



Review

Organic compounds in hydraulic fracturing fluids and wastewaters: A review

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ABSTRACT

High volume hydraulic fracturing (HVHF) of shale to stimulate the release of natural gas produces a large quantity of wastewater in the form of flowback fluids and produced water. These wastewaters are highly variable in their composition and contain a mixture of fracturing fluid additives, geogenic inorganic and organic substances, and transformation products. The qualitative and quantitative analyses of organic compounds identified in HVHF fluids, flowback fluids, and produced waters are reviewed here to communicate knowledge gaps that exist in the composition of HVHF wastewaters. In general, analyses of organic compounds have focused on those amenable to gas chromatography, focusing on volatile and semi-volatile oil and gas compounds. Studies of more polar and non-volatile organic compounds have been limited by a lack of knowledge of what compounds may be present as well as quantitative methods and standards available for analyzing these complex mixtures. Liquid chromatography paired with high-resolution mass spectrometry has been used to investigate a number of additives and will be a key tool to further research on transformation products that are increasingly solubilized through physical, chemical, and biological processes *in situ* and during environmental contamination events. Diverse treatments have been tested and applied to HVHF wastewaters but limited information has been published on the quantitative removal of individual organic compounds. This review focuses on recently published information on organic compounds identified in flowback fluids and produced waters from HVHF.

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1. Introduction

Shale gas extraction via high volume hydraulic fracturing (HVHF) has resulted in the use of 116 billion liters of fluids annually from 2012 to 2014 and yielded similar volumes of flowback and produced waters (Kondash and Vengosh, 2015). These fluids contain a complex mixture of inorganic and organic compounds used as additives (Elsner and Hoelzer, 2016; Stringfellow et al., 2014) as well as compounds extracted from the shale itself including salts, metals, radionuclides, oil and gas compounds, and natural organic matter (NOM) (Abualfaraj et al., 2014; Chapman et al., 2012; Engle and Rowan, 2014). Understanding these complex fluid mixtures is essential for understanding efficacy of additives, fluid treatment options for reuse in future HVHF jobs or discharge, and threats to the natural environment and human exposure.

The identification and quantification of individual organic compounds among the complex mixture of additives, oil and gas compounds, NOM, and transformation products requires diverse sample preparation and analytical techniques (Ferrer and Thurman, 2015a). Mass spectral techniques provide data of variable confidence ranging from having only the exact masses of interest to having confirmed structures by reference standards (Schymanski et al., 2014). Gas chromatography paired with mass spectrometry has been traditionally used to identify hydrophobic oil and gas hydrocarbons found in produced waters (Ferrer and Thurman, 2015a; Maguire-Boyle and Barron, 2014; Orem et al., 2014; Strong et al., 2013), and can be used to quantify many of the compounds in HVHF fluids and wastewaters of known toxicity (Elliott et al., 2017). Liquid chromatography paired with mass spectrometry has been shown to be useful in identifying many of the more hydrophilic organic compounds used in HVHF additives such as ethoxylated surfactants (Ferrer and Thurman, 2015a, 2015b; Getzinger et al., 2015; Hoelzer et al., 2016), but further method development requires overcoming analytical barriers such as the complex high salinity matrix. Analytical methods for describing unknown shale extracts and transformation products will require higher resolution techniques such as two dimensional gas chromatography with time of flight mass spectrometry (GC × GC-TOF-MS) (Hoelzer et al., 2016), liquid chromatography with time of flight mass spectrometry (LC-TOF-MS) (Ferrer and Thurman, 2015b; Thurman et al., 2014), and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), each requiring laborious data analysis and interpretation. Time of flight mass spectrometry can provide sufficiently high resolution that exact masses can be combined with GC or LC to determine unknown molecular formulas and structures with relatively high confidence in the absence of standards, especially when combined with fragmentation spectra (Ferrer and Thurman, 2015b; Marshall and Hendrickson, 2008; Thurman et al., 2014). Ultrahigh resolution FT-ICR-MS allows for direct determination of the assigned molecular formula based on the exact mass alone but provides no direct details on molecular structure (Marshall and Hendrickson, 2008) unless paired with MS-MS techniques. However, large numbers of possible isomers at higher masses make this approach challenging, but this challenge might be partially overcome by using LC.

Organic compounds observed in these fluids have been characterized by their mobility, persistence, toxicity, and frequency of use to understand the level of concern for human exposure via groundwater (Rogers et al., 2015). However, the combination of multiple organic compounds, inorganic compounds, and multiple phases complicates modeling the behavior of these organic compounds in the natural environment. Experimental and field studies are needed to address questions of mobility, persistence, and toxicity of HVHF fluid additives, geogenic organic compounds, and

potential transformation products.

A number of studies have worked to identify analytical methods and quantify organic compounds in HVHF fluids, flowback fluids, and produced waters, and describe how these compounds are transformed within diverse environments. However, these studies have yet to be synthesized to provide a holistic perspective on the processes controlling organic compounds within these fluids. This review aims to synthesize existing literature on organic compounds quantitatively and qualitatively identified in HVHF fluids, flowback fluids and produced waters. Additionally, this review focuses on the distribution of HVHF associated organic compounds during environmental contamination and their use as tracers of contamination, the removal efficiencies of specific organic compounds during wastewater treatment, and makes recommendations for future research.

2. Hydraulic fracturing fluid additives

The majority of organic additives included in HVHF fluid have been described by class and their frequency of use (Elsner and Hoelzer, 2016; Rogers et al., 2015). Additionally, lists of additives are publicly available through the website [FracFocus](http://fracfocus.org) (fracfocus.org) and are summarized in the EPA hydraulic fracturing study report (U.S. EPA, 2016). Organic compounds are used at every stage in the HVHF process: 1) mixing of the base fluid including solvent and surfactants, 2) as cross linkers and breakers, 3) clay stabilizers, 4) corrosion, scale, and 5) biofouling inhibitors (Elsner and Hoelzer, 2016; Stringfellow et al., 2014). Alcohols are the dominant organic class used in a number of functions including as solvents (methanol, isopropanol, ethanol), surfactants (ethylene glycol, ethoxylated alcohols and phenols) and corrosion inhibitors (propargyl alcohol) (Elsner and Hoelzer, 2016). Polymers are also used in a large number of processes including as gelling agents, friction reducers, proppant coatings, corrosion and scale inhibitors (Elsner and Hoelzer, 2016). Many synthetic polymers and biopolymers are readily biodegraded, although their monomers may be of environmental concern (Elsner and Hoelzer, 2016; Stringfellow et al., 2014). Hydrocarbons, as light and heavy petroleum distillate mixtures and individual compounds (naphthalene, tetradecane, limonene), are an additional dominant class of additives, used primarily as solvents (Elsner and Hoelzer, 2016).

Of the remaining additives, some are specifically added to be reactive. For example, strong oxidants are used as biocides (infrequently) (Kahrilas et al., 2015) and as breakers (77% of surveyed well disclosure lists) (Elsner and Hoelzer, 2016). Glutaraldehyde and dibromonitripropionamide are the dominant biocides used (27% and 24%, respectively) and behave by reacting with specific function groups (thiol, amino, sulfhydryl) and destroying protein function (Kahrilas et al., 2015; Maillard, 2002). Breakers are used to “break” polymers and reduce surface tension of the fluid, allowing flowback fluids to return to the surface. These breakers and biocides may react not only with their targets, but also on the other organic compounds present as additives or from geogenic sources and result in unknown transformation products (Hoelzer et al., 2016; Luek et al., 2017; Maguire-Boyle and Barron, 2014).

3. Flowback and produced waters

Specific organic compounds have been analyzed both qualitatively and quantitatively in more than 238 flowback and produced water samples from hydraulically fractured shale gas wells in published literature (Table 1, Fig. 1). These analyses have focused on both oil and gas related compounds (e.g., hydrocarbons, benzene, toluene, ethylbenzene and xylene [BTEX]), small organic acids related to microbial degradation, and other additives. Confidence in

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