

THESIS

CHARACTERIZATION AND TREATMENT OF PRODUCED WATER FROM  
WATTENBERG OIL AND GAS WELLS FRACTURED WITH SLICKWATER AND GEL  
FLUIDS

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Bradley A. Sick

Department of Civil and Environmental Engineering

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Master's Committee:

Advisor: Kenneth Carlson

Pinar Omur-Ozbek  
Thomas Bradley

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## ABSTRACT

# CHARACTERIZATION AND TREATMENT OF PRODUCED WATER FROM WATTENBERG OIL AND GAS WELLS FRACTURED WITH SLICKWATER AND GEL FLUIDS

Treatment of produced water for reuse as a fracturing fluid is becoming an increasingly important aspect of water management surrounding the booming unconventional oil and gas industry. Understanding variation in water quality due to fracturing fluid and produced water age are fundamental to choosing an effective treatment strategy.

This study involves the collection and analysis of produced water samples from three wells in the Wattenberg Field, located in northeast Colorado, over a 63-day study period (15 sampling events). One well was fractured with a cross-linked gel fluid, one with a slickwater fluid, and one with a hybrid of both fluids. Extensive water quality characterization was conducted on each sample to understand the impact of fracturing fluid type on temporal water quality trends. The greatest impact observed was that total organic carbon (TOC) concentrations were significantly higher in produced water samples from the wells fractured with the gel and hybrid fluids (943 to 1,735 mg/L) compared to the well fractured with the slickwater fluid (222 to 440 mg/L). Total dissolved solids (TDS) concentrations, as well as many of the component inorganics that make up TDS, were fairly consistent among the three wells. TDS concentrations at each well increased with time from roughly 18,000 mg/L at day 1 to roughly 30,000 mg/L at day 63.

Jar testing was conducted on collected samples to understand the variability in chemical coagulation/flocculation treatment due to type of fracturing fluid and well age. For the sampled wells, it was found that 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. The coagulant demand for produced waters from wells fractured with gel fluids was found to be roughly 25 to 300 % higher than that for wells fractured with slickwater fluids. The coagulant demand of produced water from each well was found to decrease with the age of the well.

Additional laboratory characterization techniques were conducted on a subset of samples in order to better understand the makeup of organic compounds in produced water, including an analysis of the distribution of the volatile portion of solids, a TOC size analysis, and an analysis of organic subcategories. It was found that the majority of organic compounds in produced water samples are smaller than 0.2  $\mu\text{m}$ , and that the relatively small portion that is larger than 1.5  $\mu\text{m}$  contributes significantly to the predominantly volatile total suspended solids (TSS) load. Carbohydrates were found to be the largest contributor to the overall organic compound load in early produced waters from wells fractured with gel fluids; petroleum hydrocarbons were found to be the largest contributor from wells fractured with slickwater fluids. Chemical coagulation was found to reduce TOC concentrations by roughly 20%, independent of this difference in makeup.

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## 1. INTRODUCTION

Water management has become a central issue surrounding the recent unconventional oil and gas boom that has resulted in a significant increase in US domestic oil and gas production over the past roughly five years. As the rate of new development stabilizes and basins begin to mature, production companies are moving toward integrated water strategies that allow for lower-impact, more cost-effective management of the large volumes of water involved with hydraulic fracturing.

Recycling produced water (i.e., wastewater) generated from already developed wells to offset the water demand of fracturing new wells will play a vital role in optimizing such strategies. This recycling process typically involves some extent of treatment in order to improve the quality of the produced water to the point that it can be effectively used as a fracturing fluid. Understanding the treatment involved and the variability of the produced water quality that is being generated is crucial for developing an effective water reuse strategy.

This phenomenon currently exists within the Wattenberg Field, located in northeastern Colorado. As development in this region matures, production companies are moving away from the previously predominant disposal model and are beginning to treat an increasing portion of their generated waste stream for reuse. In order to design effective treatment systems, production companies need to understand the quality of produced water specific to this field and the effects this water quality has on selected treatment processes.

The work presented in this thesis has been conducted in partnership with and funded by Encana Oil and Gas (USA), one of the largest operators in the Wattenberg Field. Encana operates in an area of the Wattenberg where both slickwater- and gel-based hydraulic fracturing

fluids are used. In order to develop effective water management strategies, it is important for Encana to understand the temporal trends in produced water quality, the effects fracturing fluid type has on this water quality, and the variation in treatability of produced water from wells fractured with slickwater and gel fluids.

As such, this study involved the collection and analysis of produced water samples from three Encana wells fractured with different fracturing fluids over a 63-day study period. Extensive water quality characterization was conducted on each sample. Jar testing was conducted to understand variability in coagulation/flocculation treatment due to type of fracturing fluid and well age. In addition to the work conducted in partnership with Encana, various laboratory characterization techniques were conducted on a subset of samples in order to better understand the makeup of organic compounds in produced water.

A review of published literature was conducted in order to provide a more in-depth summary of the research problem and the work completed to date. A cited summary discussion of this literature review is presented in Chapter 2, along with the clearly stated objectives of this research.

Chapter 3 includes a reformatted copy of a summary report submitted to Encana. This summary report includes a description of all of the methods used in this study, a summary of results, and a discussion of those results. Supporting material not included in this report is included in Appendices A through D.

The additional organic compound characterization tasks completed outside the scope of work established with Encana were not included in the Chapter 3 report. A description of each of these tasks and their results are presented in Chapter 4 and include an analysis of the distribution

of the volatile portion of solids, a TOC size analysis, and an analysis of organic subcategories.

Supporting material for Chapter 4 is presented in Appendix E.

Chapters 5 provides a summary of conclusions, and Chapter 6 provides a discussion of future work, both of which pertain to the entire of body of work conducted as part of this study. References are included in Chapter 7.

A produced water fact sheet was created while working with Encana and is included as Appendix E.

## 2. LITERATURE REVIEW

### 2.1 Unconventional Oil and Gas Extraction

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 easily extracted conventional oil and gas plays are becoming exhausted, extraction of oil and gas from shales and other tight source rock formations is becoming more and more attractive as a means of meeting the continued demand for this energy source. Technological improvements with directional drilling and hydraulic fracturing have allowed these previously cost-prohibitive unconventional oil and gas resources to become one of the largest and fastest growing sources of US domestic energy over the past 5 years (EIA 2013).

Natural gas currently makes up 27% of the US energy supply, and is projected to continue to makeup roughly one quarter to one third of the US energy supply throughout the next 30 years (DOE 2013). The annual production of conventional onshore and offshore natural gas resources is projected to remain constant or decrease over the next 30 years, while shale gas is expected to grow in accord with the increasing demand for natural gas (EIA 2013). Natural gas remains a versatile fuel source with an extensive existing infrastructure, playing a large role across multiple energy sectors, including as a fuel source for power generation, as an industrial feedstock, and for direct or indirect use in residential and commercial heating (EIA 2013).

In 2012, natural gas surpassed coal as the dominate source of energy in power generation for the first time in US history (EIA 2012). This transition from coal to natural gas plays an important role in decreasing greenhouse gas and toxic air emissions by the US power generation sector. Based on a study by Burham et al. (2012), shale gas life cycle greenhouse gas emissions

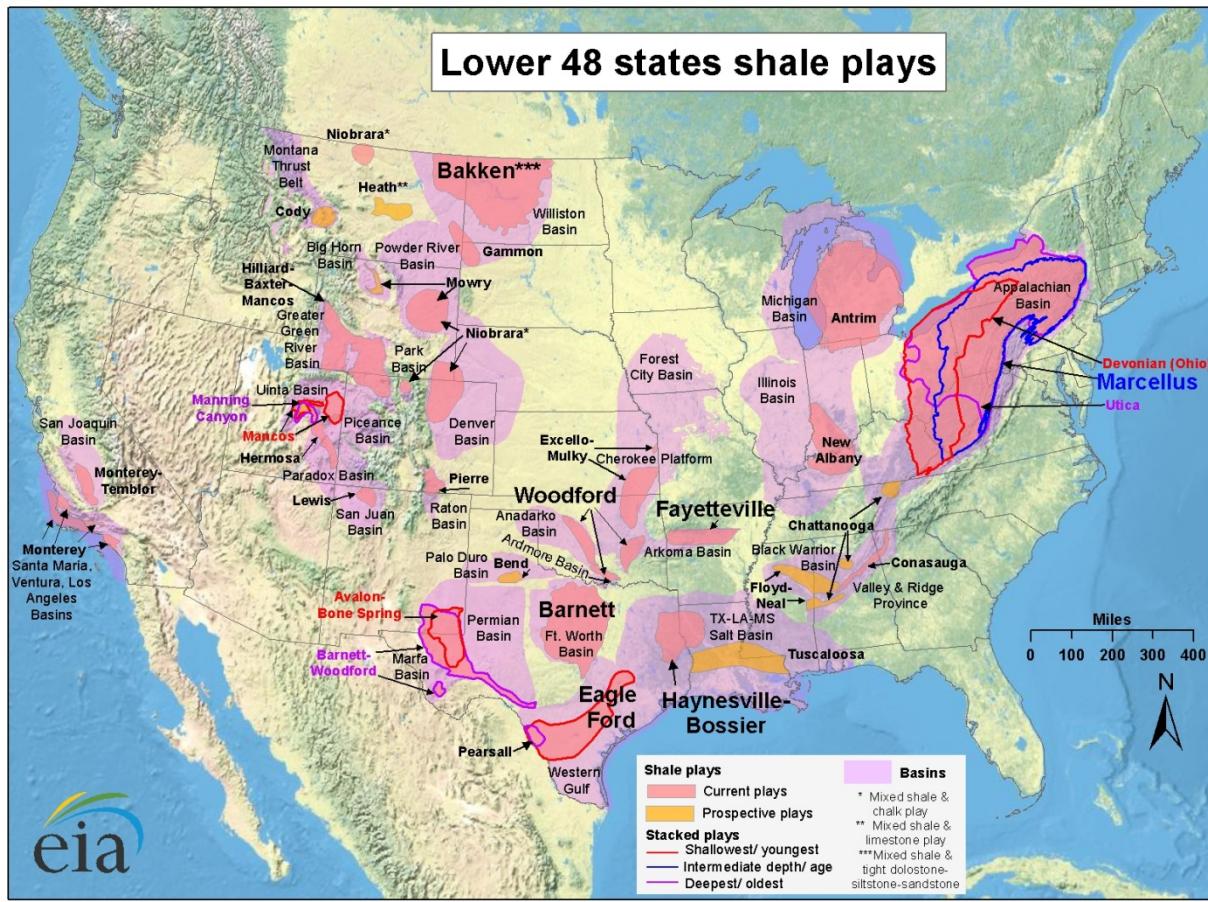
are 6% lower than conventional natural gas, 23% lower than gasoline, and 33% lower than coal. Additionally, natural gas contains less impurities and is cleaner-burning than coal, which results in a reduction of toxic air emissions such as nitrous oxides, sulfur dioxide, and mercury.

Conventional oil and gas extraction typically involves drilling a vertical well into a high-permeability reservoir formation, often composed of sandstone- or carbonate-based geology, and extracting the freely available oil and gas via either pumping or by utilizing the pressure differential between the formation pressure and the surface pressure. Direct water use for a conventional well is primarily for drilling the wellbore, but may also involve the use of water for reservoir flooding.

Unconventional wells involve drilling a borehole either vertically or horizontally into a low-permeability source rock formation, often composed of shale or tight sandstone. The source rock formation is the geologic strata in which plant- or animal-based organics were deposited, along with inorganic sediment, and thermogenically formed into the targeted petroleum product. Due to its low permeability, the formation must be stimulated in order to increase the permeability of the formation and allow the targeted hydrocarbons to flow into the borehole (EPA 2004). Hydraulic fracturing has become the most commonly used practice for stimulating unconventional wells, in which an engineered fluid is injected under high pressure into the formation in order to fracture the source rock. Hydraulic fracturing can be performed with vertical wells, but is being used more commonly with horizontal wells that penetrate a much larger portion of the targeted formation, resulting in significantly greater production efficiencies.

As presented in Figure 2.1, various unconventional shale plays are distributed throughout the contiguous US. Different basins, as well as different areas within each basin, produce various ratios of petroleum hydrocarbons, ranging from areas of the Marcellus that produce primarily

methane with few other heavier hydrocarbons (i.e., ‘dry gas’) to the Bakken, which produces primarily crude oil with only a small amount of associated gas. This variability is primarily controlled by the temperature and pressure conditions under which the target formation exists, and therefore the level of kerogen maturation within the formation (Dow 1977).



**Figure 2-1: Location of Shale Plays across US Lower 48 States (EIA 2011)**

The research summarized in this thesis was focused primarily on unconventional oil and gas extraction from the Wattenberg Field in the Denver-Julesburg Basin, located in northeastern Colorado. Though various hydrocarbon-producing intervals exist, the system of formations targeted for production in this field is commonly referred to as the Niobrara Shale. This Niobrara system is 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 average from 10- to 25-ft thick (DOE 2013). Historically, the Niobrara has primarily been an oil play with associated gas, and historical oil production has come from mostly vertical wells in the deeper, more mature portions of the formation (Pish and McDermott 2010). Since 2008, development within the field has been moving toward horizontal wells of increasing length stimulated with high-volume hydraulic fracturing (Goodwin et al. 2013).

### *2.1.1 Water Demand*

The extraction of unconventional oil and gas involves the use of large volumes of water for drilling and hydraulic fracturing and also produces large volumes of wastewater. As such, water management has become a central issue in continuing to produce this energy source. This energy-water nexus is not, however, specific to unconventional oil and gas. In terms of life cycle water use per unit of energy produced, unconventional oil and gas is one of the least water-intense forms of energy currently utilized (Mielke et al. 2010). As unconventional oil and gas extraction practices continue to mature, water intensity continues to decrease. For example, in the Barnett Shale, which is typically considered the oldest unconventional field in the US, the average length of a horizontal wellbore has nearly doubled since the mid-2000s, resulting in a 40% decrease in water-use intensity (Nicot et al. 2014).

Water demand per well varies from basin to basin based on length of horizontals, stimulation strategy, and formation characteristics. Life cycle water consumption for Marcellus wells was estimated by Jiang et al. (2013) to be 5.2 million gal per well, with direct water consumption accounting for 65% of overall water consumption and the other 35% attributed to indirect consumption (excluding gas utilization).

Average direct water use per horizontal well for one producer in the Wattenberg Field has been estimated at 2.8 million gal per well for horizontal wells and 6.5 million gal per well for extended horizontal wells (greater than 25 stages), based on a study by Goodwin et al. (2013). This study also suggested that the number of stages used to fracture a well is the best indicator of water demand per well. Horizontal wells require significantly more water than vertical wells, but horizontal wells are estimated to be less water-intense than vertical wells in terms of gallons of water used per unit of energy produced (Goodwin et al. 2012). As such, as the industry moves away from vertical wells and toward long horizontal wellbores, water-use intensity will continue to decrease. Similarly, wastewater production per unit of energy recovered may be less in unconventional wells than in conventional wells, as is the case in the Marcellus Basin (Lutz et al. 2013).

Overall, the water demand for upstream unconventional oil and gas production is large across an entire development area, basin, or state. This demand, however, is typically only a very small portion of a population's overall water use, dwarfed by other water uses such as agriculture, and therefore water stress issues caused by this demand are typically local and intermittent. For example, according to Nicot and Scanlon (2012), water withdrawals for shale gas in Texas, which is the largest US shale gas-producing state, accounts for less than 1% of statewide water withdrawals, and local impacts vary with water availability and competing demands. Similarly, Vidic et al. (2013) report that hydraulic fracturing accounts for only 0.2% of overall state withdrawal in Pennsylvania, and problems are therefore generally local and during drought periods.

### *2.1.2 Hydraulic Fracturing Wastewater*

Just as a large volume of water is required to hydraulically fracture each unconventional oil and gas well, each well also produces a significant volume of wastewater throughout the life of the well. Typically, the highest rate of wastewater generation from a well occurs immediately after the well has been hydraulically fractured and then decreases through the life of the well. During the initial ‘flowback’ period, which varies in length depending on multiple factors, but is typically on the order of days, the well will typically only produce wastewater, with very little associated oil and gas. This ‘flowback’ is generally considered to be predominantly fracturing fluid, as it has had limited time to interact with the formation, and is therefore very similar in composition to the raw fluid used to fracture the well.

Once the well starts to produce significant amounts of oil and gas, the mixed fluid stream flowing from the well consists of oil, gas, and wastewater. This wastewater is separated at the surface and, at this point, is typically referred to as ‘produced water’, as opposed to ‘flowback’. This produced water will typically continue to be produced and separated from the recovered petroleum products, thus generating a continuous wastewater stream through the life of the well. The produced water generated over the course of the life of a well is generally thought to be a combination of the fluid used to fracture the well and formation water that resided in either the target formation or neighboring formations. Significant ambiguity exists, however, both in defining when this wastewater is referred to as ‘flowback’ and when it is referred to as ‘produced water’, and also in understanding the ratio of contributions from the fracturing fluid and from formation water. As such, this entire wastewater stream will be referred to herein as ‘produced water.’

The rate and total volume of wastewater produced from each well varies from basin to basin and from well to well. Some basins are very dry and therefore result in a net water loss over the life of the well, while some basins contain a significant volume of water within the target and surrounding formations and therefore result in a net production of water over the life of the well. For example, it has been reported that produced water volume exceeds hydraulic fracturing volume in the Barnett Shale play (Nicot et al. 2014). Regardless of whether there is a net loss or gain, produced water creates a very significant waste stream.

The variable rate of produced water generation largely affects water management strategies. The Barnett, Fayetteville, and Marcellus Shales all produce a significant volume of initial produced water, which better enables the effectiveness of reuse. These three major shale plays produce approximately 500,000 to 600,000 gal of water per well in the first 10 days after completion (Mantell 2011). Similarly, in the Wattenberg Field, the rate of produced water generation generally starts off very high and then decreases over the life of the well. As much as one-third of the overall 30-year projection of total produced water from a Wattenberg well may be produced in the first 30 days after completion (Bai et al. 2013).

This wastewater stream results in various significant social, environmental, and economic costs. Social impacts are largely focused around the truck traffic required for hauling fresh and produced water. Hauling this large volume of fresh water to the site and wastewater to disposal or treatment facilities has been estimated to account for greater than half of the overall truck traffic associated with unconventional oil and gas development (NYSDEC 2010). This truck traffic can result in road damage, noise, increased accidents, and increased air pollution.

Similarly, there are various environmental costs associated with this waste stream. When produced water is treated and discharged to surface water bodies, incomplete treatment can result

in negative impact on surface water, including documented increases in chlorine concentrations downstream of treatment discharges (Olmstead et al. 2012). Treatment plant discharges may also negatively impact surface water via brominated disinfection products and other contaminants of concern, such as radioactive material (EPA 2012; Vengosh et al. 2013). Other potential environmental costs include contamination of surface and groundwater from spills or illicit discharges and increased air emissions from wastewater storage. In most cases, the direct discharge of wastewater from hydraulic fracturing has been discontinued due to strong regulations.

Economically, the transport and disposal of produced water results in a significant cost to the industry. Trucking requires many trips and is very costly, and building pipeline infrastructure requires a large capital investment and extensive planning. Treatment and disposal costs are also significant and vary greatly depending on the management strategy and other regional factors.

These social, environmental, and economic costs can be minimized by choosing optimum water management strategies that incorporate all these costs in evaluating alternatives. One attractive alternative that is being utilized more and more by the industry is the reuse of produced water to counterbalance the freshwater demand for fracturing other wells, as discussed below. This strategy has the potential to reduce the amount of overall waste that must be injected or treated to discharge standards, while also reducing water demand, public burden, environmental impacts, and overall cost of production.

## **2.2 Produced Water Quality**

Produced water quality characterization is a crucial first step in developing any wastewater management strategy, especially for understanding, designing, and optimizing

treatment for reuse. Understanding water quality will also be crucial in designing advanced treatment systems for discharge as fields near the end of development and the demand for recycled fracturing fluid diminishes. Produced water quality varies greatly, and therefore should be individually characterized when choosing a treatment strategy (Alley et al. 2011).

Fracturing fluid components and formation characteristics are likely the primary factors that influence produced water quality. Fracturing fluid components are believed to have a larger impact on younger produced water (i.e., the ‘flowback’ discussed above), while the geochemistry of the formation is believed to have a larger impact on older produced water quality, as a larger portion of the produced water is believed to be made up of formation water, and the portion that originated from the fracturing fluid has had a longer time to interact with the formation.

### *2.2.1 Fracturing Fluid Components*

Fracturing fluids are highly engineered fluids designed to maximize the recovery of hydrocarbons from a tight formation by increasing the permeability of the formation. A successful fluid will form fractures that contact as much of the formation as possible, prop open these fractures so that they do not shut back up when the pressure is released, and then flow freely out of the created fractures (Kaufman et al. 2008). Fracturing fluids are composed of a carrier fluid (typically water), a proppant (typically an engineered sand of a controlled size), and various chemical additives. The water and proppant typically make up greater than 99% of the overall fracturing fluid, and additives are selected based on the formation characteristics and the selected stimulation strategy.

Fracturing fluids can be separated into two main categories: gel fluids 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 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 (Zhu 2012). Though slickwater fluids can contain low concentrations of gelling agents, the term ‘gel fluid’ is used in the study to refer to fluids with high concentrations of gelling agents that significantly increase the viscosity of the fracturing fluid.

Before hydraulic fracturing of tight shale began in the Barnett Shale in 1997, most fracturing occurred with cross-linked gel fluids with high concentrations of proppants. With fracturing tight shales, some producers found that gel fluids had trouble flowing back from the formation after the stimulation and therefore resulted in lower production. In response to this, the use of slickwater fluids with various additives became more popular, with additive recipes continually changing to maximize production (Kaufman et al. 2008). Tight gas characteristics and fracturing strategies vary greatly, however, among and within various basins, resulting in the use of both slickwater and gel fluids today. The temperature and pressure of the target formation and the amount of fluids resident to the formation influence the selection of fluid type. Gel fluids have proved to be optimum in deep, wet, high-temperature reservoirs, where the increased viscosity more effectively carries the proppant and then readily breaks down, while slickwater fluids may be the more optimum choice in shallower, dryer, and/or low-temperature reservoirs (Zhu 2012).

Montgomery (2013) provides a discussion of typical fracturing fluid additives. A summary of this discussion is provided in bullet format below, with emphasis on the common compounds used in each additive and their purposes, as well as the differences between gel fluids and slickwater fluids. Common additives used for both slickwater and gel fluids are as follows:

- Clay control agents: Minimizes clay swelling and base fluid interaction with the reservoir mineralogy via cation exchange; typically KCl or quaternary amine compound (permanently charged ammonium cation with four organic functional groups).
- Friction reducers: Reduces friction and therefore pumping energy; many exist, commonly polyacrylic acid, polyacrylamide, or acrylamidoMethylPropaneSulfate; can be sensitive to divalent cations; gelling agents also reduce friction, so gel fluids typically have less friction-reducing compounds compared to slickwater fluids.
- Biocides: Prevents introduction of sulfate reducing bacteria to the reservoir to prevent hydrogen sulfide production that will ‘sour’ the well and also to prevent buildup of biofilm that will foul the well; many compounds exist; biocides also act to minimize enzymatic breakdown of polymers used in gel fluids.
- Surfactants: Reduces surface tension to help aid fluid recovery from the formation; many exist, including various glycol ethers.
- Gelling agents: Increases viscosity to increase fracture width and carry proppant; slickwater fluids sometimes have low concentrations of linear gelling agents (i.e., not able to be cross-linked), while gel fluids have larger concentrations of gelling agents that are often able to be cross-linked; most commonly used gelling agents are as follows:
  - *Guar or various derivatives*: Readily cross-linked and broken down; may leave an insoluble residue when broken.
  - *Cellulose or various derivatives*: Many cellulose derivatives are unable to be cross-linked and are therefore used in very high concentrations for gel fluids; very little residue.

Additives specific to gel fluids are as follows:

- Cross-linkers: Increases the molecular weight of the gelling agent by linking together polymer molecules and therefore increases the viscosity; boron cross-linkers are most common and are activated at high pH and broken at low pH; titanium and zirconium are also common and are not pH-dependent, resulting in higher-molecular-weight broken gel residue; iron, chromium, and aluminum can also cross-link gels, but are not typically used as an additive.
- Breakers: Reduces molecular weight of polymer gels to allow cleanup; primary classes of compounds used are as follows:
  - *Oxidizers*: Most often persulfates or peroxides that break the polymer backbone into its component sugars; encapsulated to control time of release; can damage the formation.
  - *Acids*: Less selective than oxidizers, often necessary for borate cross-linkers.
  - *Enzymes*: Proteins that act as catalysts to digest the polymer; not consumed by the breaking process; sensitive to temperature and pH.
- Buffers: Adjusts pH to control fluid chemistry and sometimes to control the timing of cross-linking.

Other additives may include (typically in smaller concentrations): corrosion inhibitors, scale inhibitors, non-emulsifiers, paraffin inhibitors, and iron-controlling compounds.

Fracturing fluid chemistry will impact produced water quality, particularly of early produced water. Some additives may remain in the same form in which they were added if they are not designed to react and are not affected by the high temperature and pressure present in the downhole environment. Other components, such as gelling agents, are designed to be modified

downhole and therefore return in the produced water in a different form. Another example is clay stabilizing additives, which are designed to function via ion exchange. Here, cations in the clay stabilizing agent (e.g., potassium ions or quaternary amines) are exchanged for formation cations, often predominantly sodium ions, while the chlorine component stays in the solution and returns with the produced water.

Because slickwater fluids lack the large concentration of gelling agent polymers, as well as the associated cross-linker, breaker, and sometimes buffering additives, produced water from wells fractured with slickwater fluids are more likely to be similar in composition to conventional produced waters. Similarly, 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 (e.g., residual breaker; Montgomery 2013).

### *2.2.2 Characterization Work by Others*

A fair amount of recent characterization work has been done by others for produced water in the Marcellus Shale region. Marcellus wells are typically fractured with slickwater fracturing fluids (Vidic et al. 2013), and therefore the produced water from these wells typically do not contain high organic loads associated with gel fluids. In terms of inorganics, produced water from unconventional Marcellus wells has been found to be fairly similar to conventional produced water (Haluszczak et al. 2013). This is likely attributed to the fact that inorganic constituents originate primarily from the formation.

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 (Gregory et al. 2013).

A fairly extensive Marcellus produced water quality characterization study was conducted by Hayes (2009), which reported on water quality at 19 wells sampled from day 1 to day 90 after hydraulic fracturing. Some of the sampled wells were vertical wells and some were horizontal wells. The type of fracturing fluid used in each of the 19 wells was not discussed, but it is expected that slickwater fluids were used. Averages and ranges of oil and grease, TOC, and dissolved organic carbon (DOC) concentrations for the raw fracturing fluid and produced water at day 5 and day 14 after the wells were opened is presented in Table 2-1.

**Table 2-1: Marcellus Produced Water Organics Concentrations reported by Hayes**

	<b>Fracture Fluid</b>		<b>5-Day Flowback</b>		<b>14-Day Flowback</b>	
	<i>Range</i>	<i>Average</i>	<i>Range</i>	<i>Average</i>	<i>Range</i>	<i>Average</i>
Oil and grease (mg/L)	4.6 – 255	N/A	4.6 – 655	6.3	<4.6 – 103	N/A
TOC (mg/L)	5.6 – 1,260	226	3.7 – 388	62.8	1.2 – 509	38.7
DOC (mg/L)	5 – 1,270	301	30.7 – 501	114	5 – 695	43

Based on the measured data, organic concentrations are highest in the raw fracturing fluid and decrease as the produced water ages. This suggests that organic constituents originate largely from fracturing fluid additives and not from the formation. The magnitude of measured organic concentrations published by Hayes agrees with other values reported for Marcellus produced water. Gregory et al. (2013) report values for the first 30 days of flowback from seven Marcellus unconventional horizontal wells fractured with a blended freshwater and recycled water fracturing fluid as follows: oil and grease: 4.6 – 802 mg/L (average 74 mg/L, 62 samples); TOC: 1.2 – 1,530 mg/L (average 160 mg/L, 55 samples).

Hayes (2009) concluded that fracturing fluid additives make up greater than 75% of the TOC in fracture fluids, which he attributed to polyacrylamide friction reducers, and that the decrease in TOC with age of produced water is attributed to the loss of friction-reducing compounds due to adherence to surfaces downhole. As part of this study, an extensive list of

volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) were measured. Many of the measured compounds were not detected, and those that were detected were generally below 1 mg/L. Constituents that were detected are similar to those found in conventional produced water, such as benzene, toluene, ethylbenzene, and xylene (BTEX), methylated benzenes, naphthalene, naphthenic acids, volatile acids, and simple alkanes.

A compilation of produced water quality, separated by basin type (i.e., conventional, tight, or shale), was performed by Alley et al. (2011). The majority of the data compiled by this study were published prior to 2007. Oil and grease was the only organic parameter presented in the complied data, a summary of which is presented in Table 2-2. Here, little variation is observed between the maximum oil and gas concentrations between conventional and tight gas wells, but this data is fairly inconclusive.

**Table 2-2: Produced Water Oil and Grease Concentrations Reported by Alley et al.**

Type	Number of Records	Oil and Grease Concentration (mg/L)
Conventional natural gas	4,000	2.3 - 60
Conventional oil	165	Maximum: 92
Tight gas sands	137	Maximum: 42
Shale gas	541	Not reported

McFarlane has done fairly extensive work to characterize hydrocarbons in produced water from conventional onshore and offshore wells, but this work does not include analysis of produced water from wells fractured with modern fracturing fluids. This work concludes that for conventional wells, a large component of soluble organics is made up of fatty acids, with the highest concentration of any fatty acid being 11 mg/L (McFarlane 2004). This work also focuses on the study and modeling of the solubility of petroleum-based organic compounds, thus providing insight to the magnitude of organic load in produced water by formation hydrocarbons, which appears to be fairly limited (McFarlane et al. 2002).

Overall, the body of existing work largely lacks characterization of organic compounds in unconventional wells, particularly in regard to differences in organic makeup resulting from the use of modern slickwater- and gel-based hydraulic fracturing fluids. Additionally, due to the observed variability between various basins and various wells, published water quality data for one basin or set of wells will not likely provide a confident indication of water quality of other produced waters.

### **2.3 Treatment of Produced Waters for Reuse**

Management of produced water may include disposal via injection, recycling for reuse as a fracturing fluid, or treatment for discharge or other beneficial reuse, such as agriculture. Produced water management trends 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).

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). This is changing, however, as more produced water is being recycled for reuse. For example, in Pennsylvania, reuse has increased from roughly 5% in 2008 to roughly 90% in the second half 2011, resulting in a roughly 30% reduction in average distance traveled per unit of wastewater (Rahm et al. 2013). One motivation for this change in the Marcellus is the enactment of 2010 Pennsylvania state legislation that limits discharge of TDS to less than 500 mg/L (Pa. Code § 95.10 2010). Another key factor is that the geology of the Marcellus region greatly limits disposal via underground injection (MSAC 2011).

The reuse of produced water as hydraulic fracturing fluid typically involves some time of treatment and/or blending with freshwater. Typical treatment objects for reuse include suspended solids removal, removal of 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 concerns include BaSO<sub>4</sub> and, to a lesser extent, SrSO<sub>4</sub> and CaCO<sub>3</sub> (Vidic et al. 2013).

The type and extent of treatment for each application varies greatly as a function of produced water quality. Mantell (2011) provides an overview of water treatment strategies used by Chesapeake Energy Corporation across various US basins. Each strategy depends heavily on the produced water quality specific to each basin, as outlined in the bullets below. Mantell states that the three most important factors in produced water management are quantity, rate of production, and quality of produced water. No discussion is included regarding the importance fracturing fluid type (i.e., slick versus gel) has on choosing a treatment strategy.

- Barnett: TDS typically ranges from 50,000 to 140,000 mg/L and TSS are low; abundant opportunities for injection result in less incentive to treat for reuse.
- Fayetteville: TDS < 15,000 mg/L, Ca and Mg concentrations are low; treatment for reuse is limited to simply filtration and blending.
- Haynesville: TDS > 350,000 mg/L, Ca and Mg concentrations are high; produced water is unattractive for reuse due to poor quality.

- Marcellus: TDS typically ranges from 40,000 to 90,000 mg/L, Ca and Mg concentrations are moderate to high, TSS ~160 mg/L; incentive to reuse is high, resulting in reuse of nearly 100% of early produced water via ‘improved filtering process.’

Based on interactions with production companies operating in the Wattenberg Field, a coagulation/flocculation treatment step will be a crucial component in all or most treatment processes designed to treat Wattenberg produced water for reuse as a hydraulic fracturing fluid. This process is necessary to destabilize otherwise stable, colloidal particles so that they can be removed via solid-liquid separation (e.g., dissolved air flotation, sedimentation, filtration), thus substantially reducing the concentration of suspended solids.

Hydrophilic particles contain polar or ionized surface functional groups that allow them to bond with water molecules, thus stabilizing them in aqueous solutions and preventing them from agglomerating together to form larger particles. The relative stability of a particle depends on the magnitude of its surface charge, which can be either positive or negative and is highly variable with pH (Crittenden et al. 2012). Coagulation is the process of destabilizing the particles, and flocculation is the process of these destabilized particles agglomerating together to form larger particles.

Various possible coagulation/flocculation mechanisms exist. Adsorption and charge neutralization involves charged particles adsorbing oppositely charged ions or polymers to neutralize the overall surface charge, thus allowing them to agglomerate. Adsorption and interparticle bridging involves multiple charged particles adsorbing to a long chained polymer. Enmeshment in a precipitate (i.e., ‘sweep flocculation’) involves the formation of insoluble metal precipitates that entrap colloidal particles (Crittenden et al. 2012).

In practice, coagulation is achieved via addition of a chemical coagulant, which typically consists of an iron or aluminum salt, or electrocoagulation, which involves the use of sacrificial electrodes, to provide an external source of positively charged ions. Electrocoagulation may be used for treatment of produced water, but is not included in this study.

Because coagulation/flocculation has been identified as a crucial treatment process for Wattenberg produced water reuse, it is important to have an understanding of the efficiency, mechanics, and inferences of coagulation/flocculation for produced waters from both slickwater- and gel-stimulated wells within the Wattenberg Field.

A limited amount of work has been published regarding coagulation/flocculation of produced water. Zangaeva (2010) has looked at the effect of production chemicals (namely, corrosion inhibitors and scale inhibitors) on the coagulation/flocculation process for produced waters from conventional offshore wells. This study concluded that both additives had a variable effect of flocculation, individually and in combination, with no strong trends observed between additives and effectiveness of flocculation.

Cardoso et al. (2012) present a study showing that some 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.

Preliminary unpublished results from within our research group at Colorado State University (CSU) show that coagulation/flocculation is most difficult for early produced water (i.e., immediately after the well is opened) and that coagulation/flocculation may be more easily

achieved with older produced water samples. It is also observed that the TOC concentration and difficulty of treatment follow similar temporal trends, suggesting that some organic molecules present in early flowback are interfering with coagulation/flocculation. It is important to confirm and better understand this phenomenon and to determine which component(s) of early produced water may be interfering with treatment.

## **2.4 Research Purpose and Objectives**

As unconventional oil and gas fields mature and the rate of development stabilizes, producers will have the incentive to move toward integrated water management strategies across development areas. Such strategies may involve the installation of infrastructure to move produced water to centralized facilities, where it would be combined with produced water from other nearby wells and treated as a mixed stream. In order for such a strategy to be successful for a field in which both slickwater and gel fracturing fluids are used (e.g., the Wattenberg Field), understanding the relative differences in produced water treatability as a function of fracture fluid and time will be very important. Little work has been done to study the differences in produced water quality from wells fractured with slickwater fracture fluids versus wells fractured with gel fluids, especially with keeping other factors relatively constant. Additionally, little work has been done to understand the specific organic makeup of produced waters and the effects these organic compounds have on chemical coagulation.

The purpose of this research is to gain a better understanding of the treatment of produced water from Wattenberg unconventional oil and gas wells, particularly in regard to the effects fracturing fluid and the age of produced water have on chemical coagulation. In order to move beyond empirical observations of treatability, this research aims to couple a detailed water

quality characterization of collected samples with treatment results in order to work toward better understanding treatment mechanisms and interferences. The objectives of this research are as follows:

- Collect produced water samples from three oil and gas wells—one fractured with a slickwater fluid, one fractured with a cross-linked gel fluid, and one fractured with a hybrid of both fluids—and complete a comprehensive water quality characterization on collected samples to measure the differences in produced water quality resulting from these different fracturing fluids and to track temporal trends.
- Perform jar testing on produced water samples collected from each of the three wells to measure relative differences in temporal coagulant demand trends among wells fractured with different fluids.
- Use various analytical techniques to better understand the composition of organic compounds present in produced water samples.

### 3. ENCANA PRODUCED WATER CHARACTERIZATION AND TREATABILITY STUDY

The entirety of this chapter was submitted to Encana Oil and Gas (USA) Inc. as a summary report of the work completed and to present findings for a scope of work developed in partnership with and funded by Encana. Minor omissions have been made in order to remove information regarding the specific location of the studied wells. Supporting information is presented in Appendices A through D.

#### **3.1 Introduction and Purpose**

This report presents a summary of findings from a roughly 2-month study conducted by the CSU Center for Energy and Water Sustainability in partnership with Encana Oil and Gas (USA) Inc. This study involved field collection of 15 sets of produced water samples from three separate unconventional oil and gas wells, analytical characterization of the collected samples, jar testing of the collected samples, and summary and interpretation of the observed results. The primary purpose of this report is to document the completed work and present a summary of primary observations.

The objective of this study was to characterize the quality and treatability of produced water from wells fractured with different hydraulic fracturing fluids (slickwater, cross-linked gel, and a hybrid of slickwater and cross-linked gel) in order to help answer the following research questions:

- What is the water quality of the produced water from each well, how does each vary temporally, and what are the primary differences from well to well?

- What is the difference in coagulant demand between these produced waters, and how does this demand change temporally?
- When (how long after initial production) can these different produced waters be effectively treated for reuse?
- How does precipitation of metal solids vary with dilution of produced water?

The findings of this study provide a more complete understanding of produced water quality in the Wattenberg Field, particularly in regard to the differences in produced water from wells fractured with slickwater fluids versus those fractured with cross-linked gel fluids. This information can be used to support produced water management decisions, including treating and/or blending (diluting) the produced water for reuse as a fracturing fluid, treating the produced water to a discharge standard, or disposing of the produced water via subsurface injection.

### **3.2 Summary of Wells**

Each of the studied wells is located in Weld County, Colorado. Well D was fractured with a slickwater fluid, Well G was fractured with a cross-linked gel fluid, and Well B was fractured as a hybrid, using portions of both slickwater fluid and cross-linked gel fluid. Table 3-1 provides a summary of well details for each of the studied wells.

**Table 3-1: Well Details**

Well Name	True Vertical Depth (ft)	Formation	Effective Lateral Length (ft)	Number of Stages	Fracture Fluid Type	Production Start Date
Well B	7,132	Niobrara C	4,502	28	Hybrid	11/25/13
Well D	7,064	Niobrara C	4,367	28	Slickwater	11/25/13
Well G	7,193	Codell	4,561	29	Cross-linked gel	11/26/13

The primary difference between the slickwater and the cross-linked gel fluid is that the gel fluid consists of gelling agent, crosslinker, and breaker packages that act to significantly modify the viscosity of the fracturing fluid as the well is stimulated. In contrast, the slickwater fluid does not contain these components and as such maintains a fairly consistent viscosity. A list of the primary components used in each fluid is presented in Table 3-2. This data was collected from FracFocus.org, the national chemical hydraulic fracturing chemical registry. Fracturing fluid additives reported on FracFocus.org are presented in terms of a maximum concentration and some compounds are reported as proprietary. As such, this data not represent the precise makeup of each fluid, but is useful for understanding and comparing the primary components in each fluid. In Table 3-2, compounds found only in the slickwater fluid are shaded red, compounds found only in the cross-linked gel fluid are shaded blue, and compounds found in both fluids (but at different concentrations in most cases) are shaded purple. Because concentrations presented represent the maximum potential concentration, not the actual, precise concentrations used, they should only be used to make relative comparisons.

Well B was fractured with a hybrid mixture of the slickwater fluid and the cross-linked gel fluid and as such contains all of the components listed in Table 3-2. For this well, each stage was stimulated by first injecting a slickwater fluid (roughly 40% of the total stage volume), followed by a cross-linked gel fluid (roughly 60% of the total stage volume).

As presented in Table 3-2, each fracturing fluid contains similar biocide, breaker, clay control, friction reducer, surfactant, and non-emulsifier packages. According to data reported to FracFocus.org for these wells, these packages are primarily composed of organic compounds, including choline chloride, polyacetate, petroleum distillates, and amphoteric surfactants. As noted above, the unique components of the cross-linked gel fluid consist of gelling agent,

**Table 3-2: FracFocus.org Frac Fluid Compositions for Wells B, D, and G**

Well D (Slick Water)					Well G (Cross-Linked Gel)				
Purpose	Trade Name	Ingredients	Max Conc. (mg/L)	Approximate Chem Formula	Purpose	Trade Name	Ingredients	Max Conc. (mg/L)	Approximate Chem Formula
Acidizing	HCl, 10.1 - 15%	Hydrochloric Acid	1,218	HCl	Breaker	High Perm CRB	Ammonium Persulphate	90	H8N2O8S2
Corrosion Inhibitor	CI-31	Formic Acid	9	CH2O2		Water	379	H2O	
		Oxyalkylated Fatty Acid	4.5	[COH]		Enzyme G HT-II	Tryptone	19	[CHON]
		Aromatic Aldehyde	4.5	C6H5CHO			Yeast Extract	19	N/A
		Quaternary Ammonium Compound	4.5	NR4	Buffer	BF-9L, 300 gal tote	Potassium Carbonate	315	KCO3
		Isopropanol	1.5	C3H8O			Potassium Hydroxide	158	KOH
		Methanol	0.8	CH4O		XLW-30AG, tote	Petroleum Distillates	382	C(9-16)Hx
		Cyclic Alkanes	0.8	[CH]	Crosslinker	XLW-32	Methanol	164	CH4O
		Organic Sulfur Compound	0.8	[CHS]			Boric Acid (H3BO3)	82	H3BO3
		Benzyl Chloride	0.2	C7H7Cl			Methyl Borate	82	C3H9BO3
Iron Control	Ferrotrol 300L	Citric Acid	10	C6H8O7	Gelling Agent	GW-3LDF	Guar Gum	3,355	C6H12O6/unit
Paraffin Inhibitor	Parasorb 5000, bag	Calcined Diatomaceous Earth	270	N/A			Paraffinic Petroleum Distillate	1,677	[CH]
		White Mineral Oil	125	C(15-40)Hx			Petroleum Distillates	1,677	C(9-16)Hx
		Proprietary Paraffin Inhibitor	104	N/A			Isotridecanol, ethoxylated	280	[CHO]
		Silica, Crystalline-Quartz	21	Si			1-butoxy-2-propanol	280	C7H16O2
Biocide	Alpha 452	Tetrakis(hydroxymethyl) Phosphonium Sulfate	167	C8H24O12P2S	Biocide	Alpha 452	Tetrakis(hydroxymethyl) Phosphonium Sulfate	145	C8H24O12P2S
Breaker	GBW-5	Ammonium persulphate	113	H8N2O8S2	Breaker	GBW-5	Ammonium persulphate	9	H8N2O8S2
Clay Control	ClayCare, tote	Choline Chloride	747	C5H14CINO	Friction Reducer	ClayCare, tote	Choline Chloride	668	C5H14CINO
Friction Reducer	MaxPerm-20A, bulk	Polyacetate	563	(C4H6O2)n			Polyacetate	30	(C4H6O2)n
		Petroleum Distillates	281	C(9-16)Hx			Petroleum Distillates	15	C(9-16)Hx
		Sodium Chloride	47	NaCl			Sodium Chloride	3	NaCl
		Oxyalkylated Alcohol	47	N/A			Oxyalkylated Alcohol	3	N/A
Surfactant	Flo-Back 40, tote	Amphoteric Surfactant	338	N/A	Surfactant	Flo-Back 40, tote	Amphoteric Surfactant	287	N/A
Non-emulsifier	NE-945W, 265 gl tote	Glycerine	150	C3H8O3	Non-emulsifier	NE-945W, 265 gl tote	Oxyalkylated Alcohol	20	N/A
		Oxyalkylated Alcohol	25	N/A					
		Polyethylene Glycol	25	C2nH4n+2On+1					

Note: Approximate chemical formulas presented in brackets list primary elements of composition. Chemical formula and structure are unknown

crosslinker, and breaker packages. The primary compounds that make up these packages, in terms of maximum possible concentration, are petroleum distillates (approximately 41%) and guar gum (approximately 37%), both of which are organic compounds. Also, the cross-linker package includes boric acid, which makes the element boron unique to the cross-linked gel fluid. The unique components of the slickwater fluid include acidizing, corrosion inhibitor, iron control, and paraffin inhibitor packages. Hydrochloric acid (HCl) makes up the majority of the slickwater-specific compounds, with the remaining maximum concentration of slickwater-specific compounds (i.e., excluding HCl) totaling only 556 mg/L (as compared to 8,957 mg/L for the maximum concentration of cross-linked gel-specific compounds).

### **3.3 Study Methods**

#### *3.3.1 Sample Collection and Preservation*

Fifteen sampling events were conducted between November 26, 2013 and January 30, 2014, as outlined in Table 3-3. Sampling began immediately after the start of production (11/25/13 for Wells B and D, 11/26/13 for Well G). The pre-production flowback period ranged from 3 days (Well B) to 7 days (Well D); no pre-production flowback samples were collected as part of this study. Samples were collected every 3 days for the first nine events, every 5 days for events 10 and 11, and every 7 days for events 12 through 15. All wells were shut in between 11/27/13 and 11/30/13, and as such these days were not included in the ‘days after start of production’ count.

**Table 3-3: Sampling Events**

Event Number	Sample Date	Time (days after start of production)
1	11/26/13	1
2	12/02/13	4
3	12/05/13	7
4	12/08/13	10
5	12/11/13	13
6	12/14/13	16
7	12/17/13	19
8	12/20/13	22
9	12/23/13	25
10	12/28/13	30
11	01/02/14	35
12	01/10/14	42
13	01/16/14	49
14	01/23/14	56
15	01/30/14	63

Each sample was collected from the dedicated production separator associated with each well. Samples were collected from the valve below the water-level viewing glass. The only exception is that the sample for Well G collected at the first sampling event was collected directly from the wellhead, as the well was not connected to the production separator until later that day. Roughly 5 gal of sample was collected from each well at each sampling event and allocated to appropriate containers. Samples collected for volatile compounds were collected in 40-mL VOAs with zero headspace. All other samples for water quality characterization were placed in 1-L polyethylene bottles. All VOAs and 1-L bottles were immediately placed on ice and were kept refrigerated until analyzed. The remaining roughly 4 gal was placed in a 5-gal bucket and used for jar testing.

### *3.3.2 Characterization*

Various analysis parameters were measured in an attempt to completely characterize the water quality for each sample. A complete list of measured parameters, method numbers, and

brief method descriptions are included in Tables 3-4 and 3-5. Some parameters were measured by CSU (Table 3-4), and some were measured by eAnalytics (Table 3-5), a trusted third-party laboratory commonly used by CSU for quick and cost-effective analysis of produced water samples. pH and conductivity were measured in the field during sample collection and were then later verified in the lab. Field-collected pH and conductivity readings are presented in this report.

### *3.3.3 Treatability*

Removing suspended solids via coagulation and flocculation is a crucial step in almost all produced water treatment systems. The addition of a coagulant acts to destabilize suspended particles, allowing the particles to flocculate together into larger particles that can be settled or filtered out. Different water qualities require different coagulant doses, depending on the amount and surface charge of suspended particles, as well as the presence of other compounds that may interfere with the effectiveness of the coagulant. In order to understand the differences in coagulant demand of the produced waters from each of the three studied wells, as well as the change in these coagulant demands over time, coagulation-flocculation jar testing was conducted to determine the optimum coagulant dose for each collected sample. The bench-scale jar testing plan used for this study was not intended to optimize the treatment process. Instead, a relatively simple but consistent testing plan was conducted for each sample in order to observe the relative differences in coagulant demand among the three separate produced waters, as well as the relative temporal change in each coagulant demand with time. As treatment optimization was

**Table 3-4: Analytical Methods for Parameters Measured at CSU Labs**

Parameter	Method Number	Description
pH	Hach PHC10105 gel-filled pH probe	A glass electrode is used to measure the emf of the sample against a reference solution, and the measured emf is used to determine the hydrogen ion concentration based on a three-point standard curve generated using pH buffer solutions.
Conductivity	Hach CDC401 conductivity probe	A graphite, four-pole conductivity probe is used to measure the electrical conductivity of the sample in mili-Siemens/cm
TOC	Adapted from <i>Standard Methods*</i> , Method 5301 B	A Shimadzu TOC-VCSH analyzer is used to measure TOC as the difference between total carbon (TC) and total inorganic carbon (TIC). In general, TC and TIC were both analyzed by oxidizing carbon to CO <sub>2</sub> and measuring CO <sub>2</sub> concentrations using a non-dispersive infrared detector. The TC oxidation includes a high-temperature (680 degC) combustion chamber with a platinum catalyst, allowing for more complete oxidation.
DOC	See above	Same as above, except that the sample is first filtered through a Whatman 934-AH glass microfiber filter (1.5-um-equivalent pore size).
Chemical oxygen demand (COD)	Hach Method 8000	COD is measured as the amount of O <sub>2</sub> consumed in a sample heated for 2 hours with sulfuric acid and a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion (Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> ) to green chromic ion (Cr <sup>3+</sup> ). The amount of Cr <sup>3+</sup> that is produced is then measured colorimetrically with a spectrophotometer at 620 nm.
Turbidity	EPA Method 180.1	Turbidity is measured using a Hach 2100 N turbidimeter to measure the light scattering potential ('cloudiness') of each sample. Measurements were collected in nephelometric turbidity units (NTUs).
UV254	Adapted from <i>Standard Methods*</i> , Method 5910	The ultraviolet (UV) absorbance is measured using a HACH DR/4000 spectrophotometer at 254 nm against organic-free water as a indicator of organic constituents in the sample. Results are automatically reported in absorbance per centimeter (cm <sup>-1</sup> ).
Alkalinity	<i>Standard Methods*</i> , Method 2320 B	Alkalinity was measured as the amount of hydrochloric acid (HCl) added to a sample of a given size until the titration endpoint of pH 4.5 was achieved.
Gravimetric Solids Analysis: TS, TDS, TSS, TVS, VDS, VSS	<i>Standard Methods*</i> , Method 2540	Total solids (TS), TDS, TSS, total volatile solids (TVS), volatile dissolved solids (VDS), and volatile suspended solids (VSS) analyses are conducted via evaporation, drying, filtration, muffling, and weighing. TS, TDS, and TSS samples were dried at 105 degC; TVS, VDS, and VSS samples were muffled at 550 degC. Whatman 934-AH glass microfiber filters (1.5-um-equivalent pore size) were used to filter samples.

not the goal here, this study did not compare different coagulant types and did not include the use of any flocculent aiding polymers. Instead, aluminum chlorohydrate (ACH) was selected as the sole chemical coagulant used for all jar testing. The jar testing method used generally followed ASTM D2035-13. A Phipps & Bird PB-900 programmable jar tester was used. The collected sample was allocated out into five separate square beakers (jars), allowing for five different coagulant doses to be simultaneously tested on each sample. 1 L of the well-mixed produced water sample. Doses of chemical coagulant were then added to each

**Table 3-5: Analytical Methods for Parameters Measured by eAnalytics Laboratory**

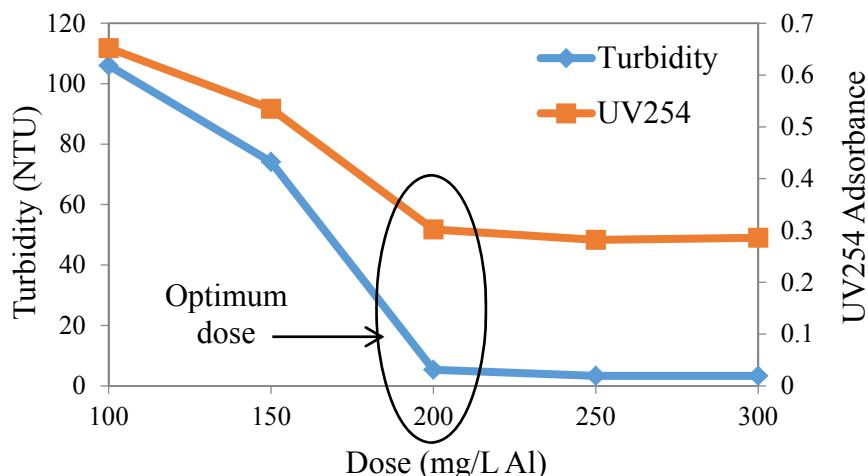
Parameter	Method Number	Description
Metals: Al, Ba, B, Ca, Fe, K, Mg, Na, Si, Sr, Zr	EPA 6010C	Samples are acid digested to pH < 2 to dissolve all metals. Inductively coupled plasma–atomic emission spectrometry (ICP-AES) is then used to measure target metals.
Ammonia (NH <sub>4</sub> )	EPA 350.1	The sample is buffered at a pH of 9.5 and is distilled into a solution of boric acid. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue and measured colorimetrically.
Bicarbonate (HCO <sub>3</sub> )	EPA 310.1	An unaltered sample is titrated to an electrometrically determined end point of pH 4.5.
Bromide (Br)	EPA 300.0	A small volume of sample is introduced into an ion chromatograph (IC). The anions of interest are separated in the IC column and are measured against a standard curve with a conductivity detector.
Chloride (Cl)	EPA 9253	Sample is adjusted to pH 8.3 and titrated with a silver nitrate solution in the presence of a potassium chromate indicator. The end point is indicated by persistence of the orange-silver chromate color.
Sulfate (SO <sub>4</sub> )	ASTM D516	Sulfate ion is converted to barium sulfate suspension under controlled, stabilized conditions. The resulting turbidity is determined by a nephelometer, spectrophotometer, or photoelectric colorimeter and compared to a standard sulfate curve.
Oil and grease	EPA 1664	(N-hexane extractable material) The sample is acidified to pH <2 and serially extracted three times with n-hexane. The extract is dried, the solvent is distilled from the extract, and then the extract is weighed gravimetrically.
Gasoline range organics (GRO)	EPA 8260C	Non-halogenated organics in the range C6 to C10 are measured using GS-MS. See method description for BTEX below.
Diesel range organics (DRO)	EPA 8015	Non-halogenated organics in the range of C10 to C28 are extracted from the sample and introduced into a gas chromatograph (GC). Detection of analytes is achieved through a flame ionization detector (FID).
Oil range organics (ORO)	EPA 8015	Non-halogenated organics in the range of C28 to C36 are extracted from the sample and introduced into a GC. Detection of analytes is achieved through an FID.
Total petroleum hydrocarbons (TPH)	See description	Sum of GRO, DRO, and ORO
BTEX	EPA 8260C	The volatile compounds are introduced into a GC. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS). Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using an appropriate calibration curve.

\*Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF

beaker at the same time. In general, the five doses used were as follows: 100, 150, 200, 250, and 300 mg/L as Al (ACH dose calculations presented in Appendix A). In some cases, 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 rpm for 1 minute, followed by flocculation mixing at 25 rpm for 20 minutes and then a 15-minute setting period.

A ‘treated’ sample was then collected from the sampling port built in to each beaker. The turbidity and UV254 absorbance was immediately measured for each of the five samples, according the methods described in Table 3-4 above. An ‘optimum dose’ was then selected out of each of the five tested doses. As illustrated in Figure 3-1, 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. Additional water quality analyses were conducted on each optimum dose ‘treated’ sample in order to measure the change between the ‘raw’ and ‘treated’ samples. These additional analyses included pH, TOC, DOC, COD, and solids (TS, TDS, TSS, TVS, VSS, VDS) and were conducted according to the methods described in Table 3-4 above.



**Figure 3-1: Selection of Optimum Dose based on Turbidity and UV254**

### 3.4 Observations/Results

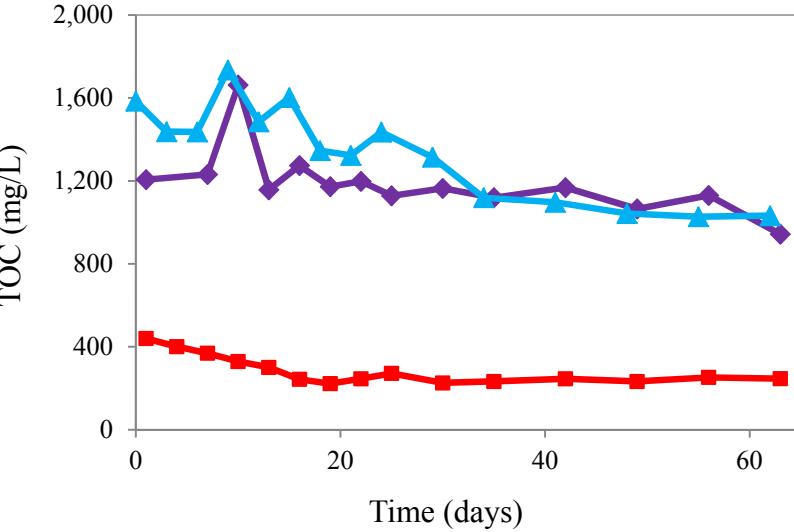
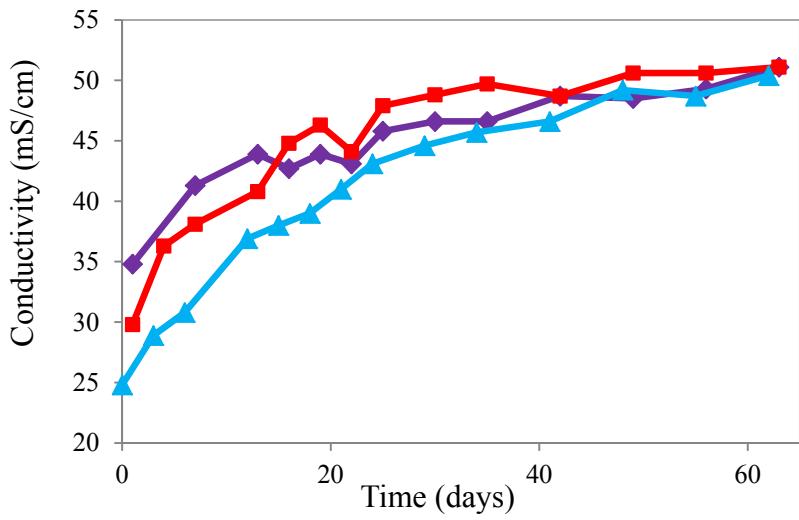
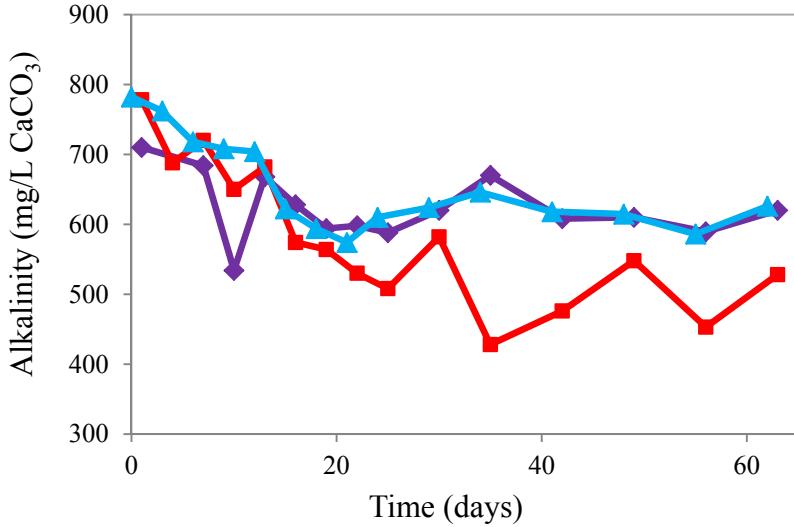
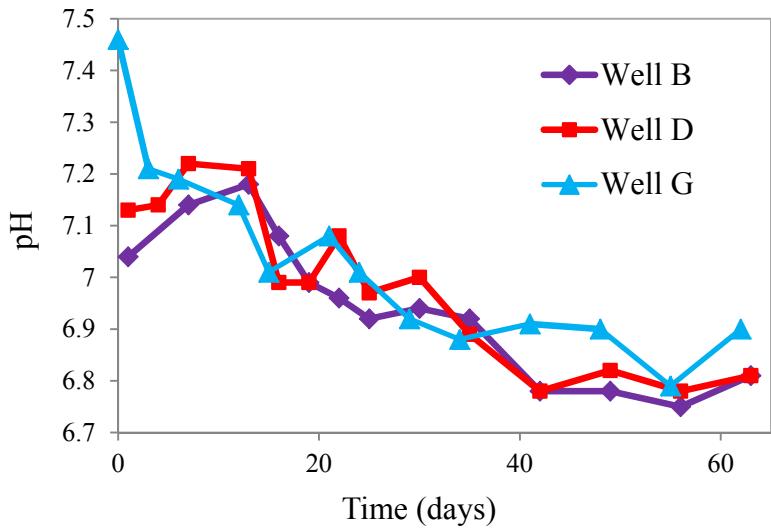
#### 3.4.1 Characterization

Extensive water quality characterization was performed on each collected sample. Temporal trends for pH, alkalinity, conductivity, and TOC are presented in Figure 3-2. In

general, there was very little difference in pH values among the various wells at each time point. All pH readings were near neutral (pH of 7), and a slightly decreasing temporal trend in pH was observed at each well. The alkalinity concentrations among the various wells at each time point were also fairly consistent, with the exception that the alkalinity concentration at Well D was significantly lower than the other two wells after roughly day 30. A slight downward temporal trend in alkalinity was observed for each well. Alkalinity concentrations were generally high over the course of the sampling period, suggesting a significant buffering capacity in each produced water stream.

Conductivity was also fairly consistent among the various 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 to 35 mS/cm at day 1 to roughly 51 mS/cm at day 63. Consistent with this observation, and as shown in Table 3-6, TDS concentrations also increased over the course of the sampling period, from roughly 17,000 to 22,000 mg/L at day 1 to roughly 34,000 mg/L at day 63. This upward trend was also observed for the majority of the component metals and ions that makeup the TDS.

TOC concentrations were significantly higher in samples from Well B and Well G than in samples from Well D. TOC concentrations in Well G were generally slightly higher than Well B over the first 30 days, at which point the TOC concentrations in these two wells converge. A slight downward temporal trend in TOC was observed for each well. DOC concentrations followed a similar trend to TOC for each well,



**Figure 3-2: pH, Conductivity, Alkalinity, and TOC Trends**

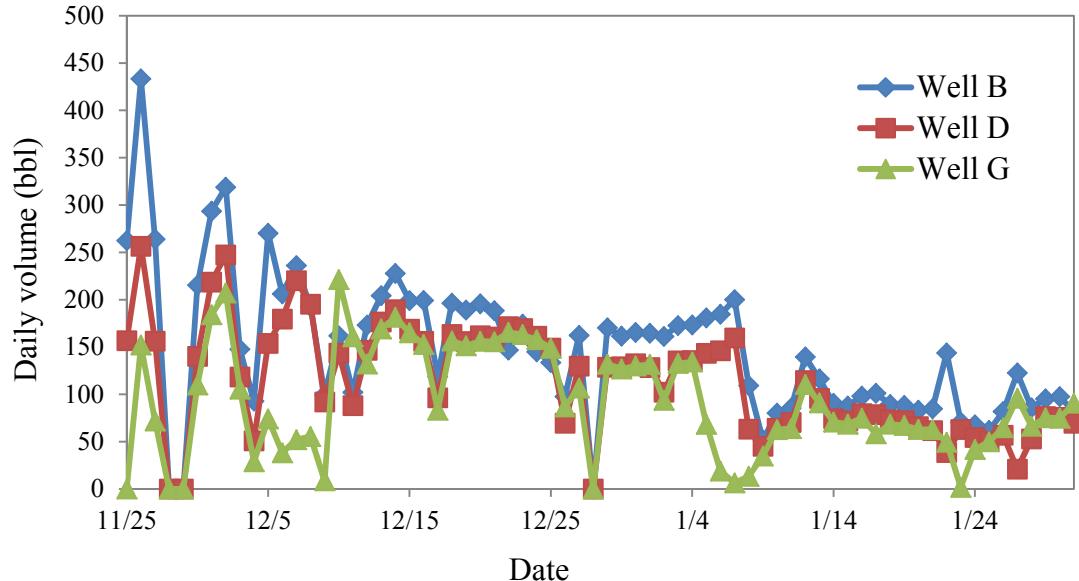
**Table 3-6: Summary of Measured Water Quality**

Parameter	Unit	Well B (Hybrid)			Well D (Slickwater)			Well G (Cross-Linked Gel)		
		Average	Range	Average	Range	Average	Range	Average	Range	Average
pH	-	6.95	6.75 – 7.18	6.99	6.78 – 7.22	7.06	6.79 – 7.46			
Conductivity	mS/cm	45.1	34.8 – 51.1	44.8	29.8 – 51.1	40.6	24.8 – 50.4			
TOC	mg/L	1,187	943 – 1,662	284	222 – 440	1,334	1,027 – 1,735			
DOC	mg/L	1,042	831 – 1,375	248	214 – 340	1,189	820 – 1,431			
COD	mg/L	4,624	3,175 – 7,120	2,354	950 – 3,750	4,943	4,050 – 8,825			
Turbidity	NTU	295	119 – 763	262	124 – 489	247	115 – 490			
UV254	Abs.	1.567	0.746 – 2.670	0.719	0.352 – 2.163	1.613	0.967 – 2.412			
Alkalinity	mg/L CaCO <sub>3</sub>	623	534 – 710	581	428 – 778	653	574 – 782			
TS	mg/L	30,960	23,427 – 35,520	30,056	18,620 – 34,830	27,332	18,087 – 34,500			
TDS	mg/L	30,352	22,913 – 34,680	29,871	18,187 – 33,840	27,029	17,380 – 33,460			
TSS	mg/L	155	41 – 339	144	40 – 220	148	38 – 322			
TVS	mg/L	2,268	1,533 – 3,518	2,104	960 – 4,320	1,995	992 – 3,247			
VDS	mg/L	2,177	1,333 – 3,420	1,961	733 – 3,810	1,930	870 – 2,700			
VSS	mg/L	101	32 – 238	74	17 – 137	106	27 – 285			
Al	mg/L	3.3	2.1 – 5.0	3.2	1.7 – 5.0	2.2	1.1 – 3.4			
Ba	mg/L	24	14 – 37	27	12 – 39	14	6 – 28			
B	mg/L	34	26 – 39	23	19 – 26	37	29 – 44			
Ca	mg/L	574	355 – 1,014	562	275 – 1,002	471	213 – 927			
Fe	mg/L	45	25 – 103	41	20 – 72	50	33 – 82			
K	mg/L	101	72 – 161	76	57 – 89	112	87 – 143			
Mg	mg/L	85	54 – 136	84	40 – 133	72	34 – 132			
Na	mg/L	10,761	7,349 – 18,608	11,173	9,583 – 12,637	9,430	6,063 – 12,428			
Si	mg/L	41	29 – 49	56	40 – 67	40	28 – 51			
Sr	mg/L	81	44 – 165	80	32 – 167	68	25 – 157			
Zr	mg/L	0.78	0.30 – 1.83	0.22	0.12 – 0.46	0.27	0.16 – 0.42			
Br	mg/L	80	54 – 102	79	48 – 102	70	45 – 93			
Cl	mg/L	16,190	11,400 – 20,570	16,883	12,150 – 19,580	14,686	9,010 – 19,050			
HCO <sub>3</sub>	mg/L	553	418 – 722	493	320 – 838	525	360 – 716			
NH <sub>4</sub>	mg/L	36	25 – 43	33	24 – 38	35	24 – 41			
SO <sub>4</sub>	mg/L	15	4 – 29	20	1 – 89	43	2 – 210			
Oil and grease	mg/L	123	40 – 435	68	17 – 304	153	10 – 872			
GRO	mg/L	208	47 – 910	127	33 – 356	243	49 – 1,392			
DRO	mg/L	76	10 – 273	54	12 – 248	124	7 – 762			
ORO	mg/L	8	7 – 12	15	5 – 34	23	5 – 77			
TPH	mg/L	281	55 – 1,068	180	48 – 398	378	56 – 2,231			
BTEX	mg/L	50	26 – 100	39	19 – 63	52	26 – 135			

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 are smaller than 1.5 um.

Table 3-6 presents the average and range of values by well for each parameter measured. Detailed characterization data are presented in Appendix B. The concentrations of divalent cations (Mg, Ca, Sr, and Ba) were significantly lower in Well G compared to the other two wells. Boron concentrations were significantly lower in Well D compared to the other two wells. All other metal and ion concentrations were fairly consistent among the various wells and showed a slight upward trend, with the exception of silicon (higher concentration in Well B, fairly flat temporal trend) and sulfate (decreasing temporal trend). No strong trends were observed for COD, turbidity, TSS, UV254, or the volatile portions of the measured solids (TVS, VSS, and VDS).

Daily water production values reported by Encana are presented in Figure 3-3 for the purpose of aiding to the discussion of measured water quality. The magnitude and general trend of daily water production does not differ greatly from well to well, with each well showing a fairly steady and gradual downward temporal trend. Between the November 25, 2013 and January 30, 2014 study period, Well B produced at total of 9,915 bbl (0.41 Mgal), Well D produced a total of 7,709 bbl (0.32 Mgal), and Well G produced a total of 6,208 bbl (0.26 Mgal).



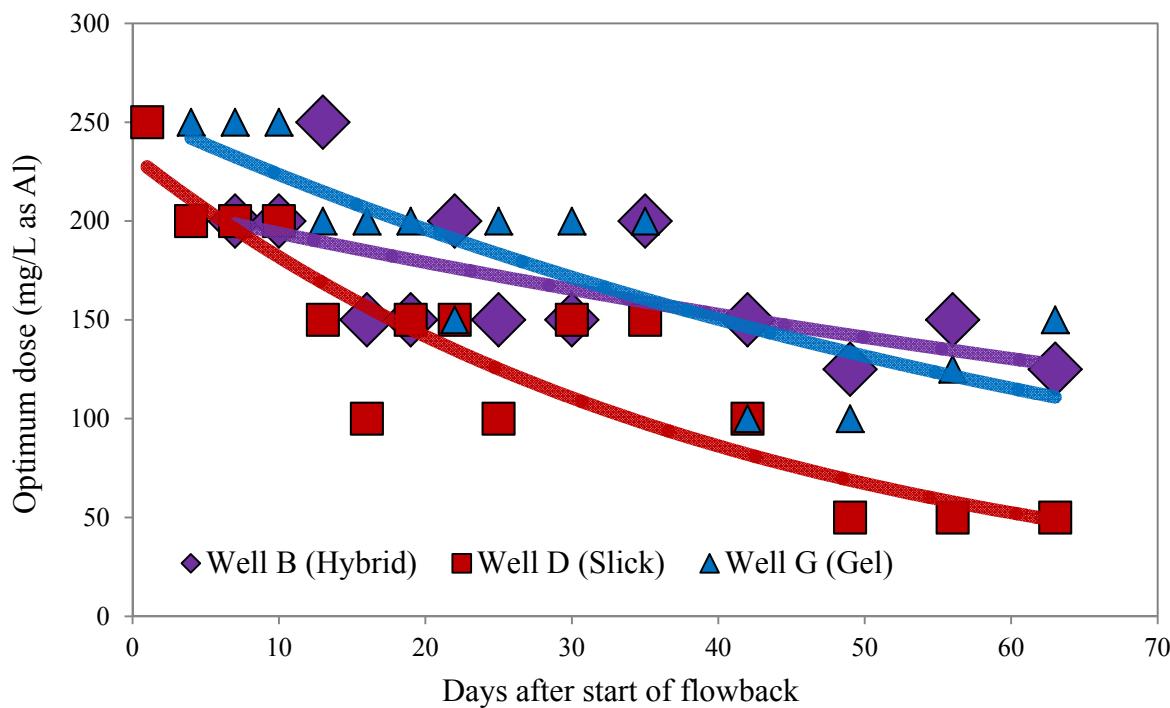
**Figure 3-3: Daily Water Production**

### 3.4.2 Treatability

The optimum coagulant dose determined for each five-point jar test is presented in Figure 3-4. The complete set of turbidity and UV254 measurements for each jar test, along with photographs of various jar tests, are presented in Appendix C. An exponential trend line was fit to each set of data in order to illustrate the general temporal trend in coagulant demand for each well. Figure 3-4 does not include the optimum dose for the day 1 sample from Well G. The optimum dose for this sample was found to be 800 mg/L (i.e., roughly three times the next highest dose). Because this sample was collected directly from the wellhead, prior to the start of production, this data point was not included in the dataset to which the trend line was fit.

Based on the observed trends, Well G (cross-linked gel fluid) has a higher coagulant demand than Well D (slickwater fluid), but this difference is fairly minor (25 to 300 % greater for cross-linked gel fluid). The observed coagulant demand at Well B (hybrid fluid), generally falls in between the other two wells, except after roughly 35 days, when the coagulant demand of produced water from Well B becomes slightly higher than produced water from Well G. The

coagulant demand of produced water from each well is observed to decrease with time. The average linear decrease ranges from 0.8 mg/L Al per day (Well B) to 2.7 mg/L Al per day (Well D).



**Figure 3-4: Temporal Changes in Optimum Coagulant Dose**

Average treatment removals of measured parameters are presented in Table 3-7. The average and standard deviation of the ‘raw’ sample refers to the average of each non-treated sample for each well over the study period. The average and standard deviation of the ‘treated’ sample refers to the average concentrations measured in each of the optimum dose samples collected after jar testing.

Mean turbidity removal was 96% or greater for at each well, resulting in an average turbidity of less than 10 NTU in all treated samples. Organics removal, as suggested by average TOC, DOC, and COD 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 D), with average treated water TSS concentrations of 93 mg/L (Well G) to 29 mg/L (Well D). No significant TDS removal was observed.

**Table 3-7: Treatment Results**

Well	Parameter	Unit	Raw		Treated		Average Removal
			Avg	StDev	Avg	StDev	
Well B (hybrid)	Turbidity	NTU	295	192	7.0	3.0	97%
	UV254	Abs.	1.567	0.460	0.483	0.129	67%
	COD	mg/L	4,624	1,002	3,942	1,577	10%
	TOC	mg/L	1,187	158	974	141	17%
	DOC	mg/L	1,042	142	957	142	8%
	TSS	mg/L	155	73	52	34	57%
	TDS	mg/L	30,352	3,148	30,528	3,040	1%
Well D (slickwater)	TVS	mg/L	2,268	575	1,985	319	9%
	Turbidity	NTU	262	114	6.0	3.1	97%
	UV254	Abs.	0.719	0.424	0.117	0.039	80%
	COD	mg/L	2,354	756	1,739	530	15%
	TOC	mg/L	284	248	234	19	12%
	DOC	mg/L	69	33	231	14	6%
	TSS	mg/L	144	49	29	19	74%
Well G (cross-linked gel)	TDS	mg/L	29,871	4,492	29,238	4,661	1%
	TVS	mg/L	2,104	864	1,951	661	3%
	Turbidity	NTU	247	2	9.4	4.5	96%
	UV254	Abs.	1.613	0.385	0.476	0.128	70%
	COD	mg/L	4,943	1,261	3,363	563	27%
	TOC	mg/L	1,334	227	1,093	202	18%
	DOC	mg/L	1,189	215	1,100	215	7%
Well G (cross-linked gel)	TSS	mg/L	148	78	93	133	56%
	TDS	mg/L	27,029	5,164	27,000	5,421	0%
	TVS	mg/L	1,995	521	1,887	427	5%

### 3.5 Discussion

This section attempts to provide justification and application of some of the primary observations regarding the characterization and treatability of the produced water generated by each well. Subsection 3.5.3 also provides results and discussion of preliminary chemical

equilibrium modeling conducted using a subset of the collected data in order to demonstrate one of the applications of the collected water quality data.

### *3.5.1 Produced Water Quality*

The pH of all produced water samples fell within the range of 6.75 to 7.5. The pH readings were fairly consistent among three studied wells, suggesting that the type of fracturing fluid (i.e., slickwater vs. gel) may not greatly influence the pH of the produced water. Alkalinity concentrations were typically greater than 500 mg/L as CaCO<sub>3</sub> over the course of the study period, suggesting a significant buffering capacity. Due to this high buffering capacity, softening (metal precipitation) via pH adjustment may require a significant chemical demand. The temporal decrease in the alkalinity trend suggests a lesser buffering capacity in older samples, especially from the slickwater well (Well B), which was observed to have a more steeply declining trend compared to the other two wells.

The high TOC concentrations (943 to 1,735 mg/L as C) in produced water from the wells fractured with cross-linked gel and hybrid fluids (Well G and Well B) is likely a result of the organic additives specific to the gel fluids (predominantly petroleum distillates and guar gum). The smaller TOC concentration (222 to 440 mg/L as C) measured in the produced water from Well D, fractured with a slickwater fluid, 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. Subsurface conductivity between wells within the targeted formation may also serve as a source of TOC in Well D (i.e., organics from the Well B fracture fluid may contribute to TOC concentrations in Well D). Petroleum hydrocarbons present in the formation may also contribute to the TOC concentrations in produced water, but based on the difference in TOC concentrations between the slickwater- and cross-link gel-

fractured wells, fracturing additives appear to have a greater impact on TOC concentration than contributions from the formation.

The lower concentration of boron in Well D is likely due to the absence of the borate-based cross-linker in the slickwater fracturing fluid. This lower boron concentration at Well D may represent the contribution of boron from the formation. Alternatively, subsurface conductivity between wells may have also allowed boron from the cross-linker used in neighboring wells to contribute to boron concentrations in Well D.

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. Early produced water (e.g., from the first 10 days of production) has had less contact time with the formation than later (i.e., older) produced water and is also typically flowing back from the well at a higher rate. As such, the water quality of earlier produced water is more similar to the raw fracturing fluid. Evidence of this includes higher concentrations of TOC and crosslinker-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 become fairly stable at roughly 30 days after production. pH, conductivity, and the majority of the metals that contribute to conductivity become more stable roughly 45 days after production.

### *3.5.2 Treatability*

Based on the jar testing results presented above, chemical coagulation was effective at a reasonable chemical dose for each of the collected produced water samples, with the exception of the pre-production sample collected from Well G. With an optimum dose of 800 mg/L as Al of ACH required for effective coagulation, this stream may require pre-treatment or may be more

cost-effective to dispose. Otherwise, produced water samples from each well were successfully treated with chemical coagulation, suggesting that the produced water waste stream could be sent to a treatment facility immediately at the start of production. The decreasing temporal trend in optimum dose suggests that treatment of produced water would require less chemical coagulant as the well ages, but the slope of this trend is fairly gradual.

Coagulant demand is observed to be higher in produced waters from Well G and Well B than in Well D, suggesting that some additive(s) specific to the cross-linked gel fluid make treatment more difficult. This difference in chemical coagulant demand is fairly minor (25 to 300 % greater for cross-linked gel fluid), however, so it would be not be unreasonable to blend these waste streams and send the blended produced water through a single treatment process.

As shown above, the chemical coagulation jar testing was successful at removing greater than 95% turbidity and roughly 50 to 75% of TSS. Additional TSS removal might be achieved with solid-liquid separation techniques beyond the 15-minute settling period used in the jar testing. The chemical coagulation process does not, however, significantly reduce the concentration of organic compounds in the produced water, nor does it remove any significant portion of TDS.

The treatability testing included in this study was not intended to provide specific treatment design criteria (e.g., specific chemical dosing requirements), but instead provides valuable insight into the relative differences in treatability among produced waters from wells fractured with different fracturing fluids, as well as relative changes in treatability with time. Similarly, treatment removals are not intended to reflect treatment removals of an overall, optimized treatment process, but instead are intended to provide a general idea of what is and

isn't removed from produced water via the chemical coagulation process. These insights will help in making decisions regarding management of this waste stream.

### *3.5.3 Chemical Equilibrium Modeling*

OLI analyzer studio, a thermodynamic aqueous chemistry modeling software package, provides many capabilities that allow for a more complete understanding of measured water quality data. Examples of two useful functions are presented here in order to demonstrate the benefits of equilibrium modeling and also to make preliminary observations. First, an analysis of ion speciation in various raw produced water samples is presented, followed by a blend ratio investigation to model the effects of blending produced water with a freshwater source.

Ion concentrations tested in the laboratory are typically reported as mg/L of the base ion (e.g., mg/L as  $\text{Ca}^{+2}$ ), but these ions do not necessarily exist in the raw solution as the base ion; they instead exist as one or many species of ion complexes (e.g.,  $\text{CaCO}_3$  or  $\text{CaSO}_4$ ). Chemical equilibrium modeling is employed to determine the form(s) in which ions actually exist in the solution. With physical parameters and ion concentrations as inputs, OLI automates the calculation of aqueous-based thermodynamic equilibrium equations and reports the distribution of real chemical species, as both aqueous and solid species, that exist in the sample. Understanding speciation may aid in understanding phenomena such as solids formation and scaling potential and can also provide a better understanding of softening and other treatment mechanisms. For this report, Well B is selected as a representative sample and days 1, 19, and 63 are used to investigate temporal variation.

Multivalent metal ions can cause potential clogging problems during hydraulic fracturing and also during well production, and it is important to investigate the speciation of all ions of interest to determine which ions present the greatest potential of scaling under a specific

condition. The results of modeled speciation of the primary cations in each sample are presented in Table 3-8. Calcium carbonate (calcite) makes up the majority of the solids in each of the analyzed samples. Each system was modeled at the measured pH of the respective sample (each near a pH of 7). At this modeled pH, magnesium, boron, zirconium, and strontium are only present in the aqueous phase. This is consistent with common softening processes, where it is known that magnesium will not start precipitating out until the pH is raised to roughly 10, at which point it will precipitate out as  $Mg(OH)_2$ .

While the solubility of barium sulfate is extremely low, the presence of barium ion in all three samples suggests that each produced water sample is sulfate-deficient and that if sulfate was introduced into the system (e.g., via dilution with a freshwater source with 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. As shown in Table 3-8, all aluminum in the solution is in the solid form of either  $NaAl(OH)_2CO_3$  or  $Al(OH)_3$ , and all ferric ions are in the form of  $Fe(OH)_3$ . These solid particles of  $Al(OH)_3$  and  $Fe(OH)_3$  are often small with a positive surface charge and therefore 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 levels to desired treatment levels.

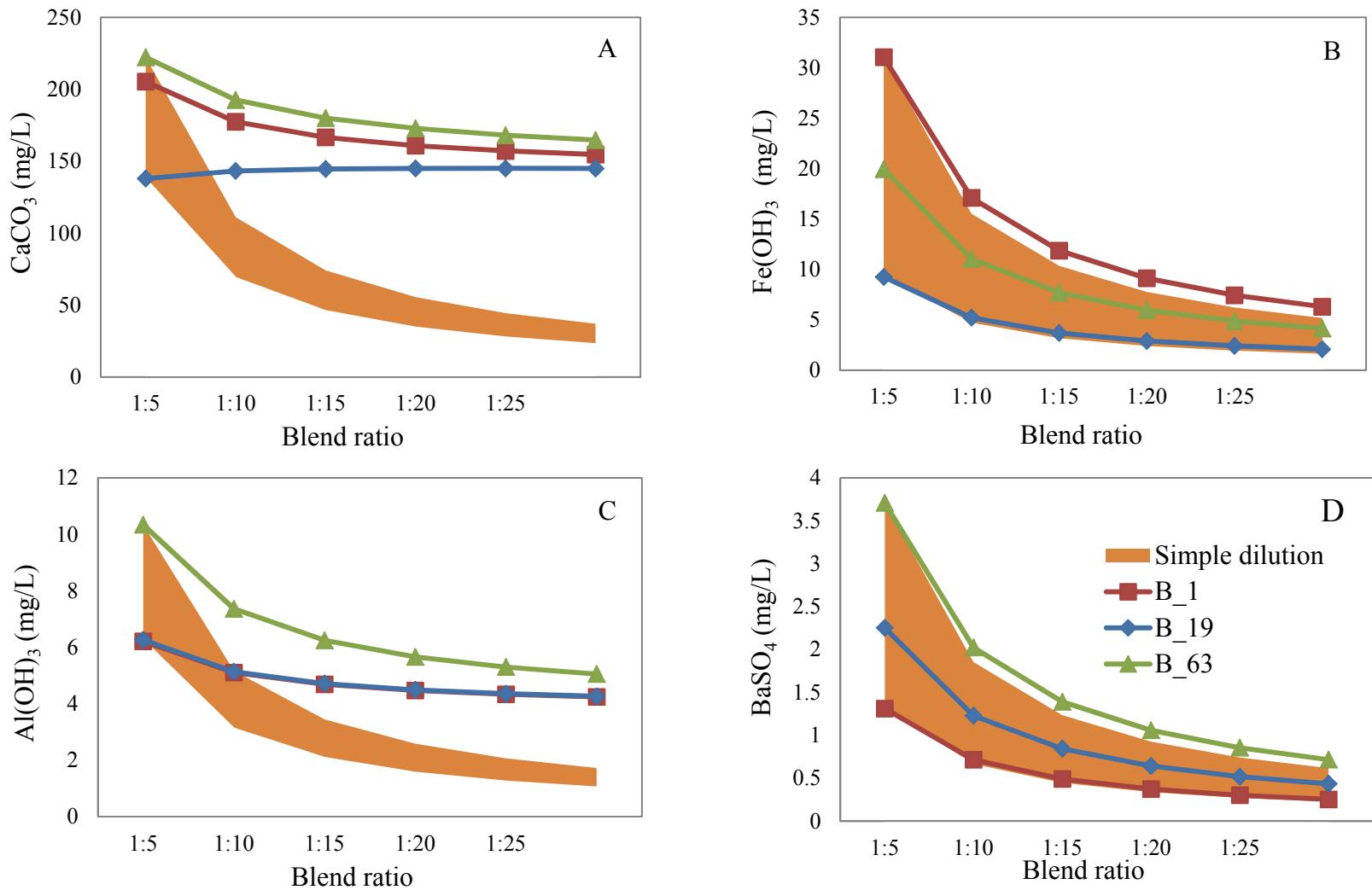
**Table 3-8: Modeled Speciation of Measured Metals for Well B**

Measured Ion	Chemical Formula	1 Day			19 Days			63 Days		
		Total mg/L	Aqueous mg/L	Solid mg/L	Total mg/L	Aqueous mg/L	Solid mg/L	Total mg/L	Aqueous mg/L	Solid mg/L
Al	Al(OH) <sub>3</sub>							14.4		14.5
	NaAl(OH) <sub>2</sub> CO <sub>3</sub>	11.3		11.3	11.5		11.5			
Ca	Ca <sup>2+</sup>	161.1	161.1		379.3	379.4		758.7	758.9	
	CaCO <sub>3</sub>	477.5	1.8	475.8	383.8	1.7	382.1	631.1	1.7	629.5
	CaH <sub>2</sub> BO <sub>3</sub> <sup>+</sup>	0.0	0.0		0.1	0.1		0.2	0.2	
	CaHCO <sub>3</sub> <sup>+</sup>	6.5	6.5		7.1	7.1		5.7	5.7	
	CaSO <sub>4</sub>	0.2	0.2		0.0	0.0		0.1	0.1	
Mg	Mg <sup>2+</sup>	51.3	51.4		79.8	79.8		134.4	134.4	
	MgCO <sub>3</sub>	0.1	0.1		0.1	0.1		0.1	0.1	
	MgHCO <sub>3</sub> <sup>+</sup>	10.5	10.5		8.3	8.3		5.5	5.5	
	MgSO <sub>4</sub>	0.2	0.2		0.0	0.0		0.0	0.0	
B	H <sub>3</sub> BO <sub>3</sub>	29.8	29.8		29.1	29.1		26.0	26.0	
	B(OH) <sub>4</sub> <sup>-</sup>	0.4	0.4		0.4	0.4		0.4	0.4	
	NaB(OH) <sub>4</sub>	0.1	0.1		0.1	0.1		0.1	0.1	
Zn	Zn <sup>2+</sup>	0.4	0.4		0.0	0.0		0.6	0.6	
	ZnCl <sup>+</sup>	0.1	0.1					0.1	0.1	
	ZnHCO <sub>3</sub> <sup>+</sup>	0.0	0.0							
Ba	Ba <sup>2+</sup>	1.8	1.8		16.8	16.8		26.5	26.5	
	BaCl <sup>+</sup>	0.4	0.4		5.0	5.0		7.3	7.3	
	BaHCO <sub>3</sub> <sup>+</sup>	0.0	0.0		0.2	0.2		0.1	0.1	
	BaSO <sub>4</sub>	20.2		20.2	5.3		5.3	7.8		7.8
Fe	Fe(OH) <sub>3</sub>	197.1		197.1	57.4		57.4	147.7		147.7
Sr	Sr <sup>2+</sup>	43.7	43.7		72.8	72.8		164.9	165.0	

The second analysis simulates the blending of produced water with a freshwater source.

The freshwater source used in this simulation is based on a typical groundwater quality in northeast Colorado (See Appendix D for freshwater quality used). Produced water may potentially be blended with a freshwater source in order to dilute the produced water to a point at which it is able to be recycled as a fracturing fluid without treatment. However, 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.

The solids concentrations at different blending ratios for four separate solids are presented in Figure 3-5. The shaded area represents the effect of simple dilution with freshwater



**Figure 3-5: Modeled Blending for Well B at Day 1, 19, and 6**

(e.g., a 1:10 blend ratio corresponds to a 90% reduction in the solids concentration), with the upper boundary of the shaded area defined by the sample with the highest solid concentration and the lower boundary of the shaded area 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. The lines represent the actual model concentrations in the system after equilibrium has been reestablished.

As shown, ferric hydroxide (Figure 3-5B) and barium sulfate (Figure 3-5D) follow the trend of simple dilution, but the concentrations of calcite (Figure 3-5A) and aluminum hydroxide (Figure 3-5C) remain 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 more flat curves shown in Figures 3-5A and 3-5C. As presented in Table 3-8, a large portion of calcium is present as the calcium ion in the raw sample. As such, when the produced water is blended with freshwater, which is usually oversaturated in terms of carbonate, additional calcium carbonate solid will be formed.

The OLI analyzer package can be used to provide a more complete analysis of each of the capabilities demonstrated above. Other potentially applicable functionalities of this software include simulating the blending of produced water from different wells and/or different ages of produced water in order to understand how streams interact and reconcile with each other, simulating a softening process with regard to pH adjustment and filter efficiency, and simulation of downhole conditions by changing the physical conditions (i.e. temperature and pressure) to explore scaling potentials present in this environment.

### **3.6 Future Work**

Further study may be desired in order to refine and expand the observations made by this study. Additional characterization studies, similar in nature to that presented here but on a separate set of wells, would aid in understanding the variability of the water quality concentrations and trends observed here. Such future studies may also include the collection of pre-production flowback samples in order to better understand this water quality. Such an understanding of pre-production water quality may also help support or refine the current justification for differences in water quality from wells fractured with different fluids. It may also be beneficial to combine water quality data from this or future sets of well, with water production data in order to better understand overall water management (e.g. dilutions, blends).

A more extensive treatability study could provide more specific treatment design criteria, including selection of appropriate components for a treatment process, and well as refining treatment parameters (e.g., sizing, dosing, and removal efficiencies). Such a study may involve the trial of different treatment processes, such as a pre-oxidation treatment process to reduce the coagulant demand. Such a process might be particularly beneficial in treating pre-production flowback and in treating produced water from wells fractured with cross-linked gel fluids. Other treatment components that require further study include the selection and use of polymer(s) as a flocculation aid and further study and comparison of solid-liquid separation techniques (dissolved air floatation, settling, filtration, etc.). Such further study would provide a better understanding of the optimal treatment process, recycled water quality, and treatment costs.

Lastly, more extensive chemical equilibrium modeling may be beneficial for better understanding blending and/or treatment designs.

## 4. ORGANIC COMPOUND CHARACTERIZATION

This chapter provides a summary of a series of tasks conducted as a first step to better understand the composition of organic compounds in produced water. This chapter expands on the organic compound characterization data presented for Wells B, D, and G discussed in Chapter 3 and also presents and discusses organic compound characterization data from two other unrelated wells located in Weld County, Colorado.

### **4.1 Introduction and Purpose**

TOC concentrations have been measured at high concentrations in various produced water samples, particularly in produced waters from wells fractured with gel-based fracturing fluids, where concentrations of greater than 1,000 mg/L are not uncommon. Based on data presented in Chapter 3, as well as other preliminary data collected within our research group, TOC concentrations seem to decrease gradually as wells age, and then stabilize at a non-zero concentration. As discussed in Chapter 2, little work has been published regarding the characterization or classification of organic compounds in produced waters. This significant organic compounds load has the potential to greatly affect how produced water is managed, particularly in regard to the treatment of this waste stream.

The objective of this study was to perform various organic-based analytical techniques on a range of produced water samples in order to help answer the following research questions:

- What is the origin of organic compounds in produced water?
- Is there a correlation between a specific classification of organic compounds and the ease of treating produced water?

- Is there a specific class of organic compounds that change over time?
- Do chemical coagulation removal efficiencies vary among different classes of organic compounds?

Analytical techniques performed in this study include the following:

- Gravimetric analysis of the volatile portion of solids
- Analysis of the size distribution of organic compounds via serial filtering
- Analysis of organic subclasses and percent removal of these subclasses via chemical coagulation

## **4.2 Organic Makeup of Fracture Fluid Used in Sampled Wells**

A list of samples collected from the five wells sampled as part of this organic compound characterization study is presented in Table 4-1. Wells B, D, and G are the same wells discussed in Chapter 3. Wells A and C are two separate wells owned by a separate operator in Weld County, Colorado. Because different operating conditions (e.g., separator timing and configuration) are present at different well sites, a description of the sample collection method and visual observation of each sample analyzed is also provided in Table 4-1. The visual observation is described in regard to the presence or absence of emulsified or free oil in the produced water, as the presence of oil in the sample will likely contribute to the overall measured organic load.

Based on observations presented in Section 3.5.1, the large difference in TOC concentrations in produced water from wells fractured with slickwater fluids versus wells fractured with gel fluids suggests that fracture fluid additives are the primary contributor to the overall organic load in produced water. As such, it is important to look at the fracture fluid

composition specific to the fluid used for each well when trying to understand the organic makeup of organic compounds in produced water.

**Table 4-1: Description of Samples Used for Organic Compound Characterization**

<b>Sample</b>	<b>Description</b>
Well B (multiple samples)	From a well fractured with a hybrid fluid, collected from production separator after start of hydrocarbon production; no emulsified oil or floating free product present
Well D (multiple samples)	From a well fractured with a slickwater fluid, collected from production separator after start of hydrocarbon production; no emulsified oil or floating free product present
Well G (multiple samples)	From a well fractured with a gel fluid, collected from production separator after start of hydrocarbon production; no emulsified oil or floating free product present
Well A_9day	From a well fractured with a gel fluid, collected from wellhead prior to hydrocarbon production; no emulsified oil or floating free product present
Well A_17day	From a well fractured with a gel fluid, collected from wellhead after start of hydrocarbon production; emulsified oil and floating free product present
Well C_4day	From a well fractured with a gel fluid, collected from wellhead prior to hydrocarbon production; no emulsified oil or floating free product present

FracFocus.org data for Wells B, D, and G were presented previously in Table 3-2. The primary compounds that make up the input organic load for these wells are petroleum distillates and the guar-based gelling agent. Well A and Well C were both fractured with the same cellulose-based (i.e., not guar-based) cross-linked gel fluid. FracFocus.org data for Wells A and C are presented in Table 4-2. The fracturing fluid for each well contained the same components, but the reported maximum concentrations for each fluid were different and as such are presented separately in Table 4-2. The cellulose-based gelling agent makes up the majority of the organic input load for this fluid. This fluid varies significantly from the gel fluids used in Wells B and G in that the gelling agent was different (cellulose versus guar) and also in that the fluid used for Wells A and C lacks the large concentration of petroleum distillates.

**Table 4-2: FracFocus.org Frac Fluid Compositions for Wells A and C**

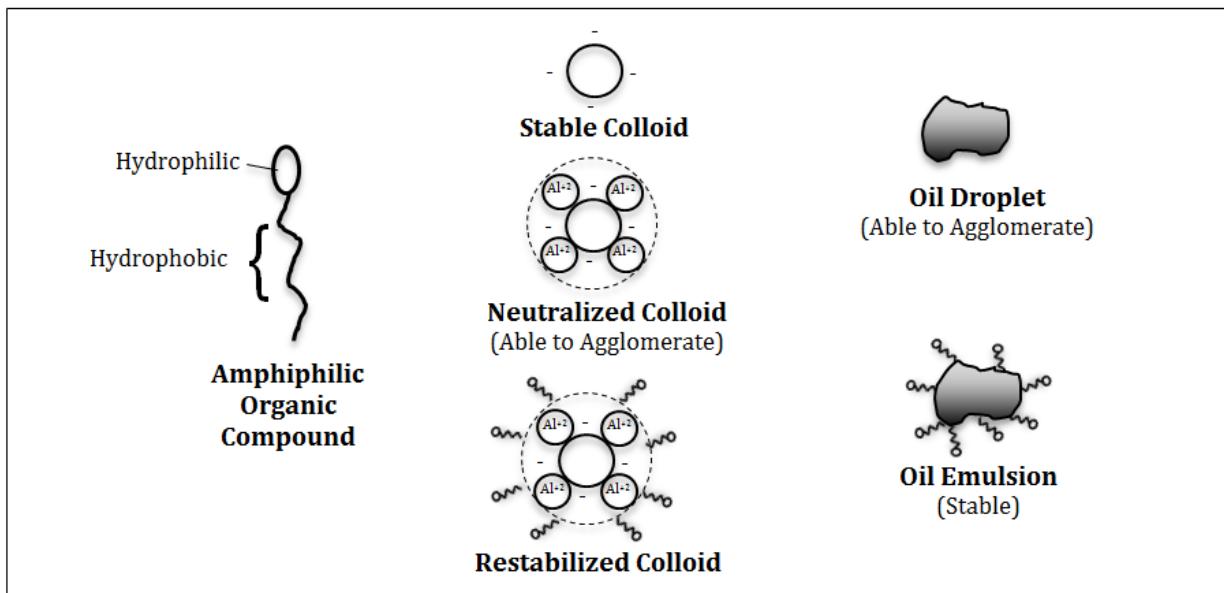
Purpose	Trade Name	Ingredients	Well A Max Conc. (mg/L)	Well C Max Conc. (mg/L)
Gelling Agent	WG-39	Polysaccharide	3,237	3,381
Buffer	BA-20 BUFFERING AGENT	Ammonium acetate	627	927
		Acetic acid	188	278
Crosslinker	CL-23 CROSSLINKER	Zirconium, acetate lactate oxo ammonium complexes	775	800
		Ammonium chloride	387	400
Non-ionic Surfactant	OilPerm A	Ethanol	347	330
		Heavy aromatic petroleum naphtha	173	165
		Poly(oxy-1,2-ethanediyl),alpha-(4-nonylphenyl)-omega-hyd oxy-, branched	28.9	27.5
		Naphthalene91-20-3	28.9	27.5
		1,2,4 Trimethylbenzene	5.8	5.5
Crosslinker	CL-41	Inorganic Salt	239	204
		Lactic Acid	289	204
Scale Inhibitor	3rd PARTY SCALE INHIBITOR	DVE4O004	335	331
Breaker	VICON NF BREAKER	Chlorous acid, sodium salt	115	233
		Sodium chloride	346	77.6
Breaker	OPTIFLO-III DELAYED RELEASE BREAKER	Ammonium persulfate	191	200
		Crystalline silica, quartz	57.3	59.9
Biocide	MC B-8520	4,4-Dimethyloxazolidine	128	239
		3,4,4-Trimethyloxazolidine	6.4	12.0
		2-Amino-2-methyl-1-propanol	1.3	2.4
Additive	CLA-WEB	Ammonium salt	118	123
Friction Reducer	FR-66	Hydrotreated light petroleum distillate	43.1	75.2
Biocide	MC B-8625	Glutaraldehyde	35.2	65.8
Breaker	SP BREAKER	Sodium persulfate	40.3	34.0
Surfactant	OilPerm B	Isopropanol	173	173
		Terpenes and Terpenoids, sweet orange-oil	173	173
		Proprietary Component	173	173

The gelling agent used in each gel-based fracturing fluid is composed of a long-chain polysaccharide. Polysaccharides are polymeric carbohydrate molecules composed of long chains of monosaccharides (i.e., sugars). Guar-based gelling agents are derived from the endosperm of the seed from the legume *Cyamopsis tetragonolobus* and are composed of a linear mannose ‘backbone’ with galactose subunits attached along this backbone at a ratio of roughly two mannose to one galactose (Aqualon 2005). Cellulose-based gelling agents are similar in nature, except glucose is typically the primary monosaccharide unit.

Amphiphilic organic compounds have both hydrophobic and hydrophilic ends and can act to stabilize both colloidal particles (e.g. particles in water) and emulsified liquids (e.g. oil in water). It is postulated that amphiphilic organic matter may interfere with the coagulation process by restabilizing neutralized particles before they are able to agglomerate into a large enough particle size that is able to be removed. Under successful coagulation, charged (stable) colloids in the produced water are neutralized by the cations provided by the coagulant dose, and the neutral particles are then able to aggregate into larger, charge-neutral floc that can be separated from the liquid stream. For early produced water samples that are difficult to treat, it is expected that colloids are successfully being neutralized, but that the neutral (i.e., unstable) colloids are restabilized by amphiphilic organic matter present in the waste stream before the neutralized colloids are able to flocculate and be removed (Figure 4-1).

In a similar manner, small emulsions of oil are neutrally surface-charged and therefore adsorb the hydrophobic end of the amphiphilic organic compounds while the hydrophilic functionality stabilizes the emulsion (Figure 4-1). It is expected that the same amphiphilic organic compounds that act to restabilize neutral particles and prevent flocculation may result in stable oil-in-water emulsions, leading to ineffective separation of produced water and crude oil.

It is hypothesized that the amphiphilic organic compounds present in produced water may be surfactants and/or polysaccharides originating from fracturing fluid additives. The concentration of these compounds is expected to be highest immediately after flowback begins and then gradually decline. This may be supported by the observed decrease in TOC and increase in treatability over time.



**Figure 4-1: Illustration of Restabilization of Colloids by Amphiphilic Organic Compounds**

### 4.3 Methods

#### 4.3.1 Gravimetric Analysis for Volatile Portions of Solids

A gravimetric analysis was conducted on all samples collected as part of the Encana study (described in Chapter 3), as well as two additional samples from Well A (9-day sample and 17-day sample). The gravimetric method used is presented in Table 3-4, with each sample measured in triplicate. TS, TSS, and TDS samples were muffled at 550 degC in order to determine the volatile fraction of each class of solids. This volatile portion serves as a rough approximation of the amount of organic matter present in the solid fraction of the produced water.

#### 4.3.2 Organic Compound Size Distribution via Serial Filtering

A size analysis of organic compounds was conducted on five samples by successively filtering the samples through various decreasing filter sizes and then measuring the TOC concentration of the filtrate. Samples were filtered through each filter type presented in Table 4-3. Each sample was run in triplicate to determine variability caused by filtering (i.e., three

separate aliquots were collected from the bulk sample bottle and each aliquot was filtered through separate sets of filters). A sample was collected from each filtrate for TOC analysis. TOC analysis was conducted using a Shimadzu TOC analyzer, which reports the difference between measured TC and TIC (see TOC method in Table 3-4). Each TOC analysis was conducted at a 1:10 dilution.

**Table 4-3: Filters Used for TOC Size Analysis**

Nominal Pore Size (um)	Material	Brand/Model
2.5	Paper	Whatman 45
1.5	Glass microfiber	Whatman 934-AH
0.45	Mixed cellulose esters	Millipore HAG047S6
0.2	Cellulose acetate	Nalgene 195-2520

#### *4.3.3 Analysis of Organic Subcategories*

In order to better understand the makeup of TOC, various organic subclasses were measured for 12 untreated produced water samples and two treated produced water samples. Measured subclasses included carbohydrates, TPH, and various VOCs and SVOCs. For the initial round of analysis, 55 VOCs and 64 SVOCs were measured for two samples (Well A\_9day and WellA\_17day) based on EPA method 8260C and 8270D, respectively, both of which target priority pollutants. These GC-MS-based methods were conducted by eAnalytics. For all other samples, only BTEX concentrations were measured (see BTEX method in Table 3-4). TPH concentrations were measured as described in Table 3-4. In addition to the 14 samples mentioned above, TPH and BTEX were measured for each sample collected from Wells B, D, and G in order to observe the temporal changes in these subcategories.

Carbohydrates were measured based on the Anthrone Method (Dulekgurgen 2004). This method involves the use of a strong acid and digestion under high-temperature conditions to break down carbohydrates into monosaccharides. The monosaccharides undergo a colorimetric

reaction with Anthrone ( $C_{14}H_{10}O$ ), and the abundance of monosaccharides measured using a spectrophotometer and compared to a standard curve generated using glucose. eAnalytics performed this analysis on all samples except the Well B, D, and G 55/56-day samples, which were measured at CSU in order to explore using a longer digestion time. Based on the results presented in Appendix E, it was decided that the prescribed 15-minute digestion time was sufficient, and it was also observed that there seems to be some interference producing a false high reading in the sample collected from Well D.

Measured concentrations for each organic subcategory were converted from mg/L as measured compound to mg/L as carbon for the sake of being able to compare each measured subcategory to the overall TOC. Carbohydrate concentrations, which are measured in mg/L as glucose, were multiplied by 0.4 (carbon makes up 40% of the molecular weight of glucose), TPH concentrations were multiplied by 0.85 (carbon makes up roughly 85% of petroleum hydrocarbons, on average), and BTEX was multiplied by 0.92 (the average percent as carbon of the four compounds). Concentrations as mg/L as carbon were then compared to the measured TOC to calculate the percent of the overall TOC concentration for each subcategory.

In order to explore the amount of each organic subcategory removed by a chemical coagulation treatment process, the three samples from Wells A and C were treated in a jar testing apparatus, and TOC and organic subclass concentrations were measured for the treated produced water. A mixed ACH and poly-aluminum chloride (PACl) chemical coagulant was used for these jar tests.

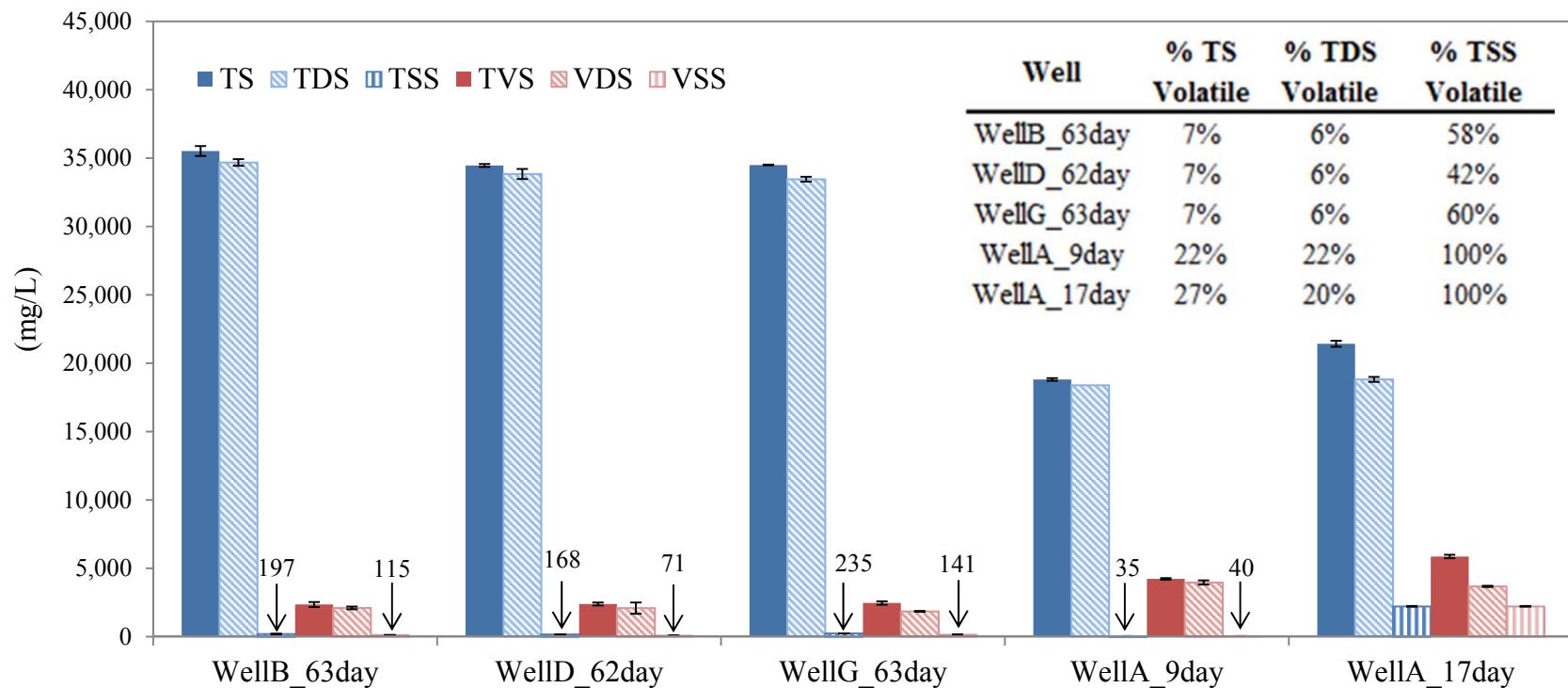
## 4.4 Results

### 4.4.1 Volatile Portions of Solids

Results for five samples are presented in Figure 4-2. Though this analysis was conducted on all samples collected as part of the Encana study, only the 62/63-day sample results for Wells B, D, and G are presented in this figure for the sake of comparing these results to the organic size distribution that was also conducted on these samples (Subsection 4.4.2). Averages of the triplicate measurements are reported, with error bars showing standard deviation. Data labels are included where values are too low for the bar to show up on the figure. A summary table of the calculated ‘percent volatile’ for each category of solids is presented in the upper-right corner of Figure 4-2.

Table 4-3 presents a summary of the average, minimum, and maximum percent volatile of each solids category for Wells B, D, and G (based on the 15 sampling events at each well). There were no strong temporal trends observed in any of these measurements (i.e., the volatile portion of TS, TDS, and TSS remained fairly constant throughout the 63-day study period). Based on the data presented in Table 4-3, the Well B, D, and G samples presented in Figure 4-2 are a good representation of the averages observed over the 63-day Encana study period.

Average percent TS and percent TDS volatile were consistent (8 to 9% and 7 to 9%, respectively) across Wells B, D, and G, and average percent TSS was highest at Well G (72%) and lowest at Well D (51%). Wells A and C had higher portions of volatile solids in all categories (i.e., TS, TDS, and TSS) compared to Wells B, D, and G. In all measured samples, the majority of the volatile solids were dissolved and the majority of TSS were volatile. Additionally, the magnitude of volatile solids concentrations (TVS, VDS, and VSS) is fairly consistent among all the measured samples.



**Figure 4-2: Solids Distributions**

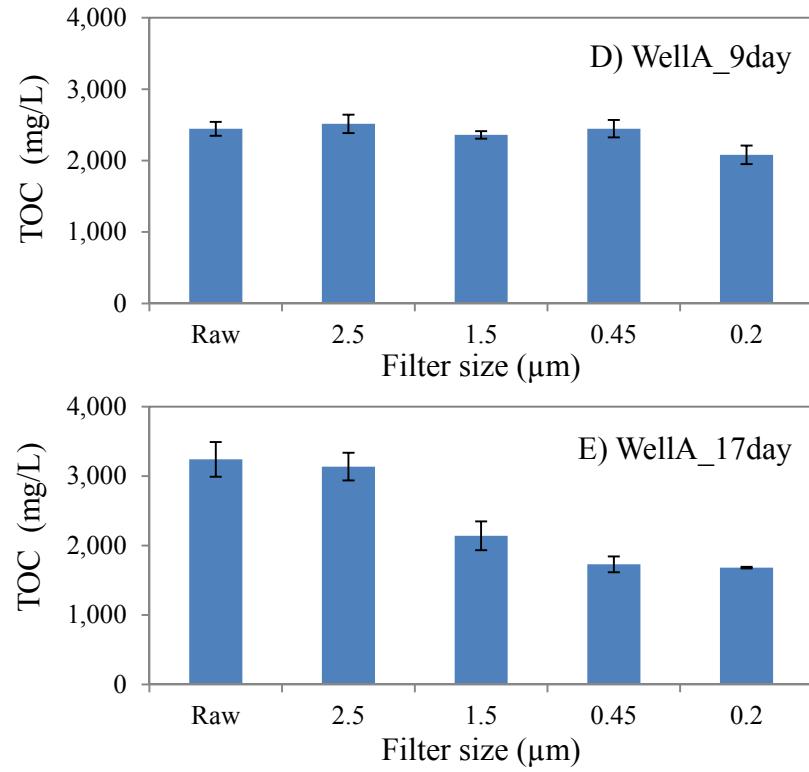
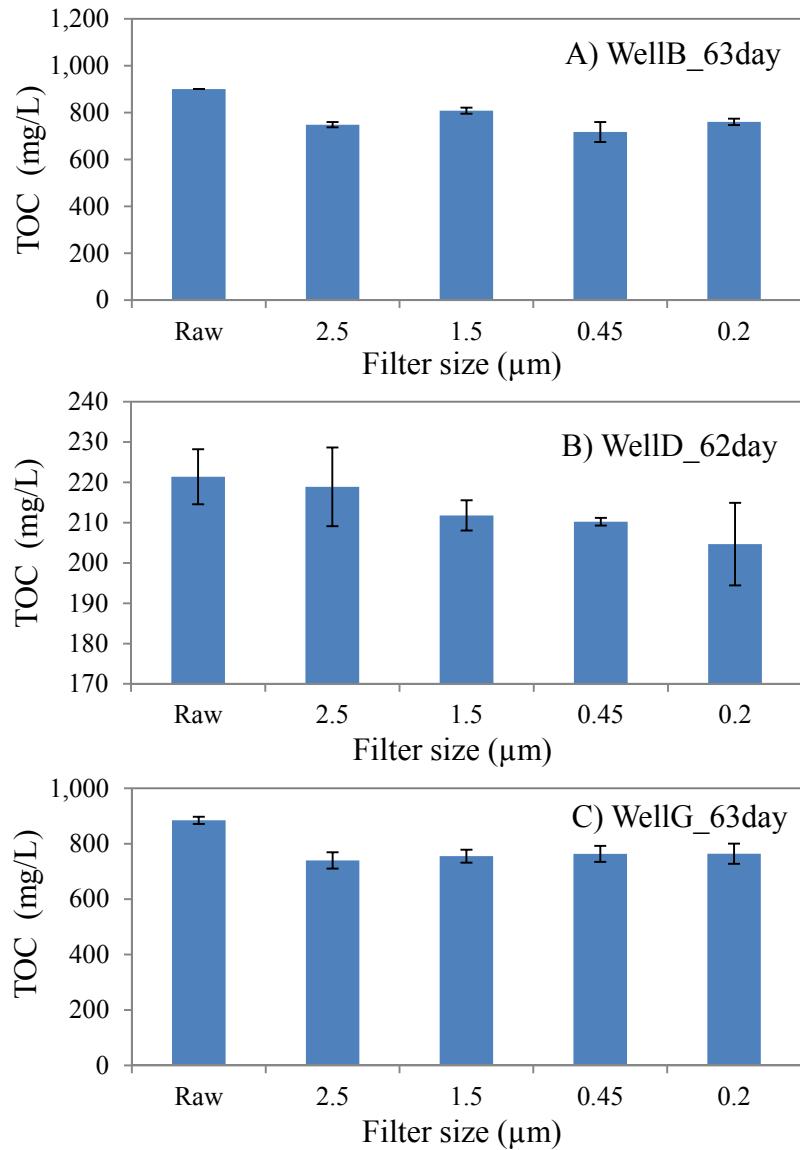
**Table 4-4: Summary of Percent Volatile Solids for all Well B, D, and G Samples**

	Well B			Well D			Well G		
	Average	Min	Max	Average	Min	Max	Average	Min	Max
% TS Volatile	8%	5%	19%	9%	5%	22%	9%	2%	27%
% TDS Volatile	7%	5%	12%	9%	4%	17%	9%	3%	19%
% TSS Volatile	66%	36%	80%	51%	33%	76%	72%	42%	89%

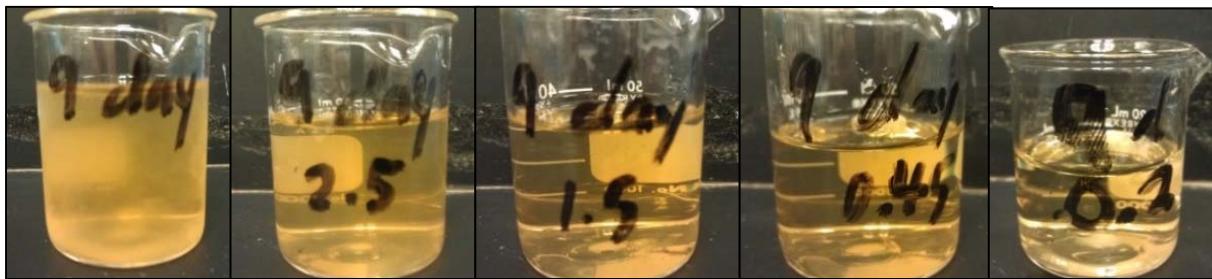
#### *4.4.2 Organic Compound Size Distribution via Serial Filtering*

Measured TOC concentrations of raw samples and samples collected after filtration through each filter size are presented in Figure 4-3. Averages of the triplicate measurements are reported, with error bars showing standard deviation. Photographs of samples WeldA\_9 day and WeldA\_16 day are presented in Figure 4-4 and Figure 4-5, respectively.

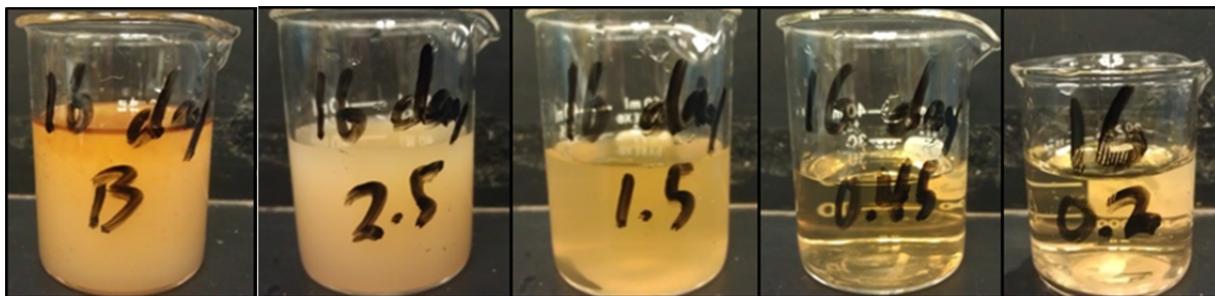
Filtering down to 0.2  $\mu\text{m}$  does not have a large impact on TOC concentrations for each of the measured samples, with the exception of sample WellA\_17day. For this sample, which contained both free and emulsified oil (Figure 4-5), there was little difference in TOC concentration between the unfiltered sample and the sample filtered at 2.5  $\mu\text{m}$ . A significant amount of organic compounds seems to be retained on a 1.5 $\mu\text{m}$  filter, where the average concentration decreases from 3,138 mg/L to 2,142 mg/L. This correlates well with the distribution of volatile solids for this sample (Figure 4-2), which suggests that roughly one-third of the volatile solids are volatile suspended solids. The TOC concentration slightly decreases after filtering through each the 0.45- $\mu\text{m}$  and 0.2- $\mu\text{m}$  filters. However, based on the observed variation, the observed decrease between 1.5- and 0.2- $\mu\text{m}$  filter sizes may not be significant. Based on a visual observation of the sample, the sample becomes incrementally less turbid after passing through the 1.5-, 0.45-, and 0.2- $\mu\text{m}$  filters. It appears that the majority of the emulsified oil is removed from the sample after passing through a 1.5- $\mu\text{m}$  filter.



**Figure 4-3: TOC Size Distributions**



**Figure 4-4: Photographs of WellA\_9 day Serially Filtered Samples**



**Figure 4-5: Photographs of WellA\_17 day Serially Filtered Samples**

#### 4.4.3 *Organic Subcategories*

Table 4-5 presents the concentration of detected VOCs and SVOCs measured in the two samples from Well A. There were 43 additional VOCs and 60 additional SVOCs analyzed that were not detected in either sample and are therefore not included in the table. Based on the VOC and SVOC concentrations measured in these two samples, it was decided that BTEX serves as a good representation of the overall VOC/SVOC concentration. As such, only BTEX was measured in all other samples.

Concentrations and percent of TOC for each measured organic subcategory are presented in Table 4-6. The percent of TOC as ‘other’ represents the remaining TOC concentration that does not fall into any of the measured subcategories. Of the 12 measured samples, carbohydrates made up 22 to 67% of the measured TOC, TPH made up 1 to >100% (but generally less than 20%) of the measured TOC, and BTEX made up 0 to 15% of TOC. As expected, carbohydrate concentrations are significantly higher in samples from wells fractured with gel-based fracturing

fluids. Carbohydrate concentrations measured in samples from Well D may be falsely high, as further discussed in Appendix E.

**Table 4-5: Detected VOCs/SVOCs in Wells A and C**

	Compound Name	Well A_9day	Well A_17day
VOCs (Method 8260C)	1,2,4-Trimethylbenzene	94	11,557
	1,3,5-Trimethylbenzene	14.7	3,117
	4-Isopropyltoluene	7.55	2,638
	Benzene	4,251	8,584
	Ethylbenzene	206	6,966
	Isopropylbenzene	14.2	2,183
	Naphthalene	43.7	2,491
	n-Butylbenzene	5.92	3,856
	n-Propylbenzene	18.2	3,875
	sec-Butylbenzene	ND	1,761
SVOCs (Method 8270D)	Toluene	3,279	23,840
	Total Xylenes	787	25,254
	2-Methylnaphthalene	ND	23,812
	Fluorene	ND	1,892
	Naphthalene	ND	2,665
	Phenanthrene	ND	2,233

All values in ug/L.

ND = Not detected.

The measured TPH value is significantly higher in sample WellA\_17day than in any other sample, likely due to the presence of free and emulsified oil in the sampling container. The measured TPH concentration is higher than the measured TOC concentration for this sample because the TOC analyzer used is not able to analyze floating free product, while the TPH method used (gravimetric measurement of extracted material) is able to measure floating free product. The unaccounted-for (or ‘other’) portion of TOC ranges from < 0 to 66%. Over the 12 measured samples, percent TOC as carbohydrates averaged 40%, percent TOC as TPH averaged 30%, percent TOC as BTEX averaged 6%, and the remaining 24% on average was unaccounted for in the subcategories measured.

No strong temporal trends were observed for any of the subcategories of organic compounds based on the collected data.

**Table 4-6: Breakdown of Organic Subcategories**

Sample Name	TOC (mg/L)	Carbs. (mg/L as C)	TPH (mg/L as C)	BTEX (mg/L as C)	Percent of TOC			
					Carbs	TPH	BTEX	Other
WellC_4day	2,788	1,029	92	-	37%	3%	-	60%
WellA_9day	2,445	1,239	34	8	51%	1%	0%	48%
WellA_17day	3,242	1,043	4,487	59	32%	138%	2%	-73%
WellB_7day	1,231	560	219	39	46%	18%	3%	33%
WellB_35day	1,119	352	221	54	32%	20%	5%	44%
WellB_56day	1,130	708	295	59	63%	26%	6%	6%
WellD_7day	369	96	338	50	26%	92%	15%	-32%
WellD_35day	233	63	41	26	27%	17%	12%	43%
WellD_56day	252	55	43	32	22%	17%	14%	47%
WellG_7day	1,436	376	81	24	26%	6%	2%	66%
WellG_35day	1,119	454	233	62	41%	21%	6%	33%
WellG_56day	1,027	687	95	42	67%	9%	4%	19%

The percent removal of each organic subcategory from the three treated samples collected from chemical coagulation jar tests is presented in Table 4-7. The overall reduction in TOC concentration ranges from 48 to 64%, while each subcategory has a measured removal of greater than 75%. BTEX removal is measured at greater than 90% for the two samples where BTEX removal was measured, and TPH removal was measured at greater than 95% for two of the three measured samples.

As presented in Chapter 3, average TOC removal from the chemical coagulation jar testing conducted on samples from Wells B, D, and G ranges from 12 to 18%. Subcategory removal was not measured for these wells.

**Table 4-7: Percent Removal of Organic Subcategories via Chemical Coagulation**

Sample Name	Percent Removal			
	TOC	Carbs.	TPH	BTEX
WellC_4day	53%	85%	94%	N/A
WellA_9day	48%	77%	77%	96%
WellA_17day	64%	87%	97%	91%

## 4.5 Discussion

The observation that the majority of the volatile solids were dissolved is consistent with the measured ratio of DOC/TOC, which suggests that the majority of organic compounds are dissolved. The serial filter results suggest that these dissolved organic compounds are smaller than 0.2  $\mu\text{m}$ . The observation that roughly three-fourths of the measured TSS concentrations was volatile suggests that particles over 1.5  $\mu\text{m}$  are mostly organic. This filter size, however, may not be retaining small colloidal inorganic particles, such as colloidal clay particles, which are typically considered to have a particle size of 0.1 to 1  $\mu\text{m}$  (Crittenden et al. 2012).

The decrease in TOC concentration and the change in visual observation after sample WellA\_17 day passed through a 1.5- $\mu\text{m}$  filter suggest that emulsified oil droplets are typically greater than 1.5  $\mu\text{m}$ . This suggests that emulsified oil may be a significant contributor to overall measured TSS concentrations. Insoluble products resulting from breaking the gelling agent and/or bacteria present in the produced water may also contribute to the mostly volatile TSS load.

BTEX generally represents a majority of the overall list of measured VOCs/SVOCs and therefore likely serves as a good indicator of the overall concentration of VOCs/SVOCs. However, unaccounted-for portions of TOC may include other VOCs/SVOCs not measured, considering that BTEX makes up greater than 5% of the TOC in many of the measured samples.

Carbohydrates make up the majority of the TOC in most produced water samples from wells fractures with gel fluids, with TPH also contributing a significant portion. A significant portion of the overall TOC concentration did not fall within any of the three subcategories measured. This may be due to the presence of organic material that does not fall within any of the measured subcategories and/or may be attributed to errors or inconsistencies in analytical techniques. For the 15 samples collected for Well D, which was fractured with a slickwater fluid, TPH made up the majority of the measured TOC concentration (greater than 50% on average).

No strong temporal trends were observed for any of the subcategories of organic compounds based on the collected data. Similarly, the volatile portion of TS, TDS, and TSS for Wells B, D, and G remained fairly constant throughout the 63-day study period. Comparing this with the observation from Chapter 3 that the coagulate demand decreased with time (i.e., produced water becomes easier to treat as the well ages), treatability may not correlate well with any of these measured subcategories.

The overall reduction in TOC concentration ranges from 48 to 64%, while each subcategory has a measured removal of greater than 75%. This suggests that the unaccounted-for portion of organic compounds is not removed. It should also be noted, however, that the measured percent removal of carbohydrates in the treated Well A and Well C samples may be falsely high due to the long holding time and lack of refrigeration of the sample prior to treatment.

## 5. CONCLUSIONS

The following conclusions are drawn from the results, discussion, and supporting information 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.

1. 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.
2. 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).
3. 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.
4. Carbohydrates are the largest contributor to the overall organic compound load in early produced waters from wells fractured with gel fluids; petroleum hydrocarbons are the largest contributor from wells fractured with slickwater fluids. Chemical coagulation decreases TOC concentrations by roughly 20% for both produced waters independent of this difference in makeup.
5. 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.

6. Chemical coagulant demand for produced waters from wells fractured with gel fluids is roughly 25 to 300 % higher than that for wells fractured with slickwater fluids, with the demand from each produced water type decreasing with the age of the well.
7. 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.

## 6. FUTURE WORK

The following tasks can build on the work presented herein in order to help further understand the impacts different fracturing fluids have on produced water quality, particularly in regard to the makeup of organic compounds.

1. Additional characterization work is needed for a larger number of wells, fractured with both slickwater and gel fluids, in order to determine the variability in observed differences in produced water quality resulting from the different fracturing fluids.
2. It would be beneficial for future sampling and analysis campaigns to include pre-production flowback samples, as well as samples beyond the 63-day study period used in this study.
3. Additional organic compound characterization is needed to more completely understand the makeup of organic compounds. This includes work to understand the portion of TOC that did not fall into any of the measured organic compound subcategories investigated in this study.
4. Further work is needed to refine the Anthrone Method or choose an alternative method for measuring carbohydrates in produced water samples, particularly in regard to finding a method that will not result in the interferences suggested by samples from Well D.
5. More work is needed to better understand the mechanisms of coagulant interference, which may involve measuring surfactant concentrations and whether there is a correlation between surfactant concentration and coagulant demand. An alternative idea would be to spike older (> 30 days after production) produced water samples with various levels of fracturing additives (starting with those most expected to interfere with treatment) and

then run jar testing on spiked samples to determine the relative effect of various additives on the coagulation process.

6. Determine an appropriate method for measuring the concentration of surfactants in produced water.
7. Investigate the surface charge of suspended particles (zeta potential) in produced water samples, as well as the change in zeta potential time and the change in zeta potential after a chemical coagulation process.
8. Expand size characterization of organic compounds into the sub-micron range.
9. Incorporate measured produced water quality and treatability data into an overall water management model, which couples the variable water quality and water quantity being produced from an entire field consisting of wells of different ages and fractured with different fluids, in order to predict the overall water quality coming into a treatment plant if all produce water streams from a field were blended and centrally managed.

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## APPENDIX A: COAGULANT DOSES

ACH was used as the coagulant for jar testing. Solid, granular ACH with a molecular formula of  $\text{Al}_2(\text{HO})_5\text{Cl} \cdot 2\text{H}_2\text{O}$  and a molecular weight of 210.48 g/mol was used to make a stock solution. 100 g of solid ACH was dissolved in water to a total volume of 1 L to create a 100,000 mg/L ACH (25,638 mg/L as Al) stock solution. The volume of this stock solution added to each 1 L jar test sample per desired dose is presented in Table A-1. The most commonly used doses are highlighted in gray. Each dose is in units of mg/L as Al, not mg/L as ACH, for the sake of being able to compare this coagulant to other aluminum-based coagulants.

**Table A-1: Volumes of 100,000 mg/L ACH Stock Solution Used for Jar Testing**

Al Dosage (mg/L as Al)	mL of Stock
12.5	0.49
25	0.98
50	1.95
75	2.93
100	3.90
150	5.85
200	7.80
250	9.75
300	11.70
450	17.55
600	23.40
800	31.20

## APPENDIX B: DETAILED CHARACTERIZATION DATASET

This appendix includes a detailed characterization dataset for samples collected from the three wells described in Chapter 3. A summary of all collected data is presented in Tables B-1 through B-3. Analytical methods for the collected data are described in Table 3-4 and Table 3-5 of Chapter 3. Figures B-1 through B-5 present water quality trends not already presented in Chapter 3.

**Table B-1: Summary of Wet Chemistry**

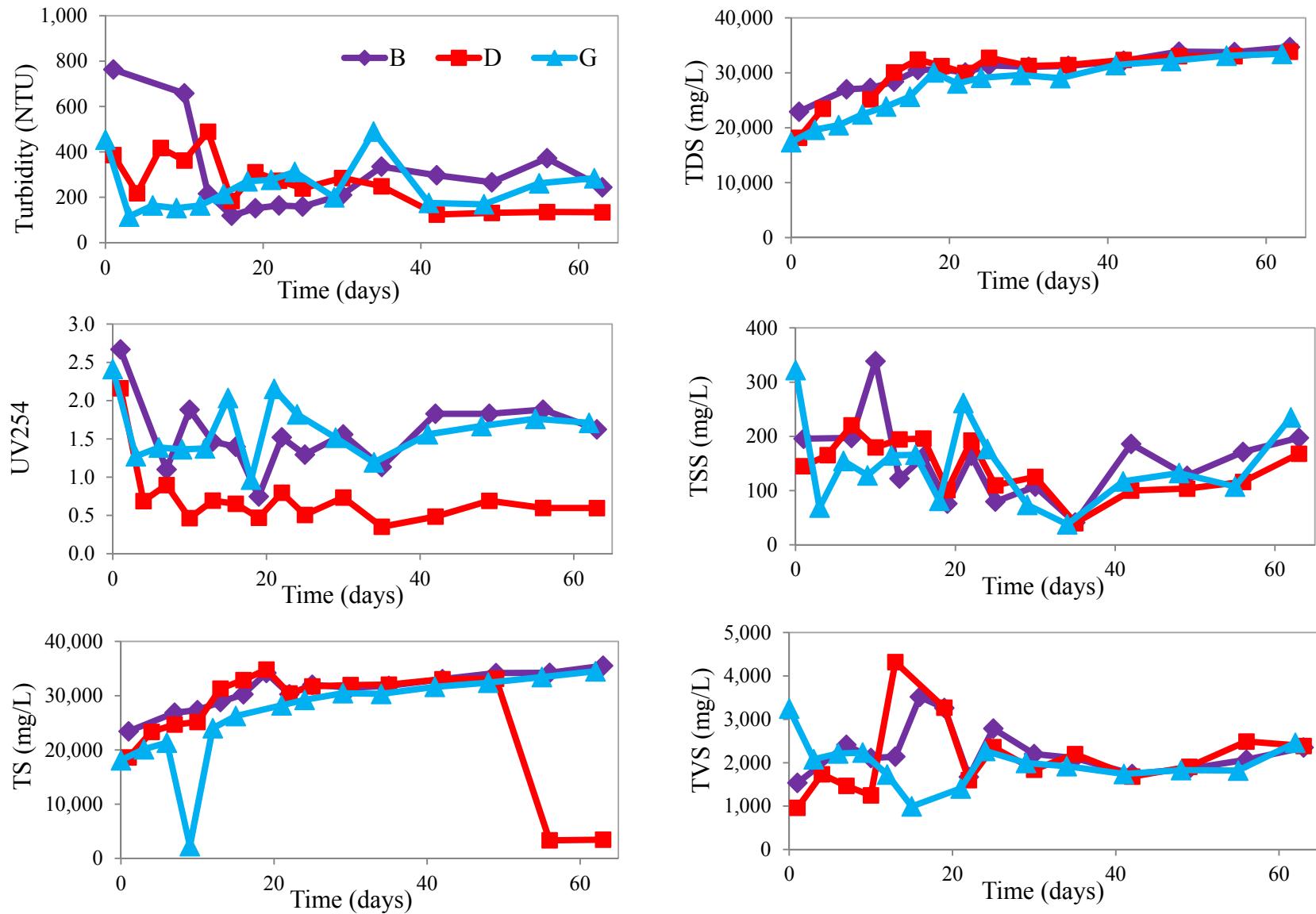
Sample Date	Sample Time	Elapsed Time (days)	Field pH	Field Cond. (mS/cm)	Lab pH	Lab Cond. (mS/cm)	Turb (NTU)	UV254 Abs.	Alkalinity mg/L CaCO <sub>3</sub>	TS (mg/L)	TDS (mg/L)	TSS (mg/L)	TVS (mg/L)	VDS (mg/L)	VSS (mg/L)
<b>Well B: Hybrid (Slickwater and Cross-Linked Gel)</b>															
11/26/13	2:45 PM	1	7.04	34.8	7.10	31.4	763	2.670	710	23,427	22,913	196	1,533	1,333	142
12/05/13	9:15 AM	7	7.14	41.3	7.27	37.2	176.5	1.101	684	26,853	27,000	197	2,413	2,553	91
12/08/13		10			7.02	38.0	658	1.882	534	27,340	27,227	339	2,107	2,000	238
12/11/13	1:15 PM	13	7.18	43.9	7.31	39.8	216	1.465	668	28,833	28,383	122	2,140	1,623	76
12/14/13	12:00 PM	16	7.08	42.7	7.30	39.0	118.5	1.398	628	30,260	30,520	162	3,518	3,420	98
12/17/13	3:00 PM	19	6.99	43.9	7.05	40.7	152	0.746	594	34,200	30,633	76	3,260	3,220	47
12/20/13	9:00 AM	22	6.96	43.1	7.27	42.2	164	1.520	598	30,260	30,047	164	1,673	1,847	70
12/23/13	10:15 AM	25	6.92	45.8	7.13	44.3	159	1.295	588	32,020	31,367	80	2,787	2,620	55
12/28/13	9:00 AM	30	6.94	46.6	7.11	44.1	210	1.558	620	31,467	31,087	107	2,200	2,193	84
01/02/14	9:45 AM	35	6.92	46.6	7.09	44.2	335	1.134	670	31,813	31,253	41	2,107	1,953	32
01/10/14	9:30 AM	42	6.78	48.7	7.06	46.1	297	1.829	608	33,047	32,200	186	1,740	1,700	131
01/16/14	9:45 AM	49	6.78	48.5	7.19	46.2	266	1.829	610	34,180	33,850	127	1,860	1,960	94
01/23/14	10:00 AM	56	6.75	49.3	7.07	46.7	372	1.882	589	34,220	33,767	171	2,070	1,953	137
01/30/14	9:45 AM	63	6.81	51.1	7.15	46.7	244	1.625	620	35,520	34,680	197	2,350	2,100	115
<b>Well D: Slickwater</b>															
11/26/13	2:15 PM	1	7.13	29.8	7.27	27.3	386	2.163	778	18,620	18,187	145	960	733	110
12/02/13	4:00 PM	4	7.14	36.3	7.45	33.7	218	0.688	688	23,340	23,460	165	1,733	1,750	110
12/05/13	9:30 AM	7	7.22	38.1	7.15	36.7	418	0.897	720	24,680		220	1,467	1,362	105
12/08/13		10			7.06	38.6	362	0.465	650	25,147	25,180	180	1,247	1,120	83
12/11/13	1:00 PM	13	7.21	40.8	7.03	40.1	489	0.694	682	31,320	30,080	195	4,320	3,810	137
12/14/13	12:15 PM	16	6.99	44.8	7.49	43.0	183.5	0.652	574	32,890	32,420	196			98
12/17/13	3:15 PM	19	6.99	46.3	7.13	42.3	311	0.470	564	34,830	31,240	101	3,270	3,233	37
12/20/13	9:15 AM	22	7.08	44.1	7.50	44.3	273	0.797	530	30,413	29,987	192	1,600	1,513	63
12/23/13	10:30 AM	25	6.97	47.9	7.19	45.7	239	0.507	508	31,720	32,740	110	2,360	2,300	60
12/28/13	9:15 AM	30	7.00	48.8	7.06	46.2	285	0.734	582	31,960	31,247	125	1,840	1,520	69
01/02/14	10:00 AM	35	6.89	49.7	7.20	46.2	249	0.352	428	32,040	31,420	40	2,200	2,247	17
01/10/14	9:45 AM	42	6.78	48.7	7.11	48.3	124	0.485	476	33,040	32,340	100	1,680	1,520	39
01/16/14	10:00 AM	49	6.82	50.6	7.05	47.8	131	0.691	548	33,133	33,030	104	1,907	1,880	51
01/23/14	10:15 AM	56	6.78	50.6	7.21	47.5	135	0.597	453	33,240	33,027	116	2,490	2,373	58
01/30/14	10:00 AM	63	6.81	51.1	7.14	49.2	134	0.596	528	34,460	33,840	168	2,387	2,087	71
<b>Well G: Cross-Linked Gel</b>															
11/26/13	3:15 PM	1	7.46	24.8	7.54	23.3	454	2.412	782	18,087	17,380	322	3,247	2,700	285
12/02/13	4:15 PM	4	7.21	28.9	7.65	27.0	115	1.273	762	20,127	19,633	69	2,080	2,247	48
12/05/13	9:45 AM	7	7.19	30.8	7.14	29.4	164	1.388	718	21,333	20,460	155	2,213	2,140	66
12/08/13		10			7.05	31.1	152	1.364	708	22,620	22,433	128	2,233	2,060	114
12/11/13	1:30 PM	13	7.14	36.9	7.09	34.2	164	1.376	704	24,000	23,850	165	1,727	1,747	140
12/14/13	12:30 PM	16	7.01	38.0	7.25	34.0	215	2.035	622	26,253	25,650	166	992	870	122
12/17/13	3:30 PM	19	7.44	39.0	7.05	36.4	271	0.967	594	30,080	81				48
12/20/13	9:30 AM	22	7.08	41.0	7.11	39.5	277	2.154	574	28,233	28,060	262	1,407	1,813	141
12/23/13	10:45 AM	25	7.01	43.1	7.04	40.4	312	1.821	610	29,240	29,100	177	2,273	2,300	152
12/28/13	9:30 AM	30	6.92	44.6	7.01	42.4	200	1.516	624	30,460	29,613	74	1,993	1,820	57
01/02/14	10:15 AM	35	6.88	45.7	6.99	42.7	490	1.193	646	30,340	29,027	38	1,920	2,120	27
01/10/14	10:00 AM	42	6.91	46.6	7.10	44.8	175	1.560	618	31,633	31,420	117	1,740	1,680	81
01/16/14	10:15 AM	49	6.9	49.2	7.11	45.0	169	1.668	614.6	32,393	32,160	132	1,830	1,820	89
01/23/14	10:30 AM	56	6.79	48.7	7.13	47.1	262	1.763	586	33,433	33,113	107	1,820	1,860	74
01/30/14	10:15 AM	63	6.9	50.4	7.12	47.6	284	1.710	626	34,500	33,460	235	2,460	1,847	141

**Table B-2: Summary of Measured Ions**

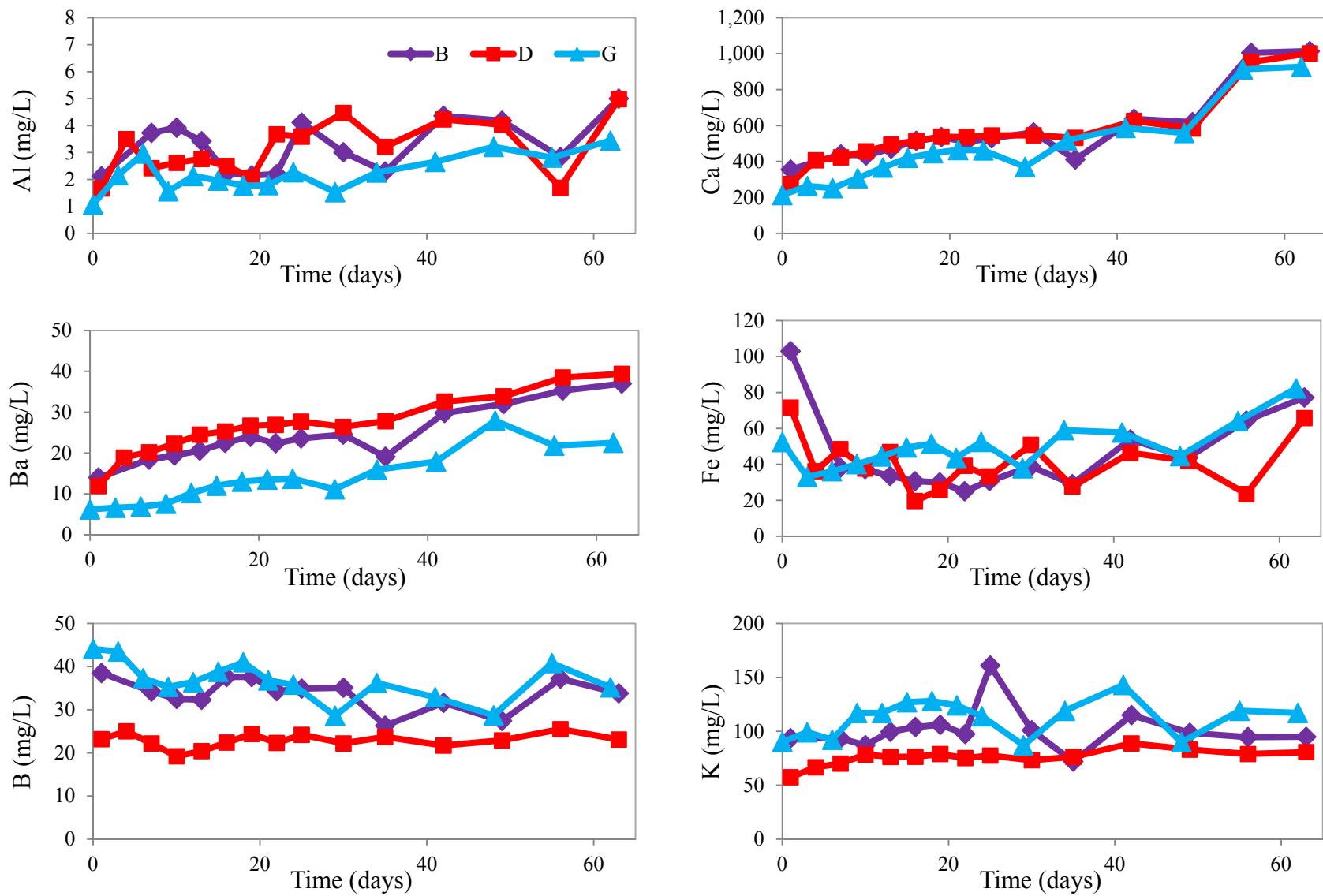
Sample Date	Sample Time	Elapsed Time (days)	Al (mg/L)	Ba (mg/L)	B (mg/L)	Ca (mg/L)	Fe (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Si (mg/L)	Sr (mg/L)	Zn (mg/L)	Br (mg/L)	Cl (mg/L)	HCO <sub>3</sub> (mg/L)	NH <sub>4</sub> (mg/L)	SO <sub>4</sub> (mg/L)	Sum of Ions (mg/L)
<b>Well B: Hybrid (Slickwater and Gel)</b>																			
11/26/13	2:45 PM	1	2.12	14.0	38.5	355	103.0	93.6	54.4	7,349	44.0	43.8	0.496	59.9	11,985	722	25.3	29.4	20,920
12/05/13	9:15 AM	7	3.73	18.4	34.2	439	38.1	93.4	68.6	18,608	47.2	57.2	0.847	54.2	11,400	610	31.1	22.0	31,526
12/08/13		10	3.92	19.4	32.5	433	37.3	87.1	64.9	8,267	40.5	57.5	0.304	70.1	14,400	605	34.0	28.8	24,181
12/11/13	1:15 PM	13	3.42	20.6	32.3	471	33.5	99.6	72.1	8,795	42.2	61.0	0.918	72.8	15,100	605	35.0	23.3	25,468
12/14/13	12:00 PM	16	2.23	22.5	37.6	515	30.6	104.0	78.1	12,286	49.1	69.6	0.580	78.1	15,590	595	33.0	15.1	29,507
12/17/13	3:00 PM	19	2.15	24.0	37.6	536	30.0	106.0	82.2	10,943	47.2	72.8	<10	81.1	17,950	482	38.0	5.3	30,437
12/20/13	9:00 AM	22	2.20	22.4	34.3	510	25.0	97.4	79.5	9,056	36.4	74.9	0.569	72.3	14,430	486	38.0	14.3	24,979
12/23/13	10:15 AM	25	4.11	23.6	34.9	529	30.7	161.0	81.6	10,421	36.7	78.7	<10	81.4	16,210	418	38.0	10.3	28,159
12/28/13	9:00 AM	30	3.01	24.5	35.1	562	38.8	101.0	86.2	13,408	40.1	82.5	<10	102.0	20,570	668	40.0	22.4	35,784
01/02/14	9:45 AM	35	2.29	19.1	26.3	411	29.0	71.9	64.3	8,666	29.0	61.5	<10	81.3	16,240	542	40.0	14.3	26,298
01/10/14	9:30 AM	42	4.36	29.8	31.6	637	53.9	115.0	98.5	12,452	41.4	92.3	<0.10	97.2	19,450	542	43.0	6.2	33,694
01/16/14	9:45 AM	49	4.18	32.0	27.4	619	43.8	98.6	84.9	12,057	33.6	77.4	<0.10	81.0	19,120	510	35.0	4.0	32,828
01/23/14	10:00 AM	56	2.83	35.3	37.2	1,005	64.4	94.6	136.0	9,541	38.3	135.0	1.830	93.0	18,620	480	39.0	6.0	30,329
01/30/14	9:45 AM	63	5.00	37.0	33.8	1,014	77.2	94.9	136.0	8,807	44.9	165.0	0.727	93.0	15,600	480	37.0	5.0	26,631
<b>Well D: Slickwater</b>																			
11/26/13	2:15 PM	1	1.67	11.9	23.2	275	71.6	57.4	40.1	10,203	64.3	32.3	0.129	47.7	14,530	838	23.7	88.6	26,309
12/02/13	4:00 PM	4	3.50	18.9	25.0	407	36.2	66.7	58.7	11,431	66.1	49.9	<0.1	61.1	15,090	722	25.3	29.4	28,091
12/05/13	9:30 AM	7	2.42	20.2	22.2	423	48.5	70.0	67.1	9,583	67.0	55.7	0.121	56.7	12,150	540	35.8	29.0	23,171
12/08/13		10	2.62	22.3	19.2	457	37.7	78.4	68.1	12,637	60.1	59.9	<10	72.9	15,600	590	28.0	30.1	29,763
12/11/13	1:00 PM	13	2.76	24.5	20.4	494	46.9	76.3	74.8	9,710	62.7	63.8	0.169	76.8	16,200	540	32.0	9.9	27,435
12/14/13	12:15 PM	16	2.50	25.3	22.4	515	19.6	76.4	78.1	12,286	58.2	69.9	<10	66.3	18,540	478	35.0	9.9	32,283
12/17/13	3:15 PM	19	2.06	26.7	24.4	538	25.8	78.9	82.4	11,316	61.2	73.7	<10	84.3	18,290	417	31.0	19.7	31,071
12/20/13	9:15 AM	22	3.68	26.9	22.3	536	39.2	75.2	83.4	10,233	56.0	78.9	<10	79.6	16,290	422	36.0	13.6	27,996
12/23/13	10:30 AM	25	3.59	27.7	24.2	545	33.3	77.5	84.4	12,627	50.7	81.4	<10	91.6	19,580	405	36.0	16.2	33,684
12/28/13	9:15 AM	30	4.47	26.4	22.2	546	50.9	73.2	81.5	10,782	54.7	80.2	<10	102.0	17,160	542	36.0	13.8	29,575
01/02/14	10:00 AM	35	3.21	27.8	23.7	532	27.7	76.3	86.1	12,050	43.4	83.6	<10	92.5	18,530	323	38.0	19.8	31,957
01/10/14	9:45 AM	42	4.23	32.6	21.7	626	46.4	88.8	96.5	10,191	52.4	92.1	<0.10	81.3	16,180	395	35.0	10.6	27,954
01/16/14	10:00 AM	49	4.03	33.9	22.9	584	41.9	83.1	86.2	11,583	39.7	78.8	<0.10	87.0	17,850	480	36.0	1.0	31,012
01/23/14	10:15 AM	56	1.69	38.5	25.5	954	23.5	79.0	133.0	11,077	44.9	136.0	0.463	90.0	18,050	320	36.0	4.0	31,014
01/30/14	10:00 AM	63	4.98	39.4	23.1	1,002	65.8	80.7	133.0	11,888	64.3	167.0	<0.10	95.0	19,200	380	36.0	8.0	33,187
<b>Well G: Cross-Linked Gel</b>																			
11/26/13	3:15 PM	1	1.07	6.2	44.1	213	52.4	90.3	33.5	6,063	43.4	25.3	<0.1	45.2	9,010	716	34.1	210.0	16,588
12/02/13	4:15 PM	4	2.16	6.6	43.5	263	33.0	99.1	41.1	7,765	43.7	33.3	<0.1	45.2	11,415	653	23.7	48.6	20,516
12/05/13	9:45 AM	7	2.96	6.9	37.3	252	36.2	92.2	42.2	7,258	37.1	34.1	0.225	47.4	10,200	595	27.3	37.0	18,706
12/08/13		10	1.56	7.6	35.3	307	40.1	117.0	48.8	7,117	41.9	41.0	<0.10	56.8	11,400	480	29.0	50.7	19,774
12/11/13	1:30 PM	13	2.13	10.2	36.4	366	44.4	117.0	57.9	7,940	42.4	47.1	<0.10	58.3	11,990	360	40.0	40.1	21,152
12/14/13	12:30 PM	16	1.96	12.0	38.8	420	49.4	127.0	66.2	8,763	50.8	57.2	<10	60.7	14,330	542	32.0	44.7	24,596
12/17/13	3:30 PM	19	1.77	13.0	41.0	446	51.5	128.0	71.9	10,152	48.0	63.1	<10	69.3	16,330	593	35.0	30.8	28,074
12/20/13	9:30 AM	22	1.79	13.5	36.8	464	43.6	124.0	73.1	8,994	39.0	68.8	<10	71.3	13,940	541	38.0	61.5	24,510
12/23/13	10:45 AM	25	2.27	13.7	35.8	462	52.5	114.0	72.2	12,428	38.6	69.1	<10	85.4	19,050	522	35.0	14.8	32,995
12/28/13	9:30 AM	30	1.53	11.1	28.6	370	37.8	87.0	58.3	10,546	28.1	56.3	<10	80.4	15,990	621	41.0	45.1	28,002
01/02/14	10:15 AM	35	2.26	15.9	36.2	518	59.0	119.0	84.7	11,255	39.2	79.9	<10	87.5	17,510	441	39.0	31.9	30,319
01/10/14	10:00 AM	42	2.65	17.9	32.9	587	57.7	143.0	90.8	9,522	40.1	85.9	<0.10	78.8	15,630	443	38.0	11.9	26,782
01/16/14	10:15 AM	49	3.21	27.9	28.7	559	44.6	89.9	80.1	10,869	35.4	79.4	<0.10	84.0	16,860	465	36.0	6.0	29,268
01/23/14	10:30 AM	56	2.81	21.8	40.8	913	64.1	119.0	132.0	11,292	35.1	128.0	0.418	90.0	18,140	460	37.0	2.0	31,478
01/30/14	10:15 AM	63	3.44	22.5	35.2	927	82.3	117.0	130.0	11,490	42.3	157.0	0.159	92.5	18,500	440	37.0	13.0	32,089

**Table B-3: Summary of Measured Organics**

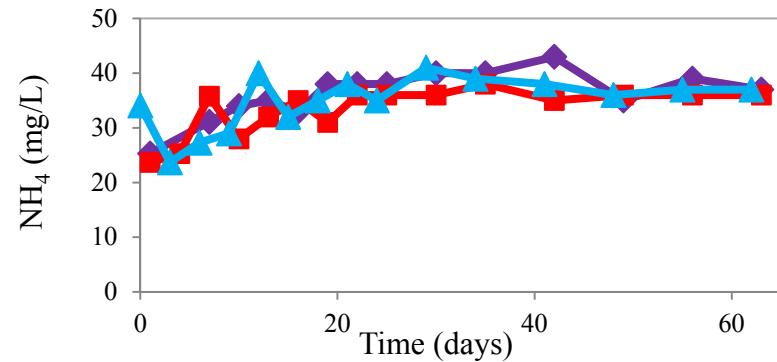
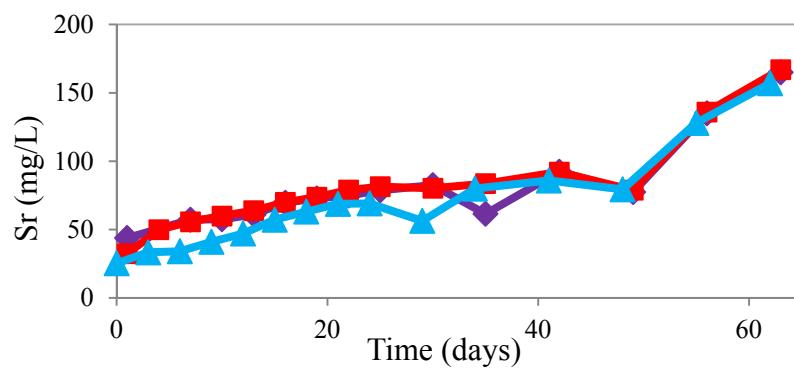
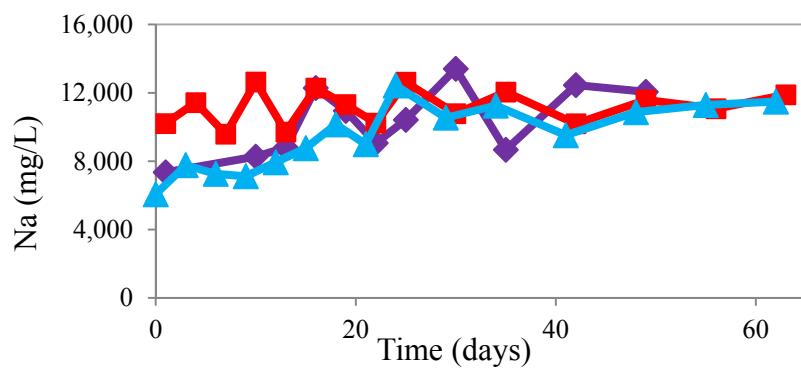
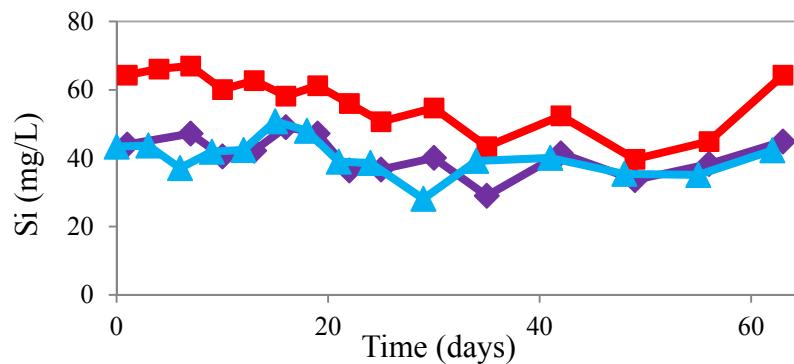
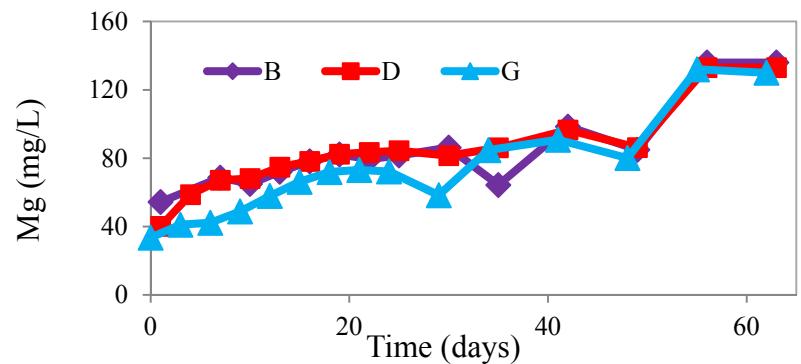
Sample Date	Sample Time	Elapsed Time (days)	TOC (mg/L)	DOC (mg/L)	Carbs. (mg/L)	COD (mg/L)	Oil and Grease (mg/L)	TPH (mg/L)				Benzene (ug/L)	Toluene (ug/L)	Ethyl-benzene (ug/L)	Total Xylenes (ug/L)	BTEX (mg/L)
								GRO	DRO	ORO	TPH					
<b>Well B: Hybrid (Slickwater and Cross-Linked Gel)</b>																
11/26/13	2:45 PM	1	1,206			6,150	61.1	92.8	57.4	7.84	158	9,072	9,597	885	6,097	26
12/05/13	9:15 AM	7	1,231	1,134	1402	4,515	73.8	209	48.2	<5.0	257	14,749	15,678	1,482	10,119	42
12/08/13		10	1,662	1,375		7,120	435	910	146	11.9	1,068	21,561	33,067	5,660	39,342	100
12/11/13	1:15 PM	13	1,157	1,006		3,620	191	184	9.89	<5.0	194	14,952	15,951	1,243	8,733	41
12/14/13	12:00 PM	16	1,274	1,133		4,445	81.3	215	76.9	<5.0	292	18,518	18,925	1,827	13,650	53
12/17/13	3:00 PM	19	1,172	1,063		3,175	<5.0	54.9	<5.0	<5.0	55	13,560	11,569	662	4,859	31
12/20/13	9:00 AM	22	1,198	1,117		4,580	64.5	130	52.5	<5.0	183	15,503	13,733	1,134	8,649	39
12/23/13	10:15 AM	25	1,128	1,068		3,765	41.2	113	30.4	<5.0	143	15,438	14,051	1,084	8,130	39
12/28/13	9:00 AM	30	1,164	1,116		4,550	88.4	99.1	80.4	<5.0	180	17,585	17,389	1,335	9,765	46
01/02/14	9:45 AM	35	1,119	945	882	4,210	40.2	224	28.8	6.74	260	21,157	20,483	2,004	14,993	59
01/10/14	9:30 AM	42	1,168	914		4,340	57.1	242	42.7	6.6	291	20,420	23,406	2,111	14,260	60
01/16/14	9:45 AM	49	1,065	935		5,050	49.3	47.3	38.6	<5.0	86	18,919	20,484	1,865	12,953	54
01/23/14	10:00 AM	56	1,130	911	1772	4,900	121	243	104	<5.0	347	21,043	19,712	2,779	20,709	64
01/30/14	9:45 AM	63	943	831		4,310	291	150	273	<5.0	423	19,082	17,185	1,881	12,618	51
<b>Well D: Slickwater</b>																
11/26/13	2:15 PM	1	440			950	34.2	159	44.7	5.27	209	16,479	16,471	1,476	10,188	45
12/02/13	4:00 PM	4	401	251		2,270	31.5	234	35.7	<5	270	17,211	18,765	1,811	12,537	50
12/05/13	9:30 AM	7	369	340	241	3,080	112	356	42.2	<5	398	15,830	20,444	2,276	15,498	54
12/08/13		10	329	260		1,685	37.5	269	56.3	6.97	332	22,875	23,127	1,967	14,566	63
12/11/13	1:00 PM	13	301	284		2,265	77.6	281	25.7	<5	307	13,890	17,894	2,212	16,087	50
12/14/13	12:15 PM	16	243	250		2,490	89.7	101	83.4	<5.0	184	20,362	17,799	1,153	8,590	48
12/17/13	3:15 PM	19	222	238		1,231	<5.0	48.3	<5.0	<5.0	48	12,429	10,411	495	3,640	27
12/20/13	9:15 AM	22	246	217		2,105	56.3	33.3	48.2	<5.0	82	7,874	7,115	471	3,604	19
12/23/13	10:30 AM	25	272	256		2,165	46.8	50.4	40.2	<5.0	91	11,922	10,907	664	4,934	28
12/28/13	9:15 AM	30	226	244		2,850	46.9	77.2	36.8	<5.0	114	15,874	14,753	1,014	7,808	39
01/02/14	10:00 AM	35	233	214	157	2,085	17.4	35.5	12.3	<5.0	48	12,756	10,916	591	4,389	29
01/10/14	9:45 AM	42	246	226		2,510	32.6	96.2	29.6	<5.0	126	13,880	14,407	1,059	7,305	37
01/16/14	10:00 AM	49	233	227		3,750	42.3	47.3	38.6	<5.0	86	10,869	10,582	633	4,544	27
01/23/14	10:15 AM	56	252	233	137	2,350	17.8	35	15.2	<5.0	50	16,503	12,685	724	5,156	35
01/30/14	10:00 AM	63	246	225		3,525	304	77.4	248	34.1	360	17,230	14,353	1,101	7,945	41
<b>Well G: Cross-Linked Gel</b>																
11/26/13	3:15 PM	1	1,584			8,825	872	1392	762	77.3	2,231	17,266	54,294	7,846	55,858	135
12/02/13	4:15 PM	4	1,437	1,431		4,050	30.6	153	8.91	<5	162	14,886	15,674	1,250	9,716	42
12/05/13	9:45 AM	7	1,436	1,391	942	4,465	9.6	74.7	13.5	6.91	95	10,026	9,340	702	5,578	26
12/08/13		10	1,735	1,333		4,795	104	235	40.3	<5	275	21,426	21,711	1,570	12,396	57
12/11/13	1:30 PM	13	1,485	1,413		5,355	154	284	90	<5	374	17,100	20,437	2,122	16,529	56
12/14/13	12:30 PM	16	1,602	1,420		4,105	74	91.3	69.5	<5.0	161	16,824	16,053	936	7,556	41
12/17/13	3:30 PM	19	1,346	1,332		4,165	13.4	49.2	7.26	<5.0	56	11,302	10,032	517	4,138	26
12/20/13	9:30 AM	22	1,323	1,118		6,680	175	170	143	8.41	321	10,734	12,670	1,256	10,185	35
12/23/13	10:45 AM	25	1,435	1,318		4,820	174	267	148	9.02	424	18,064	20,127	2,145	16,884	57
12/28/13	9:30 AM	30	1,314	1,184		4,360	28.3	64	18.4	<5.0	82	15,659	14,475	1,001	7,950	39
01/02/14	10:15 AM	35	1,119	1,009	1136	4,390	25.9	251	18.5	5.03	275	20,806	23,493	2,471	20,731	68
01/10/14	10:00 AM	42	1,097	1,024		4,405	68.7	218	58.6	5.5	282	19,736	23,283	1,961	14,377	59
01/16/14	10:15 AM	49	1,043	974		4,340	43.8	181	40.1	<5.0	221	13,877	15,482	1,241	9,386	40
01/23/14	10:30 AM	56	1,027	883	1720	5,005	43.6	71.8	39.4	<5.0	111	20,797	16,222	1,056	8,030	46
01/30/14	10:15 AM	63	1,032	820		4,380	471	148	398	50.1	596	19,252	17,932	1,708	13,015	52



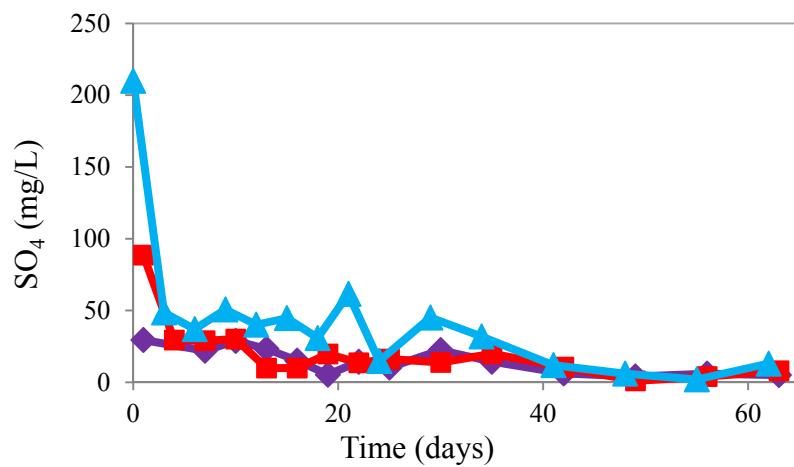
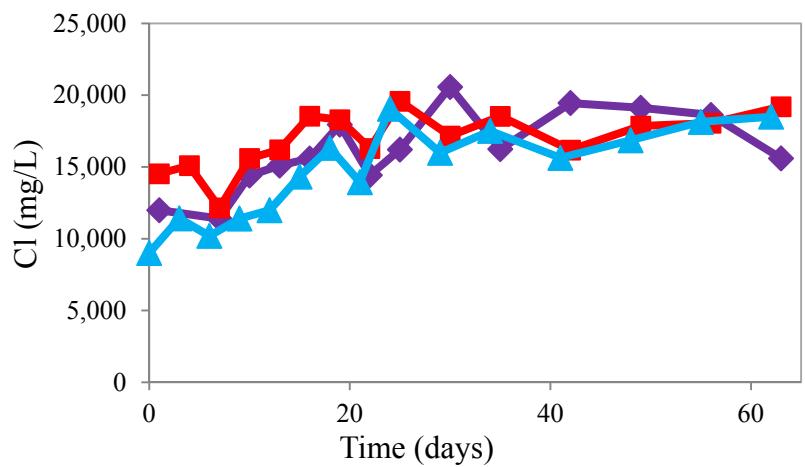
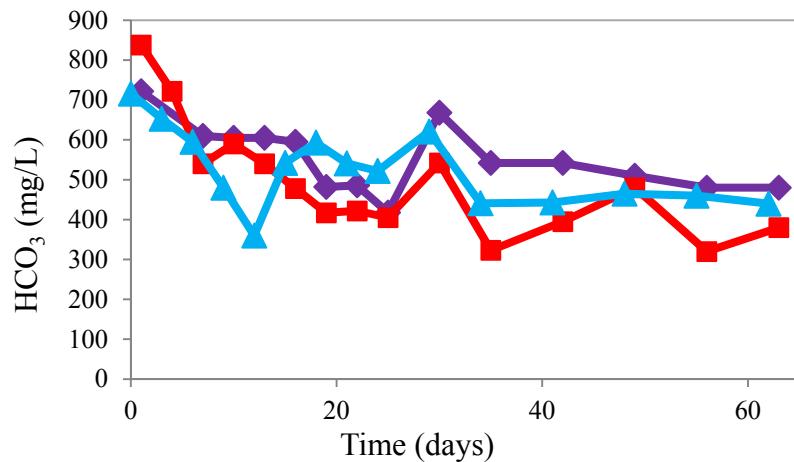
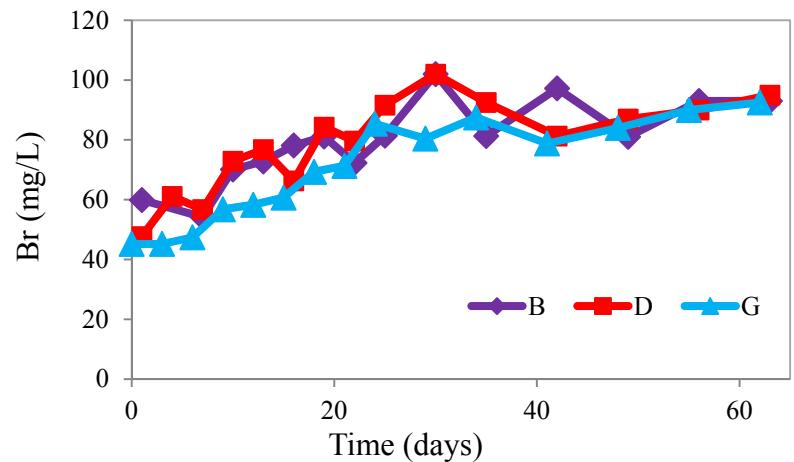
**Figure B-1: Turbidity, UV254, TS, TDS, TSS, and TVS Trends for Wells B, D, and G**



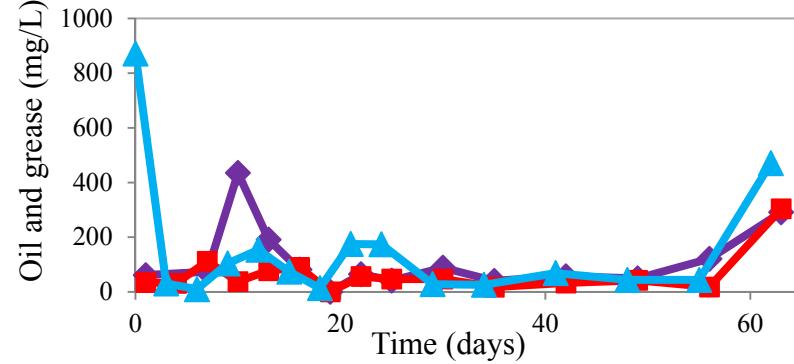
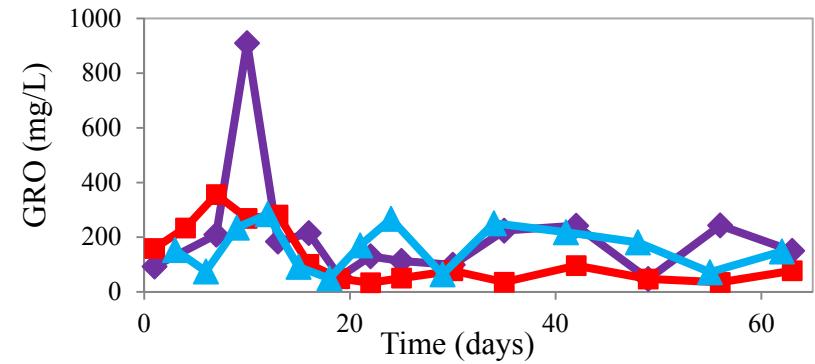
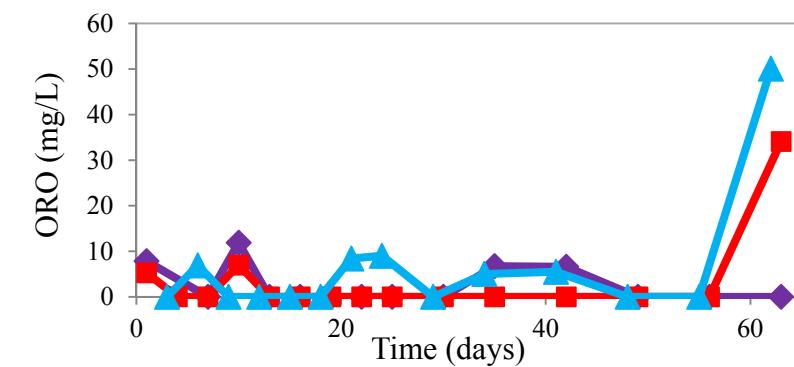
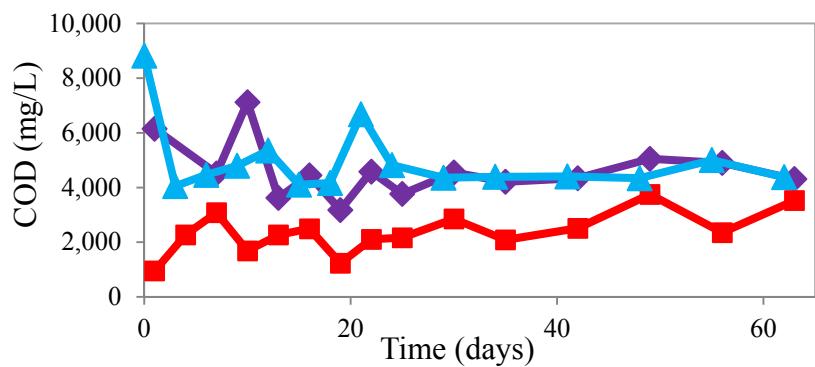
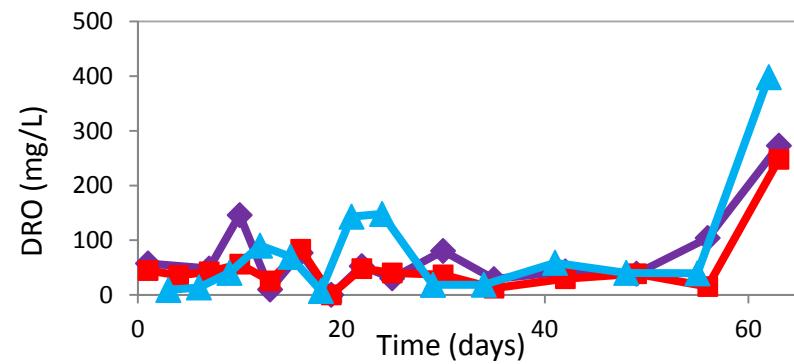
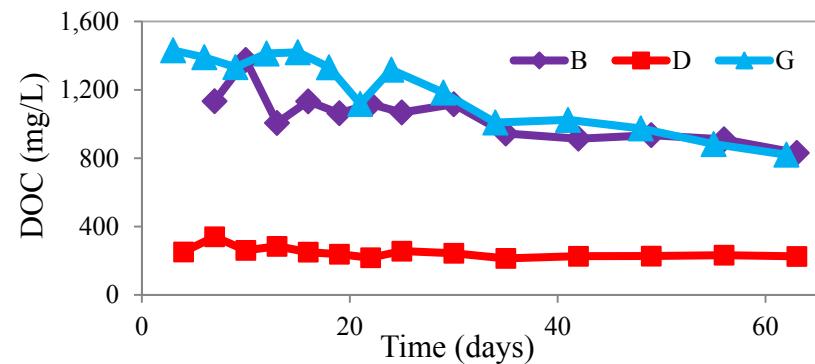
**Figure B-2: Al, Ba, B, Ca, Fe, and K Trends for Wells B, D, and G**



**Figure B-3: Mg, Na, NH<sub>4</sub>, Si, and Sr Trends for Wells B, D, and G**



**Figure B-4:** Br, Cl, HCO<sub>3</sub>, and SO<sub>4</sub> Trends for Wells B, D, and G



**Figure B-5: DOC, COD, GRO, DRO, ORO, and O&G Trends for Wells B, D, and G**

## APPENDIX C: DETAILED JAR TESTING RESULTS

Measured UV254 and turbidity data for each jar test conducted for Wells B, D, and G are included in Tables C-1 through C-6. The selected optimum dose for each set of jar tests is highlighted in blue. Turbidity readings were taken after both 15-minute and 25-minute settling periods for a majority of the jar tests. Optimum samples collected for treatment removal testing were taken after the 15-minute setting period. Photographs of various completed jar tests are presented in Figures C-1 through C-3. A photograph of typical flow formation during the slow mix (flocculation) stage is presented in Figure C-4.

A settling test was conducted to observe the change in measured turbidity as a result of increased setting time. This test was conducted using the 9- and 10-day samples from Wells B, D, and G. Results from this experiment are presented in Figure C-5. As observed, there is little decrease in measured turbidity after a settling time of 25 minutes for the measured samples.

**Table C-1: Jar Testing Raw Data for Well B (1 of 2)**

Sample Date	Analysis Date	Time Point (days)	AI Concentration	15 Min Settling		25 Min Settling	
				UV254	Turbidity (NTU)	Turb. Removal%	Turbidity (NTU)
12/5/2013	12/27/2013	7	Raw	2.670	223		
			100	0.652	106	52.5	17.9
			150	0.535	74.1	66.8	10.5
			200	0.302	5.35	97.6	3.28
			250	0.282	3.35	98.5	2.41
			300	0.286	3.35	98.5	3.59
12/8/2013	12/24/2013	10	Raw		358		
			50	0.952	136	62.0	
			100	0.844	108	69.8	
			150		71	80.2	
			200	0.685	2.93	99.2	
			250	0.341	3.4	99.1	
12/11/2013	12/21/2013	13	Raw		237		
			100	0.330	68.1	71.3	
			150	0.309	35.4	85.1	
			200	0.296	52.1	78.0	
			250	0.474	4.02	98.3	
			300	0.282	17.2	92.7	
12/14/2013	12/21/2013	16	Raw		222		
			100	0.464	8.75	96.1	
			150	0.485	3.43	98.5	
			200	0.362	3.95	98.2	
			250	0.322	2.8	98.7	
			300	0.332	4.01	98.2	
12/17/2013	12/21/2013	19	Raw		174		
			100	0.364	10.7	93.9	
			150	0.358	3.82	97.8	
			200	0.357	6.5	96.3	
			250	0.369	14.1	91.9	
			300	0.423	6.18	96.4	
12/20/2013	1/9/2014	22	Raw		289		
			100	0.347	23.5	91.9	11.7
			150	0.315	10	96.5	4.8
			200	0.293	8.35	97.1	3.1
			250	0.309	4.02	98.6	5.3
			300	0.318	4.45	98.5	6.0

**Table C-2: Jar Testing Raw Data for Well B (2 of 2)**

Sample Date	Analysis Date	Time Point (days)	Al Concentration	15 Min Settling		25 Min Settling	
				UV254	Turbidity (NTU)	Turb. Removal%	Turbidity (NTU)
12/23/2013	1/8/2014	25	Raw		157		
			100	0.351	12.6	92.0	5.47
			150	0.320	5.64	96.4	3.01
			200	0.324	4.74	97.0	2.52
			250	0.315	4.53	97.1	6.37
			300	0.373	12.4	92.1	22.6
12/28/2013	1/2/2014	30	Raw		521		
			100	0.607	30.9	94.1	18
			150	0.505	11.2	97.9	6.24
			200	0.547	11.4	97.8	5.93
			250	0.573	10.2	98.0	8.28
			300	0.656	12.7	97.6	20.4
1/2/2014	1/3/2014	35	Raw		321		
			100	0.680	28.3	94.6	16.5
			150	0.672	11.8	97.7	7.65
			200	0.610	8.07	98.5	6.24
			250	0.726	13.4	97.4	10.3
			300	0.842	25.7	95.1	25.9
1/10/2014	1/10/2014	42	Raw		351		
			100	0.578	20.9	94.0	12.2
			150	0.499	7.26	97.9	5.85
			200	0.462	4.05	98.8	3.89
			250	0.472	3.74	98.9	3.11
			300	0.488	3.51	99.0	5.97
1/16/2014	1/16/2014	49	Raw		266		
			50	0.693	33.1	87.6	20.2
			75	0.657	24.7	90.7	15.9
			100	0.621	14.5	94.5	9.97
			125	0.597	9.81	96.3	6.01
			150	0.576	9.69	96.4	5.56
1/23/2014	1/23/2014	56	Raw		390		
			50	0.740	66.8	82.9	31.6
			75	0.648	34.2	91.2	19.5
			100	0.557	20.3	94.8	13.9
			125	0.587	17.1	95.6	9.3
			150	0.552	11.2	97.1	6.53
1/30/2014	1/30/2014	63	Raw		330		
			50	0.687	33.5	89.8	20.1
			75	0.645	18.7	94.3	19.8
			100	0.620	15.4	95.3	12.3
			125	0.600	11.9	96.4	8.81
			150	0.587	11.6	96.5	11

**Table C-3: Jar Testing Raw Data for Well D (1 of 2)**

Sample Date	Analysis Date	Time Point (days)	Al Concentration	15 Min Settling		25 Min Settling	
				UV254	Turbidity (NTU)	Turb. Removal%	Turbidity (NTU)
11/26/2013	12/24/2013	1	Raw		427		
			25	0.416	82.1	80.8	
			50	0.653	143	66.5	
			100	0.526	113	73.5	
			150	0.322	74.5	82.6	
			200	0.324	83	80.6	
			250	1.22	99.7		
12/2/2013	12/27/2013	4	Raw		360		
			100	0.334	162	55.0	11.7
			150	0.219	66.8	81.4	4.9
			200	0.094	2.77	99.2	100.0
			250	0.102	4.57	98.7	4.48
			300	0.109	2.23	99.4	1.73
12/5/2013	12/27/2013	7	Raw		622		
			100	0.233	89.5	85.6	15.1
			150	0.119	105	83.1	5.88
			200	0.098	2.28	99.6	3.13
			250	0.197	13.5	97.8	3.4
			300	0.149	24	96.1	3.35
							99.5
12/8/2013	12/24/2013	10	Raw		379		
			25	0.280	121	68.1	
			50	0.307	134	64.6	
			100	0.185	60.9	83.9	
			150	0.073	54.8	85.5	
			200	0.137	3.53	99.1	
			250	0.099	1.58	99.6	
12/11/2013	12/21/2013	13	Raw		706		
			100	0.198	6.48	99.1	
			150	0.203	3.64	99.5	
			200	0.569	3.93	99.4	
			250	1.029	108	84.7	
			300	1.036	135	80.9	
12/14/2013	21-Dec	16	Raw		273		
			100	0.152	5.33	98.0	
			150	0.157	3.06	98.9	
			200	0.147	2.51	99.1	
			250	0.142	2.58	99.1	
			300	0.149	6.24	97.7	
12/17/2013	1/9/2014	19	Raw		80.7		
			100	0.080	7.88	90.2	3.81
			150	0.074	8.3	89.7	2.97
			200	0.090	5.12	93.7	2.05
			250	0.077	3.9	95.2	3.48
			300	0.127	13.5	83.3	13.7
12/20/2013	1/2/2014	22	Raw		427		
			100	0.121	15.4	96.4	6.58
			150	0.094	7.09	98.3	2.3
			200	0.120	17.4	95.9	2.81
			250	0.108	6.32	98.5	4.13
			300	0.160	19.2	95.5	11.6
							97.3

**Table C-4: Jar Testing Raw Data for Well D (2 of 2)**

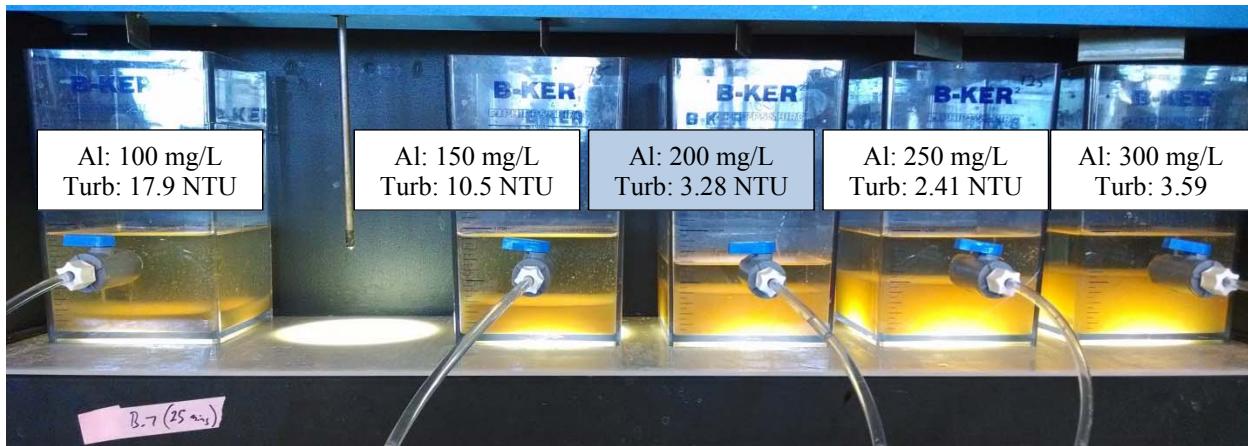
Sample Date	Analysis Date	Time Point (days)	Al Concentration	15 Min Settling		25 Min Settling	
				UV254	Turbidity (NTU)	Turb. Removal%	Turbidity (NTU)
12/23/2013	1/8/2014	25	Raw		148		
			100	0.086	7.87	94.7	3.17
			150	0.089	6.02	95.9	3.14
			200	0.079	4.85	96.7	1.9
			250	0.096	6.61	95.5	3.48
			300	0.139	16.3	89.0	10
12/28/2013	1/2/2014	30	Raw		767		
			100	0.163	26.3	96.6	5.52
			150	0.152	14.1	98.2	4.91
			200	0.128	10.9	98.6	5.38
			250	0.206	14.3	98.1	10.4
			300	0.435	60.8	92.1	52
1/2/2014	1/3/2014	35	Raw		275		
			100	0.125	11.5	95.8	7.08
			150	0.127	7	97.5	4.08
			200	0.189	13.2	95.2	12.3
			250	0.642	291	-5.8	237
			300	0.727	305	-10.9	306
1/10/2014	1/10/2014	42	Raw		266		
			100	0.112	5.54	97.9	3.13
			150	0.106	2.75	99.0	1.09
			200	0.101	2.06	99.2	1.01
			250	0.120	1.44	99.5	1.18
			300	0.129	6.9	97.4	5.97
1/16/2014	1/16/2014	49	Raw		254		
			50	0.055	6.52	97.4	6.11
			75	0.034	5.52	97.8	3.33
			100	0.017	3.64	98.6	2.05
			125	0.019	4.04	98.4	1.88
			150	0.010	3.2	98.7	1.63
1/23/2014	1/23/2014	56	Raw		136		
			50	0.106	6.7	98.3	4.16
			75	0.104	5.43	98.6	2.68
			100	0.980	2.93	99.2	1.68
			125	0.094	2.63	99.3	1.65
			150	0.108	3.38	99.1	2.23
1/30/2014	1/30/2014	63	Raw		380		
			50	0.149	7.42	97.8	7.51
			75	0.144	6.36	98.1	3.38
			100	0.127	4.05	98.8	2.58
			125	0.126	3.58	98.9	2.39
			150	0.126	3.52	98.9	2.2

**Table C-5: Jar Testing Raw Data for Well G (1 of 2)**

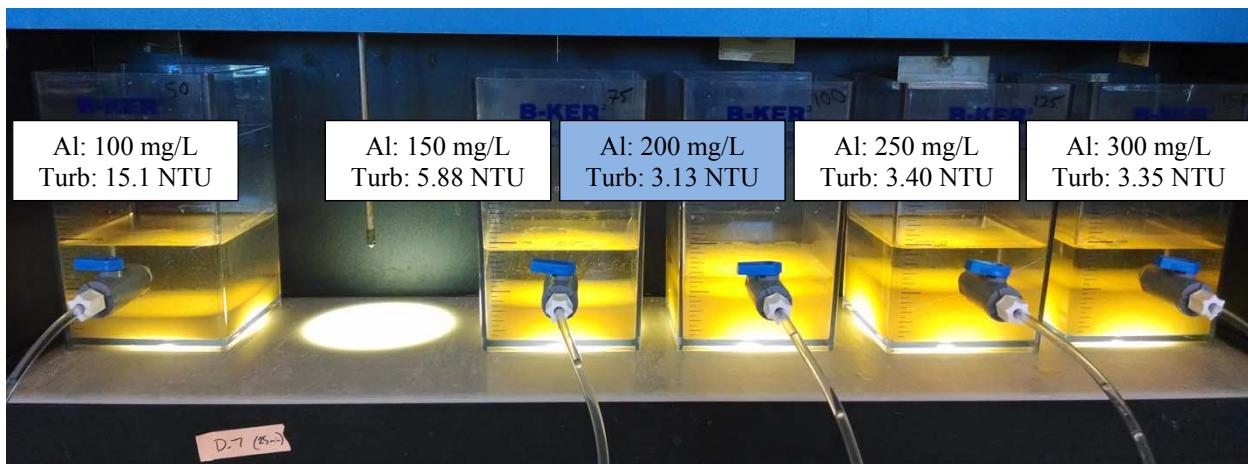
Sample Date	Analysis Date	Time Point (days)	Al Concentration	15 Min Settling		25 Min Settling	
				UV254	Turbidity (NTU)	Turb. Removal%	Turbidity (NTU)
11/26/2013	1/8/2014	0	Raw		330		
			250		56.9	82.8	48.8
			300		49.6	85.0	41.7
			350		48.9	85.2	38.2
			400		60.36	81.7	50.4
			450		69.3	79.0	55.8
			600	0.386	18.7	94.3	13.2
			700	0.440	12.3	96.3	12.8
			800	0.407	10.2	96.9	10.4
12/2/2014	12/27/2013	3	Raw		113		
			100	0.962	110	2.7	29
			150	0.965	125	-10.6	23.4
			200	0.769	104	8.0	19.7
			250	0.331	6.55	94.2	2.96
			300	0.340	6.7	94.1	14
12/5/2013	12/27/2013	6	Raw		176		
			100	0.630	78.5	55.4	33.7
			150	0.586	89.9	48.9	24.7
			200	0.568	71.7	59.3	19.6
			250	0.335	9.43	94.6	4.34
			300	0.285	2.51	98.6	2.14
12/8/2013	12/24/2013	9	Raw		132		
			100	0.360	95.6	27.6	
			150	1.347	136	-3.0	
			200	0.712	49.6	62.4	
			250	0.460	11.4	91.4	
			300	0.478	10.6	92.0	
12/11/2013	12/21/2013	12	Raw		187		
			100	0.484	19.1	89.8	
			150	0.513	8.9	95.2	
			200	0.388	4.77	97.4	
			250	0.369	2.74	98.5	
			300	0.325	2.37	98.7	
			600	0.694			
			900	2.142			
			1200	1.842			
			1600	1.687			
12/14/2013	12/21/2013	15	Raw		325		
			100	0.818	67.7	79.2	
			150	0.583	27.4	91.6	
			200	0.456	9.44	97.1	
			250	0.472	8.27	97.5	
			300	0.371	8.63	97.3	
12/17/2013	1/9/2014	18	Raw		273		
			100	0.390	31.9	88.3	17.9
			150	0.350	22.7	91.7	8.04
			200	0.301	8.3	97.0	4.5
			250	0.259	5.86	97.9	5.15
			300	0.308	5.24	98.1	7.96

**Table C-6: Jar Testing Raw Data for Well G (2 of 2)**

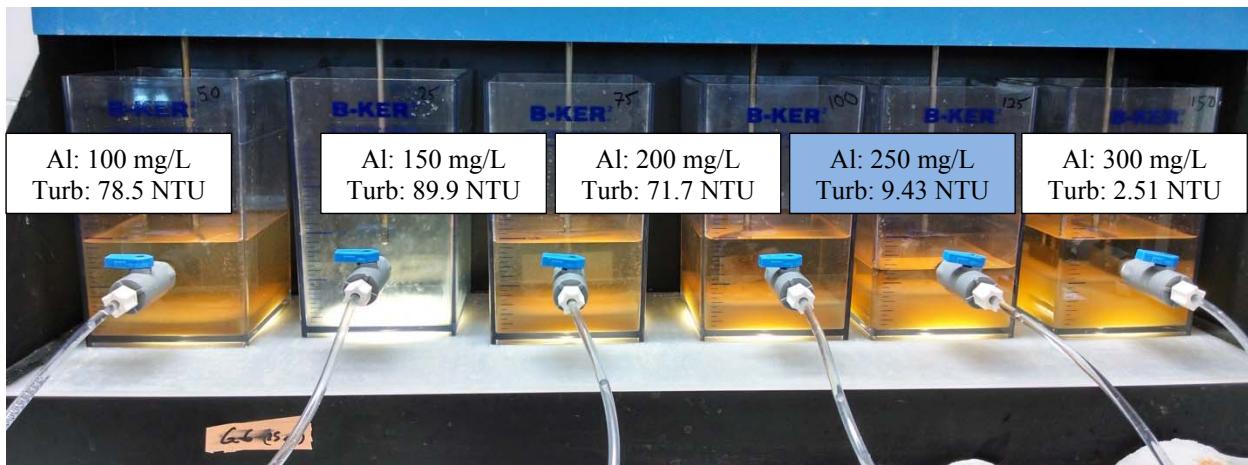
Sample Date	Analysis Date	Time Point (days)	Al Concentration	15 Min Settling		25 Min Settling	
				UV254	Turbidity (NTU)	Turb. Removal%	Turbidity (NTU)
12/20/2014	1/2/2014	21	Raw		468		468
			100	0.564	83.2	82.2	30
			150	0.410	22.4	95.2	10.7
			200	0.429	22.9	95.1	9.28
			250	0.427	22.2	95.3	9.01
			300	0.468	21.7	95.4	21.1
12/23/2013	1/8/2014	24	Raw		373		
			100	0.414	29	92.2	15.3
			150	0.365	11.8	96.8	6.96
			200	0.354	8.05	97.8	6.26
			250	0.349	5.95	98.4	6.88
			300	0.360	6.93	98.1	8.65
12/28/2014	1/2/2014	29	Raw		426		426
			100	0.627	132	69.0	43.2
			150	0.577	876	-105.6	35.3
			200	0.638	14.6	96.6	11.1
			250	0.601	20.8	95.1	19.4
			300	0.689	103	75.8	96.9
1/2/2014	1/3/2014	34	Raw		439		
			100	0.630	30	93.2	19.6
			150	0.629	14.2	96.8	10.2
			200	0.567	10.8	97.5	6.61
			250	0.663	10.7	97.6	9.72
			300	1.290	137	68.8	92.4
1/10/2014	1/10/2014	41	Raw		357		
			100	0.576	6.52	98.2	5.76
			150	0.547	5.04	98.6	4.82
			200	0.529	4.84	98.6	4.63
			250	0.499	3.29	99.1	3.56
			300	0.492	3.83	98.9	4.04
1/16/2014	1/16/2014	48	Raw		168.5		
			50	0.685	15.1	91.0	10.9
			75	0.654	10.3	93.9	8.32
			100	0.699	7.65	95.5	14
			1250	0.615	6.888	95.9	7.08
			150	0.572	5.24	96.9	5.08
1/23/2014	1/23/2014	56	Raw		218		
			50	0.650	22.3	94.3	15.6
			75	0.651	25.1	93.6	19.9
			100	0.592	10.3	97.4	7.34
			125	0.569	7.05	98.2	9.41
			150	0.569	6.91	98.2	5.16
1/30/2014	1/30/2014	63	Raw		287		
			50	0.719	25.7	92.2	16.5
			75	0.686	20.13	93.9	12.8
			100	0.665	16.1	95.1	12.2
			125	0.642	11.9	96.4	7.5
			150	0.624	10.3	96.9	6.06



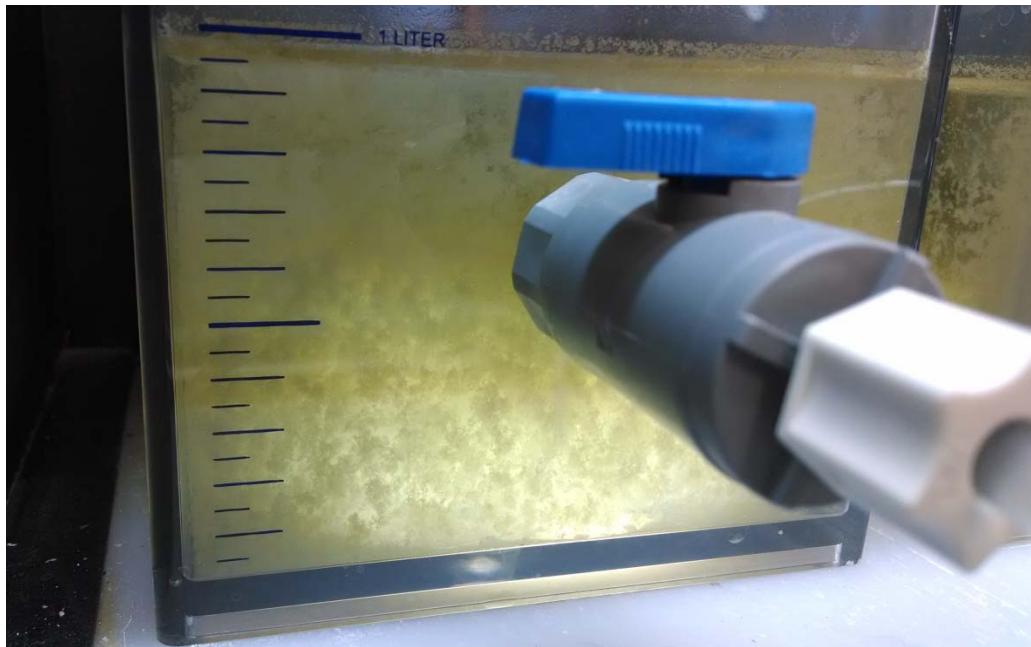
**Figure C-1: Photograph of Well B\_7 Day Completed Jar Tests**



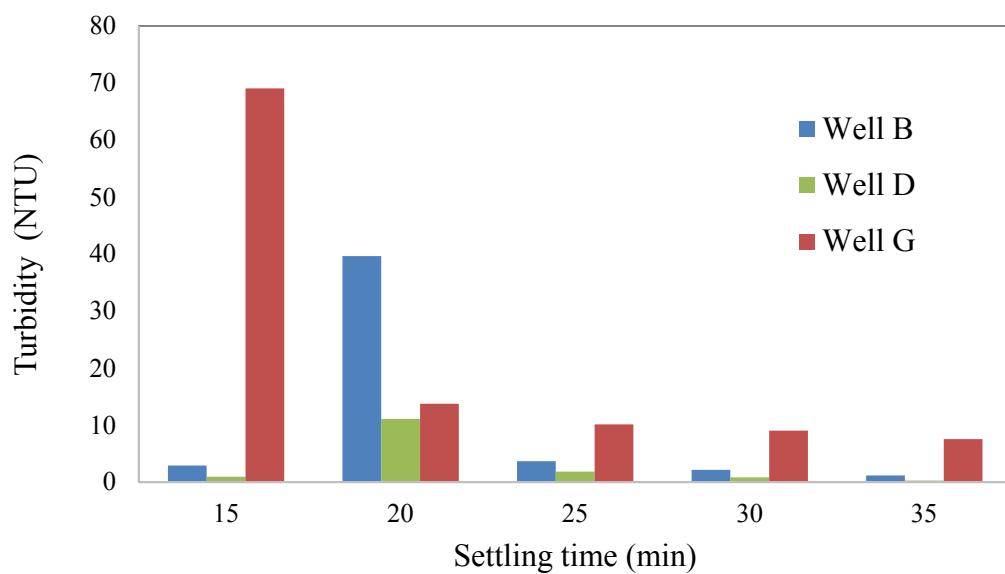
**Figure C-2: Photograph of Well D\_7 Day Completed Jar Tests**



**Figure C-3: Photograph of Well G\_6 day Completed Jar Tests**



**Figure C-4: Photograph of Typical Floc Formation during Slow Mixing**



**Figure C-5: Change in Turbidity in Jar Tests due to Increased Settling Time**

## APPENDIX D: GROUNDWATER WATER QUALITY USED FOR DILUTION MODELING

Table D-1 presents the water quality of a typical groundwater source in northeast Colorado. This water quality was used as the freshwater quality for the dilution modeling presented in Chapter 3. This water quality is based on the analysis of an actual groundwater source.

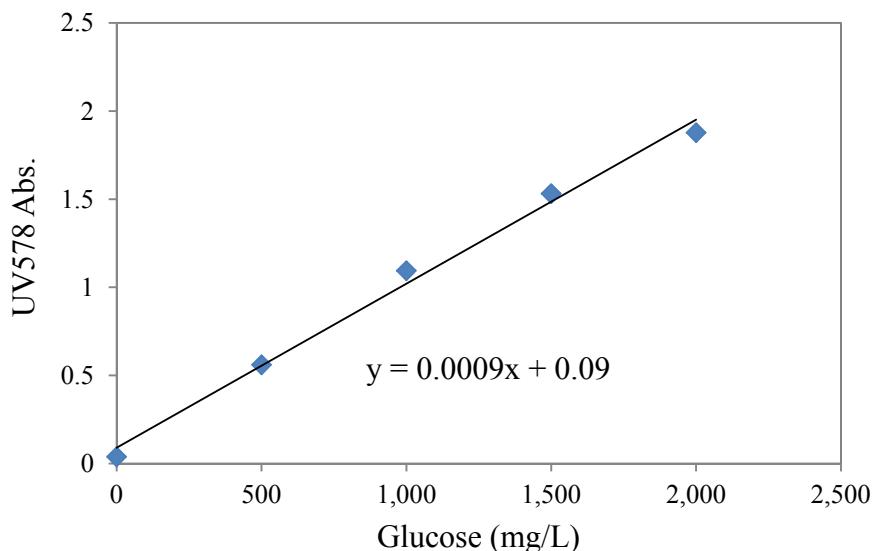
**Table D-1: Water Quality of a Typical NE Colorado Groundwater Source**

Parameter	Concentration (mg/L)
pH	8.3
Alkalinity	305
Aluminum	0.439
Barium	0.01
Calcium	60.4
Iron	0.196
Magnesium	23.8
Potassium	4.15
Sodium	330
Strontium	1.51
Zinc	0.174
Bicarbonate	305
Chloride	35.3
Sulfate	429
Boron	2.11497

## APPENDIX E: ANTHRONE METHOD FOR CARBOHYDRATES

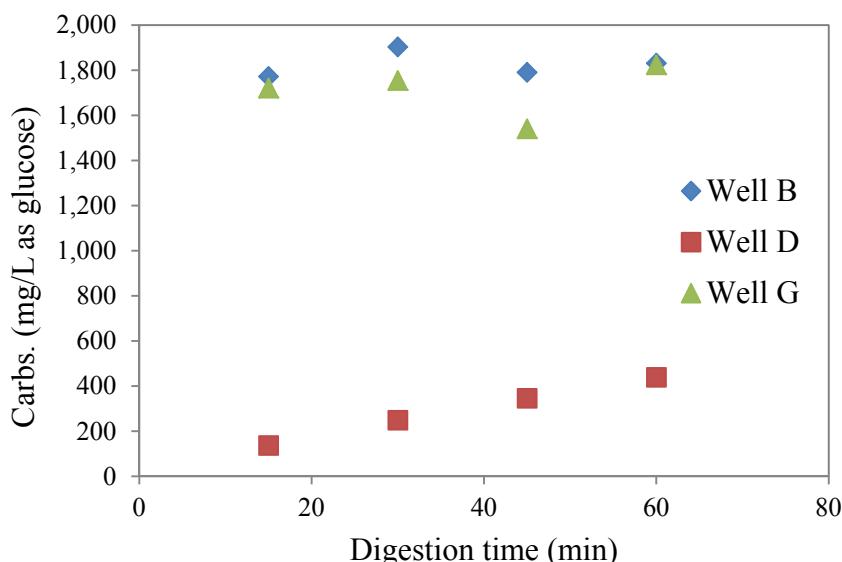
As discussed in Chapter 4, the Anthrone Method was used to measure the concentration of carbohydrates in the collected samples. The method used was adapted from Dulekgurgen (2004). In general, this method estimates total sugars (i.e., saccharides) by breaking carbohydrates (i.e., polysaccharides) into simple sugars (i.e., monosaccharaides) using a strong acid and a thermal digestion period. Anthrone, an aromatic organic compound, reacts with the sugars present to give a colored compound. The amount of total sugars in the solution is then estimated by measuring the absorbance of the color-reacted sample and comparing this absorbance to a standard glucose calibration curve.

This method was followed according to the cited protocol, with the exception that different glucose concentrations were used to generate a standard curve based on the expected concentration of carbohydrates in the produced water samples. The values used for the standard curve are presented in Figure E-1.



**Figure E-1: Glucose Calibration Curve**

Because this method relies on the breaking down of carbohydrates into their component sugars in order for them to be measured, and because the guar-based carbohydrates in the produced water samples were expected to be fairly complex, and therefore potentially difficult to break down, an experiment was conducted to measure the effect of an increased digestion time of the measured carbohydrate concentration. The tested hypothesis here was that increasing the digestion time may allow complex carbohydrates in produced water samples that contain guar-based gelling agents to be broken down more completely and therefore be more accurately measured. Results from this experiment are shown in Figure E-2.



**Figure E-2: Impact of Increased Digestion Time on Measured Carbs. Concentration**

As shown in Figure E-2, the measured carbohydrate concentration in samples from Well B and Well G did not increase significantly with a digestion time beyond the prescribed 15 minutes. The measured carbohydrate concentration in the sample from Well D did, however, increase with each successive increase in digestion time. This result was the opposite of what was expected to happen; Well B and Well G were fractured with a gel-based fluid and therefore are expected to contain significant concentrations of carbohydrates, while Well D was fractured

with a slickwater fluid and therefore would not be expected to contain a significant concentration of carbohydrates.

This result suggests that the prescribed 15-minute digestion time is sufficient for measuring carbohydrate concentrations and that increasing the digestion time only results in higher readings for what is thought to be some interfering color-producing compound in the sample from Well D.

Regarding future work, it would be desirable to find an alternative method for measuring carbohydrate concentrations in produced water samples that does not result in this observed interference from samples that contain lower concentrations of carbohydrates. One such method that may be explored is outlined in the following publication:

Hoeman. (2011.) “Method for identification and analysis of polysaccharide-based hydraulic-fracture flowback fluid.” *Society of Petroleum Engineers*.

## APPENDIX F: PRODUCED WATER FACT SHEET

(See next page)

# PRODUCED WATER



NE COLORADO FACT SHEET

JANUARY 2014

## What is Produced Water?

Hydraulic fracturing is a proven method used to extract oil and gas resources from deep, tight shale formations. The process consists of pumping roughly 4 to 10 million gallons of fracturing fluid (99.5% water and sand) into a deep geologic formation in order to fracture the rock and allow the migration of oil and gas into the wellbore. Once a well is hydraulically fractured, the well will produce a mixed stream of oil, water, and gas over the 20 to 30 year life of the well. At the surface, this mixed stream is separated. The water separated from this stream is referred to as *produced water*. This waste stream must be transported away from the wellhead, via trucking or pipeline, to either an industrial treatment facility or a disposal well.

## How much is there?

The rate of water production from a hydraulically fractured well is generally highest when the well is young, and then decreases as the well ages. Over the 20 to 30 year life of the well, roughly 2 to 6 million gallons of produced water may be generated.

## What's in Produced Water?

A research team at Colorado State University has collected and analyzed over 40 produced water samples from multiple Encana wells in NE Colorado. The table below presents the range of measured water quality concentrations. As presented in the table, some of the measured parameters originate from the hydraulic fracturing fluid used to fracture the well, while some parameters originate from the geologic formation.

Parameter	Measured Concentration	Unit	Origin	Reference Concentration
pH	6.88 - 7.64		N/A	Drinking water: 6.5 – 8.5
Oil and Grease	10 - 200	mg/L	Mineral oil additives and petroleum from the formation	Domestic wastewater: 50 – 150 mg/L
Total Organic Carbon	200 - 1,800	mg/L	Various organic fracturing fluid additives and dissolved petroleum from the formation	Pulp and paper wastewater: 500 – 5,000 mg/L
BTEX*	20 - 100	mg/L	Petroleum from the formation and potentially minor contribution from trace fracturing fluid additives	
Total Dissolved Solids (TDS)**	17,000 - 33,000	mg/L	Geologic formation and fracturing fluid additives	Typical Seawater: 34,500 mg/L
Chloride	9,000 - 20,500	mg/L	Geologic formation	Typical Seawater: 19,000 mg/L
Sodium	6,000 - 18,500	mg/L	Geologic formation	Typical Seawater: 10,500 mg/L
Calcium	215 - 560	mg/L	Geologic formation	Typical Seawater: 400 mg/L
Bromide	45 - 100	mg/L	Geologic formation and fracturing fluid additives	Typical Seawater: 65 mg/L
Strontium	25 - 83	mg/L	Geologic formation	Typical Seawater: 13 mg/L

\* BTEX consists of the sum of the concentrations of Benzene, Toluene, Ethylbenzene, and Total Xylenes. These are volatile organic compounds commonly associated with petroleum compounds and their derivatives.

\*\* Total Dissolved Solids (TDS) is a bulk parameter representing the sum of each dissolved ion in the solution. TDS primarily consists of chloride, sodium, and calcium, as shown above. Smaller components of TDS include other common minerals and metals, such as magnesium, potassium, barium, bromide, strontium, aluminum, iron, ammonium, and sulfate, all naturally occurring.