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Temporal characterization and statistical analysis of flowback and produced waters and their potential for reuse

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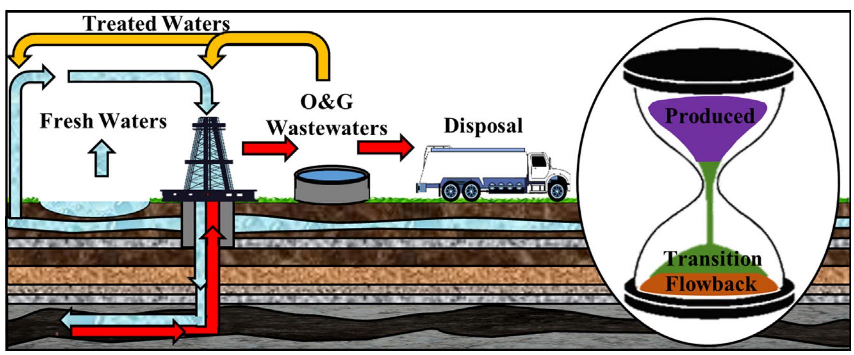
HIGHLIGHTS

- High resolution sampling and analysis of water chemistry during the flowback period
- Temporal pattern of synthetic and geogenic components present in waters described.
- Alkalinity and iron may limit the reuse of these waters in HF.
- Three unique groupings in the chemical data corresponded to different stages in flowback period.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydraulic fracturing (HF) has allowed for the utilization of previously unattainable shale oil and gas (O&G) resources. After HF is complete, the waters used to increase the facies' permeability return uphole as wastewaters. When these waters return to the surface, they are characterized by complex organic and inorganic chemistry, and can pose a health risk if not handled correctly. Therefore, these waters must be treated or disposed of properly. However, the variability of these waters' chemical composition over time is poorly understood and likely limits the applicability of their reuse. This study examines the water chemistry of a hydraulically fractured site in the Niobrara formation throughout the flowback period. Samples were collected every other day for the first 18 days, then on a regular basis for three months. We identified HF fluid additives, including benzalkonium chlorides (BACs), alkyl ethoxylates (AEOs), and polyethylene glycols (PEGs), as well as geogenic components present in flowback and produced waters, their overall temporal pattern, and variables affecting the reuse of these waters. Observations indicate that alkalinity and iron may limit the reuse of these waters in HF, while chloride and alkalinity may limit the use of these waters for well-casing cement. The presence of numerous surfactant homologs, including biocides, was also observed, with the highest levels at the beginning of the flowback period. Principal component analysis identified three unique groupings in the chemical data that correspond to different stages in the flowback period: (1) the flowback stage (days 1–2); (2) the transition stage (days 6–21); and (3) the produced water stage (days 21–87). Results from this study will be important when designing decision

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frameworks for assessing water treatment options, particularly if onsite treatment is attempted. Successful reclamation of these waters may alleviate stress on water resources that continues to negatively impact the U. S.

1. Introduction

The impact of horizontal fracturing of oil and gas (O&G) wells on the environment, particularly with reference to water acquisition and use, has been highly debated (DiGiulio and Jackson, 2016; Gallegos et al., 2015; Nicot et al., 2012; Vengosh et al., 2014; Vidic et al., 2013). A typical horizontal fracturing operation may require up to 20,000 m^3 (5 million gallons) of water, commonly referred to as source water, to complete a single well. In northeast Colorado, within the Denver-Julesburg (DJ) basin, source water is often acquired from surface water and groundwater, with a small fraction coming from recycled water from O&G actives (Freyman, 2014). The overall water demand for hydraulic fracturing (HF) in the state is roughly 5 billion gallons per year, with approximately 89% (~4.45 billion gallons) of the water use coming from Weld County and Garfield County (Freyman, 2014). This demand equates to approximately 1.3% of the total freshwater use in these counties (U.S. Geologic Survery, 2010) and nearly twice the amount of water that Boulder County uses for municipal purposes (Freyman, 2014). Yet, 100% of the wells within the DJ basin are located in an area of high or extreme water stress (Freyman, 2014) exacerbated by high residential, agricultural, and other industrial water demands.

After the well fracturing is complete, injection waters return to the surface as O&G wastewaters (Bai et al., 2013; Hayes, 2009; King, 2012). In the beginning of this 'flowback period', these wastewaters are thought to be more representative of the injection waters rather than deep subsurface fluids know as formation waters, and are referred to as flowback waters (Bai et al., 2013; Hayes, 2009; King, 2012). As the flowback period continues, the flowback water begins to acquire the characteristics of the O&G formation water; subsequently, the water coming from the well is referred to as produced waters (Bai et al., 2013; Hayes, 2009; King, 2012). In Colorado, over 16 billion gallons of produced water are brought to the surface annually (Goodwin et al., 2013), while the annual U.S. produced water volume is 870 billion gallons (Thacker et al., 2015) – a substantial fraction of this water volume is in need of treatment to satisfy Clean Water Act standards. More produced water is brought to the surface in the US than source water needed for HF-in 2014 the total HF water use in the U.S. was 97.5 billion gallons (Freyman, 2014); thus, it is possible to create a closed system for HF water reuse. However, the handling and transportation of these fluids may make complete reuse economically infeasible.

Produced waters are comprised of a geogenic portion, consisting of compounds native to the geologic formation, and additives, which contain chemicals used to stimulate the formation of fractures and aid in well production (Elsner and Hoelzer, 2016; Ferrer and Thurman, 2015; Kahrilas et al., 2014; Regnery et al., 2016; Thacker et al., 2015; Thurman et al., 2016). The geogenic portion of these waters contain numerous organic and inorganic constituents that potentially hinder the ability of reuse (Fakhru'l-Razi et al., 2009; Freedman et al., 2017; Mohan et al., 2013). Not surprisingly, these waters also contain petroleum hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs) (Hayes, 2009; Regnery et al., 2016; Thacker et al., 2015). The synthetic portion of these waters is generally composed of two major components: polyethylene glycols (PEGs) and alkyl ethoxylates (AEOs) (Thurman et al., 2016, 2014). Recent studies showed that these compounds accounted for approximately 20% of the liquid chromatography (LC)-compatible dissolved organic compounds present in O&G wastewater in the DJ Basin (Thurman et al., 2016, 2014). These chemicals serve a variety of purposes in the fracturing process and are commonly used as surfactants, clay stabilizers, and friction reducers (Ground Water Protection Commission and Council and Interstate Oil and Gas Compact, 2013; Thurman et al., 2016).

Due to their complexity, produced waters are difficult and costly wastewaters to treat once they reach the surface. In the U.S., 95.2–98% of produced water is re-injected; of this, 55% is injected to maintain formation pressure and increase the output of producing wells, while ~40% is injected for disposal (Clark and Veil, 2009). Both of these have the detrimental effect of uncontrollable subsurface flow and variable formation pressure, which led the state of Oklahoma to ban some regional injection due to costly seismic effects (Tobben and Nguyen, 2016). The remaining 5% of the water is disposed of using alternative methods, with only a small fraction reclaimed for beneficial use (Clark and Veil, 2009). Recently, there have been increased interests from the industry, the scientific community, and the public in using produced waters from O&G operations as a new source of water for areas with water scarcity (Collins, 2016; Freedman et al., 2017; Freyman, 2014; Lester et al., 2015).

In addition to reuse in O&G activities, these waters may serve as a supplement or an alternative to fresh water for crop irrigation, livestock watering, municipal and industrial uses, as well as other beneficial uses (Dickhout et al., 2017; Meng et al., 2016; Pica et al., 2017; Tiedeman et al., 2016). Although alternative uses for these waters could greatly benefit communities, careful consideration of their chemical and biological composition must be given before treatment or reuse. Additionally, characterization of these waters is equally important when applying management practices and handling potential surface spills (McLaughlin et al., 2016; Rogers et al., 2017). While identifying components in these waters is imperative, the changing site conditions pose additional unique problems. Unlike common industrial wastewaters, O&G wastewaters from HF and well production are temporally variable (Hayes, 2009; Mohan et al., 2013; Rosenblum et al., 2017). Because wastewater treatment systems are designed for a given range of contaminant concentrations, the changing influent conditions can pose technical problems. Thus, understanding the temporal variability of produced water composition is fundamental to water treatment system design.

Numerous studies have characterized produced and flowback waters; however, many of these studies take a spatial approach, looking at multiple wells at one-time point (Barbot et al., 2013; Khan et al., 2016; Lester et al., 2015; Luek et al., 2017; Luek and Gonsior, 2017; Mohan et al., 2013; Thacker et al., 2015; Vengosh et al., 2013; Wunsch et al., 2013). Although a few studies have analyzed waters temporally, limited data are available, particularly pertaining to the synthetic fraction of the water, as well as the potential for microbial community variation (Cluff et al., 2014; Hayes, 2009; Kim et al., 2016). Understating the temporal variability of flowback and produced water quality will affect the treatment and reuse of these waters, particularly when considering inorganic constituents that may cause mineral scaling in treatment processes.

The composition of microbial communities may affect the end use of produced waters, but could also inform the nature of subsurface microbiology in a given formation (Colman et al., 2017). A large suite of studies have characterized microbial communities associated with hydraulically fractured shales such as the Marcellus and Barnett formations, but little is known about the microbial ecology of the Niobrara formation (Davis et al., 2012; Mohan et al., 2013). Prior investigations have revealed a dominance of strict/facultative anaerobic, fermentative bacteria such as the genera *Halolactibacillus*, *Marinobacter*, and *Halomonas*. Members of the orders *Halanaerobiales*, *Clostridiales*, and *Synergistia* have been reported to be present in the Barnett and Marcellus