Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23665

146 (2019) 39–56
April

Investigating the influence of hydraulic fracturing fluid type and well age on produced water quality: chemical composition, and treatment and reuse challenges

Seongyun Kim*, Bradley Sick, Pinar Omur-Ozbek, Kenneth H. Carlson

Department of Civil and Environmental Engineering, Colorado State University, 1372 Campus Delivery, Fort Collins, Colorado 80523–1372, United States. email: seongyunkim7@gmail.com (S. Kim), bradsick@hotmail.com (B. Sick), pinar.omur-ozbek@colostate.edu (P. Omur-Ozbek), kcarlson@engr.colostate.edu (K.H. Carlson)

Received 17 September 2018; Accepted 23 December 2018

ABSTRACT

This study involves the analysis of produced water from three wells of different fracturing fluid types over a 63-d period. Total organic carbon concentration was higher in produced water samples from the wells fractured with the gel and hybrid fluids compared with the well fractured with the slickwater frac fluid. Total dissolved solids concentrations at each well increased with time from 18,000 to 30,000 mg/L. Liquid chromatography–mass spectrometry was performed to characterize the organic matter from different wells. Chemical equilibrium modeling was utilized to model the speciation of measured ions and to predict the precipitation of metal solids from blending produced water with a fresh groundwater source. Chemical coagulation was successful at reducing the turbidity of all produced water samples. Coagulation–flocculation jar testing was conducted on each sample to determine the variability in optimum dose as a function of fracturing and well age. The optimum dose for produced waters from wells fractured with gel fluids was determined about 25%–300% higher than that for wells fractured with slickwater fluids.

Keywords: Produced water; Hydraulic fracturing; Coagulation testing; Slickwater; Cross-linked gel; Liquid chromatography–mass spectrometry (LC-MS)

1. Introduction

Oil and natural gas have played an integral role in the development of today's global industrial society and remain an important part of the current global energy portfolio. As more readily extracted conventional oil and gas resources are exhausted, technological improvements with horizontal drilling and hydraulic fracturing have allowed previously cost-prohibitive unconventional resources to become one of the largest and fastest growing sources of US domestic energy over the past 5 years [1].

Although unconventional oil and gas are among the least water-intense forms of energy currently utilized [2], water demand for hydraulic fracturing and the associated wastewater generation result in significant water management challenges. Each hydraulically fractured well requires roughly 2 to 7 million gallons of water, [3–9] which is mixed with sand and chemical additives to form an engineered fluid that is injected under high pressure into the formation in order to create and prop open fractures [5,10,11].

Once a well has been hydraulically fractured, it is opened and fluid is allowed to return to the surface. Initially, a high flow rate of predominantly water, often referred to as "flowback", is returned to the surface. Within hours to weeks after the well is opened, the well begins producing a significant amount of oil and/or gas and is put into production. During the production phase, a mixed stream of oil and/or gas and water is generated, typically at a decreasing rate over the

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* Corresponding author.

1944-3994/1944-3986

life of the well. Water separated from this mixed stream is typically referred to as "produced water", and results in a constant generation of wastewater over the operating life of a well. The rate of wastewater production from a well is typically greatest when the well is initially opened and then sharply declines. As much as one-third of the overall 30-y projection of total produced water may be produced in the first 30 d after completion [12].

Produced water management options depend on many factors, including availability of injection and disposal wells, availability of water treatment infrastructure, regulations, and overall pace and scale of development [13]. Sourcing and hauling water for fracturing fluid and hauling and disposing of generated wastewater to and from well sites results in significant operating costs as well as a variety of social and environmental risks and impacts [14]. In 2007, the vast majority of produced water in the United States, 95.2% of the reported volume, was managed through injection [15]. There are reports regarding the chemical and physical characteristics of produced water from conventional and unconventional oil and gas reservoirs and the possible treatment options for produced water [16–19]. More recently, treatment and reuse (i.e., recycling) of produced water to counterbalance the freshwater demand for fracturing other wells is becoming a more integral part of produced water management to minimize total dissolved solids (TDS) [20,21]. This strategy has the potential to reduce the amount of overall wastewater that must be injected or treated to discharge standards, while also reducing water demand, public burden, environmental impacts, and overall cost of production.

The recycling process typically involves some degree of treatment and/or blending with freshwater in order to improve the quality of the produced water to the point that it can be effectively used as a fracturing fluid. Typical treatment objectives for reuse include removal of suspended solids and scale-forming components, and disinfection. High suspended solids and/or bacterial 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 [22]. Major scaling concerns include $BaSO_4$ and, to a lesser extent, $SrSO_4$ and $CaCO_3$ [23].

An understanding of the quality and variability of produced water is crucial in designing effective water management strategies and treatment systems. Maguire-Boyle and Barron [24] investigated on the organic compound in produced water by chromatography mass spectrometry (GC/MS) analysis. It has been shown that the age of a well has a significant impact on produced water quality, particularly over the first few months of production [25,26]. It is also expected that the type of fracturing fluid used to stimulate a well may have a significant impact on produced water quality.

Fracturing fluids can be separated into two main categories: gel and slickwater fluids. A gel fluid uses high concentrations of a polymer gelling agent, which often has the ability to be cross-linked for the purpose of greatly increasing the viscosity of the fracturing fluid. Slickwater fluids use low concentrations of viscosity-increasing polymer or no polymer at all and typically use lower proppant concentrations [27]. 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 [28].

This study analyzed data from 15 sets of produced water samples collected over a 63-d study period from three wells fractured with different fracturing fluids. Extensive water quality characterization was performed on each sample. Chemical coagulation jar testing was conducted to understand variability in optimum treatment dose due to type of fracturing fluid and well age. The studied wells were unconventional oil and gas wells located in the Wattenberg Field of the Denver-Julesburg Basin, located in northeastern Colorado. The system of formations targeted for production in this field is commonly referred to as the Niobrara Shale, an Upper Cretaceous hybrid shale/carbonate with production depths ranging from 1,800 to 2,700 m and an overall thickness of roughly 100 m, with carbonate-rich targets for horizontal laterals that range from 3 to 7 m thick [29]. Many operators utilize both slickwater and gel hydraulic fracturing fluids in this field and wastewater management often involves a decision of whether or not to combine wastewater streams from wells fractured with different fluids or from wells of different ages. It is essential to understand whether the fracturing fluids behave differently and may be blended and treated together for possible reuse.

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

2. Materials and methods

2.1. Well characteristics

The study involved field collection of 15 sets of produced water samples from three separate unconventional oil and gas wells located in Weld County, Colorado. Table 1 and Fig. 1 provide information on the studied wells.

The wells were located on the same centralized pad and targeted the same formation, but were stimulated with a different fracturing fluid package (Tables 2 and 3). FracFocus [30], the national hydraulic fracturing chemical registry, was used to identify the names and maximum concentrations of compounds used in each fracturing fluid package.

Well S was fractured with a slickwater fluid, the primary chemical additive of which was hydrochloric acid (HCl). Other unique components of the slickwater fluid, which constitute a total maximum concentration of 556 mg/L, include acidizing, corrosion inhibitor, iron control, and paraffin inhibitor packages.

Well G was fractured with a cross-linked gel fluid, unique components of which include gelling agent, cross-linker, and breaker packages. The primary compounds that make up these packages, in terms of maximum possible concentration, are petroleum distillates (~41%) and guar gum (~37%), both

Table 1
Properties of studied wells

Well name	Job start	Job end	Production start date	True vertical depth (m)	Effective lateral length[a] (m)	Lateral number of stages[b]	Input water volume (L)	Fracture fluid type
Well S	10/21/2013	10/26/2013	11/25/13	2,153	1,331	28	15,090,279	Slickwater
Well G	11/4/2013	11/9/2013	11/26/13	2,192	1,390	29	15,577,257	Cross-linked gel
Well H	10/28/13	11/3/2013	11/25/13	2,173	1,372	28	16,447,394	Hybrid

[a] Effective lateral length: length from the top of the upper most perforation to the bottom of the deepest perforation.
[b] Lateral number of stages: number of stages in the total horizontal length.

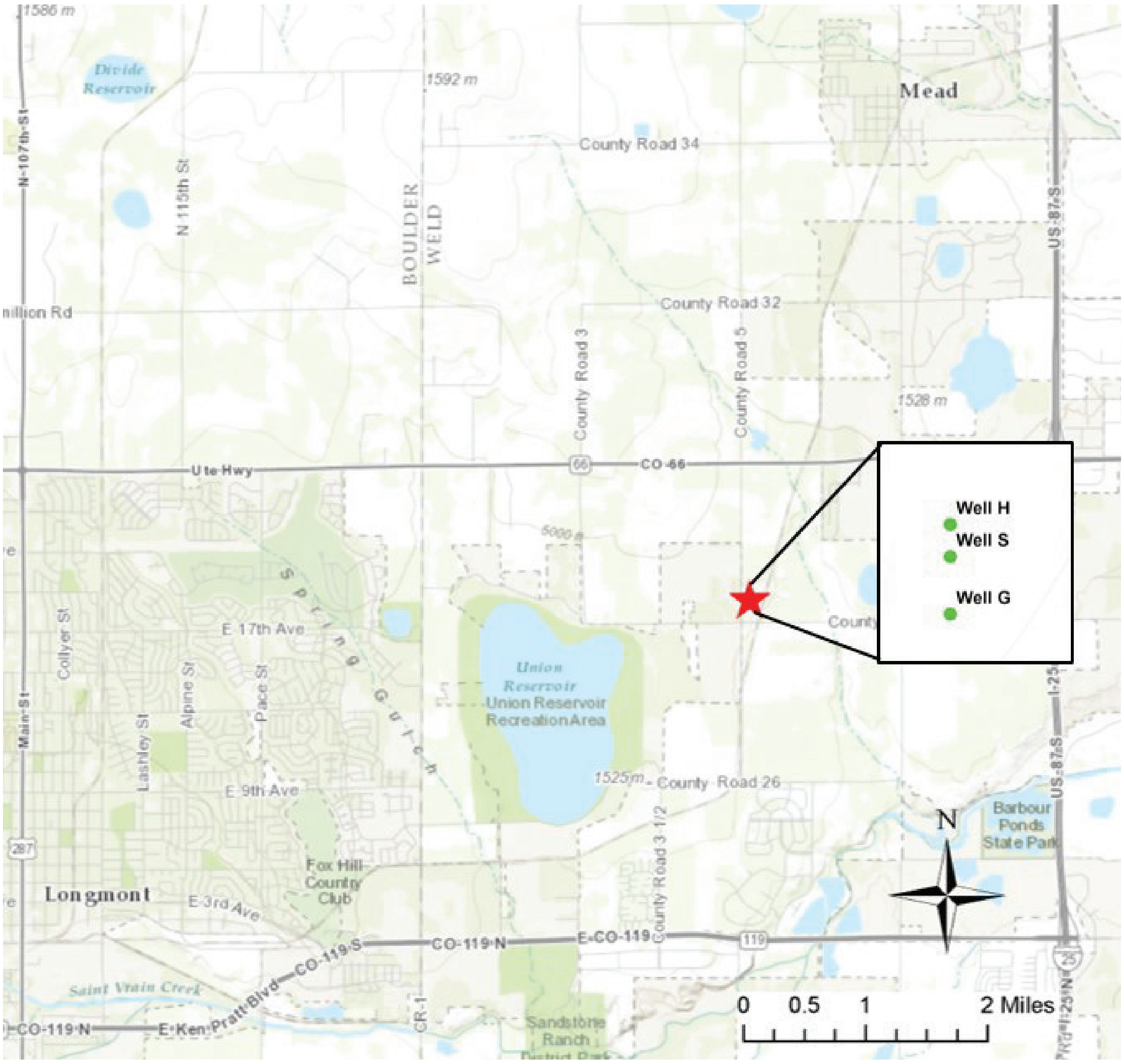


Fig. 1. Map of the configuration of three unconventional oil and gas wells located in Weld County, Colorado.

of which are organic compounds that significantly modify the viscosity of the fracturing fluid as the well is stimulated. It should be noted that the slickwater fluid used in Well S did not contain these modifying components of the gel fluid and, as such, maintained a fairly consistent viscosity. The cross-linker package also includes boric acid, which makes the element boron unique to the cross-linked gel fluid.

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

Table 2
FracFocus.org Frac fluid compositions for Well S

Well S				
Purpose	Trade name	Ingredients	Max concentration (mg/L)	Approximate chemical formula
Acidizing	HCI, 10.1%–15%	Hydrochloric acid	1,218	HCI
Corrosion inhibitor	Cl-31	Formic acid	9	CH_2O_2
		Oxyalkylated fatty acid	4.5	[COH]
		Aromatic aldehyde	4.5	C_6H_5CHO
		Quaternary ammonium compound	4.5	NR_4
		Isopropanol	1.5	C_3H_8O
		Methanol	0.8	CH_4O
		Cyclic alkanes	0.8	[CH]
		Organic sulfur compound	0.8	[CHS]
		Benzyl chloride	0.2	C_7H_7Cl
Iron control	Ferrotrol 300L	Citric acid	10	$C_6H_8O_7$
Paraffin inhibitor	Paras orb 5000,bag	Calcined diatomaceous earth	270	N/A
		White mineral oil	125	$C_{(15\text{-}40)}H_X$
		Proprietary paraffin inhibitor	104	N/A
		Silica, crystalline-quartz	21	Si
Biocide	Alpha452	Tetrakis(hydroxymethyl) phosphonium sulfate	167	$C_8H_{24}O_{12}P_2S$
Breaker	GBW-5	Ammonium persulfate	113	$H_8N_2O_8S_2$
Clay control	Clay care, tote	Choline chloride	747	$C_5H_{14}CINO$
Friction reducer	MaxPerm-20A, bulk	Polyacetate	563	$(C_4H_6O_2)n$
		Petroleum distillates	281	$C_{(9\text{-}16)}Hx$
		Sodium chloride	47	NaCl
		Oxyalkylated alcohol	47	N/A
Surfactant	Flo-Back 40, tote	Amphoteric surfactant	338	N/A
Non-emulsifier	NE-945W, 265gl tote	Glycerine	150	$C_3H_8O_3$
		Oxyalkylated alcohol	25	N/A
		Polyethylene glycol	25	$C_{2n}H_{4n}+2O_n+1$

Both the slickwater and cross-linked gel fracturing fluids contained similar biocide, breaker, clay control, friction reducer, surfactant, and non-emulsifier packages. The primary components of these packages, in terms of maximum possible concentration, are the following organic compounds: choline chloride, polyacetate, petroleum distillates, and amphoteric surfactants [31].

2.2. Sample collection

Fifteen sampling events were conducted over a 63-d period. Sampling began immediately after the start of oil and gas production (referred to as day 0). The pre-production flowback period ranged from 3 d for Well H to 7 d for Well S; no pre-production flowback samples were collected as a part of this study. Samples were collected every 3 d for the first nine events; every 5 d for events 10 and 11; and every 7 d for events 12–15.

All samples were collected from a dedicated production separator associated with each well. The only exception was the first sample collected from Well G, which was collected directly from the wellhead. Approximately 18 L of sample were collected from each well at each sampling event and allocated to appropriate containers. Volatile compounds analysis samples were collected in glass vials, headspace free. All other samples for water quality characterization were placed in 1-L polyethylene bottles. All vials and bottles were immediately placed on ice and kept refrigerated until analyzed. All samples were analyzed within a week after sampling. The remaining samples from each collection, ~15 L, were placed in 18-L container and used for jar testing.

2.3. Analtyical methods

Conductivity and pH, respectively, were measured in the field and verified in the lab using probes (CDC401 and PHC10105, Hach, Loveland, CO, USA). Field-collected pH and conductivity readings are presented in this study. Alkalinity was measured using standard method 2320B; TDS and total suspended solids (TSS) were determined using Standard Method 2540 [32]. Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured using a

Table 3
FracFocus.org Frac fluid compositions for Well G

Well G				
Purpose	Trade name	Ingredients	Max concentration (mg/L)	Approximate chemical formula
Breaker	High Perm CRB	Ammonium persulfate	90	$H_8N_2O_8S_2$
Breaker	Enzyme G HT-II	Water	379	H_2O
		Tryptone	19	[CHON]
		Yeast extract	19	N/A
Buffer	BF-9L, 300 gal tote	Potassium carbonate	315	KCO_3
		Potassium hydroxide	158	KOH
Cross-linker	XLW-30AG,tote	Petroleum distillates	382	$C_{(9\text{-}16)}Hx$
Cross-linker	XLW-32	Methanol	164	CH_4O
		Boric acid (H_3BO_3)	82	H_3BO_3
		Methyl borate	82	$C_3H_9BO_3$
Gelling agent	GW-3LDF	Guar gum	3,355	$C_6H_{12}O_6$/unit
		Paraffinic petroleum distillate	1,677	[CH]
		Petroleum distillate	1,677	$C_{(9\text{-}16)}Hx$
		Isotridecanol, ethoxylated	280	[CHO]
		1-Butoxy-2-propanol	280	$C_7H_{16}O_2$
Biocide	Alpha452	Tetrakis(hydroxymethyl) phosphonium sulfate	145	$C_8H_{24}O_{12}P_2S$
Breaker	GBW-5	Ammonium persulfate	9	$H_8N_2O_8S_2$
Clay control	Clay care, tote	Choline chloride	668	$C_5H_{14}ClNO$
Friction reducer	MaxPerm-20A, bulk	Polyacetate	30	$(C_4H_6O_2)n$
		Petroleum distillates	15	$C_{(9\text{-}16)}H_X$
		Sodium chloride	3	NaCl
		Oxyalkylated alcohol	3	N/A
Surfactant	Flo-Back 40, tote	Amphoteric surfactant	287	N/A
Non-emulsifier	NE-945W, 265gl tote	Oxyalkylated alcohol	20	N/A

TOC-VCSH analyzer, Shimadzu (Kyoto, Japan). Whatman microfilters (1.5 µm pore size) were used for DOC analysis. Whatman microfiber filters (0.45 µm pore size) were used for TDS, and TSS analyses. Turbidity was measured with a Hach 2100N turbidimeter, according to EPA Method 180.1 [33]. The ultraviolet (UV) absorbance was measured with a HACH DR/4000 spectrophotometer at 254 nm (referred to as UV254). Al, Ba, B, Ca, Fe, K, Mg, Na, Si, Sr, and Zr concentrations were determined using inductively coupled plasma–atomic emission spectrometry (ICP-AES) after acid digestion of samples to pH below 2. Chloride was measured using a silver nitrate titration, according to EPA method 9253. Bromide was measured using an ion chromatograph, according to EPA method 300. Sulfate was measured using American Society for Testing and Materials (ASTM) method D516 [34]. Ammonia was measured using EPA method 350.1. All samples collected from the production oil–water separators (i.e., 15 samples from each of the three wells) were analyzed for each of the listed parameters.

2.4. Jar testing to determine optimum dose

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

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

At the end of the setting period, a sample was collected from the sampling port built into each jar. Sample turbidity was immediately measured for each of the five sub-samples. Of the five doses tested, an optimum dose was selected as the lowest dose at which an increase to the next dose resulted in less than 1.5% increase in net turbidity (NTU) removal. Additional water quality analyses were conducted on each optimum dose sample in order to measure treatment removals. These additional analyses included pH, UV254 absorbance, TOC, DOC, TSS, and TDS [31].

2.5. LC-MS method

Samples from three sampling events were further analyzed by LC-MS run under ESI mode. 20 mL of samples from Well S and Well G were collected in glass vials at 4, 25, and 56 d. A C18 column was used for separation, the nebulizer pressure was set to 30 psig and the scan spectra were collected in an *m*/*z* range of 50–1,600. The carrier flow rate was 0.4 mL/min. 5 µL of sample was injected and each run lasted 18 min at 30°C. The mobile phase A was 0.1% formic acid in water and B was 0.1% formic acid in acetonitrile. The mobile phase gradients during the run were 95%–80% A for 1–8 min, 80–5% A for 8–17 min, and 5–95% A for 17–18 min.

2.6. Chemical equilibrium modeling

Ion concentrations tested in the laboratory are reported as mg/L of the base ion, such as mg/L as Ca^{+2}. However, these ions do not necessarily exist in the raw solution as the base ion; instead, they exist as one or several species of ion complexes such as $CaCO_3$ or $CaSO_4$. Multivalent metal ions can cause potential clogging problems during hydraulic fracturing and also during well production. Chemical equilibrium modeling can determine the form(s) in which ions actually exist in the solution; such speciation knowledge can help in understanding phenomena such as solids formation and scaling potential and support decisions regarding softening and other treatment options [31].

This study utilized OLI Stream Analyzer (OLI Systems, Cedar Knolls, NJ), a chemical equilibrium modeling software that provides thermodynamic equilibrium equations for the physical and chemical understanding of aqueous-phase systems [35], to determine what form or forms the measured ions exist in the sample and the distribution of chemical species as both aqueous and solid species. The limitation and assumptions of OLA analyzer were summarized in supporting information (Table S1). Speciation modeling was conducted on samples collected from Well H on Days 1, 19, and 63 to reflect temporal variation. Each system was modeled at the measured pH of the respective sample (~pH 7).

Untreated produced water is sometimes blended with freshwater to dilute the solution to a quality that can be used for fracturing without treatment. This study also used OLI Stream Analyzer to model the expected precipitation of metal solids that would result from blending produced water from Well H with a freshwater source that reflects typical groundwater quality of Northeast Colorado. Water quality of a typical Northeastern Colorado groundwater is summarized in Table 4. In addition, the average pH is 8.3.

3. Results and discussion

3.1. Produced water characterization

Temporal trends for pH, alkalinity, conductivity, and TOC are presented in Fig. 2. The pH of all produced water samples was within 6.75–7.5, with a slightly decreasing temporal trend in pH observed at each well. However, hydrochloric acid might promote changes in alkalinity and increases in Ca, Mg, and Sr in produced water and occur usually within 48 h after flowback water began. The observation reported on supporting information (Figs. S1 and S2) where Ca, Mg, and Sr were significantly lower in Well G, indicating that there might be occurred many of acid-driven reactions at Well H and Well S which is used HCl as a primary additives.

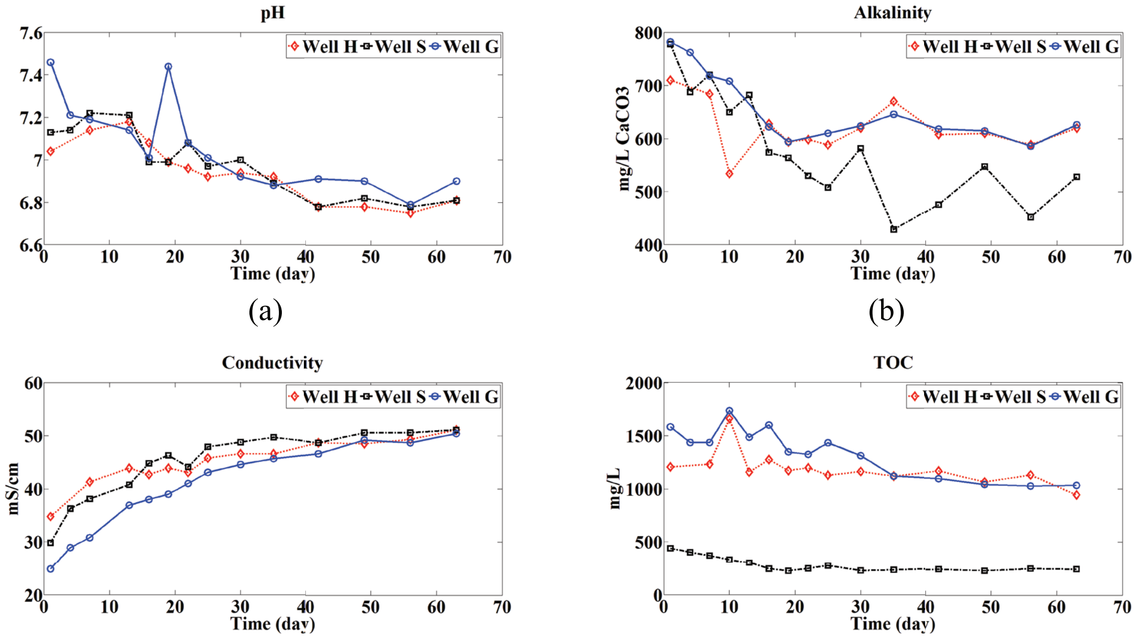
Table 4
Water quality of a typical Northeastern Colorado groundwater source

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

Alkalinity concentrations among the three wells at each time point were fairly consistent; the exception was the alkalinity concentration at Well S, which was significantly lower than the other two wells after Day 30. A slight downward temporal trend in alkalinity was observed for every well. Alkalinity concentrations were typically greater than 500 mg/L as $CaCO_3$ during the study period, suggesting a significant buffering capacity. Due to this high buffering capacity, a softening process using pH adjustment to precipitate metals could require a significant chemical demand. The temporal decrease in the alkalinity trend suggests a lesser buffering capacity in older samples, especially from Well S, which was observed to have a more steeply declining trend compared with the other two wells.

Conductivity was fairly consistent among the three wells at each time point, with Well G generally having a slightly lower conductivity than the other two wells over the sampling period. Conductivity readings were strongly correlated with TDS concentrations. An upward temporal trend in conductivity was observed at each well, increasing from 25–35 mS/cm at Day 1 to approximately 51 mS/cm at Day 63. The trends of measured inorganic ions of temporal variability and different fracturing type are shown in supporting information (Figs. S1 and S2). TDS concentrations also increased over the course of the sampling period, from approximately 17,000 to 22,000 mg/L at Day 1 to approximately 34,000 mg/L at Day 63. Chloride and sodium made-up the primary inorganic constituent ions, followed by calcium and bicarbonate. Chloride, sodium, and the majority of the component metals and inorganic ions measured followed trends similar to TDS. Exceptions included bicarbonate, sulfate, and silicon which showed a slight decreasing temporal trend.

One way ANOVA was performed to check difference in water quality parameters from each well by flowback time. With a few exceptions, metals and inorganic ions



(a) (b)

(c) (d)

Fig. 2. Temporal trends of pH (a), alkalinity (b), conductivity (c), and TOC (d) measurements. Day 0 corresponds to the first day that the wells were put online for production (3 to 7 d after the wells were opened).

concentrations were fairly consistent from well to well (i.e., did not seem to be impacted by fracture fluid type). One exception was that the concentrations of divalent cations (Ca [*p*-value = 0.42], Mg [*p*-value = 0.45], and Sr [*p*-value = 0.62]) were significantly lower in Well G samples, compared with samples from the other two wells. The other exception was that boron concentrations were less in Well S samples compared with those from the other two wells. The lower concentration of boron in Well S is likely due to the absence of the boron-based cross-linker in the slickwater fracturing fluid. The low boron concentration at Well S may represent the introduction of boron from the formation. The boron concentration difference between Well S and other wells supports the assumption that there was negligible fluid communication between the wells due to their relatively close proximity.

The rest of water quality parameters trends of three wells and the age of wells are shown in supporting information (Figs. S3 and S4). No significant trends were observed for turbidity (*p*-value = 0.86) or TSS (*p*-value = 0.75). Turbidity readings ranged from 115 to 763 NTU, with average turbidity at each well ranging from 247 NTU at Well G, 295 NTU at well H to 262 NTU at Well S. TSS readings ranged from 38 to 339 mg/L, with average TSS at each well ranging from 144 mg/L at Well S, 155 mg/L at well H to 148 mg/L at Well G.

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

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

The observed temporal increase in TDS and decrease in TOC in each produced water stream is likely due to the increased impact on water quality from the formation and decreased impact from fracturing fluid additives with time. Produced water samples collected during the first 10 d of production had less contact time with the formation and typically are flowing back from the well at a higher rate than produced water collected later in the study. As such, the water quality of earlier produced water samples is more similar to the raw fracturing fluid; these samples exhibit higher concentrations of TOC and cross-linker-associated salts – in this case, boron – and lower concentrations of dissolved salts contributed by the formation. These trends, however, tend to stabilize as the well ages. The data presented here show that TOC and alkalinity concentrations became fairly stable at approximately 30 d after production. pH, conductivity, and the majority of the metals and ions that contribute to conductivity became more stable about 45 d after production.

The observed trend in TDS in this study is similar to other published data, with the difference being the magnitude of the stabilized TDS concentration, which can vary greatly from field to field. For example, TDS concentrations in Marcellus produced water has been observed to increase dramatically over the first roughly 30 d after the well is opened and then stabilize at values between roughly 60,000 and 1,40,000 mg/L [24].

Average TOC concentrations reported from the study by Vidic et al. [23] for Marcellus wells, which are typically fractured with slickwater fluids are generally less than 250 mg/L and are reported to decrease or stabilize with time [24,26]. These published results are consistent with the TOC concentrations measured for slickwater fluids in this study.

Daily water production values are presented in supporting information (Fig. S5). The magnitude and general trend of daily water production does not differ greatly from well to well, with each well showing a gradual downward temporal trend.

3.2. Chemical coagulation jar testing

The optimum dose was selected out of each of the five tested doses. As shown in Fig. 3, this optimum dose was selected as the smallest dose where an increase in dose does not result in a significant increase in turbidity or UV_{254} removal.

The optimum coagulant dose determined for each five-point jar test is presented in Fig. 4. The optimum dose for 1 d sample from Well G was found to be 800 mg/L – about three times the next highest dose. Fig. 4 does not include the optimum dose for the Day 1 sample from Well G collected prior to connection of the well to the production oil–water separator. Because this sample was collected directly from the well head, prior to the start of production, this data point was not included in the dataset.

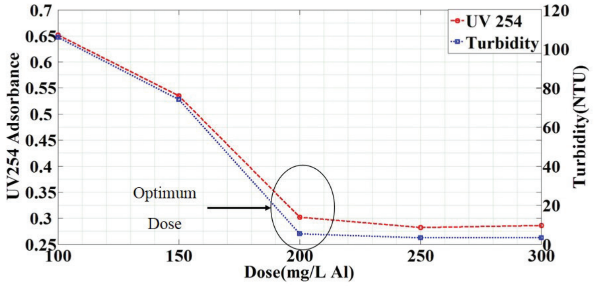


Fig. 3. Selection of optimum dose based on turbidity and UV_{254}.

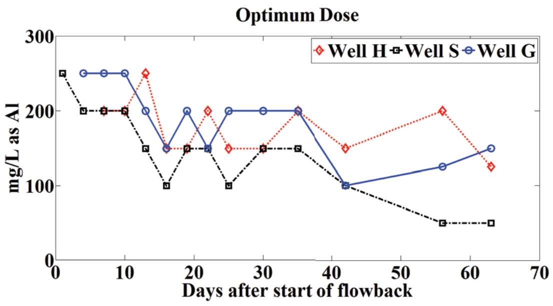


Fig. 4. Temporal trends in optimum aluminum chlorohydrate coagulant dose.

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

Average removal of measured parameters following the optimal coagulant dose for all samples from given well tested is presented in Table 5. Organics removal, as suggested by average TOC and DOC removals, was generally less than 20% for each well. TOC removal was higher than DOC removal, suggesting that larger organic molecules are more effectively removed by the coagulation process. TSS removal ranged from 56% (Well G) to 74% (Well S), with average treated water TSS concentrations of 93 mg/L (Well G) to 29 mg/L (Well S). No significant TDS removal was observed. Mean turbidity removal was 96% or more for samples from each well, resulting in an average turbidity of all treated samples measuring less than 10 NTU.

Organics removal results are consistent with other published literature. Cardoso et al. [36] showed that dissolved organic material with a negative surface charge (e.g., humic acids and fulvic acids) can be removed via coagulation/flocculation and solid/liquid separation, but low-weight particles with no surface charge, such as carbohydrates, are not removed via coagulation/flocculation [36]. 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.

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

Table 5
Average removal of selected constituents for 0 to 63 d produced water samples using chemical coagulation

Parameter	Average removal (%)		
	Well S	Well G	Well H
Turbidity (NTU)	97	96	97
UV_{254} (Abs.)	80	70	67
TOC (mg/L)	12	18	17
DOC (mg/L)	6	7	8
TSS (mg/L)	74	56	57
TDS (mg/L)	1	0	1

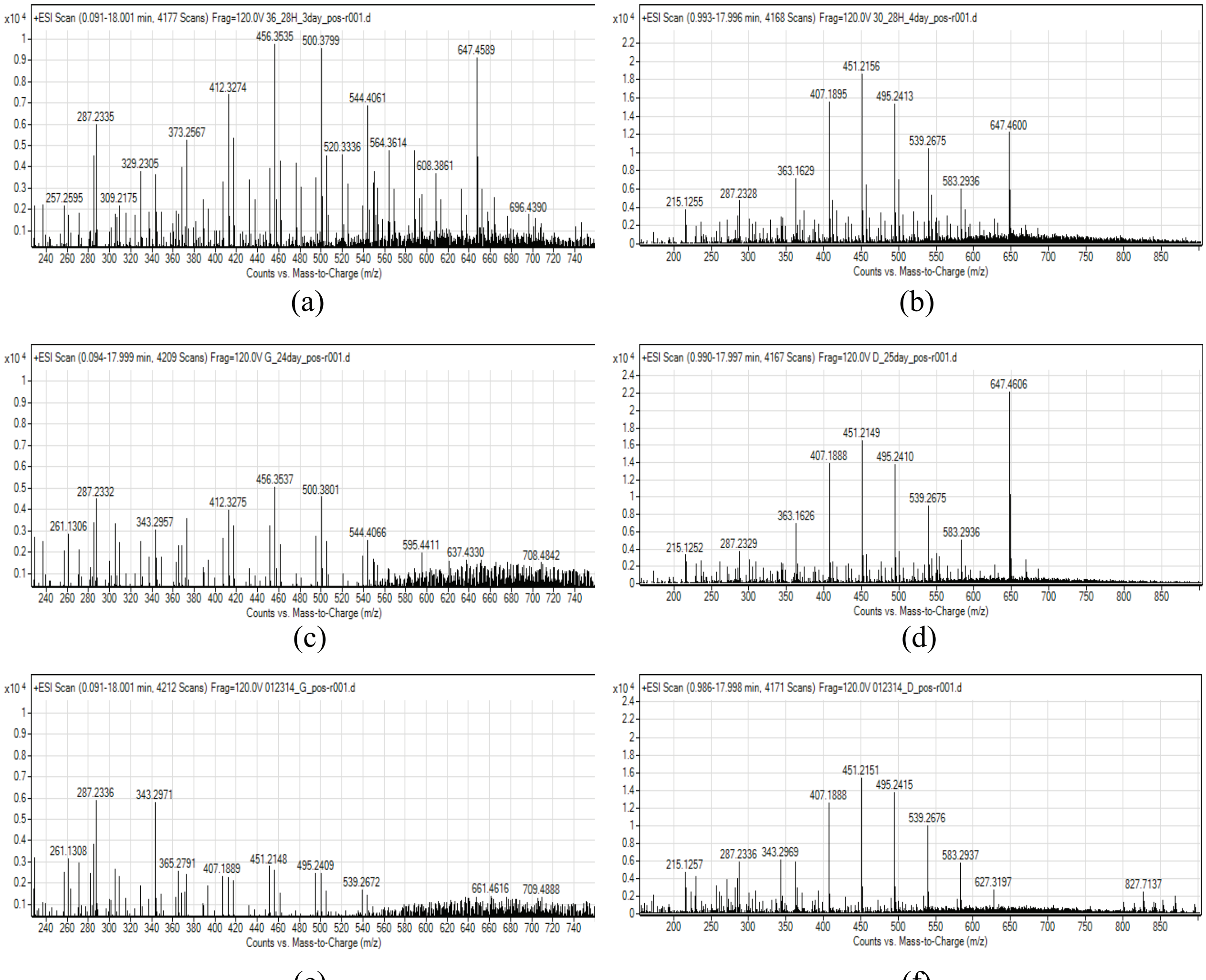
as well as the relative changes in treatability with time. Similarly, measuring removal of parameters with each coagulation treatment was not conducted to identify an overall, optimized treatment process; instead, the data collected provides a general idea of what is and isn't removed from produced water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

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

3.3. LC-MS analysis for comparison between gel well flowback and slickwater well flowback with temporal variability

Flowback water samples 4, 25, and 56 d from Well G and Well S were analyzed by LC-MS and the Agilent mass hunter qualitative analysis. Fig. 5 shows the mass spectra from the Well G at 4 d (a), 25 d (c) and 56 d (e) and Well S at 4 d (b), 25 d (d), 56 d (f) with relative abundances. Although there are different relative abundances of peaks for the same well age samples for Well G and Well S, similar organic compounds were detected at each well. The detected different organic compounds indicate that there was likely no communication between Well G and Well S due to the closed distance.

LC-MS data were further analyzed to identify the organic compounds in both gel and slick wells with temporal variability by using Agilent Technology Software linked to a library based on the exact mass of chemicals used for hydraulic fracturing between 2005 and 2009 in the United States [37]. Benzenecarboperoxoic acid, 1,1-dimethylethyl ester, cocamidopropyl betaine, dipropylene glycol, phthalic anhydride, polyethylene glycol and triethylene glycol were



(a) (b)

(c) (d)

(e) (f)

Fig. 5. Mass spectra of detected organic constituents with relative abundance using LC/MS for Well G at (a) 4 d, (c) 25 d, (e) 56 d and Well S at (b) 4d, (d) 25 d, (f) 56 d.

detected in both Well G and Well S. Some of the organic compounds were not detected in the early samples while others were not detected in the later samples indicating the presence or absence of degradation byproducts or compounds extracted from shale formation during fracturing. 1-Methoxy-2-propanol, 3,4,4-trimethyloxazolidine, aldol, dodecylbenzene sulfonate isopropanolamine, ethoxylated octyl phenol, ethyl acetoacetate, methyl salicylate, *n*,*n*′-methylenebisacrylamide, polyethylene-polypropylene glycol, propanol, [2-(2-methoxymethylethoxy) methylethoxyl] and triamcinolone were detected only in Well G, meaning that they are likely degradation products of the gel additives (Table 6).

The distribution of constituents obtained from positive spectra and compared wells for temporal variability are presented in Fig. 6. Organic carbon compound classes were sorted by different range groups. The class distribution of the carbon fraction showed similar trends for both Well G and Well S. The carbon classes from both wells indicate that early flowback water tends to have a higher number of carbon classes than later flowback water. The most abundant compounds in 4-d Well S sample were C31-C44, and C21–30 compounds were predominant in 25-d Well S whereas the compounds in 56-d Well S sample were evenly distributed except over C44. The 4-d Well G sample showed the highest concentrations in C31-C44, similar to Well S, and the 25-d Well G was dominant in the C31-C44 range.

Early flowback water required more aluminum for better coagulation (Fig. 4), indicating a higher organic matter optimum dose. To check how carbon classes distribution

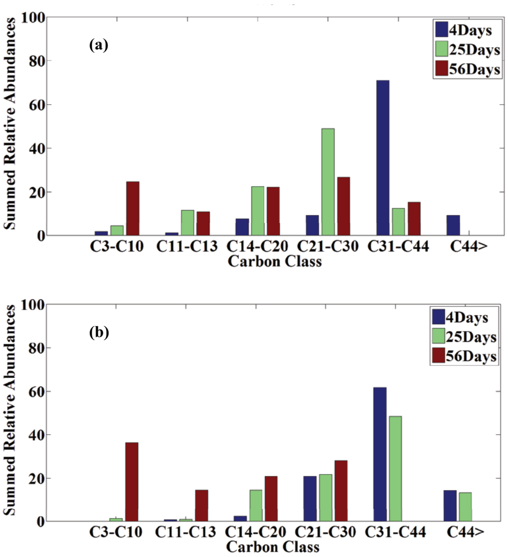


Fig. 6. Comparison of carbon classes with relative abundances for temporal variability with different well fractured (a) Well S and (b) Well G.

Table 6
Chemical found in flowback water for Well S and Well G with temporal variability

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

affect coagulation, linear regression analysis was performed. Since there are many ranges of carbon classes, classes were grouped (C3-C30) to make two dimensional plot. The total abundance of C3–30 and C>30 is 100. A relatively strong correlation was obtained (R^2 > 0.8 in both) as presented in Fig. 7. As can be observed from Fig. 7, 20% of the abundance of compounds was from C3–30 and the remaining 80% was from C>30. The sample which are 20% of C3-C30 and 80% of C>30 was needed 200 mg/L as Al and the sample which are 85% of C3–C30 and 15% of C>30 was needed 50 mg/L as Al, confirming that organic matter with a higher number of carbons increases coagulation demand.

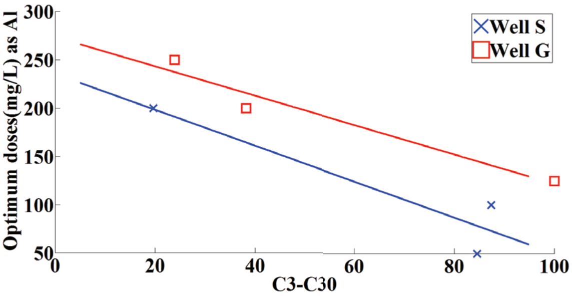


Fig. 7. Optimum doses trend in summed carbon between 3 to 30 from Well S and Well G.

3.4. Ion speciation in selected produced water samples

The results of chemical speciation modeling for samples collected from Well H on Days 1, 19, and 63 are summarized in Table 7. Calcium carbonate (calcite) makes up the majority of the inorganic solids in each of the analyzed samples, followed by ferric hydroxide and barium sulfate. At the modeled pH (each near a pH of 7), magnesium, boron, zirconium, and strontium are only present in the aqueous phase; this finding is consistent with common softening processes, where it is known that magnesium will not start precipitating until the pH is raised to roughly 10, at which point it will precipitate out as $Mg(OH)_2$. While the solubility of barium sulfate is extremely low, the presence of the barium ion in all three samples suggests that each produced water sample is sulfate-deficient and that if sulfate was introduced into the system – by means of dilution with a freshwater source of a high sulfate concentration – barium sulfate could become a significant scaling concern. Trivalent cations such as aluminum and iron have a strong tendency to hydrolyze in a solution and to precipitate out as hydroxide complexes. It was found that all aluminum in the solution was present in the solid form of either $NaAl(OH)_2CO_3$ or $Al(OH)_3$, and all ferric ions were 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; therefore, they present as a colloidal suspension. As such, a coagulation treatment process may be required to

Table 7
Modeled speciation on measured metals for well H

Measured Ion	Chemical formula	1 d			19 d			63 d		
		Total	Aqueous	Solid	Total	Aqueous	Solid	Total	Aqueous	Solid
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Al	$Al(OH)_3$	–	–	–	–	–	–	14.4	–	14.5
	$NaAl(OH)_2CO_3$	11.3	–	11.3	11.5	–	11.5	–	–	–
Ca	Ca^{2+}	161.1	161.1	–	379.3	379.4	–	758.7	758.9	–
	$CaCO_3$	477.5	1.8	475.8	383.8	1.7	382.1	631.1	1.7	629.5
	$CaH_2BO_3^+$	0.0	0.0	–	0.1	0.1	–	0.2	0.2	–
	$CaHCO_3^+$	6.5	6.5	–	7.1	7.1	–	5.7	5.7	–
	$CaSO_4$	0.2	0.2	–	0.0	0.0	–	0.1	0.1	–
Mg	Mg^{2+}	51.3	51.4	–	79.8	79.8	–	134.4	134.4	–
	$MgCO_3$	0.1	0.1	–	0.1	0.1	–	0.1	0.1	–
	$MgHCO_3^+$	10.5	10.5	–	8.3	8.3	–	5.5	5.5	–
	$MgSO_4$	0.2	0.2	–	0.0	0.0	–	0.0	0.0	–
B	H_3BO_3	29.8	29.8	–	29.1	29.1	–	26.0	26.0	–
	$B(OH)_4^-$	0.4	0.4	–	0.4	0.4	–	0.4	0.4	–
	$NaB(OH)_4$	0.1	0.1	–	0.1	0.1	–	0.1	0.1	–
Zn	Zn^{2+}	0.4	0.4	–	0.0	0.0	–	0.6	0.6	–
	$ZnCl^+$	0.1	0.1	–	–	–	–	0.1	0.1	–
	$ZnHCO_3^+$	0.0	0.0	–	–	–	–	–	–	–
Ba	Ba_2^+	1.8	1.8	–	16.8	16.8	–	26.5	26.5	–
	$BaCl^+$	0.4	0.4	–	5.0	5.0	–	7.3	7.3	–
	$BaHCO_3^+$	0.0	0.0	–	0.2	0.2	–	0.1	0.1	–
	$BaSO_4$	20.2	–	20.2	5.3	–	5.3	7.8	–	7.8
Fe	$Fe(OH)_3$	197.1	–	197.1	57.4	–	57.4	147.7	–	147.7
Sr	Sr^{2+}	43.7	43.7	–	72.8	72.8	–	164.9	165.0	–

remove these suspended solids from the solution in order to lower aluminum and iron concentrations to desired treatment levels.

3.5. Blended water modeling

Modeled concentrations of solid calcium carbonate, ferric hydroxide, aluminum hydroxide, and barium sulfate with blending ratios ranging from one part produced water to five parts fresh water (1:5) to one part produced water to 30 parts fresh water are presented in Fig. 8 for each of the three samples modeled. A shaded area is also provided for each solid in Fig. 8, which represents the concentration of each solid due to simple dilution. The upper boundary of each shaded area is defined by the sample with the highest solid concentration, and the lower boundary of the shaded area is defined by the sample with the lowest solids concentration. This shaded area does not consider changes in solids concentrations due to the reestablishment of equilibrium resulting from blending. As shown in Fig. 8, ferric hydroxide (Fig. 8(b)) and barium sulfate (Fig. 8(d)) follow the trend of simple dilution but the concentration of calcite (Fig. 8(a)) and aluminum hydroxide (Fig. 8(c)) remains relatively constant with an increase in the blend ratio. With larger ratios of freshwater mixed with produced water, the dissolved portion of calcium and aluminum tend to reproduce more solids, which compensate the effect of dilution and lead to the flatter curves shown in Fig. 8(a) and Fig. 8(c).

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

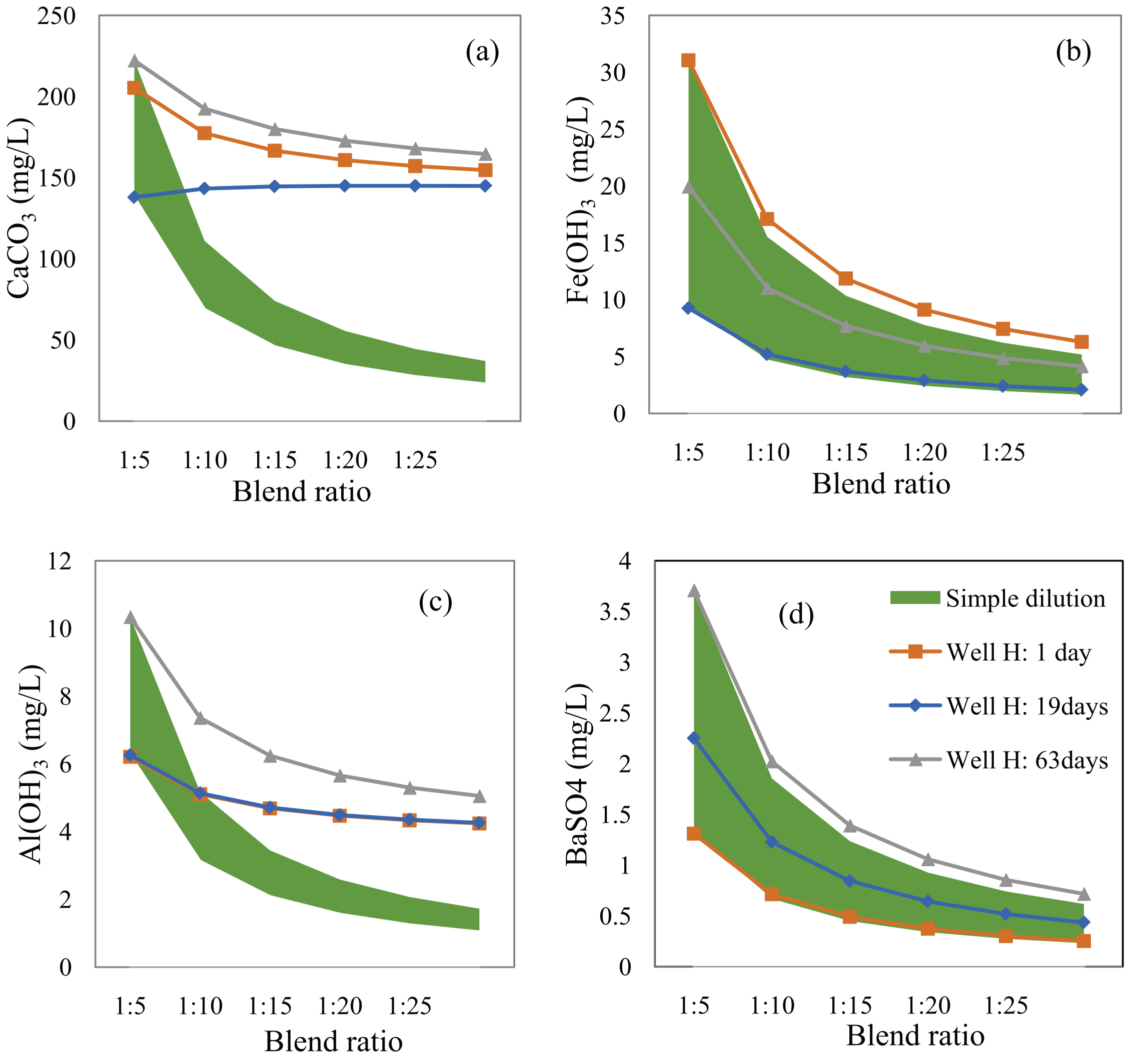


Fig. 8. Modeled blending of Well H samples collected at Days 1, 19, and 63 with calcite (a), ferric hydroxide (b), aluminum hydroxide (c) and barium sulfate (d).

4. Conclusions

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

- Fracturing fluid additives have a significant impact on at least the first 63 d of produced water quality, particularly in regard to the effect additive packages specific to cross-linked gel fluids have on the organic makeup of produced water.
- Produced water from wells fractured with gel fluids have a significantly greater organic compound load (>1,000 mg/L) compared with produced water from wells fractured with slickwater fluids (approximately 200–400 mg/L).
- Fracturing fluid additives have a greater impact on TOC concentrations in produced water over the first 63 d of production than contributions from the formation.
- Chemical coagulation decreases TOC concentrations by roughly 20% for produced waters from wells fractured with both gel and slickwater fluids, independent of their difference in makeup.
- Chemical coagulation can successfully reduce the turbidity of produced waters from wells fractured with both slickwater and gel fluids immediately after the start of production.
- Chemical coagulant demand for produced waters from wells fractured with gel fluids is roughly 25%–400% higher than that for wells fractured with slickwater fluids, with the demand from each produced water type decreasing with the age of the well.
- Similar organic compounds are detected from wells of fractured with slickwater fluid and fracture with gel fluids by using LC-MS and higher carbon group are needed more aluminum dose for coagulation process.
- Fracturing fluid additives have a large enough effect on the treatability of produced water that the impacts of different fracturing fluid types should be considered when blending produced water streams for water management and treatment.
- When produced water is blended with a fresh water source, solid species present in the system will not necessarily be diluted as expected due to the redistribution of chemical species caused by changes in equilibrium.

Acknowledgments

The authors would like to acknowledge Encana Corp. for providing samples and providing insight with the hydraulic fracturing operation. Funding for this research was provided by Encana Corp. and a Colorado State University internal grant. The authors acknowledge the technical support and work of Bradly Sick.

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Supplementary material

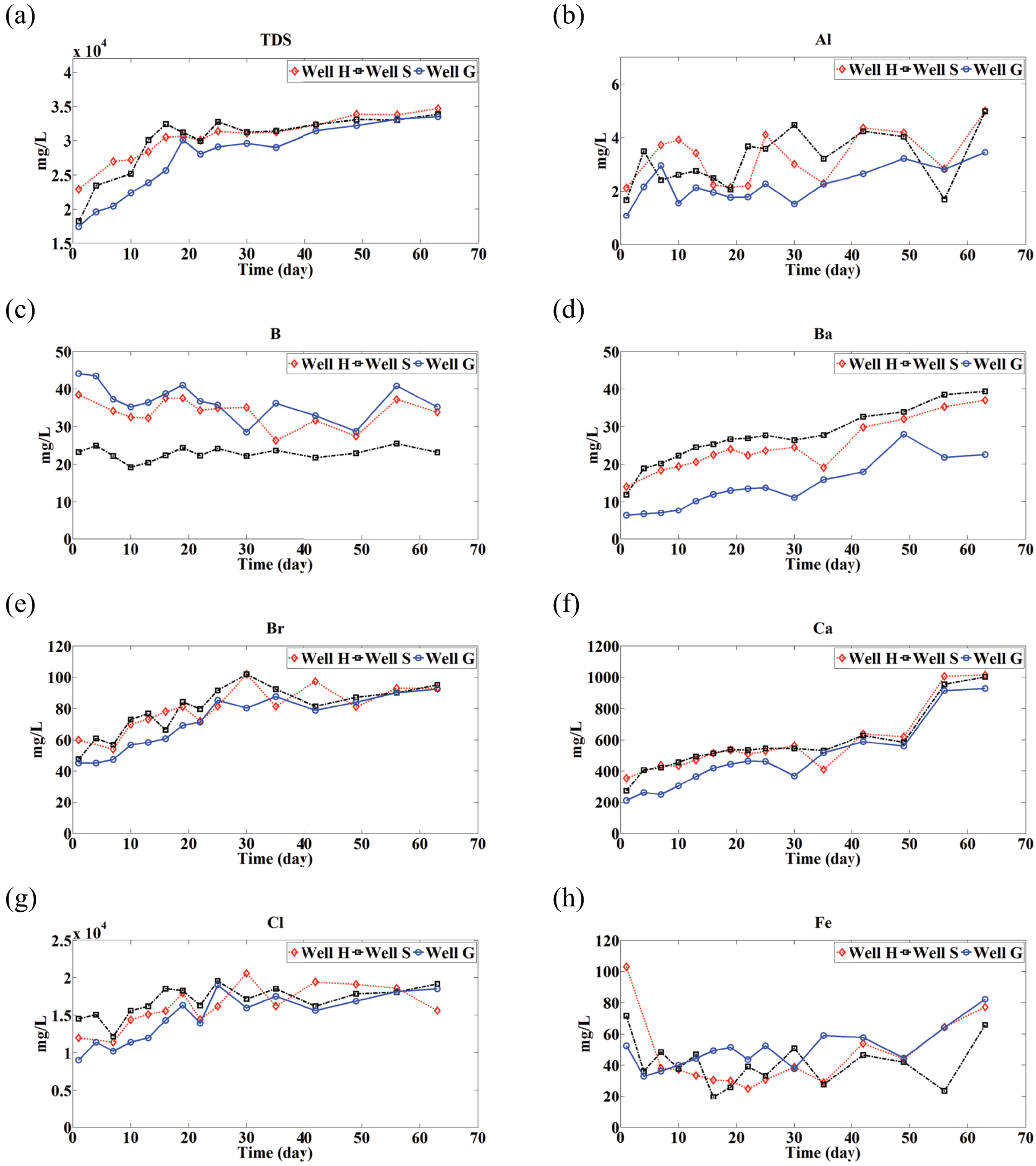

Fig. S1. (a) TDS, (b) Al, (c) B, (d) Ba, (e) Br, (f) Ca, (g) Cl, and (h) Fe trends for Wells H, S, and G.

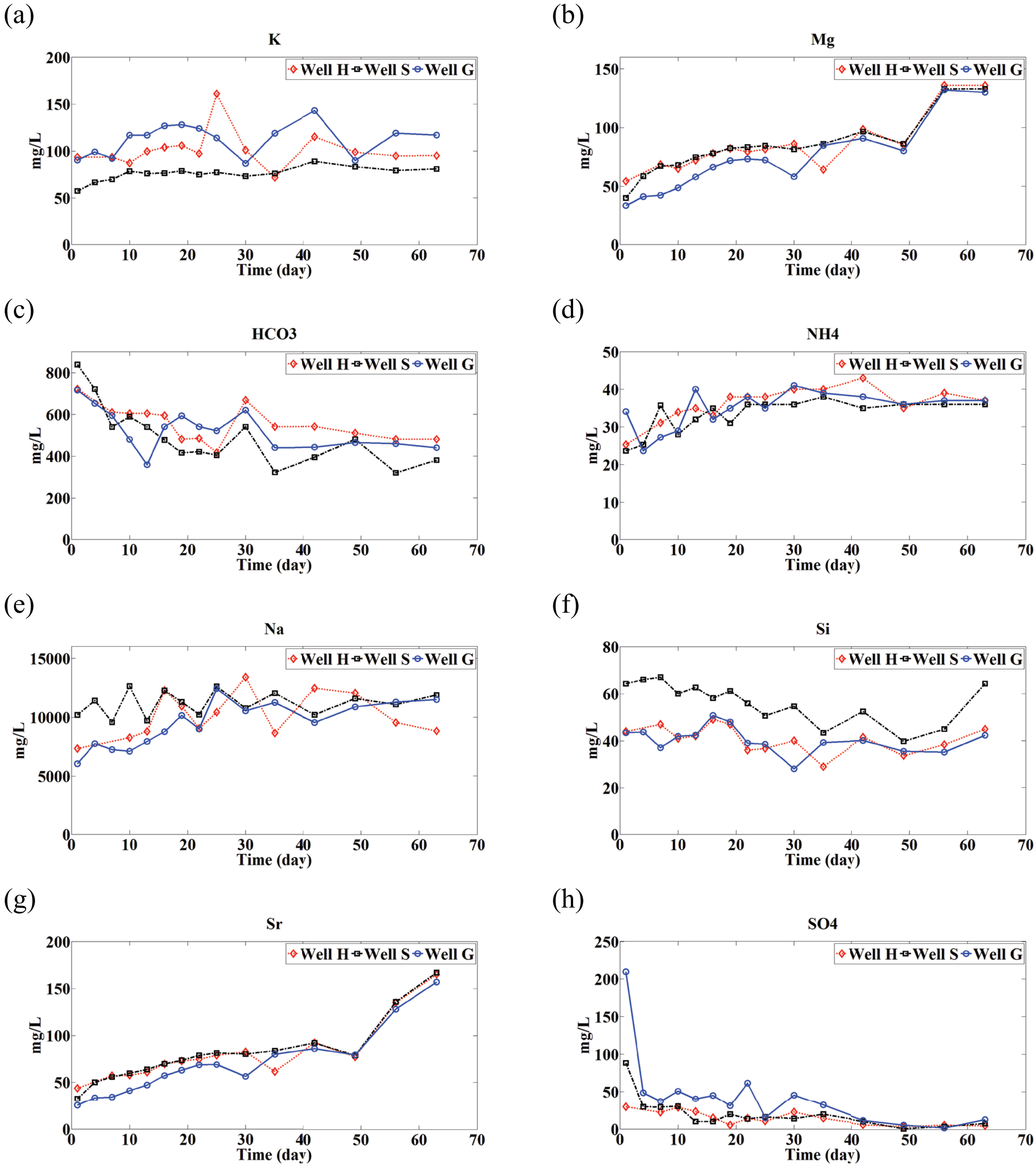

Fig. S2. (a) K, (b) Mg, (c) HCO_3, (d) NH_4, (e) Na, (f) Si, (g) Sr, and (h)SO_4 trends for Wells H, S, and G.

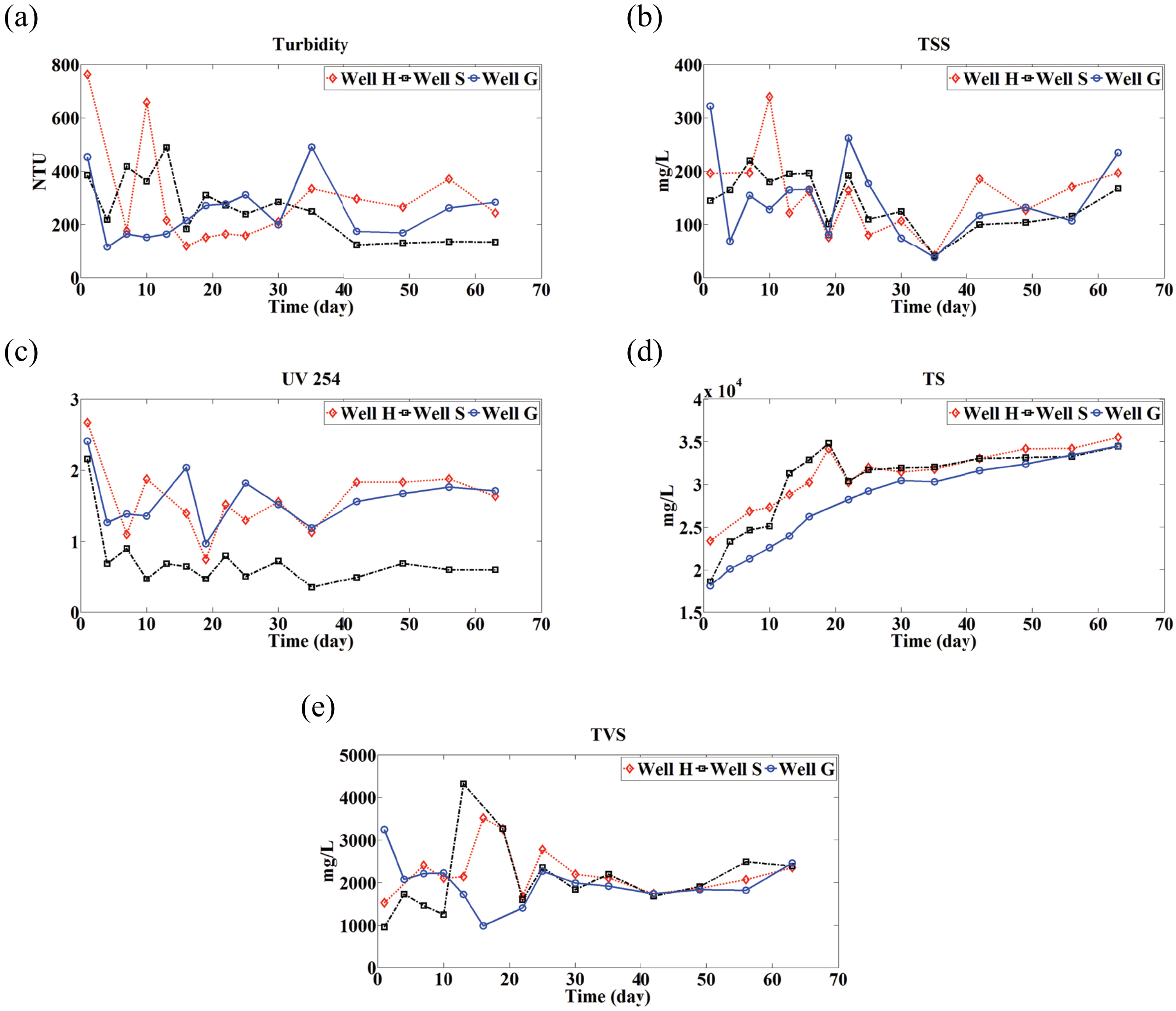

Fig. S3. (a) Turbidity, (b) TSS, (c) UV_{254}, (d) TS, and (e) TVS trends for Wells H, S, and G.

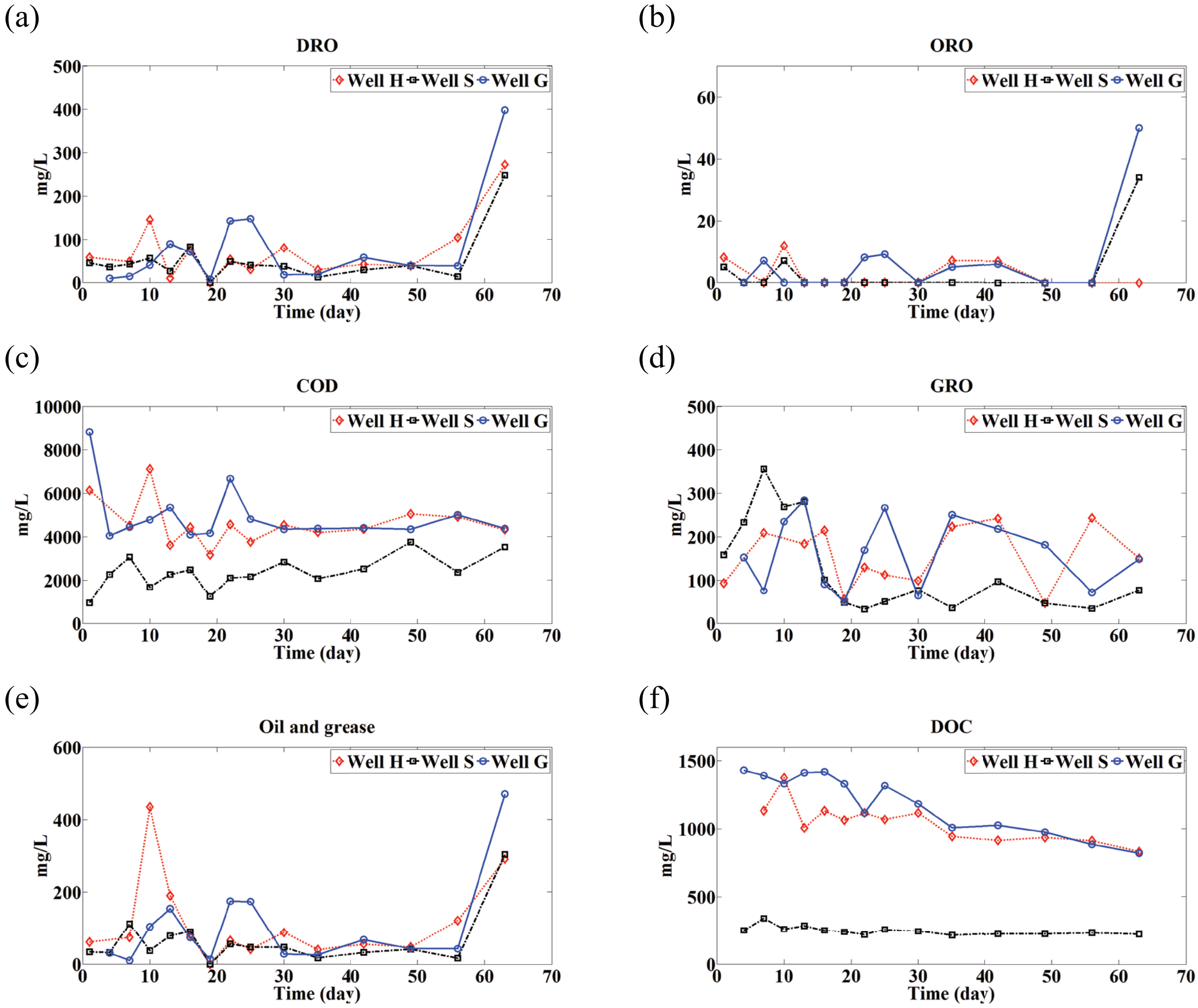

Fig. S4. (a) DRO, (b) ORO, (c) COD, (d) GRO, (e) oil and grease, and (f) DOC trends for Wells H, S, and G.

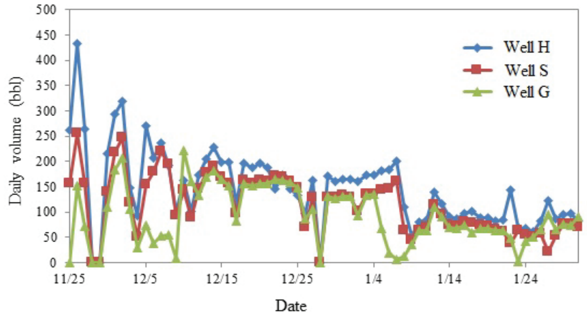

Fig. S5. Daily water production.

Table S1
Summary of limitation and assumption of using OLI analyzer for both aqueous phase and non-aqueous phase

Aqueous phase	Non-aqueous phase
Water content >65% Temperature: –50 to 300	Enhanced SRK equation of state was applied to determined non-aqueous and vapor fugacity coefficient
Pressure: 0 to 1,500 atm Ionic strength: 0 to 30	Vapor critical of temperature, pressure, volume, and acentric factor are correlated to find a Fugacity coefficient