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Organic and inorganic composition and microbiology of produced waters from Pennsylvania shale gas wells

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ABSTRACT

Hydraulically fractured shales are becoming an increasingly important source of natural gas production in the United States. This process has been known to create up to 420 gallons of produced water (PW) per day, but the volume varies depending on the formation, and the characteristics of individual hydraulic fracture. PW from hydraulic fracturing of shales are comprised of injected fracturing fluids and natural formation waters in proportions that change over time. Across the state of Pennsylvania, shale gas production is booming; therefore, it is important to assess the variability in PW chemistry and microbiology across this geographical span. We quantified the inorganic and organic chemical composition and microbial communities in PW samples from 13 shale gas wells in north central Pennsylvania. Microbial abundance was generally low (66–9400 cells/mL). Non-volatile dissolved organic carbon (NVDOC) was high (7–31 mg/L) relative to typical shallow groundwater, and the presence of organic acid anions (e.g., acetate, formate, and pyruvate) indicated microbial activity. Volatile organic compounds (VOCs) were detected in four samples (~1 to 11.7 µg/L): benzene and toluene in the Burket sample, toluene in two Marcellus samples, and tetrachloroethylene (PCE) in one Marcellus sample. VOCs can be either naturally occurring or from industrial activity, making the source of VOCs unclear. Despite the addition of biocides during hydraulic fracturing, H₂S-producing, fermenting, and methanogenic bacteria were cultured from PW samples. The presence of culturable bacteria was not associated with salinity or location; although organic compound concentrations and time in production were correlated with microbial activity. Interestingly, we found that unlike the inorganic chemistry, PW organic chemistry and microbial viability were highly variable across the 13 wells sampled, which can have important implications for the reuse and handling of these fluids.

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1. Introduction

Natural gas resources are an important part of America's energy resource portfolio, playing an integral role in the development of sustainable energy that protects both environmental and national security interests (Arthur et al., 2009; Moniz et al., 2011). Production of natural gas from shale is a rapidly expanding practice that may account for up to 50% of all natural gas produced in the U.S. by 2040 (AEO, 2013). Unconventional development of shale gas is accomplished by using methods that combine horizontal drilling and hydraulic fracturing (HF) (Arthur et al., 2009). During HF, fracturing fluids are injected into the formation under high pressure to create small fractures, allowing methane to escape (Arthur et al., 2009). Fracturing fluids are primarily composed of

freshwater, proppants (e.g., sand) and chemical additives, such as friction reducers, biocides, and scale reducers. The additives (<2% by mass) improve gas production by increasing proppant delivery to fractures and maintaining the integrity of the well by reducing the likelihood of microbial fouling, well souring, or scale build up. One to four million gallons of water may be required to hydraulically fracture a well with 10–50% of the injected fluids returning to the surface (Paugh et al., 2008; Arthur et al., 2009; Soeder and Kappel, 2009). These large volumes of returned fluids present water management challenges (Lutz et al., 2013), and operators are increasingly reusing these fluids in order to reduce the amount of freshwater required and the amount of wastewater requiring disposal.

After the initial fracturing of the shale, injected fluid returns to the surface primarily within the first 2 weeks of production, and pumping continues to produce a mixture of fracturing fluids and water naturally present in the fractured geologic formation. Due

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to the mixing that occurs in the subsurface, all waters produced following HF will be referred to as produced waters (PW) in this study. The PW initially largely reflects the composition of the injected fluid, which is commonly composed of recycled brine diluted with freshwater to a salinity typically <50,000 mg/L (King, 2012). Over time, the PW starts to largely reflect the chemical composition of the formation water. In the Marcellus Shale, PWs have elevated total dissolved solids (TDS, ~200,000 mg/L) (Hayes, 2009; Rowan et al., 2010, 2015; Haluszczak et al., 2013) and are enriched in naturally occurring radioactive materials relative to other formations (Rowan et al., 2011). The variable inorganic chemistry can affect the suitability of PW for reuse or the strategy for disposal (Paugh et al., 2008).

In order to assess the potential environmental impact of PW and evaluate handling and disposal options, we need to fully understand the chemistry and microbiology of these fluids. Although the inorganic chemical composition of produced waters from Marcellus Shale wells has been characterized (Hayes, 2009; Chapman et al., 2012; Barbot et al., 2013; Rowan et al., 2015), knowledge on the presence of organic compounds is limited (Strong et al., 2013; Cluff et al., 2014; Orem et al., 2014). Hydrocarbons and synthetic organic chemicals, possibly from hydraulic fracturing chemical additives, were observed in PW samples from Marcellus Shale wells after 250 days of production (Orem et al., 2014). The concentrations of organic chemicals used for hydraulic fracturing, e.g., solvents, biocides, and scale inhibitors, generally declined after onset of production but residual quantities persisted after more than 8 months in production (Cluff et al., 2014). However, the variability in the presence of organics in Marcellus Shale PW is largely unknown because previous studies either analyzed samples from only single well sites or only reported presence/absence.

Microbial activity can negatively affect the success of gas recovery and recycling of PW through well souring or corrosion (Fichter et al., 2008), but also can contribute to the biodegradation of potential environmental contaminants in PW. Recent work shows that microbial populations change during production, with different community compositions present in pre-fracturing fluids compared to PW recovered over the lifetime of production (Struchtemeyer et al., 2011; Struchtemeyer and Elshahed, 2012; Murali Mohan et al., 2013a, 2013b; Strong et al., 2013; Cluff et al., 2014). In the Marcellus Shale, communities shifted during production toward halophilic and hydrocarbon-degrading lineages (Murali Mohan et al., 2013a; Strong et al., 2013; Cluff et al., 2014). Lineages in low abundance in pre-fracturing fluids (<2%) increased in abundance and dominated the community on exposure to subsurface conditions, which may have implications for reuse of PW as populations tolerant to the subsurface conditions in the shale could be positively selected (Murali Mohan et al., 2013a). However, a shift toward hydrocarbon degrading populations, as seen by Strong et al. (2013), could be exploited for the treatment of these wastes prior to disposal. Work is also needed to assess the potential of halophiles in PW that form H₂S, which can cause well souring.

Shale gas production is ongoing and rapidly expanding across the state of Pennsylvania; therefore, it is important to assess the variability in PW chemistry and microbiology across this geographical span. We hypothesized that the chemical composition, and the microbial abundance and viability in PW, would be similar in shale gas wells within 2 counties in north central PA. In this study, we quantitatively characterized the chemical composition (inorganic and organic chemistry) and microbiology of PW from 13 Pennsylvania shale gas wells located along a 22-mile transect through Tioga and Lycoming counties. Our results show that TDS was high in all wells, but the organic chemistry and microbiology was highly variable. Halophilic microorganisms, including *Halanaerobium* species that were detected previously in Marcellus

Shale PW (Murali Mohan et al., 2013a; Cluff et al., 2014), were cultured from 4 wells, showing that these organisms are viable and their presence and activity could affect the reuse and handling of PW.

2. Materials and methods

2.1. Study site and sampling

PW were sampled from the gas–liquid separator tank of 13 shale gas production wells in Tioga and Lycoming Counties in north central Pennsylvania (Fig. 1). All of the wells were constructed using horizontal drilling methods, completed by hydraulic fracturing, and when sampled, the majority had been in production from 10 to 38 months, with the Burket well in production only 5 months (Table 1). Additives to enhance gas recovery, such as biocides, were only added to the fracturing fluids used at the time of well completion and no reinjection of chemical additives was performed during production (personal communication from the well operator). Twelve wells were producing from Middle Devonian Marcellus Shale, whereas well ST460-Burket was producing from the shallower Upper Devonian Burket Shale (Table 1). ST460-Burket was located at the same well pad as ST460-MS, which produced from Marcellus Shale.

Samples of PW were obtained directly from a valve on the separator tank (as described in Rowan et al., 2015), minimizing contact with air. The separator is a low oxygen to oxygen-free environment at pressures near those at the well head where methane and produced water accumulate and separate. The PW accumulated over a period of hours to days in the separators before being pumped into large water storage tanks that were emptied weekly to monthly. Based on information compiled in the IHS database (IHS, 2014), the wells in our study produced an estimated 4–736 barrels of water per month (median of 109 barrels per month) in 2012, the year our samples were collected.

The pH of the samples was measured directly using field probes. Samples for major cation and trace element analyses were filtered in the field through a 0.45 μm pore size filter, and acidified with double distilled nitric acid. Samples collected for anion analyses were filtered in the field through a 0.45 μm pore size filter. Samples were collected for non-volatile dissolved organic carbon (NVDOC) analyses by filtering through 0.20-μm Supor® filters (Pall, Port Washington, NY) into 2 40-mL prebaked glass bottles, then preserved with hydrochloric acid to a pH of <2. Sample bottles were filled without headspace. Samples for volatile organic compound (VOC) analyses were collected without filtration in 2 40-mL prebaked glass bottles and preserved with hydrochloric acid to a pH of <2; bottles were filled without headspace. Samples for low-molecular-weight organic acid anion (LMWOA) analyses were collected without filtration in 2 40-mL prebaked glass bottles. Sample bottles were filled 1/2 full and frozen as soon as possible (in a freezer or on dry ice). Unfiltered samples collected for microbiology were collected aseptically into sterile 2 L glass media bottles without headspace to minimize exposure to air. All water samples were stored on wet ice in the field and during transport to the laboratory, where they were refrigerated upon arrival, with the exception of LMWOA samples, which were kept frozen. Reservoir temperature and depth was obtained from the well operator.

2.2. Analytical techniques

The major and trace element analyses were conducted at the U.S. Geological Survey (USGS) in Reston, VA, USA. Anion concentrations were determined by ion chromatography (Dionex ICS 1000 IC, equipped with an electrochemical detector and AS14 column)

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