



**In-Situ Transformation of Hydraulic Fracturing Surfactants
from Well Injection to Produced Water**

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In-Situ Transformation of Hydraulic Fracturing Surfactants from Well Injection to Produced Water

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Borch^{d,e,f}, and J. Alexandra Hakala^{a,*}

Environmental Significance Statement

Hydraulic fracturing fluid (HFF) has been formulated through decades of conventional sandstone and carbonate oil and gas production and may not respond similarly in unconventional shale plays. Laboratory and field studies are required to understand how these compounds might respond to these newly accessible reservoir conditions. We observed *in-situ* transformation of HFF surfactants from injected HFF to produced water and over the course of production with implications for produced water treatment and reuse, HFF environmental tracers, and well productivity. The observed subsurface transformations illustrate the need for more investigations into the effects of mineralogy, subsurface chemistry, and microbial processes across various substrates (e.g. Fayetteville, Bakken, Marcellus, Utica shales) on the downhole fate of HFFs and their transformation mechanisms.

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Abstract

Chemical changes to hydraulic fracturing fluids (HFFs) within fractured
unconventional reservoirs may affect hydrocarbon recovery and, in turn, the
environmental impact of unconventional oil and gas development. Ethoxylated alcohol
surfactants, which include alkyl ethoxylates (AEOs) and polyethylene glycols (PEGs), are
often present in HFF as solvents, non-emulsifiers, and corrosion inhibitors. We present
detailed analysis of polyethoxylates in HFF at the time of injection into three
hydraulically-fractured Marcellus Shale wells and in the produced water returning to
the surface. Despite the addition of AEOs to the injection fluid during almost all stages,
they were rarely detected in the produced water. Conversely, while PEGs were nearly
absent in the injection fluid, they were the dominant constituents in the produced

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3 28 water. Similar numbers of ethoxylate units support downhole transformation of AEOs to
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5 29 PEGs through central cleavage of the ethoxylate chain from the alkyl group. We also
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7 30 observed a decrease in the average ethoxylate (EO) number of the PEG-EOs in the
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9 31 produced water over time, consistent with biodegradation during production. Our
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11 32 results elucidate an overlooked surfactant transformation pathway that may affect the
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14 33 efficacy of HFF to maximize oil and gas recovery from unconventional shale reservoirs.
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18 34 Keywords: Hydraulic Fracturing Fluid, Produced Water, Surfactant Transformation,
19 35 Marcellus Shale
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24 36 **Introduction**

27 37 Unconventional oil and gas production from shale source rock involves injecting
28
29 38 millions of liters of hydraulic fracturing fluid (HFF) at high pressures to stimulate oil and
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31 39 gas extraction from the shale by creating fractures that enhance permeability.^{1,2} Mixtures
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33 40 of HFF consist primarily of water and proppant with additives such as surfactants, biocides,
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35 41 and scale and corrosion inhibitors meant to aid in fracture development, oil and gas
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37 42 production, and extend the lifetime of the well.^{2,3} Ethoxylated alcohols, e.g. polyethylene
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39 43 glycols (PEGs) and alkyl ethoxylates (AEOs), are commonly added as solvents, scale
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41 44 inhibitors, and non-emulsifiers, and are included in mixtures of acid corrosion inhibitors
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43 45 and biocides.³⁻⁶ Both AEOs and PEGs have been detected previously as components of
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45 46 injected fracturing fluids, flowback waters, and produced waters associated with
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47 47 hydraulically-fractured oil and gas reservoirs.^{5,7,8}
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52 48 Common HFF constituents may be used to identify contamination from oil and gas
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54 49 production in public water supplies and natural aquatic environments.^{5-7,9-11} Ethoxylated
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3 50 surfactants have been suggested as tracers to monitor impacts of oil and gas operations in
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5 51 both waters¹² and sediments.¹³ However, a greater understanding of changes in fluid
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7 52 composition from injection through flowback and production is necessary to know which
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9 53 compounds will be applicable for environmental monitoring and to inform HFF wastewater
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11 54 treatment.¹⁴ Furthermore, changes in fluid composition between injection and
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13 55 flowback/production^{8, 15, 16} can indicate sorption to or reaction with the wellbore and
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15 56 reservoir,¹⁷⁻²⁰ including biologically and mineral surface-mediated reactions,^{15, 21-23} which
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17 57 may impact unconventional reservoir productivity.

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22 58 During shut-in, reactions that affect mineral surface wettability, e.g. modification of
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24 59 surfactant structures,²⁴⁻²⁹ may affect long-term hydrocarbon production from the fractured
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26 60 reservoir.^{24, 27, 30-35} In addition, the degradation potential of HFF compounds at earth
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28 61 surface conditions has been illustrated in the context of groundwater and agricultural field
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30 62 contamination,^{4, 21, 23, 36-38} including the potential to form unintended byproducts such as
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32 63 acetone.³⁹ Sequential loss of ethoxylate (EO) groups from AEOs, PEGs, and nonylphenol
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34 64 ethoxylates to generate species with a lower EO number has been widely reported,
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36 65 including in HFF degradation studies.^{23, 40, 41} However, because central cleavage of the
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38 66 ethylene oxide (EO) substituents from the alkyl chain to form PEGs has only been shown to
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40 67 occur under aerobic conditions,⁴¹⁻⁴⁴ this mechanism has largely been overlooked for HFF as
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42 68 shale reservoirs naturally exist under anoxic conditions.⁴⁵ Further, while adsorption has
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44 69 been shown to be important for AEO removal in laboratory microcosms,^{23, 38} the ability of
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46 70 dark Fenton processes to generate oxidative radicals that can degrade high molecular
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48 71 weight surfactants has only recently been elucidated in the context of subsurface oil and
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50 72 gas reservoirs.⁴⁶ Still, a better understanding of subsurface surfactant transformation will
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3 73 inform produced water treatment and reuse and provide knowledge on the effects of
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5 74 injected surfactants on shale properties related to well productivity such as mineral surface
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8 75 wettability. Increased hydrocarbon recovery from individual wells lessens the
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10 76 environmental impact of unconventional oil and gas development⁴⁷ by decreasing the
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12 77 amount of land⁴⁸⁻⁵⁰ and water⁵¹⁻⁵³ used per unit of oil and gas produced, and also favors the
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15 78 economics of shale gas development.

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17 79 Deep shale formations typically exist under reducing conditions, as has been
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19 80 illustrated for the Marcellus Shale.⁴⁵ However, recent laboratory-based studies focused on
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21 81 HFF-Marcellus Shale interactions showed that mixed redox conditions may exist in
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23 82 fractured shales upon introduction of HFF.¹⁷⁻¹⁹ Though reconstruction of metabolic
24
25 83 pathways^{22, 54-56} and genomic evidence^{15, 57-59} reveal the importance of alternative terminal
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27 84 electron acceptors and viral predation in microbial community dynamics, there exists a
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29 85 need to better characterize biogeochemical reactions in hydraulically-fractured shales that
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31 86 can transform injected HFF components. A prior study of the Niobrara formation reported
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33 87 a loss of AEOs from the injection fluid but could not follow transformation of AEOs to PEGs
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35 88 as PEGs were also present in the injected HFF.⁸

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40 89 The objective of our study was to improve our understanding of *in-situ*
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42 90 transformation of substituted ethoxylates in the injection water from individual fracturing
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44 91 stages based on a detailed characterization of produced water from multiple wells in the
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46 92 same lithology. Due to the absence of PEGs in the injected fluid, our data provide new
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48 93 insights into the downhole *transformation* of AEOs to PEGs that can occur in hydraulically
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50 94 fractured unconventional reservoirs and bear general implications for hydrocarbon
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53 95 production and produced water quality.
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Experimental

Field Sample Collection and Processing

Samples were collected from three hydraulically fractured horizontal wells in southwestern Pennsylvania in June, 2012. The target formation was the Marcellus Shale with a depth of 2500 meters, reservoir temperature between 55°C and 75°C, and pressure between 240 and 280 psi. Details on fracturing stages and produced water can be found in the supporting information. Fracfocus.org information showed that PEGs were only present as an additive in the biocide mixture used (Table S1). Because of the proprietary nature of these chemical mixtures, the fracfocus.org data may be incomplete. Acknowledging the limits of this dataset, fracfocus.org was used *only* to identify from which disclosed mixtures the targeted surfactants may have originated and was *not* used to characterize injected HFF or produced water. The presence of chemicals in and the characterization of injected HFF and produced waters was *solely* based on mass spectrometry analysis of actual samples. Samples were collected in 1 L HDPE Nalgene bottles and transferred back to the laboratory for analysis. A 40 mL aliquot was transferred into a pre-cleaned amber vial and acidified with a 6 N HCl stock solution (Fisher Chemical, Fairlawn, NJ, USA) to drop the pH between 2.5 and 3.0. This acidification step was performed on both injected HFF and produced water samples, and thus did not result in acid-catalyzed transformation of AEOs that would alter our interpretation of the results. The samples were refrigerated at 4°C until the organic compounds could be extracted from the sample (no more than 24 hours).

Organic compounds were extracted using solid phase extraction SEP Pak C-18 cartridges (P/N WAT051910, Waters Corporation, Milford, MA, USA) to remove salts. Each

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3 119 cartridge had 360 mg of Silica-based C-18 sorbent with a particle size ranging from 55 to
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5 120 105 μm . The columns were attached to 10 mL syringes, conditioned with 6 mL of Optima
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8 121 LC/MS grade acetonitrile (Fisher Chemical, Fairlawn, NJ, USA), and rinsed with 6 mL of
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10 122 Optima LC/MS grade water (Fisher Chemical, Fairlawn, NJ, USA). After rinsing the columns,
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12 123 6 mL of solution were loaded onto the columns, rinsed with 6 mL of LC/MS grade water
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15 124 and eluted off the column using 6 mL of LC/MS grade acetonitrile. The eluent was collected
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17 125 in a 20 mL borosilicate scintillation vial with a urea cap containing a poly seal cone liner
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20 126 and refrigerated for no more than 24 hours prior to analysis. Samples were removed from
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22 127 the refrigerator, allowed to equilibrate at room temperature for one hour, then transferred
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24 128 to 2 mL glass vials using borosilicate pipettes prior to accurate mass analysis by
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27 129 quadrupole time-of flight-mass spectrometry (QTOF-MS).
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30 **Accurate Mass Analysis**

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33 131 Accurate mass analysis was performed using an Infinity 1290 Liquid
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35 132 Chromatography System (LC) coupled with a 6520B QTOF-MS from Agilent Technologies
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37 133 (Santa Clara, CA, USA) equipped with electrospray Jet Stream Technology operating in
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40 134 positive ion mode operating under the following parameters: capillary voltage: 3500 V;
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42 135 nebulizer pressure: 30 psig; drying gas: 12 L/min; drying gas temperature: 325 $^{\circ}\text{C}$;
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44 136 fragmentor voltage: 80 V (injected HFF) and 100 V (produced water); skimmer voltage: 65
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47 137 V; octopole RF: 750 V. Mass spectra were recorded across a mass range of 100 to 800 m/z
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49 138 at 2 GHz and processed with Agilent MassHunter software. Samples were injected into the
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51 139 QTOF-MS without column separation using an infusion method, which by-passed the LC
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54 140 column by replacing it with an inert fitting. Direct injection likely did not influence our
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3 141 results through ion suppression or preferential ionization as we observed PEGs and AEOs
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5 142 together in multiple samples. In addition, we performed analyses on a serial dilution of a
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8 143 PEG/AEO mixture that illustrated no preferential ionization of PEGs over AEOs that would
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10 144 impact our interpretation of the results (Figure S1). Quantification of any ion suppression
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12 145 of AEOs by PEGs is not possible at this point as a full suite of commercially available
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14 146 standards for quantifying PEGs and AEOs is unavailable. A 50:50 by volume solution of
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17 147 LC/MS grade acetonitrile and LC/MS grade water was used to carry the infused samples to
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20 148 the QTOF-MS. Quantification of compounds could not be performed as commercial
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22 149 standards for every identified compound were unavailable at the time of analysis.¹² As a
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24 150 result, a mass balance of AEOs and PEGs could not be calculated because of potential
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27 151 differences in ESI ionization efficiency between AEOs and PEGs, but relative abundance
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29 152 could be semi-quantitatively determined from MS counts for each compound.
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33 153 **Results and Discussion**

34 35 36 154 **Hydraulic Fracturing Fluid and Produced Water Chemistry**

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38 155 The QTOF-MS spectra of hydraulic fracturing fluids (HFFs) and produced waters
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40 156 showed an array of analytes with an average $\Delta m/z$ of 44.026 (Figure S3) difference,
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42 157 indicative of compounds that differ by one EO unit (C_2H_4O), such as ethoxylated
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44 158 surfactants.⁶⁰⁻⁶³ These ethoxylated compounds can be separated by their Kendrick mass
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47 159 defect⁶⁴ (KMD, calculated using an ethoxylate correction factor of 44/44.0262) into distinct
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50 160 groups with masses and KMDs that match previous observations of C_{12} and C_{14} AEOs and
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52 161 PEGs (Tables S2–S5).^{5,6} By using KMDs and matching our spectra to previously published
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3 162 literature where AEOs and PEGs have been putatively identified,^{5,6} we are confident in our
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5 163 assignment of AEO and PEG formulas to these spectra.

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8 164 For the most part, AEOs were the dominant compounds detected in all sampled
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10 165 fracturing stages with the exception of well 2 stages 7, 8, and 11 (Figures 1, S2). Alkyl
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12 166 ethoxylates were present in the friction reducer and corrosion inhibitor used to fracture
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14 167 the three wells studied, whereas polyethylene glycols were present only in the biocide
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16 168 (Table S1). Because PEGs were only present in the biocide mixture disclosed to
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18 169 fracfocus.org and AEOs were only present in the friction reducer and corrosion inhibitor
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20 170 disclosed (Table S1), we were able to infer the additives used in each fracturing stage by
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22 171 the presence or absence of AEOs and PEGs. For instance, the presence of AEOs in nearly all
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24 172 stages indicate that friction reducer and corrosion inhibitor were used in nearly all
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26 173 fracturing stages. However, for well 2, stages 8 and 11, the presence of PEGs and the
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28 174 absence of AEOs allows us to infer that biocide was likely used in the absence of friction
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30 175 reducer and corrosion inhibitor. In fact, except for well 2, stage 7 and well 3, stage 4—
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32 176 where both PEGs and AEOs were present—the mass spectra suggest that, when corrosion
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34 177 inhibitor and/or friction reducer was used (i.e., AEOs were present), little or no biocide was
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36 178 included (i.e., PEGs were not present).

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39 179 Conversely to what was found in the injected HFF, mass spectra of produced water
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41 180 showed almost no contribution from AEOs, but a constant presence of PEGs (Figures 1, S2,
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43 181 S3; Tables S2, S6–S8). In fact, AEOs were found in only one early produced water sample
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45 182 (well 2, 279 BBL), where their signal was less than 5% of the total signal. Comparison of
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47 183 PEG counts to chloride chemistry (Figure S5) shows that, while mixing with the reservoir
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49 184 brine occurs,⁶⁵ this mixing did not dilute the PEG compounds in the produced water. Thus,
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3 185 changes in the AEO and PEG chemistry from injection to production were not related to
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5 186 mixing with or dilution by the reservoir brine.
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9 187 **Fate of Hydraulic Fracturing Fluid Surfactants**

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11 188 Adsorption of AEOs has been suggested as a removal mechanism in activated
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14 189 sludge⁶⁶ and laboratory microcosms,²³ especially of longer alkyl-chained AEOs, and may be
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16 190 expected given the strong hydrophobicity of the alkyl group.⁶⁷ However, the appearance of
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18 191 PEGs in the produced water mass spectra suggests transformation of AEOs to PEGs as an
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21 192 important removal pathway. This pathway is best supported by comparing the absence of
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23 193 PEGs in the injection HFF mass spectra of Well 1 to the absence of AEOs and accompanying
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25 194 appearance of PEGs in the produced water mass spectra of Well 1 (Figures 1, S2). In
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28 195 addition, the EO number distribution of the PEGs found in the produced water was similar
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30 196 to the EO number distribution of the AEOs found in the injected HFF for all wells (Figures 1,
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32 197 S2), consistent with transformation by cleavage of the alkyl group from the polyethoxylated
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35 198 chain.^{41, 42, 44, 68}
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37 199 Central cleavage of AEOs can occur through acid-catalyzed hydrolysis,⁶⁸ and the
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40 200 fracfocus.org reports (summarized in Table S1) indicate that HCl may have been used
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42 201 during the fracturing of these wells. However, the fracfocus.org data is notably incomplete
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44 202 as discussed in the methods, and the *reported* use of HCl to fracfocus.org does not equate to
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46 203 the *actual* use of HCl. Further, we did not observe any acid-catalyzed hydrolysis in the
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49 204 injected fluid spectra after acidification with HCl in the field to a pH roughly equal to where
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51 205 the acid slug would drop the HFF (~2.5-3 as supported by the ~0.6-0.9% HCl
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54 206 concentration, Table S1). Therefore, it is unlikely that acid hydrolysis played a large role in
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3 207 our observed transformation of AEOs to PEGs. Mineral surface-catalyzed hydrolysis (Figure
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5 208 2c) of ester bonds in organic pollutants has been illustrated^{69,70} and may have played some
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8 209 role in the patterns we observed. Radical oxygen species from Fenton reactions with
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10 210 molecular oxygen may also play a role as they have been shown to cause central scission of
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12 211 polyacrylamides under reservoir pressures and temperatures (Figure 2a).⁴⁶ Central
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14 212 cleavage is also a well-documented aerobic biodegradation pathway for AEOs, thought to
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16 213 occur only with molecular oxygen as the terminal electron acceptor (Figure 2b).^{41,42,44}
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18 214 Whereas anaerobic biodegradation of AEOs more commonly results in terminal ethoxylate
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20 215 cleavage as a result of fermentation⁴⁰ and would not result in the formation of PEGs with
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22 216 similar EO numbers as observed in our samples.

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26 217 Though the Marcellus shale naturally exists under reducing conditions,⁴⁵ complex
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28 218 redox gradients and iron oxidation in the presence of HFF have been observed,^{17,18}
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30 219 suggesting aerobic conditions or oxidants may have been introduced into the subsurface
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32 220 with the HFF. Given the illustrated oxidative nature of HFF,^{18,19} and that HFF is mixed at
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34 221 the surface under atmospheric conditions, i.e. oxic, initial injection of HFF may have carried
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36 222 the molecular oxygen necessary for central cleavage of the AEOs by aerobic biodegradation
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38 223 or radical oxygen species. In addition, aerobic microbial communities have been observed
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40 224 in injected HFF and early produced water,^{15,22} supporting the possibility of aerobic
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42 225 biodegradation immediately following HFF injection in the subsurface. Our data also
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44 226 suggest that, surprisingly, biocides and AEOs were only injected together in well 2, stage 7
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46 227 (Table S1), indicating that, in all other stages where AEOs were present, microbial activity
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48 228 would not have been affected by biocides. Further, previous studies suggest any biocides
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50 229 used would have little effect on the microbial communities downhole.^{22,56,59,71} We did not
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3 230 observe any specific degradation products (e.g., carboxylated or formate ethoxylates) or
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6 231 residual alcohols in positive or negative ESI mass spectra. Still, we propose central cleavage
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8 232 by aerobic biodegradation or radical oxygen species (Figure 2a,b) as the most likely
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10 233 mechanisms responsible for the observed transformations of AEOs to PEGs from the
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12 234 injected HFF to the produced water.

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15 235 We also observed a decrease in the EO number of the PEGs in the produced water
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17 236 over time (Figure 3). Hydroxyl radicals have been shown to reduce the EO number of
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19 237 polyethoxylated phenols in oxic conditions (Figure 2d).⁷² A decrease in EO number of
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21 238 polyethoxylates has also been observed during aerobic biodegradation from chain
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23 239 shortening of higher molecular weight PEGs.^{73,74} Conversely, a more recent study showed
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25 240 preferential consumption of lower EO number PEGs in aerobic microcosms of HFF leading
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27 241 to increased relative abundance of longer chained PEGs over time.³⁷ Because anaerobic
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29 242 biodegradation likewise leads to sequential chain shortening of polyethoxylates,^{40,75} we
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31 243 cannot definitively state that the observed chain shortening occurred aerobically or
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33 244 anaerobically. However, downhole environments shift to more reducing^{18,19} and
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35 245 anaerobic^{15,22} conditions over time, including the use of alternative electron acceptors⁵⁵⁻⁵⁷
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37 246 and the degradation of higher molecular weight surfactants.⁷⁶ Therefore, we submit that
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39 247 anaerobic biodegradation is the most likely cause of the PEG chain shortening observed
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41 248 (Figure 2e) but cannot rule out aerobic biodegradation without further targeted
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43 249 experimentation.
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250 **Environmental Significance**

251 The observed subsurface transformation of AEOs to PEGs illustrates the need for
252 more investigations into the effects of mineralogy, subsurface chemistry, and microbial
253 processes across various substrates (e.g. Fayetteville, Bakken, Marcellus, Utica shales) on
254 the downhole fate of HFFs. For instance, others have observed AEOs in produced water
255 from the Denver-Julesburg Basin, and suggest those compounds as a tracer for HFF
256 contamination.⁵ However, our data suggest AEOs would not be useful as a tracer for HFF
257 contamination from Marcellus wells as they may be transformed to PEGs during the shut-in
258 period. Downhole transformation of HFF components also has environmental implications
259 for water treatment and reuse as well as fate, toxicity, and transport of components in
260 hydraulic fracturing wastewaters and spills. Because AEOs are more hydrophobic than
261 PEGs, AEOs may be more easily removed during water treatment via adsorption methods
262 such as activated carbon, whereas PEGs are more susceptible to biodegradation.⁷⁷ Cleavage
263 of the EO group from substituted ethoxylates may also have adverse health implications for
264 other ethoxylated compounds that have been associated with unconventional oil and gas
265 development, such as nonylphenol ethoxylates,¹³ which would be transformed to more
266 toxic and endocrine disrupting nonylphenols,⁷⁸ affecting the ability to reuse produced
267 water.

268 Unsuspected transformation of HFF surfactants (e.g. AEOs) may also alter the
269 intended efficacy of the HFF fluid, affecting hydrocarbon recovery. Changes in the
270 surfactant chemistry, e.g. from hydrophobic AEOs to hydrophilic PEGs, can alter mineral
271 surface wettability,²⁴⁻²⁹ which directly affects the flow of oil and gas through subsurface
272 fracture networks and, in turn, the long-term productivity of the well.^{39, 42, 45-50} Maintaining

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3 273 the long-term productivity of wells drilled into unconventional reservoirs is necessary to
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5 274 mitigate the environmental impact of unconventional oil and gas production.⁴⁷ Increased
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8 275 recovery factors for leased areas involves lowering the surface footprint to obtain the same
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10 276 amount of oil and gas, decreasing the land⁴⁸⁻⁵⁰ and water⁵¹⁻⁵³ used per unit of oil and gas
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12 277 produced, thereby lessening the environmental disruption of unconventional oil and gas
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15 278 production.

19 279 **Conclusions**

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22 280 We presented a field study illustrating *in-situ* transformation of HFF surfactants
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24 281 from injection to production. Our data indicate that AEOs are likely transformed to PEGs
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26 282 via central cleavage through Fenton generated hydroxyl radical attack or aerobic
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29 283 biodegradation, both processes that require molecular oxygen. While unconventional
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31 284 reservoirs generally exist under reducing conditions, our observations show that molecular
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33 285 oxygen may be present in the injected HFF in high enough concentrations to trigger
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35 286 oxidative reactions in the subsurface. Such reactions, both inorganic and organic, may have
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37 287 consequences for resource extraction from unconventional oil and gas wells. More detailed
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39 288 investigations of individual surfactant homologues under various temperature, pressure,
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41 289 redox, and chemical conditions (e.g. Fe(II) activity) are required to fully understand the
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43 290 surfactant reaction mechanisms and kinetics possible in the subsurface. Such studies
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45 291 should also focus on mineral surface properties such as wettability to understand how
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47 292 these reactions may impact oil and gas extraction.
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293 **Disclaimer**

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15 319 these samples.
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19 320 **Supporting Information**

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22 321 Supporting information includes detailed information on hydraulic fracturing fluid
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24 322 (HFF) components as reported to fracfocus.org, tables of surfactants identified in HFF from
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27 323 all stages of all wells and from all produced water samples from all wells, and
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30 324 representative mass spectra of injected HFF and produced water.
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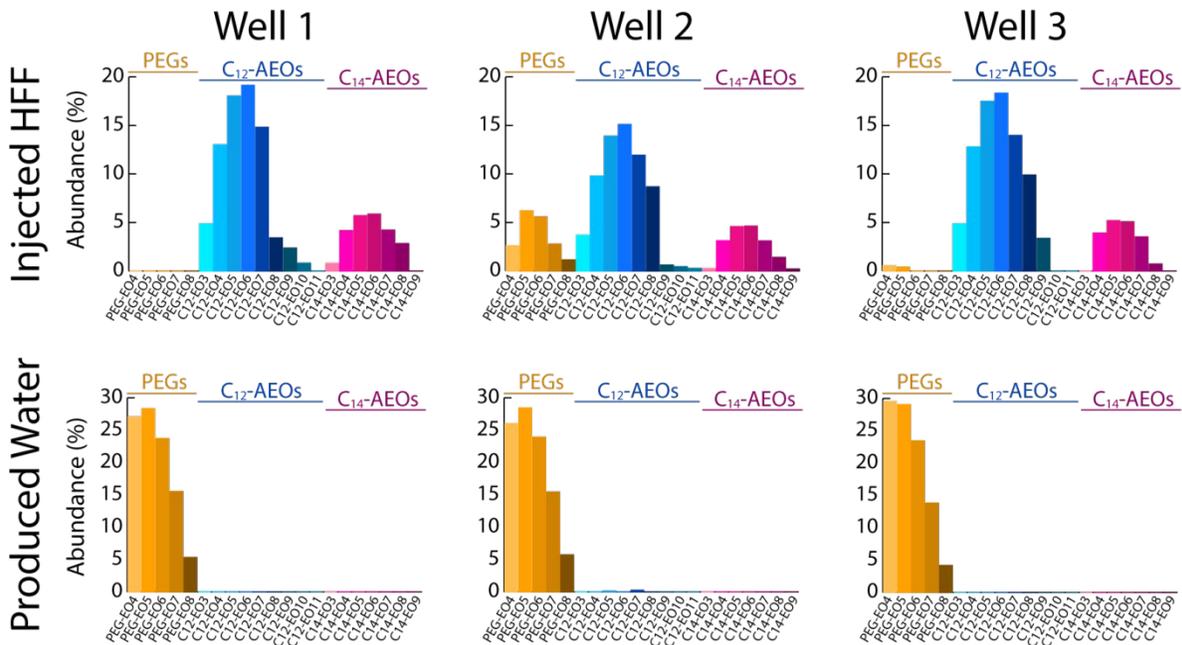
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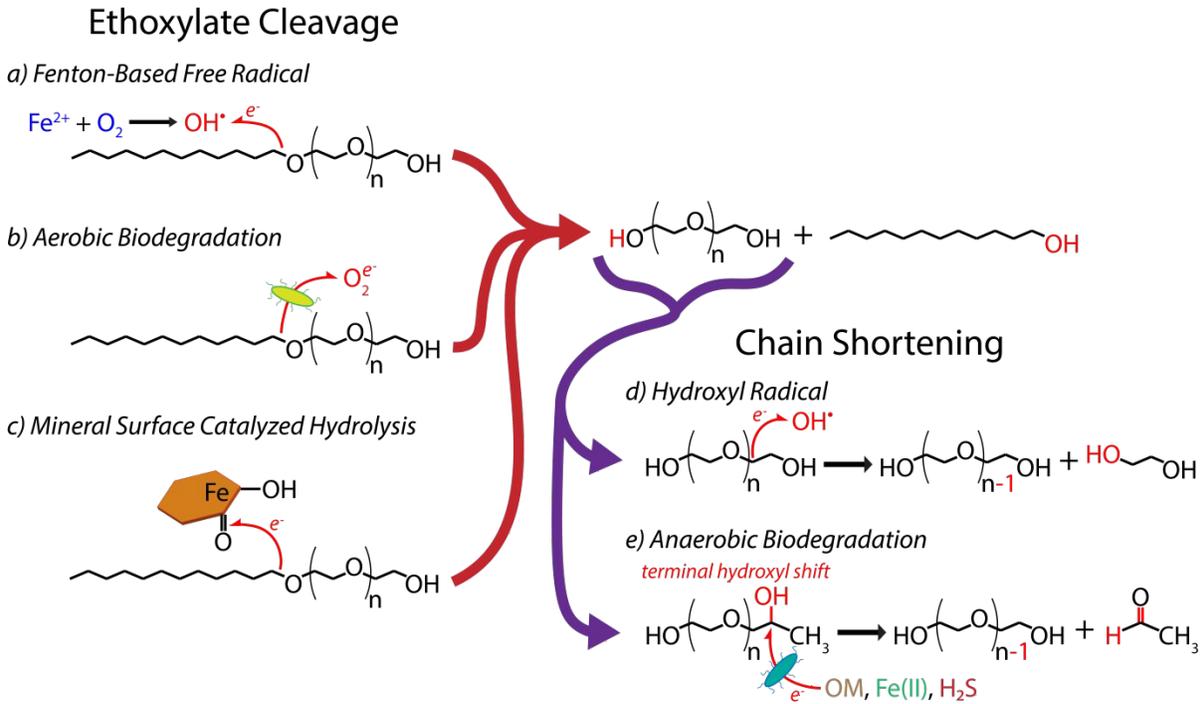
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608
 609 **Figure 1.** Relative abundance (as %) of AEOs (C₁₂-E03 to E011, C₁₄-E03 to E09) and PEGs
 610 (PEG-E04 to E08) for all injected hydraulic fracturing fluid (HFF) and produced water
 611 samples from wells 1, 2, and 3 showing a shift from AEO dominance to PEG dominance
 612 from injection to production. Well 1 in particular illustrates the transformation of AEOs to
 613 PEGs from injection to production given the absence of PEGs in the injected HFF and the
 614 appearance of PEGs in the produced water with the concomitant disappearance of AEOs
 615 from the produced water.



616
617 **Figure 2.** Proposed reaction mechanisms for central ethoxylate cleavage by a) Fenton-
618 based free radical processes as illustrated by Xiong *et al.*⁴⁵, b) aerobic biodegradation as
619 observed in multiple studies,⁴¹⁻⁴⁴ or c) mineral surface catalyzed hydrolysis.^{69,70} Both a)
620 and b) mechanisms require molecular oxygen. All cleavage mechanisms result in
621 polyethylene glycol formation with the same ethoxylate number as the parent alkyl
622 ethoxylate. Also shown are proposed reaction mechanisms for chain shortening by d)
623 hydroxyl radical as observed by Destailats *et al.*⁶⁹ for polyethoxylated phenols or e)
624 anaerobic biodegradation beginning with a terminal hydroxyl shift as observed by multiple
625 studies^{23,40,72} and which may be followed by fermentation of the acetaldehyde to acetate
626 and ethanol.

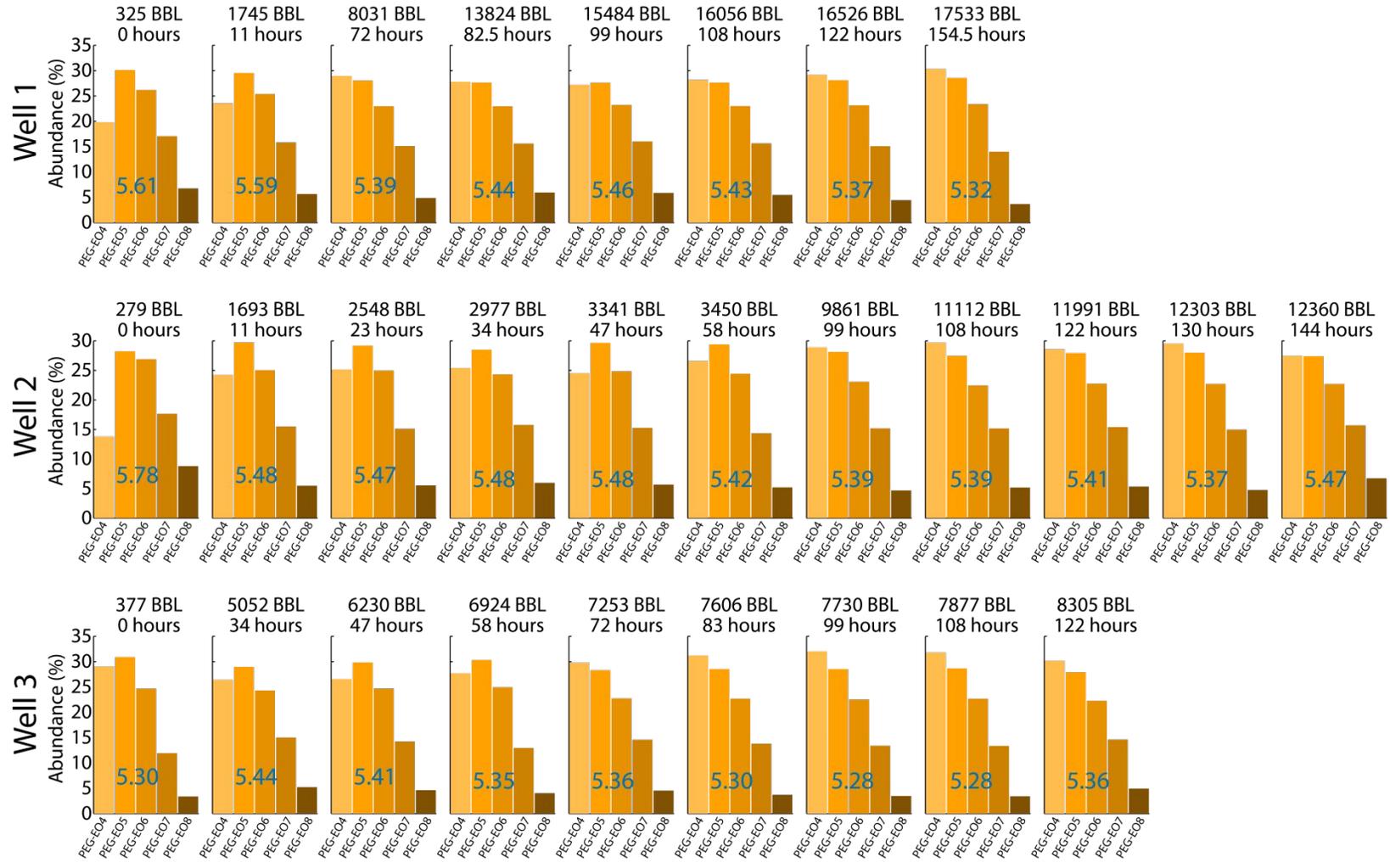
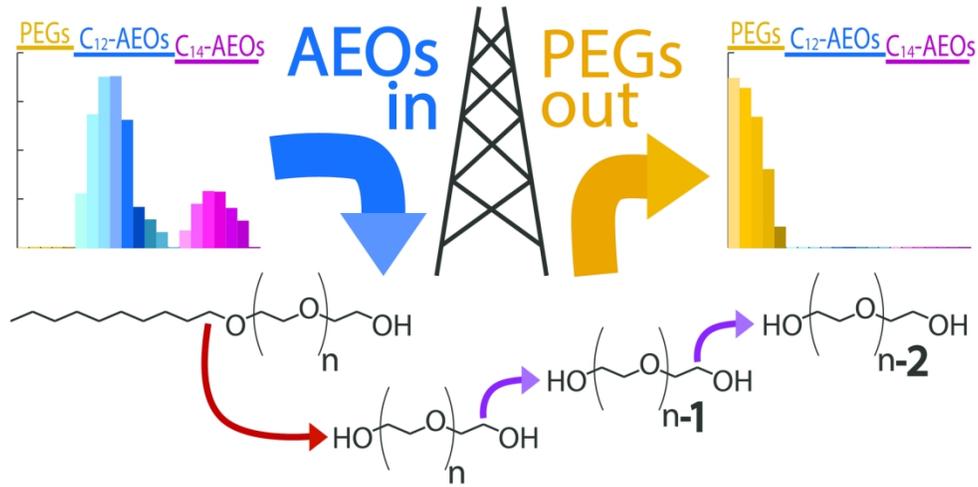


Figure 3. Relative abundance (as %) of PEG-EOs (EO4 to EO8) over the course of production marked by barrels of water (BBL) and time from when the first produced water sample was collected (in hours) showing a shift to lower EO number PEGs over the course of production. Average EO number of PEGs is shown in blue to further illustrate the reduction in PEG-EO number over the course of production



80x40mm (600 x 600 DPI)