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1 **Organic Compounds in Hydraulic Fracturing Fluids and Wastewaters: A Review**

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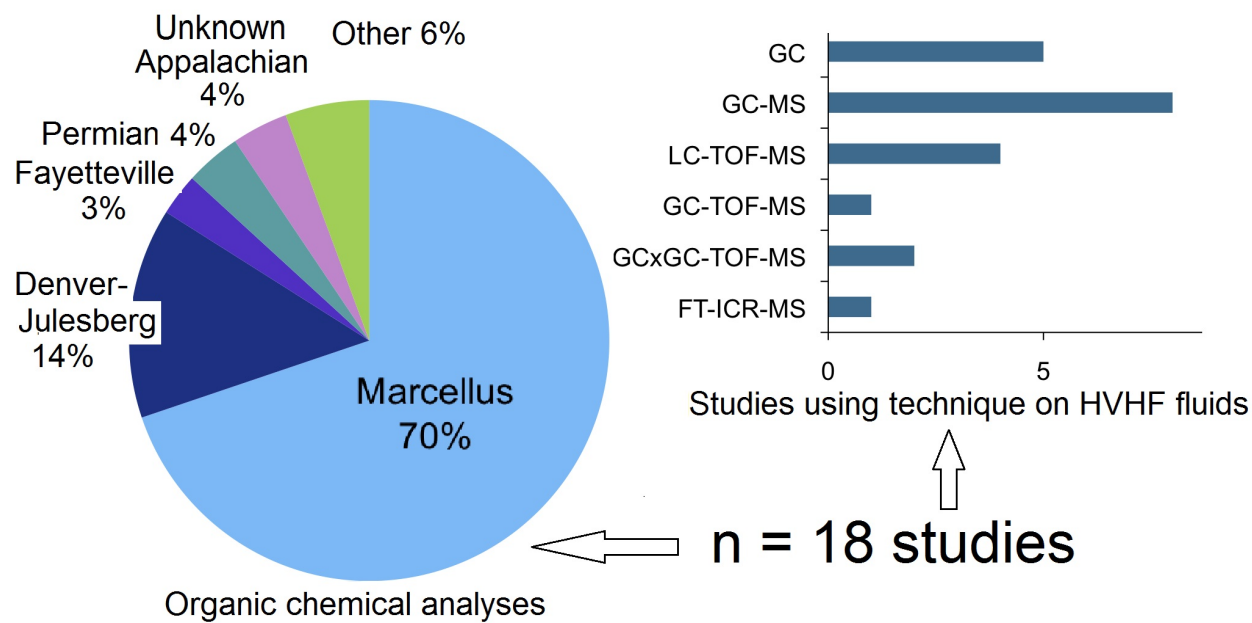
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15 ***Key words: high volume hydraulic fracturing, fracking, flowback fluid, produced water***

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

26 Abstract

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

45

45 **1. Introduction**

46 Shale gas extraction via high volume hydraulic fracturing (HVHF) has resulted in the use
47 of 116 billion liters of fluids annually from 2012-2014 and yielded similar volumes of flowback
48 and produced waters (Kondash and Vengosh, 2015). These fluids contain a complex mixture of
49 inorganic and organic compounds used as additives (Elsner and Hoelzer, 2016; Stringfellow et
50 al., 2014) as well as compounds extracted from the shale itself including salts, metals,
51 radionuclides, oil and gas compounds, and natural organic matter (NOM) (Abualfaraj et al.,
52 2014; Chapman et al., 2012; Engle and Rowan, 2014). Understanding these complex fluid
53 mixtures is essential for understanding efficacy of additives, fluid treatment options for reuse in
54 future HVHF jobs or discharge, and threats to the natural environment and human exposure.

55 The identification and quantification of individual organic compounds among the
56 complex mixture of additives, oil and gas compounds, NOM, and transformation products
57 requires diverse sample preparation and analytical techniques (Ferrer and Thurman, 2015a).
58 Mass spectral techniques provide data of variable confidence ranging from having only the exact
59 masses of interest to having confirmed structures by reference standards (Schymanski et al.,
60 2014). Gas chromatography paired with mass spectrometry has been traditionally used to
61 identify hydrophobic oil and gas hydrocarbons found in produced waters (Ferrer and Thurman,
62 2015a; Maguire-Boyle and Barron, 2014; Orem et al., 2014; Strong et al., 2013), and can be used
63 to quantify many of the compounds in HVHF fluids and wastewaters of known toxicity (Elliott
64 et al., 2017). Liquid chromatography paired with mass spectrometry has been shown to be useful
65 in identifying many of the more hydrophilic organic compounds used in HVHF additives such as
66 ethoxylated surfactants (Ferrer and Thurman, 2015a, 2015b; Getzinger et al., 2015; Hoelzer et
67 al., 2016), but further method development requires overcoming analytical barriers such as the

68 complex high salinity matrix. Analytical methods for describing unknown shale extracts and
69 transformation products will require higher resolution techniques such as two dimensional gas
70 chromatography with time of flight mass spectrometry (GC×GC-TOF-MS) (Hoelzer et al.,
71 2016), liquid chromatography with time of flight mass spectrometry (LC-TOF-MS) (Ferrer and
72 Thurman, 2015b; Thurman et al., 2014), and Fourier transform ion cyclotron resonance mass
73 spectrometry (FT-ICR-MS), each requiring laborious data analysis and interpretation. Time of
74 flight mass spectrometry can provide sufficiently high resolution that exact masses can be
75 combined with GC or LC to determine unknown molecular formulas and structures with
76 relatively high confidence in the absence of standards, especially when combined with
77 fragmentation spectra (Ferrer and Thurman, 2015b; Marshall and Hendrickson, 2008; Thurman
78 et al., 2014). Ultrahigh resolution FT-ICR-MS allows for direct determination of the assigned
79 molecular formula based on the exact mass alone but provides no direct details on molecular
80 structure (Marshall and Hendrickson, 2008) unless paired with MS-MS techniques. However,
81 large numbers of possible isomers at higher masses make this approach challenging, but this
82 challenge might be partially overcome by using LC.

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

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

100

101 **2. Hydraulic Fracturing Fluid Additives**

102 The majority of organic additives included in HVHF fluid have been described by class
103 and their frequency of use (Elsner and Hoelzer, 2016; Rogers et al., 2015). Additionally, lists of
104 additives are publicly available through the website FracFocus (fracfocus.org) and are
105 summarized in the EPA hydraulic fracturing study report (U.S. EPA, 2016). Organic compounds
106 are used at every stage in the HVHF process: 1) mixing of the base fluid including solvent and
107 surfactants, 2) as cross linkers and breakers, 3) clay stabilizers, 4) corrosion, scale, and 5)
108 biofouling inhibitors (Elsner and Hoelzer, 2016; Stringfellow et al., 2014). Alcohols are the
109 dominant organic class used in a number of functions including as solvents (methanol,
110 isopropanol, ethanol), surfactants (ethylene glycol, ethoxylated alcohols and phenols) and
111 corrosion inhibitors (propargyl alcohol) (Elsner and Hoelzer, 2016). Polymers are also used in a
112 large number of processes including as gelling agents, friction reducers, proppant coatings,

113 corrosion and scale inhibitors (Elsner and Hoelzer, 2016). Many synthetic polymers and
114 biopolymers are readily biodegraded, although their monomers may be of environmental concern
115 (Elsner and Hoelzer, 2016; Stringfellow et al., 2014). Hydrocarbons, as light and heavy
116 petroleum distillate mixtures and individual compounds (naphthalene, tetradecane, limonene),
117 are an additional dominant class of additives, used primarily as solvents (Elsner and Hoelzer,
118 2016).

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

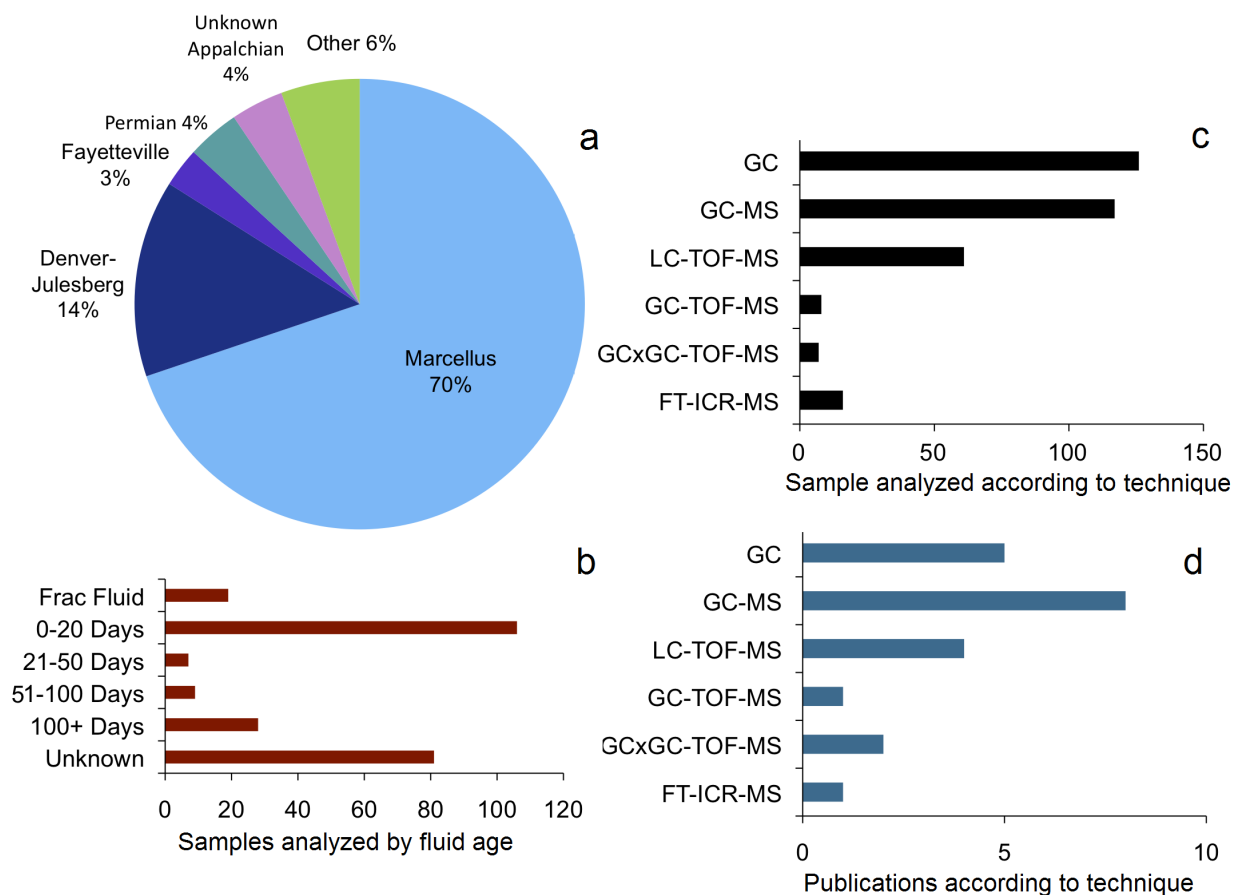
129 **3. Flowback and Produced Waters**

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

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

140 Seventy percent of the samples analyzed for organic compounds have been collected
141 from the Marcellus shale basin, which makes up ~37% of unconventional natural gas production
142 but less than 0.01% of oil production (*Drilling Productivity Report*, 2017). Gas chromatography
143 has been used extensively in these studies for volatile and semi-volatile organic compound
144 (VOC, SVOC) analyses (Table 1). Ion chromatography (IC) has also been used to analyze small
145 organic acids (Akob et al., 2015; Lester et al., 2013). High resolution LC-TOF-MS has been used
146 to investigate specific additives, focusing mostly on samples from Weld County, Colorado in the
147 Denver-Julesberg basin (Ferrer and Thurman, 2015b; Rosenblum et al., 2016; Thurman et al.,
148 2014). Organic analyses have also been performed on samples collected from the Barnett shale
149 (Maguire-Boyle and Barron, 2014; Thurman et al., 2014), the Wolfcamp and Cline shales in the
150 Permian basin (Khan et al., 2016), New Albany shale (Orem et al., 2014), an unknown formation
151 in Texas (Thacker et al., 2015), a single sample from each of the Eagle Ford, Fayetteville,
152 Burket, and unspecified formations in Pennsylvania, Nevada, and Louisiana.

153



154

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

158
159

160 **Table 1.** Published reports and peer-reviewed literature analyzing organic compounds in shale
 161 gas flowback and produced waters. ^qquantitative; ^scompared to standards; ^lcompared to spectral
 162 library [^]sample origins not precisely specified and up to 5 may overlap with samples reported by
 163 Lester et al., 2015; Rosenblum et al., 2016. *MBA, methyl blue active substances (for anionic
 164 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)

166 A number of known and suspect additives have been identified in flowback and produced
167 waters, although not all studies had access to the corresponding list of additives or the HVHF
168 fluid alone prior to injection (Cluff et al., 2014; Hayes, 2009; Hoelzer et al., 2016; Lester et al.,
169 2015; Orem et al., 2014; Rosenblum et al., 2016; Strong et al., 2013; Thacker et al., 2015;
170 Wolford, 2011). Quantitative analyses for known organic additives are still limited by a lack of
171 standards and standard methods and many compounds can only be putatively identified. Several
172 surfactants/dispersants have been identified including ethoxylated alcohols (Cluff et al., 2014;
173 Lester et al., 2015; Thurman et al., 2014), ethoxylated phenols (Orem et al., 2014), glycols
174 (Hayes, 2009; Orem et al., 2014; Robert Wolford, 2011; Rosenblum et al., 2016), alkyl amines
175 (Thacker et al., 2015), cocamide compounds (Ferrer and Thurman, 2015b; Thacker et al., 2015),
176 2-butoxyethanol (Thacker et al., 2015), and bulk anionic surfactants (as methyl blue active
177 substances) (Ziemkiewicz and He, 2015). Of these surfactants, only ethylene glycol and
178 propylene glycol were reported quantitatively and neither of these studies appear in the peer
179 reviewed literature (Hayes, 2009; Wolford, 2011). The biocides alkyl dimethyl benzyl
180 ammonium chloride, glutaraldehyde, and hexahydro-1,3,5-trimethyl-1,3,5-triazine-2-thione have
181 been detected but only the latter was quantified (Ferrer and Thurman, 2015b; Orem et al., 2014).
182 The triazine biocide was initially detected in flowback at very high levels (1.5 mg L^{-1}) but
183 returned to very low levels ($10 \text{ } \mu\text{g L}^{-1}$) within one week of well operation (Orem et al., 2014).
184 Phthalates have been identified in several flowback and produced water samples (Hayes, 2009;
185 Hoelzer et al., 2016; Lester et al., 2015; Maguire-Boyle and Barron, 2014; Orem et al., 2014). In
186 quantitative analyses of phthalates, di-n-octyl-phthalate peaked in Marcellus shale early
187 flowback ($5600 \text{ } \mu\text{g L}^{-1}$) and rapidly declined (Orem et al., 2014), but no clear pattern was
188 observed in nineteen Marcellus shale well time series for diethyl phthalate, di-n-butyl phthalate,

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

190 Citric acid, used for iron control, was reported in Marcellus flowback samples at high
191 concentrations (9, 53, and 70 mg L⁻¹) but was not identified in any produced water samples
192 within the same study (Wolford, 2011). 2,2,4-trimethyl-1,3,-pentanediol (solvent) and tridecane
193 (fuel component) were also traced in a Marcellus shale well across flowback and produced
194 waters, and while both peaked around the second day of flowback, both remained above 200 µg
195 L⁻¹ in produced waters (Orem et al., 2014). The gelling agent guar gum was analyzed for but
196 neither detected nor quantified in twenty-two Denver-Julesberg flowback and produced water
197 samples (Ferrer and Thurman, 2015b). Bisphenol F and 2-butoxy ethanol were reported in a
198 Texas produced water sample (Thacker et al., 2015), and a number of other additives have been
199 reported non-quantitatively in several shale plays including a dioctadecyl ester of phosphate
200 (lubricant), and some fluorinated organic compounds (possible flowpath tracers) (Hoelzer et al.,
201 2016; Maguire-Boyle and Barron, 2014).

202

203 *3.2 Geogenic organic compounds from additives and/or shale*

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

212 TOF-MS (Hoelzer et al., 2016; Maguire-Boyle and Barron, 2014; Orem et al., 2014; Strong et
213 al., 2013), but only twenty four of these compounds have been reported quantitatively above the
214 limit of detection in the peer reviewed literature (Akob et al., 2015; Lester et al., 2015;
215 Ziemkiewicz and He, 2015; Ziemkiewicz, 2013). Reported concentrations of these quantifiable
216 organic compounds are given in supplemental online materials (Table S1, Figure S1), including
217 data from two non-peer reviewed sources (Hayes, 2009; Wolford, 2011). Dissolved methane as
218 well as other light gases including ethane, propane, and butane will not be discussed here as they
219 are by default present in productive wells. Overall, extractable hydrocarbons decreased in
220 concentration during flowback and were lowest in produced water in a large number of analyzed
221 samples (Orem et al., 2014). In broad spectrum reports of organic compounds in flowback and
222 produced waters using various types of gas chromatography, aliphatic compounds were the
223 dominant class identified (Hoelzer et al., 2016; Maguire-Boyle and Barron, 2014; Orem et al.,
224 2014; Strong et al., 2013). Out of 986 compounds tentatively identified using GCxGC-TOF-MS
225 in a Marcellus shale produced water, 61% of the identified compounds were aliphatic, and 24%
226 were cycloaliphatic (Strong et al., 2013). Aromatic compounds represented 13% of the
227 remaining compounds. PAHs accounted for 2% in this Marcellus shale produced water, and a
228 substantial number of aromatic compounds and PAHs were also identified by other broad
229 spectrum reports of organic compounds (Hoelzer et al., 2016; Maguire-Boyle and Barron, 2014;
230 Orem et al., 2014). A new analytical technique has been developed for quantification of PAHs
231 and other SVOCs in HVHF wastewater pairing solid-phase extraction with GC-MS (Regnery et
232 al., 2016).

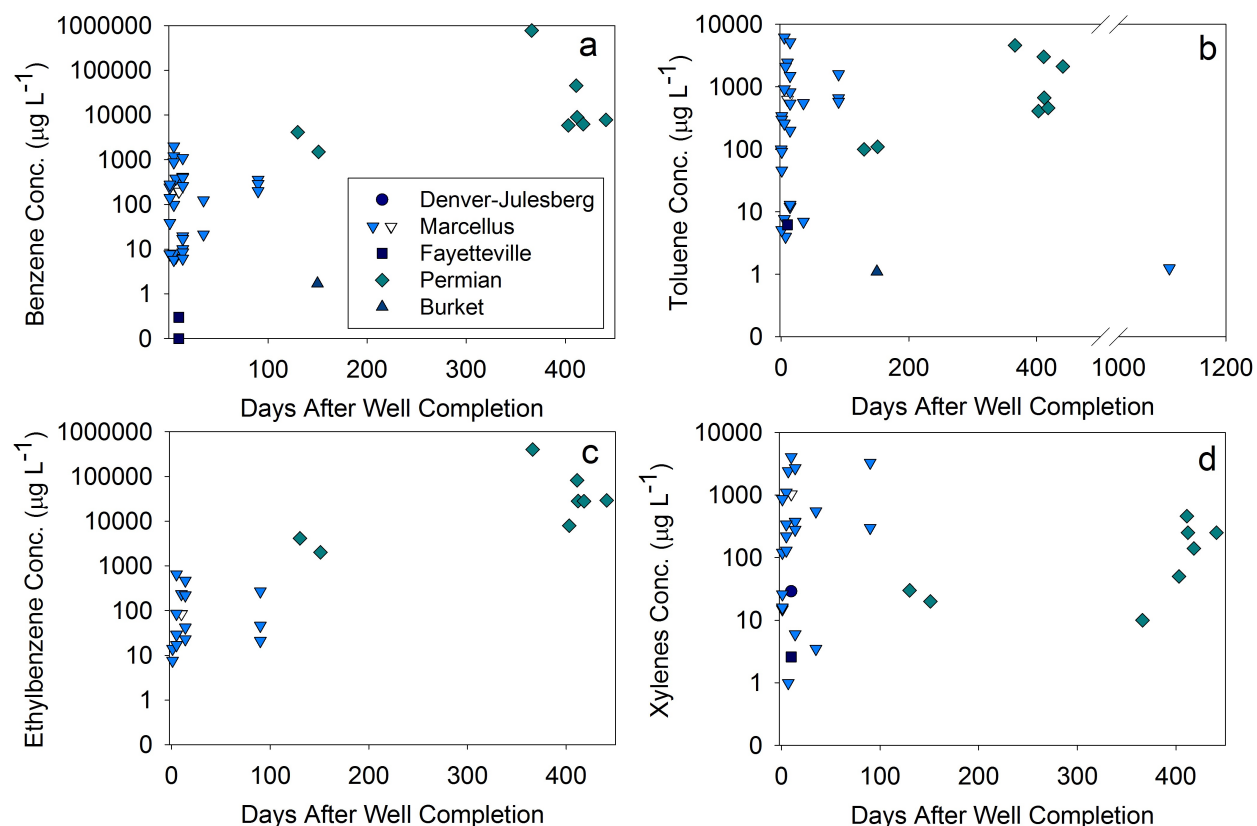
233 BTEX compounds were both the most frequently analyzed organic compounds in
234 flowback and produced water and the most frequently detected organic compounds above

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

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

258 naphthalenes were identified but not quantified in Barnett and Marcellus shales (Maguire-Boyle
259 and Barron, 2014). Methyl phenol and dimethylphenol were detected in much higher
260 concentrations in a composite flowback sample from the Denver-Julesberg basin than PAHs
261 ($150\text{-}830\text{ ug L}^{-1}$ vs. $<10\text{ug L}^{-1}$) (Lester et al., 2015), but similar concentration ranges of both the
262 phenolic and PAH compounds were observed in the Marcellus (Hayes, 2009). A number of
263 oxygen containing resins/asphaltenes were identified in Marcellus, Barnett and Eagle Ford shale
264 produced waters (Maguire-Boyle and Barron, 2014).

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



271
 272 **Figure 2.** Concentrations (log scale) of benzene (a), toluene (b), ethylbenzene (c), and xylene (d)
 273 in flowback and produced water samples by days after HVHF well completion from literature
 274 (Akob et al., 2015; Hayes, 2009; Hoelzer et al., 2016; Khan et al., 2016; Lester et al., 2015;
 275 Wolford, 2011; Ziemkiewicz, 2013; Ziemkiewicz and He, 2015). Open triangles indicate mean
 276 of 13 Marcellus samples (Ziemkiewicz and He, 2015), colored triangles represent individual data
 277 points. Fayetteville samples are shown on day 10 for comparison but were collected within the
 278 first three weeks (Hoelzer et al., 2016). Note: benzene and ethylbenzene are given on a different
 279 scale than toluene and xylenes.
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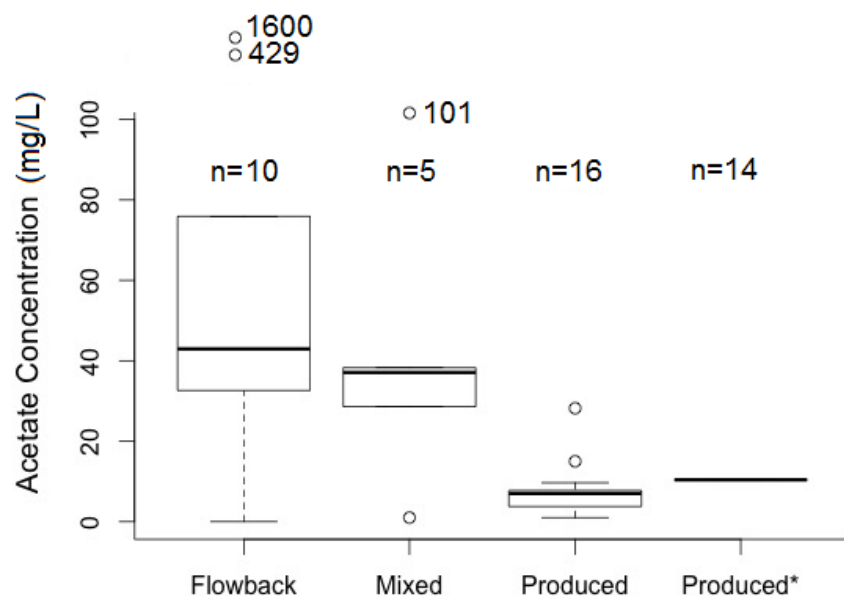
281 3.3 Transformation products of organic constituents

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

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

290 A number of small organic acids are produced through microbial transformation under
291 the anaerobic conditions frequently observed in HVHF wastewater via fermentation (Müller,
292 2008). Small organic acids were analyzed in a handful of studies, although not all report
293 quantitative results. Acetate was measured in seven studies (**Figure 3**), formate in three (Akob et
294 al., 2015; Strong et al., 2013; Thacker et al., 2015), and citrate (Wolford, 2011), lactate,
295 propionate, butyrate, and pyruvate (Akob et al., 2015) were each analyzed in one study. Acetate,
296 propionate, and butyrate were measured in the Hayes dataset with high method detection limits
297 (10mg L^{-1}) but are not included due to questionable reliability (Hayes, 2009). Acetate and other
298 organic acids are likely produced during the anaerobic degradation of additives and potentially
299 geogenic substances as hydrocarbons are degraded to acetate under anaerobic conditions (e.g.,
300 Callbeck et al., 2013). Indeed, fermentative classes of bacteria capable of producing organic
301 acids were identified in flowback samples where acetate was identified (Cluff et al., 2014;
302 Murali Mohan et al., 2013b). Acetate concentrations were highest in flowback samples,
303 presumably due to the high concentrations of degradable organic additives such as ethoxylates,
304 guar gum, and glycols. The highest concentration of acetate observed (1600 mg L^{-1}) was in a
305 composite flowback sample, and was three times higher than the next highest sample and an
306 order of magnitude higher than most flowback samples (Lester et al., 2015). Aeration of
307 flowback fluid resulted in acetate decreasing below detection limits, which is not surprising as
308 fermentation would no longer be occurring and any acetate previously produced would likely be
309 readily mineralized *in situ* under aerobic conditions (Murali Mohan et al., 2013b). Produced

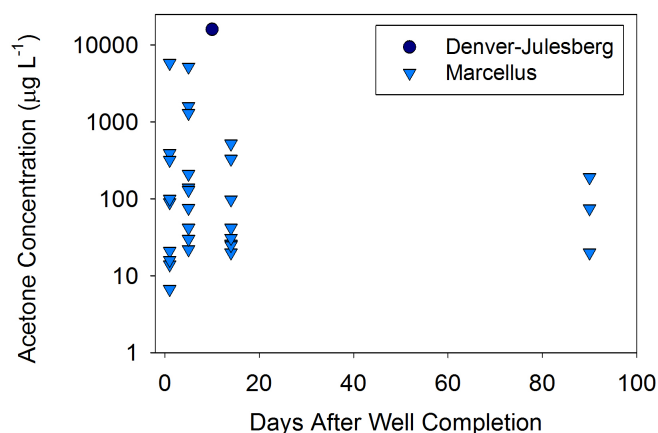
310 water samples contained much lower acetate concentrations. In 14 Marcellus shale produced
 311 water samples (**Figure 3, Produced***), the mean acetate concentration was 10.6 mg L^{-1} , but the
 312 range was not reported (Orem et al., 2014). In 16 other produced water samples, the mean acetate
 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).



327

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

332

333 Acetone in flowback may originate from its use as an additive, may be a transformation

334 product via anaerobic fermentation via pyruvate (Rosenfeld and Simon, 1950), or may be

335 associated with both sources. Acetone concentrations were highly variable in flowback samples

336 (most ND, median 90 µg L⁻¹ in positive detections, mean of 1,060 µg L⁻¹ in n=37 positive

337 detections) and acetone was not measured in any samples after 90 days (Figure 4). The highest

338 observed concentration was measured in a composite flowback sample (16,000 µg L⁻¹) (Lester et

339 al., 2015), and several other flowback samples had acetone concentrations ranging from 10² - 10³

340 µg L⁻¹ (Hayes, 2009). Interestingly, in at least one supply water sample (used for mixing to make

341 HVHF fluid), acetone concentrations were even higher than in flowback (Hayes, 2009),

342 suggesting that this supply water was likely a recycled fluid that contained high levels of acetone

343 as an additive or degradable organic additives that underwent fermentation to form acetone. In a

344 simulated bioreactor “spill” of HVHF fluids, acetone was produced as a degradation product (see

345 Section 4.2) (Kekacs et al., 2015).

346 19% of the 404 identified organic compounds in Fayetteville shale flowback fluid and

347 produced waters using GCxGC-TOF-MS were suspected to be formed through subsurface
348 reactions (Hoelzer et al., 2016). Many of these compounds included carbonyl groups (Hoelzer et
349 al., 2016) that may indicate degradation of geopolymers or hydrolysis products of delayed-
350 release acids used as breakers (Hoelzer et al., 2016; Orem et al., 2014, 2010). In Marcellus shale
351 produced waters, 2,2,4-trimethyl-1,3-pentanediol was identified at high concentrations (130 -
352 500 $\mu\text{g L}^{-1}$) in flowback and remained at those concentrations in the produced waters even 234
353 days after HVHF (Orem et al., 2014). This compound has not been identified as an additive
354 previously, but a related compound, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, has been
355 used industrially as a solvent and may potentially be related to the source of this derivative
356 (Orem et al., 2014). A direct transformation product of the known additive, azobis
357 (isobutyronitrile), tetramethylsuccinonitrile was identified by GCxGC-TOF-MS in Fayetteville
358 shale produced waters (Hoelzer et al., 2016). Dimerization and trimerization of the frequently
359 used biocide glutaraldehyde under the variable salinity, temperature, and pressure conditions
360 reflecting a shale gas well has been tested under laboratory conditions (Kahrilas et al., 2016), but
361 has not been observed in flowback and produced waters (Ferrer and Thurman, 2015b).
362 Additionally, hydroxylated phenols identified in flowback fluids are likely degradation products
363 of alkylphenol ethoxylate additives (Hoelzer et al., 2016).

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

370 compounds (chloromethyl propanoate, chloromethyl pentanoate, chloromethyl hexanoate,
 371 chloromethyl octanoate) identified by Hoelzer and colleagues are suspected HVHF additives
 372 (Hoelzer et al., 2016). Four studies have identified a number of additional halogenated organic
 373 compounds that are likely transformation products and several potential mechanisms for the
 374 formation of these compounds are hypothesized (Hayes, 2009; Hoelzer et al., 2016; Luek et al.,
 375 2017; Maguire-Boyle and Barron, 2014). Maguire-Boyle and Barron (2014) identified the
 376 corresponding non-halogenated aliphatic compound for each halogenated compound and
 377 suggested that the halide salts or free halogens created during oxidative treatments could cause
 378 the observed halogenation (Maguire-Boyle and Barron, 2014). Similarly, Hoelzer and colleagues
 379 indicated radicalic substitution, nucleophilic substitution, and electrophilic addition in the
 380 presence of halides and free halogen species as the proposed halogenation mechanisms (Hoelzer
 381 et al., 2016). In streambed sediments downstream of a deep well injection facility, several
 382 halogenated organic compounds including 1,54-dibromotetrapentacontane were identified (Orem
 383 et al., 2017).

384
 385 **Table 2.** Halogenated organic compounds identified in flowback and produced waters. *Italicized*
 386 compounds are explicit and suspect fracturing fluid additives. Note: Compounds identified in
 387 Hayes (2009) rely on EPA methods with quantification using reference standards; Hoelzer et al.,
 388 (2016) and Maguire-Boyle and Barron (2014) match ions using spectral libraries and report
 389 confidence in assignment in their supplemental materials. Halogenated chemical formulas in
 390 Luek et al., (2017) not included due to lack of structural information.
 391

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	<i>Hoelzer et al., 2016</i>
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	<i>Hoelzer et al., 2016</i>
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	<i>Hoelzer et al., 2016</i>
<i>Chloromethyl octanoate</i>	C ₉ H ₁₇ ClO ₂	GCxGC-TOF-MS	<i>Hoelzer et al., 2016</i>
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

392 4. Environmental Contamination

393 4.1 Contamination Events

394 In the peer-reviewed literature, specific organic compounds have been identified in
395 surface water, sediments, and groundwater and have been linked to recent HVHF activities
396 (Cozzarelli et al., 2017; DiGiulio and Jackson, 2016a; Drollette et al., 2015; Gross et al., 2013;
397 Hildenbrand et al., 2016, 2015; Kassotis et al., 2014; Llewellyn et al., 2015; Orem et al., 2017).
398 These suspected contamination events were documented in the Bakken, Powder River Basin,
399 Marcellus, Permian, Barnett, and Denver-Julesberg basins, and next to a deep well injection
400 facility in West Virginia. The EPA has also published five “retrospective case studies”
401 investigating the impacts of HVHF on drinking water sources in five different locations between
402 2011-2013. (*Retrospective Case Study in Killdeer, North Dakota: Study of the Potential Impacts*
403 *of Hydraulic Fracturing on Drinking Water Resources*, 2015, *Retrospective Case Study in*
404 *Northeastern Pennsylvania: Study of the Potential Impacts of Hydraulic Fracturing on Drinking*
405 *Water Resources*, 2015, *Retrospective Case Study in Southwestern Pennsylvania Study of the*

406 *Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, 2015, Retrospective*
407 *Case Study in the Raton Basin, Colorado: Study of the Potential Impacts of Hydraulic*
408 *Fracturing on Drinking Water Resources, 2015, Retrospective Case Study in Wise County,*
409 *Texas: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources,*
410 2015). Organic analyses have focused on additives and oil and gas related compounds; inorganic
411 tracers of HVHF including anions and metals have also been analyzed in these samples to
412 understand the potential contamination events.

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

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

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

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

458 In northeastern Pennsylvania, groundwater samples were collected from private
459 residential wells (9-231 m depth) and analyzed for GC-amenable compounds (Drollette et al.,
460 2015). Gas related organic compounds were detected in 9 of 59 wells and diesel related organic
461 compounds were detected in 23 of 41 wells in highly variable concentrations (Drollette et al.,
462 2015). BTEX compounds were identified in 6 samples at trace levels below EPA drinking water
463 maximum contaminant level recommendations (Drollette et al., 2015). The highest
464 concentrations of observed organic compounds were identified within 1 km of a shale gas well as
465 well as in close proximity to a well that caused an environmental health and safety violation.
466 Based on geochemical fingerprinting tools, the authors concluded that the groundwater
467 contamination was likely due to surface spills associated with HVHF activities rather than via
468 subsurface contamination. Additionally, a disclosed additive, bis(2-ethylhexyl) phthalate, was
469 identified in the same two samples with the highest diesel related organic compounds
470 concentrations. Foaming was also observed in three residential drinking water wells in northern
471 Pennsylvania located in close proximity to HVHF wells (Llewellyn et al., 2015). Commercial
472 laboratories were unable to detect any compounds during this known contamination event other
473 than methane that exceeded regulatory drinking water standards and recommendations, but 2-

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

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

487 Following complaints of residents, the EPA investigated groundwater contamination in
488 Pavilion, WY suspected to be associated with the HVHF of shallow gas wells through the
489 installation of several shallow and deep groundwater monitoring wells (DiGiulio and Jackson,
490 2016a; DiGiulio et al., 2011). Multiple phases of monitoring were performed beginning with
491 existing residential and municipal wells, followed by shallow monitoring wells, and finally by
492 two explicitly drilled deep monitoring wells (235 m, 295 m) (DiGiulio et al., 2011). Shallow
493 wells had high levels of BTEX, diesel and gas related compounds, and other hydrocarbons, but
494 ultimately were suspected of contamination by the use of surface unlined pits where fluids
495 including diesel used for gas extraction were stored (DiGiulio and Jackson, 2016a). However,
496 organic compounds identified in deep groundwater monitoring wells were different than those

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

511 In the EPA retrospective case studies (*Retrospective Case Study in Killdeer, North*
512 *Dakota: Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources,*
513 *2015, Retrospective Case Study in Northeastern Pennsylvania: Study of the Potential Impacts of*
514 *Hydraulic Fracturing on Drinking Water Resources, 2015, Retrospective Case Study in*
515 *Southwestern Pennsylvania Study of the Potential Impacts of Hydraulic Fracturing on Drinking*
516 *Water Resources, 2015, Retrospective Case Study in the Raton Basin, Colorado: Study of the*
517 *Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, 2015, Retrospective*
518 *Case Study in Wise County, Texas: Study of the Potential Impacts of Hydraulic Fracturing on*
519 *Drinking Water Resources, 2015), a suite of organic compounds including VOCs, SVOCs, and*

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

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

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

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

573

574 4.2 Simulated bioreactor “spills”

575 Two published studies have simulated spills of HVHF fluids at the bench scale under
576 aerobic conditions. In each of these studies, a synthetic mixture of HVHF fluid additives was
577 mixed with natural microbial communities and the organic additives quantified over 7-180 days.
578 In an aerobic solution inoculated with an activated sludge microbial community, the overall
579 dissolved organic carbon (DOC) content decreased by 52% in 6.5 days in freshwater and a 20 g
580 L⁻¹ saline solution. At higher salinities (40 g L⁻¹ and 60 g L⁻¹), DOC did not change significantly
581 over the same time period. Acetone, a degradation product, increased by two orders of
582 magnitude, and volatile additives such as naphthalene and benzene were rapidly decreased in
583 concentration, likely due to volatilization (Kekacs et al., 2015). In the second study, varying
584 combinations of fracturing fluid additives were mixed with agricultural soil and the *in situ*
585 microbial community and their changes tracked to understand co-contaminant interactions over
586 180 days (McLaughlin et al., 2016). The presence of glutaraldehyde biocide impeded the
587 degradation of polyethylene glycol surfactants, and high salt levels also severely inhibited their

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

590

591 **5. Flowback and Produced Water Treatment**

592 High total dissolved solids (TDS) create a significant challenge for the treatment of
593 flowback and produced waters (Gregory et al., 2011; Kondash et al., 2017), hence wastewaters
594 are frequently sent to Class II disposal wells (U.S. EPA, 2016). TDS varies by basin and
595 increases over the lifetime of the well (Kondash et al., 2017); high levels of TDS limit direct
596 reuse due to scaling problems and reduced effectiveness of friction reducers (Gregory et al.,
597 2011; Kamel and Shah, 2009). The fate of the treated effluent determines the type and amount of
598 treatment required. The treatment for reuse in HVHF requires a different level of treatment (e.g.,
599 precipitation of scaling cations, disinfection, (Lester et al., 2015)) than other beneficial reuses or
600 discharge to the environment (Estrada and Bhamidimarri, 2016; Gregory et al., 2011). High TDS
601 formation produced waters, such as the Bakken or Marcellus, cannot be directly reused and TDS
602 must be first reduced either by using dilution or treatment, which is in contrast to formations
603 such as the Niobrara or Eagle Ford, that have much lower TDS (Kondash et al., 2017).

604 The wide variety of treatment methods used for flowback and produced waters have been
605 reviewed previously (Drewes et al., 2009; Estrada and Bhamidimarri, 2016; Fakhru'l-Razi et al.,
606 2009; Gregory et al., 2011; U.S. EPA, 2016). Traditional oil and gas centralized waste treatment
607 and municipal treatment facilities (no longer in use) have not been shown to sufficiently remove
608 key contaminants from HVHF wastewaters prior to discharging to streams (Ferrar et al., 2013;
609 Getzinger et al., 2015; Warner et al., 2013). Thermal distillation and crystallization technologies
610 efficiently remove TDS but may be energy intensive, while membrane technologies such as

611 reverse osmosis, forward osmosis, and nanofiltration are prone to clogging and fouling and are
612 more effective when combined with pre-treatment technologies (Coday et al., 2014; Estrada and
613 Bhamidimarri, 2016; Gregory et al., 2011; Jang et al., 2017; Riley et al., 2016; Shaffer et al.,
614 2013).

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

622 Bench-scale experiments have examined the removal efficiencies of a number of organic
623 compounds frequently found in HVHF wastewaters. Guar gum, a common HVHF additive likely
624 to foul membranes, was effectively removed biologically (~90%) at low TDS using an activated
625 sludge mixture (Lester et al., 2014). In a different synthetic HVHF wastewater, forward osmosis
626 rejected >99.9% of oil while acetic acid rejection was much lower at only 82% (23 °C) and 74%
627 (60 °C) (Zhang et al., 2014). More hydrophobic compounds, including alkanes and polycyclic
628 aromatic hydrocarbons, were removed with 90-99% efficiency using forward osmosis (Bell et
629 al., 2017). Powdered activated carbon (PAC) combined with coagulants were tested for removal
630 efficiency of total petroleum hydrocarbons and polyethylene glycols from actual HVHF
631 flowback and produced waters. PAC was shown to be effective at high doses (750 mg L⁻¹, 1,000
632 mg L⁻¹ PAC) for polyethylene glycol removal in all cases and in three out of four wastewaters
633 for total petroleum hydrocarbons (Rosenblum et al., 2016). However, these specific classes

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

636

637 **6. Considerations and Future Research**

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

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

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

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

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

676

677 **7.0 Conclusions**

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

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

689

690

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