

21 **Abstract:** Hydraulic fracturing (HF) of shale and other permeable rock formations to
22 release gas and oil is a water-intensive process that returns a significant amount of
23 flowback and produced water (FPW). Due to the complex chemical composition of HF
24 fluids and FPW, this process has led to public concern on the impacts of FPW disposal,
25 spillage and spreading to regional freshwater resources, in particular to shallow
26 groundwater aquifers. To address this, a better understanding of the chemical
27 composition of HF fluid and FPW, as well as the chemical environmental fate properties
28 such as their persistence, mobility and toxicity, are needed. Such research would
29 support risk-based management strategies for the protection of regional water quality,
30 including both the phase-out of problematic chemicals and better hydraulic safeguards
31 against FPW contamination. This article presents recent strategies to advance the
32 assessment and analysis of HF and FPW associated organic chemicals.

33 **Keywords:** hydraulic fracturing, chemical, pollution, water resources, mobility

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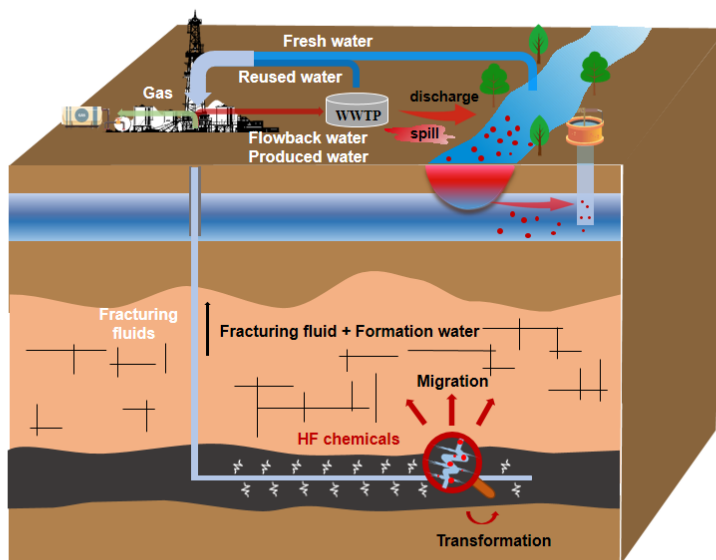
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43 **Introduction**

44 In many countries advances in horizontal drilling and hydraulic fracturing (HF)
45 techniques has led to increasing extraction of gas and oil from shales and other low
46 permeable geological formations ¹. In China HF industries are playing an essential role
47 in transitioning away from coal, and thereby reducing emissions of air pollutants
48 (particulates, SO_x, NO_x) and greenhouse gas emissions, as well as transitioning to
49 renewable energy sources ². However, HF processes pose special concerns on regional
50 water resources, due to the high-volume consumption of fresh water ³. As demonstrated
51 in Figure 1, fresh water is mixed with numerous HF chemical additives, which are then
52 injected into a deep-horizon to fracture low-permeability shale and rocks to facilitate
53 gas and oil extraction. This process introduces a high pressure environment
54 underground, and creates fractures, faults and joints through which fracturing fluid
55 could penetrate along these permeable pathways ⁴. Hydraulic fracturing also produces
56 a significant amount of wastewater, referred to as flowback and produced water, which
57 is referred to collectively as FPW. Flowback water is the returned water containing most
58 of the HF fluids and produced water is that containing the geological water that contains
59 most of the gas and oil. FPW contains numerous synthetic chemicals, geogenic
60 compounds and transformation byproducts ⁵. Release of these compounds towards the
61 surrounding environment may pose risks to regional water resources, in particular to
62 shallow groundwater aquifers ^{6,7}. So far, a detailed chemical characterization of HF
63 chemicals remains lacking. This hinders constructing environmental emission
64 inventories of HF-associated organic pollutants. A process-based understanding of
65 subsurface fate of HF chemicals during gas and oil extraction processes is an essential

66 task for making risk-based water management strategies, and therefore requiring
67 guidance through careful chemical analysis.



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70 **Figure 1.** Schematic illustration of hydraulic fracturing (HF) processes and possible pathways
71 of how HF chemicals can impact water quality.

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73 **Chemical fingerprint of hydraulic fracturing activities**

74 **Identifying hydraulic-fracturing associated chemicals.** FPW carries both geogenic
75 compounds (e.g. PAHs, hydrocarbons) and HF chemicals of a wide range of
76 physicochemical properties. Characterizing the organic chemical compositions of FPW
77 therefore requires sophisticated instrumental efforts. This involves co-deployment of
78 different analytical tools to analyze this wide variety of substances, ranging from very
79 mobile polar substances to large hydrophobic oils. So far, information revealed from

80 chemical disclosure and compound-specific characterization of flowback water are still
81 inadequate to complete an emission inventory of HF-associated chemicals. Recently,
82 high-resolution mass spectrometry such as time-of-flight mass spectrometry (TOF-MS)
83 coupled to liquid chromatography (LC) or two-dimensional gas chromatography (GC),
84 is increasingly applied to identify unknown organic compounds and transformation
85 products ^{8, 9}. Additionally, Fourier transform ion cyclotron resonance mass
86 spectrometry (FT-ICR-MS) is an emerging tool to characterize the elemental
87 composition of organic components in FPW. For instance, a very recent study revealed
88 that oxygen-containing compounds such as unsaturated phenols were predominant in
89 flowback water¹⁰. Another recent study applied a reversed phase HPLC coupled to
90 Orbitrap MS for non-target analysis and semi-quantification of organic compounds in
91 flowback water samples. Specifically, in total seven series of homologues were
92 identified at different confidence levels ¹¹. One of the most challenging classes of
93 contaminants for analysis are water-soluble polymers, like polyacrylamide (PAM), that
94 are used in large volumes as viscosity enhancers (Xiong et al. 2018). In the subsurface,
95 these can transform to a complex mixture of oligomers and polymeric fragments that
96 are difficult to quantify, and therefore to understand their fate and risk ^{12, 13}. Only
97 recently have methods been proposed to measure such substances in water, such as the
98 use of combining size exclusion chromatography (SEC) with an MS by way of in-
99 source fragmentation to reduce the number of mass fragments ¹⁴. This calls for
100 implementation and integration of targeted and non-targeted analytical tools for
101 identifying hydraulic fracturing associated chemical fingerprints. Moreover, mobile

102 organic pollutants are co-eluting with brines, and the inorganic ions could introduce
103 matrix-effect by lowering ionization efficiency of the mobile analytes using LC¹⁵. Thus,
104 prior to instrumental analysis proper pretreatment techniques are essential to remove
105 salts from flowback water samples.

106 The identification of transformation pathways of chemicals in FPW is key to understand
107 their ultimate fate and impacts. However, the concentration of chemicals in FPW are
108 influenced by concurrent downhole processes such as dilution, transformation, and
109 sorption, which makes the identification of transformation products complex.

110 Compound specific isotope analysis (CISA) determines stable isotopic compositions in
111 organic molecules, providing a valuable approach to characterize organic contaminants
112 subsurface transformation processes^{16, 17}. Specifically, CSIA could identify geogenic
113 and anthropogenic sources of a certain organic compound through isotopic
114 fingerprinting. Moreover, monitoring the specific isotope fractionation of organic
115 compounds allows to prove the occurrence of subsurface transformation processes,
116 even when the substrate concentration is variable due dilution by formation water. As
117 part of this, stable halogen (i.e. $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$) CSIA could potentially serve as a
118 unique tool to characterize both halogenation and dehalogenation transformations of
119 different HF chemicals in high-saline environments^{18, 19}.

120 **Persistent, mobile and toxic substances.** Underground injection of hydraulic
121 fracturing fluids raises continuous concerns for regional shallow groundwater aquifers,
122 since fracturing chemicals might cause groundwater contamination. Among the
123 hundreds of HF chemicals, special attention should be paid to compounds with high

124 persistence (P) and aqueous mobility (M), particularly toxic ones (which are referred to
125 as PMT substances), which are slow to degrade and can rapidly spread in the subsurface
126 ^{20, 21}. Once these are accidentally released into surrounding water environment, they
127 might potentially pass natural barriers, and finally pollute and accumulate within
128 drinking water resources ^{22, 23}. Besides persistent, bioaccumulative and toxic (PBT)
129 chemicals, more focus on these chemicals is expected for PMT chemicals, as Europe is
130 introducing new chemical regulations on this class of contaminant²². The known PMTs
131 including tetrachloroethene, 1,4-dioxane and 1,2,4-trimethylbenzene, have already
132 been detected in the HF wastewaters. Some PMT contaminants unique to hydraulic
133 fracturing could serve as an ‘identifier’ for accidental spill or leakage of wastewater
134 towards surrounding fresh water environments. Recent advances on chemical
135 disclosure frameworks, such as FracFocus (<https://fracfocus.org/>), have substantially
136 increased the transparency of HF chemicals, providing numerous open-source
137 databases that are useful for chemical risk assessments and environmental impact
138 analysis ²⁴. To predict HF chemicals impact on regional water quality, it is beneficial to
139 evaluate the chemicals degradability and aqueous mobility based on experimental data.
140 When the experimental data are unavailable “*in-silico*” tools are often applied to
141 identify and to prioritize the associated PMT chemicals ^{21, 25}. Also, regular monitoring
142 and chemical analysis of surrounding groundwater and surface water samples should
143 include specific PMT compounds, in order to provide proof of the extent of spreading/or
144 contaminant of the substances with the greatest hazard of spreading long distances. This
145 type of chemical fingerprinting will support oil and gas industries making sound risk-

146 based water and wastewater management strategies. More description of fate processes
147 and simulation studies to base this fingerprinting and management strategies on are
148 presented in the next sections.

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150 **Subsurface attenuation of hydraulic fracturing chemicals**

151 **Transformation and products.** Under elevated temperature, pressure, and halide
152 concentrations, fracturing chemicals can undergo various (bio)chemical reactions in
153 subsurface environment. So far, most studies have focused on abiotic reactions of HF
154 chemicals. For instance, one recent study analyzed alkyl ethoxylate (AEO) surfactants
155 in fracturing fluid and produced water; the study suggested that the absence of AEOs
156 in produced water was due to the subsurface transformation of AEOs to polyethylene
157 glycols (PEGs) by cleaving the ethoxylate chain from the alkyl group ²⁶. Hydrolysis
158 processes occur for putative acids such as alkanoyl anhydrides, alkanoyl chlorides, and
159 chloromethyl alkanooates. These chemicals were introduced as “breakers” to destruct
160 water-based guar gum to facilitate gas and fluid transport in subsurface fractures ²⁷.
161 Although some chemical additives are non-toxic and have short half-lives, their
162 subsurface transformation processes still might release various problematic byproducts.
163 For example, 2,2-dibromo-3-nitropropionamide (DBNPA), a frequently disclosed
164 fracturing biocide, could form different toxic halogenated PM(T) transformation
165 products, including dibromoacetonitrile, trihalomethanes (THMs) and haloacetonitriles
166 ²⁸. Moreover, subsurface formation water contains high-levels of halide ions (i.e.
167 chloride, bromide and iodide) that could be incorporated into organic molecules via

168 halogenation reactions^{27, 29}. In the presence of strong oxidants such as ammonium
169 persulfate and sodium chlorite as breakers, halide ions can form molecular halogens
170 that would elevate the yield of halomethanes in the subsurface^{8, 27}. Thus, an improved
171 understanding of these relevant transformation mechanisms is required to avoid
172 formation of unwanted organohalides in flowback water.

173 **Simulation studies.** Downhole conditions in shale wells are featured by higher
174 temperature and pressure. Specifically, the well temperatures typically range from 40 °C
175 to 100 °C, and the bottom hole pressure depends on well depth and could vary from
176 1800 psi to 4500 psi³⁰. To help overcome the difficulty in characterizing transformation
177 products of HF chemicals *in-situ*, controlled experiments using high-pressure reactors
178 could be utilized to simulate the transformation of chemicals in complex subsurface
179 environments. High-pressure reactors have been recently designed for this purpose. For
180 instance, stainless steel reactors were designed to simulate the subsurface chemistry of
181 one HF chemical biocide, glutaraldehyde (GA)³¹. The reactor could elevate reaction
182 pressures up to 3000 psi (i.e. 207 bars) and temperatures up to 350 °C. Their results
183 indicated that GA undergoes polymerization reactions, forming dimers and trimers as
184 byproducts, and precipitates out at ~140 °C and/or at higher pH values³¹. Notably, the
185 temperature plays a more vital role on GA transformations, rather than the applied
186 pressure³¹. However, the low throughput hinders experimental simulations of multiple
187 organic compounds. To overcome this shortcoming, one high-throughput reactor was
188 developed that consists of 15 independent reactors equipped with pressure pumps and
189 a temperature-control system that is based on an external thermal bath³⁰. The individual

190 reactors could be operated simultaneously at a maximum pressure of 5000 psi (345
191 bars), where the maximum temperature was dependent on the boiling point of liquids
192 filled in the external thermal bath. By utilizing this simulator, different HF chemicals'
193 transformation pathways and the formation of specific reaction products have been
194 better characterized. For instance, this study revealed that ammonium persulfate, one
195 frequently used oxidative breaker, could halogenate cinnamaldehyde. Specifically, they
196 found that halide ions are first oxidized to hypohalogenic acids such as HOCl, HOBr,
197 HOI, and then are attached to α,β -unsaturated molecular bonds. Moreover, they also
198 reported that ammonium persulfate could directly react with cinnamaldehyde to form
199 benzene derivatives (Sumner and Plata, 2018b). New halogenation mechanisms were
200 also revealed by which epichlorohydrin undergoes ring-opening pathways via chloride
201 and hydroxide addition processes. Another recent experimental study indicated that
202 citric acid could trigger the formation of THMs, when it is in contact with cross-linked-
203 gel matrix, especially in the presence of high-level chemical breakers ²⁹.

204 **FPW wastewater reuse and treatment**

205 **Wastewater reuse.** Underground fracturing consumes vast amounts of fresh water
206 resources, and later returns high-volume wastewater to the surface. So far, deep-well
207 injection and reuse as fracturing fluids are the two common ways to dispose the FPW
208 wastewater. However, deep-well injection is limited by the availability of suitable wells,
209 and is often avoided due to the pressure from local regulations and permits. When oil
210 and gas industries are located in (semi) arid regions, reuse of hydraulic fracturing
211 wastewater is a practical solution for onsite wastewater reuse, since this could

212 significantly reduce fresh water consumption and the cost for water treatment ³².
213 Generally, wastewater is recycled and often mixed with fresh water in arid regions for
214 both internal and external use ³³. For internal reuse, the flowback water is collected and
215 mainly treated by adding fracturing chemical additives in order to maintain the
216 fracturing efficiency. It is worth noting that PMT substances used for this purpose might
217 accumulate in the wastewater during the fracturing and chemical re-feeding processes
218 ³⁴. This might increase the risk of groundwater contamination by fracturing chemicals,
219 particularly PMT substances. Externally, the wastewater that is treated intensively can
220 be re-used for irrigation, livestock drinking and/or surface discharge. However, external
221 reuse of this wastewater requires expensive, efficient treatment techniques to deal with
222 high-saline composition in addition to numerous organic and inorganic solutes (Table
223 1); leaving desalination processes, like reverse osmosis, a requirement for effective
224 external water treatment, as described in the next section.

225 **Table 1** Example of basic and advanced water treatment techniques used for the removal of organic contaminants from hydraulic fracturing wastewater.

Treatment techniques	Description	Target compounds	Sample location	Removal fraction	Refs.
basic treatment	filtration	Benzene	Wattenberg field in northeast Colorado	95%	35
		Toluene		97%	
		Ethylbenzene		97%	
membrane treatment	ultrafiltration-reverse osmosis	Dimethylbenzylamine	Weiyuan in Sichuan Basin, China	78.3%	10
		Indoline		96.3%	
		6-methyl-quinoline		100%	
adsorption	granular activated carbon	naphthalene sulfonate	a Baltic shale gas basin in Poland	-*	36
		hexaethyleneglycol		-	
		octaethyleneglycol		-	
		decaethyleneglycol		-	
		hodecaethyleneglycol		-	
advanced oxidation processes	Fe ⁰ /persulfate/O ₃	propanoic acid	a shale gas well in southwest China	-	37
		isobutyric acid		-	
		isovaleric acid		-	
		butanoic acid, 2-methyl-		-	
		4-methylhexanoic acid		-	
		benzenemethanethiol		-	
		ethyl nonyl ester		-	
		1-pentadecanamine, n,n-dimethyl-		-	
		1-phenyl-2-benzylaminopropane		-	
		2-(2-Butoxyethoxy) ethanol		-	
	ozonation		a Baltic shale gas basin in Poland	-	36

oxidative treatment	microwave-activated persulfate process	benzene	shale gas field in southwest China	0.61%	38
		hexamethyldisiloxane		100%	
		methylbenzene		29.96%	
		3,4-dihydrogen-2 h-pyran		100%	
		2,2,4,6,6-pentmethyl heptane		40.66%	
		chloriso-octane		100%	
		myristic acid		100%	
		diisobutyl phthalate		100%	
		palmitic acid		45.65%	
		oleamide		100%	
		antioxidant 2246		54.86%	
		2-ethylhexyl hydrogen phthalate		61.15%	
		erucic acid amide		26.13%	

226 *information not available

227 **Wastewater treatment.** The basic treatment technologies, including centrifugation,
228 hydrocyclones, flotation, medium filtration, coagulation/flocculation, and evaporation,
229 are often applied for wastewater pretreatment to remove suspended solids and oil ³⁶.
230 Current advanced water treatment techniques are membrane separation, thermal
231 distillation, adsorption using activated carbon or ionic resins, and advanced oxidation
232 for the removal of dissolved organic compounds. An overview of different treatment
233 techniques is summarized in Table 1.

234 Membrane based techniques, including reverse osmosis membranes and ultrafiltration,
235 have been applied for HF wastewater treatment ³⁹. Efficient removal of specific organic
236 contaminants from HF wastewater often requires combination of different membrane
237 techniques. For instance, ultrafiltration was coupled with reverse osmosis membranes
238 in order to treat wastewater collected from Weiyuan extraction field in China ¹⁰. The
239 results showed that the targeted organic contaminants, dimethylbenzylamine, indoline
240 and 6-methyl-quinoline, were removed from the water by 78.3%, 96.3%, and 100%,
241 respectively ¹⁰. Notably, the membrane-based water treatment systems could produce
242 concentrated residual waters, rather than break down the organic contaminants. In order
243 to prevent further environmental pollution, careful disposal and treatment schemes are
244 definitely required to manage the membrane concentrates⁴⁰.

245 Adsorption is a practical approach to remove various organic contaminants from HF
246 wastewater ⁴¹. Activated carbon (AC) is the most common sorbent in adsorbent based
247 systems, and these have been applied to successfully remove polyaromatic
248 hydrocarbons (PAHs) from HF wastewater, but no satisfactory removal was obtained

249 for phthalates⁴². This might be due to weaker sorption of phthalates in comparison with
250 PAHs. Granular activated carbon has also been added to flowback water to sorb
251 dissolved organic contaminants. The results showed that heavy organic molecules such
252 as hexaethyleneglycol and dodecaethyleneglycol are preferentially removed from the
253 water³⁶. Very recently, novel green sorbents such as porous biochar aerogel was also
254 applied for HF wastewater treatment, leading to a higher removal efficiency for
255 hydrophobic organic compounds⁴³.

256 Advanced oxidation processes (AOPs), including ozonation, Fenton-based techniques
257 and heterogeneous photocatalysis, have been increasingly applied for the removal of
258 organic contaminants in HF wastewaters⁴⁴. For instance, a micro-scale
259 Fe⁰/Persulfate/O₃ treatment approach was developed to treat flowback water, and it was
260 observed that different organic compounds were successfully reduced via
261 transformation processes³⁷. Organic contaminant removal efficiency by AOPs might
262 be greatly influenced by water chemistry such as halide ion concentrations in HF
263 wastewaters⁴⁵, potentially leading to persistent, mobile byproducts. Thus, desalination
264 of HF wastewater will be a crucial step for sustainable AOP treatment. On the other
265 hand, AOPs could be introduced as a pretreatment method and combined with other
266 treatment techniques such as bioactive filtration to obtain higher removal efficiencies
267 for dissolved organic contaminants in HF wastewaters⁴⁶. Given that removal of
268 different organic contaminants from wastewater is technically challenging, evaluation
269 of different wastewater treatment strategies should be well guided by compound
270 specific chemical analysis. Moreover, a combination of different water treatment

271 techniques would be beneficial for an organic-contaminant targeted wastewater
272 treatment strategy. The additives that are ultimately added to water used for shale gas
273 extraction should be ideally chosen for their ease in removal in the water treatment
274 processes occurring on site.

275 **Conclusions**

- 276 • Adequate chemical characterization involving an assessment of the persistency,
277 mobility and toxicity of hydraulic fracturing chemicals and their transformation
278 products is helpful to prioritize compounds of concerns to water resources for risk-
279 based decisions and to establish a reasonable monitoring program for surrounding
280 water quality.
- 281 • Understanding the fate and transport of hydraulic fracturing chemicals in the
282 subsurface environment will support the optimization of gas extraction operations
283 to avoid unwanted byproducts such as halogenated methanes and other toxic HF
284 chemicals brought to the surface.
- 285 • A chemical-based water management strategy is necessary for reuse and treatment
286 of hydraulic fracturing wastewaters. Special attention should be paid to PMT and
287 PBT chemicals to prevent their release toward regional environment.
- 288 • High-quality experimental data on HF chemicals persistency, bioaccumulation,
289 mobility and toxicity are needed to identify high-volume PMT and PBT substances.
290 Particularly, our knowledge on toxic effects of HF chemicals remains limited due
291 to the lack of the toxicity data as well as relevant studies demonstrating toxicity of
292 the identified HF chemicals. This will support source reduction of the prioritized

293 hazardous organic pollutants, and also will promote further development of
294 environmentally friendly chemical substituents, and lower the cost of treatment
295 operations needed to protect regional water resources and surrounding environment.

296

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305 **References**

- 306 1. A. Vengosh, W. A. Mitch and L. M. McKenzie, Environmental and Human Impacts of
307 Unconventional Energy Development, *Environmental Science & Technology*, 2017, **51**, 10271-
308 10273.
- 309 2. C. Zhong, A. Zolfaghari, D. Hou, G. G. Goss, B. D. Lanoil, J. Gehman, D. C. W. Tsang, Y. He and D.
310 S. Alessi, Comparison of the Hydraulic Fracturing Water Cycle in China and North America: A
311 Critical Review, *Environmental Science & Technology*, 2021, **55**, 7167-7185.
- 312 3. A. J. Kondash, N. E. Lauer and A. Vengosh, The intensification of the water footprint of hydraulic
313 fracturing, *Science Advances*, 2018, **4**.
- 314 4. D. T. Birdsell, H. Rajaram, D. Dempsey and H. S. Viswanathan, Hydraulic fracturing fluid
315 migration in the subsurface: A review and expanded modeling results, *Water Resources*
316 *Research*, 2015, **51**, 7159-7188.
- 317 5. W. T. Stringfellow, M. K. Camarillo, J. K. Domen, W. L. Sandelin, C. Varadharajan, P. D. Jordan, M.
318 T. Reagan, H. Cooley, M. G. Heberger and J. T. Birkholzer, Identifying chemicals of concern in
319 hydraulic fracturing fluids used for oil production, *Environ Pollut*, 2017, **220**, 413-420.
- 320 6. S. Jasechko and D. Perrone, Hydraulic fracturing near domestic groundwater wells, *Proceedings*
321 *of the National Academy of Sciences*, 2017, **114**, 13138-13143.
- 322 7. J. Gao, C. Zou, W. Li, Y. Ni, F. Liao, L. Yao, J. Sui and A. Vengosh, Hydrochemistry of flowback
323 water from Changning shale gas field and associated shallow groundwater in Southern Sichuan

- 324 Basin, China: Implications for the possible impact of shale gas development on groundwater
325 quality, *Sci Total Environ*, 2020, **713**, 136591.
- 326 8. J. L. Luek and M. Gonsior, Organic compounds in hydraulic fracturing fluids and wastewaters:
327 A review, *Water Res*, 2017, **123**, 536-548.
- 328 9. P. K. Piotrowski, B. A. Weggler, E. Barth-Naftilan, C. N. Kelly, R. Zimmermann, J. E. Saiers and F.
329 L. Dorman, Non-Targeted chemical characterization of a Marcellus shale gas well through
330 GC × GC with scripting algorithms and high-resolution time-of-flight mass spectrometry, *Fuel*,
331 2018, **215**, 363-369.
- 332 10. Y. Sun, M. Wu, T. Tong, P. Liu, P. Tang, Z. Gan, P. Yang, Q. He and B. Liu, Organic compounds in
333 Weiyuan shale gas produced water: Identification, detection and rejection by ultrafiltration-
334 reverse osmosis processes, *Chemical Engineering Journal*, 2021, **412**.
- 335 11. C. Sun, Y. Zhang, D. S. Alessi and J. W. Martin, Nontarget profiling of organic compounds in a
336 temporal series of hydraulic fracturing flowback and produced waters, *Environ Int*, 2019, **131**,
337 104944.
- 338 12. B. Xiong, R. D. Loss, D. Shields, T. Pawlik, R. Hochreiter, A. L. Zydney and M. Kumar,
339 Polyacrylamide degradation and its implications in environmental systems, *npj Clean Water*,
340 2018, **1**, 17.
- 341 13. H. P. H. Arp and H. Knutsen, Could We Spare a Moment of the Spotlight for Persistent, Water-
342 Soluble Polymers?, *Environmental Science & Technology*, 2020, **54**, 3-5.
- 343 14. S. Huppertsberg, D. Zahn, F. Pauelsen, T. Reemtsma and T. P. Knepper, Making waves: Water-
344 soluble polymers in the aquatic environment: An overlooked class of synthetic polymers?,
345 *Water Research*, 2020, **181**, 115931.
- 346 15. K. Müller, D. Zahn, T. Frömel and T. P. Knepper, Matrix effects in the analysis of polar organic
347 water contaminants with HILIC-ESI-MS, *Analytical and Bioanalytical Chemistry*, 2020, **412**,
348 4867-4879.
- 349 16. A. S. Ojeda, E. Phillips and B. Sherwood Lollar, Multi-element (C, H, Cl, Br) stable isotope
350 fractionation as a tool to investigate transformation processes for halogenated hydrocarbons,
351 *Environmental Science: Processes & Impacts*, 2020, **22**, 567-582.
- 352 17. J. Zimmermann, L. J. S. Halloran and D. Hunkeler, Tracking chlorinated contaminants in the
353 subsurface using compound-specific chlorine isotope analysis: A review of principles, current
354 challenges and applications, *Chemosphere*, 2020, **244**, 125476.
- 355 18. B. Jin, J. Zhang, W. Xu, M. Rolle, J. Liu and G. Zhang, Simultaneous determination of stable
356 chlorine and bromine isotopic ratios for bromochlorinated trihalomethanes using GC-qMS,
357 *Chemosphere*, 2021, **264**, 128529.
- 358 19. Y. Liu, S. Liu, Q. Wang, S. Gligorovski, G. Zhang and B. Jin, Stable chlorine isotope analysis of
359 triclosan using GC-qMS: Method development and applications, *Applied Geochemistry*, 2021,
360 **129**, 104961.
- 361 20. J. D. Rogers, T. L. Burke, S. G. Osborn and J. N. Ryan, A Framework for Identifying Organic
362 Compounds of Concern in Hydraulic Fracturing Fluids Based on Their Mobility and Persistence
363 in Groundwater, *Environmental Science & Technology Letters*, 2015, **2**, 158-164.
- 364 21. C. Huang, B. Jin, M. Han, Y. Yu, G. Zhang and H. P. H. Arp, The distribution of persistent, mobile
365 and toxic (PMT) pharmaceuticals and personal care products monitored across Chinese water
366 resources, *Journal of Hazardous Materials Letters*, 2021, **2**, 100026.
- 367 22. S. E. Hale, H. P. H. Arp, I. Schliebner and M. Neumann, Persistent, mobile and toxic (PMT) and

- 368 very persistent and very mobile (vPvM) substances pose an equivalent level of concern to
369 persistent, bioaccumulative and toxic (PBT) and very persistent and very bioaccumulative (vPvB)
370 substances under REACH, *Environmental Sciences Europe*, 2020, **32**, 155.
- 371 23. B. Jin, C. Huang, Y. Yu, G. Zhang and H. P. H. Arp, The Need to Adopt an International PMT
372 Strategy to Protect Drinking Water Resources, *Environmental Science & Technology*, 2020, **54**,
373 11651-11653.
- 374 24. C. B. Hill, O. P. Yadav and E. Khan, Hydraulic Fracturing Chemical Disclosure Policy and Data
375 Analysis: Metrics and Trends in Transparency, *Environ Sci Technol*, 2021, **55**, 3918-3928.
- 376 25. Z. Zheng, G. M. Peters, H. P. H. Arp and P. L. Andersson, Combining in Silico Tools with
377 Multicriteria Analysis for Alternatives Assessment of Hazardous Chemicals: A Case Study of
378 Decabromodiphenyl Ether Alternatives, *Environmental Science & Technology*, 2019, **53**, 6341-
379 6351.
- 380 26. B. C. McAdams, K. E. Carter, J. Blotevogel, T. Borch and J. A. Hakala, In situ transformation of
381 hydraulic fracturing surfactants from well injection to produced water, *Environmental Science:
382 Processes & Impacts*, 2019, **21**, 1777-1786.
- 383 27. K. Hoelzer, A. J. Sumner, O. Karatum, R. K. Nelson, B. D. Drollette, M. P. O'Connor, E. L. D'Ambro,
384 G. J. Getzinger, P. L. Ferguson, C. M. Reddy, M. Elsner and D. L. Plata, Indications of
385 Transformation Products from Hydraulic Fracturing Additives in Shale-Gas Wastewater, *Environ
386 Sci Technol*, 2016, **50**, 8036-8048.
- 387 28. A. J. Sumner and D. L. Plata, Halogenation Chemistry of Hydraulic Fracturing Additives under
388 Highly Saline Simulated Subsurface Conditions, *Environ Sci Technol*, 2018, **52**, 9097-9107.
- 389 29. A. J. Sumner and D. L. Plata, Oxidative Breakers Can Stimulate Halogenation and Competitive
390 Oxidation in Guar-Gelled Hydraulic Fracturing Fluids, *Environ Sci Technol*, 2019, **53**, 8216-8226.
- 391 30. A. J. Sumner and D. L. Plata, Exploring the hydraulic fracturing parameter space: a novel high-
392 pressure, high-throughput reactor system for investigating subsurface chemical
393 transformations, *Environ Sci Process Impacts*, 2018, **20**, 318-331.
- 394 31. G. A. Kahrilas, J. Blotevogel, E. R. Corrin and T. Borch, Downhole Transformation of the
395 Hydraulic Fracturing Fluid Biocide Glutaraldehyde: Implications for Flowback and Produced
396 Water Quality, *Environ Sci Technol*, 2016, **50**, 11414-11423.
- 397 32. D. Liu, J. Li, C. Zou, H. Cui, Y. Ni, J. Liu, W. Wu, L. Zhang, R. Coyte, A. Kondash and A. Vengosh,
398 Recycling flowback water for hydraulic fracturing in Sichuan Basin, China: Implications for gas
399 production, water footprint, and water quality of regenerated flowback water, *Fuel*, 2020, **272**.
- 400 33. J. M. Estrada and R. Bhamidimarri, A review of the issues and treatment options for wastewater
401 from shale gas extraction by hydraulic fracturing, *Fuel*, 2016, **182**, 292-303.
- 402 34. J. Rosenblum, E. M. Thurman, I. Ferrer, G. Aiken and K. G. Linden, Organic Chemical
403 Characterization and Mass Balance of a Hydraulically Fractured Well: From Fracturing Fluid to
404 Produced Water over 405 Days, *Environmental Science & Technology*, 2017, **51**, 14006-14015.
- 405 35. Z. Y. Zhang, X. W. Du, K. H. Carlson, C. A. Robbins and T. Z. Tong, Effective treatment of shale oil
406 and gas produced water by membrane distillation coupled with precipitative softening and
407 walnut shell filtration, *Desalination*, 2019, **454**, 82-90.
- 408 36. A. Butkovskiy, A. H. Faber, Y. Wang, K. Grolle, R. Hofman-Caris, H. Bruning, A. P. Van Wezel and
409 H. H. M. Rijnaarts, Removal of organic compounds from shale gas flowback water, *Water
410 Research*, 2018, **138**, 47-55.
- 411 37. H. Zhang, Z. K. Xiong, F. Z. Ji, B. Lai and P. Yang, Pretreatment of shale gas drilling flowback fluid

412 (SGDF) by the microscale Fe-0/persulfate/O-3 process (mFe(0)/PS/O-3), *Chemosphere*, 2017,
413 **176**, 192-201.

414 38. W. M. Chen, Z. Y. Luo, C. W. Wu, P. Wen and Q. B. Li, Oxidative removal of recalcitrant organics
415 in shale gas flowback fluid by the microwave-activated persulfate process, *Environmental*
416 *Science and Pollution Research*, 2019, **26**, 684-693.

417 39. H. Chang, T. Li, B. Liu, R. D. Vidic, M. Elimelech and J. C. Crittenden, Potential and implemented
418 membrane-based technologies for the treatment and reuse of flowback and produced water
419 from shale gas and oil plays: A review, *Desalination*, 2019, **455**, 34-57.

420 40. E. W. Tow, M. S. Ersan, S. Kum, T. Lee, T. F. Speth, C. Owen, C. Bellona, M. N. Nadagouda, A. M.
421 Mikelonis, P. Westerhoff, C. Mysore, V. S. Frenkel, V. deSilva, W. S. Walker, A. K. Safulko and D.
422 A. Ladner, Managing and treating per- and polyfluoroalkyl substances (PFAS) in membrane
423 concentrates, *AWWA Water Sci*, 2021, **3**, 1-23.

424 41. M. A. Al-Kaabi, N. Zouari, D. A. Da'na and M. A. Al-Ghouthi, Adsorptive batch and biological
425 treatments of produced water: Recent progresses, challenges, and potentials, *J Environ*
426 *Manage*, 2021, **290**, 112527.

427 42. A. Butkovskiy, H. Bruning, S. A. E. Kools, H. H. M. Rijnaarts and A. P. Van Wezel, Organic
428 Pollutants in Shale Gas Flowback and Produced Waters: Identification, Potential Ecological
429 Impact, and Implications for Treatment Strategies, *Environ Sci Technol*, 2017, **51**, 4740-4754.

430 43. Y. H. Liu, P. Tang, Y. M. Zhu, W. C. Xie, P. Yang, Z. H. Zhang and B. C. Liu, Green aerogel adsorbent
431 for removal of organic compounds in shale gas wastewater: High-performance tuning and
432 adsorption mechanism, *Chemical Engineering Journal*, 2021, **416**.

433 44. M. Coha, G. Farinelli, A. Tiraferri, M. Minella and D. Vione, Advanced oxidation processes in the
434 removal of organic substances from produced water: Potential, configurations, and research
435 needs, *Chemical Engineering Journal*, 2021, **414**.

436 45. P. Tang, B. C. Liu, Y. L. Zhang, H. Q. Chang, P. Zhou, M. B. Feng and V. K. Sharma, Sustainable
437 reuse of shale gas wastewater by pre-ozonation with ultrafiltration-reverse osmosis, *Chemical*
438 *Engineering Journal*, 2020, **392**.

439 46. P. Tang, W. C. Xie, A. Tiraferri, Y. L. Zhang, J. Zhu, J. Li, D. Lin, J. C. Crittenden and B. C. Liu,
440 Organics removal from shale gas wastewater by pre-oxidation combined with biologically
441 active filtration, *Water Research*, 2021, **196**.

442