Temporal characterization of flowback and produced water quality from a hydraulically fractured oil and gas well

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Keywords: Unconventional drilling, Hydraulic fracturing, Denver-Julesburg Basin, Produced Water, Flowback, NORM, Water Quality, Water Reuse

Abstract

This study examined water quality, naturally-occurring radioactive materials (NORM), major ions, trace metals, and well flow data for water used and produced from start-up to operation of an oil and gas producing hydraulically-fractured well (horizontal) in the Denver-Julesburg (DJ) Basin in northeastern Colorado. Analysis was conducted on the groundwater used to make the fracturing fluid, the fracturing fluid itself, and nine flowback/produced water samples over 220 days of operation. The chemical oxygen demand of the wastewater produced during operation decreased from 8,200 to 2,500mg/L, while the total dissolved solids (TDS) increased in this same period from 14,200 to roughly 19,000 mg/L. NORM, trace metals, and major ion levels were generally correlated with TDS, and were lower than other shale basins (e.g. Marcellus and Bakken). Although at lower levels, the salinity and its origin appear to be the result of a similar mechanism to that of other shale basins when comparing Cl^-/Br^- , Na^+/Br^- , and $\text{Mg}^{2+}/\text{Br}^-$ ratios. Volumes of returned wastewater were low with only 3% of the volume injected (11 million liters) returned as flowback by day 15 and 30% returning by day 220. Low levels of TDS indicate a more treatment-amenable wastewater, but low volumes of flowback could limit onsite reuse in the DJ Basin. These results offer insight into the temporal water quality changes in the days and months following flowback, along with considerations and implications for water reuse in future hydraulic fracturing or for environmental discharge.

50

51 1. Introduction

52 The use of unconventional drilling technologies (hydraulic fracturing and horizontal
53 drilling) has rapidly increased over the past 15 years. This is especially the case in
54 Colorado, where the number of active wells (both vertical and horizontal) increased from
55 22,228 to 53,228 between 2000 and 2015 (COGCC, 2015). The majority of the
56 unconventional drilling in Colorado currently takes place within the Wattenberg Field,
57 which has around 24,500 active wells in 2017 (COGCC, 2017). The Wattenberg Field is
58 the most productive area of the Denver-Julesburg Basin (DJ Basin), and contains several
59 formations, including the Niobrara Formation and the Codell Sandstone Member. The
60 benefit this intense activity has had on the U.S. economy and the region is tempered by
61 its potential impact on the local environment (Adgate et al., 2014) and, more pressingly,
62 on regional water quantity and quality (Goodwin et al., 2014; Vidic et al., 2013). These
63 concerns about water quantity arise from the significant volumes of water used in the
64 fracturing fluids during hydraulic fracturing, which range from 7 to 33 million liters per
65 well (Kondash and Vengosh, 2015; Malakoff, 2014). Following the hydraulic fracturing
66 process the well is flowed back, returning large volumes of water to the surface along
67 with the oil and gas, generating a stream of wastewater throughout the life of the well that
68 could negatively impact the regional water quality in the event of a spill or release
69 (Torres et al., 2016; Vidic et al., 2013).

70

71 Over 95 percent of this wastewater in the US is disposed of to Class II wells via deep
72 well injection (Clark and Veil, 2009; McCurdy, 2011). While this method is considered

to be the most economic and best practice for these wastewaters, it has recently been linked to seismic activity and potential environmental contamination (Ellsworth, 2013; Kassotis et al., 2016). These environmental impacts coupled with many shale basins being in semiarid regions, magnifies the importance of understanding these wastewaters (e.g. water quality, origins of salinity, to volumes returned) and increasing their treatment and reuse.

Oil and gas wastewaters generated by hydraulically-fractured wells are commonly called flowback and produced water. Flowback is typically defined by the oil and gas industry as the point when the well is flowed back to allow the flow of oil, gas, and water to the surface. Once this mixture is directed towards separators for on-site production facilities (i.e., oil/gas/water separators), the resulting water is termed produced water. Flowback and produced waters consist of a variety of constituents that are either present within the fracturing fluid used during the fracturing process, or contributed from the formation itself (Barbot et al., 2013; Gregory et al., 2011; Thurman et al., 2017). Additives used within fracturing fluids vary by operator and from formation to formation, but typically consist of surfactants, biocides, friction reducers, gelling agents, and gel breakers, each of which serves a role during the hydraulic fracturing process (Rogers et al., 2015; Stringfellow et al., 2014; Thurman et al., 2014). These components, especially the gel-based fracs, increase the organic chemical load of the returning wastewaters. This organic chemical load has been shown to decrease with time (Esmaeilirad et al., 2015) as the returning wastewater begins to resemble formation water (i.e. produced water).

Formation-based constituents consist of total dissolved solids (TDS), hydrocarbons, naturally occurring radioactive material (NORM), metals, and other elements (Alley et al., 2011; Zhang et al., 2014). These parameters are known to increase to levels present in the native formation water, particularly TDS. Since TDS is generally considered the greatest challenge in the treatment and reuse of produced water, understanding the rate at which mixing of the formation and injected waters occurs along with insights into the origin of the TDS (i.e. salinity) is important when considering reuse strategies. Furthermore, most research on NORM has focused on environmental monitoring, wastewater treatment, and radioanalytical chemistry of uranium (U), radium (Ra), and Ra decay products arising from flowback and produced waters, particularly from the Marcellus Shale (Nelson et al., 2015b, 2014; USGS, 2011; Zhang et al., 2014). However, very little is known about the concentration of NORM in flowback and produced waters in other formations of Devonian age, such as the Niobrara formation of the DJ Basin in northeastern Colorado.

A more detailed view of the water quality characteristics of returning wastewaters and their volumes over time is needed to guide treatment and re-use efforts, and catalog indicator constituents in the event of a spill or release. Accordingly, the objectives of this study were to examine a single well in the Denver-Julesburg Basin over more than 7 months to (1) determine basic water quality, elemental composition, the origin and nature of salinity, and NORM concentrations of waters used and produced, (2) measure the volume of the returning flowback and produced waters over time; and (3) suggest reuse strategies and implications for the oil and gas wastewaters, based on the findings.

119

120 **2. Methods**

121 2.1. Site and Sampling Description

122 Water samples were collected from a single horizontally-fractured well on a multi-well
123 pad in the Wattenberg Field (Weld County, CO). The oil and gas producing well (wet),
124 had 28 stages (~1800m) targeting the Niobrara formation, and occurred at a depth of
125 2100 m. During the hydraulic fracturing process, a water sample was collected from a
126 storage tank onsite, prior to the generation of a gel-based fracturing fluid. The water
127 sample originated from shallow groundwater, from a nearby well. In addition to the
128 groundwater, a sample of gelled fracturing fluid was also collected. The gelled fracturing
129 fluid was broken using concentrated tert-butyl peroxide at 10%, and was heated for 1
130 hour at 110°C to return this complex mixture (semi-solid) to a liquid state that could be
131 investigated using standard wastewater analysis techniques. This method was selected
132 since 10% tert-butyl peroxide was used in this well as the breaker, and since the operator
133 noted that high-temperatures were required for breaking. This resulted in several
134 preliminary experiments at 10% tert-butyl peroxide under different temperatures, with
135 110°C being chosen, since it yielded a completely dissolved mixture.

136

137 Flowback of the well was initiated after hydraulic fracturing and a one-month shut-in
138 following the wells completion (shut-in: well closed after hydraulic fracturing to allow
139 for other wells onsite to be fractured or to finish the construction of production facilities
140 prior to flowing back a well), with the first water sample being collected on the first day
141 of flowback (D1). The second water sample was collected on the fourth day of flowback

(D4). After day four, the well was again shut in to set up for onsite production (oil/water/gas separator), which lasted three days. Following this period, another water sample was collected on the seventh day (D7) of flowback (not counting the three-day shut in). Water samples were also taken on the 15th (D15), 22nd (D22), 55th (D55), 80th (D80), 130th (D130), and 220th (D220) day following the flowing back of the well. D1 and D4 were taken from a flowback tank (emptied every 4-6 hours) for our individual well, whereas D7 to D220 were collected from an oil/water/gas separator (sampling port) that isolated the individual well, from the other hydraulically fractured wells on-site. After collection in burned glass amber bottles (1L, headspace free), the water samples were immediately transported to the lab (~2 hr after collection) and stored at 4°C for up to 5 days prior to analysis. The wells water production was collected from the separators onsite meter (i.e. daily water production), while the total volume used for fracturing fluid was obtained from the well's FracFocus (FracFocus) report and was verified by the operator.

2.2. General Water Quality, Inorganic Ions, and Metals Analysis

Total dissolved solids (TDS), total suspended solids (TSS), and volatile suspended solids (VSS) were determined by Standard Methods (Eaton and Franson, 2005). The pH was determined using a ThermoSci Orion meter (Thermo Scientific). Turbidity was measured with a turbidimeter (Hach 2100N). Chemical oxygen demand (COD) was measured using kits (Hach method 8000) after dilution to reduce Cl⁻ interference and a spectrophotometer (Hach DR5000). Alkalinity was determined using Hach method 8203. These parameters

were selected as classic indicators of wastewater, that have also been used to assess oil and gas wastewater (Lester et al., 2015; Metcalf and Eddy, 2014; Riley et al., 2016).

The Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado Boulder performed the inorganic ion and metal analysis. Metals and trace elements were measured by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer SCIEX Elan DRC-e). Anions were measured by ion chromatography (Dionex Series 4500I). Major cations were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; ARL 3410+, Thermo Scientific). These three methods have been used in previous flowback and produced water research, resulting in them being selected for the research conducted here (Barbot et al., 2013; Kim et al., 2016; Lester et al., 2015; Riley et al., 2016; Warner et al., 2013).

2.3. Naturally-Occurring Radioactive Material Analysis

All samples for radionuclide analysis (with the exception of ^{238}U) were collected unfiltered, shipped to the State Hygienic Laboratory at the University of Iowa, and acidified (nitric, Fisher ACS Plus, pH<2) for several days prior to analysis. All samples were counted for 60,000 s on high-purity germanium (HPGe) gamma spectrometers (Canberra or ORTEC, running GammaVision version 7.02, Env32 analysis method) as previously described (Nelson et al., 2014). The State Hygienic Laboratory at the University of Iowa is accredited by the U.S. National Environmental Laboratory Accreditation Program (NELAP, www.nelac-institute.org); all HPGe measurements and quality control measures met standards established by NELAP. After HPGe, sub-samples

were prepared by American Society for Testing and Materials (ASTM) method D7535–09 and counted (60,000 s) by gas-flow proportional counting (Canberra LB4200) to determine levels of ^{210}Pb (<http://www.astm.org/Standards/D7535.htm>). Note that Pb pre-concentration varied slightly from the ASTM method: Fe carrier was decreased from 20 to 2 mg and 10 mg KMnO_4 was added prior to Pb pre-concentration and separation on Pb resin (Eichrom Technologies, LLC, Lisle, Illinois). Sub-samples (0.5 L, $n = 3$) were prepared for isotope-dilution alpha spectrometry using polonium-209 (^{209}Po ; 25 mBq tracer; Eckert and Ziegler CRM 92565) as a tracer to determine levels of ^{210}Po . Polonium was separated by autodeposition onto silver or nickel disks based on established methods and counted (360,000 s minimum) in vacuum-controlled alpha spectrometers as previously described (Knight et al., 2014; Nelson et al., 2015a). Radioactivity concentrations of ^{210}Pb and ^{210}Po in this dataset represent total activities (residual solids and soluble).

Activities of ^{238}U were determined by mass spectrometry (ICP-MS, Elan DRC-e) at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado Boulder. Ratios of uranium-238 radioactivity concentrations to uranium-234 radioactivity concentrations ($^{234}\text{U}/^{238}\text{U}$) were determined by alpha spectrometry using Eichrom method (ACW02) and uranium-232 (^{232}U ; 50 mBq tracer; Eckert and Ziegler CRM 92403) as a tracer. All radioactivity concentrations were decay corrected to the time of collection using standard decay correction equations.

3. Results and Discussion

3.1 Composition of Groundwater, Fracturing Fluid, and Flowback/Produced water Over Time

210 The water quality data for groundwater, fracturing fluid, and the flowback/produced
 211 water samples are presented in Table 1. The groundwater had COD, turbidity, alkalinity,
 212 and TDS levels similar to those commonly found in the regional groundwater (Arapahoe
 213 Aquifer;(COGCC, 2007). This moderately-saline water contained metal concentrations
 214 below the median for regional water-table monitoring wells, while inorganic ion levels
 215 were higher than the median (Musgrove et al., 2014). The broken gelled fracturing fluid
 216 had a COD of 115,000 mg/L substantially higher than the ground water, while its TDS
 217 was greater at 3,330 mg/L. These results would be expected, considering the substantial
 218 amounts of chemical additives used to make the fracturing fluid that would contribute a
 219 significant level of COD. The TDS was also expected, since it was anticipated that the
 220 TDS would originate from the ground water (2,120 mg/L) along with some of the
 221 additives, either organic or inorganic, that would be dissolved and thus contribute to the
 222 TDS. However, it should be noted that although the TDS was higher (Table 1), the major
 223 ions and trace metals detected were lower for the fracturing fluid then the ground water
 224 (Table 2), which was not anticipated.

225

226 Table 1: Water quality data for the groundwater, fracturing fluid (Frac Fluid), and the
 227 returning flowback and produced water samples. Volume returned and its percentage of
 228 the total volume (cumulative) used to fracture the well (~11,000,000 L) are included.

Time (days)	Cumulative Volume Returned (L)	Cumulative Volume Returned (%)	COD (mg/L)	pH	Alkalinity (mg/L)	Turbidity (NTU)	TSS (mg/L)	VSS (mg/L)	TDS (mg/L)
GW			46.8	7.37	119	9.7	850	350	2,120
Frac Fluid			115,000	4.65	600	552	*ND	*ND	3,330
1	31,000	0.3%	8,215	7.42	1,070	1,835	10,900	7,000	14,220
4	110,000	1.0%	3,900	7.10	700	109	6,400	3,100	14,613

7	180,000	1.6%	4,725	7.05	850	177	7,550	3,350	17,763
15	306,000	2.8%	4,305	6.90	570	194	7,550	3,200	18,586
22	365,000	3.3%	3,825	6.56	440	371	7,600	4,750	19,433
55	1,410,000	12.7%	2,837	6.83	612	196	9,200	4,525	15,320
80	1,830,000	16.5%	2,890	6.89	553	283	5,467	3,900	16,967
130	2,630,000	23.7%	2,650	7.01	479	214	4,100	1,800	17,482
220	3,330,000	29.8%	2,543	6.80	475	223	3,433	2,467	18,756

229 *Non-detect (ND)

230

231 The flowback sample collected on D1 was expectedly different than the groundwater,
232 with regards to all of the water quality variables investigated (except pH), given the
233 addition of fracturing fluid chemicals and storage in the borehole for over a month prior
234 to flowback (Table 1 and 2). However, it was anticipated that the broken fracturing fluid
235 and the D1 sample would be similar in water quality, because only 31,000 L returned by
236 D1. This 31,000 L is around a quarter of the borehole's volume, which suggests that the
237 D1 sample would not reach the formation and would reside in the borehole only (120,000
238 L; 0.2 m x 3.6 km [borehole dimensions]). Due to this, it was anticipated that the samples
239 TDS of the samples would be similar to the groundwater (i.e. water used to make the
240 fracturing fluid), while its COD would be similar to the fracturing fluid. Neither
241 occurred, with the TDS being around 7 times that of the groundwater, and the COD being
242 14 times less than that of the fracturing fluid. This is likely from the TDS being
243 introduced by the formation through various mechanisms (i.e. mixing, migration, and
244 extraction of formation brine), while the levels of COD could be due to natural
245 attenuation (i.e., diluted, degraded, or sorbed in the borehole).

246

247 The D1 TDS levels support the notion that the injected water was likely mixed to some
248 degree with saline formation brine (TDS discussed in greater detail in section 3.2). The

COD levels could also be explained by dilution and mixing with formation brines, while other potential mechanisms, such as adsorption/absorption or biological degradation could have also contributed to the lower than expected COD levels observed. It is likely that the injected fracturing fluid was mixed to some degree (i.e. diluted) with the naturally occurring formation water that had lower levels of COD (higher TDS). Another possible mechanisms, was sorption, since there are vast amounts of mud, shale, hydrocarbons, and other components that could be present within the borehole that could remove COD from the flowback. In addition, it is also possible that biodegradation occurred down-hole, even in the presence of biocides, which have been shown to be less effective than anticipated in fracturing wastewaters (Vikram et al., 2014). The notion of biodegradation is further supported by the elevated alkalinity levels (Connolly et al., 1990; Porowski, 2001; Warner et al., 2013) – the alkalinity of the groundwater was 119 mg/L (as CaCO_3 ; Table 1) and increased almost an order of magnitude by the first day of flowback (D1, 1070 mg/L CaCO_3 ; The increase in alkalinity suggests that methanogenesis or fermentation occurred, which is also reinforced by the removal of SO_4^{2-} , which may have acted as an electron acceptor under anaerobic conditions (Figure 1b; Haluszczak et al., 2013; Ziemkiewicz and He, 2015). However, it should be noted that the decreasing levels of SO_4^{2-} could have been related to Sr^{2+} or Ba^{2+} precipitation (SrSO_4 or BaSO_4), which did increase to a higher degree (Sr^{2+} ; 2.5x and Ba^{2+} ; 2.8x) than other trace elements over the course of the study, except Mg^{2+} (Table 2; Haluszczak et al., 2013; Ziemkiewicz and He, 2015) Therefore, it is probable that these three mechanisms all occurred to some degree with the month-long shut-in playing a significant role. That is, the shut-in likely provided the time for diffusion or transport of

oil and water through the borehole (i.e. mixing to diffusion), which is supported by the well producing 40% oil (vol:vol) on D1, as well as time for sorption and biodegradation, resulting in these levels of COD and TDS on D1.

The sample collected on D4 had a similar TDS value to that of D1, and also likely returned prior to reaching the formation fissures (110,000 L; Table 1). However, the sample had reductions greater than 50% of numerous water quality variables (e.g. 50%, COD; 59%, TSS; and 65%, alkalinity), illustrating the change that occurred from D1 to D4. This rapid change over a short number of days was not seen for the remainder of the study, as demonstrated by samples returning between D7 to D22 that had steady decreases in COD and pH and increases in TSS, turbidity, and TDS (Table 1). After D7, the volume returned was greater than that of the borehole volume (Table 1), which indicates those waters were likely influenced by the formation (i.e. imbibition) and the naturally occurring formation water to a greater degree (i.e. further dilution by formation water, extraction of tightly bound pore water, or natural attenuation) than the samples returned on D1 and D4.

The samples collected on D55 to D80 exhibited a decrease in COD and TSS of 17% and 40% respectively, but had smaller changes for other water quality variables, such as TDS (<17,000 mg/L). After D80, COD decreased slowly and TDS progressively increased to D220 (Figure 1a). These results illustrate the substantial water quality changes that occur over the first few days of flowback and how water quality variability then steadies out during the well production period for certain variables. Similar results for TDS were seen

for two other wells that were studied overtime in the DJ-Basin, with the researchers TOC values showing trends similar to those of our COD results (0 day to 200 days; (Kim et al., 2016). These differences over time will impact the management options for possible reuse of the wastewater (discussed in section 3.4), with COD being the variable of significant change, not TDS, which is generally seen in other shale basins (Cluff et al., 2014).

Figure 1: Variation of (A) COD and TDS of the groundwater, flowback, and produced water samples with time, and (B) alkalinity and SO_4^{2-} of the groundwater, flowback, and produced water with time. Note: The time point “0” is the groundwater used to generate the fracturing fluid.

3.2. Origin of Salinity in Flowback and Produced Waters

The TDS of the flowback and produced waters were much lower than the TDS of flowback and produced waters from other US shale formations (Barnett, 60,000 mg/L; Woodford, 110,000 mg/L; Permian, 140,000 mg/L; Marcellus Shale, 180,000 mg/L; Osborn et al., 2012; Warner et al., 2013), but similar to the TDS of the Fayetteville Shale and other flowback and produced waters collected in the Denver-Julesburg Basin (Niobrara Shale; Esmaeilirad et al., 2015; Lester et al., 2015; Warner et al., 2013). The composition of the waters returned from this well were predominantly Na-Cl- HCO_3 with negative MCl_2 values for all samples ($\text{MCl}_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Ba}^{2+} + \text{Sr}^{2+} - \text{SO}_4^{2-} - \text{CO}_3^{2-}$; Connolly et al., 1990; McCaffrey et al., 1987), while sodium and chloride comprised greater than 95% of the TDS concentration.

Table 2: Major ions and trace elements identified in the groundwater and flowback/produced water samples over time.

Constituent	Sample										
	Ground Water	Frac Fluid	D1	D4	D7	D15	D22	D55	D80	D130	D220
Major Ions (mg/L)											
Cl^-	1,160	360	6,524	7,886	7,640	9,435	10,359	8,806	10,036	9,927	11,650
Br^-	0.7	5.6	86.0	101.4	111.2	124.5	128.6	109.3	128.4	143.7	168.5
SO_4^{2-}	121.1	8.96	74.9	64.0	65.6	42.6	38.9	14.4	21.1	31.6	8.7
HCO_3^-	145.0		1,303	853.5	1,036	695.1	536.7	746.4	674.4	584.1	579.3

Trace Elements (mg/L)											
Mn ²⁺	0.02	DL	0.5	0.88	0.66	0.88	0.97	0.50	0.43	0.41	0.34
Fe ³⁺	0.5	0.9	43.4	69.3	51.1	64.3	54.5	30.4	28.9	33.0	19.2
Mg ²⁺	20.8	3.7	15.3	20.7	26.2	34.5	38.4	26.8	26.8	34.3	38.1
Si	3.9	DL	46.7	47.8	46.5	47.8	43.6	47.7	48.0	48.8	37.2
Al ³⁺	0.03	DL	0.4	0.84	3.3	DL	DL	DL	DL	DL	0.01
Ca ²⁺	77.3	18.5	171.7	197.9	163.3	229.2	256.6	185.1	226.5	243.1	266.9
Na ⁺	587.4	145.7	4,385	4,858	4,659	5,799	6,095	5,717	6,128	6,187	6,934
K ⁺	5.9	26.3	21.5	23.9	32.7	49.0	54.7	27.8	30.2	26.5	30.2
Ba ²⁺	0.05	0.02	4.8	6.6	7.3	10.9	14.2	9.3	9.7	12.8	13.7
Sr ²⁺	0.6	0.06	15.7	20.5	22.9	31.4	39.5	25.7	31.4	35.6	40.0

322 Detection Limit (DL) for Al³⁺ 0.0001 mg/L; Mn²⁺ 0.0003 mg/L; Si 0.025 mg/L

323 The ratio of chloride, sodium, and magnesium to bromide (Cl⁻/Br⁻, Na⁺/Br⁻ and Mg²⁺/Br⁻)
324 can provide insight to the origins of the salinity in oil and gas wastewaters (Balashov et
325 al., 2015; Barbot et al., 2013; Haluszczak et al., 2013; Stewart et al., 2015; Warner et al.,
326 2013; Ziemkiewicz and He, 2015). The water returned from this well was characterized
327 by Cl⁻/Br⁻ ratios of 68-80 (Figure 2a), which is lower than the Cl⁻/Br⁻ ratio found in other
328 flowback and produced waters in the Denver-Julesburg Basin (91-156, Rosenblum et al.,
329 2016; 156, Lester et al., 2015, and 212-228, Esmaeilirad et al., 2016), but similar to Cl⁻
330 /Br⁻ ratios found in flowback and produced water from the Fayetteville Shale (Warner et
331 al., 2013). These Cl⁻/Br⁻ values are also similar for some Marcellus Shale flowback and
332 produced waters, although the Marcellus samples have much higher Cl⁻ and Br⁻
333 concentrations (Figure 2a; Chapman et al., 2012; Hayes, 2009). Similarly, the ratio of
334 Na⁺/Br⁻ and Mg²⁺/Br⁻ are also comparable to other shale basins (Figures 2b and 2c;
335 Hayes, 2009; Warner et al., 2013). The Cl⁻/Br⁻, Na⁺/Br⁻, and Mg²⁺/Br⁻ plot along the
336 fresh water dilution line described in Dresel and Rose (2010) suggesting that the injected
337 waters (low TDS) under went mixing with the subsurface brine. Therefore, the data then
338 suggests that the origin of the flowback and produced waters salinity is from evaporated
339 seawater modified by halite precipitation and dilution by meteoric water (i.e. dilution of

injected water by evaporated seawater; Haluszczak et al., 2013; Hayes, 2009; McCaffrey et al., 1987; Warner et al., 2013).

The notion that these flowback and produced waters originated from modified evaporated seawater that was diluted by the injected water is further supported by performing a simple mass balance. This was done similarly to that of Kondash et al. (2017), using the following equation with the results presented in SI Figure 1.

$$\text{Percentage of Final TDS} = \frac{TDS(t) - TDS(\text{initial})}{TDS(\text{Final}) - TDS(\text{initial})} \times 100$$

The results show that on D1 nearly 70% of the TDS was associated with the formation, while by D7 it was more than 90% (SI Figure 1). This result indicates that the salinity of these flowback and produced waters originated from the formation, as has been demonstrated for other basins (Rowan et al., 2015; Warner et al., 2014). However, the time it took to reach this fraction of final TDS does not follow the current literature (Kondash et al., 2017). The flowback on D7 had 90% of its TDS originate from the formation. In the Marcellus and Barnett shales, it took nearly 60 days for the returning waters to reach 85% (Kondash et al., 2017). This suggests that the diffusion of the salts into the flowback water occurred at a faster rate, and is likely explained by the 30-day shut-in period; that provided the time for mixing and diffusion of the TDS into the returning flowback water.

Figure 2: Levels of (A) Cl^- , (B) Mg^{2+} , and (C) Ca^{2+} plotted versus Br^- in flowback and produced waters in Colorado (Denver-Julesburg Basin [DJ (this study) and DJ Literature; Esmailirad et al., 2015; Lester et al., 2014; Riley et al., 2016; Rosenblum et al., 2016), Arkansas (Fayetteville; Warner et al., 2013), Pennsylvania (Marcellus; Hayes, 2009), and Seawater Evaporation (McCaffrey et al., 1987).

Another consideration for the salinity of the flowback and produced waters from the Denver-Julesburg Basin is understanding why the salinity (i.e. TDS) minimally changed over the study and by what process the salinity was introduced. For Marcellus brines, (Balashov et al., 2015) suggested that a temporal increase of salt concentration in flowback can be explained by salt diffusion from capillary-bound or free brine present in the shale matrix to the injected water that fills the fractures after hydraulic fracturing. This process may be responsible for the TDS concentrations in the Denver-Julesburg Basin samples because we saw high concentrations of TDS on D1 that likely occurred as a result of the 30-day shut-in period prior to flowing back the well. This shut-in period would have provided the time for diffusion of salts from the capillary-bound or free brine in the shale matrix to the injected fluid in the new fractures. This theory is supported by the volume of oil produced by D1 (40% vol:vol), along with the small increase in TDS over the 220 day study period (Figure 2). Balashov et al. (2015) also proposed that this diffusion of capillary-bound or free brine will continue to increase the concentration of TDS for up to 12 months, at which point a pseudo-steady state of salinity and TDS concentration will be achieved. The TDS concentrations measured in the produced water from our well follow a trend over time (Figure 2) similar to that measured by Balashov et al. (2015) and support their theory about achieving a pseudo-steady state, which appears to have occurred by the end of our study.

3.3. Naturally Occurring Radioactive Materials

A comparative analysis of ^{238}U and ^{234}U in the groundwater and subsequent flowback and produced waters from the well over time indicated that U radioactivity (and mass) levels

were highest in groundwater (34 mBq/L or 2.75 µg/L), while levels in flowback/produced waters steadily declined from 14 mBq/L (1.16 µg/L) on D1 and below detection by D220 (<0.02 mBq/L or <0.002 µg/L; Figure 3A). Similar to Phan et al. (2015), we observed that levels of U were highest in the water returning from the well on D1 (14.3 mBq/L or 1.16 µg/L), but steadily decreased over time and remained less than 1 mBq/L (<0.1 µg/L).³⁷ The ratio of $^{234}\text{U}/^{238}\text{U}$ was lower in the groundwater (1.28) than those observed initially in flowback/produced water (e.g., D1 $^{234}\text{U}/^{238}\text{U} = 2.07$; Figure 3C). The initial enrichment of ^{234}U at D1 decreased with subsequent sampling of produced water over time, which suggests that although the total levels of U decreased, a new source of U (such as interstitial fluids in the Niobrara formation) was introduced to the produced waters. Despite this transient increase in $^{234}\text{U}/^{238}\text{U}$ ratios, the total radioactivities of ^{234}U and ^{238}U combined remain below public health guidelines for $^{\text{nat}}\text{U}$ ingestion according to the Safe Drinking Water Act (i.e., 30 µg/L $^{\text{nat}}\text{U}$; US EPA, 2000) U levels in this dataset represent total U (residual solids and aqueous phase), with future work needed to determine the relative contributions of U levels in soluble and particulate phases.

The data presented here corroborates with the only other published study the authors could find on U levels from the Niobrara formation, Tourtelot (1956), whom observed U concentrations in the Niobrara formation were generally less than 10 mg/kg (≤ 120 Bq/kg). For comparison, portions of the Marcellus Shale contain approximately 100 mg/kg (~ 1200 Bq/kg). Thus, based on the relatively lower concentrations of ^{238}U parent radionuclide in the targeted Niobrara formation (Tourtelot, 1956), we expected

and observed levels of NORM in flowback and produced waters lower than those from Marcellus Shale wells reported by others (Barbot et al., 2013; Haluszczak et al., 2013; USGS, 2011). Additionally, we observed radiochemical disequilibrium (Fig 3A-C) which likely arose from various water chemistry factors (pH, redox conditions, concentration of divalent cations, etc.).

Several researchers have investigated ^{226}Ra and ^{228}Ra in Marcellus Shale waste (Barbot et al., 2013; Nelson et al., 2015a, 2014; USGS, 2011); however, to our knowledge no information is available about the levels of these radionuclides in the Denver-Julesburg basin wastewaters. In contrast to observations for U, we observed the lowest value of ^{226}Ra in groundwater (at or below critical level, 58 Bq/L), while the highest level of ^{226}Ra was observed on D15 (3,150 mBq/L, Figure 3A). In all samples, levels of ^{228}Ra were below critical levels (i.e., < 150 mBq/L), but still ten times the drinking water standard of 185 mBq/L (US EPA, 2000) Notably, the levels of ^{226}Ra and ^{228}Ra in the flowback or produced waters were substantially lower than typical levels of ^{226}Ra and ^{228}Ra reported from Marcellus Shale wastewaters (670,000 mBq/L and 76,000 mBq/L respectively (Nelson et al., 2015a, 2014). Due to the high levels of SO_4^{2-} observed in waters in this study, Ra is likely in the insoluble RaSO_4 form ($K_{\text{sp}} = 4.25 \times 10^{-11}$; Kirby and Salutsky, 1964; Zielinski et al., 2001). Ra levels in this dataset represent total Ra (residual solids and aqueous phase). Future studies aim to determine the relative contributions of soluble Ra (i.e., Ra^{2+}) from insoluble Ra (i.e., RaSO_4).

There is a paucity of literature on the radioactivity concentrations of ^{210}Pb and ^{210}Po in flowback/produced water from an unconventional well over time (Figure 3B). In a

closed-system like the Niobrara, we expect that ^{210}Pb and ^{210}Po to be in secular equilibrium (i.e., radioactivity levels should be equal to one another and all progenitors (Nelson et al., 2015c). We observed radiochemical disequilibrium (Figure 3B) between ^{210}Pb ($t_{1/2} = 22.2$ years) and its decay product ^{210}Po ($t_{1/2} = 138.4$ days), which suggests differences in solubility in waters characterized in this study (NNDC, n.d.). (“National Nuclear Data Center, NuDat 2 database [Internet]. <http://www.nndc.bnl.gov/nudat2/>: National Nuclear Data Center, Brookhaven National Laboratory; 2013. Available from: <http://www.nndc.bnl.gov/nudat2/>,” n.d.) We observed that levels of ^{210}Pb were lowest in the groundwater (3.4 mBq/L) and generally increased over time along with stable Pb concentrations, with the highest ^{210}Pb radioactivity concentration observed on D220 (43 mBq/L). All values of ^{210}Pb remain below US Environmental Protection Agency (US EPA) guidelines for ^{210}Pb exposure by ingestion (115mBq/L).³⁷ Radioactivity concentrations of ^{210}Po were also low—well below US EPA drinking water guidelines (555 mBq/L for alpha emitters; US EPA, 2000) Similar to ^{210}Pb , the lowest value for ^{210}Po was observed in the groundwater (2.4 mBq/L), with higher values observed (maximum 9.0 mBq/L) with subsequent sampling of flowback/produced water. Thus, the observed disequilibrium between ^{210}Pb and ^{210}Po suggests differences in water chemistry for these two radionuclides, i.e., the increased levels of ^{210}Pb relative to ^{210}Po cannot be exclusively explained by mobilization of residual solids. Radioactivity concentrations of ^{210}Pb and ^{210}Po were low and present minimal occupational and public health risk; however, their ingrowth is supported by ^{226}Ra and should be considered in any long-term waste management strategy (Nelson et al., 2015a).

Figure 3: Variation of (A) ^{226}Ra ; (B) ^{210}Po , ^{210}Pb , and ^{238}U ; and (C) the ratio of ^{234}U to ^{238}U over time from the groundwater (0) to 220 days after flowing back the well. Note the different scale in the y-axis for B.

3.4 Implications for Treatment and Reuse

The reuse of local flowback and produced water is challenging for a number of reasons including variable water quality, low flowback volumes, and lack of guidance on reuse water quality targets for the industry. This has resulted in minimal treatment in the DJ-basin to date, which is compounded by the volumes returned. These low water volumes, make onsite reuse for other fracturing operations a challenge without a regional facility to collect enough water (11 million liters) from multiple wells (approximately 36 wells based on the volumes measured herein by day 15), to fracture one additional well. However, the potential for reuse in the Denver-Julesburg Basin, and specifically the Wattenberg Field, should not be discounted because there are currently over 24,000 wells in operation, and many more planned (COGCC, 2017).

A centralized treatment facility that is designed to manage flowback and produced water for the basin, could provide tailored water either for future hydraulic fracturing or generate water of environmental discharge quality. In either case, the first treatment step would likely be the removal of suspended solids and scale-forming agents. The flowback and produced waters studied showed substantial levels of suspended solids that decreased over time (Table 1), along with some scale-forming constituents that either decreased (HCO_3^-) or increased (Ca^{2+} , Sr^{2+} , Ba^{2+}). Suspended solids could be targeted with coagulation-flocculation-based methods (chemical or electrocoagulation), which have shown to be effective for turbidity and suspended solids removal for Denver-Julesburg Basin waters, even at low concentrations of chemical coagulant (FeCl_3 , 5 mg/L; Lobo et

al., 2016; Rosenblum et al., 2016) The addition of water softening could also be implemented to target scale forming constituents, which would likely be necessary given the increasing levels of divalent cations in the flowback and produced waters over time (Esmailirad et al., 2015).

Treatments targeting future hydraulic fracturing would also need to consider both organic and some inorganic constituents because they are known to affect the viscosity of gel-based fracturing fluids. Esmailirad et al. (2016b) showed mono-, di-, and trivalent cations, along with phosphorus and total organic carbon (TOC), can reduce the viscosity of gel-based fracturing fluids. Guar-based fluids made from recycled produced water were negatively impacted by Na^+ ($> 5,000 \text{ mg/L}$), Ca^{2+} ($>200\text{mg/L}$), Fe^{3+} ($>75 \text{ mg/L}$), and PO_4^{3-} ($>3 \text{ mg/L}$), while Esmailirad et al. (2016a) demonstrated TOC ($> 1000 \text{ mg/L}$) was a factor for a carboxyl methyl cellulose gel-based fluid. Based on these results, Na^+ and Ca^{2+} are of concern by D15, while Fe^{3+} and PO_4^{3-} concentrations would not be of concern for any of the flowback or produced waters studied. Softening-based methods or dilution (3:1 treated produced water to fresh water) could achieve appropriate inorganic ion concentrations (Esmailirad et al., 2015). Lastly, water treatment processes should include microorganism inactivation that could be achieved through a variety of disinfection methods such as UV light, chlorine, ozone, or biocide addition (Kidder et al., 2011; Lester et al., 2015).

If improved water quality is desired for specific industrial uses or environmental discharge, the TDS, dissolved organic carbon (DOC) concentration, and chemical oxygen

demand (COD) must be addressed by further treatment. While TDS levels for flowback and produced waters were lower than those found in other oil and gas basins in the United States, there are high COD levels. The removal of DOC and COD are often done through biological processes, activated carbon adsorption, and advanced oxidation processes. Adsorption-based processes are likely not sustainable due to the levels of COD and volumes of water, and advanced oxidation processes are challenging due to the hydroxyl radical scavenging potential of these specific waters (e.g., alkalinity). The high levels of COD, coupled with relatively low TDS suggest that biological processes could be an appropriate technology. Biological treatment of conventional produced water has been demonstrated (Liu et al., 2013; Lu et al., 2009; Zhao et al., 2006), yet less is known regarding biological treatment for flowback or produced waters (Akyon et al., 2015; Kekacs et al., 2015; Lester et al., 2014). The TDS levels in the DJ would not prohibit biological processes, but would still hinder the COD removal rate and reduce the total COD removal (Lefebvre and Moletta, 2006; Lester et al., 2014). Therefore, acclimation of a salt-tolerant community or the use of specific halophiles would better support the treatment of flowback and produced samples detailed here (Lefebvre and Moletta, 2006). Potential treatment technologies include an acclimated activated sludge, moving bed biofilm reactor, biological activated filtration, microbial mats, and a membrane bioreactor (Akyon et al., 2015; Boschee, 2014). Lester et al. (2015) reported a BOD/COD ratio of about 0.9 in a DJ flowback sample and saw 50% DOC removal in 6 hrs with a sequencing batch reactor, suggesting that an acclimated biological processes could be a good option for DOC and COD removal in the basin wastewaters.

TDS levels throughout the 220 days of the wastewater production exceeded recommend TDS values for livestock watering recommendations (TDS < 10,000 mg/L; ALL Consulting, 2003) and the long-term irrigation recommendations (< 2,000 mg/L) of the EPA (US EPA, 2004). Based on the TDS for these produced waters, reverse osmosis (RO) would be an ideal treatment for the region. In addition to TDS, RO treatment would also have the expected benefit of removing heavy metals (Fu and Wang, 2011). Prior to RO, pre-treatment steps (discussed above) should target suspended solids (coagulation-flocculation), scaling agents (water softening), DOC/COD (biodegradation), along with micro- or ultra- filtration to minimize potential fouling of the RO membranes. Compared to other basins that have flowback or produced waters with TDS levels greater than RO brines, achieving irrigation standards (TDS 500-2000 mg/L; Lester et al., 2015) or water of even higher quality (TDS < 500 mg/L) is reasonably achievable for Denver-Julesburg Basin waters.

3.4.1 Consideration for Industrial Reuse or Environmental Discharge

Several inorganic ions or metals commonly found in flowback and produced waters pose potential health risks, and would need to be addressed during treatment. Heavy metals associated with industrial wastewater that are of environmental health concern (e.g., Cu, Cr, and Ni) and found in flowback and produced waters were all less than 0.5 mg/L, while Pb was above the drinking water action level (0.015 mg/L) for just D130 (0.224 mg/L). These levels of heavy metals (e.g., Cu, Cr, and Ni) are similar to those found in municipal wastewater treatment plants (Karvelas et al., 2003; Olujimi et al., 2012). Bromide levels are also important to consider (86-143 mg/L; Table 1) because bromide

can react with organic matter to form harmful disinfection byproducts (i.e., bromomethanes, bromophenols, bromate) during chlorine disinfection of waters (Landis et al., 2016; Ziemkiewicz and He, 2015).

The low radioactivity concentrations observed in flowback and produced waters were consistent with the low levels of the parent radionuclide (^{238}U) present in the Niobrara formation and would not be a significant concern (Tourtelot, 1956). The highest value of ^{226}Ra (3,280 mBq/L) observed in this study was approximately 0.5 % the level of ^{226}Ra observed in Marcellus Shale produced water (670,000 mBq/L; Nelson et al., 2014). The levels of NORM in the wastewaters characterized in this study are below US EPA guidelines for discharge to wastewater treatment plants (i.e., 22,200 mBq/L ^{226}Ra ; 22,000 mBq/L ^{228}Ra ; 111,000 mBq/L ^{238}U ; Zhang et al., 2014). Although these levels are low compared to other basins, their removal could be addressed through co-precipitation with barium or other alkaline earth metals (Zhang et al., 2014). Alternatively NORM (with the exception of radon [Rn]) could likely be removed from flowback and produced fluids through membrane based processes (e.g. RO; Huikuri et al., 1998; Montaña et al., 2013). Monitoring of solids and sludges generated during treatment processes may warrant future study as NORM could become concentrated in certain treatment trains. This is of particular concern for solids from flocculation-coagulation and rejection streams (i.e. brines) from membrane based processes. Radioactive ingrowth of decay products is a concern in flowback and produced fluids, particularly for short-lived decay products of ^{226}Ra (Nelson et al., 2015a). Field studies and monitoring may be warranted for waters enriched in ^{226}Ra .

577

578 4. Conclusions

579 This research presents an in-depth analysis of flowback from a single well and produced
580 water over time, illustrating how water quality changes along with considerations for
581 treatment and reuse in the DJ-basin. The importance of volumes returned when
582 considering reuse approaches (centralized facility vs. on-site treatment) is illustrated, and
583 strategies are provided for treatment regardless of the age of the well. This is the result of
584 most water quality parameters (except COD and alkalinity), metals (except, Fe^{+3} , Ba^{+2} ,
585 and Sr^{+2}), and anion (except SO_4^{-2}) levels minimally changing over time in this well. This
586 research is important for other oil and gas producing basins, since it provides a
587 comparison for the changes that take place from the initial ground water, fracturing fluid,
588 flowback, and produced water over time. However, it must be noted that this study
589 investigated a single well in the DJ-basin, not permitting these results to capture the
590 heterogeneity of all wells in Colorado or from other basins (Hoelzer et al., 2016).
591 Nonetheless, this research is critical for the growing body of literature on flowback and
592 produced water, that ideally leads to improved reuse and appropriate management of
593 produced water within the oil and gas industry.

594

595 **Acknowledgments**

596 This work was supported by the AirWaterGas Sustainability Research Network, and was
597 funded by the National Science Foundation under Grant No. CBET-1240584. Opinions,
598 findings, recommendations, and conclusions conveyed in this paper are those of the
599 author(s) and do not necessarily reflect the views of the National Science Foundation.

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. The researchers would also like to acknowledge Dr. Stephen Osbourn for his technical insight, our industry collaborators that permitted access and took the time to help us collect the samples, and the five anonymous reviewers for their insightful comments that improved the manuscript.

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Supplementary Information

SI Figure 2: Percentage of TDS associated with the formation. This was done using the TDS of the groundwater (TDS initial) and the D220 TDS (TDS final), using the following equation $Percentage\ of\ Final\ TDS = \frac{TDS(x) - TDS(initial)}{TDS(Final)} \times 100$, with TDS (x) being a specific time (i.e. D1, D4, etc.).

SI Figure 1: Volume (bbl) of water returned over time from the single well studied. The volumes were measured every 24 hours from flow meters connected to separators (oil/water/gas). On days when specific volume was not measured, the average well flow returned five days before and after were used to calculate that days returned volume.