University of New Hampshire

University of New Hampshire Scholars' Repository

Civil and Environmental Engineering
Scholarship

Civil and Environmental Engineering

10-15-2017

Organic compounds in hydraulic fracturing fluids and wastewaters: A review

Jenna L. Luek

University of New Hampshire, Durham, Jenna.Luek@unh.edu

Michael Gonsior

University of Maryland

Follow this and additional works at: https://scholars.unh.edu/civeng_facpub

Comments

This is an Accepted Manuscript of an article published by Elsevier in Water Research in 2017, available online:

<https://dx.doi.org/10.1016/j.watres.2017.07.012>. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Recommended Citation

Luek, J.L., Gonsior, M. 2017. A Review of Organic Compounds in Hydraulic Fracturing Fluids and Wastewaters. Water Research 123, 536-548. DOI:10.1016/j.watres.2017.07.012

This Article is brought to you for free and open access by the Civil and Environmental Engineering at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Civil and Environmental Engineering Scholarship by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact Scholarly.Communication@unh.edu.

Organic Compounds in Hydraulic Fracturing Fluids and Wastewaters: A Review

Jenna L. Luek^{1} and Michael Gonsior¹*

1. University of Maryland Center for Environmental Science, Chesapeake Biological

Laboratory, Solomons, Maryland 20688, USA

Water Research, accepted manuscript. Published article can be found at:

<https://doi.org/10.1016/j.watres.2017.07.012>

© 2017. This manuscript version is made available under the CC-BY-NC-ND 4.0 license:

<http://creativecommons.org/licenses/by-nc-nd/4.0/>

**Corresponding Author: Jenna Luek, Telephone: +14126054898, Email: jluek88@gmail.com*

Key words: high volume hydraulic fracturing, fracking, flowback fluid, produced water

16 Graphical Abstract

17

18

19 Highlights

- 20 • GC and GC-MS are key analytical techniques used for organic chemical analysis
- 21 • BTEX, acetate, and acetone are the most frequently analyzed organic compounds
- 22 • Diverse halogenated organic compounds have been detected in flowback fluids
- 23 • Organic additives have been used to infer environmental contamination
- 24 • Development of new standards and standard methods for quantification are needed

25

26

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 compounds 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.

1. Introduction

Shale gas extraction via high volume hydraulic fracturing (HVHF) has resulted in the use of 116 billion liters of fluids annually from 2012-2014 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 (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 dibromonitrilopropionamide 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 identification of organic compounds is variable, with some compounds identified quantitatively

using standards while others rely on spectral libraries or match of exact mass due to a lack of standards and standardized methods (Schymanski et al., 2014). The use of quantitative techniques (^q), standards (^s), or spectral libraries (^l) is indicated in Table 1 by publication and technique.

Seventy percent of the samples analyzed for organic compounds have been collected from the Marcellus shale basin, which makes up ~37% of unconventional natural gas production but less than 0.01% of oil production (*Drilling Productivity Report*, 2017). Gas chromatography has been used extensively in these studies for volatile and semi-volatile organic compound (VOC, SVOC) analyses (Table 1). Ion chromatography (IC) has also been used to analyze small organic acids (Akob et al., 2015; Lester et al., 2013). High resolution LC-TOF-MS has been used to investigate specific additives, focusing mostly on samples from Weld County, Colorado in the Denver-Julesburg basin (Ferrer and Thurman, 2015b; Rosenblum et al., 2016; Thurman et al., 2014). Organic analyses have also been performed on samples collected from the Barnett shale (Maguire-Boyle and Barron, 2014; Thurman et al., 2014), the Wolfcamp and Cline shales in the Permian basin (Khan et al., 2016), New Albany shale (Orem et al., 2014), an unknown formation in Texas (Thacker et al., 2015), a single sample from each of the Eagle Ford, Fayetteville, Burket, and unspecified formations in Pennsylvania, Nevada, and Louisiana.

Figure 1. Summary of flowback and produced water samples analyzed to date for organic compounds in 18 studies given in Table 1. a) by basin b) fluid age c) analytical technique and d) number of publications by analytical technique.

Table 1. Published reports and peer-reviewed literature analyzing organic compounds in shale gas flowback and produced waters. ^qquantitative; ^scompared to standards; ^lcompared to spectral library [^]sample origins not precisely specified and up to 5 may overlap with samples reported by Lester et al., 2015; Rosenblum et al., 2016. *MBA, methyl blue active substances (for anionic surfactants).

Basin/Shale Gas Formation (state) [#]	Fluid Type (time of sampling)	Analytical Method for Organic Compound Identification (targeted classes)	Number of Samples	Source
Marcellus (PA), Burket (PA)	Produced (5 months - 38 months)	GC-MS (VOCs ^{q,s} , IC (organic acids)	13	(Akob et al., 2015)
Marcellus (PA)	Flowback and Produced	GC (alkenes, alkanes, acetate ^l), LC-TOF-MS (ethoxylated surfactants)	31	(Cluff et al., 2014)
Denver-Julesberg (CO)	Flowback and Produced	LC-TOF-MS (gels, surfactants, biocides ^s)	22 [^]	(Ferrer and Thurman, 2015b)

Marcellus (PA, WV)	Flowback (Day 1, 5, 14) Produced (Day 90)	GC-MS (VOCs, SVOCs, pesticides ^{q,s}) GC-ECD (PCBs ^{q,s}) GC-FID (ethylene glycol ^{q,s})	78	(Hayes, 2009)
Fayetteville (AR)	Flowback (Week 0-3) Produced (Week 50)	GC-FID (VOCs ^{q,s}), GC-MS (SVOCs), GCxGC-FID and GCxGC-TOF-MS (SVOCs)	6	(Hoelzer et al., 2016)
Permian-Wolfcamp, Cline (TX)	Produced (Day 130-441)	GCxGC-TOF-MS (VOCs ^{q,s,l} , SVOCs ^{q,s,l})	8	(Khan et al., 2016)
Marcellus (WV), Denver-Julesberg (CO), Utica (OH), ND, PA, WV	Flowback, Produced, Compression liquids	FT-ICR-MS (dissolved ionizable (ESI-) organics)	16	(Luek et al., 2017)
Denver-Julesberg (CO)	Flowback composite (unknown timing)	IC (acetic acid ^q), GC-MS (VOC, SVOC ^{q,s}) LC-TOF-MS (trace organic chemicals)	1	(Lester et al., 2015)
Marcellus (PA)	Flowback	HPLC (organic acids ^q)	3	(Murali Mohan et al., 2013b)
Marcellus (PA), Eagle Ford (TX), Barnett (NM)	Produced (unknown)	GC-MS (aliphatic, aromatic, resin, asphaltenes, halogenated ^l)	3	(Maguire-Boyle and Barron, 2014)
Marcellus (PA) New Albany (IN, KY)	Flowback and Produced (time series)	GC-MS (PAHs, , aromatic amines, phenols, heterocyclic and other aromatic & aliphatic compounds, phthalates, fatty acids ^{q,s,l}), HPLC (volatile fatty acids ^q)	Unknown (>14)	(Orem et al., 2014)
Denver-Julesberg (CO)	Produced (Unknown)	LC-TOF-MS (polyethylene glycols), GC-FID (total petroleum hydrocarbons)	4	(Rosenblum et al., 2016)
Marcellus (Greene County, PA)	Produced water (18 months)	GCxGC-TOF-MS (aliphatic, cycloaliphatic, and aromatic compounds, and PAHs)	1	(Strong et al., 2013)
Unknown (TX)	Unknown	GC-MS (VOCs ^{q,l} , SVOCs), LCMS-IT-TOF (surfactant), IC (organic acids ^q)	3	(Thacker et al., 2015)
Denver-Julesberg (CO), Barnett (TX), PA, NV, LA	Flowback and Produced	LC-TOF-MS (ethoxylated surfactants ^s)	12 [^]	(Thurman et al., 2014)
Marcellus (PA)	Flowback, Produced and Flowback/Produced Mixture	GC-FID (acetic acid, ethylene glycol, 1,2-propanediol ^{q,s}) HPLC (citric acid ^{q,s})	10	(Wolford, 2011)
Marcellus (WV)	Flowback (Day 0, 7, 14, 35)	Unreported, listed as EPA certified labs	13	(Ziemkiewicz, 2013)
Marcellus (WV)	Flowback	GC-MS (VOCs ^{q,s}) GC-FID (petroleum hydrocarbons ^{q,s}) MBA* (surfactants ^{q,s})	13	(Ziemkiewicz and He, 2015)

A number of known and suspect additives have been identified in flowback and produced waters, although not all studies had access to the corresponding list of additives or the HVHF fluid alone prior to injection (Cluff et al., 2014; Hayes, 2009; Hoelzer et al., 2016; Lester et al., 2015; Orem et al., 2014; Rosenblum et al., 2016; Strong et al., 2013; Thacker et al., 2015; Wolford, 2011). Quantitative analyses for known organic additives are still limited by a lack of standards and standard methods and many compounds can only be putatively identified. Several surfactants/dispersants have been identified including ethoxylated alcohols (Cluff et al., 2014; Lester et al., 2015; Thurman et al., 2014), ethoxylated phenols (Orem et al., 2014), glycols (Hayes, 2009; Orem et al., 2014; Robert Wolford, 2011; Rosenblum et al., 2016), alkyl amines (Thacker et al., 2015), cocamide compounds (Ferrer and Thurman, 2015b; Thacker et al., 2015), 2-butoxyethanol (Thacker et al., 2015), and bulk anionic surfactants (as methyl blue active substances) (Ziemkiewicz and He, 2015). Of these surfactants, only ethylene glycol and propylene glycol were reported quantitatively and neither of these studies appear in the peer reviewed literature (Hayes, 2009; Wolford, 2011). The biocides alkyl dimethyl benzyl ammonium chloride, glutaraldehyde, and hexahydro-1,3,5-trimethyl-1,3,5-triazine-2-thione have been detected but only the latter was quantified (Ferrer and Thurman, 2015b; Orem et al., 2014). The triazine biocide was initially detected in flowback at very high levels (1.5 mg L^{-1}) but returned to very low levels ($10 \text{ } \mu\text{g L}^{-1}$) within one week of well operation (Orem et al., 2014). Phthalates have been identified in several flowback and produced water samples (Hayes, 2009; Hoelzer et al., 2016; Lester et al., 2015; Maguire-Boyle and Barron, 2014; Orem et al., 2014). In quantitative analyses of phthalates, di-n-octyl-phthalate peaked in Marcellus shale early flowback ($5600 \text{ } \mu\text{g L}^{-1}$) and rapidly declined (Orem et al., 2014), but no clear pattern was observed in nineteen Marcellus shale well time series for diethyl phthalate, di-n-butyl phthalate,

di-n-octyl-phthalate, or bis-(2-ethylhexyl) phthalate (Hayes, 2009).

Citric acid, used for iron control, was reported in Marcellus flowback samples at high concentrations (9, 53, and 70 mg L⁻¹) but was not identified in any produced water samples within the same study (Wolford, 2011). 2,2,4-trimethyl-1,3,-pentanediol (solvent) and tridecane (fuel component) were also traced in a Marcellus shale well across flowback and produced waters, and while both peaked around the second day of flowback, both remained above 200 µg L⁻¹ in produced waters (Orem et al., 2014). The gelling agent guar gum was analyzed for but neither detected nor quantified in twenty-two Denver-Julesberg flowback and produced water samples (Ferrer and Thurman, 2015b). Bisphenol F and 2-butoxy ethanol were reported in a Texas produced water sample (Thacker et al., 2015), and a number of other additives have been reported non-quantitatively in several shale plays including a dioctadecyl ester of phosphate (lubricant), and some fluorinated organic compounds (possible flowpath tracers) (Hoelzer et al., 2016; Maguire-Boyle and Barron, 2014).

3.2 Geogenic organic compounds from additives and/or shale

Ultrahigh resolution mass spectrometry has been used to identify more than 30,000 organic compounds in shale oil.^{20,22} Although shale gas is more aged than shale oil and likely contains fewer organic compounds, interactions of the fracturing fluid with shale likely extracts a very large number of geogenic organic compounds from both oil and gas producing wells. Combined with a number of petrogenic additives such as petroleum distillates, kerosene, BTEX, mixed alkanes, and naphthalenes, many geogenic compounds may be present in any given flowback fluid or produced water. Indeed, more than a thousand geogenic organic compounds have been identified in flowback and produced waters using GC-FID, GC-MS, and GCxGC-

TOF-MS (Hoelzer et al., 2016; Maguire-Boyle and Barron, 2014; Orem et al., 2014; Strong et al., 2013), but only twenty four of these compounds have been reported quantitatively above the limit of detection in the peer reviewed literature (Akob et al., 2015; Lester et al., 2015; Ziemkiewicz and He, 2015; Ziemkiewicz, 2013). Reported concentrations of these quantifiable organic compounds are given in supplemental online materials (Table S1, Figure S1), including data from two non-peer reviewed sources (Hayes, 2009; Wolford, 2011). Dissolved methane as well as other light gases including ethane, propane, and butane will not be discussed here as they are by default present in productive wells. Overall, extractable hydrocarbons decreased in concentration during flowback and were lowest in produced water in a large number of analyzed samples (Orem et al., 2014). In broad spectrum reports of organic compounds in flowback and produced waters using various types of gas chromatography, aliphatic compounds were the dominant class identified (Hoelzer et al., 2016; Maguire-Boyle and Barron, 2014; Orem et al., 2014; Strong et al., 2013). Out of 986 compounds tentatively identified using GCxGC-TOF-MS in a Marcellus shale produced water, 61% of the identified compounds were aliphatic, and 24% were cycloaliphatic (Strong et al., 2013). Aromatic compounds represented 13% of the remaining compounds. PAHs accounted for 2% in this Marcellus shale produced water, and a substantial number of aromatic compounds and PAHs were also identified by other broad spectrum reports of organic compounds (Hoelzer et al., 2016; Maguire-Boyle and Barron, 2014; Orem et al., 2014). A new analytical technique has been developed for quantification of PAHs and other SVOCs in HVHF wastewater pairing solid-phase extraction with GC-MS (Regnery et al., 2016).

BTEX compounds were both the most frequently analyzed organic compounds in flowback and produced water and the most frequently detected organic compounds above

detection limits (Figure 2). In the Marcellus shale, BTEX concentrations were highest in flowback over the first 90 days, but were detectable at low concentrations in produced waters even several years after the initial HVHF event. Toluene, ethylbenzene, and xylene concentrations in flowback were up to two orders of magnitude lower than benzene quantified concurrently. Fayetteville, Burket, and Denver-Julesberg samples were only analyzed in early flowback and had similar levels to the Marcellus shale (Akob et al., 2016; Hoelzer et al., 2016; Lester et al., 2015). In the Permian basin, produced water after 130-441 days of operation had consistently high levels of benzene, toluene, and ethylbenzene, of hundreds of mg L^{-1} , while xylenes concentration were three orders of magnitude lower, similar to Marcellus flowback (Khan et al., 2016). High BTEX concentrations found in the Permian could be associated with oil production compared to the generally dry Marcellus shale gas. A clear distinction was made in a side by side comparison of BTEX in a dry and a wet Marcellus shale gas; wet gas concentrations were two orders of magnitude higher for all ions than dry gas, peaking in wet gas seven days after HVHF (benzene = $375 \mu\text{g L}^{-1}$, toluene = $2,100 \mu\text{g L}^{-1}$, xylenes (m,p) = $2,400 \mu\text{g L}^{-1}$) [ethylbenzene not reported] (Ziemkiewicz, 2013).

Aromatic compounds including polycyclic aromatic hydrocarbons have been quantitatively reported in a number of studies. Phenol, 2-methylphenol, 3&4-methylphenol, 2,4-dimethylphenol, 2-methylnaphthalene, phenanthrene, and pyrene were all quantified in a composite Denver-Julesberg basin flowback sample (Lester et al., 2015) and in Marcellus shale flowback and produced waters (Hayes, 2009). 1,2,4-trimethylbenzene and isopropylbenzene were quantified in Fayetteville flowback fluids and Marcellus shale flowback and produced waters (Hoelzer et al., 2016). New Albany shale produced waters also frequently contained alkyl naphthalenes, phenanthrenes, and pyrene (Orem et al., 2014). Alkylated benzenes and alkylated

naphthalenes were identified but not quantified in Barnett and Marcellus shales (Maguire-Boyle and Barron, 2014). Methyl phenol and dimethylphenol were detected in much higher concentrations in a composite flowback sample from the Denver-Julesburg basin than PAHs (150-830 ug L⁻¹ vs. <10ug L⁻¹) (Lester et al., 2015), but similar concentration ranges of both the phenolic and PAH compounds were observed in the Marcellus (Hayes, 2009). A number of oxygen containing resins/asphaltenes were identified in Marcellus, Barnett and Eagle Ford shale produced waters (Maguire-Boyle and Barron, 2014).

Polychlorinated biphenyls (PCBs) and pesticides were analyzed for the Hayes report (Hayes, 2009) in nineteen wells over the first ninety days after HVHF, but were only detected sporadically in very low concentrations and the report concluded that testing for these compounds in future wastewater analyses was unnecessary. These compounds have not been specifically targeted in any other study, and no evidence has been provided for a potential source for these compounds in fracturing additives.

Figure 2. Concentrations (log scale) of benzene (a), toluene (b), ethylbenzene (c), and xylene (d) in flowback and produced water samples by days after HVHF well completion from literature (Akob et al., 2015; Hayes, 2009; Hoelzer et al., 2016; Khan et al., 2016; Lester et al., 2015; Wolford, 2011; Ziemkiewicz, 2013; Ziemkiewicz and He, 2015). Open triangles indicate mean of 13 Marcellus samples (Ziemkiewicz and He, 2015), colored triangles represent individual data points. Fayetteville samples are shown on day 10 for comparison but were collected within the first three weeks (Hoelzer et al., 2016). Note: benzene and ethylbenzene are given on a different scale than toluene and xylenes.

3.3 Transformation products of organic constituents

Transformations in HVHF fluids of organic compounds may occur through physico-chemical or biological processes. Indeed, specific additives are designed to chemically transform and “break” polymers in the fracturing fluid to reduce surface tension before flowback begins (Stringfellow et al., 2014). Despite the use of biocides, high bacterial cell counts have been identified both in the injected fluids and in flowback and produced waters (Cluff et al., 2014;

Mohan et al., 2014; Murali Mohan et al., 2013a). Hence, a combination of physical, chemical and biologically mediated reactions ultimately drive the transformation of organic compounds in these fluids (Elsner and Hoelzer, 2016; Hoelzer et al., 2016).

A number of small organic acids are produced through microbial transformation under the anaerobic conditions frequently observed in HVHF wastewater via fermentation (Müller, 2008). Small organic acids were analyzed in a handful of studies, although not all report quantitative results. Acetate was measured in seven studies (**Figure 3**), formate in three (Akob et al., 2015; Strong et al., 2013; Thacker et al., 2015), and citrate (Wolford, 2011), lactate, propionate, butyrate, and pyruvate (Akob et al., 2015) were each analyzed in one study. Acetate, propionate, and butyrate were measured in the Hayes dataset with high method detection limits (10mg L^{-1}) but are not included due to questionable reliability (Hayes, 2009). Acetate and other organic acids are likely produced during the anaerobic degradation of additives and potentially geogenic substances as hydrocarbons are degraded to acetate under anaerobic conditions (e.g., Callbeck et al., 2013). Indeed, fermentative classes of bacteria capable of producing organic acids were identified in flowback samples where acetate was identified (Cluff et al., 2014; Murali Mohan et al., 2013b). Acetate concentrations were highest in flowback samples, presumably due to the high concentrations of degradable organic additives such as ethoxylates, guar gum, and glycols. The highest concentration of acetate observed (1600 mg L^{-1}) was in a composite flowback sample, and was three times higher than the next highest sample and an order of magnitude higher than most flowback samples (Lester et al., 2015). Aeration of flowback fluid resulted in acetate decreasing below detection limits, which is not surprising as fermentation would no longer be occurring and any acetate previously produced would likely be readily mineralized *in situ* under aerobic conditions (Murali Mohan et al., 2013b). Produced

310 water samples contained much lower acetate concentrations. In 14 Marcellus shale produced
 311 water samples (**Figure 3, Produced***), the mean acetate concentration was 10.6 mg L^{-1} , but the
 312 range was not reported (Orem et al., 2014). In 16 other produced water samples, the mean acetate
 313 concentration was 7.0 mg L^{-1} . Formate was not detected in two of the three studies in which it
 314 was analyzed, and in those where it was not detected acetate was also absent (Strong et al., 2013;
 315 Thacker et al., 2015). Butyrate was not detected in any of the 13 produced water samples it was
 316 analyzed in, but propionate, lactate, formate, and pyruvate were detected in produced water
 317 samples at low levels ($<4 \text{ mg L}^{-1}$ each) and acetate in slightly higher concentrations (mean 5.8
 318 mg L^{-1}). These are indications for continued bacterial activity (Akob et al., 2015).

319

320

321 **Figure 3.** Boxplot of acetate/acetic acid concentrations in quantified samples reported in literature (Akob et al.,
 322 2015; Lester et al., 2015; Murali Mohan et al., 2013b; Orem et al., 2014; Strong et al., 2013; Thacker et al., 2015;
 323 Wolford, 2011). Box gives median and 25th and 75th percentiles, whisker represent 90th percentile, and individual
 324 points show outliers. Acetate values below detection for one produced and two HVHF wastewater samples were not
 325 included in the box plot (Strong et al., 2013; Thacker et al., 2015). Mixed is a combination of flowback and
 326 produced water (Wolford, 2011). Produced* represents mean of 14 samples reported by (Orem et al., 2014).

Figure 4. Acetone concentrations in flowback and produced water to 90 days compiled from literature values (Akob et al., 2015; Hayes, 2009; Hoelzer et al., 2016; Lester et al., 2015; Wolford, 2011; Ziemkiewicz, 2013; Ziemkiewicz and He, 2015). Acetone analyses were not performed on samples collected more than 90 days after HVHF well completion.

Acetone in flowback may originate from its use as an additive, may be a transformation product via anaerobic fermentation via pyruvate (Rosenfeld and Simon, 1950), or may be associated with both sources. Acetone concentrations were highly variable in flowback samples (most ND, median $90 \mu\text{g L}^{-1}$ in positive detections, mean of $1,060 \mu\text{g L}^{-1}$ in $n=37$ positive detections) and acetone was not measured in any samples after 90 days (Figure 4). The highest observed concentration was measured in a composite flowback sample ($16,000 \mu\text{g L}^{-1}$) (Lester et al., 2015), and several other flowback samples had acetone concentrations ranging from 10^2 - $10^3 \mu\text{g L}^{-1}$ (Hayes, 2009). Interestingly, in at least one supply water sample (used for mixing to make HVHF fluid), acetone concentrations were even higher than in flowback (Hayes, 2009), suggesting that this supply water was likely a recycled fluid that contained high levels of acetone as an additive or degradable organic additives that underwent fermentation to form acetone. In a simulated bioreactor “spill” of HVHF fluids, acetone was produced as a degradation product (see Section 4.2) (Kekacs et al., 2015).

19% of the 404 identified organic compounds in Fayetteville shale flowback fluid and

produced waters using GCxGC-TOF-MS were suspected to be formed through subsurface reactions (Hoelzer et al., 2016). Many of these compounds included carbonyl groups (Hoelzer et al., 2016) that may indicate degradation of geopolymers or hydrolysis products of delayed-release acids used as breakers (Hoelzer et al., 2016; Orem et al., 2014, 2010). In Marcellus shale produced waters, 2,2,4-trimethyl-1,3-pentanediol was identified at high concentrations (130 - 500 $\mu\text{g L}^{-1}$) in flowback and remained at those concentrations in the produced waters even 234 days after HVHF (Orem et al., 2014). This compound has not been identified as an additive previously, but a related compound, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, has been used industrially as a solvent and may potentially be related to the source of this derivative (Orem et al., 2014). A direct transformation product of the known additive, azobis (isobutyronitrile), tetramethylsuccinonitrile was identified by GCxGC-TOF-MS in Fayetteville shale produced waters (Hoelzer et al., 2016). Dimerization and trimerization of the frequently used biocide glutaraldehyde under the variable salinity, temperature, and pressure conditions reflecting a shale gas well has been tested under laboratory conditions (Kahrilas et al., 2016), but has not been observed in flowback and produced waters (Ferrer and Thurman, 2015b). Additionally, hydroxylated phenols identified in flowback fluids are likely degradation products of alkylphenol ethoxylate additives (Hoelzer et al., 2016).

A number of studies have putatively identified halogenated organic compounds in flowback and produced waters that are much more diverse than the limited number of known halogenated additives (Table 2). Perfluorinated organic compounds identified in the Eagle Ford shale produced waters were suggested to be tracers used for reservoir mapping (Maguire-Boyle and Barron, 2014). Methylene chloride is the only explicitly disclosed halogenated organic compound identified in flowback and produced waters, but four additional halogenated organic

compounds (chloromethyl propanoate, chloromethyl pentanoate, chloromethyl hexanoate, chloromethyl octanoate) identified by Hoelzer and colleagues are suspected HVHF additives (Hoelzer et al., 2016). Four studies have identified a number of additional halogenated organic compounds that are likely transformation products and several potential mechanisms for the formation of these compounds are hypothesized (Hayes, 2009; Hoelzer et al., 2016; Luek et al., 2017; Maguire-Boyle and Barron, 2014). Maguire-Boyle and Barron (2014) identified the corresponding non-halogenated aliphatic compound for each halogenated compound and suggested that the halide salts or free halogens created during oxidative treatments could cause the observed halogenation (Maguire-Boyle and Barron, 2014). Similarly, Hoelzer and colleagues indicated radicalic substitution, nucleophilic substitution, and electrophilic addition in the presence of halides and free halogen species as the proposed halogenation mechanisms (Hoelzer et al., 2016). In streambed sediments downstream of a deep well injection facility, several halogenated organic compounds including 1,54-dibromotetrapentacontane were identified (Orem et al., 2017).

Table 2. Halogenated organic compounds identified in flowback and produced waters. *Italicized* compounds are explicit and suspect fracturing fluid additives. Note: Compounds identified in Hayes (2009) rely on EPA methods with quantification using reference standards; Hoelzer et al., (2016) and Maguire-Boyle and Barron (2014) match ions using spectral libraries and report confidence in assignment in their supplemental materials. Halogenated chemical formulas in Luek et al., (2017) not included due to lack of structural information.

Compound	Molecular Formula	Method	Source
Chloromethane	CH ₃ Cl	GC/MS EPA Method SW846 8260B	Hayes 2009
<i>Dichloromethane</i>	<i>CH₂Cl₂</i>	<i>GC/MS EPA Method SW846 8260B</i>	<i>Hayes 2009</i>
<i>Dichloromethane</i>	<i>CH₂Cl₂</i>	<i>GCxGC-TOF-MS</i>	<i>Hoelzer et al., 2016</i>
<i>Dichloromethane</i>	<i>CH₂Cl₂</i>	<i>GC/MS</i>	<i>Maguire-Boyle and Barron 2014</i>
Trichloromethane	CHCl ₃	GC/MS	Maguire-Boyle and Barron 2014
Tetrachloroethene	C ₂ Cl ₄	GC/MS EPA Method SW846 8260B	Hayes 2009

1,1-dichloroethane	C ₂ H ₄ Cl ₂	GC/MS	Maguire-Boyle and Barron 2014
1,1'-oxybis[1,1]-dichloromethane	C ₂ H ₄ Cl ₂ O	GC/MS	Maguire-Boyle and Barron 2014
<i>Chloromethyl propanoate</i>	C ₄ H ₇ ClO ₂	GCxGC-TOF-MS	Hoelzer et al., 2016
bis(2-chloroethyl) ether	C ₄ H ₈ Cl ₂ O	GC/MS EPA Method SW846 8260B	Hayes 2009
1-chloro-5-iodo-pentane	C ₅ H ₁₀ ClI	GCxGC-TOF-MS	Hoelzer et al., 2016
1,1-dimethyl-3-chloropropanol	C ₅ H ₁₁ ClO	GCxGC-TOF-MS	Hoelzer et al., 2016
Hexachlorobenzene	C ₆ Cl ₆	GC/MS EPA Method SW846 8270C	Hayes 2009
2-(chloromethyl) tetrahydropyran	C ₆ H ₁₁ ClO	GCxGC-TOF-MS	Hoelzer et al., 2016
2-chlorocyclohexanol	C ₆ H ₁₁ ClO	GCxGC-TOF-MS	Hoelzer et al., 2016
<i>Chloromethyl pentanoate</i>	C ₆ H ₁₁ ClO ₂	GCxGC-TOF-MS	Hoelzer et al., 2016
1-chloro-3,3-dimethyl-butane	C ₆ H ₁₃ Cl	GCxGC-TOF-MS	Hoelzer et al., 2016
1,2,3-trichlorobenzene	C ₆ H ₃ Cl ₃	GC/MS EPA Method SW846 8260B	Hayes 2009
1,2,4-trichlorobenzene	C ₆ H ₃ Cl ₄	GC/MS EPA Method SW846 8260B	Hayes 2009
1,4-dichlorobenzene	C ₆ H ₄ Cl ₂	GC/MS EPA Method 624	Hoelzer et al., 2016
2,6-dichlorophenol	C ₆ H ₄ Cl ₂ O	GC/MS EPA Method SW846 8270C	Hayes 2009
2,4-dichloro-5-oxo-2-hexenedioic acid	C ₆ H ₄ Cl ₂ O ₅	GC/MS	Maguire-Boyle and Barron 2014
Dichlorophenol	C ₆ H ₄ ClO	GC/MS EPA Method SW846 8260B	Hayes 2009
2,2-dichloro-3,6-dimethyl-1-Oxa-2-silacyclohexa-3,5-diene	C ₆ H ₈ Cl ₂ OSi	GC/MS	Maguire-Boyle and Barron 2014
3-chloro-1,1,2,2-tetramethyl-cyclopropane	C ₇ H ₁₃ Cl	GCxGC-TOF-MS	Hoelzer et al., 2016
<i>Chloromethyl hexanoate</i>	C ₇ H ₁₄ ClO ₂	GCxGC-TOF-MS	Hoelzer et al., 2016
<i>Chloromethyl octanoate</i>	C ₉ H ₁₇ ClO ₂	GCxGC-TOF-MS	Hoelzer et al., 2016
1-chlorohexadecane	C ₁₆ H ₃₃ Cl	GC/MS	Maguire-Boyle and Barron 2014
1-chlorooctadecane	C ₁₈ H ₃₇ Cl	GC/MS	Maguire-Boyle and Barron 2014
Trichlorodocosylsilane	C ₂₂ H ₄₅ Cl ₃ Si	GC/MS	Maguire-Boyle and Barron 2014
1-chloroheptacosane	C ₂₇ H ₅₅ Cl	GC/MS	Maguire-Boyle and Barron 2014
Bromomethane	CH ₃ Br	GC/MS EPA Method SW846 8260B	Hayes 2009
Tribromomethane	CHBr ₃	GC/MS EPA Method SW846 8260B	Hayes 2009
2-bromo-hexane	C ₆ H ₁₃ Br	GCxGC-TOF-MS	Hoelzer et al., 2016
1-bromo-2-methyl-cyclohexane	C ₇ H ₁₃ Br	GCxGC-TOF-MS	Hoelzer et al., 2016
4-bromoheptane	C ₇ H ₁₅ Br	GCxGC-TOF-MS	Hoelzer et al., 2016
2-piperidinone, N-[4-bromo-n-butyl]	C ₉ H ₁₆ BrNO	GCxGC-TOF-MS	Hoelzer et al., 2016
2-bromo-tricyclo[3.3.1.1(3,7)]decane	C ₁₀ H ₁₅ Br	GCxGC-TOF-MS	Hoelzer et al., 2016
3-bromo-cyclodecene	C ₁₀ H ₁₇ Br	GCxGC-TOF-MS	Hoelzer et al., 2016
4,5-dibromo-, (R*,R*)-decane	C ₁₀ H ₂₀ Br ₂	GCxGC-TOF-MS	Hoelzer et al., 2016
1,12-dibromododecane	C ₁₂ H ₂₄ Br ₂	GC/MS	Maguire-Boyle and Barron 2014

14-bromo-1-tetradecene	C ₁₄ H ₂₇ Br	GC/MS	Maguire-Boyle and Barron 2014
1-bromopentadecane	C ₁₅ H ₃₁ Br	GC/MS	Maguire-Boyle and Barron 2014
7-bromomethyl-pentadec-7-ene	C ₁₆ H ₃₁ Br	GCxGC-TOF-MS	Hoelzer et al., 2016
1-bromohexadecane	C ₁₆ H ₃₃ Br	GC/MS	Maguire-Boyle and Barron 2014
1-bromooctadecane	C ₁₈ H ₃₇ Br	GC/MS	Maguire-Boyle and Barron 2014
1,54-dibromotetrapentacontane	C ₅₄ H ₁₀₈ Br ₂	GC/MS	Maguire-Boyle and Barron 2014
3-iodo-propanoic acid,	C ₃ H ₅ IO ₂	GCxGC-TOF-MS	Hoelzer et al., 2016
2-iodo-3-methyl-butane	C ₅ H ₁₁ I	GCxGC-TOF-MS	Hoelzer et al., 2016
5-iodopentan-2-one	C ₅ H ₉ IO	GCxGC-TOF-MS	Hoelzer et al., 2016
1-iodo-nonane	C ₉ H ₁₉ I	GCxGC-TOF-MS	Hoelzer et al., 2016
1-iodo-2-methylundecane	C ₁₂ H ₂₅ I	GCxGC-TOF-MS	Hoelzer et al., 2016
1-iodo-2-methylundecane	C ₁₂ H ₂₅ I	GC/MS	Maguire-Boyle and Barron 2014
1-iodo-tetradecane	C ₁₄ H ₂₉ I	GCxGC-TOF-MS	Hoelzer et al., 2016
Bromodichloromethane	CHBrCl ₂	GCxGC-TOF-MS	Hoelzer et al., 2016
1,3-dioxolane, 2-(3-bromo-5,5,5-trichloro-2,2-dimethylpentyl)	C ₁₀ H ₁₆ BrCl ₃ O ₂	GCxGC-TOF-MS	Hoelzer et al., 2016
1-bromo-11-iodoundecane	C ₁₁ H ₂₂ BrI	GC/MS	Maguire-Boyle and Barron 2014

4. Environmental Contamination

4.1 Contamination Events

In the peer-reviewed literature, specific organic compounds have been identified in surface water, sediments, and groundwater and have been linked to recent HVHF activities (Cozzarelli et al., 2017; DiGiulio and Jackson, 2016a; Drollette et al., 2015; Gross et al., 2013; Hildenbrand et al., 2016, 2015; Kassotis et al., 2014; Llewellyn et al., 2015; Orem et al., 2017). These suspected contamination events were documented in the Bakken, Powder River Basin, Marcellus, Permian, Barnett, and Denver-Julesberg basins, and next to a deep well injection facility in West Virginia. The EPA has also published five “retrospective case studies” investigating the impacts of HVHF on drinking water sources in five different locations between 2011-2013. (*Retrospective Case Study in Killdeer, North Dakota: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015, *Retrospective Case Study in Northeastern Pennsylvania: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015, *Retrospective Case Study in Southwestern Pennsylvania Study of the*

Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, 2015, Retrospective Case Study in the Raton Basin, Colorado: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, 2015, Retrospective Case Study in Wise County, Texas: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, 2015). Organic analyses have focused on additives and oil and gas related compounds; inorganic tracers of HVHF including anions and metals have also been analyzed in these samples to understand the potential contamination events.

The only large volume surface spill of HVHF wastewaters (11.4 million liters) extensively analyzed for organic compounds and published in the literature occurred in Blacktail Creek in North Dakota (Bakken formation) in January of 2015. Streamwater water and stream bed sediment samples were collected in February and June of 2015 for a large number of organic and inorganic chemical analyses, biological, and toxicological analyses (Cozzarelli et al., 2017). SVOCs including 1,3,5-trimethylbenzene, 1,2,3,4-tetramethylbenzene, and 1-methylnaphthalene were quantified in unfiltered water samples in a location of an oily sheen downstream from the spill location. However, these compounds were absent from filtered water samples, suggesting that many of these organic compounds might have been particle-bound. Trace SVOCs were identified in streambed sediment below reporting limits, but the authors suggested that the spill pathway over 10s of meters of soil could have resulted in substantial sorption of hydrophobic organic compounds to soil prior to the spill entering the stream (Cozzarelli et al., 2017). Surface contamination of streamwaters and streambed sediments were also investigated outside of a deep well injection facility in West Virginia to determine if the large volumes of HVHF wastewater transported and unloaded on site resulted in contamination of the nearby environment (Akob et al., 2016; Orem et al., 2017). Extensive organic chemical analyses were performed targeting oil

and gas compounds, known HVHF chemical additives, disinfection by-products, and additional SVOCs including halogenated compounds (Orem et al., 2017). In streamwater, only tetra-hydro-thiophene 1,1-dioxide, a compound used for cleaning natural gas, was consistently identified downstream of the facility. In sediments, a complex mixture of organic compounds was identified which included a number of halogenated organic compounds (trifluoroacetate/alkanes and halogenated alkanes), some of which have been identified previously in HVHF fluids (Maguire-Boyle and Barron, 2014) and wastewaters while others are of unknown origin. Although the results are complex and indicate possible broader contamination in the region upstream of the facility, the distribution of organic compounds combined with inorganic analyses (Akob et al., 2016) indicated clear environmental contamination from the HVHF wastewater disposal facility.

The largest groundwater investigation to investigate the impacts of HVHF were performed using private and public groundwater wells from aquifers overlying the Permian (n=42 wells, multiple time points) and Barnett basins (n=550, n=100) (Fontenot et al., 2013; Hildenbrand et al., 2016, 2015). Samples in both basins were analyzed using GC-MS and headspace-gas chromatography (HS-GC) for a number of organic compounds identified in HVHF fluid as well as others associated with oil and gas development. BTEX compounds, chlorinated solvents (dichloromethane, chloroform), and low molecular weight alcohols were detected in a number of Barnett region samples, with only toluene and methanol distributions indicative of surface spills (Hildenbrand et al., 2015). Ethanol was found alongside high bromide concentrations, another tracer of HVHF wastewater (Hildenbrand et al., 2015). Permian basin groundwater wells were sampled at four time points, during which unconventional oil and gas development increased significantly (Hildenbrand et al., 2016). Following the initial time point,

ethanol and dichloromethane elevated significantly at an additional time point, and a number of other organic compounds associated with oil and gas development and degradation (isopropyl alcohol, propargyl alcohol, acetaldehyde, cyclohexane, toluene, xylene, ethylbenzene) that were not present in the initial sampling campaign were identified (Hildenbrand et al., 2016). The authors ultimately concluded that their findings indicated the transient nature of potential contamination events in developed areas (Hildenbrand et al., 2016).

In northeastern Pennsylvania, groundwater samples were collected from private residential wells (9-231 m depth) and analyzed for GC-amenable compounds (Drollette et al., 2015). Gas related organic compounds were detected in 9 of 59 wells and diesel related organic compounds were detected in 23 of 41 wells in highly variable concentrations (Drollette et al., 2015). BTEX compounds were identified in 6 samples at trace levels below EPA drinking water maximum contaminant level recommendations (Drollette et al., 2015). The highest concentrations of observed organic compounds were identified within 1 km of a shale gas well as well as in close proximity to a well that caused an environmental health and safety violation. Based on geochemical fingerprinting tools, the authors concluded that the groundwater contamination was likely due to surface spills associated with HVHF activities rather than via subsurface contamination. Additionally, a disclosed additive, bis(2-ethylhexyl) phthalate, was identified in the same two samples with the highest diesel related organic compounds concentrations. Foaming was also observed in three residential drinking water wells in northern Pennsylvania located in close proximity to HVHF wells (Llewellyn et al., 2015). Commercial laboratories were unable to detect any compounds during this known contamination event other than methane that exceeded regulatory drinking water standards and recommendations, but 2-

butoxyethanol was identified in the foaming waters using GCxGC-qTOF-MS. 2-butoxyethanol is an ingredient in the Airfoam HD additive frequently used during HVHF (Llewellyn et al., 2015).

In Weld County, CO, 218 groundwater samples were analyzed for BTEX following 77 industry reported spills of oil or produced waters. Following remediation at several sites, benzene remained above the maximum contaminant limit for groundwater in 59% of sites, and above these levels outside of the remediation area in 37% of sites (Gross et al., 2013). In Garfield County, CO, groundwater samples were collected in a high density shale gas drilling region and analyzed for the endocrine disruption capacity (EDC) of the solid phase extracts of these fluids (Kassotis et al., 2014). In 39 samples, 89% of samples exhibited estrogenic activity, 41% anti-estrogenic, 12% androgenic, and 46% anti-androgenic activity; significantly higher than nearby drilling sparse control sites. These high EDC activities were suspected to be related to groundwater contamination due to HVHF activities from any of the more than 100 known EDCs found in HVHF additives (Kassotis et al., 2014).

Following complaints of residents, the EPA investigated groundwater contamination in Pavilion, WY suspected to be associated with the HVHF of shallow gas wells through the installation of several shallow and deep groundwater monitoring wells (DiGiulio and Jackson, 2016a; DiGiulio et al., 2011). Multiple phases of monitoring were performed beginning with existing residential and municipal wells, followed by shallow monitoring wells, and finally by two explicitly drilled deep monitoring wells (235 m, 295 m) (DiGiulio et al., 2011). Shallow wells had high levels of BTEX, diesel and gas related compounds, and other hydrocarbons, but ultimately were suspected of contamination by the use of surface unlined pits where fluids including diesel used for gas extraction were stored (DiGiulio and Jackson, 2016a). However, organic compounds identified in deep groundwater monitoring wells were different than those

identified in surface wells and a number of known synthetic organic compounds used for HVHF were identified (DiGiulio and Jackson, 2016a; DiGiulio et al., 2011). These included isopropanol (biocide, surfactant, breakers, foaming agents), nonylphenol and octylphenol (surfactants), diethylene glycol, triethylene glycol, tetraethylene glycol (solvent, foaming agent), 2-butoxyethanol (gelling agent), and a suspected degradation product of possible undisclosed additives, tert-butyl alcohol (DiGiulio and Jackson, 2016a; DiGiulio et al., 2011). Aromatic solvent, diesel oil, heavy aromatic petroleum naphtha, toluene, xylene and petroleum raffinates (material remaining following extraction of specific petroleum products) were reported as fracturing fluid additives in the nearby well, and a number of compounds reflecting these additives were identified in the monitoring wells including BTEX, trimethylbenzenes, naphthalenes, and phenols (DiGiulio and Jackson, 2016a; DiGiulio et al., 2011). Diesel and gas related organic compounds in 23 of 28 nearby domestic well samples correlated with reports of foul odors (DiGiulio et al., 2011). Phthalates, acetone, 2-butanone, and 3-methyl-2-pentanone, benzoic acid, and other small organic acids were also identified in the groundwater samples.

In the EPA retrospective case studies (*Retrospective Case Study in Killdeer, North Dakota: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015, *Retrospective Case Study in Northeastern Pennsylvania: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015, *Retrospective Case Study in Southwestern Pennsylvania Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015, *Retrospective Case Study in the Raton Basin, Colorado: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015, *Retrospective Case Study in Wise County, Texas: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015), a suite of organic compounds including VOCs, SVOCs, and

DRO and GRO compounds were analyzed in groundwater and surface water samples based on complaints of changes in water quality. In the Northeastern PA and Southwestern PA case studies (Marcellus shale), low level and sporadic detections of organic compounds including phthalates, toluene, benzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, chloroform, acetone, phenol, 2-butoxyethanol, and phthalates as well as DRO and GRO were suspected laboratory and field contaminants and inconsistent with contamination due to hydraulic fracturing activities due to a lack of other potential indicators such as chloride, TDS, Ba, or Sr (*Retrospective Case Study in Northeastern Pennsylvania: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015, *Retrospective Case Study in Southwestern Pennsylvania Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*, 2015). Similarly, detections of these compounds as well as xylene in the Killdeer aquifer were presumed to be laboratory contaminants with the exception of tert-butyl alcohol (TBA) at two groundwater sites. At these sites, along the groundwater flowpath from a documented well blowout, TBA was elevated ($975 \mu\text{g L}^{-1}$) and had a documented HVHF fluid source. TBA as well as chloride decreased over the four time points, consistent with the movement of a contaminant plume through the wells (U.S. EPA, 2015b). Acetate and formate, indicators of hydrocarbon degradation, were detected in 31% of wells and 10% of wells, respectively, in the sampled groundwaters (U.S. EPA, 2015b). In Wise County, TX (Barnett Shale), VOCs were detected, including tert-butyl alcohol, methyl tert-butyl ether, ethyl tert-butyl ether, tert-amyl methyl ether, m+p-xylene, o-xylene, 1,2,4-trimethylbenzene, and benzene; however, the sources of the compounds was considered unidentified because there were not repeated detections and no glycol ethers indicative of hydraulic fracturing (U.S. EPA, 2015e). In the Raton Basin, CO, (coal bed methane) a large number of organic chemicals were detected,

representing possible HVHF fluid additives, as well potential natural sources (U.S. EPA, 2015c). VOCs such as BTEX detected in this study were interpreted to originate from water-rock interactions or enhanced solubilization due to the solvent-like properties of the injection fluid (U.S. EPA, 2015c). Again, TBA was detected in some sites at high levels (maximum 1,310 $\mu\text{g L}^{-1}$), but the observation was interpreted as not necessarily representing contamination from a HVHF fluid event because neither TBA or its parent compounds were disclosed, and sufficient spatial data or adequate pre-HVHF controls did not exist (U.S. EPA, 2015c).

These studies and their critics bring up common issues in interpreting environmental data and associating the observations with a specific contamination source. First, in nearly all scenarios, relatively few baseline data exists for sampling locations as all extensive studies have been completed in response to perceived threats or changes. Baseline data for organic compounds are rarer than for inorganic ions and are completely absent for specific tracers that may be strong indicators of a HVHF source. Reference sites in the same geologic region are sometimes used as a control variable, but these are also susceptible to contamination from past events, especially considering shale gas regions are co-located in conventional oil and gas regions that have been drilled for longer time periods. Unfortunately, baseline data cannot retroactively be collected and this will continue to be a critical issue in interpreting data. A second common critique is of the observations of some compounds associated with HVHF, but an absence of others associated with HVHF (Connor et al., 2016; McHugh et al., 2016, 2014). Fontenot, Meik and colleagues responded in describing the role changing pH and redox conditions plays on dissolved metal concentrations (Fontenot et al., 2014; Meik et al., 2016). DiGiulio and Jackson responded by explaining that heterogeneity in itself is indicative of anthropogenic impact if groundwater samples are obtained from the same formation (DiGiulio

and Jackson, 2016b). Previous research has shown the differences in groundwater transport of contaminants based on the strength of their interaction with the geologic formation and soils, as reactive or nonreactive solutes (Brusseau, 1994; Burr et al., 1994; Mackay et al., 1986). Nonreactive solutes such as chloride will be transported faster than reactive organic compounds associated with HVHF fluids which may be retarded through interactions with the geologic formations and organic carbon present in these formations (Allen-King et al., 2002; Mackay et al., 1986).

4.2 Simulated bioreactor “spills”

Two published studies have simulated spills of HVHF fluids at the bench scale under aerobic conditions. In each of these studies, a synthetic mixture of HVHF fluid additives was mixed with natural microbial communities and the organic additives quantified over 7-180 days. In an aerobic solution inoculated with an activated sludge microbial community, the overall dissolved organic carbon (DOC) content decreased by 52% in 6.5 days in freshwater and a 20 g L⁻¹ saline solution. At higher salinities (40 g L⁻¹ and 60 g L⁻¹), DOC did not change significantly over the same time period. Acetone, a degradation product, increased by two orders of magnitude, and volatile additives such as naphthalene and benzene were rapidly decreased in concentration, likely due to volatilization (Kekacs et al., 2015). In the second study, varying combinations of fracturing fluid additives were mixed with agricultural soil and the *in situ* microbial community and their changes tracked to understand co-contaminant interactions over 180 days (McLaughlin et al., 2016). The presence of glutaraldehyde biocide impeded the degradation of polyethylene glycol surfactants, and high salt levels also severely inhibited their

degradation. Polyacrylamide was not degraded over the duration of the experiment, but did react with the biocide glutaraldehyde (McLaughlin et al., 2016).

5. Flowback and Produced Water Treatment

High total dissolved solids (TDS) create a significant challenge for the treatment of flowback and produced waters (Gregory et al., 2011; Kondash et al., 2017), hence wastewaters are frequently sent to Class II disposal wells (U.S. EPA, 2016). TDS varies by basin and increases over the lifetime of the well (Kondash et al., 2017); high levels of TDS limit direct reuse due to scaling problems and reduced effectiveness of friction reducers (Gregory et al., 2011; Kamel and Shah, 2009). The fate of the treated effluent determines the type and amount of treatment required. The treatment for reuse in HVHF requires a different level of treatment (e.g., precipitation of scaling cations, disinfection, (Lester et al., 2015)) than other beneficial reuses or discharge to the environment (Estrada and Bhamidimarri, 2016; Gregory et al., 2011). High TDS formation produced waters, such as the Bakken or Marcellus, cannot be directly reused and TDS must be first reduced either by using dilution or treatment, which is in contrast to formations such as the Niobrara or Eagle Ford, that have much lower TDS (Kondash et al., 2017).

The wide variety of treatment methods used for flowback and produced waters have been reviewed previously (Drewes et al., 2009; Estrada and Bhamidimarri, 2016; Fakhru'l-Razi et al., 2009; Gregory et al., 2011; U.S. EPA, 2016). Traditional oil and gas centralized waste treatment and municipal treatment facilities (no longer in use) have not been shown to sufficiently remove key contaminants from HVHF wastewaters prior to discharging to streams (Ferrar et al., 2013; Getzinger et al., 2015; Warner et al., 2013). Thermal distillation and crystallization technologies efficiently remove TDS but may be energy intensive, while membrane technologies such as

reverse osmosis, forward osmosis, and nanofiltration are prone to clogging and fouling and are more effective when combined with pre-treatment technologies (Coday et al., 2014; Estrada and Bhamidimarri, 2016; Gregory et al., 2011; Jang et al., 2017; Riley et al., 2016; Shaffer et al., 2013).

Few individual organic compounds have been tracked through industrial treatment facilities, although any given treatment train could neglect a number of organic compounds, additives, and transformation products. The effectiveness of a given treatment method on organic compounds is frequently reported only for regulated hydrocarbons such as total oil and grease (Drewes et al., 2009), or other bulk measurements including dissolved organic carbon (DOC), chemical oxygen demand and 3D excitation-emission matrix fluorescence (e.g., Hickenbottom et al., 2013; Lobo et al., 2016; Riley et al., 2016).

Bench-scale experiments have examined the removal efficiencies of a number of organic compounds frequently found in HVHF wastewaters. Guar gum, a common HVHF additive likely to foul membranes, was effectively removed biologically (~90%) at low TDS using an activated sludge mixture (Lester et al., 2014). In a different synthetic HVHF wastewater, forward osmosis rejected >99.9% of oil while acetic acid rejection was much lower at only 82% (23 °C) and 74% (60 °C) (Zhang et al., 2014). More hydrophobic compounds, including alkanes and polycyclic aromatic hydrocarbons, were removed with 90-99% efficiency using forward osmosis (Bell et al., 2017). Powdered activated carbon (PAC) combined with coagulants were tested for removal efficiency of total petroleum hydrocarbons and polyethylene glycols from actual HVHF flowback and produced waters. PAC was shown to be effective at high doses (750 mg L⁻¹, 1,000 mg L⁻¹ PAC) for polyethylene glycol removal in all cases and in three out of four wastewaters for total petroleum hydrocarbons (Rosenblum et al., 2016). However, these specific classes

represented only a fraction of the DOC, and much of the DOC was not removed (52-90%) using PAC (Rosenblum et al., 2016).

6. Considerations and Future Research

Reviewing and synthesizing the literature on HVHF organic compounds remains challenging due to inconsistencies in reporting information such as age of fluids and sampling techniques (storage conditions, head-space free, etc.). Building on the suggested reporting parameters listed by Bibby and colleagues (2013): (1) shale play/formation (2) fracturing/stimulation approach (3) well age (4) water quality (bulk parameters, inorganics), we suggest reporting additional information helpful in interpreting organic analyses: (5) Sample location (well, separator, collection tank) (6) Sampling information (bottle type, head-space free, storage conditions and duration).

Gas chromatography paired with mass spectrometry has been the most frequently used technique for organic compound analysis of HVHF fluids and wastewaters. GC and GC-MS have a large number of standardized methods for VOCs and SVOCs including oil and gas compounds in HVHF fluids. Continued research on these compounds is critical in understanding basin to basin variability, differences in HVHF techniques, and quantifying many known toxic compounds (Elliott et al., 2017). Quantification using standard methods is essential for tracking the distribution of HVHF fluids and wastewaters when they accidentally enter the environment.

The Marcellus shale region is the dominant location of HVHF fluid samples analyzed for organic compounds, followed by the Denver-Julesburg basin. Although the Marcellus is the dominant shale gas producer, oil is not co-produced in this formation (*Drilling Productivity Report*, 2017), indicating a lower complexity background organic carbon pool compared to a

shale oil (Bae et al., 2010). Analysis of the Denver-Julesburg, Permian, and other co-producing gas and oil basins will inevitably differ in their distribution of geogenic organic compounds compared to gas-only basins. Future research should work to diversify basin coverage across gas, oil, and co-producing basins to understand the variability in geogenic signatures and diversity of HVHF fluid systems. Treatment goals and techniques also vary by basin and further investigation into the removal rates of specific organic compounds of interest is needed across treatment schemes developed across all basins (i.e., halogenated organic compounds, BTEX, known toxic additives).

DOC concentrations compared to concentrations of specific organic compounds show that a large portion of the organic carbon pool remains uncharacterized. Additional research needs to build on recent progress developing new analytical methods that can overcome the extremely complex high salinity matrix for known additives and identified transformation products in these fluids, particularly using LC-MS techniques. Continued research using alternative extraction methods and high-resolution non-targeted techniques will allow for the identification of the diverse transformation products in HVHF fluids and wastewaters during treatment as well as environmental contamination events. New standards must be made available for known additives, geogenic organic compounds, and newly identified transformation products to further progress in this field and gain a broad understanding of the fate of organic compounds in HVHF.

7.0 Conclusions

Organic compounds are used as HVHF fluid additives and a number of these have been detected in these flowback and produced waters. Geogenic compounds and transformation

products from biotic and abiotic processes have also been identified in these wastewaters. BTEX, acetate, and acetone are the most frequently analyzed and detected organic compounds, and VOC and SVOCs are commonly analyzed. However, non-targeted techniques have highlighted the diversity of organic compounds that may be present in a given fluid for which new standards and analytical methods need to be developed. Organic chemical additives have been used in combination with inorganic chemical tracers to infer and track environmental contamination events. Further analytical development will benefit these investigations, allowing quantitative comparisons of new organic chemical tracers highly specific to HVHF to be made against background levels.

Acknowledgements

Financial assistance was obtained from NSF CBET Award #1604475/1604432 to Michael Gonsior and Paula Mouser. This is contribution (xxxx, to be filled in after acceptance of manuscript) of the University of Maryland Center for Environmental Science, Chesapeake Biological Laboratory.

References

- Abualfaraj, N., Gurian, P.L., Olson, M.S., 2014. Characterization of Marcellus Shale Flowback Water. *Environ. Eng. Sci.* 140716083132007. doi:10.1089/ees.2014.0001
- Akob, D.M., Cozzarelli, I.M., Dunlap, D.S., Rowan, E.L., Lorah, M.M., 2015. Organic and inorganic composition and microbiology of produced waters from Pennsylvania shale gas wells. *Appl. Geochem.* 60, 116–125. doi:10.1016/j.apgeochem.2015.04.011
- Akob, D.M., Mumford, A.C., Orem, W., Engle, M.A., Klimes, J.G., Kent, D.B., Cozzarelli, I.M., 2016. Wastewater Disposal from Unconventional Oil and Gas Development Degrades Stream Quality at a West Virginia Injection Facility. *Environ. Sci. Technol.* 50, 5517–5525. doi:10.1021/acs.est.6b00428
- Allen-King, R., Grathwohl, P., Ball, W.P., 2002. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. *Adv. Water Resour.* 25, 985–1016.
- Bae, E., Na, J.-G., Chung, S.H., Kim, H.S., Kim, S., 2010. Identification of about 30 000 Chemical Components in Shale Oils by Electrospray Ionization (ESI) and Atmospheric Pressure Photoionization (APPI) Coupled with 15 T Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) and a Comparison to Conventional Oil. *Energy Fuels* 24, 2563–2569. doi:10.1021/ef100060b
- Bell, E.A., Poyner, T.E., Newhart, K.B., Regnery, J., Coday, B.D., Cath, T.Y., 2017. Produced water treatment using forward osmosis membranes: Evaluation of extended-time performance and fouling. *J. Membr. Sci.* 525, 77–88. doi:10.1016/j.memsci.2016.10.032
- Bibby, K.J., Brantley, S.L., Reible, D.D., Linden, K.G., Mouser, P.J., Gregory, K.B., Ellis, B.R., Vidic, R.D., 2013. Suggested Reporting Parameters for Investigations of Wastewater from Unconventional Shale Gas Extraction. *Environ. Sci. Technol.* 47, 13220–13221. doi:10.1021/es404960z
- Brusseau, M.L., 1994. Transport of reactive contaminants in heterogeneous porous media. *Rev. Geophys.* 32, 285–313.
- Burr, D.A., Sudicky, E.A., Naff, R.L., 1994. Nonreactive and reactive solute transport in three-dimensional heterogeneous porous media: Mean displacement, plume spreading, and uncertainty. *Water Resour. Res.* 30, 791–815.
- Callbeck, C.M., Agrawal, A., Voordouw, G., 2013. Acetate Production from Oil under Sulfate-Reducing Conditions in Bioreactors Injected with Sulfate and Nitrate. *Appl. Environ. Microbiol.* 79, 5059–5068. doi:10.1128/AEM.01251-13
- Chapman, E.C., Capo, R.C., Stewart, B.W., Kirby, C.S., Hammack, R.W., Schroeder, K.T., Edenborn, H.M., 2012. Geochemical and Strontium Isotope Characterization of Produced Waters from Marcellus Shale Natural Gas Extraction. *Environ. Sci. Technol.* 46, 3545–3553. doi:10.1021/es204005g
- Cluff, M.A., Hartsock, A., MacRae, J.D., Carter, K., Mouser, P.J., 2014. Temporal Changes in Microbial Ecology and Geochemistry in Produced Water from Hydraulically Fractured Marcellus Shale Gas Wells. *Environ. Sci. Technol.* 48, 6508–6517. doi:10.1021/es501173p
- Coday, B.D., Xu, P., Beaudry, E.G., Herron, J., Lampi, K., Hancock, N.T., Cath, T.Y., 2014. The sweet spot of forward osmosis: Treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. *Desalination* 333, 23–35. doi:10.1016/j.desal.2013.11.014

- Connor, J.A., Walker, K., Molofsky, L., Baca, E., Gie, E., McHugh, T., 2016. Comment on “Impact to Underground Sources of Drinking Water and Domestic Wells from Production Well Stimulation and Completion Practices in the Pavillion, Wyoming, Field.” *Environ. Sci. Technol.* 50, 10769–10770.
- Cozzarelli, I.M., Skalak, K.J., Kent, D.B., Engle, M.A., Benthem, A., Mumford, A.C., Haase, K., Farag, A., Harper, D., Nagel, S.C., Iwanowicz, L.R., Orem, W.H., Akob, D.M., Jaeschke, J.B., Galloway, J., Kohler, M., Stoliker, D.L., Jolly, G.D., 2017. Environmental signatures and effects of an oil and gas wastewater spill in the Williston Basin, North Dakota. *Sci. Total Environ.* 579, 1781–1793. doi:10.1016/j.scitotenv.2016.11.157
- DiGiulio, D.C., Jackson, R.B., 2016a. Impact to Underground Sources of Drinking Water and Domestic Wells from Production Well Stimulation and Completion Practices in the Pavillion, Wyoming, Field. *Environ. Sci. Technol.* 50, 4524–4536. doi:10.1021/acs.est.5b04970
- DiGiulio, D.C., Jackson, R.B., 2016b. Response to Comment on “Impact to Underground Sources of Drinking Water and Domestic Wells from Production Well Stimulation and Completion Practices in the Pavillion, Wyoming Field.” *Environ. Sci. Technol.* 50, 10771–10772. doi:10.1021/acs.est.6b04300
- Dominic C. DiGiulio, Richard T. Wilkin, Carlyle Miller, Gregory Oberley, 2011. Investigation of Ground Water Contamination near Pavilion, Wyoming (Draft No. EPA 600/R-00/000). US Environmental Protection Agency.
- Drewes, J., T. Cath, J. Debroux, J. Veil, 2009. An Integrated Framework for Treatment and Management of Produced Water: Technical Assessment of Produced Water Treatment Technologies (No. RPSEA Project 07122-12.).
- Drilling Productivity Report For key tight oil and shale regions, 2017. . U.S. Energy Information Administration.
- Drollette, B.D., Hoelzer, K., Warner, N.R., Darrah, T.H., Karatum, O., O’Connor, M.P., Nelson, R.K., Fernandez, L.A., Reddy, C.M., Vengosh, A., Jackson, R.B., Elsner, M., Plata, D.L., 2015. Elevated levels of diesel range organic compounds in groundwater near Marcellus gas operations are derived from surface activities. *Proc. Natl. Acad. Sci.* 112, 13184–13189. doi:10.1073/pnas.1511474112
- Elliott, E.G., Ettinger, A.S., Leaderer, B.P., Bracken, M.B., Deziel, N.C., 2017. A systematic evaluation of chemicals in hydraulic-fracturing fluids and wastewater for reproductive and developmental toxicity. *J. Expo. Sci. Environ. Epidemiol.* 27, 90–99.
- Elsner, M., Hoelzer, K., 2016. Quantitative Survey and Structural Classification of Hydraulic Fracturing Chemicals Reported in Unconventional Gas Production. *Environ. Sci. Technol.* 50, 3290–3314. doi:10.1021/acs.est.5b02818
- Engle, M.A., Rowan, E.L., 2014. Geochemical evolution of produced waters from hydraulic fracturing of the Marcellus Shale, northern Appalachian Basin: A multivariate compositional data analysis approach. *Int. J. Coal Geol.* 126, 45–56. doi:10.1016/j.coal.2013.11.010
- Estrada, J.M., Bhamidimarri, R., 2016. A review of the issues and treatment options for wastewater from shale gas extraction by hydraulic fracturing. *Fuel* 182, 292–303. doi:10.1016/j.fuel.2016.05.051
- Fakhru’l-Razi, A., Pendashteh, A., Abdullah, L.C., Biak, D.R.A., Madaeni, S.S., Abidin, Z.Z., 2009. Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.* 170, 530–551. doi:10.1016/j.jhazmat.2009.05.044

- Ferrar, K.J., Michanowicz, D.R., Christen, C.L., Mulcahy, N., Malone, S.L., Sharma, R.K., 2013. Assessment of Effluent Contaminants from Three Facilities Discharging Marcellus Shale Wastewater to Surface Waters in Pennsylvania. *Environ. Sci. Technol.* 130314103725000. doi:10.1021/es301411q
- Ferrer, I., Thurman, E.M., 2015a. Chemical constituents and analytical approaches for hydraulic fracturing waters. *Trends Environ. Anal. Chem.* 5, 18–25. doi:10.1016/j.teac.2015.01.003
- Ferrer, I., Thurman, E.M., 2015b. Analysis of hydraulic fracturing additives by LC/Q-TOF-MS. *Anal. Bioanal. Chem.* 407, 6417–6428. doi:10.1007/s00216-015-8780-5
- Fontenot, B.E., Hunt, L.R., Hildenbrand, Z.L., Carlton Jr., D.D., Oka, H., Walton, J.L., Hopkins, D., Osorio, A., Bjorndal, B., Hu, Q.H., Schug, K.A., 2013. An Evaluation of Water Quality in Private Drinking Water Wells Near Natural Gas Extraction Sites in the Barnett Shale Formation. *Environ. Sci. Technol.* 47, 10032–10040. doi:10.1021/es4011724
- FracFocus, website: fracfocus.org, n.d.
- Getzinger, G.J., O'Connor, M.P., Hoelzer, K., Drollette, B.D., Karatum, O., Deshusses, M.A., Ferguson, P.L., Elsner, M., Plata, D.L., 2015. Natural Gas Residual Fluids: Sources, Endpoints, and Organic Chemical Composition after Centralized Waste Treatment in Pennsylvania. *Environ. Sci. Technol.* 49, 8347–8355. doi:10.1021/acs.est.5b00471
- Gregory, K.B., Vidic, R.D., Dzombak, D.A., 2011. Water Management Challenges Associated with the Production of Shale Gas by Hydraulic Fracturing. *Elements* 7, 181–186. doi:10.2113/gselements.7.3.181
- Gross, S.A., Avens, H.J., Banducci, A.M., Sahmel, J., Panko, J.M., Tvermoes, B.E., 2013. Analysis of BTEX groundwater concentrations from surface spills associated with hydraulic fracturing operations. *J. Air Waste Manag. Assoc.* 63, 424–432. doi:10.1080/10962247.2012.759166
- Hayes, T., 2009. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas (Final Report). Gas Technology Institute.
- Hickenbottom, K.L., Hancock, N.T., Hutchings, N.R., Appleton, E.W., Beaudry, E.G., Xu, P., Cath, T.Y., 2013. Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations. *Desalination* 312, 60–66. doi:10.1016/j.desal.2012.05.037
- Hildenbrand, Z.L., Carlton, D.D., Fontenot, B.E., Meik, J.M., Walton, J.L., Taylor, J.T., Thacker, J.B., Korlie, S., Shelor, C.P., Henderson, D., Kadjo, A.F., Roelke, C.E., Hudak, P.F., Burton, T., Rifai, H.S., Schug, K.A., 2015. A Comprehensive Analysis of Groundwater Quality in The Barnett Shale Region. *Environ. Sci. Technol.* 49, 8254–8262. doi:10.1021/acs.est.5b01526
- Hildenbrand, Z.L., Carlton, D.D., Fontenot, B.E., Meik, J.M., Walton, J.L., Thacker, J.B., Korlie, S., Shelor, C.P., Kadjo, A.F., Clark, A., Usenko, S., Hamilton, J.S., Mach, P.M., Verbeck, G.F., Hudak, P., Schug, K.A., 2016. Temporal variation in groundwater quality in the Permian Basin of Texas, a region of increasing unconventional oil and gas development. *Sci. Total Environ.* 562, 906–913. doi:10.1016/j.scitotenv.2016.04.144
- Hoelzer, K., Sumner, A.J., Karatum, O., Nelson, R.K., Drollette, B.D., O'Connor, M.P., D'Ambro, E.L., Getzinger, G.J., Ferguson, P.L., Reddy, C.M., Elsner, M., Plata, D.L., 2016. Indications of Transformation Products from Hydraulic Fracturing Additives in Shale-Gas Wastewater. *Environ. Sci. Technol.* 50, 8036–8048. doi:10.1021/acs.est.6b00430

- Jang, E., Jeong, S., Chung, E., 2017. Application of three different water treatment technologies to shale gas produced water. *Geosystem Eng.* 20, 104–110. doi:10.1080/12269328.2016.1239553
- Kahrilas, G.A., Blotevogel, J., Corrin, E.R., Borch, T., 2016. Downhole Transformation of the Hydraulic Fracturing Fluid Biocide Glutaraldehyde: Implications for Flowback and Produced Water Quality. *Environ. Sci. Technol.* 50, 11414–11423. doi:10.1021/acs.est.6b02881
- Kahrilas, G.A., Blotevogel, J., Stewart, P.S., Borch, T., 2015. Biocides in Hydraulic Fracturing Fluids: A Critical Review of Their Usage, Mobility, Degradation, and Toxicity. *Environ. Sci. Technol.* 49, 16–32. doi:10.1021/es503724k
- Kamel, A., Shah, S.N., 2009. Effects of salinity and temperature on drag reduction characteristics of polymers in straight circular pipes. *J. Pet. Sci. Eng.* 67, 23–33. doi:10.1016/j.petrol.2009.02.004
- Kassotis, C.D., Tillitt, D.E., Davis, J.W., Hormann, A.M., Nagel, S.C., 2014. Estrogen and Androgen Receptor Activities of Hydraulic Fracturing Chemicals and Surface and Ground Water in a Drilling-Dense Region. *Endocrinology* 155, 897–907. doi:10.1210/en.2013-1697
- Kekacs, D., Drollette, B.D., Brooker, M., Plata, D.L., Mouser, P.J., 2015. Aerobic biodegradation of organic compounds in hydraulic fracturing fluids. *Biodegradation*. doi:10.1007/s10532-015-9733-6
- Khan, N.A., Engle, M., Dungan, B., Holguin, F.O., Xu, P., Carroll, K.C., 2016. Volatile-organic molecular characterization of shale-oil produced water from the Permian Basin. *Chemosphere* 148, 126–136. doi:10.1016/j.chemosphere.2015.12.116
- Kondash, A., Vengosh, A., 2015. Water Footprint of Hydraulic Fracturing. *Environ. Sci. Technol. Lett.* 150918090943001. doi:10.1021/acs.estlett.5b00211
- Kondash, A.J., Albright, E., Vengosh, A., 2017. Quantity of flowback and produced waters from unconventional oil and gas exploration. *Sci. Total Environ.* 574, 314–321. doi:10.1016/j.scitotenv.2016.09.069
- Lester, Y., Ferrer, I., Thurman, E.M., Sitterley, K.A., Korak, J.A., Aiken, G., Linden, K.G., 2015. Characterization of hydraulic fracturing flowback water in Colorado: Implications for water treatment. *Sci. Total Environ.* 512–513, 637–644. doi:10.1016/j.scitotenv.2015.01.043
- Lester, Y., Sharpless, C.M., Mamane, H., Linden, K.G., 2013. Production of Photo-oxidants by Dissolved Organic Matter During UV Water Treatment. *Environ. Sci. Technol.* 47, 11726–11733. doi:10.1021/es402879x
- Lester, Y., Yacob, T., Morrissey, I., Linden, K.G., 2014. Can We Treat Hydraulic Fracturing Flowback with a Conventional Biological Process? The Case of Guar Gum. *Environ. Sci. Technol. Lett.* 1, 133–136. doi:10.1021/ez4000115
- Llewellyn, G.T., Dorman, F., Westland, J.L., Yoxtheimer, D., Grieve, P., Sowers, T., Humston-Fulmer, E., Brantley, S.L., 2015. Evaluating a groundwater supply contamination incident attributed to Marcellus Shale gas development. *Proc. Natl. Acad. Sci.* 112, 6326–6330. doi:10.1073/pnas.1420279112
- Lobo, F.L., Wang, H., Huggins, T., Rosenblum, J., Linden, K.G., Ren, Z.J., 2016. Low-energy hydraulic fracturing wastewater treatment via AC powered electrocoagulation with biochar. *J. Hazard. Mater.* 309, 180–184. doi:10.1016/j.jhazmat.2016.02.020

- Luek, J.L., Schmitt-Kopplin, P., Mouser, P.J., Petty, W.T., Richardson, S.D., Gonsior, M., 2017. Halogenated organic compounds identified in hydraulic fracturing wastewaters using ultrahigh resolution mass spectrometry. *Environ. Sci. Technol.* doi:10.1021/acs.est.6b06213
- Mackay, D.M., Freyberg, D.L., Roberts, P.V., Cherry, J.A., 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer 1. Approach and Overview of Plume Movement. *Water Resour. Res.* 22, 2017–2029.
- Maguire-Boyle, S.J., Barron, A.R., 2014. Organic compounds in produced waters from shale gas wells. *Env. Sci Process. Impacts* 16, 2237–2248. doi:10.1039/C4EM00376D
- Maillard, J.-Y., 2002. Bacterial target sites for biocide action. *J. Appl. Microbiol.* 92.
- Marshall, A.G., Hendrickson, C.L., 2008. High-Resolution Mass Spectrometers. *Annu. Rev. Anal. Chem.* 1, 579–599. doi:10.1146/annurev.anchem.1.031207.112945
- McHugh, T., Molofsky, L., Daus, A., Connor, J., 2014. Comment on “An Evaluation of Water Quality in Private Drinking Water Wells Near Natural Gas Extraction Sites in the Barnett Shale Formation.” *Environ. Sci. Technol.* 48, 3595–3596. doi:10.1021/es405772d
- McHugh, T., Molofsky, L., Fitzgerald, L., Connor, J., 2016. Comment on “A Comprehensive Analysis of Groundwater Quality in The Barnett Shale Region.” *Environ. Sci. Technol.* 50, 496–497. doi:10.1021/acs.est.5b05067
- McLaughlin, M.C., Borch, T., Blotvogel, J., 2016. Spills of Hydraulic Fracturing Chemicals on Agricultural Topsoil: Biodegradation, Sorption, and Co-contaminant Interactions. *Environ. Sci. Technol.* doi:10.1021/acs.est.6b00240
- Mohan, A.M., Bibby, K.J., Lipus, D., Hammack, R.W., Gregory, K.B., 2014. The Functional Potential of Microbial Communities in Hydraulic Fracturing Source Water and Produced Water from Natural Gas Extraction Characterized by Metagenomic Sequencing. *PLoS ONE* 9, e107682. doi:10.1371/journal.pone.0107682
- Müller, V., 2008. Bacterial fermentation. *eLS*.
- Murali Mohan, A., Hartsock, A., Bibby, K.J., Hammack, R.W., Vidic, R.D., Gregory, K.B., 2013a. Microbial Community Changes in Hydraulic Fracturing Fluids and Produced Water from Shale Gas Extraction. *Environ. Sci. Technol.* 47, 13141–13150. doi:10.1021/es402928b
- Murali Mohan, A., Hartsock, A., Hammack, R.W., Vidic, R.D., Gregory, K.B., 2013b. Microbial communities in flowback water impoundments from hydraulic fracturing for recovery of shale gas. *FEMS Microbiol. Ecol.* 86, 567–580. doi:10.1111/1574-6941.12183
- Orem, W., Tatu, C., Varonka, M., Lerch, H., Bates, A., Engle, M., Crosby, L., McIntosh, J., 2014. Organic substances in produced and formation water from unconventional natural gas extraction in coal and shale. *Int. J. Coal Geol.* 126, 20–31. doi:10.1016/j.coal.2014.01.003
- Orem, W., Varonka, M., Crosby, L., Haase, K., Loftin, K., Hladik, M., Akob, D.M., Tatu, C., Mumford, A., Jaeschke, J., Bates, A., Schell, T., Cozzarelli, I., 2017. Organic geochemistry and toxicology of a stream impacted by unconventional oil and gas wastewater disposal operations. *Appl. Geochem.* 80, 155–167. doi:10.1016/j.apgeochem.2017.02.016
- Orem, W.H., Voytek, M.A., Jones, E.J., Lerch, H.E., Bates, A.L., Corum, M.D., Warwick, P.D., Clark, A.C., 2010. Organic intermediates in the anaerobic biodegradation of coal to methane under laboratory conditions. *Org. Geochem.* 41, 997–1000. doi:10.1016/j.orggeochem.2010.03.005

- Regnery, J., Coday, B.D., Riley, S.M., Cath, T.Y., 2016. Solid-phase extraction followed by gas chromatography-mass spectrometry for the quantitative analysis of semi-volatile hydrocarbons in hydraulic fracturing wastewaters. *Anal Methods* 8, 2058–2068. doi:10.1039/C6AY00169F
- Riley, S.M., Oliveira, J.M.S., Regnery, J., Cath, T.Y., 2016. Hybrid membrane bio-systems for sustainable treatment of oil and gas produced water and fracturing flowback water. *Sep. Purif. Technol.* 171, 297–311. doi:10.1016/j.seppur.2016.07.008
- Rogers, J.D., Burke, T.L., Osborn, S.G., Ryan, J.N., 2015. A framework for identifying organic compounds of concern in hydraulic fracturing fluids based on mobility and persistence in groundwater. *Environ. Sci. Technol. Lett.* 150515152302002. doi:10.1021/acs.estlett.5b00090
- Rosenblum, J.S., Sitterley, K.A., Thurman, E.M., Ferrer, I., Linden, K.G., 2016. Hydraulic fracturing wastewater treatment by coagulation-adsorption for removal of organic compounds and turbidity. *J. Environ. Chem. Eng.* 4, 1978–1984. doi:10.1016/j.jece.2016.03.013
- Rosenfeld, B., Simon, E., 1950. THE MECHANISM OF THE BUTANOL-ACETONE FERMENTATION I. THE RÔLE OF PYRUVATE AS AN INTERMEDIATE. *J. Biol. Chem.* 186, 395–404.
- Schymanski, E.L., Jeon, J., Gulde, R., Fenner, K., Ruff, M., Singer, H.P., Hollender, J., 2014. Identifying Small Molecules via High Resolution Mass Spectrometry: Communicating Confidence. *Environ. Sci. Technol.* 140129110454000. doi:10.1021/es5002105
- Shaffer, D.L., Arias Chavez, L.H., Ben-Sasson, M., Romero-Vargas Castrillón, S., Yip, N.Y., Elimelech, M., 2013. Desalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions. *Environ. Sci. Technol.* 47, 9569–9583. doi:10.1021/es401966e
- Stringfellow, W.T., Domen, J.K., Camarillo, M.K., Sandelin, W.L., Borglin, S., 2014. Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing. *J. Hazard. Mater.* 275, 37–54. doi:10.1016/j.jhazmat.2014.04.040
- Strong, L.C., Gould, T., Kasinkas, L., Sadowsky, M.J., Aksan, A., Wackett, L.P., 2013. Biodegradation in Waters from Hydraulic Fracturing: Chemistry, Microbiology, and Engineering. *J. Environ. Eng.* 140, B4013001.
- Thacker, J., Carlton, D., Hildenbrand, Z., Kadjo, A., Schug, K., 2015. Chemical Analysis of Wastewater from Unconventional Drilling Operations. *Water* 7, 1568–1579. doi:10.3390/w7041568
- Thurman, E.M., Ferrer, I., Blotvogel, J., Borch, T., 2014. Analysis of Hydraulic Fracturing Flowback and Produced Waters Using Accurate Mass: Identification of Ethoxylated Surfactants. *Anal. Chem.* 86, 9653–9661. doi:10.1021/ac502163k
- U.S. EPA, 2016. Hydraulic Fracturing for Oil and Gas: Impacts from the Hydraulic Fracturing Water Cycle on Drinking Water Resources in the United States (Final Report). (No. EPA/600/R-16/236F). U.S. Environmental Protection Agency, Washington, DC.
- U.S. EPA, 2015a. Retrospective Case Study in Northeastern Pennsylvania: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources (No. EPA/600/R-14/088). US Environmental Protection Agency.
- U.S. EPA, 2015b. Retrospective Case Study in Killdeer, North Dakota: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources (No. EPA/600/R-14/103). US Environmental Protection Agency.

- 968 U.S. EPA, 2015c. Retrospective Case Study in the Raton Basin, Colorado: Study of the Potential
 969 Impacts of Hydraulic Fracturing on Drinking Water Resources (No. EPA/600/R-14/091).
 970 US Environmental Protection Agency.
- 971 U.S. EPA, 2015d. Retrospective Case Study in Southwestern Pennsylvania Study of the Potential
 972 Impacts of Hydraulic Fracturing on Drinking Water Resources (No. EPA/600/R-14/084).
 973 US Environmental Protection Agency.
- 974 U.S. EPA, 2015e. Retrospective Case Study in Wise County, Texas: Study of the Potential
 975 Impacts of Hydraulic Fracturing on Drinking Water Resources (No. EPA/600/R-14/090).
 976 US Environmental Protection Agency.
- 977 Warner, N.R., Christie, C.A., Jackson, R.B., Vengosh, A., 2013. Impacts of Shale Gas
 978 Wastewater Disposal on Water Quality in Western Pennsylvania. *Environ. Sci. Technol.*
 979 131002090059009. doi:10.1021/es402165b
- 980 Woford, R., 2011. Characterization of organics in marcellus shale flowback and produced
 981 waters. Pennsylvania State University.
- 982 Zhang, S., Wang, P., Fu, X., Chung, T.-S., 2014. Sustainable water recovery from oily
 983 wastewater via forward osmosis-membrane distillation (FO-MD). *Water Res.* 52, 112–
 984 121. doi:10.1016/j.watres.2013.12.044
- 985 Ziemkiewicz, P., 2013. Characterization of liquid waste streams from shale gas development.
 986 AGH Drill. Oil Gas 30, 297. doi:10.7494/drill.2013.30.1.297
- 987 Ziemkiewicz, P.F., He, Y.T., 2015. Evolution of water chemistry during Marcellus Shale gas
 988 development: A case study in West Virginia. *Chemosphere* 134, 224–231.
 989 doi:10.1016/j.chemosphere.2015.04.040
 990