



A Framework for Identifying Organic Compounds of Concern in Hydraulic Fracturing Fluids Based on Their Mobility and Persistence in Groundwater

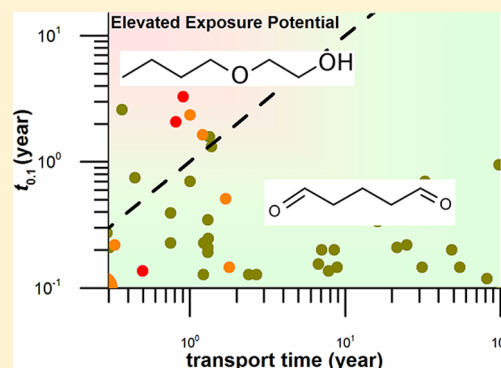
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S Supporting Information

ABSTRACT: We developed a screening framework for identifying organic components of hydraulic fracturing fluid with increased probability of exposure via groundwater based on mobility, persistence, toxicity, and frequency of use. Of 996 organic fracturing fluid compounds identified by the U.S. Environmental Protection Agency and FracFocus for four states, data were available to perform an initial screening of 659 compounds for sufficient mobility and persistence to reach a water well under fast and slow groundwater transport scenarios. For the fast transport scenario, 15 compounds identified on at least 50 FracFocus reports were predicted to have an elevated exposure potential, which was defined as $\geq 10\%$ of the initial concentration remaining at a transport distance of 94 m, the average setback distance in the United States. Of these 15 compounds, two were identified on $>20\%$ of FracFocus reports (naphthalene and 2-butoxyethanol), four were compounds identified on $>5\%$ of reports, and three had health-based standards.



INTRODUCTION

Significant technological advances in horizontal drilling and hydraulic fracturing are allowing extraction of hydrocarbons from low-permeability formations that were previously not developed because of limited recovery.¹ Rapid expansion of the use of these technologies has generated concern about degradation of water quality in aquifers.^{1–5} Fracturing fluids are pumped into the shale formation at high pressures to induce fractures and carry proppants to hold open the fractures and create a flow path for the hydrocarbons to the well. A typical fracturing fluid composition includes $\sim 90\%$ water, $\sim 9\%$ proppants, and $\sim 1\%$ chemical additives, including surfactants, friction reducers, gelling agents, and biocides.^{6,7} Each additive is a mixture of compounds, the types and concentrations of which vary substantially on the basis of basin characteristics as well as operator specifications.⁶

Subsurface pathways that may result in the release of fracturing fluids to aquifers include failure of well integrity, improperly abandoned wells, and existing faults or fractures in geologic formations between the target formations and aquifers.^{1–3,6} The probability of groundwater contamination by these pathways is generally thought to be low.⁸ Surface pathways include spills from the transport, storage, and handling of fracturing fluid additives as well as flowback water from the formation.^{2,3,9} Surface spills and releases are the more likely groundwater contamination pathway.^{2,5,8,10}

Human exposure to a harmful fracturing fluid constituent requires transport to a potential receptor,⁵ and the broad variety of compounds possibly used in fracturing fluids poses a challenge when evaluating transport potential.⁶ Previous studies of potential drinking water contamination by fracturing fluids have focused on characterizing the toxicity of the individual compounds,^{11–14} with consideration of environmental exposure potential for only a limited number of compounds^{9,13,14} and not mixtures.¹⁵ The variety of compounds hinders baseline groundwater monitoring due to analytical limitations of a comprehensive analysis of possible constituents.¹⁶ Effective groundwater monitoring should focus on constituents most likely to be present.¹⁷

Our objectives are (1) to develop a screening framework for identifying fracturing fluid compounds that are sufficiently mobile and persistent to be transported through aquifers by comparing the time for a compound to degrade to a predicted groundwater transport time and (2) to perform an initial screening using available data for 659 compounds. Degradation products and mixture interactions were not considered.

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Table 1. Frequently Used Organic Compounds in Hydraulic Fracturing Fluids and Corresponding Screening Framework Parameters^a

compound	additive purpose ^b	FracFocus frequency (%) ^c	toxicity cat. ^d	K_d (L kg _{sed} ⁻¹) ^e	$t_{1/2}$ (d)	ref ^f
methanol	corrosion inhibitor, surfactant, nonemulsifier, scale inhibitor, biocide, cross-linker	76.5	HAI	1×10^{-3}	1	25
hydrotreated light petroleum distillates	friction reducer, gelling agent, cross-linker	70.0	no HAI	2×10^2	231	28
2-propanol	corrosion inhibitor, nonemulsifier, surfactant	50.1	no HAI	3×10^{-3}	14	26
ethylene glycol	cross-linker, scale inhibitor, corrosion inhibitor, friction reducer	49.7	HAI	2×10^{-4}	24	25
guar gum	gelling agent	45.2	no HAI	3×10^{-1}	0.1	29
ethanol	surfactant, biocide	34.2	no HAI	2×10^{-3}	2	27
glutaraldehyde	biocide	33.3	no HAI	2×10^{-3}	0.3	27
propargyl alcohol	corrosion inhibitor	32.7	HAI	2×10^{-3}	13	27
acetic acid	buffer, iron control	31.7	no HAI	7×10^{-6}	7	28
citric acid	iron control	23.4	no HAI	3×10^{-9}	0.4	28
heavy aromatic petroleum naphtha	surfactant, nonemulsifier, inhibitor, corrosion inhibitor	23.3	no HAI	7×10^{-1}	6	21
2-butoxyethanol	surfactant, corrosion inhibitor, nonemulsifier	22.8	HAI	8×10^{-3}	56	26
naphthalene	surfactant, nonemulsifier, corrosion inhibitor	22.0	HAI	7×10^{-1}	258	25
sorbitan monooleate	friction reducer, biocide, corrosion inhibitor	20.7	no HAI	2×10^{-3}	20	28

^aCompounds were designated frequently used if they were identified on >20% of FracFocus disclosure reports. ^bFunction of additive in which each compound was identified as an ingredient, reported by the EPA.⁵³ FracFocus does not report the specific purpose of each compound within an additive, and a compound may be used as an ingredient in multiple additives.⁵³ ^cPercentage of FracFocus reports identifying use of compound out of 50024 reports acquired for the states of Colorado, North Dakota, Pennsylvania, and Texas. ^dIndicates availability of health assessment information (HAI). No frequently used compounds had health-based standards (MCLs). ^eCalculated according to eq 3. ^fReferences for degradation kinetics data.

METHODS

Compound Sources and Selection. A total of 996 unique organic compounds were identified. Of these, 641 were identified from unique Chemical Abstract Service (CAS) numbers reported on FracFocus Chemical Disclosure Registry reports¹⁸ acquired for Colorado (7772 reports), North Dakota (5662), Pennsylvania (4312), and Texas (32278) as of November 2014. By 2012, all four states required disclosure on FracFocus.¹⁹ Additional compounds were identified from a list compiled by the Environmental Protection Agency (EPA).²⁰ Some compounds were identified on both lists (331); however, 355 were identified only by the EPA. Compounds were not consistently reported on FracFocus until 2011,¹⁸ while the EPA list includes compounds disclosed between 2005 and 2010. Consequently, there are compounds considered in this analysis that operators may no longer use but are of interest with respect to potential legacy contamination. Compounds that are considered proprietary may not be identified by CAS number on the FracFocus reports.¹⁹ Finally, both the EPA list and FracFocus include compounds with no apparent use in fracturing fluids, for instance, due to errors in the reported CAS number. To account for compounds with no indication of current or apparent use in fracturing fluids, compounds were only designated as having an elevated exposure potential if they were predicted to have $\geq 10\%$ of the initial concentration remaining at the setback distance and were identified on ≥ 50 FracFocus reports (0.1% of reports acquired).

Of the 996 compounds, CAS numbers or unique structures could not be identified for 337 compounds (Methods of the Supporting Information); these were classified as “no data” and were not screened, which left 659 organic compounds to be screened. Degradation products of the screened compounds were not considered.

Screening Framework. Compounds were screened by comparing the time to degrade to 10% of the initial

concentration ($t_{0.1}$) against the transport time to a distance of 94 m (t_{94}), the national average required setback distance.¹⁹ The average setback distance represents a horizontal transport distance for a contaminant from an oil and gas well to a domestic well. The framework simulates horizontal transport in an aquifer from a point of release (e.g., a failed well casing, a spill that has migrated through the vadose zone) to a drinking water well. Two transport scenarios were considered: a highly porous aquifer with relatively fast groundwater velocity and a less porous aquifer with slower velocity. Compounds identified on ≥ 50 FracFocus reports and predicted to have $\geq 10\%$ of the initial concentration remaining at the transport distance were predicted to have an elevated exposure probability.

Mobility. The transport time of each compound, t_{94} , was calculated using an average linear groundwater velocity, v_w , as

$$t_{94} = \frac{d_c R}{v_w} \quad (1)$$

where d_c is the setback distance (94 m) and R is the retardation coefficient, calculated as

$$R = 1 + \rho_s \left(\frac{1}{n} - 1 \right) K_d \quad (2)$$

where ρ_s is the density of the aquifer sediment (assumed to be 2.65 kg L⁻¹), n is the porosity, and K_d is the distribution coefficient (liters per kilogram of sediment). The distribution coefficient was estimated to include sorption of the neutral form of the compound to organic matter and sorption of the cationic form of organic bases by ion exchange:

$$K_d = \alpha_n K_{oc} f_{oc} + \alpha_c K_{d,ex} \quad (3)$$

where α_n is the neutral fraction of the organic compound, α_c is the cationic fraction of organic bases, K_{oc} (liters per kilogram of organic carbon) is the organic carbon partition coefficient, $K_{d,ex}$ (liters per kilogram of sediment) is the ion exchange coefficient, and f_{oc} is the fraction of organic carbon of the sediment

(assumed to be $0.001 \text{ kg}_{\text{oc}} \text{ kg}_{\text{sed}}^{-1}$). The K_{oc} of each compound was estimated by the EPA's widely used Estimation Program Interface (EPI) Suite program.²¹ We estimated $K_{\text{d,ex}}$ for 83 bases that were $\geq 10\%$ ionized at pH 7 assuming a low cation exchange capacity consistent with an alluvial sediment allowing fast transport (Methods of the Supporting Information). Ion exchange was considered negligible for ionized organic acids because the anion exchange capacity of typical alluvial aquifer sediments is relatively low.^{22,23}

The transport time was calculated for scenarios of fast (v_w of 1 m day^{-1}) and slow (v_w of 0.01 m day^{-1}) groundwater flow. The fast transport scenario is consistent with velocities reported for alluvial deposits.²⁴

Persistence. Persistence was evaluated using a "tenth-life", $t_{0.1}$, which was calculated from a compound's half-life ($t_{1/2}$) as

$$t_{0.1} = t_{1/2} \left[\frac{\ln(0.1)}{\ln(0.5)} \right] \quad (4)$$

For 312 compounds, biodegradation and hydrolysis half-lives were determined from published experimental data.^{21,25–35} When available, degradation kinetics in groundwater attenuation studies or anaerobic environments were chosen over aerobic kinetics to better represent likely conditions in a groundwater contaminant plume. For the other 347 compounds, experimental degradation data were not available. These compounds were screened using an estimated time required for complete primary biodegradation in an aerobic aquatic environment predicted by BIOWIN 4, which calculated a rating corresponding to an expected degradation time range (Table S2 of the Supporting Information).^{21,36} Half-lives assigned to the BIOWIN-predicted time range intervals³⁷ were used to adjust the predictions to an estimated $t_{0.1}$ (Methods of the Supporting Information).

Toxicity. Compounds were evaluated for potential toxicity using National Primary Drinking Water Regulations (NPDWR)³⁸ and health assessment information, including oral reference doses, inhalation reference concentrations, and carcinogenic risk slope factors published by the EPA Integrated Risk Information System (IRIS).³⁹ Three categories were defined: 14 compounds had a maximum contaminant level (MCL) that could be enforced under NPDWR, 53 compounds had published health assessment information (e.g., reference doses) but no MCL, and 592 compounds had no MCL and no health assessment information.

Frequency of Use. The frequency of use was assessed by counting the number of FracFocus reports on which a compound's CAS number appeared. Table 1 summarizes the screening parameters for 14 frequently used compounds identified on $>20\%$ of FracFocus reports. Frequency of use was assessed on a national scale and could misrepresent the prevalence of a compound regionally.

RESULTS AND DISCUSSION

Compounds with Elevated Exposure Potential. For the fast transport scenario, 41 compounds screened using published degradation data were predicted to have $\geq 10\%$ of the initial concentration remaining at the transport distance (Figure 1). Of these, 15 compounds were also identified on ≥ 50 FracFocus reports and were predicted to have an elevated exposure potential (Table 2). Because some compounds excluded or rarely identified on FracFocus could be relevant for assessing potential legacy contamination, all compounds predicted to be

sufficiently mobile and persistent were identified (Table S1 of the Supporting Information); however, they were considered to have an elevated exposure potential only if they were identified on ≥ 50 reports.

Three of the 15 compounds with elevated exposure potential have health-based standards (MCLs): acrylamide and the petroleum hydrocarbons ethylbenzene and xylenes. The occurrence of these compounds at concentrations above their MCLs would necessitate regulatory action. Acrylamide was identified on 3.2% of FracFocus reports as a residual ingredient in nonhazardous acrylamide polymers commonly used in fracturing fluids as friction reducers.^{13,40} The petroleum hydrocarbons were rarely identified as individual additives on FracFocus (e.g., ethylbenzene, 0.30% of reports), but they are minor constituents of some petroleum-based additives like hydrotreated light petroleum distillates [$<0.5\%$ (w/v)],^{41,42} identified as an ingredient in friction reducers on 70.0% of reports. Benzene, also a minor constituent of petroleum distillates, was predicted to be sufficiently mobile and persistent by the screening framework but was individually identified on <50 reports.

Six of the 15 compounds with elevated exposure potential have health assessment information (e.g., reference doses), but no MCLs. The occurrence of these compounds at concentrations above their reference doses could be a concern for human health but would not necessitate regulatory action. Two of six were frequently used: 2-butoxyethanol (22.8% of FracFocus reports) and naphthalene (22.0%). Both compounds are commonly identified as ingredients in surfactants, corrosion inhibitors, and nonemulsifiers, and naphthalene is a constituent of some petroleum-based additives.^{41,43} A recent study detected trace concentrations of 2-butoxyethanol in addition to unresolved complex mixtures of organic compounds in a domestic water well, concluding that drilling or fracturing fluids used in nearby gas wells likely caused the observed groundwater contamination.⁴⁴ *N,N*-Dimethylformamide, an ingredient in corrosion inhibitors, was identified on 9.1% of FracFocus reports. Three of the six compounds were rarely identified ($<5\%$ of reports).

The remaining six of the 15 compounds with elevated exposure potential did not have health assessment information; these compounds are currently not assessed in the EPA IRIS database. Three of the six were more commonly used in fracturing fluids [polysorbate 80 (12.6% of FracFocus reports), 2-mercaptoethanol (8.7%), and 2-ethylhexanol (7.2%)], and the other three compounds were rarely identified.

For the fast transport scenario, six of the compounds screened using the BIOWIN-estimated biodegradation time ranges were predicted to have $\geq 10\%$ of the initial concentration remaining at the transport distance, and four of the six were predicted to have elevated exposure potentials but were rarely identified on FracFocus (Table 2 and Figure S2 of the Supporting Information). In the slow transport scenario, no compounds were predicted to have an elevated exposure potential because degradation to $<10\%$ of the initial concentration occurred by the time the compounds reached the transport distance (Figures S1 and S2 of the Supporting Information).

Frequently Used Compounds. Frequently used compounds identified on $>20\%$ of FracFocus reports are labeled in Figure 1. Ethylene glycol, sorbitan monooleate, 2-propanol, and propargyl alcohol were plotted just below the region designating elevated exposure potential. Both ethylene glycol

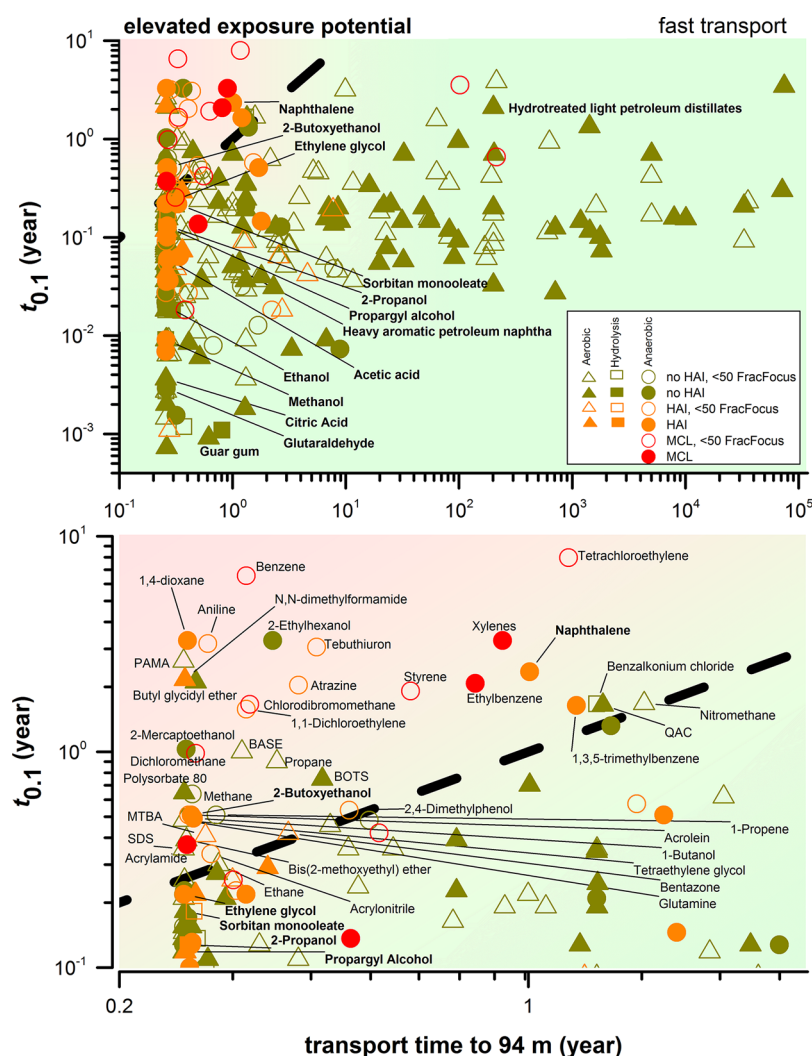


Figure 1. Screening framework plot of time to 10% of initial concentration ($t_{0.1}$) vs. transport time to 94 m (the average setback distance in the United States) for 312 compounds with degradation data available. (top) The elevated exposure potential zone ($\geq 10\%$ of the initial concentration predicted to remain at the setback distance) is defined as the area above the 1:1 line; (bottom) the elevated exposure potential zone is shown in detail. The transport time is calculated for the fast groundwater transport scenario. The 41 compounds predicted to have $\geq 10\%$ of their initial concentration remaining at the transport distance are labeled in the bottom plot (compound abbreviations are defined in Table 2 and Table S1 of the Supporting Information). Frequently used compounds (appearing on $>20\%$ of FracFocus reports) are indicated by bold labels. Toxicity is represented using three categories: compounds with maximum contaminant levels (MCL, red symbols), compounds with health assessment information but not MCLs (HAI, orange symbols), and compounds without MCLs and HAI (no HAI, yellow symbols). Empty symbols represent data for compounds appearing on <50 FracFocus reports and filled symbols those appearing on ≥ 50 reports. The symbol shape indicates whether the half-life used to calculate the $t_{0.1}$ value represents anaerobic biodegradation (circles), aerobic biodegradation (triangles), or abiotic hydrolysis (squares).

and propargyl alcohol have oral reference doses, and while ethylene glycol's dose is relatively high, occurrence at concentrations above the reference dose could be a health concern.

Frequently used compounds of elevated exposure potential could be utilized as indicators of contamination by fracturing fluids. Groundwater monitoring programs and studies evaluating potential migration of fracturing fluids have focused on conservative ions such as chloride and bromide;^{17,45,46} however, the source of these ions is not readily distinguished.^{45,46} The screening framework may be applied to prioritize future research needs, including measuring fate and transport parameters for frequently used mobile and persistent compounds relevant to human health risk assessments or that

could be considered for groundwater monitoring programs to help indicate fracturing fluid migration.

Uncertainty and Limitations. The persistence assessment is highly uncertain because degradation data are limited for many fracturing fluid compounds² and kinetics can vary depending on site conditions.^{32,47} Most of the biodegradation half-lives used to calculate $t_{0.1}$ were measured or estimated in oxic environments, and kinetics under anoxic conditions common to groundwater contaminant plumes are generally slower than aerobic rates.^{47,48} The half-life assumed in the screening framework allows for the comparison of a broad variety of compounds; however, degradation rates used will not be applicable for all site conditions. The lack of published degradation data required that 53% of compounds were screened using estimates of aerobic biodegradation time ranges.

Table 2. Compounds Predicted To Have an Elevated Exposure Potential Because They Were Identified on ≥ 50 FracFocus Reports (0.1% of reports acquired) and Predicted To Have $\geq 10\%$ of the Initial Concentration Remaining at the 94 m Transport Distance (the average setback distance in the United States)

compound	additive purpose ^a	FracFocus frequency (%) ^b	toxicity cat. ^c	$t_{0.1}$ (year) ^d	t_{94} (year) ^e
acrylamide	friction reducer	3.2	MCL	0.37 (an)	0.26
ethylbenzene	corrosion inhibitor	0.30	MCL	2.1 (an)	0.81
xylene ^f	corrosion inhibitor, surfactant, solvent	2.3	MCL	3.3 (an)	0.90
1,3,5-trimethylbenzene	surfactant	0.75	HAI	1.6 (an)	1.2
1,4-dioxane	surfactant	1.2	HAI	3.3 (an)	0.26
1-butanol	surfactant	2.1	HAI	0.49 (an)	0.27
2-butoxyethanol	surfactant, corrosion inhibitor, nonemulsifier	22.8	HAI	0.51 (an)	0.27
N,N-dimethylformamide	corrosion inhibitor	9.1	HAI	2.2 (ae)	0.26
naphthalene	surfactant, nonemulsifier, corrosion inhibitor	22.0	HAI	2.4 (an)	1.0
2-ethylhexanol	nonemulsifier, surfactant	7.2	no HAI	3.3 (an)	0.37
2-mercaptoethanol	iron control	8.7	no HAI	1.0 (an)	0.26
benzene, 1,1'-oxybis-, tetrapropylene derivatives, sulfonated, sodium salts (BOTS)	scale inhibitor, surfactant	1.3	no HAI	0.75 (ae)	0.44
butyl glycidyl ether	resin	0.93	no HAI	2.1 (ae)	0.27
polysorbate 80	surfactant	12.6	no HAI	0.65 (ae)	0.26
quaternary ammonium compounds, dicoco alkyldimethyl, chlorides (QAC)	corrosion inhibitor, biocide	4.7	no HAI	1.7 (ae)	1.3
bis(hexamethylenetriamine penta methylene phosphonic acid) (BMPA)	scale inhibitor	1.2	no HAI	0.55 (ae) ^g	0.26
diethylenetriaminepenta (methylene-phosphonic acid) (DMPA)	scale inhibitor	0.16	no HAI	0.55 (ae) ^g	0.26
FD&C blue no. 1	gelling agent	0.39	no HAI	0.34 (ae) ^g	0.26
tetrakis(triethanolamino) zirconium(IV) (TTZ)	cross-linker	2.8	no HAI	0.34 (ae) ^g	0.26

^aFunction of additive in which each compound was identified as an ingredient, reported by the EPA.⁵³ FracFocus does not report the specific purpose of each compound within an additive, and a compound may be used as an ingredient in multiple additives.⁵³ ^bPercentage of FracFocus reports identifying the use of a compound out of 50024 reports acquired for the states of Colorado, North Dakota, Pennsylvania, and Texas. ^cIndicates whether a compound has health-based standards (MCL), no MCL but health assessment information available (HAI), or no MCL and no health assessment information (no HAI). ^dCalculated according to eq 4. The conditions for which the compound's half-life was reported are noted for anaerobic biodegradation (an), aerobic biodegradation (ae), or abiotic hydrolysis (hy). ^eEstimated according to eq 1 for fast transport scenario. ^f"Xylenes" refers to the mixture of three isomers (ortho, meta, and para). Toxicity studies performed for the mixture.³⁹ Fate and transport parameters were determined for *m*-xylene because it is the dominant isomer in the mixture (45–70%).²⁷ ^gEstimated $t_{0.1}$ adjusted from the expected time range required for complete aerobic biodegradation predicted by BIOWIN 4.²¹

While models such as BIOWIN 4 are useful as an initial screening tool,^{36,49} the uncertainty of these predictions and the difficulty of extrapolating rates from one condition to another⁴⁷ illustrate the need for data on the degradation of many compounds used in fracturing fluids under conditions relevant for groundwater transport.

We did not consider possible interactions between co-contaminants, which may include solubility enhancement by cosolvents, mobility enhancement by association with surfactants,⁵⁰ or biodegradation inhibition by biocides.^{13,29} We also did not account for any chemical transformations that compounds may undergo downhole, or the formation of additional organic compounds in produced water.^{51,52} The degradation of some fracturing fluid compounds may yield intermediate products that are more hazardous than the parent compound,^{14,48} but the behavior of these degradation products was not considered.

Uncertainties in framework parameters, including the dependency of sorption on site-specific conditions and the variability of degradation rates, could push compounds above or below the 10% remaining threshold. Limitations such as neglecting possible mixture interactions, omitting degradation products and any intermediates formed downhole, and the exclusion of fate and transport parameters relevant to specific pathways (e.g., volatilization and dispersion) could also

influence the exposure potential. The 10% remaining threshold will not be appropriate for all scenarios because some compounds are hazardous at trace quantities and groundwater concentrations could vary considerably depending on the mass released and transport pathway. The toxicity assessment is limited because mixture toxicity was not considered and some hazardous compounds may not be included in the EPA's IRIS database. While it remains challenging to predict the exposure potential of fracturing fluid compounds in groundwater, the initial screening results prioritize compounds with elevated potential for human exposure based on our current knowledge. More data on the fate and transport of fracturing fluid organic constituents and their transformation products are needed to improve our understanding of the exposure potential in groundwater.

■ ASSOCIATED CONTENT

§ Supporting Information

Additional details about the methods and results (all compounds predicted to have $\geq 10\%$ remaining, slow scenario, predicted biodegradation time frames), screening parameters, and compounds classified as "no data". The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.5b00090.

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Notes

The authors declare no competing financial interest.

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