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Volatile-organic molecular characterization of shale-oil produced water from the Permian Basin

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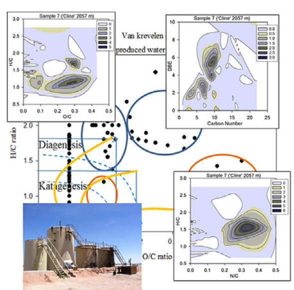
HIGHLIGHTS

- 1st high-resolution VOC MS data for the shale-oil produced water from Permian.
- Shale-oil water VOC high-resolution GC-ToF-MS identified 1400 compounds.
- 3D van Krevelen and DBE diagrams fingerprinting framework for high-resolution MS.
- Source composition & solubility controlled the composition of the produced water.
- Partial treatment may support beneficial reuse for fracturing or bio-energy.

GRAPHICAL ABSTRACT



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ABSTRACT

Growth in unconventional oil and gas has spurred concerns on environmental impact and interest in beneficial uses of produced water (PW), especially in arid regions such as the Permian Basin, the largest U.S. tight-oil producer. To evaluate environmental impact, treatment, and reuse potential, there is a need to characterize the compositional variability of PW. Although hydraulic fracturing has caused a significant increase in shale-oil production, there are no high-resolution organic composition data for the shale-oil PW from the Permian Basin or other shale-oil plays (Eagle Ford, Bakken, etc.). PW was collected from shale-oil wells in the Midland sub-basin of the Permian Basin. Molecular characterization was conducted using high-resolution solid phase micro extraction gas chromatography time-of-flight mass spectrometry. Approximately 1400 compounds were identified, and 327 compounds had a >70% library match. PW contained alkane, cyclohexane, cyclopentane, BTEX (benzene, toluene, ethylbenzene, and xylene), alkyl benzenes, propyl-benzene, and naphthalene. PW also contained heteroatomic compounds containing nitrogen, oxygen, and sulfur. 3D van Krevelen and double bond equivalence versus carbon number analyses were used to evaluate molecular variability. Source composition, as well as solubility, controlled the distribution of volatile compounds found in shale-oil PW. The salinity also increased with depth, ranging from 105 to 162 g/L total dissolved solids. These data fill a gap for shale-oil PW composition, the associated petroleomics plots provide a fingerprinting framework, and the results for

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the Permian shale-oil PW suggest that partial treatment of suspended solids and organics would support some beneficial uses such as onsite reuse and bio-energy production.

1. Introduction

Produced water (PW), as the largest waste stream generated during oil and gas production, is a mixture of formation water naturally present in reservoirs and water injected into reservoirs for pressure support, hydraulic fracturing, or reservoir treatment (Veil et al., 2004; Ahmadun et al., 2009). Understanding the sources and chemistry of formation waters is critical in oil-field management and petroleum exploration for many reasons such as planning for saltwater disposal and secondary recovery projects, proper treatment of production fluids to prevent corrosion and enhance phase separation (Ostroff, 1979). Also, predicting and locating variations in PW quality supports evaluating potential beneficial uses and treatment needs (Ahmadun et al., 2009).

Recent advances in horizontal drilling and hydraulic fracturing have caused a significant increase in unconventional hydrocarbon production including shale gas, coal-bed methane, tight oil, oil sands, and shale oil (Alley et al., 2011; Maguire-Boyle and Barron, 2014). Alley et al. found that PW compositions vary between each conventional and unconventional hydrocarbon production formation types (Alley et al., 2011). Orem et al. found that PW can be significantly altered from that of the formation for up to 250 days after hydraulic fracturing due to influence from compounds added during hydraulic fracturing (Orem et al., 2014), and Rowan et al. observed hydraulic fracturing flowback in PW from shale gas for up to 90 days (Rowan et al., 2015). Although compositions are highly variable, PWs contain dissolved inorganic salts (e.g. sodium, chloride, etc.), chemical additives used for drilling and well operations (e.g., hydraulic fracturing and/or corrosion inhibitor, biocide, and friction reducers), dissolved oil components (e.g. petroleum compounds), naturally occurring radioactive materials, suspended solids, and dissolved gases (Veil et al., 2004; Silset et al., 2010).

Several researchers have examined, to some extent, the organic composition within PW from various formations around the world (Utvik, 1999; Faksness et al., 2004; Sirivedhin and Dallbauman, 2004; Tellez et al., 2005; Lu et al., 2006; Dorea et al., 2007; Silset et al., 2010; Horner et al., 2011; Wang et al., 2012; Eftekhardadkhah and Oye, 2013; Maguire-Boyle and Barron, 2014; Orem et al., 2014). The composition and volume of PW varies as a function of the geologic formation and the age of the field (Dudasova et al., 2009). Tellez et al. used gas chromatography–mass spectroscopy (GC–MS) to evaluate PW from Permian Basin (Tellez et al., 2005). This work was conducted prior to the vast increases in unconventional oil production in the Permian, and there are no previously published investigations of PW from tight oil reservoirs within the Permian Basin, which is the most productive tight oil play in the US (Guerra et al., 2011). Recently, production in the Permian Basin has been >2 million barrels of oil per day (U.S.E.I.A., 2015). Despite use of GC–MS in several of these prior studies, the reported results focused on bulk trends in organic composition or on select compounds that could be separated and quantified. Wang et al. was the only paper that did use high-resolution MS and examined the complex mixture within PW from a conventional oil field in Wyoming using petroleomics analysis approaches including van Krevelen and double-bond equivalent (DBE) versus carbon number plots (Wang et al., 2012).

High-resolution GC–MS is critical for detailed organic-compositional fingerprinting and characterization of hydrocarbon mixtures. Gas chromatography-time of flight-mass spectroscopy (GC-ToF-MS) and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) are two of the few instruments that have been able to resolve the thousands of compounds in both crude oil and shale oil (Stanford et al., 2007; Avila et al., 2012; Cho et al., 2012, 2013; Jin et al., 2012; Kekalainen et al., 2013; Lababidi et al., 2013). The majority of this work used FT-ICR-MS for hydrocarbon analysis, whereas GC-ToF-MS has not been used as much even with its high-resolution capability for low polarity and nonpolar organic mixtures. Moreover, results plotted in van Krevelen diagrams have been typically used for oil maturation and source comparison (Kim et al., 2003; Wu et al., 2004), and they also appear well suited to amplify and expose compositional differences within and between complex organic mixtures such as PWs.

Despite prior work, there is still vast uncertainty in the molecular-level composition of PWs derived from unconventional hydrocarbon production formations. To our knowledge, no organic composition data are available from the unconventional shale-oil PW being produced from the Permian Basin or other shale-oil plays (Eagle Ford, Bakken, etc.). The goal of this study was to characterize the volatile organic compositional variability of late stage shale-oil PW from the Permian Basin using high-resolution GC–MS. Late stage PW, generally collected months or years after wells go into production is more indicative of the native formation water (Rowan et al., 2015), as opposed to analysis of early stage and flowback PW, which is particularly focused on the compounds used for hydraulic fracturing. Injected fracturing compounds are already reported for all wells in Texas through the FracFocus database. The organic compositional data for the PW samples was compared to the organic composition of oil and shale oil. Comparison of PWs quality with standards for drinking water was also used to examine beneficial use and treatment options.

2. Materials and methods

2.1. Permian Basin hydrogeology

The Permian Basin province, containing multiple sub-basins located in western Texas and eastern New Mexico, is one of the most productive hydrocarbon plays within North America, containing conventional oil, tight oil, and natural-gas resources (Guerra et al., 2011). Due to the depositional history, there are significant variations in lithology, geochemistry, and hydrologic properties of the hydrocarbon reservoirs. Fig. 1 presents the stratigraphic column of Midland Basin within the Permian Basin with the lithologic setting. At their deepest points the two sub-basins, the Midland and Delaware Basins, contain approximately 4600 m and 10,700 m of sediments, respectively, overlying Precambrian basement. Pre-Pennsylvanian strata that consist primarily of those contained in the precursor to the Permian Basin, the Tobosa Basin, are composed of marine carbonates and shales. Permian-age sediments include a sequence of geologic strata including evaporites, carbonates, discontinuous fluvial-deltaic arkosic sandstones, very fine siltstone and marine shales (Fig. 1). Historically, much of the hydrocarbon production was derived from conventional structural and stratigraphic traps in Guadalupian and Leonardian age reservoirs