.421	420.3334	44.0261
13.333	552.4118	44.025	13.4	464.3595	44.0257
14.96	570.4234	44.0258	14.531	492.3902	44.0264
13.304	596.4368		13.353	508.3852	44.0262
			15.004	526.3958	44.0265
			14.465	536.4166	
14.92	614.4492	44.0263			
14.88	658.4755	44.0245	13.321	552.4114	44.0272
14.841	702.5	44.0264	13.294	596.4386	
14.801	746.5264				
			14.964	570.4223	44.0264
			14.923	614.4487	
	Average	44.0258		Average	44.0263
	Standard Deviation	0.0012		Standard Deviation	0.0003

Table 6.5. Mass difference of propylated glycols from RWA and FWA in both “relatively hydrophilic and hydrophobic zones”.

RWA			FWA		
Retention time	Measured mass(m/z)	Mass difference	Retention time	Measured mass(m/z)	Mass difference
9.032	197.1151	58.0424	10.087	331.2102	58.0423
10.87	255.1575		10.777	389.2525	
5.762	215.1234	58.0441	12.894	424.3283	58.0414
8.437	273.1675		15.041	482.3697	
8.437	273.1675	58.0415	14.824	462.3572	58.0431
10.102	331.209	58.0427	15.613	520.4003	
10.793	389.2517				
			15.227	491.3738	58.0472
10.027	358.2216	58.0491	16.01	549.421	
9.515	416.2707				
			15.613	520.4003	58.0417
9.997	400.2916	58.0428	16.422	578.442	
10.596	458.3344				
			16.01	549.421	58.0424
10.486	414.3072	58.0426	16.892	607.4634	
10.989	472.3498				
			12.254	558.4228	58.0423
10.545	620.4227	58.0429	12.706	616.4651	
10.918	678.4656				
			16.422	578.442	58.0422
			17.428	636.4842	
10.601	664.4488	58.0428	12.706	616.4651	58.0414
10.955	722.4916		13.152	674.5065	
			13.582	732.548	58.0422
10.603	669.404	58.042	14.008	790.5902	
10.954	727.446				
			14.008	790.5902	58.0423
8.6	682.4229	58.0425	14.42	848.6325	
9.642	740.4654				
10.651	708.4746	58.0422			
10.99	766.5168				
	Average	58.0431		Average	58.0425
	Standard Deviation	0.0019		Standard Deviation	0.0016

6.3.2 Identification of organic compounds

Due to the lack of standard solutions, qualitative analysis of samples was conducted using Agilent software B.06.00 based on the exact mass of compounds used for hydraulic fracturing (USHRC, 2011). The identified organic compounds in RWA and FWA are exhibited in Figure 6.5. All compounds were detected at less than 5ppm mass accuracy. The qualitative analysis based on LC-MS for RWA and FWA shows that they have approximately the same compounds including acetone, aldol, alkoxylated phenol formaldehyde resin, diethylbenzene, dipropylene glycol, d-Limonene, ether salt, ethylbenzene, n-dodecyl-2-pyrrolidone, dodecylbenzenesulfonate isopropanolamine, polyethylene glycol, and triethylene glycol. Since these compounds were detected in samples that were exposed to thermal processing at 120°C for 5 hours twice, these compounds do not seem to be easily degraded under temperature and oxidation conditions expected during hydraulic fracturing. Cyclohexanone, di (ethylene glycol) ethyl ether acetate, diethylene glycol, dipropylene glycol monomethyl ether (2-methoxymethylethoxy propanol), ethoxylated octyl phenol and toluene were detected in RWA but not identified in FWA. These compounds might be from the recycled water (perhaps a different frac fluid since the recycled water was from a commercial treatment plant) and not easily removed from conventional water treatment. While quantitative analysis is not possible without chemical standards, relative abundances analysis of each organic compound from RWA and FWA can be compared (Figure 6.5). For example, according to Figure 6.5, if the acetone concentration of RWA is 100ug/L, FWA is 20 ug/L.

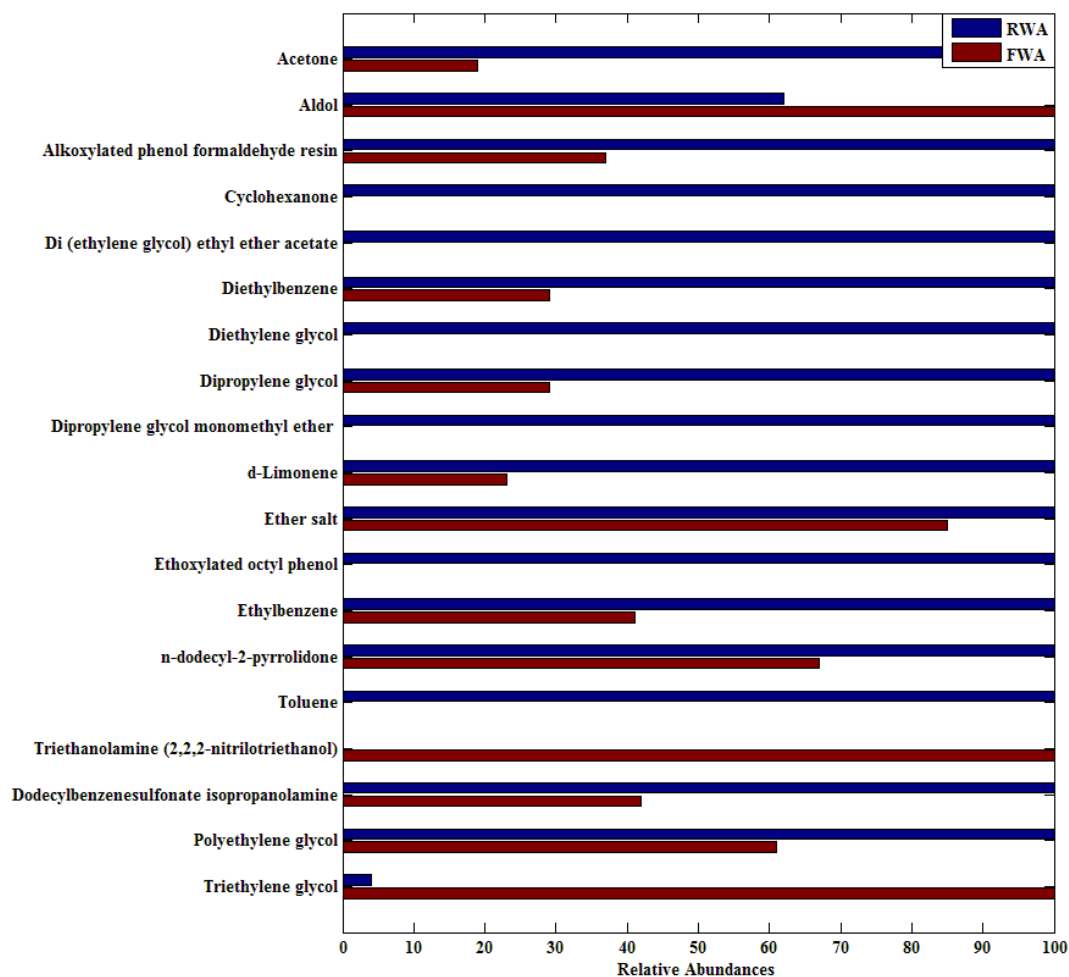


Figure 6.5. Identified organic compounds from both RWA and FWA with relative abundances.

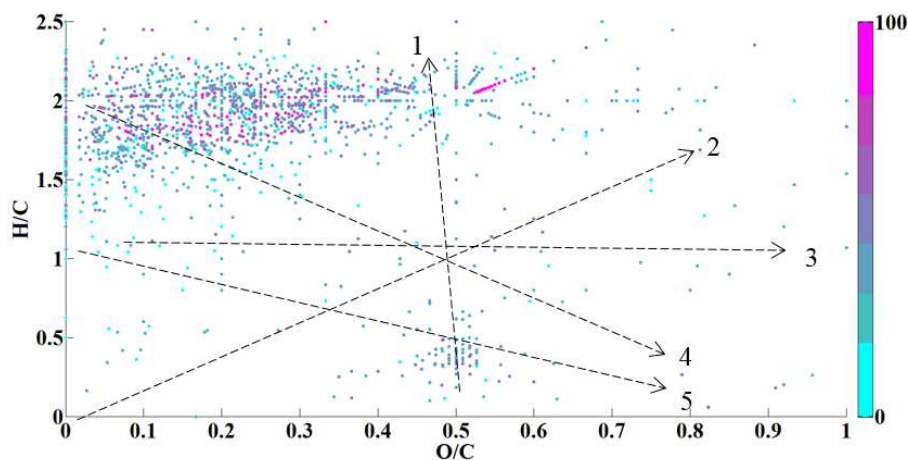
6.3.3 Organic compounds characterization trends from FWA and RWA

Thousands of peaks are detected in the LC-MS analysis and the van Krevelen diagrams that were used. The van Krevelen diagram is a cross plot of ratios of hydrogen to carbon (H: C) on the y-axis and oxygen to carbon (O: C) on the x-axis with a color bar that indicates mass spectral relative abundance. The van Krevelen diagram (Figure 6.6) shows that most of the compounds

were detected between H/C ratio of 1.5 to 2.5 and O/C ratio of 0 to 0.3. It means that organic compounds from both FWA and RWA have a relatively low degree of oxidation (O/C ratio less than 0.3) and a high saturation level (H/C ratios higher than 1.5). Some of the compounds also were detected roughly at H/C of ratio 0.5 and O/C ratio of 0.5, meaning a higher degree of oxidation and a greater amount of unsaturation. The van Krevelen diagram for FWA and RWA show almost the same pattern of relative abundance (color bar on Figure 6.6).

Additionally, linear trends between data in the van Krevelen plot can suggest structural relationships among families of compounds, making it easy to identify various chemical reactions (Kim, et al, 2003; Grannas, et al, 2006). Five trend lines (1, 2, 3, 4 and 5) are shown in Figure 6.6, indicating (1) hydrogenation/ dehydrogenation; (2) hydration/condensation; (3) oxidation/reduction; (4) methylation/demethylation; (5) carboxylation/decarboxylation (Grannas, et al, 2006).

(a)FWA



(b)RWA

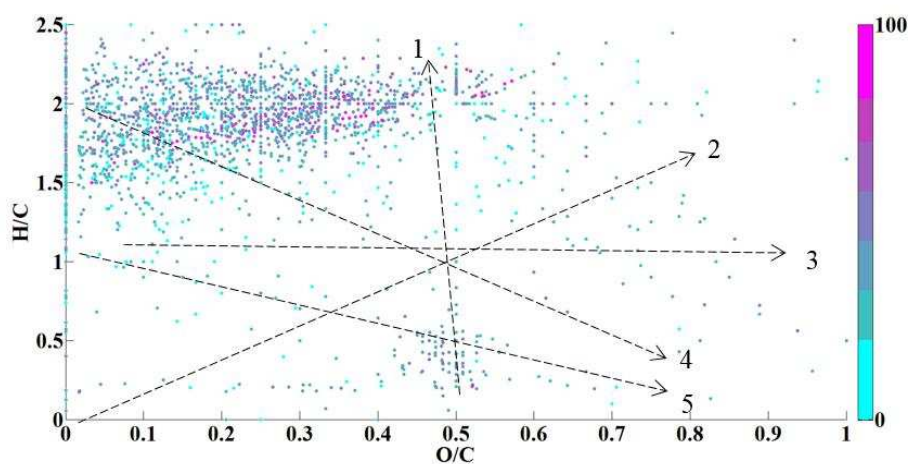


Figure 6.6. Van Krevelen diagram for O/C and H/C ratio of FWA (a) and RWA (b) indicating relative abundance by color bar. Arrows illustrate specific chemical reactions: (1) hydrogenation/dehydrogenation; (2) hydration/condensation; (3) oxidation/reduction; (4) methylation/demethylation; (5) carboxylation/decarboxylation.

FWA and RWA from both the relatively hydrophilic and hydrophobic zones are further analyzed by the Kendrick mass defect analysis (Kendrick, 1963; Hughey, et al, 2001; Marshall and Rodgers, 2008). Naphthenic acids of produced samples from oil sands have been analyzed by the Kendrick mass defect method based on the CH_2 functional group equaling exactly 14.0000

(Barrow, et al, 2010). Recently, ethoxylated homologues of produced water samples from unconventional oil and gas wells has been analyzed by Thurman et al (2014). However, the Kendrick mass defect analysis has not been applied for fracturing fluid of the ethylene oxide unit and propylated glycol.

The ethylene oxide unit ($\text{CH}_2\text{CH}_2\text{O}$) was applied for both samples (FWA and RWA) and a Kendrick mass defect analysis was performed. Kendrick exact masses (KEM) were calculated as follows:

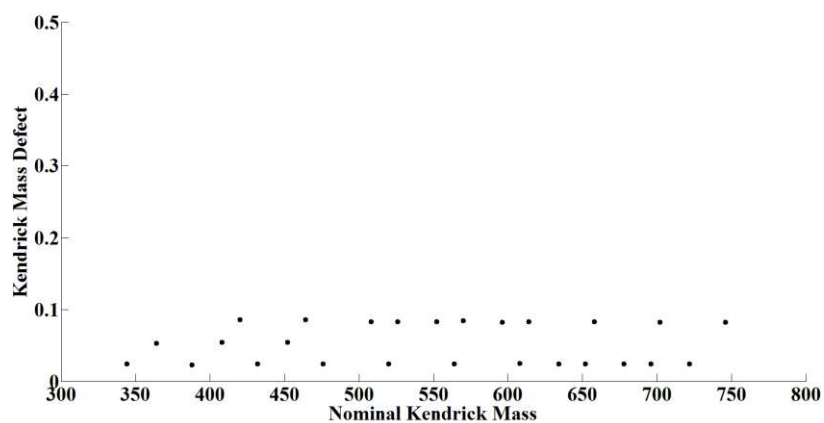
$$KEM = \text{Measured Mass} \times \frac{44.000}{44.0262} \quad (3)$$

To apply the Kendrick mass defect analysis for propylated glycol ($\text{CH}_3\text{-CH-CH}_2\text{-O}$), equation (2) was used.

$$KEM = \text{Measured Mass} \times \frac{58.000}{58.0418} \quad (2)$$

Kendrick mass defect (KMD) is the difference between Kendrick exact mass (KEM) and Kendrick normal mass. Figure 6.7 shows Kendrick mass defect analysis results of FWA and RWA for the ethylene oxide unit ($\text{CH}_2\text{CH}_2\text{O}$). As shown in Figure 6.7, most of KMD are scattered between 0 and 0.1, except two points from FWA which have approximately 0.5 of KMD. These values of KMD for both FWA and RWA are smaller than KMD values usually found in petroleum products sample ((Hughey, et al, 2001). KMD from both FWA and RWA are also smaller than KMD from produced water samples based on ethylene oxide (Thurman, et al, 2014). KMD based on propylated glycol equaling 58.000/58.0418 mass units are shown in Figure 6.8. Most of KMD from RWA are close to 1 and only a few KMD are less than 0.1 while most values from FWA are less than 0.1 and just two KMD value are close to 1.

(a) RWA



(b) FWA

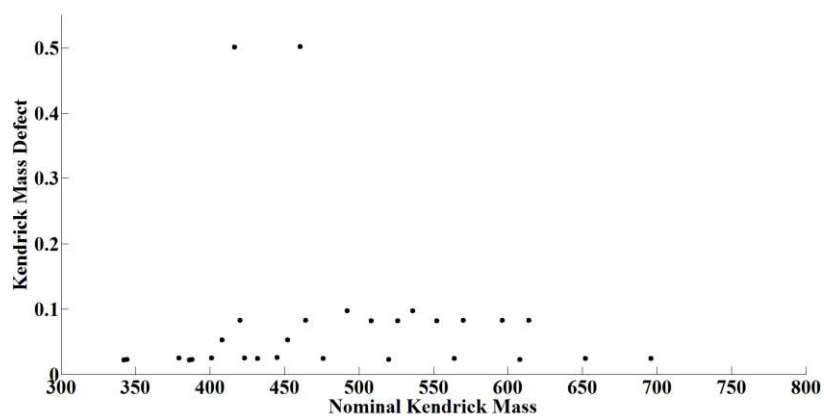
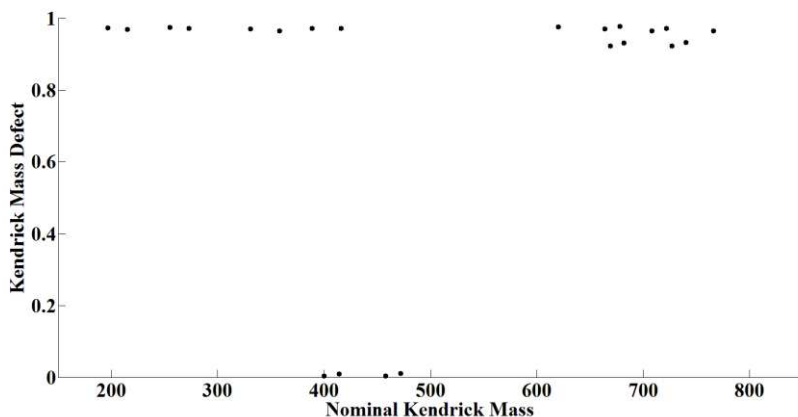


Figure 6.7. Kendrick mass defect diagram of ethylene oxide equaling 44.000/44.062 mass unit from RWA (a) and FWA (b).

(a) RWA



(b) FWA

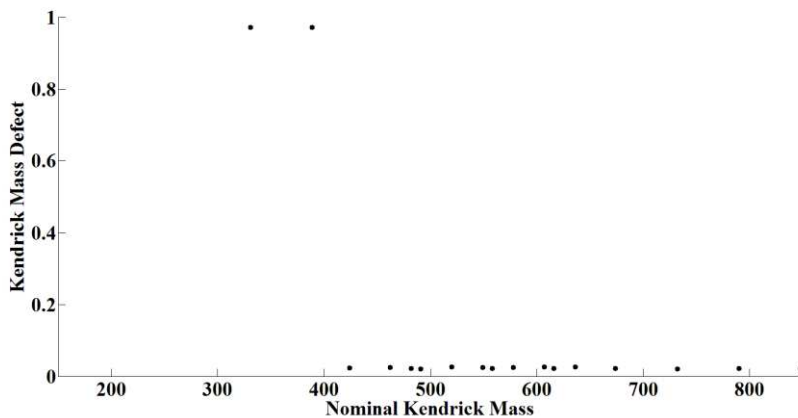


Figure 6.8. Kendrick mass defect diagram of propylated glycol equaling 58.000/58.0418 mass unit from RWA (a) and FWA (b).

In addition, the double bond equivalent (DBE) analysis was performed by LC-MS spectra. DBE can give information on the number of rings, the number of double bonds and hydrogen deficiency in a given molecular formula. DBE values were calculated by the following equation:

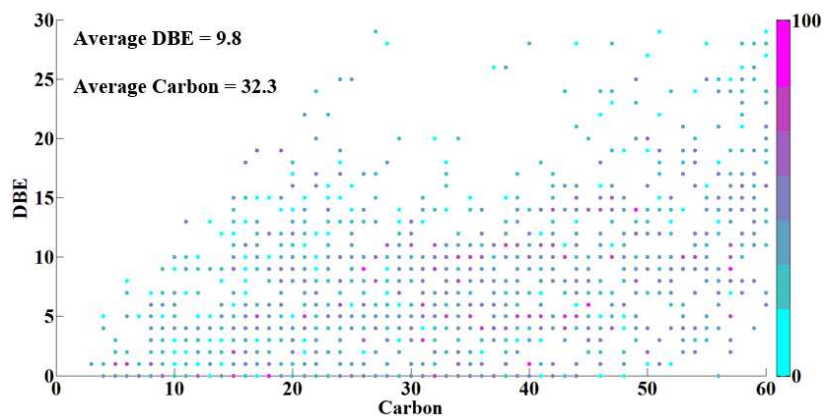
$$\text{DBE} = c - \frac{(h + l)}{2} + \frac{n}{2} + 1 \quad (3)$$

for formulas of $C_cH_hN_nO_oS_sCl_l$.

The results of DBE versus carbon distributions are presented in Figure 6.9. DBE and carbon numbers ranged from 0 to 30 and 0 to 60 individually. According to Figure 6.9, each water analyzed has a similar distribution pattern but different relative abundances. FWA had a higher average carbon number of 32.3 and a DBE of 9.8 but not significantly different from the average carbon number of 31.5 and DBE of 9.5 in RWA. The average difference of DBE between FWA and RWA does not indicate an aromatic difference because there is only a 0.3 average DBE value difference rather than a 3 DBE value that would be expected if an aromatic ring was removed. The distribution of DBE for asphaltene from petroleum were between 20 and 35 which is a higher distribution of DBE than FWA and RWA (Arnaud, 2009). The DBE value from produced water samples from Wyoming were distributed between 0 and 16 which are much less than FWA and RWA (Wang, et al, 2012).

The normalized ratio abundances for RWA and FWA grouped into four categories of carbon content (C_{21-30} , C_{31-40} , C_{41-50} and C_{51-60}) are shown in Figure 6.10. As can be seen in Figure 6.10, RWA and FWA comprise predominantly $C_{21}-C_{40}$. RWA has more abundance than FWA at carbon numbers between $C_{21}-C_{40}$ but less abundance when greater than C_{41} . These results are similar to the mass spectrum data in Figure 6.2 that showed FWA having a greater abundance than RWA at later retention times because higher number of carbon chains are detected at later retention times.

(a) FWA



(b) RWA

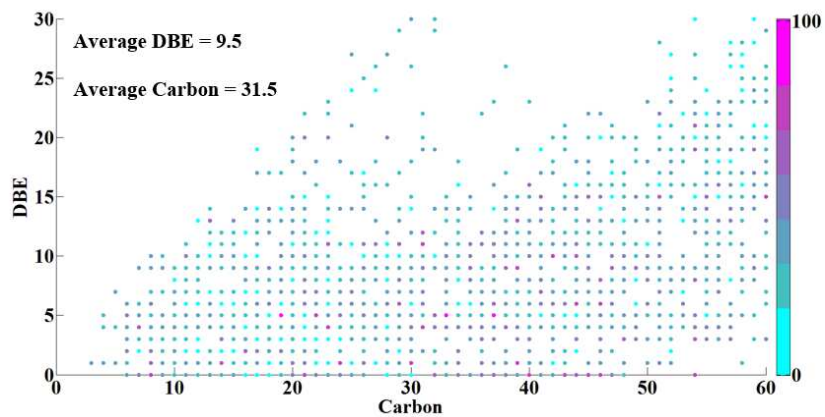


Figure 6.9. Double bond equivalent (DBE) versus carbon number distribution of (a) FWA and (b) RWA. The color bar indicates relative abundances.

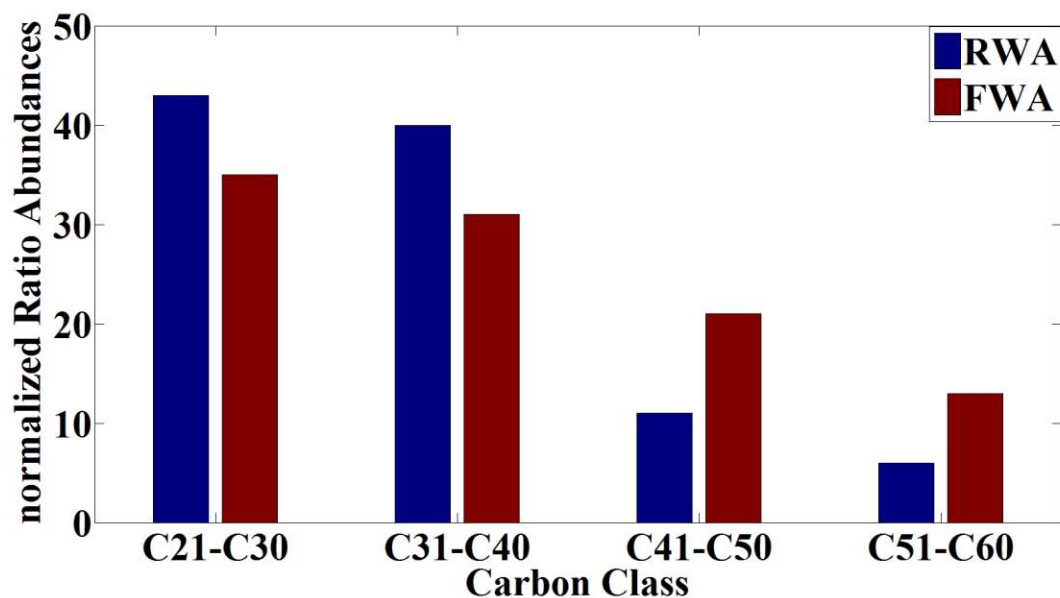


Figure 6.10. Comparison of the relative abundance of carbon compound classes for FWA and RWA.

6.4 Conclusions

- In this study, frac fluid with recycled water and frac fluid with fresh water were compared by Liquid chromatography-mass spectroscopy with electrospray ionization when subjected to downhole temperature and oxidation conditions which is a same condition of hydraulic fracturing process.
- Ethylene oxide and propylated glycol functional unit were detected from both recycled water with frac additives and fresh water with frac additives, showing very similar mass deferent pattern in mass spectra from both samples.
- Qualitative analysis was performed through Agilent qualitative analysis software B.06.00 based on the exact mass of the chemical compound which was used for hydraulic fracturing in the Unites States between 2005 and 2009. The qualitative analysis shows that they have approximately the same compound from both samples.

- To further analyze the sample, van Krevelen diagram, carbon distributions versus double bond equivalent and comparison of the relative abundance of carbon compound class were applied to both samples, showing all similar pattern between samples.

7. Organic and inorganics from flowback and produced water from shale gas operation: treatment and identification of glycols using gas chromatography-mass spectrometry⁴

7.1 Introduction

The shale oil and gas development in the United States is expected to play an integral role in today's exponential increasing energy demand (GNS, 2012), and advanced technology of directional drilling and hydraulic fracturing has allowed the unconventional oil and gas wells to become one of the fastest growing energy sources in the U.S (AEO, 2013). Hydraulic fracturing requires approximately 2 to 7 million gallons of water for each well (Goodwin, et al, 2013; Hickenbottom, et al, 2013; Lee, et al, 2011; Nicot and Scanlon, 2012; Ranm, 2011; Stephenson, et al, 2011; Suarez, 2012), which is ~98-99% water and sand with 1-2% of chemical additives to make up the fracturing fluid (USDOE 2009; Lee, et al, 2011; Spellman, 2012). The volume of water recovered is approximately 20 to 40% of the initial water input, during 3-4 weeks after flowback water started to be collected, indicating that most of the fracturing fluid additives remain in the geological formation during this period (Bai, et al, 2013). It is important to identify the constituents in the flowback water so that a proper treatment or disposal technique can be determined for its handling.

Glycols (ethylene and propylene), hydrotreated distillates, methanol and various ethoxylated compounds are the most commonly used ingredients for hydraulic fracturing process (Carter, et al, 2013). Carter et al (2013) determined that ethylene and propylene glycols form

⁴ As Submitted to Environmental Science and Technology
Seongyun Kim^a, Ken Carlson^a, Pinar Omur-Ozbek^a

^aDepartment of Civil and Environmental Engineering, Colorado State University, Fort Collins, CO 80523-1372, USA

approximately 15% of fracturing additives. Ethylene glycol monobutyl ether and ethylene glycol are third and fourth most widely used chemical for hydraulic fracturing process between 2005 and 2009 in the United States (USHRC, 2011).

Flowback/produced water quality from hydraulic fracturing may have different characteristics depending on the formations, specifically total dissolved solids (TDS) levels (e.g. Marcellus ~ 180,000ppm, Barnett~60,000ppm, and Dever-Joulesberg 35,000ppm) (Vengosh, et al, 2014; Osborn, et al, 2012).

Li et al (2016) compared produced water quality of between wells fractured with fresh water and recycled water and identified by particle size distribution measurement and X-ray photoelectron spectroscopy (XPS), suggesting recycled water was more compatible with shale formation and cleaned out faster. Today more than 60 % of recycled produced water from produced water is reinjected into wells isolated from underground drinking sources in the natural gas industry (Hayes and Arthur, 2004). To minimize the TDS effects, produced water are mixed with enough fresh waters for the subsequent fracturing jobs (Jenner and Lamadrid, 2013)

The strategy of treatment process for flowback/produced water depends on the use of the effluent (Jenner and Lamadrid, 2013; Lutz, et al, 2013). The flowback water maybe used to fracture other wells, however, the quality of the water should be at a certain level for a successful operation.

Produced water can be evaporated off to reduce the amount of waste and injected into the well of storage. However, this method is not suitable strategy due to the lack of appropriate geology for injection in certain region (Lutz, et al, 2013). In other cases the wastewater, which is not treated, can be injected into subsurface located below groundwater formation (USDOE, 2009; USDOA, 2011; Rahm, 2011; Spellman, 2012; Jenner and Lamadrid, 2013).

There are several studies focused on treatment and reuse of flowback water. (Esmaeilirad, et al, 2015; Rosenblum, et al, 2016). High TDS water can be difficult to treat with wastewater treatment processes such as biological treatment, ultrafiltration and forward osmosis (Lester, et al, 2014; Lefebvre, et al, 2004; Altaee and Hilal, 2004). Also due to presence of various chemicals introduced as fracturing additives, including toxic chemicals (e.g. 2-butoxyethanol, ethylene glycol, etc.) or biocides (e.g., glutaraldehyde), biological treatment is not a reasonable choice (Rogers, et al, 2015; Stringfellow, et al, 2014). High levels of total organic carbon (TOC) in flowback/produced water can negative impact on the membrane processes and make it difficult to use as a direct treatment option (Pandey, et al, 2012). Coagulation is widely utilized for both domestic and industrial wastewater treatment because it is very efficient in removing suspended and colloidal particles (Alexander, et al, 2012; Wang, et al, 2014). Flowback/produced water has similar water quality characteristics to wastewater such as high TDS and TSS (Mukherjee, et al, 2015), and hence coagulation is applied for its treatment (Esmaeilirad, et al, 2015; Rosenblum, et al, 2016). Activated carbon is the most often used as an adsorbent from the treatment of water, municipal and industrial wastewater because of its capability of adsorbing organic contaminants and its reasonable costs (Zhang, et al, 2013). In addition, activated carbon process have also been proven to be useful to reduce the hydrocarbons from hypersaline salt waters (Karapanagiotic, 2007) and surfactants within flowback/produced water (Wu and Pendleton, 2001). Rosenblum et al (2016) investigated the chemical coagulants and powdered activated carbon to lower level of water quality parameters such as dissolved organic carbon, polyethylene glycols and total petroleum hydrocarbons from produced water in Colorado. The electrocoagulation, ultrafiltration, granulated activated carbon adsorption and reverse osmosis were performed to investigate how water quality

parameter from produced water effectively removed especially total organic carbon and total dissolved solids for the purpose of an irrigation of switch grass and canola (Caschette, 2016).

All (2003) suggests salinity, sodicity and toxicity are main critical factors for crop irrigation. Desirable for drinking water are recommended less than 500 mg/L of TDS. Treated water with 1000 to 3000 mg/L of TDS are considered as useful for irrigation and treated water with greater than 3000 mg/L unfit for drinking and irrigation (Davis and De Wiest, 1966).

It is critical to determine the treatment efficiency especially for the additives that are toxic to humans and aquatic habitat. The intake of ethylene glycol can cause kidney failure, brain damage and even death (Kruse, 2012). A lethal dose of ethylene glycol in humans has been estimated to be approximately 100ml/70kg of person (Andrews and Snyder, 1991). Propylene glycol has been certified as generally recognized as safer than ethylene glycol for use and propylene glycol have been used for a wide variety of cosmetic, foods and alcoholic beverages. Propylene glycol is required high levels of biochemical oxygen demand (BOD) during degradation process which can give negative effect on aquatic life, consuming oxygen required by aquatic organism. High levels of dissolved oxygen (DO) is needed for decomposing propylene glycol in the water column (USEPA, 2012). Serious damage of propylene glycols occurs over 4g/L at plasm conditions which considers exceptionally high intake over a short period of time (WHO, 1995), informing that it could be almost impossible to happen to take that levels by consuming foods, except for alcoholic beverages.

Total petroleum hydrocarbons (TPH) is a mixture chemical, usually found in produced water from oil gas development, and are totally made from carbon and hydrogen. TPH is generally used as an indicator of oil spill contamination at the field. TPH treatment in produced water is

critical because TPH can affect negative effects on human and water quality if released to the environment.

The objective of this study was to determine the efficiency of electrocoagulation, ultrafiltration, granular activated carbon and reverse osmosis processes to remove total dissolved solids (TDS), total organic carbon (TOC), dissolved organic carbon (DOC), BTEX, propylene glycol, ethylene glycol, ethylene glycol monobutyl ether, total petroleum hydrocarbon (TPH) and turbidity of produced water from unconventional oil and gas wells in Colorado.

7.2 Materials and methods

7.2.1 Sample collection, location and storage

The flowback/produced water samples were collected from Weld County located in the Denver Julesburg Basin from 10/27/2015 to 4/8/2016. 20ml of samples were collected in glass vials to use for GC-MS. Samples were stored at 4 °C after sample collection and after treatments. Samples were blended from flowback/produced water coming from entire wells in Weld County Colorado since wastewater samples were collected from a tank in a central processing facility directly.

7.2.2 Treatment process and sample collection

The water samples were treated with a series of water treatment processes as shown in Figure 7.1. Samples were collected in 40 mL amber glass vials after every treatment unit to observe the change in water quality parameters for identification of glycols by gas chromatography–mass spectrometry. The specifics of the treatment processes are presented in Figure 7.1.

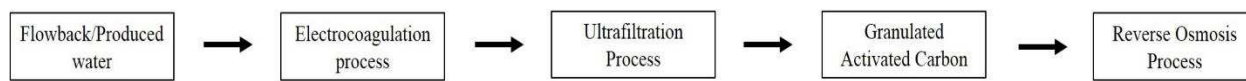


Figure 7.1. The description of analysis process and wastewater treatment plan.

7.2.2.1 Electrocoagulation

Jar testing performed by two metal plates linked to a power supply for one anode and one cathode for the first phase of the treatment study. A continuous flow electrocoagulation utilized the same power supply as a second phase testing in addition to a SHURflo diaphragm pump (model No. 8000-953-238) which consist of six stacked iron plate and anode/cathode electrolytic cell connection. Phipps and Bird 900 Model Jar Tester was used at a paddle speed of 15 rpm for flocculation. 60 liter were treated with mixer at 50 rpm paddle speed. Adding of deionized water with microbubbles stimulated dissolved air floatation. Addition of deionized water occurred microbubbles which was pressurized vessel at 80psi

7.2.2.2 Ultrafiltration

A Mann + Hummel UA420-BT housing and UA420-E hollow fiber filter were utilized for the ultrafiltration process. The pore size was 0.05um and polyacrylonitrile (PAN) was modified as a membrane material of a hydrophilic. The SHURflo diaphragm pump (model No. 8000-953-238) was also used to pump water at a flowrate of 0.5 gpm.

7.2.2.3 Granular activated carbon process

Three columns were used for granular activated carbon (GAC) testing by applying 3" and 4 " diameter PVC piping, caps, nozzles, and plastic tubing. Tubing was used for linking the bottom of each column and running upward to the entrance of the next column. Acid washed 12x30 mesh activated charcoal coconut shell (Charcoal House, GAC1230C-AW) was used for adsorption media with a total empty bed contact time (EBCT) of 7.96 hours. Total volume of three columns

was 23,894.59 cm^3 and flowrate (Msterflex l/s peristaltic pump) was 50mL/min. GAC1230C-AW adsorption media provided isotherms and ten different masses of GAC (5 to 50 % of mass) were applied to where measured and each combined with a 400 mL of ultrafiltration brine. The same condition of Phipps and Bird jar test was applied (described in electrocoagulation section) for mixing each 400 mL beaker of ultrafiltration brine and coconut charcoal at a paddle speed of 25rpm for 1 hour. Whatman #3 (pore size 6um) was used for filtering the brine/GAC mixture to remove suspended inorganic carbon particles before measuring TOC.

7.2.2.4 Reverse osmosis

Sterlitech SEPA CF Cell Crossflow Filtration Unit was selected for reverse osmosis (RO) and GE Osmonics flat sheet RO membranes were used for estimating different material and operating pressures. Both characteristics of AG and SE series were summarized in Table 7.1.

Table 7.1. Summary of Reverse Osmosis (RO).

	AG-Series	SE-Series
Membrane Material	Polyamide	Thin Film
Typical Operating Pressure/Flux	200 psi/10-20 GFD	425 psi/5-20 GFD
Maximum Operating Pressure	450 psi (with tape) and 600 psi (with outer wrap)	600 psi with temperature below 35°C
Salt rejection	95.5% as NaCl	98.9% as NaCl
Application	Brackish Water	Industrial/Wastewater

7.2.3 GC-MS method

7.2.3.1 Sample preparation

Ethylene glycol butyl ether (CAS # 111-76-2), propylene glycol (CAS # 57-55-6), 1, 3-propanediol (CAS # 504-63-2) and ENVI-Carb Plus were obtained from Sigma Aldrich and an ethylene glycol (CAS # 106-21-1) was purchased from Fisher Scientific.

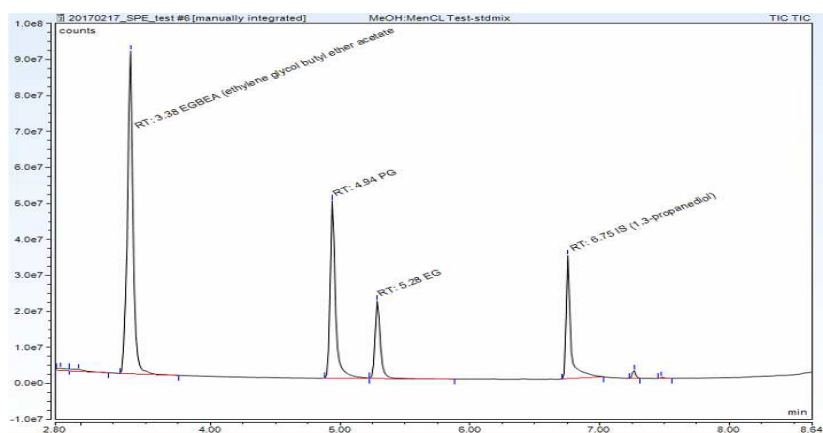
SPE extraction was conducted following the method described in reference (Sidisky, et al., 2010) with minor modifications. Briefly, the cartridge was first conditioned by a sequential rinses of 1 mL methylene chloride, 2x2mL methanol, and 3 mL LC grade water. Solvents were pushing through the cartridge by manual pushing down the plunger of the glass syringe that sat on top of the cartridge. Then 5 mL of sample spiked with 100 uL of 500 ug/mL of 1,3-propandiol (IS) in water was applied onto the cartridge, followed by a 10-min drying under vacuum. Then the glycols were eluted with 2 mL of methanol: methylene chloride (8:2, by vol) after a 1-min soaking. The eluate was stored at 4°C until analysis and injected as is without volume adjustment. Note that vacuum/pressure application was not monitored. Vacuum applied during 10-min drying was generated from fume hood vacuum outlet, and the pressure for pushing liquid through the cartridge during sample loading and elution steps was from the syringe. Two samples from each treatment were randomly chosen as sample blank without the addition of IS, and extracted by SPE. Samples for calibration curves were prepared by diluting authentic standards in methanol and spiked in with the same amount of IS as in actual samples. Curve samples were directly injected without going through SPE extraction.

7.2.3.2 Gas chromatography-mass spectrometry analysis

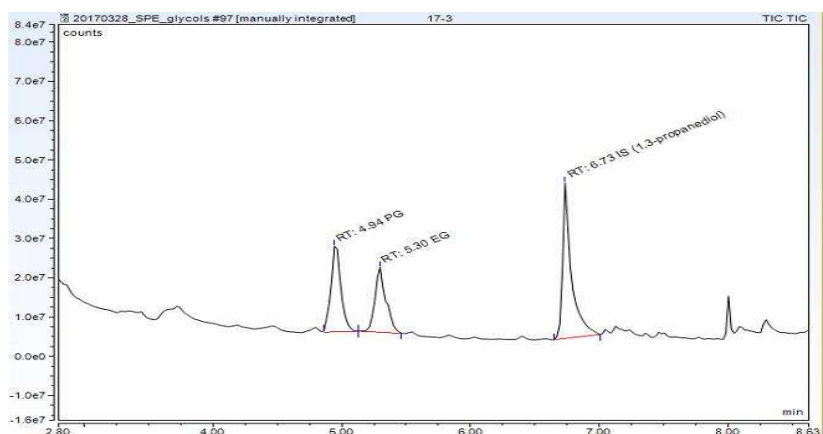
SPE extracted samples and curve samples were analyzed using a Trace 1310 GC coupled to a Thermo ISQ-LT MS. Samples (2 µL) were injected at a 5:1 split ratio, and the inlet was held

at 250°C and transfer line was held at 240°C. SCFA separation was achieved on a 30m DBWAXUI column (J&W, 0.25 mm ID, 0.25 μ m film thickness). Oven temperature was held at 110°C for 1 min, ramped at 10°C/min to 160°C, then ramped to 240°C at 30°C/min. Helium carrier gas flow was held at 1.2 mL/min. SIM mode was used to scan mass 31, 33, 41, 43, 45, 57, 58, 61, 62, 75, 87, 100 at a rate of 10 scans/sec under electron impact mode. Three injections of methanol blank were made in between sample runs in order to remove carryover signals. Figure 7.2 show total ion chromatogram of standard and samples. Figure 7.3 presents mass spectra of ethylene glycol monobutyl ether, propylene glycol, ethylene glycol and internal standard.

(a)



(b)



7.2.3.3 Calibration curve

We have initially prepared the curve samples in water and taken the samples through SPE extraction, as same as actual samples would. Concentrations used for this first set of curve were 5, 10, 15, and 30 ug/mL, as suggested in reference (Sidisky, et al., 2010). But the results showed that most of samples were approximately at 0.1- 5 ug/mL. Then we ran a second set of curve with concentrations 0.2, 1, 2, 10, and 20 ug/mL (See Figure 7.4). Because we ran out of cartridges so that the second set of curve were from standard mix dissolved in methanol, which were then directly injected to GC-MS. Both curves showed good linearity over the ranges. The final results were calculated based on the second curve using 4 points of 0.2, 1, 2, and 10 ug/mL.

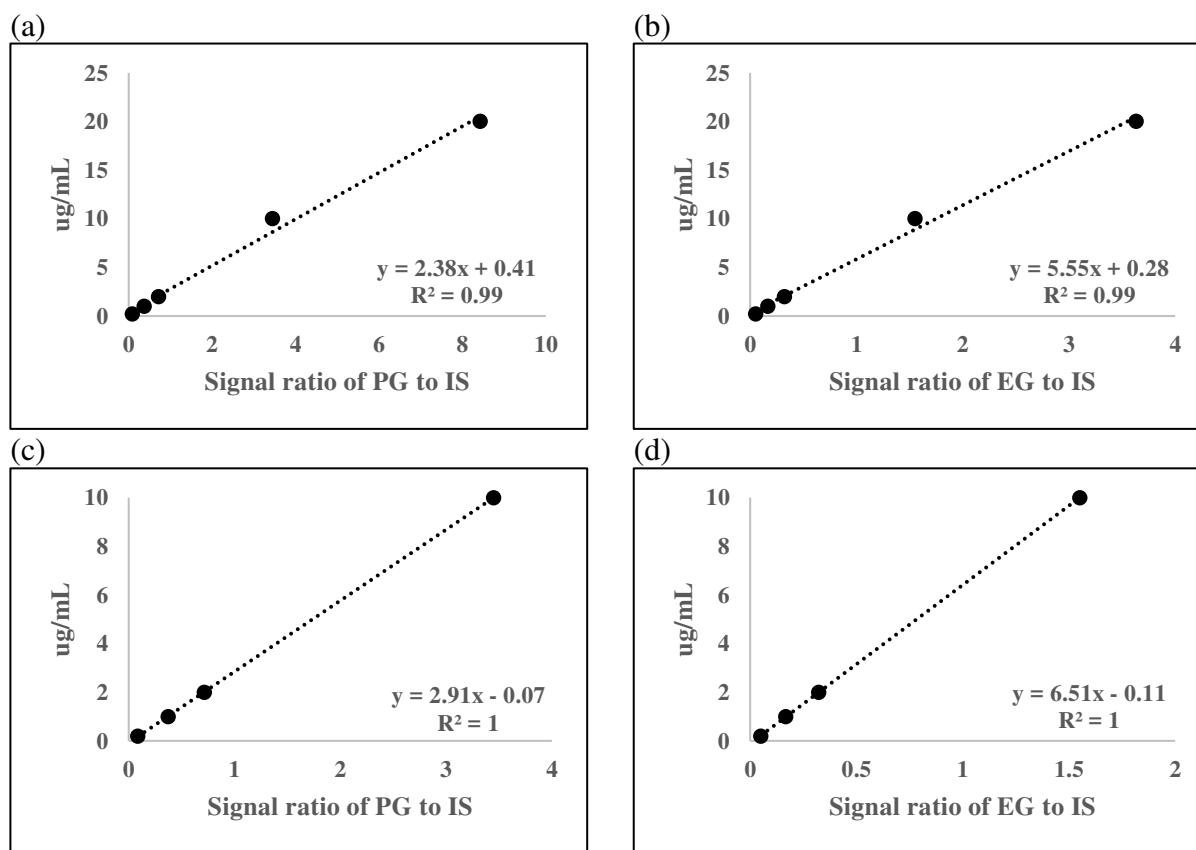


Figure 7.4. Calibration curve for PG ((a) and (c)) and EG ((b) and (d)) for GC-MS analysis.

7.2.3.4 Quality control

Due to the lack of cartridges, pooled QC method was replaced by preparing and running 3 replicates of one actual sample, one sample was randomly chosen. Coefficient of variations of overall analytical procedure including sample prep and data acquisition were calculated based on these 3 replicates. Coefficient of variations of ethylene glycol and propylene glycol from 3 replicated SPE preparation were 8% and 12%, respectively.

7.2.3.5 1,3-propanedial signal in samples without IS spiking

Signal intensity of 1,3-propandiol in samples varied from 1.5×10^4 to 4.2×10^4 , which approximated to $< 6\%$ of signal intensity of spiked IS level. Variations were also seen within treatment, therefore, the background level was not subtracted. Spiked IS signals were used as is (Table 7.2).

Table 7.2. IS (1,3-propanedial) levels in randomly chosen samples (Note: two samples per treatment).

Treatment Processes	Peak area	Average (n=2)
Raw water	33256	42460
	51664	
H2O2/EC treatment	34595	34267
	33939	
Ultrafiltration	44204	40929
	37654	
GAC process	29566	18503
	7440	
RO	9321	15394
	21466	

7.2.4 Water quality analysis

A Shimadzu TOC-VCSH analyzer is used to measure TOC. Standard method 2540 and EPA method 180.1 were applied to measure TDS and turbidity individually. TPH, BTEX, Ca, Mg,

HCO₃, Na, Cl and B were measured from ALS Global Environmental Laboratory (Fort Collins, CO).

7.2.5 Statistical analysis

Water quality parameters (TDS, TOC, DOC, PG and EG) were analyzed by analysis of variance (ANOVA) and Tukey's test for multiple pairwise comparisons. Statistical results were done in R version 3.20. If p-value is less than 0.05, water qualities between wastewater treatments were considered significant.

7.3 Results and discussion

7.3.1 Water quality parameters in the raw flowback water

Flowback/produced water were collected from the central processing facility for treatability testing and water quality characteristics varies from sampling data points due to the temporal variability from central processing facility of produced water quality. Produced water characteristics from the central processing facility were summarized in Table 7.3.

Table 7.3. Summary of produced water quality.

Variable	Minimum	Maximum	Average	# Data Points	Time Period
TOC (mg/L)	1,200	2,173	1,783	11	
TDS (mg/L)	13,600	27,539	21,978	12	
pH	6.5	6.7	6.6	3	
ORP (mV)	-88	-23	-58	3	
Ca (mg/L)	190	270	227	4	10/27/2015- 4/8/2016
Mg (mg/L)	ND	36	22	4	
HCO ₃ (mg/L)	600	750	660	3	
Na (mg/L)	6,300	6,900	6,526	4	
Cl (mg/L)	11,000	17,000	13,000	4	
B (mg/L)	19	22	25	4	

ND: Not Detected

Produced water samples had pH values around 6.6. High levels of TOC measured in the samples indicate high concentration of dissolved cross-linker or high concentration remaining in

the fracturing fluid. Relatively high variation of TDS concentrations is due to the temporal variation and the older produced have higher TDS concentration than the younger produced water. Chloride, sodium, bicarbonate and calcium were the primary ions in produced water. Kim et al (2016) reported similar finding of TOC (approximately 2,000 mg/L) and TDS (approximately 10,000 mg/L to 25,000mg/L) regarding flowback and produced water quality which were sampled from two wells with different fracturing fluid to study temporal variation in Northeast, Colorado during 200 days. Boron and magnesium were also included as water quality parameters.

7.3.2 Total dissolved solids

Electrocoagulation (EC) and ultrafiltration (UF) did not achieve significant TDS removal (1.1% of removal by EC and 3.1% of removal by UF) (Figure 7.5), showing there was not a statically significant difference between raw water and UF (p-value between raw water and EC = 0.99, p-value between EC and UF = 0.99) (Table 7.4). While activated carbon usually removes most dissolved organic compounds from wastewater, removal of TDS after the granular activated carbon (GAC) was approximately 16% (21,500 mg/L of TDS to 18,470mg/L of TDS). Some inorganic compounds can be adsorbed on the GAC sorbent by accumulating depending on the quality of wastewater and the most usually found adsorbed metal is calcium (Lambert, et al, 2002) which is the one of the main inorganics in produced water (Kim, et al, 2016; Barbot, et al, 2013). Aluminum, iron and magnesium also adsorbed on the GAC sorbent (Lambert, et al, 2002). It indicates that 16% removal of TDS caused from the accumulation of these inorganic in GAC bed. RO is effectively capable of removing 95 to 99% of the TDS (ALL, 2003; Barrufet, et al, 2005; Funston, et al, 2002) depending on certain factors such as initial water quality, membrane characteristics and equipment (ALL, 2003). The reverse osmosis (RO) removed almost 90% of TDS (18,470mg/L of TDS to 2550mg/L of TDS), showing still higher levels of TDS for reuse

because treated water with higher than 2,000mg/L of TDS can be only reused to tolerant plants and permeable soils for crop irrigation (USEPA, 2004).

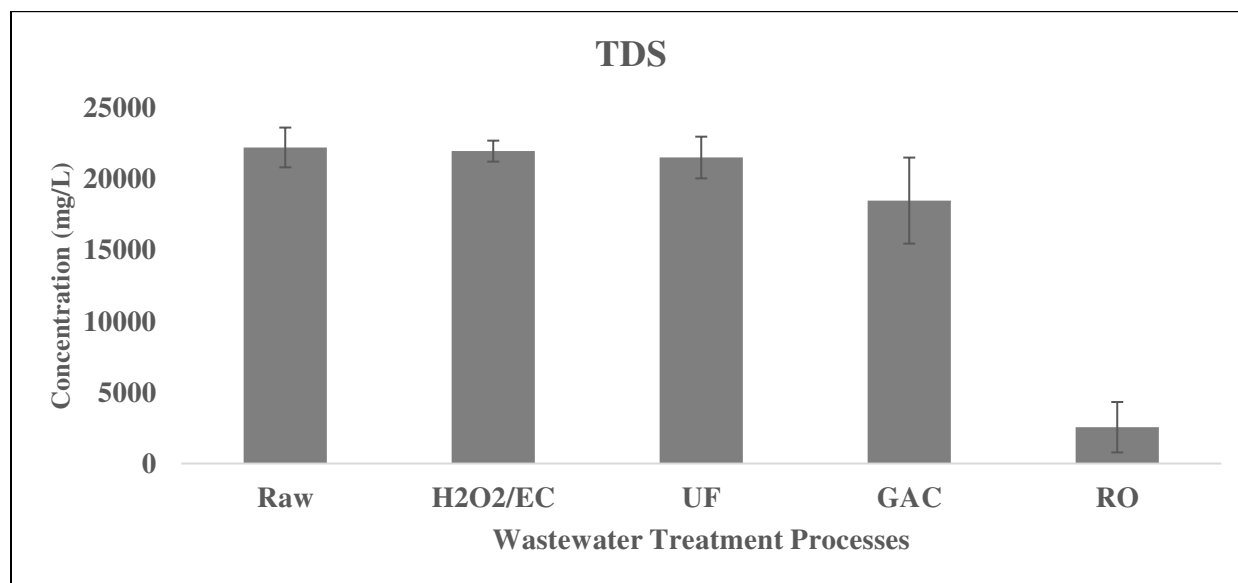


Figure 7.5. Total Dissolved Solids (TDS) results of each water treatment processes (electrocoagulation (EC), ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO)). Error bars indicate standard deviation.

Table 7.4. Analysis of variance (ANOVA) and Tukey's test for multiple pairwise comparisons for TDS of before and after treatment.

(i)	(j)	Mean Difference (i-j)	Sig
Raw water	H2O2/EC	-260.0	0.99
	UF	-66.7	0.99
	GAC	-3733.3	0.17
	RO	-19653.3	<0.001
H2O2/EC	UF	-326.7	0.99
	GAC	-3473.3	0.22
	RO	-19393.3	<0.001
UF	GAC	-3800.0	0.16
	RO	-15920.0	<0.001
GAC	RO	-19720.0	<0.001

7.3.3 Total petroleum hydrocarbon

As shown in Figure 7.6, raw water contained 179mg/L of TPH which was mostly made up by GRO (150 mg/L). Raw water TPH levels were significantly higher than reported by Rosenblum et al. (2016) as 8 mg/L to 20mg/L of TPH in produced water in Colorado. TPH was removed greater than 90 % by using powdered activated carbon (PAC) (dose of 1,000mg/L) (Rosenblum, et al, 2016). TPH removal of 80% was achieved after EC (with 90% removal of GRO) while DRO only attained a 54% removal (16.0 mg/L to 7.3 mg/L) and ORO achieved a 51% removal (13mg/L to 6.30mg/L), indicating that larger carbon chain TPH (DRO (C10-C28) and ORO (C28-C36)) is not easily removed compared to smaller carbon chain TPH (GRO (C5-C10)). After the UF treatment process, more than 95 % of GRO, ORO and DRO were removed. ORO levels were down to not detectable levels after UF. TPH level after UF were still required treatment to meet discharge standards (less than 1mg/L) as a ground remediation. Produced water had a 100% removal of TPH after granular activated carbon (GAC), indicating that TPH could be very efficiently removed without RO.

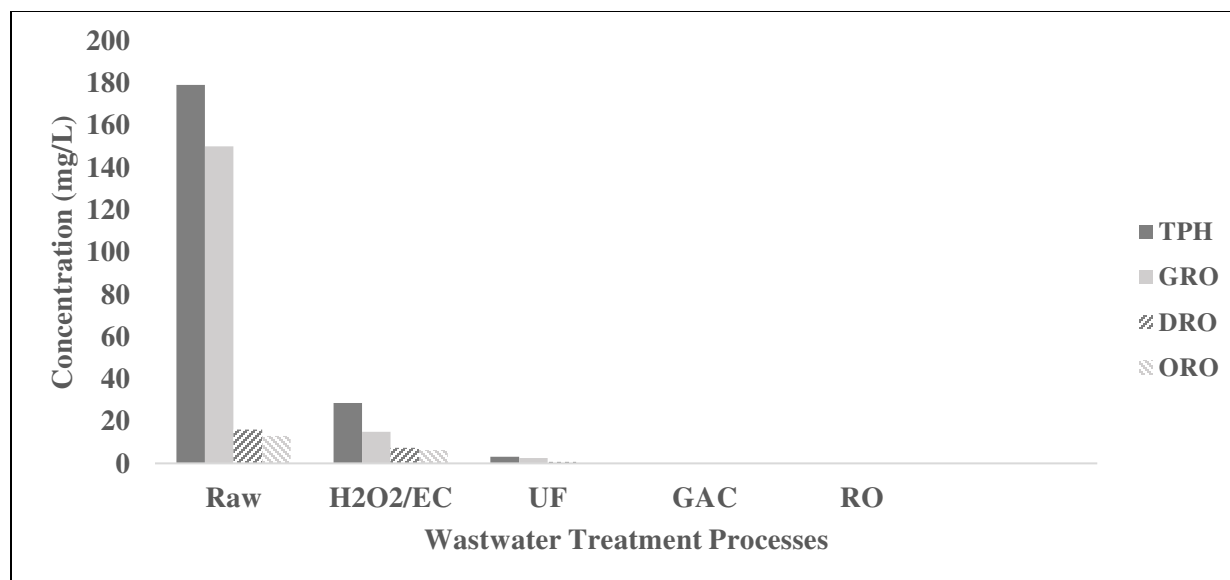


Figure 7.6. Total petroleum hydrocarbons (TPH) of each water treatment processes (electrocoagulation (EC), ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO)).

Electrocoagulation (EC) process has been shown to readily remove Total Petroleum Hydrocarbons (TPH) up to 80 % under the best working conditions (Perez, et al, 2015). Activated carbon is a commonly used method for wastewater treatment of municipal wastewater, organic wastewater due to the ability of absorbing a wide range of organic compounds. Previous studies showed TPH removal up to more than 95 % after GAC or PAC from an initial value of 9,300 mg/L to average final concentration of 360 mg/L and 12 mg/L respectively with 5 to 25 g of activated carbon (Ayotamuno, et al, 2006).

7.3.4 Turbidity

The turbidity can be varied depending on the wells' location and the time after flowback water began. Sick et al (2014) reported an average turbidity between 247 to 295 NTU depending on different fracturing fluid type during 60 days after flowback water began in Colorado. The reported turbidity removal was higher than 96 % and less than 10 NTU remained after coagulation

process by using an aluminum as a coagulant (Sick, 2014). The raw produced water had 172 NTU of turbidity as shown in Figure 7.7. Several previous studies confirmed that turbidity can be easily removed by electrocoagulation process (Bukhari, 2007; Merzouk, et al, 2009; Kobya, et al. 2003). Softening prior to electrocoagulation process was more effective in removing turbidity with 88% to 99% removal of produced water from unconventional oil and gas wells in Colorado (Esmaeilirad, et al, 2015). EC removed 85% of turbidity (172 NTU to 24 NTU) and UF removed almost 99% of turbidity (24 NTU to 1.1 NTU).

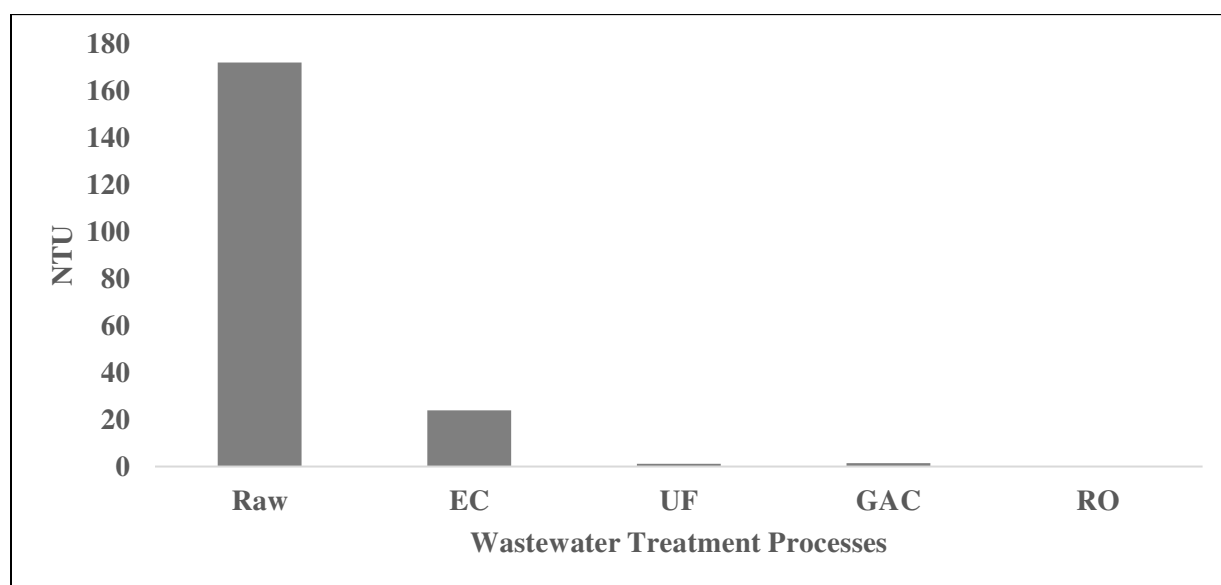


Figure 7.7. Turbidity of each water treatment processes (electrocoagulation (EC), ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO)).

7.3.5 Total organic carbon and dissolved organic carbon

The total organic carbon (TOC) levels in flowback/produced were previously measured in samples from shale oil and gas wells and stabilized approximately 2,000 mg/L with temporal variation and fracturing fluid types (Kim, et al, 2016).

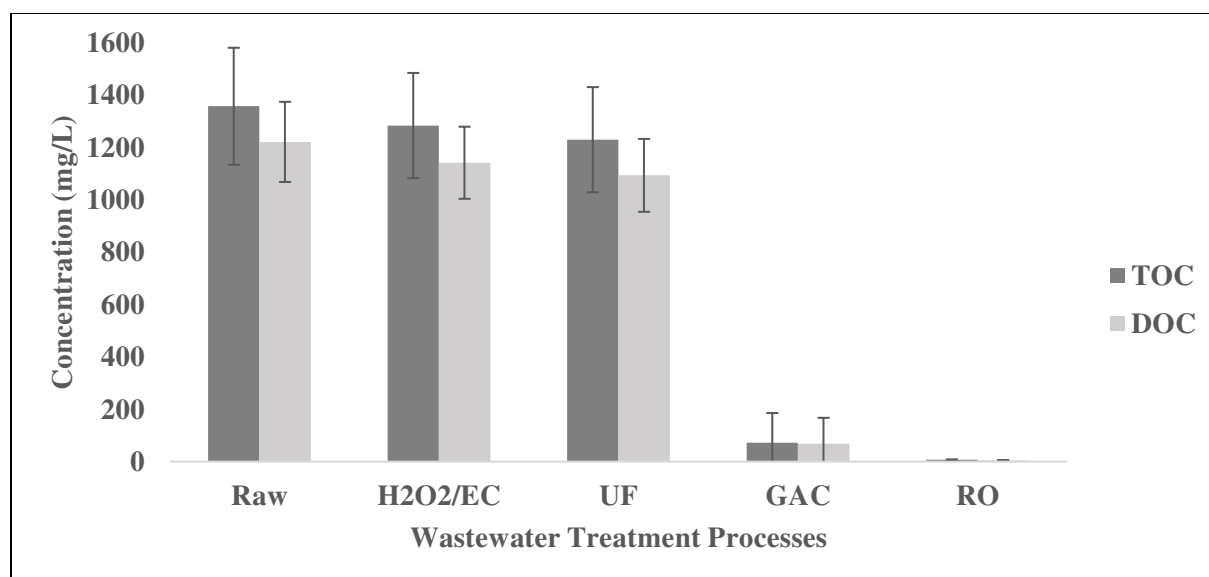


Figure 7.8. Total Organic carbon (TOC) and Dissolved Organic Carbon (DOC) results of each water treatment processes (electrocoagulation (EC), ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO)). Error bars indicate standard deviation.

TOC concentration can include particulate carbon such as high carbon mass particles or oils that can be removed by filtration process. The electrocoagulation and ultrafiltration removed 9.3% of TOC concentration (1356 mg/L to 1229 m/L) and 10.4% of DOC concentration (1220mg/L to 1093mg/L), showing almost TOC concentration is comprised of dissolved carbon rather than particulate carbon (Figure 7.8). About 95% reduction in TOC and DOC were achieved by GAC, proving activated carbon as one of the best methods to remove organic carbon. Both p-values for TOC and DOC between UF and GAC were less than 0.001, meaning that TOC and DOC from UF are statically lower than after GAC's (Table 7.5 and Table 7.6). 95% of TOC and DOC removal by GAC in this study were much higher removal than previously reported by Rosenblum et al. (2016) that shows removals between 9.5 % to 23.3 % by applying PAC with 1,000mg/L dose from vertical wells and horizontal wells in oil and gas field (Rosenblum, et al, 2016). While there is no statistical difference of TOC (p-value = 0.983) and DOC (p-value = 0.95) between GAC and RO, reverse osmosis (RO) process made up to 99% of removal of both TOC

(72 mg/L to 7 mg/L) and DOC (68 mg/L to 5mg/L) concentration within samples. 99% of TOC removal exhibited higher efficiency of previous results which are approximately 90% of TOC removal by a surfactant modified zeolite (SMZ)/membrane bioreactor (MBR)/RO system (Kwon, et al, 2008; Brookes, 2005). EC process achieved greater than 80% TPH removal while only 5% of DOC was removed by EC, indicating that DOC form only small fraction of TPH and 5% of DOC removal caused from TPH removal.

Table 7.5. Analysis of variance (ANOVA) and Tukey's test for multiple pairwise comparisons for TOC of before and after treatment.

(i)	(j)	Mean Difference (i-j)	Sig
Raw water	H2O2/EC	-73.3	0.98
	UF	-127.3	0.88
	GAC	-1284.67	<0.001
	RO	-1356.67	<0.001
H2O2/EC	UF	-54.0	0.99
	GAC	-1211.3	<0.001
	RO	-1283.3	<0.001
UF	GAC	-1157.3	<0.001
	RO	-1229.3	<0.001
GAC	RO	-72.0	0.983

Table 7.6. Analysis of variance (ANOVA) and Tukey's test for multiple pairwise comparisons for DOC of before and after treatment.

(i)	(j)	Mean Difference (i-j)	Sig
Raw water	H2O2/EC	-79.7	0.92
	UF	-127.7	0.69
	GAC	-1152.0	<0.001
	RO	-1220.7	<0.001
H2O2/EC	UF	-48.0	0.99
	GAC	-1072.3	<0.001
	RO	-1141.0	<0.001
UF	GAC	-1024.3	<0.001
	RO	-1093.0	<0.001
GAC	RO	-68.7	0.95

7.3.6 Propylene glycol and ethylene glycol

5 set of wastewater samples were analyzed by GC-MS for identifying ethylene glycol, propylene glycol and ethylene glycol monobutyl ether. Removal of EG and PG from hydraulic fracturing wastewater through EC, UF, GAC and RO is illustrated in Figure 7.9.

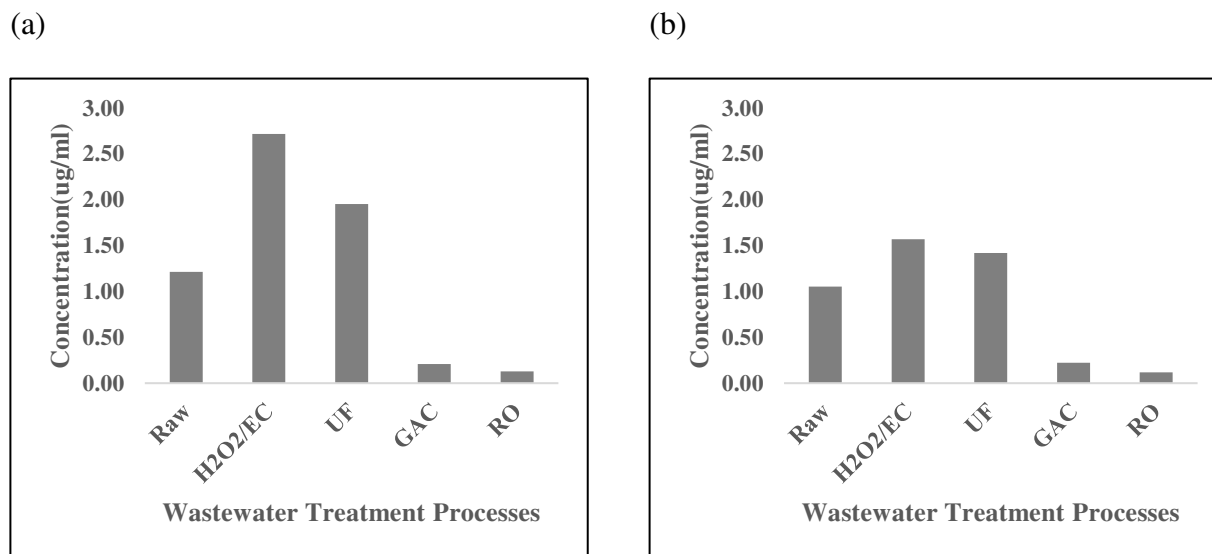


Figure 7.9. PG (a) and EG (b) of average concentration from 5sets samples via wastewater treatment processes.

Ethylene glycol monobutyl ether was not detected in any sample, suggesting that ethylene glycol monobutyl ether might not be used for frac additives in this study wells or degraded through the high pressure and the high temperature under formation. PG concentration is little higher than EG concentration. PG ranged from 0.07 ug/ml to 5.39 ug/ml and EG level varied between 0.07 ug/ml to 5.52 ug/ml, showing both PG and EG have highest concentration from 4th sample set (see Table 7.7).

Table 7.7. Summary of EG and PG concentration of raw produced water and each treatment processes.

	Sample No.	Raw(ug/ml)	H2O2/EC(ug/ml)	UF(ug/ml)	GAC(ug/ml)	RO(ug/ml)
EG	1	0.08	0.58	0.44	0.24	0.13
	2	0.09	0.57	0.53	0.18	0.15
	3	0.06	0.35	0.32	0.17	0.09
	4	4.96	5.52	5.23	0.36	0.12
	5	0.07	0.84	0.57	0.16	-
Average		1.05	1.57	1.42	0.22	0.12
PG	1	0.64	1.56	1.79	0.44	0.25
	2	1.08	1.86	1.54	0.13	0.12
	3	0.10	0.65	0.49	0.10	0.08
	4	4.12	5.39	4.84	0.20	0.07
	5	0.12	4.13	1.10	0.18	-
Average		1.21	2.72	1.95	0.21	0.13

Average concentration of PG and EG shows a decreasing trend through the treatment processes, and GAC found to remove both PG (drinking water limit (1ug/ml) and EG to meet acceptable limits for drinking water. P-value for PG and EG between GAC and RO are 0.99 and 0.89, meaning that there is not significant different between GAC and RO for PG and EG (Table 7.8 and Table 7.9)

PG (p-value = 0.06) and EG (p-value <0.001) concentrations in raw produced water samples were detected at significantly lower concentrations than after H2O2/EC. Given the raw water from hydraulic fracturing, there might be still interferences from hydraulic fracturing additives or geological formations for recovery in chromatogram even if specific SPE method was applied. Figure 7.5 shows that TDS concentration was not affected by treatment processes until RO was applied, meaning that salts in produced water do not have a significant impact on recovery for PG and EG in the chromatogram.

TOC and DOC (Figure 7.8) are not likely to affect PG and EG in raw water because there were little decrease between EC and UF from raw produced water samples. TPH (Figure 7.6) and

turbidity (Figure 7.7) were drastically decreased by EC processes, assumed TPH and turbidity might act as interferences in raw produced water samples. Sidisky et al (2010) concluded that the presence of salt and oil does not affect the recovery of PG and EG through GC-MS method by applying ENVI-carb plus cartridges for SPE method. Suspended solids is considered as a blockage of SPE cartridge (Tadeo, 2008) and between turbidity and suspended solid have a strong positive linear relationship (Hannouche, et al, 2011), indicating that turbidity cause low recovery of PG and EG in raw water samples. Pre-filtration is necessary to reduce turbidity and enhance the recovery of PG and EG in raw water. However, any pre-filtration was not applied for raw water in this study. PG and EG concentration of raw produced water might be higher than PG and EG concentration of after H2O2/EC concentration of PG and EG.

Table 7.8. Analysis of variance (ANOVA) and Tukey's test for multiple pairwise comparisons for PG of before and after treatment.

(i)	(j)	Mean Difference (i-j)	Sig
Raw water	H2O2/EC	1.56	0.06
	UF	0.75	0.63
	GAC	-0.27	0.98
	RO	-0.34	0.96
H2O2/EC	UF	-0.82	0.54
	GAC	-1.84	0.02
	RO	-1.91	0.02
UF	GAC	-1.02	0.34
	RO	-1.09	0.28
GAC	RO	-0.07	0.99

Table 7.9. Analysis of variance (ANOVA) and Tukey's test for multiple pairwise comparisons for EG of before and after treatment.

(i)	(j)	Mean Difference (i-j)	Sig
Raw water	H2O2/EC	0.51	<0.001
	UF	-0.39	<0.001
	GAC	-0.11	0.56
	RO	-0.05	0.97
H2O2/EC	UF	-0.12	0.51
	GAC	-0.39	<0.001
	RO	-0.46	<0.001
UF	GAC	-0.28	0.01
	RO	-0.34	<0.001
GAC	RO	-0.06	0.89

7.3.7 Benzene, toluene, ethylbenzene and xylene

The soluble organic compounds in produced water are polar compounds and composed of relatively lower carbon chains (Fakhru'l-Razi, et al, 2009). The concentration of oil in produced water varied with water production volume, type of oil, and well ages (Stephenson, 1992). Aromatic compounds, which cause natural environments toxicity, are not easily removed by separation technique of oil and water (Fakhru'l-Razi, et al, 2009). Due to the variety of organics added for hydraulic fracturing process, the concentration of Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) can reach 600mg/L in flowback/produced water (API, 2002). The capability of ultrafiltration, granular activated carbon and reverse osmosis process to remove benzene, toluene, ethylbenzene, and xylenes (BTEX) from produced water is presented in Figure 7.10. Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) of each water treatment processes (ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO)). BTEX concentration of raw produced water was measured at 9,380ug/L and mainly made up by benzene (5,200ug/L) and toluene (3,200ug/L). A significant removal of BTEX (greater than 95% removal) was achieved

after GAC process for produced water (3,482ug/L to 166ug/L), showing a similar result of 96 % removal of BTEX by GAC because GAC process is used generally to remove organic compounds during water treatment (Caetano, et al, 2016). BTEX levels after GAC meet discharge requirements except for benzene (discharge permit: benzene (5ug/L), ethylbenzene (100ug/L), toluene (100ug/L) and xylene (200 ug/L) ³⁹ and satisfy drinking water standard without benzene (drinking water standard: benzene (5ug/L), ethylbenzene (700ug/L), toluene (1000ug/L) and xylene (10,000 ug/L)) (WRC). Benzene is under strict regulation for drinking water because it can cause cancer (WRC).

The UF removed more than 60% of BTEX (9,380ug/L to 3,482ug/L), agreeing with results from the study by Bilstad and Espedal (1996) which showed 54% removal of benzene, toluene and xylene (BTX) from produced water in North Sea through UF (Bilstad and Espedal, 1996).

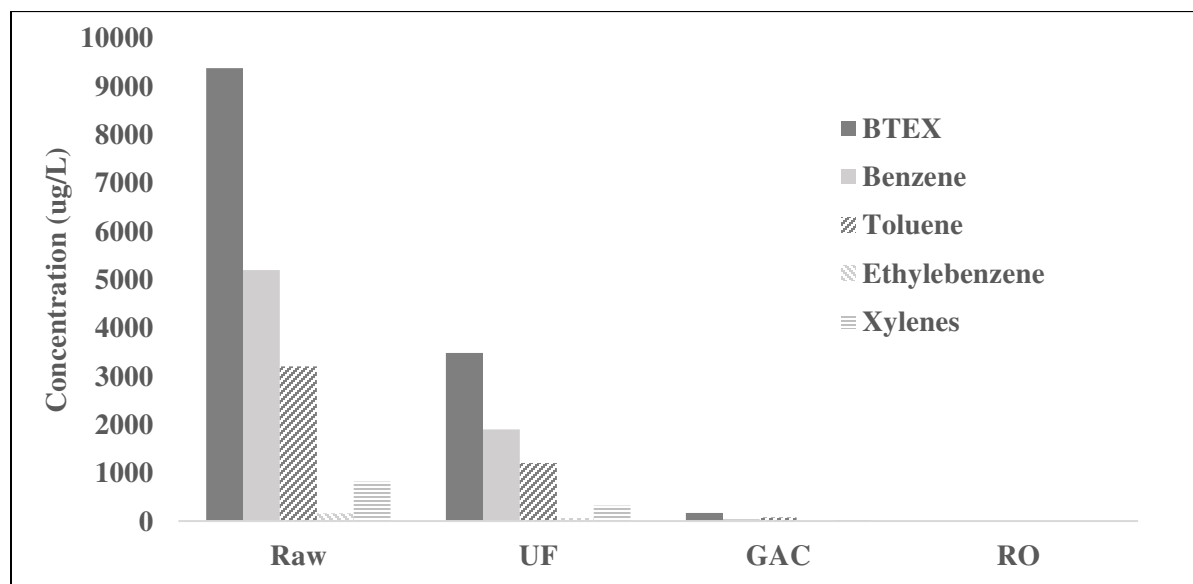


Figure 7.10. Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) of each water treatment processes (ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO)).

7.4 Conclusion

This work has investigated organic, inorganic compounds and other water quality parameters in flowback/produced water and the application of treatment processes including electrocoagulation (EC), ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO). Gas chromatography–mass spectrometry with solid phase extraction was applied to detect propylene glycol (PG), ethylene glycol (EG) and ethylene glycol monobutyl ether (EGME). While EGME was not detected in any produced water samples, PG concentration varied between 0.07ug/ml and 5.39ug/ml and EG was between 0.07 ug/ml to 5.52ug/ml via wastewater treatment process.

GAC removed both PG and EG down to an acceptable level and GAC was approved as an effective treatment method for removal of organic compounds including PG, EG, TPH, BTEX, TOC, and DOC. Turbidity and TPH were effectively removed by EC and most of turbidity and TPH were removed after UF process. TDS only effectively removed through RO. Almost 90% of TDS (2550mg/L) was removed by RO which is still high level of reuse for various purpose.

8. Conclusion

The overall objective of this dissertation is to:

Characterize organic and inorganic compounds flowback/produced water from horizontal shale wells in the Wattenberg field in terms of temporal variability and different fracturing additives, and evaluate the application of wastewater treatment processes.

Chapter 4 and Chapter 5 illustrated the analysis of inorganic and organic in flowback/produced with temporal variation and different fracturing fluid type. In chapter 4, flowback/produced water were studied from two wells over 200 days. One of the frac fluids had an initial pH greater than 10 and used a guar-based gel and the second fluid contained a non-guar polysaccharide based polymer with an initial pH of less than 6. Main inorganics in flowback/produced water were observed to be chloride, calcium and sodium, each gradually increasing over the 200-day period in a similar manner to TDS and show significant positive correlation with TDS (coefficient of determinant (over 0.85)). Recoveries of zirconium, potassium and aluminum were between from 3 % to 33 % and notable differences were observed between frac fluids from a mass balance approach over the 200-day period. In chapter 5, flowback/produced water were characterized from three study wells in terms of different fracturing fluid types over 63 days and applied chemical coagulation for treatment and comparison. Gel fracturing fluid have a significant greater organic compound slickwater fracturing fluids in produced water. Chemical coagulation decreases TOC concentrations by approximately 20% for produced waters.

To study the impacts on organic compounds from recycled water with frac additives and fresh water with frac additives, chapter 6 focused on comparing the organic compounds from fresh

water with frac additives and recycled water with frac additives by LC-QTOF. Results show that similar pattern of organic compound group from recycled water with frac additives and freshwater with frac additives.

Chapter 7 focused on investigating organic and inorganic compounds impact on wastewater treatment from the flowback/produced water. Electrocoagulation (EC), ultrafiltration (UF), granular activated carbon (GAC) and reverse osmosis (RO) were applied as treatment processes for this study. Propylene glycol (PG), ethylene glycol (EG) and ethylene glycol monobutyl (EGME) ether in produced water samples were investigated by GC-MS and EGME were not detected any produced water samples. PG were detected from 0.07ug/ml to 5.39ug/ml and EG were between 0.07 ug/ml to 5.52ug/ml, presenting the decreased trend via treatment processes. GAC was found to be removal of both PG and EG until an acceptable drinking water criteria. EC removed both turbidity (85%) and TPH (80%) and UF removed most of turbidity and TPH. GAC shows removed most of organic compounds including BTEX, TOC and DOC. TDS was not effectively removed until GAC which contributed 15% of TDS removal. Roughly 90% of TDS was removed by RO.

9. References

- AEO, 2012. Annual Energy Outlook 2012 with Projections to 2035. DOE/EIA-0383(2012); United States Energy Information Administration: Washington, DC, USA.
- AEO, 2013. Annual Energy Outlook 2013 with projections to 2040. DOE/EIA-0383(2013); United States Energy Information Administration: Washington , DC, USA.
- Ahmadun, F. R., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., Abidin, Z. Z. (2009). Review of technologies for oil and gas produced water treatment. *Journal of Hazard and Material*, 170, 530–551.
- Aja, S.U., Wood, S. A., Williams-Jones, A. E. (1996). The aqueous geochemistry of Zr and the solubility of some Zr-bearing minerals. *Applied Geochemistry*, 10, 603-620.
- ALL, 2003. Consulting. Handbook on Coal Bed Methane Produced Water: Management and Beneficial Use Alternatives. Prepared For: Ground Water Protection Research Foundation U.S. Department of Energy National Petroleum Technology Office Bureau of Land Management: Tulsa, Oklahoma, USA.
- Allen, R.M., Robinson, K. (1993). Environmental Aspects of Produced Water Disposal. Paper presented at the Middle East Oil Show, Bahrain.
- Altaee, A., Hilal N. (2014). Dual-stage forward osmosis/ pressure retarded osmosis process for hypersaline solutions and fracking wastewater treatment. *Desalination*, 350, 79-85.
- Andrew, A. S., Whitford, D. J., Berry, M. D., Barclay, S. A., Giblin, A. M. (2005). Origin of salinity in produced waters from the Palm Valley gas field, Northern Territory, Australia. *Applied Geochemistry*, 20 (4), 727–747.

- API, 2002. Predictors of water-soluble organics in produced water- A literature review. American Petroleum Institute. Washington, D.C, USA.
- APHA, 2012. Standard methods for the examination of water and wastewater. American Public Health Association (APHA): Washington, DC, USA.
- Arnaud, C. H. (2009). Digging into asphaltenes, *Chem. Eng. News*, 87(38), 12–17.
- Arps, J.J. (1944). Analysis of Decline Curves: *Trans. AIME* , 160, 228-47
- Arthur, J. D., Uretsky, M., Wilson, P. (2010). Water Resources and Use for Hydraulic Fracuring in the Marcellus Shale Region. ALL consulting. 1-22.
- Ayotamuno, M. J., Kogbara, R. B., Ogaji, S. O. T., Probert, S. D. (2006). Petroleum contaminated ground-water: Remediation using activated carbon. *Applied Energy*, 83(11), 1258-1264.
- Bai, B., Goodwin, S. A., Carlson, K. H. (2013). Modeling of frac flowback and produced water volume from Wattenberg oil and gas field: *Jour. Petrol. Sci. and Eng*, 108, 383–392.
- Bansal, K.M., Caudle, D.D. (1998). Interferences With Produced Water Treatment for Dispersed Oil Removal. Paper presented at the SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production, Caracas, Venezuela.
- Barbot, E., Vidic, N. S., Gregory, K. B., Vidic, R. D. (2013). Spatial and Temporal Correlation of Water Quality Parameters of Produced Waters from Devonian-Age Shale following Hydraulic Fracturing. *Environ. Sci. Technol*, 47 (6), 2562-2569.
- Barrow, M. P., Witt, M., Headley, J. V., Peru, K. M. (2010). Athabasca Oil Sands Process Water: Characterization by Atmospheric Pressure Photoionization and Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Anal. Chem*, 82 (9), 3727–3735.

- Barrufet, M. A., David, B. B., Mareth, B. (2005). Modeling and operation of oil removal and desalting oilfield brines with modular units. SPE Annual Technical Conference and Exhibition. 2005.
- Bilstad, T., Espedal, E. (1996). Membrane separation of produced water. *Water Science and Technology*, 34(9), 239-246.
- Bostick, H.D.T., Luo, H. (2001). Characterization of Soluble Organics in Produced Water. vol. 27.
- Brookes, A. (2005). Immersed membrane bioreactors for produced water treatment. Ph.D. Dissertation, thesis, Cranfield University School of Water Sciences, Cranfield, UK, 2005.
- Bukhari, A. A. (2007). Investigation of the electro-coagulation treatment process for the removal of total suspended solids and turbidity from municipal wastewater. *Bioresource Technology*, 99 (5) 914–921.
- Caetano, M. O., Schneider, I. A. H., Gomes, L. P., Kieling, A. G., Miranda, L. A. S. (2016). A compact remediation system for the treatment of groundwater contaminated with BTEX and TPH. *Environmental Technology*, 1408-1420.
- Cardoso, C., Filho, F., Mahmoudkhani, A., De Caprio, A., Costa, M., Nair, M. (2012). Facilitating treatment of produced water from offshore platforms by an oxidation/coagulation/flocculation approach. *Society of Petroleum Engineers*, 153643.
- Carlson, 2013. Water implications of shale gas development. Kenneth Carlson. Presentation, August 2013
- Carter, K. E., Hammack, R. W., Hakala, J. A. (2013). Hydraulic Fracturing and Organic Compounds - Uses, Disposal and Challenges. *Society of Petroleum Engineering*, 165692.

- Caschette, D. (2016). Development of an Electrocoagulation based treatment train for produced water with high concentration of organic matter. M.S. Dissertation, Colorado State University, Fort Collins, Co.
- Chadha, D.K. (1999). A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data; *Hydrogeol J*, 7:431–439.
- Chen, P., Mohanty, K.K. (2013). Surfactant-mediated spontaneous imbibition in carbonate rocks at harsh reservoir conditions. *Soc. Pet. Eng.*
- Chiron, S., Sauvard, E., Jeannot, R. (2000) Determination of nonionic polyethoxylate surfactants in wastewater and sludge samples of sewage treatment plants by liquid chromatography-mass spectrometry. *Analisis*, 28 (6), 535-542.
- Clapper, D.K., Watson, S.k. (1996). Shale stabilising drilling fluid employing saccharide derivatives. EP patent 702 073, assigned to Baker Huges Inc., 20 March 1996.
- Clark, C.E., Veil, J.A. (2009). Produced water volumes and management practices in the United States. US Department of Energy, Argonne National Laboratory.
- Clark, C. E., Burnham, A., Harto, C. B., Horner, R. M. (2012). The Technology and policy of hydraulic fracturing and potential environmental impacts of shale gas development. *Environmental Practice*, 14(4), 249-261.
- COGCC, 2012. Water Sources and Demand for the Hydraulic Fracturing of Oil and Gas Wells in Colorado from 2010 through 2015; Colorado Oil and Gas Conservation Commission: Denver, CO, USA.
- Dammel, J. A., Bielicki, J. M., Pollak, M. F., Wilson, E. J. (2011). A tale of two technologies: hydraulic fracturing and geologic carbon sequestration. *Environ .Sci. Technol*, 45, 5075–5086.

- Doyle, D.H., Brown, A.B., (2000). Produced Water Treatment and Hydrocarbon Removal with Organoclay. Paper presented at the SPE Annual Technical Conference and Exhibition, Dallas, Texas.
- Duruibe, J. O., Ogwuegbu, M. O. C., Egwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Science*, 2(5), 112-118.
- Dusterhoft, R., McGowen, J., Ghalambor, A. (2009). Frac-Pack Fluids. In Frac-Packing Handbook Ghalambor, A., Ali, S.A., Norman, W.D. Eds.; Society of Petroleum Engineers, Richardson, USA, pp 33-64.
- Dyer, J. A., Trivedi, P., Scrivner, N.C., Sparks, D.L. (2003). Lead sorption onto ferrihydrite. 2. Surface complexation modeling. *Environ Sci Technol*, (37), 915–922.
- Ekberg, C., Källvenius, G., Albinsson, Y., Brown, P.L. (2004). Studies on the Hydrolytic Behavior of Zirconium(IV): J. *Solution Chem*, 33, 47-79.
- Ekins, P., Vanner, R., Firebrace, J. (2007). Zero emissions of oil in water from offshore oil and gas installations: economic and environmental implications. *Journal of Cleaner Production*, vol. 15, no. 13–14, 1302–1315.
- Esmailirad, N., Carlson, K., Ozbek, P. (2015). Influence of softening sequencing on electrocoagulation treatment of produced water. *Journal of hazardous materials*, 283, 721-729.
- Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., Abidin, Z. Z. (2009). Review of technologies for oil and gas produced water treatment. *Journal of hazardous materials*, 170, 2, 530-551.
- FFCF, 2000. Fracturing Fluid Characterization Facility Final Report; DE-FC21-92MC29077; Fracturing Fluid Characterization Facility: University of Oklahoma, Norman, USA.

- Frac Focus Chemical Disclosure Registry, 2013. Hydraulic Fracturing: The Process, <http://fracfocus.org/> (accessed on September, 30. 2013)
- Funston, R., Ganesh, R., Leong, L. Y. C. (2002). Evaluation of Technical and Economic Feasibility of Treating Oilfield Produced Water to Create a “New” Water Resource.
- GNS, 2012. Geopolitics and Natural Gas; 2009-2012 Triennium Work Report; International Gas Union: Oslo, Norway, 2012.
- Gonzalez, S., Petrovic, M., Barcelo, D. (2007). Advanced liquid chromatography mass spectrometry (LC-MS) methods applied to wastewater removal and the fate of surfactants in the environment. *Trac-Trend Anal Chem*, 26 (2), 116-124.
- Goodwin, S., Douglas, C. (2012). Life Cycle Analysis of Water Use and Intensity of Oil and Gas Recovery in Wattenberg Field, Colo. *Oil & Gas Journal*, 110, 48-59.
- Goodwin, S., Carlson, C., Bai, B., Rein, L., Knox, K., Douglas, C. (2013). Improved water use estimates for drilling and hydraulic fracturing in northeast Colorado. *Journal of Water Resource and Protection*, (5), 1262-1267.
- Grannas, A. M., Hockaday, W. C., Hatcher, P. G., Thompson, L. G. (2006). Mosley-Thompson, E. New revelations on the nature of organic matter in ice cores. *J.Geophys.Res*, 111 (D4).
- Gregory, K. B., Vidic, R. D., Dzombak, D. A. (2011). Water management challenges associated with the production of shale gas by hydraulic fracturing. *Elements*, 7 (3), 181-186.
- Hannouche, A., Chebbo, G., Ruban, G., Tassin, B., Lemaire, B. J., Joannis, C. (2011). Relationship between turbidity and total suspended solids concentration within a combined sewer system. *Water Science and Technol*, 64(12), 2445-2452.
- Hansen, S.H. (1994). Review of potential technologies for the removal of dissolved components from produced water. *Chemical Engineering Research Design*, 72, pp. 176–188.

- Hayes, T. (2009). Sampling and analysis of water streams associated with the development of Marcellus shale gas. Gas Technology Institute, Bridgeville, PA, USA.
- Hickenbottom, K.L., Hancock, N.T., Hutching, N.R., Appleton, E.W., Beaudry, E.G., Xu, P., Cath, T.Y. (2013). Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations. *Desalinatio*, (312), 60-66.
- Horner, J. E., Castle, J. W., Rodgers, J. H. (2011). A risk assessment approach to identifying constituents in oilfield produced water for treatment prior to beneficial use. *Ecotoxicol Environ Safe*, 74(4), 989-999.
- Howarth, R.W., Santoro, R. (2011). Methane and the greenhouse gas footprint of natural gas from shale formations. *Climatic Change*, 113(2):679–690.
- HUFFPOST, 2013. Colorado Oil Spills Hearing Called For By Rep. Jared Polis, Following Flooding at https://www.huffingtonpost.com/2013/09/27/colorado-flood-oil-spills_n_4004919.html(last access on 10/8/13)
- Hughey, C. A., Hendrickson, C. L., Rodgers, R. P., Marshall, A. G., Qian, K. N. (2001). Kendrick mass defect spectrum: A compact visual analysis for ultrahigh- resolution broadband mass spectra. *Anal. Chem*, 73 (19), 4676-4681.
- Jalali, M. (2011). Nitrate pollution of groundwater in Toyserkan, western Iran: *Environ Earth Sci*, 62:907–913.
- Jaramillo, P., Griffin, W. M., Matthews, H. S. (2007). Comparative life-cycle air emissions of coal, domestic natural gas, LNG, and SNG for electricity generation. *Environ .Sci. Technol*, 41, 6290 -6296.

- Jenner, S., Lamadrid, A. J. (2013). Shale gas vs. coal: Policy implications from environmental impact comparisons of shale gas, conventional gas, and coal on air, water and land in the United States. *Energy Policy*, 53, 442-453.
- Karapanagiotic, H.K. (2007). Removal of phenanthrene from saltwater solutions using activated carbon. *Desalination*, 210 , 274–280.
- Kargbo, D. M., Wilhelm, R. G., Campbell, D. J. (2010). Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. *Environ. Sci. Technol*, 44, 5679-5684.
- Kaufman, P. B., Penny, G. S., Paktinat, J. (2008). Critical Evaluation of Additives Used in Shale Slickwater Fracs. Presented at the SPE Shale Gas Production Conference, Fort Worth, Texas, USA, 16-18 November 2008. SPE-119900-MS.
- Kendrick, E. (1963). A mass scale based on CH₂ = 14.0000 for high resolution mass spectrometry of organic compounds. *Anal. Chem*, 35 (13), 2146–2154.
- Kim, S., Kramer, R. W., Hatcher, P. G. (2003). Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the Van Krevelen diagram. *Anal. Chem*, 75 (20), 5336 – 5344.
- Kim, S., Ozbek, P., Dhanasekar, A., Prior, A., Carlson, K. (2016). Temporal analysis of flowback and produced water composition from shale oil and gas operations: Impact of frac fluid characteristics. *Journal of Petroleum Science and Engineering*, 147, 202-210.
- Kimball, B. (2010). Water treatment technologies for global unconventional gas plays. U.S.–China Industry Oil and Gas Forum. Fort Worth, TX ,September 16, 2010.
- Koby, M., Can, O. T., Bayramoglu, M. (2003). Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes. *Journal of Hazardous Materials*, 100, 163–178.

- Kwon, S., Sullivan, E. J., Katz, L., Kinney, K. A., Bowman, R. S. (2008). Pilot-scale test of a produced water-treatment system for initial removal of organic compounds. SPE Annual Technical Conference and Exhibition, Denver, Colorado, USA. 2008.
- Lambert, S. D., Guillermo, S. M., Graham, N. J. (2002). Deleterious effects of inorganic compounds during thermal regeneration of GAC: a review. *Journal of American Water Works Association*, 94(12), 109-119.
- Lee, D. S., Herman, J. D., Elsworth, D., Kim, H. T., Lee, H.S. (2011). A critical Evaluation of Unconventional Gas Recovery from the Marcellus Shale, Northeastern United States. *Ksce J Civ Eng*, 15, (4), 679-687.
- Lefebvre, O., Habouzit, F., Bru, V., Delgenes, J.P., Godon, J.J., Moletta, R. (2004). Treatment of hypersaline industrial wastewater by a microbial consortium in a sequencing batch reactor. *Environmental Technology*, 25, 543-553.
- Lester Y., Yacob T., Mossissey I., Linden K. (2014). Can we treat Hydraulic Fracturing Flowback with a Conventional Biological Process? The Case of Guar Gum. *Environ. Sci. Technol. Lett*, 1(1), 133-136.
- Lubczenko, 2004. The Saltwatch resource book - part a: what is salinity? Retrieved from http://www.derm.qld.gov.au/education/teachers/land/resources/resource_book_a.pdf
- Lutz, B. D., Lewis, A. N., Doyle, M. W. (2013). Generation, transport, and disposal of wastewater associated with Marcellus Shale gas development. *Water Resources Research*, 49, 647-656.
- Maciejczek, A., Mass, V., Rode, K., Pasch, H. (2010). Analysis of poly (ethylene oxide)-b-poly (propylene oxide) block copolymers by MALDI-TOF mass spectrometry using collision induced dissociation. *Polymer*, 51 (26), 6140-6150.

- Mahmoud, M.A., Abdelgawad, K.L. (2015). Chelating-agent enhanced oil recovery for sandstone and carbonate reservoirs. *Soc. Pet. Eng.*
- Marshall, A. G., Rodgers, R. P. (2008). Petroleomics: chemistry of the underworld. *Proc. Natl. Acad. Sci, U.S.A.* 105 (47), 18090–18095.
- Mantell, M.E. (2010). Produced Water Reuse and Recycling Challenges and Opportunities Across Major Shale Plays, Chesapeake Energy, available online at http://www.epa.gov/hfstudy/09_Mantell_-_Reuse_508.pdf
- Mantell, M.E. (2011). Chesapeake Energy Corporation, Produced water reuse and recycling challenges and opportunities across major shale plays. EPA Hydraulic Fracturing Technical Workshop #4: Water Resources Management, Washington, DC.
- McCormack, P., Jones, P., Hetheridge, M. J., Rowland, S. J. (2001). Analysis of oilfield produced waters and production chemicals by electrospray ionisation multi-stage mass spectrometry (ESI-MSn). *Water Research*, vol. 35, no. 15, pp. 3567–78
- Merzouk, B., Gourich, B., Sekki, A., Madani, K., Chibane, M. (2009). Removal turbidity and separation of heavy metals using electrocoagulation–electroflotation technique, a case study. *Journal of Hazardous Materials*, 164 (1) pp. 215–222.
- Mielke, E., Anadon, L.D., Narayanamurti, V. (2010). Water consumption of energy resource extraction, processing, and conversion, a review of the literature for estimates of water intensity of energy-resource extraction, processing to fuels, and conversion to electricity. Energy Technology Innovation Policy Discussion Paper. Belfer Center for Science and International Affairs, Harvard Kennedy School, Harvard University, Cambridge, MA. 2010-15
- Montgomery, C. (2013). Fracturing Fluid Components. *Intech*.

- NETL, 2013. Modern shale gas development in the United States: an update. National Energy Technology Laboratory Strategic Center for Natural Gas and Oil, Morgantown, WV, USA.
- Nicot, J.P., Scanlon, B.R. (2012). Water Use for Shale-Gas Production in Texas, US. *Environ Sci Technol.* 46, (6), 3580-3586.
- NOAA, 2013. http://www.nws.noaa.gov/oh/hdsc/aep_storm_analysis/8_Colorado_2013.pdf(last access on 10/8/13)
- Olmstead, S.M., Muehlenbachs, L.A., Shih, J., Chu, Z., Krupnick, A.J. (2013). Shale gas development impacts on surface water quality in Pennsylvania. *Proceedings of the National Academy of Sciences.* 110 (13), 4962–4967.
- Osborn, S.G., McIntosh, J.C., Hanor, J.S., Biddulph, D. (2012). Iodine- $^{129}\text{Sr}/^{86}\text{Sr}$, and trace element geochemistry of Northern Appalachian Basin brines; Evidence for basinal-scale fluid migration and clay mineral diagenesis. *American Journal of Science*, 312,263-287.
- O’Sullivan, F., Paltsev, S. (2012). Shale gas production: Potential versus actual greenhouse gas emissions. *Environmental Research Letters*, 7(4).
- Pandey S., Jegatheesan V., Baskaran K., Shu L. (2012). Fouling in reverse osmosis (RO) membrane in water recovery from secondary effluent: a review, *Reviews in Environmental Science and Biotechnology.* 125-145.
- Parasanna, M. V., Chidambaram., S., Gireesh, T. V., Jabir Ali, T. V. (2011). A study on hydrochemical characteristics of surface and subsurface water in and around Perumal Lake, Cuddalore district, Tamil Nadu, South India: *Environ Earth Sci*, 63:31–47.
- Perez, L.S., Rodriguez, O. M., Reyna, S., Sanchez-Salas, J. L., Lozada, J. D., Quiroz, M. A., Bandala, E. R. (2015). Oil refinery wastewater treatment using coupled electrocoagulation

- and fixed film biological processes. *Physics and Chemistry of the Earth, Parts A/B/C* – In Press.
- Petrovic, M., Diaz, A., Ventura, F., Barcelo, D. (2001). Simultaneous determination of halogenated derivatives of alkylphenol ethoxylates and their metabolites in sludges, river sediments, and surface, drinking, and wastewaters by liquid chromatography-mass spectrometry. *Anal Chem*, 73 (24), 5886-5895.
- Rahm, B.G, Riha, S. J. (2012). Toward strategic management of shale gas development: regional, collective impacts on water resources. *Environmental Science and Policy*, 17: 12-23.
- Rahm, B.G., Bates, J.T., Bertoia, L.R., Galford, A.E., Yoxtheimer, D.A. (2013). Wastewater management and Marcellus Shane gas development: trends, drivers, and planning implications. *Journal of Environmental Management*, 120, 105-113.
- Rahm, D. (2011). Regulating hydraulic fracturing in shale gas plays: The case of Texas. *Energy policy*, 39, 2974-2981.
- Rogers, J.D., Burke, T.L., Osborn, S.G., Ryan, J.N. (2015). A framework for identifying organic compounds of concern in hydraulic fracturing fluids based on mobility and persistence in groundwater. *Environ. Sci. Technol. Lett*, 2 (6) 158–164.
- Rosenblum, J. S., Sitterley, K. A., Thurman, E. M., Ferrer, I., Linden, K. G. (2016). Hydraulic fracturing wastewater treatment by coagulation adsorption for removal of organic compounds and turbidity. *Journal of Environmental Chemical Engineering*, 4 (2), 1978–1984.
- Sharp, K. V., Adrian, R. J. (2004). Transition from laminar to turbulent flow in liquid filled microtubes. *Experiments in Fluids* 36 (Compendex): 741-747

- Sick, B. (2014). Characterization and treatment of produced water from Wattenberg oil and gas wells fractured with slick and gel fluids. M.S. Dissertation, Colorado State University, Fort Collins, CO, 2014.
- Sidisky, L. M., Stenerson, K. K., Betz, W. R., Keeler, M. J., McCoy, M., Brown, J. (2010). The extraction of glycols from water using ENVI-carb plus solid phase extraction cartridge. Sigma-Aldrich application note T410135.
- Sirivedhin, T., Dallbauman, L. (2004). Organic matrix in produced water from the Osage-Skiatook Petroleum Environmental Research site, Osage county, Oklahoma. *Chemosphere*, 57 (6), 463–469.
- Soeder, D. J., Kappel, W. M. (2009). Water resources and natural gas production from the Marcellus Shale. USGS Fact Sheet; 2009-3032; U.S. Geologic Survey: 2009.
- SOW, 2012. Shalesshork Organization Website. 2012. <http://shaleshock.org/drilling-101/>
- Spellman, F.R. (2012). Environmental impacts of hydraulic fracturing. CRC Press: Boca Raton, FL, USA, 2012.
- Stephenson, M. T. (1992). A survey of produced water studies. In produced water: technological/Environmental Issues and Solutions; Ray, J. P., Engelhardt, F. R. Eds.; Plenum Publishing Corp: New York. pp.1-12.
- Stephenson, T., Valle, J. E., Riera-Palou, X. (2011). Modeling the Relative GHG Emissions of Conventional and Shale Gas Production: *Environ Sci Technol*, 45, (24), 10757-10764.
- Stewart, M., Arnold, K. (2011). Produced water treatment field manual [electronic resource] / Maurice Stewart, Ken Arnold: Waltham, MA : Gulf Professional Pub., c2011.

- Stringfellow, W.T., Domen, J. K., Camarillo, M. K., Sandelin, W. L., Borglin, S. (2014). Physical, Chemical, and biological characteristics of compounds used in hydraulic fracturing. *Journal of hazardous materials*, 275 pp37-54.
- Suarez, A. A. (2012). The expansion of unconventional production of natural gas (tight gas, gas shale and coal bed methane). *Advances in Natural Gas Technology*.
- Subba Rao, N., A. Subrahmanyam., S. Ravi Kumar., N. Sribivasulu., G. Babu Rao., P. Surya Rao, and G. Venkatram Reddy (2012). Geochemistry and quality of groundwater of Gummanampadu sub-basin Guntur District, Andhra Pradesh, India: *Environ Earth Sci*.
- Tadeo, J. L, 2008. eds. Analysis of pesticides in food and environmental samples. CRC Press.
- Tibbetts, P. J. C., Buchanan, I. T., Gawel, L. J., Large, R. (1992). A Comprehensive Determination of Produced Water Composition. Produced Water SE-9, vol. 46, J. Ray and F. R. Engelhardt, Eds. Springer US, pp. 97–112.
- Thurman, E. M., Ferrer, I., Blotevogel, J., Borch, T. (2014). Analysis of hydraulic fracturing flowback and produced waters using accurate mass: Identification of ethoxylated surfactants. *Anal Chem*, 86(19), 9653-9661.
- Thurman, E. M., Ferrer, I., Rosenblum, J., Linden, K., Ryan, J.N. (2017). Identification of polypropylene glycols and polyethylene glycol carboxylates in flowback and produced water from hydraulic fracturing. *Journal of hazardous materials*, 323 ,11-17.
- USDOE, 2009 a .State Oil and Natural Gas Regulations Designed to Protect Water Resources. U.S. Department of Energy: Washington, D.C, USA.
- USDOE, 2009b. Modern shale gas development in the United States. A Primer; U.S. Department of Energy Office of Fossil Energy and National Energy Technology Laboratory: Morgantown, WV, USA.

- USEIA, 2013. Technically Recoverable Shale Oil and Shale Gas Resources: An Assessment of 137 Shale Formations in 41 Countries Outside the United States. United States Energy Information Administration: Washington, DC, USA
- U.S EIA, 2015. The seven major U.S. shale plays. Director Global Recruitment Clover Global Solution,LP.<http://www.usasymposium.com/bakken/docs/Clover%20Global%20Solution,s,LP%20-%20The%20Seven%20Major%20US%20Shale%20Plays.pdf>
- USEPA, 2004. Manual Guidelines for Water Reuse; EPA/625/R-92/004; United States Environment Protection Agency: Washington, DC, 2004; <http://www.ehproject.org/PDF/ehkm/water-reuse2004.pdf>
- USEPA, 2012. United States Environmental Protection Agency. (2012). from <http://www.epa.gov/>
- USHRC, 2011. Chemicals Used in Hydraulic Fracturing,; United States House of Representatives Committee on Energy and Commerce Minority Staff.: Washington, D.C, USA.
- Van Gijtenbeek, K., Neyfeld, A., Prudnikova, A. (2006). One Molar Salt Solutions used for Clay Control in Waterbased Frac Fluids in West Siberia. Presented at the SPE Russian Oil and Gas Technical Conference and Exhibition, Moscow, Russia 2006/1/1/. SPE-101203-MS.
- Veil, J. A., Puder, M. G., Elcock, D., Redweik Jr., R. J. (2004). A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. Prepared by Argonne National Laboratory for the US Department of Energy, National Energy Laboratory, January. 2004.
- Vengosh, A., Jackson, R. B., Warner, N., Darrah, T. H., Kondash, A. (2014). A critical Review of the Risks to Water Resources from Unconventional Shale Gas Development and hydraulic Fracturing in the United States. *Environmental Science and Technology*, 48 (15), pp 8334–8348.

- Vidic, R.D., Brantley, S.L., Vandenbossche, J.M., Yoxtheimer, D., Abad, J.D. (2013). Impact of shale gas development on regional water quality. *Science*, 340(6134), 1235009.
- Wang, X. J., Goual, L., Colberg, P. J. S. (2012). Characterization and treatment of dissolved organic matter from oilfield produced waters. *Journal of hazardous materials*, 217, 164-170.
- Weber-Scannell, P.K., Duffy, L.K., Weber-Scannell, P.K., Duffy, L.K. (2007). Effects of total dissolved solids on aquatic organisms: a review of literature and recommendation for salmonid species. *American Journal of Environmental Sciences*, 3(1), 1-6.
- WRC, water research center; <http://www.water-research.net/index.php/standards/primary-standards>
- Wu, S. H., Pendleton, P. (2001). Adsorption of anionic surfactant by activated carbon: effect of surface chemistry, ionic strength, and hydrophobicity. *Journal of Colloid and Interface Science*, 243 pp306-315..
- Zhang, W., Yang, X., Wang, D. (2013). Complete removal of organic contaminants from hypersaline wastewater by the integrated process of powder activated carbon adsorption and thermal fenton oxidation, *Ind. Eng. Chem Res*, 2013, 52 pp5765– 5771.

Appendix A: detailed characterization dataset

This appendix includes a detailed characterization for wastewater samples collected from two wells described in Chapter 4. Table A-1 and Table A-2 is summary of produced water characteristics from Frac Fluid A well and Table A-3 and Table A-4 is summary of produced water characteristics from Frac Fluid B well with temporal variations described in Chapter 4.

Table A-1 Summary of produced water characteristics from Frac Fluid A

Time (days)	pH	HCO ₃	TDS	Carbohydrate (mg/kg)	HCO ₃ (mg/L)	Cl- (mg/L)	Al (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Fe (mg/L)
0.00	7.36	346	1140	3.97	350.75	1462	0.772	0.183	1.22	178	5.35
0.08	7.49	386	1820	600.4	610	2963	0.987	0.46	2.16	156	13.7
0.17	6.99	1159	7520	4199	1464	7408	3.41	1.72	11.7	97	26.2
0.25	7.12	1139	7520	4512	1570.75	8889	2.9	2.17	12.8	108	29
0.33	7.08	1159	8000	4363	1464	6000	2.6	2.04	12.2	111	26.6
0.42	7.13	1139	8530	4771	1715.32	5926	2.6	2.07	13.8	109	26.4
0.50	7.24	1200	8760	4833	1830	5928	2.75	2.55	11.9	116	25.9
0.58	7.09	1159	9140	4988	1488.2	7408	4.1	2.49	13.9	113	27.9
0.67	7.06	1139	9140	4742	1543.3	8889	3.66	2.55	11.7	112	25.9
0.75	7.03	1057	9140	4642	1549.4	5926	3.62	2.22	15.1	119	29.3
0.83	7.01	1118	9140	4779	1464	8889	3.88	2.66	14.2	118	29.8
0.92	7.04	1078	9140	5077	1433.5	8889	3.66	2.32	14.5	118	31.6
1.00	7.01	1098	9140	5051	1433.5	8889	2.98	3.1	9.1	127	32.7
1.25	7.16	1118	9840	6028	1427.4	11852	4.05	2.88	14.9	124	32
1.50	7.24	1200	9840	5103	1445.7	11555	-	-	-	-	-
1.75	7.27	1179	9840	4537	1464	11852	0.821	5.29	12.7	135	35.3
2.00	7.64	1118	9840	5472	1586	10371	4.4	2.98	9.12	117	31.3
2.25	7.52	1098	10200	5246	1769	8889	4.37	3.3	9.21	102	33.2
2.50	7.72	1078	10200	5626	1720.2	10371	4.04	2.85	8.95	111	30.5
2.75	7.59	1200	10200	6043	1775.1	10371	2.42	2.68	14.1	129	38.2
3.00	7.56	1139	9840	6422	2745	11832	4.52	2.94	9.12	107	25.8
4.00	7.62	1139	9840	6457	1830	5926	3.13	3.08	9.64	115	36
4.50	7.52	1078	10700	6151	1555.5	5926	2.37	3.08	10.3	125	36.9
5.00	7.94	1118	9140	5570	1445.7	10371	-	-	-	-	-
5.50	7.64	1098	10700	5189	1952	-	1.96	3.01	17.4	146	55.7
6.50	7.44	1118	10700	5610	1213.9	5926	2.57	3.23	9.9	125	42.9
8.17	7.32	1017	11000	-	1586	5500	1.85	3.38	13.6	163	62.6
9.50	7.47	1037	11800	-	1952	11852	1.42	3.2	15.5	153	60.9
10.50	7.15	1037	12300	-	1342	11000	1.79	3.52	15.2	177	71.5
11.50	6.72	-	13580	-	-	-	1.7	3.62	15.7	166	82
12.50	7.21	-	14022	-	-	-	1.9	3.93	18.3	179	79.8
30.50	6.72	-	17416	-	-	-	1.21	4.92	20.5	233	87.2
69.50	6.85	-	19977	-	-	-	1.12	5.49	16.9	268	72.9
102.54	6.77	-	21001	-	-	-	1.69	11	24.7	364	79.7
145.53	6.85	-	21066	-	-	-	1.91	9.19	21.8	512	76.8
203.53	6.62	-	23883	-	-	-	1.25	9.66	17.4	302	95.2

Table A-2 Summary of produced water characteristics from Frac Fluid A

Time (days)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Sr (mg/L)	Cl (mg/L)	SO4 (mg/L)	HCO3 (mg/L)	Si (mg/L)	Zr (mg/L)	COD (mg/L)	TOC (mg/L)
0.00	39.2	13.9	167	1.78	80.5	486	276	15.2	0.278	230	466.1
0.08	33.7	15.6	749	2.56	553	552	358	16.3	2.1	530	687.9
0.17	14	35.6	2745	8.89	3870	387	1350	41.9	55.9	510	
0.25	15.3	34.7	3279	10.2	4440	337	1200	43.1	37.9	640	2643
0.33	14.7	35.3	2851	10.5	3970	264	1010	42	30.6	850	2439
0.42	14.8	35	3516	11.2	4800	382	1230	44.1	32.6	780	2465
0.50	14.2	34.7	4023	11.3	5600	297	1210	43.1	38.1	370	2749
0.58	14.9	34.2	3435	11.9	4950	311	1190	46.5	66.6	490	2753
0.67	14.1	34.1	4007	11.8	5750	352	1240	43.2	63	570	2545
0.75	15.6	35.7	4130	12.7	5880	331	1220	48.3	58.3	840	2637
0.83	15.5	35.1	3608	12.7	4970	316	1090	47.7	63.2	750	2775
0.92	15.5	35.7	3947	12.8	5590	332	1200	47.4	57	860	2415
1.00	15.7	62.6	3654	14.5	5520	214	888	-	-	749	2456
1.25	15.8	34.8	3992	13.4	5760	350	1200	48.2	66.8	2340	2408
1.50	-	-	-	-	-	-	-	-	-	1880	2408
1.75	22.4	192	5576	21.4	8880	65	876	-	-	6640	2849.4
2.00	15	62.8	3230	13.5	5040	262	930	-	-	1299	2411
2.25	15.4	62.2	3641	13.8	5460	197	984	-	-	5265	2618.4
2.50	14.7	60	3589	13.1	5455	170	984	-	-	8840	2357.4
2.75	16.9	34.3	3905	14.5	5450	257	1170	45.2	33.2	13325	975.5
3.00	13.7	62.9	3158	12.4	4800	225	1020	-	-	9635	3117
4.00	15.7	60.8	3445	14.4	5400	161	912	-	-	8025	2556.9
4.50	16.2	62.1	3692	14.9	5880	256	936	-	-	-	-
5.00	-	-	-	-	-	-	-	-	-	3530	-
5.50	19.4	38.2	4839	17.2	6960	196	1000	48.3	22.1	8480	2302
6.50	16.9	63.3	4244	15.9	6480	193	861			8085	2161
8.17	20	38.7	4958	17.8	7240	155	1116	45	23.5	1130	2352.6
9.50	20.7	37.6	4797	18.6	6970	169	1080	42.1	14.6	7160	755.1
10.50	21.6	38.9	5599	19.4	8120	130	1210	44	22.6	2010	1759
11.50	22.1	40.2	5754	20.2	8280	124	986	43.6	16.7	1820	1998
12.50	24.6	41.8	5827	22.2	8390	105	940	47.4	23	7780	2053
30.50	33.8	48	6912	32.1	10320	55.4	880	44.9	4.07	1680	1577
69.50	35.3	48	8414	36.3	12660	126	612	44.5	0.05	1275	1318
102.54	51.8	102	8573	55.2	12645	80.9	838	47.1	0.131	820	1199
145.53	49.6	65.6	9754	46.5	18150	31	590	41.5	0.563	-	1759
203.53	40.7	55.8	8251	42.3	13200	42	720	32.1	0.05	-	1510

Table A-3. Summary of produced water characteristics from Frac Fluid B

Time (days)	pH	HCO ₃	TDS	Carbohydrate (mg/kg)	HCO ₃ (mg/L)	Cl- (mg/L)	Al (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Fe (mg/L)
0.00	7.26	325	1180	0.64	518.5	1482	0.858	0.097	2.82	185	10.3
0.08	6.76	935	8000	3000	1982.5	8889	0.96	1.85	13.5	95.7	56.8
0.17	7.06	1118	10700	4807	1494.5	10371	1.17	3.46	15.1	95.7	57.6
0.25	6.88	1200	10700	4601	1525	11852	1.07	3.53	13.5	105	56.5
0.33	6.96	1179	10700	4090	1622.6	8000	0.97	3.44	16.9	102	56.1
0.42	7.03	1179	10700	4867	2100	9500	0.917	3.59	16.4	106	53.1
0.50	7.06	1118	10700	4637	1604.3	8000	1.01	3.54	14	101	48.3
0.58	7.05	813	10700	4149	1506	10371	1.06	3.79	18.4	110	54.5
0.67	7.08	1281	10700	5100	701.5	7408	1.12	3.72	18.2	111	53.7
0.75	7.03	1240	10700	3731	1482.3	8889	1.17	3.58	17.5	105	50.4
0.83	7.05	1281	11000	3976	1464	8889	1.16	3.72	17.5	106	53.6
0.92	7.06	1118	11000	3891	1433.5	10371	1.21	3.77	19	111	56.3
1.00	7.1	1179	11000	5297	1378.6	10371	1.62	4.16	12.8	102	50.7
1.25	7.44	1220	11400	4423	1482.3	11852	1.18	3.34	15.4	104	39.6
1.50	7.47	1220	10700	4321	1396.9	11555	1.34	3.54	18.4	107	31.3
1.75	7.41	1261	11000	4310	1506.7	10371	4.01	3.26	9.58	117	31
2.00	7.59	1200	10700	4917	1586	16297	1.31	4.13	11.4	100	27.6
2.25	7.38	1220	11400	4522	1555.5	10371	1.25	3.92	19.3	117	37.1
2.50	7.53	1179	11400	4268	1482.3	10371	1.1	3.71	15.3	111	32.4
2.75	7.63	1322	9140	5979	1836.1	8889	3.2	2.82	14.6	127	42.5
3.00	7.31	1118	10700	5974	1628.7	10371	1.33	4.28	11.5	101	27.5
3.50	7.31	1078	9840	5943	2098.4	10371	1.4	4.23	11.1	104	27.7
4.00	7.37	1078	11000	5642	1372.5	-	1.53	4.63	13.3	114	31.4
4.50	7.49	1159	11800	5163	1360.3	11852	1.11	3.93	11.4	104	16
5.00	7.33	1159	11800	5070	1043.1	7408	1.17	4.55	14.5	112	35.5
5.50	7.56	1220	11800	5458	-	-	1	4.17	11.9	114	16
6.50	7.61	1159	11400	5035	1653.1	7408	1.44	4.59	12.3	121	22.4
8.17	7.56	1057	11800	-	2074	7500	0.881	4.1	16	133	21.4
9.50	7.65	1078	12800	-	2745	8889	0.783	3.91	16.7	132	20.4
10.50	7.47	1139	12800	-	1403	8000	0.911	4.26	17.7	141	28.1
11.50	6.53	-	14534	-	-	-	0.904	4.61	17.8	144	45.7
12.50	6.06	-	15110	-	-	-	0.89	4.98	19	144	60.6
20.50	6.78	-	16967	-	-	-	0.935	6.4	18	184	72.5
69.50	6.69	-	22218	-	-	-	1.22	9.75	17.9	287	98.7
102.50	6.43	-	23627	-	-	-	1.79	31.2	25.2	361	154
146.50	6.45	-	25548	-	-	-	1.75	14.9	22	371	211
202.50	6.38	-	22090	-	-	-	1.29	15.5	17.8	326	201

Table A-4. Summary of produced water characteristics from Frac Fluid B.

Time (days)	Mg (mg/L)	K (mg/L)	Na (mg/L)	Sr (mg/L)	Cl (mg/L)	SO4 (mg/L)	HCO3 (mg/L)	Si (mg/L)	Zr (mg/L)	COD (mg/L)	TOC (mg/L)
0.00	42.1	27.7	179	1.94	89.9	361	288	10.6	0.433	240	360.6
0.08	19.1	129	2971	9.67	4200	629	1070	39	14.9	1470	2903.4
0.17	16.3	93.2	4463	13.6	6480	127	1240	45.7	25.1	600	2430
0.25	16.4	99.1	4615	13.5	6630	141	1210	45.1	19.7	800	2373
0.33	18.1	103	4787	14.4	6870	179	1170	47.7	16.2	760	2397
0.42	17.7	103	4652	14.6	6600	191	1220	48.7	13.2	360	2391
0.50	16.3	99.1	4774	13.8	6960	1278	1250	45.4	16.9	940	2452
0.58	18.6	107	4762	15.2	6720	186	1090	51.4	19.2	2200	2512
0.67	18.3	105	4706	15.4	6790	190	1080	51.5	21.7	840	2934
0.75	17.9	102	4616	14.7	6510	111	1200	49.2	24.8	610	1955
0.83	17.9	102	4371	15.1	6360	90.6	1190	50.1	25.1	920	2539
0.92	18.8	105	4804	15.9	6930	154	1170	53.7	26.6	470	2448
1.00	16.5	171	4183	14.7	6300	117	960			905	2833
1.25	16.7	95.6	4831	14.5	6980	106	1100	46.2	25.3	2325	2454
1.50	18.3	98.6	4896	15.4	7170	130	1160	49.2	31.8	6140	2985
1.75	15.3	88.8	3253	13.8	5100	293	1008	-	-	8800	2515
2.00	16.4	177	4026	15.5	6120	103	960	-	-	250	2416
2.25	19.5	102	5039	16.9	7220	103	1050	53.5	26.1	1380	2453
2.50	18	103	5554	15.6	8040	103	1320	49.5	24.9	5540	2203
2.75	16.9	34	4158	14.5	6020	226	1210	47.1	53.1	12180	3450
3.00	17	175	4216	16.2	6650	104	933	-	-	10025	2671.8
3.50	17.4	179	4506	16.2	7020	88.2	865	-	-	11775	2417
4.00	18.4	184	4377	17.1	6960	99.1	996	-	-	660	2236
4.50	17.4	176	4360	16.4	6840	57.1	972	-	-	2370	2638
5.00	18.9	170	4513	17.3	7020	97.6	984	-	-	4610	2432
5.50	19	188	4616	17.4	7080	101	936	-	-	7030	2252
6.50	19.6	190	4929	18.1	7380	62.9	972	-	-	2215	2319
8.17	21.8	-	5721	19	8250	44.2	1050	44.3	13.8	5480	2215
9.50	22.4	105	6458	19.9	9360	31.1	1060	37.1	8.77	4000	1930.2
10.50	23.3	102	6273	20.9	9120	43.6	990	42.8	12.1	7410	1334.7
11.50	24	103	6280	21.8	9070	49.6	890	48.3	10	5120.000	2416
12.50	25	107	6507	22.6	9600	30.1	970	50.9	11	1170	1864
20.50	29.7	116	7351	26.7	10820	6.2	738	49.5	8.15	1040	1727
69.50	98.7	104	9268	39.7	13980	21.2	528	46.4	0	90	1526
102.50	59.6	217	9786	64.4	16378	18.3	852	49.8	0.107	225	1501
146.50	55.4	126	10296	54	18400	22	360	42.7	0.05	-	1807
202.50	48.9	107	9568	50.2	14950	11	840	34.4	0.05	-	1536

Appendix B: Detailed flowback/produced water characteristics

This appendix show flowback/produced water characteristic from three different fracturing fluid type with temporal variation exhibited in Chapter 5.

Table B-1 through B-4 are summary of produced water characteristics from Well H, Table B-5 Through B-8 are summary of produced water characteristics from Well S and Table B-9 through B12 are summary of produced water characteristics from Well G with temporal variations described in Chapter 5

Table B-1 Summary of produced water characteristics from Well H

Time (days)	pH	Conductivity (mS/cm)	TOC (mg/L)	DOC (mg/L)	COD (mg/L)	Turbidity (NTU)	CaCO ₃ (mg/L)	HCO ₃ (mg/L)	TS (mg/L)	TDS (mg/L)
1	7.10	31.4	1,206	-	6,150	763	710	866	23,427	22,913
7	7.27	37.2	1,231	1,134	4,515	176.5	684	834	26,853	27,000
10	7.02	38.0	1,662	1,375	7,120	658	534	651	27,340	27,227
13	7.31	39.8	1,157	1,006	3,620	216	668	815	28,833	28,383
16	7.30	39.0	1,274	1,133	4,445	118.5	628	766	30,260	30,520
19	7.05	40.7	1,172	1,063	3,175	152	594	725	34,200	30,633
22	7.27	42.2	1,198	1,117	4,580	164	598	730	30,260	30,047
25	7.13	44.3	1,128	1,068	3,765	159	588	717	32,020	31,367
30	7.11	44.1	1,164	1,116	4,550	210	620	756	31,467	31,087
35	7.09	44.2	1,119	945	4,210	335	670	817	31,813	31,253
43	7.06	46.1	-	-	4,340	297	608	742	-	-
49	-	-	-	-	-	-	-	-	-	-

Table B-2 Summary of produced water characteristics from Well H

Time (days)	TSS (mg/L)	TVS (mg/L)	VDS (mg/L)	VSS (mg/L)	Al (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)
1	196	1,533	1,333	142	2	14	39	355	103	94
7	197	2,413	2,553	91	4	18	34	439	38	93
10	339	2,107	2,000	238	4	19	33	433	37	87
13	122	2,140	1,623	76	3	21	32	471	34	100
16	162	3,518	3,420	98	2	23	38	515	31	104
19	76	3,260	3,220	47	2	24	38	536	30	106
22	164	1,673	1,847	70	2	22	34	510	25	97
25	80	2,787	2,620	55	4	24	35	529	31	161
30	107	2,200	2,193	84	3	25	35	562	39	101
35	41	2,107	1,953	32	2	19	26	411	29	72
43	-	-	-	-	-	-	-	-	-	-
49	-	-	-	-	-	-	-	-	-	-

Table B-3 Summary of produced water characteristics from Well H

Time (days)	Mg (mg/L)	Na (mg/L)	Si (mg/L)	Sr (mg/L)	Zn (mg/L)	Br (mg/L)	Cl (mg/L)	HCO ₃ (mg/L)	NH ₄ (mg/L)	SO ₄ (mg/L)	Oil and Grease (mg/L)
1	54	7,349	44	44	0	60	11,985	722	25	29	61.1
7	69	18,608	47	57	1	54	11,400	610	31	22	73.8
10	65	8,267	41	58	0	70	14,400	605	34	29	435
13	72	8,795	42	61	1	73	15,100	605	35	23	191
16	78	12,286	49	70	1	78	15,590	595	33	15	81.3
19	82	10,943	47	73	<.10	81	17,950	482	38	5	<5.0
22	80	9,056	36	75	1	72	14,430	486	38	14	64.5
25	82	10,421	37	79	<.10	81	16,210	418	38	10	41.2
30	86	13,408	40	83	<.10	102	20,570	668	40	22	88.4
35	64	8,666	29	62	<.10	81	16,240	542	40	14	40.2
43	-	-	-	-	-	-	-	-	-	-	-
49	-	-	-	-	-	-	-	-	-	-	-

Table B-4 Summary of produced water characteristics from Well H

Time (days)	GRO (mg/L)	DRO (mg/L)	ORO (mg/L)	TPH (mg/L)	Benzene (ug/L)	Toluene (ug/L)	Ethylbenzene (ug/L)	Xylenes (ug/L)	BTEX (mg/L)
1	92.8	57.4	7.84	158	9,072	9,597	885	6,097	26
7	209	48.2	<5.0	257	14,749	15,678	1,482	10,119	42
10	910	146	11.9	1,068	21,561	33,067	5,660	39,342	100
13	184	9.89	<5.0	194	14,952	15,951	1,243	8,733	41
16	215	76.9	<5.0	292	18,518	18,925	1,827	13,650	53
19	54.9	<5.0	<5.0	55	13,560	11,569	662	4,859	31
22	130	52.5	<5.0	183	15,503	13,733	1,134	8,649	39
25	113	30.4	<5.0	143	15,438	14,051	1,084	8,130	39
30	99.1	80.4	<5.0	180	17,585	17,389	1,335	9,765	46
35	224	28.8	6.74	260	21,157	20,483	2,004	14,993	59
43	-	-	-	-	-	-	-	-	-
49	-	-	-	-	-	-	-	-	-

Table B-5 Summary of produced water characteristics from Well S

Time (days)	pH	Conductivity (mS/cm)	TOC (mg/L)	DOC (mg/L)	COD (mg/L)	Turbidity (NTU)	CaCO ₃ (mg/L)	HCO ₃ (mg/L)	TS (mg/L)	TDS (mg/L)
1	7.27	27.3	440		950	386	778	949	18,620	18,187
4	7.45	33.7	401	251	2,270	218	688	839	23,340	23,460
7	7.15	36.7	369	340	3,080	418	720	878	24,680	-
10	7.06	38.6	329	260	1,685	362	650	793	25,147	25,180
13	7.03	40.1	301	284	2,265	489	682	832	31,320	30,080
16	7.49	43.0	243	250	2,490	183.5	574	700	32,890	32,420
19	7.13	42.3	222	238	1,231	311	564	688	34,830	31,240
22	7.50	44.3	246	217	2,105	273	530	647	30,413	29,987
25	7.19	45.7	272	256	2,165	239	508	620	31,720	32,740
30	7.06	46.2	226	244	2,850	285	582	710	31,960	31,247
35	7.20	46.2	233	214	2,085	249	428	522	32,040	31,420
43	7.11	48.3	-	-	2,510	124	476	581	-	-
49	-	-	-	-	-	-	-	-	-	-

Table B-6 Summary of produced water characteristics from Well S

Time (days)	TSS (mg/L)	TVS (mg/L)	VDS (mg/L)	VSS (mg/L)	Al (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)
1	145	960	733	110	2	12	23	275	72	57
4	165	1,733	1,750	110	4	19	25	407	36	67
7	220	1,467	1,362	105	2	20	22	423	49	70
10	180	1,247	1,120	83	3	22	19	457	38	78
13	195	4,320	3,810	137	3	25	20	494	47	76
16	196	-	-	98	3	25	22	515	20	76
19	101	3,270	3,233	37	2	27	24	538	26	79
22	192	1,600	1,513	63	4	27	22	536	39	75
25	110	2,360	2,300	60	4	28	24	545	33	78
30	125	1,840	1,520	69	4	26	22	546	51	73
35	40	2,200	2,247	17	3	28	24	532	28	76
43	-	-	-	-	-	-	-	-	-	-
49	-	-	-	-	-	-	-	-	-	-

Table B-7 Summary of produced water characteristics from Well S

Time (days)	Mg (mg/L)	Na (mg/L)	Si (mg/L)	Sr (mg/L)	Zn (mg/L)	Br (mg/L)	Cl (mg/L)	HCO ₃ (mg/L)	NH ₄ (mg/L)	SO ₄ (mg/L)	Oil and Grease (mg/L)
1	40	10,203	64	32	0	48	14,530	838	24	89	34.2
4	59	11,431	66	50	<0.1	61	15,090	722	25	29	31.5
7	67	9,583	67	56	0	57	12,150	540	36	29	112
10	68	12,637	60	60	<.10	73	15,600	590	28	30	37.5
13	75	9,710	63	64	0	77	16,200	540	32	10	77.6
16	78	12,286	58	70	<.10	66	18,540	478	35	10	89.7
19	82	11,316	61	74	<.10	84	18,290	417	31	20	<5.0
22	83	10,233	56	79	<.10	80	16,290	422	36	14	56.3
25	84	12,627	51	81	<.10	92	19,580	405	36	16	46.8
30	82	10,782	55	80	<.10	102	17,160	542	36	14	46.9
35	86	12,050	43	84	<.10	93	18,530	323	38	20	17.4
43	-	-	-	-	-	-	-	-	-	-	-
49	-	-	-	-	-	-	-	-	-	-	-

Table B-8 Summary of produced water characteristics from Well S

Time (days)	GRO (mg/L)	DRO (mg/L)	ORO (mg/L)	TPH (mg/L)	Benzene (ug/L)	Toluene (ug/L)	Ethylbenzene (ug/L)	Xylenes (ug/L)	BTEX (mg/L)
1	159	44.7	5.27	209	16,479	16,471	1,476	10,188	45
4	234	35.7	<5	270	17,211	18,765	1,811	12,537	50
7	356	42.2	<5	398	15,830	20,444	2,276	15,498	54
10	269	56.3	6.97	332	22,875	23,127	1,967	14,566	63
13	281	25.7	<5	307	13,890	17,894	2,212	16,087	50
16	101	83.4	<5.0	184	20,362	17,799	1,153	8,590	48
19	48.3	<5.0	<5.0	48	12,429	10,411	495	3,640	27
22	33.3	48.2	<5.0	82	7,874	7,115	471	3,604	19
25	50.4	40.2	<5.0	91	11,922	10,907	664	4,934	28
30	77.2	36.8	<5.0	114	15,874	14,753	1,014	7,808	39
35	35.5	12.3	<5.0	48	12,756	10,916	591	4,389	29
43	-	-	-	-	-	-	-	-	-
49	-	-	-	-	-	-	-	-	-

Table B-9 Summary of produced water characteristics from Well G

Time (days)	pH	Conductivity (mS/cm)	TOC (mg/L)	DOC (mg/L)	COD (mg/L)	Turbidity (NTU)	CaCO3 (mg/L)	HCO3 (mg/L)	TS (mg/L)	TDS (mg/L)
0	7.54	23.3	1,584		8,825	454	782	954	18,087	17,380
3	7.65	27.0	1,437	1,431	4,050	115	762	930	20,127	19,633
6	7.14	29.4	1,436	1,391	4,465	164	718	876	21,333	20,460
9	7.05	31.1	1,735	1,333	4,795	152	708	864	22,620	22,433
12	7.09	34.2	1,485	1,413	5,355	164	704	859	24,000	23,850
15	7.25	34.0	1,602	1,420	4,105	215	622	759	26,253	25,650
18	7.05	36.4	1,346	1,332	4,165	271	594	725	-	30,080
21	7.11	39.5	1,323	1,118	6,680	277	574	700	28,233	28,060
24	7.04	40.4	1,435	1,318	4,820	312	610	744	29,240	29,100
29	7.01	42.4	1,314	1,184	4,360	200	624	761	30460	29613
34	6.99	42.7	1,119	1,009	4,390	490	646	788	30340	29027
42	7.10	44.8	-	-	4,405	175	618	754	-	-
48	-	-	-	-	-	-	-	-	-	-

Table B-10 Summary of produced water characteristics from Well G

Time (days)	TSS (mg/L)	TVS (mg/L)	VDS (mg/L)	VSS (mg/L)	Al (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)
0	322	3,247	2,700	285	1	6	44	213	52	90
3	69	2,080	2,247	48	2	7	44	263	33	99
6	155	2,213	2,140	66	3	7	37	252	36	92
9	128	2,233	2,060	114	2	8	35	307	40	117
12	165	1,727	1,747	140	2	10	36	366	44	117
15	166	992	870	122	2	12	39	420	49	127
18	81	-	-	48	2	13	41	446	52	128
21	262	1,407	1,813	141	2	14	37	464	44	124
24	177	2,273	2,300	152	2	14	36	462	53	114
29	74	1993	1820	57	2	11	29	370	38	87
34	38	1920	2120	27	2	16	36	518	59	119
42	-	-	-	-	-	-	-	-	-	-
48	-	-	-	-	-	-	-	-	-	-

Table B-11 Summary of produced water characteristics from Well G

Time (days)	Mg (mg/L)	Na (mg/L)	Si (mg/L)	Sr (mg/L)	Zn (mg/L)	Br (mg/L)	Cl (mg/L)	HCO ₃ (mg/L)	NH ₄ (mg/L)	SO ₄ (mg/L)	Oil and Grease (mg/L)
0	34	6,063	43	25	<0.1	45	9,010	716	34	210	872
3	41	7,765	44	33	<0.1	45	11,415	653	24	49	30.6
6	42	7,258	37	34	0	47	10,200	595	27	37	9.6
9	49	7,117	42	41	<0.10	57	11,400	480	29	51	104
12	58	7,940	42	47	<0.10	58	11,990	360	40	40	154
15	66	8,763	51	57	<.10	61	14,330	542	32	45	74
18	72	10,152	48	63	<.10	69	16,330	593	35	31	13.4
21	73	8,994	39	69	<.10	71	13,940	541	38	62	175
24	72	12,428	39	69	<.10	85	19,050	522	35	15	174
29	58	10,546	28	56	<.10	80	15,990	621	41	45	28.3
34	85	11,255	39	80	<.10	88	17,510	441	39	32	25.9
42	-	-	-	-	-	-	-	-	-	-	-
48	-	-	-	-	-	-	-	-	-	-	-

Table B-12 Summary of produced water characteristics from Well G

Time (days)	GRO (mg/L)	DRO (mg/L)	ORO (mg/L)	TPH (mg/L)	Benzene (ug/L)	Toluene (ug/L)	Ethylbenzene (ug/L)	Xylenes (ug/L)	BTEX (mg/L)
0	1392	762	77.3	2,231	17,266	54,294	7,846	55,858	135
3	153	8.91	<5	162	14,886	15,674	1,250	9,716	42
6	74.7	13.5	6.91	95	10,026	9,340	702	5,578	26
9	235	40.3	<5	275	21,426	21,711	1,570	12,396	57
12	284	90	<5	374	17,100	20,437	2,122	16,529	56
15	91.3	69.5	<5.0	161	16,824	16,053	936	7,556	41
18	49.2	7.26	<5.0	56	11,302	10,032	517	4,138	26
21	170	143	8.41	321	10,734	12,670	1,256	10,185	35
24	267	148	9.02	424	18,064	20,127	2,145	16,884	57
29	64	18.4	<5.0	82	15,659	14,475	1,001	7,950	39
34	251	18.5	5.03	275	20,806	23,493	2,471	20,731	68
42	-	-	-	0	-	-	-	-	0
48	-	-	-	0	-	-	-	-	0

Appendix C: Detailed information of GC-MS results for PG and EG analysis described in Chapter 7.

Treatment processes	Signal Intensity			Ratio with the internal standard		Concentration (ug/ml)	
	PG	EG	IS	PG/IS	EG/IS	PG	EG
Raw water	244513	29033	992194	0.246437	0.029261	0.64	0.08
H2O2/EC treatment	486811	91608	871674	0.558478	0.105094	1.56	0.58
Ultrafiltration	402383	52764	630507	0.63819	0.083685	1.79	0.44
GAC process	141737	42915	811213	0.174722	0.052902	0.44	0.24
RO	83122	27055	755409	0.110036	0.035815	0.25	0.13
Raw	249773	19482	631552	0.395491	0.030848	1.08	0.09
H2O2/EC treatment	612015	95945	924039	0.662326	0.103832	1.86	0.57
Ultrafiltration	454018	81141	823466	0.55135	0.098536	1.54	0.53
GAC process	51276	32517	743535	0.068962	0.043733	0.13	0.18
RO	60440	36155	925813	0.065283	0.039052	0.12	0.15
Raw	38737	17335	657655	0.058902	0.026359	0.10	0.06
H2O2/EC treatment	176996	49541	709767	0.249372	0.069799	0.65	0.35
Ultrafiltration	168527	56761	864860	0.19486	0.06563	0.49	0.32
GAC process	41167	29607	683313	0.060246	0.043329	0.10	0.17
RO	38524	22067	743461	0.051817	0.029681	0.08	0.09
Raw	1032720	558293	718596	1.437136	0.776922	4.12	4.96
H2O2/EC treatment	1261463	582098	674442	1.87038	0.863081	5.39	5.52
Ultrafiltration	1494032	726997	886905	1.684546	0.819701	4.84	5.23
GAC process	74599	57056	792479	0.094134	0.071997	0.20	0.36
RO	43757	29710	853720	0.051255	0.034801	0.07	0.12
Raw	51175	21875	779491	0.065652	0.028063	0.12	0.07
H2O2/EC treatment	1001215	100824	695643	1.439266	0.144936	4.13	0.84
Ultrafiltration	333375	87050	830953	0.401196	0.104759	1.10	0.57
GAC process	66218	31679	766977	0.086336	0.041304	0.18	0.16