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Critical Review

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Quantitative Survey and Structural Classification of Hydraulic Fracturing Chemicals Reported in Unconventional Gas Production

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ABSTRACT

Much interest is directed at the chemical structure of hydraulic fracturing (HF) additives in unconventional gas exploitation. To bridge the gap between existing alphabetical disclosures by function / CAS number and emerging scientific contributions on fate and toxicity, we review the structural properties which motivate HF applications, and which determine environmental fate and toxicity. Our quantitative overview relied on voluntary U.S. disclosures evaluated from the FracFocus registry by different sources and on a House of Representatives ("Waxman") list. Out of over 1000 reported substances, classification by chemistry yielded succinct subsets able to illustrate the rationale of their use, and physicochemical properties relevant for environmental fate, toxicity and chemical analysis.

While many substances were non-toxic, frequent disclosures also included notorious groundwater contaminants like petroleum hydrocarbons (solvents), precursors of endocrine disruptors like nonylphenols (non-emulsifiers), toxic propargyl alcohol (corrosion inhibitor), tetramethyl ammonium (clay stabilizer), biocides or strong oxidants. Application of highly oxidizing chemicals, together with occasional disclosures of putative delayed acids and complexing agents (i.e., compounds *designed* to react in the subsurface) suggests that relevant transformation products may be formed. To adequately investigate such reactions, available information is not sufficient, but instead a full disclosure of HF additives is necessary.

INTRODUCTION

In recent years, few technologies have been discussed in such controversial terms as hydraulic fracturing (HF) and the chemicals involved. Contrasting with a long history of small volume HF in the conventional exploitation of gas and oil, hydraulic fracturing has reached a new dimension with the application of multi-stage HF in long horizontal wells with large volumes of fracking fluid for the recovery of unconventional gas [1], i.e. gas resources trapped in low-permeable coal, sandstone and shale [2]. For exploitation, vertical drilling to the target formation – in the case of shale, typically between 1000 m and 4000 m deep [3] – is followed by horizontal drilling and (partial) emplacement of a protective well casing. The casing is perforated in the depth of the target formation and hydraulic fracturing is applied to stimulate the formation by creating additional permeabilities for the gas to escape [4, 5]. From the same vertical borehole, multiple horizontal drills can be performed in different directions. They reach up to 3 km into the gas-bearing formations [6] and are fractured in several stages. Vertical drillings are closely spaced, which results in a considerable area coverage, which brings fracking activities close to residential areas and can negatively affect communities [7-10].

The share of unconventional gas in total gas output is projected to increase from 14% in 2012 to 32% in 2035 [11]. This development brings about promising economic perspectives - not only for the USA, where a reference case of the U.S. Energy Information Administration projects a growth for shale gas of 2.6% per year until 2040 [12] - but also in 41 other countries on different continents where shale gas has been found to reside in a total of 137 formations [13]. At the same time, opposition from homeowners and environmental interest groups is increasing. Reports of spills, accidents and potential harmful effects of chemicals released as a result of HF have emerged [14-17]. Uncertainty about the potential impacts of HF have led to moratoria (Quebec, New Brunswick) or bans (Bulgaria, France, Tunisia, New York State, Vermont)[18, 19].

Particular concern surrounds the chemicals that may return to the surface as a result of hydraulic fracturing. Both "fracking chemicals" – substances that are injected together with the HF fluid to optimize the fracturing performance – and geogenic substances are of relevance. These compounds can emerge in the flowback (the part of the injected HF fluid that returns to the surface), in the produced water (the water that emerges during gas production and originates from the target formation) or in a mixture of both [20-22]. The concentrations of additives typically make up between 0.5% and 3% of an injected gel-based fluid (reported by mass or volume of the fluid, depending on the source) [3, 23-25]. Given that a typical fracturing operation requires around 9000 to 29000 m^3 [26] of water, this translates into kilograms to tens of tons of the respective compounds. In 2005, underground injections of these substances for HF operations related to oil & gas were exempted from all U.S. federal regulations aiming to protect the environment (Clean Water Act, Save Drinking Water Act, Clean Air Act, Super Fund Law, Resource Recovery and Conservation Act, Toxic Release Inventory); in Germany, HF operations have been regulated by the Federal Law of Mining which currently does not require Environmental Impact Assessments including public disclosure of these chemicals [27]. Knowledge about fracturing chemicals and geogenic substances, however, is warranted for several reasons [28]:

Air emissions are reported to arise from well drilling, the gas itself or condensate tanks [7, 9, 15, 29], whereas spills and accidents [14, 16, 17, 30] pose the danger of surface and shallow groundwater contamination. *Monitoring strategies* are therefore warranted to screen for "indicator" substances of potential impacts. For such indicator substances, adequate sampling approaches and *analytical methods* need to be developed and optimized [31-34]. Identification and classification of HF chemicals and their functional groups is further important to assess the *possibility of subsurface reactions* in the formation which may potentially generate new, as yet unidentified transformation products which resurface with the flowback. For the same reason chemical knowledge is important for optimized *wastewater treatment* strategies: to eliminate problematic substances and to avoid unwanted by-product formation [35, 36]. Knowledge of the most frequently used HF chemicals is further essential for *risk assessment* (environmental behavior, toxicity) [24, 37]. Finally, an overview of reported HF chemicals can provide unbiased scientific input into current public debates and enable a *critical review of Green Chemistry* approaches. Figure 1 (white boxes) illustrates how recent contributions from different ends have aimed to close these knowledge gaps.

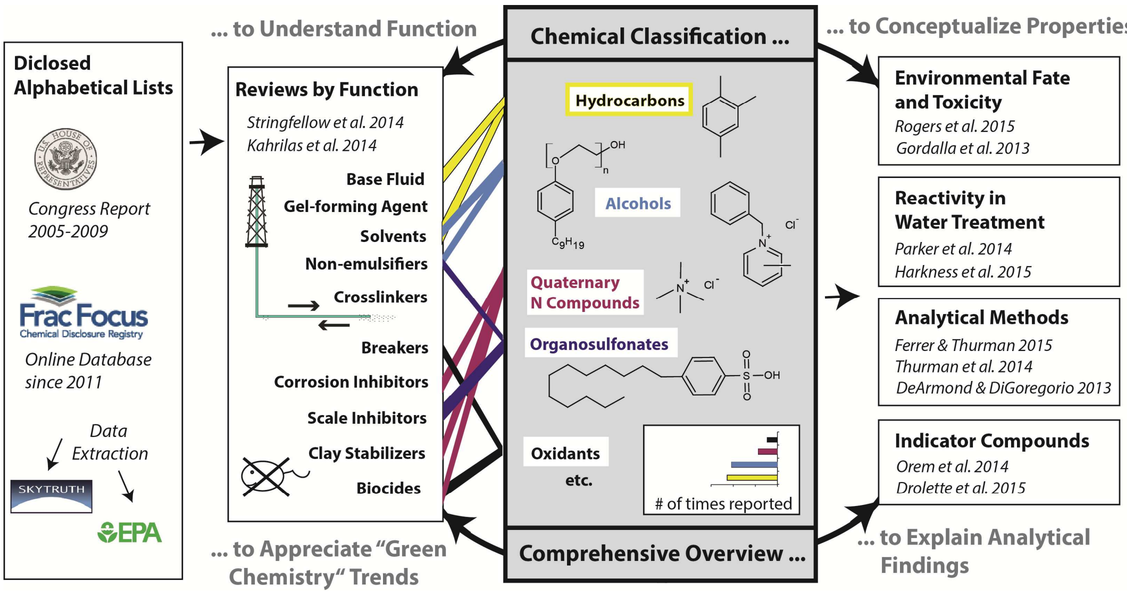


Figure 1. Information on HF additives disclosed by operators (left-hand side) and explored by scientific publications (right-hand side). The structural classification of the present contribution (grey box) enables understanding of, the chemical purpose in the HF process and may help conceptualize, resultant reactivity and the physicochemical properties relevant for environmental fate. The quantitative character of the survey (grey box, bottom), finally, demonstrates to what extent certain chemicals are used and may catalyze the recognition of unexpected (= non-disclosed) analytical findings.

More and more data on HF chemicals used in the U.S. are being disclosed by operators[38-40] (left-hand side of Figure 1), however, these reports are not necessarily complete (substances contributing to less than 0.1% of the chemicals need not be declared). Also, we experienced that information from FracFocus 2.0 [39] – the most comprehensive database of voluntary declarations in the U.S. since 2011 – is not easily extracted (for a summary of restrictions see the Task Force Report on FracFocus 2.0 [41], pages 17, 18). Until recently, the non-profit organization "SkyTruth" provided the only quantitative extract of records, and only for the period between January 2011 and May 2013 [42]. In spring 2015, the U.S. EPA released a dataset extracted independently from FracFocus for essentially the same time period (2011-2013)[43]. A recent publication[44] extracted data up to Nov 2014, however, only for a sub selection of U.S. states. Another source of information is the U.S. House of Representatives Report on chemicals used in HF between 2005 and 2009 [38] (herein referred to as "Waxman List"). In all of these compilations, compounds are listed alphabetically or by their CAS-number. This has the disadvantage that the same (or similar) chemical structures may turn up under different names and CAS-numbers. If websites provide selections of compounds [45-47], entries are typically listed according to their function in the HF process (friction reducer, clay stabilizer, etc.) rather than grouped by chemical structure [45-47].

Scientific contributions are starting to mine the information disclosed by operators and to analyze compounds in actual samples to assess environmental impacts (right-hand side of Figure 1). This includes reviews of HF chemicals[48, 49], predictions of their environmental lifetime and exposure[44], assessments of toxicity[24, 37, 50], investigations of reactivity in water treatment[35, 51], choice of adequate analytical methods[31-34] and the search for potential indicator compounds[32, 52]. These contributions also typically start from alphabetical / CAS-number lists or classify chemicals by their function in the HF process[48, 49]. Some of them include in addition a ranking by disclosure. However, to understand the environmental chemistry of HF chemicals it is not the name or the function in the HF process that is most informative. Instead, the *chemical structure* lends substances the characteristics that make them attractive as HF chemicals, and which determine the physicochemical properties that govern environmental behavior and the choice of adequate analytical methods. Figure 1 illustrates that structure and function are not necessarily identical: the same chemical structure may serve different functions, and the same effect may be achieved by different chemical structures.

Our contribution, therefore, aims to bridge this gap by bringing forward a comprehensive *chemical classification* of HF chemicals (grey box in Figure 1). A dedicated Table in each chapter illustrates the most frequently disclosed and structurally informative compounds of each class. This enables a discussion on *why* a certain substance is used in the HF process and what possible alternatives exist. This classification by chemical structure is used to discuss physicochemical properties[49] together with environmental fate and toxicity [37], and this insight is taken to select putative HF indicator substances together with promising analytical methods. Reference is made to expedient recent reviews[44, 49]. In particular, our Supporting Information provides octanol-water and Henry's law coefficients from the U.S. EPA[43] as well as log K_{oc} values, regulatory data and estimated environmental half-lives from Rogers et al.[44] to catalyze further assessments (see comprehensive list in the SI). Finally, the categorization by compound class enables a straightforward search by chemical structure and, therefore, offers a crucial starting point to interpret analytical findings in actual flowback and groundwater analyses. Identified substances may be matched with similar structures from disclosed databases to decode, on the one hand, the rationale of their putative use, and to recognize, on the other hand, unexpected (= non-disclosed) findings.

To make this overview as representative as possible, we relied on quantitative information (i.e., chemicals are ranked according to the frequency with which they were reported) from the Waxman List and FracFocus (in three independent extracts: SkyTruth, EPA and Rogers et al.[42-44]) in the United States as the world's largest producer of unconventional gas. To fully exploit this information, we provide our overview in three ways. The *Supporting Information* provides the *full data set* in the form of an Excel document, where chemicals are listed by compound class, but can also be searched by name, function, CAS-number. In addition, available compound-specific information (Henry's law constant, octanol-water coefficient, regulatory data, environmental half-lives) and the number of disclosures in the three databases are provided. A chemical classification is also provided by *Tables* in the manuscript which select the most frequently reported compounds (and some additional, interesting hits) according to their *chemical structure.* Finally, a concluding *Figure* in the manuscript (Figure 3) illustrates which substances and compound classes were most frequently reported for each particular *purpose* in order to link our contribution to existing literature and to consider which typical chemicals are disclosed in an average HF operation.

METHODOLOGY

For the years 2005-2009 our overview is based on the Waxman list, which states *in how many commercial products* a substance was reported as ingredient. For the time January 2011 to July 2013 it relies on the FracFocus Chemical Disclosure Registry – here, the information is on the *number of products multiplied by the times the product was reported*. Both databases also differ in that only substances with a valid CAS number are included from the FracFocus Registry, whereas all disclosures are included from the Waxman list. Because of the difficulty in extracting data from the FracFocus Registry – for a summary of current restrictions see the Task Force Report on FracFocus 2.0[41] (pages 17, 18) – we made use of three existing data sets from independent data analysis of FracFocus: by the non-profit organization "SkyTruth" [42], by the U.S. EPA[43] and by Rogers et al.[44]. The data provided by "SkyTruth" and the U.S. EPA are both extracted from the FracFocus Chemical Disclosure Registry 1.0. The difference between them is that the "SkyTruth" extract of our study includes multiple disclosures in the same fracturing event, whereas the U.S. EPA analysis states at how many fracturing events an additive was reported – without counting duplicate disclosures for the same fracturing event. The same type of information is available from Rogers et al.[44]. Here, data were extracted from the FracFocus Chemical Disclosure Registry 2.0 including disclosures until November 2014, however, only for the U.S. states Colorado, North Dakota, Pennsylvania, and Texas. Even though the data have, therefore, different absolute numbers, the combined information from the different databases allows reconstructing, and reaffirming, relative trends in the original source (the FracFocus database). Finally, since all data rely on voluntary disclosure by industry, they are subject to intrinsic limitations: chemicals may not be listed if their proportion in the HF additive was below 0.1%, or if they were considered proprietary. For a summary of all sources (original source, type of information, comments) see Table S1 in the Supporting Information.

After combining the entries from the four databases, we reviewed the resulting list and grouped chemicals according to their structure. In addition, identical entries reported under different names were merged (e.g., Polyethylene glycol monoundecyl ether, "Poly-(oxy-1,2-ethanediyl)-alpha-undecyl-omega-hydroxy" (CAS-No. 34398-01-1) and "Ethoxylated undecyl alcohol" (CAS-No. 127036-24-2)). Further, entries of acids and conjugated bases were merged when they were not reported for pH control, but instead as complexing agents, surfactants, etc., such as for "Ethylenediaminetetraacetic acid" (CAS-No. 60-00-4), "Disodium EDTA" (CAS-No. 139-33-3), "Disodiumethylenediaminetetra-acetate dehydrate" (CAS-No. 6381-92-6), "Trisodium ethylenediaminetetraacetate" (CAS-No. 150-38-9), "Tetrasodium ethylenediaminetetraacetate" (CAS-No. 64-02-8). Entries were also merged when the chemical structure was poorly defined and CAS numbers were missing, but when – judging by the available information – compounds were indistinguishable, such as "Alcohol alkoxylate", "Alkyl alkoxylate" and "Oxyalkylated alcohol". This procedure did not only reduce the number of entries, but it also allowed breaking down the list into manageable sub-lists according to substance classes: "Gases and Non-functionalized Hydrocarbons", "Alcohols, Ethers, Alkoxylated Alcohols", "Carboxylic Acids" etc. These sub-lists correspond to the classification typically found in textbooks [53, 54] and they allow for an overview of the chemical functional groups used and why – even if the same functionality serves different purposes in the HF process.

RESULTS AND DISCUSSION

Types of Hydraulic Fracturing Fluids and Required Properties

All hydraulic fracturing operations require a base fluid (carrier medium) which must be of sufficiently low friction to convey a high hydraulic pressure into the target formation so that fissures are generated. In the process it must further acquire sufficient viscosity to prevent loss of the base fluid into the formation, and to transport proppants to keep the fissures open. Subsequently, it must become of sufficiently low viscosity to flow back so that the gas is released through the fissures and can be recovered at the surface. In addition, the well must not be plugged, and the well surface must be protected against corrosion during the operation. Depending on the chemistry and the depth of the geological formation, different types of HF fluids can be chosen for these purposes [55, 56]. In formations of shallow depth, gas fracks (where proppants are transported in foamed or gelled gas) or slickwater fracks (where they are suspended in water with a blend of friction reducers) have the advantage that they do not require as many additives. For example, slickwater fracks do not require gels and gel breakers. [56] However, the fluid viscosity of slickwater is typically not sufficient to keep proppants suspended long enough for HF operations in greater depths. [55, 56]. For this reason, gel fracks such as outlined in Figure 2 are commonly applied, where the base fluid (water in most cases, other fluids if the formation is water-sensitive) contains a gelling agent that keeps proppants suspended for a longer time. For optimum HF performance, the mixture is of low friction at first, then becomes viscous through the use of polymer cross-linkers, and subsequently becomes non-viscous again by the use of breakers that cut polymer (cross-)linkages. Alternatives are viscoelastic Surfactants (VES) which contain surfactant molecules that self-organize into three dimensional structures with similar properties as crosslinked gels, but tolerant to salt content and easier to break [57, 58]. Figure 2 illustrates further that a HF fluid must also contain substances that protect the well surface against corrosion (corrosion inhibitors), prevent the collapse of clay structures in the formation (clay stabilizers), and prevent the clogging of wells by precipitates (scale inhibitors) or biofouling (biocides).

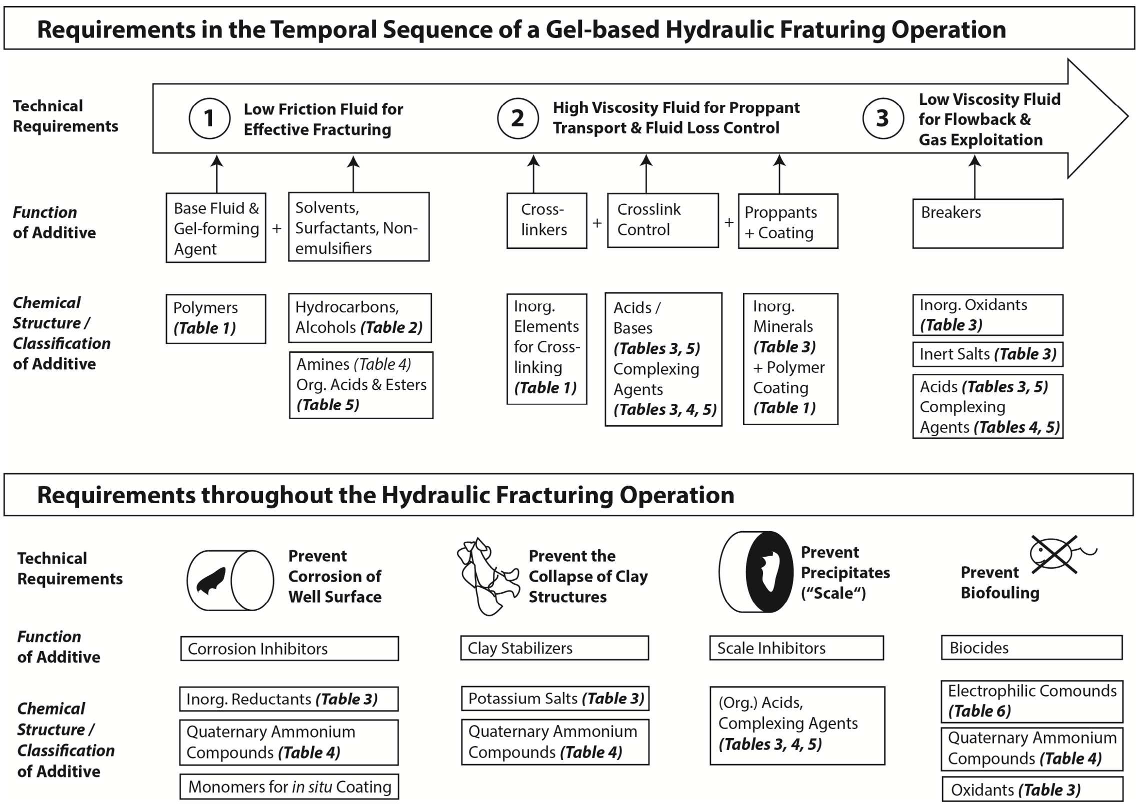


Figure 2. Requirements of a gel-based HF operation and additives grouped by their *technical function* and their *chemical classification* (corresponding to the Tables in the manuscript).

Figure 2 illustrates how such *functional* requirements are related to chemical *substance classes* and, therefore, provides a roadmap through this review. Each substance class is treated in a dedicated chapter. An associated Table links chemical properties with functionalities in the HF process by listing the most frequently disclosed (based on FracFocus extracts by the EPA, SkyTruth, Rogers et al [42-44]. and on the Waxman List [38]), or structurally most informative compounds of each class. The same structural properties are subsequently discussed with respect to environmental fate and monitoring strategies based on Henry's law constants / logK_{ow} compiled by the EPA[43] and based on logK_{oc} data provided in Rogers et al.[44]. All data are included in our comprehensive compilation in the SI. Each chapter ends by discussing which compounds are likely relevant based on toxicity[24, 44] and on environmental persistence[44] (this information is also integrated into the SI), and by identifying possible indicator compounds and analytical methods. After this treatment by *substance class*, the review is concluded by a section which takes up the perspective of *function* again. By graphically ranking the most frequently disclosed additives for the separate functions in the HF process, an overview is given of which additives are most likely to be encountered in an "average" HF operation based on the information of operators and what chemical alternatives exist.

1. Polymers and Crosslinkers

Chemical Properties Relevant in the HF Process. Table 1 lists disclosed synthetic polymers and biopolymers together with inorganic elements that are conducive to condensation / crosslinking. As illustrated by the functions and the frequency of disclosure, polymer properties – i.e., the linkage of bonds in three-dimensional structural networks – are used as protective layers against corrosion at the well surface, for proppant coating, but most prominently for gel formation within the HF fluid. A gelling agent must first create a low-friction fluid, but provide in addition functional groups that can be crosslinked at any desired time to form three-dimensional cross linkages for enhanced viscosity. These properties can be provided either by biopolymers such as guar gum and derivatized cellulose or by synthetic (co)polymers of polyacrylamides and polyacrylates.

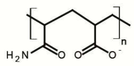
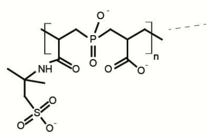
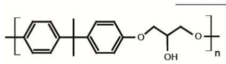
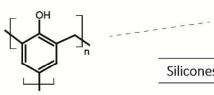
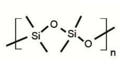
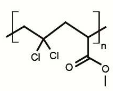
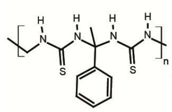
Table 1 illustrates that crosslinking of carbohydrate-based biopolymers is only possible with hydroxyl groups that are in *cis*-position to each other. The scheme in Table 1 illustrates that the galactose units in guar gum have precisely this orientation explaining the abundant use of this natural resource as gel-forming agent. Table 1 further illustrates that polymers without this *cis*-orientation of OH groups (such as cellulose) are sometimes derivatized with hydroxypropyl or carboxymethyl groups to make them water-soluble and to enable such crosslinking. To establish crosslinks, complexation of -OH groups can be achieved with either borate or metal ions. Borate has the advantage that the complexation can be reversed by adding acid as a breaker (left scheme in Table 1), but it has the disadvantage that linkages are not stable at high temperatures[56]. Metal ions have the advantage of temperature stability, but the crosslinking is not as easily reversed and some metal ions (e.g., Zr^{IV}) form precipitates when brought into contact with water [56]. Until crosslinking, Zr^{IV} therefore, needs to be kept in an organic solvent by careful choice of appropriate organic ligands (right scheme in Table 1). The right choice of ligands may also allow a gradual release of Zr^{IV} leading to delayed crosslinking[59].

Compared to biopolymers, synthetic polyamide/-acrylate polymers have the advantage that they can be deliberately designed for a spectrum of functionalities. Without crosslinking they act as friction reducers and are, therefore, typical additives in slickwater fracks[56]. If the percentage of acrylate-derived carboxyl groups is increased, these groups can be crosslinked with metal ions to provide three-dimensional structures of elevated viscosity. The same carboxyl groups can also scavenge metal ions from solution and act as scale inhibitor (see chapter below) – an effect that is enhanced by the introduction of additional phosphinate moieties (Second entry of Table 1).

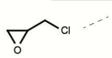
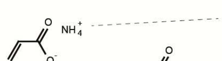
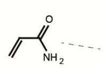
The frequency of reported guar gum versus polyacrylamide / acrylate applications suggests that biopolymers, and therefore gel-based fracks, are at least two to three times preferred over synthetic polymers in putative slickwater fracks. The listing of inorganic elements in Table 1 further suggests that low-temperature gel fracks with borate are twice as frequent as high-temperature fracks with zirconium. Disclosures, finally, suggest that zirconium has almost completely substituted the previous use of more toxic Cr^{VI}. Of the synthetic polymers, polyacrylamide/polyacrylate (co)polmers, phenol/formaldehyde epoxy resins and thiourea copolymers are most frequently disclosed (all about 10%). Epoxy resins are reported for general use as proppant coatings (Table 1) and thiourea polymers as corrosion inhibitors (Table 1).

Table 1. Most frequently reported synthetic polymers, biopolymers and inorganic cross-linkers, together with corresponding reaction schemes. n.r.: not representative; n.i.: not included. Degradation half-lives are from ref. [44]. A more comprehensive list of compounds together with physicochemical properties is provided in the S.I.

Synthetic Polymers

Structure	Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
	Acrylamides / Acrylates			8.8	n.r.	7238	31	
	Copolymer of acrylamide and sodium acrylate	Gel Forming Agent, Friction Reducer	Econo-FR400 (RockPile Energy): Friction Reducer; FRW-15A (Baker Hughes): Friction Reducer (w Distillates/ Sorbitan Monooleate/ Nonyl phenol ethoxylate);	4.1	n.i.	1954	1	25987-30-8
	Acrylic Acid, with (Sodium-2-acryl-amido-2-methyl-1-propanesulfonate and sodium phosphinate)	Scale Inhibitor	6028-SI (ESP Petrochemical): Scale Inhibitor	0.75	n.i.	752	0	110224-99-2, 129898-01-7, 71050-62-9
	Acrylamide (copolymer)	Gel Forming Agent, Friction Reducer	AG-57L (Baker Hughes): Gelling Agent (with Acrylamide Copolymer/Distillate); FRW-200 (FTSI): Friction reducer (with Surfactant/ Acrylamide/ Acrylate/ Distillates/ Ethoxylated alcohols etc);	0.24	0.0	569	3	38193-60-1, 108388-79-0
	Other Vinyl Polymers			0.6	n.r.	1990	11	
	Propylene pentamer	Gel Forming Agent,	Plexgel 907 LEB (Chemplex): Slurried Guar (w/ Petroleum Distillates/C-11 to C-14 n-alkanes); WGA-1LEB (A&C): Water Gelling Agent;	0.46	n.i.	1574	1	15220-87-8
	Phenol / Formaldehyde / Epoxy Polymers			13.3	n.r.	11184	54	
	Bisphenol A/ Epichlorohydrin resin	Proppant Coating	ER-25 (Halliburton): Resin (w/ Butyl glycidyl ether/ Dipropylene glycol monomethyl ether); EXPEDITE 350 COMPONENT A (Halliburton): Resin (with Methanol);	0.82	n.i.	498	5	25068-38-6
	Phenol-formaldehyde resin	Proppant Coating	SB Excel (Halliburton): Proppant (with Quartz); RCS (All Meshes) (Operator): Proppant (with Quartz/ Hexa-methylenetetramine);	10.9	n.i.	8087	32	9003-35-4
	Silicones			0.98	3.5	1628	7	
	Siloxanes and silicones, dimethyl,			n.i.	0.53	339	0	63148-52-7
	Halogenated Polymers			0.67	n.r.	1058	1	
	Vinylidene chloride/methyl-acrylate copolymer			0.58	n.i.	928	0	25038-72-6
	Others			11.2	n.r.	7648	20	
	Thiourea polymer w/ formaldehyde & 1-phenylethanone	Corrosion Inhibitor	CI-27 (Baker Hughes): Corrosion Inhibitor	10.0	n.i.	7101	3	68527-49-1

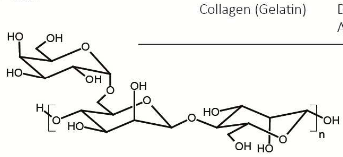
Monomers

Structure	Chemical	Function	Examples of Reported Commercial Products	EPA Eval.	Rogers et al.	Sky Truth	Waxman	CAS -Number
	Epichlorohydrin	Proppant Coating	Superior EXP-PCH 20/50 (Nabors Completion and Production Services): Proppants (with Quartz); HyperProp G2, 20/40 Baker Hughes: Proppant	0.19	0.43	877	5	25085-99-8, 106-89-8
	Bisphenol A			0	0.028	9	0	80-05-7
	Ammonium Acrylate			0.07	2.1	291	0	10604-69-0
	Acrylamide			0.52	3.2	658	2	79-06-1

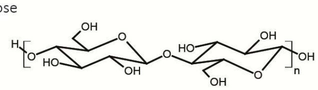
Biopolymers

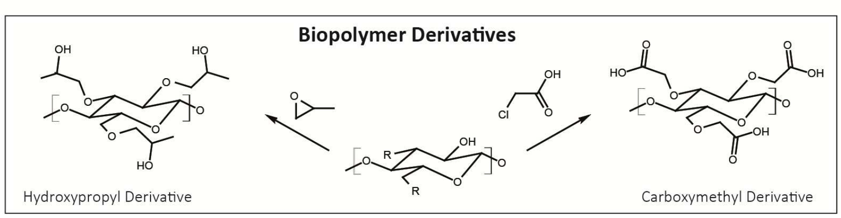
Chemical	Function	Examples of Reported Commercial Products	EPA Eval.	Rogers et al.	Sky Truth	Waxman	CAS -Number
Biopolymers			25.1	45.5	27528	123	
Guar gum, Guar gum derivatives	Gel Forming Agent	GW-4LDF (Baker Hughes): Gelling Agent (w Petroleum Distillates); WG-36 GELLING AGENT (Halliburton); J580 (Schlumberger): Gelling Agent;	21.1	45.2	23424	53	9000-30-0
Carboxymethyl Cellulose	Gel Forming Agent	XLBHT-2 (Superior Well Services): Cross-linkers	0.11	n.i.	1782	0	9004-32-4
Collagen (Gelatin)	Diverting Agent	BioSealers (Baker Hughes): Degradable Sealers (with Glutaraldehyde);	0.14	n.i.	82	6	9000-70-8

Guar Gum



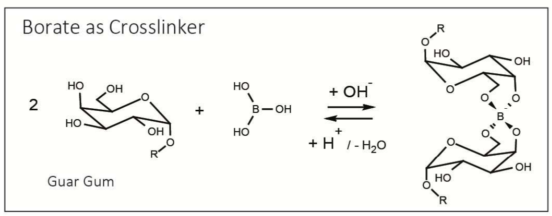
Cellulose

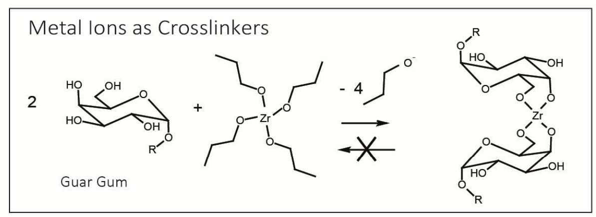




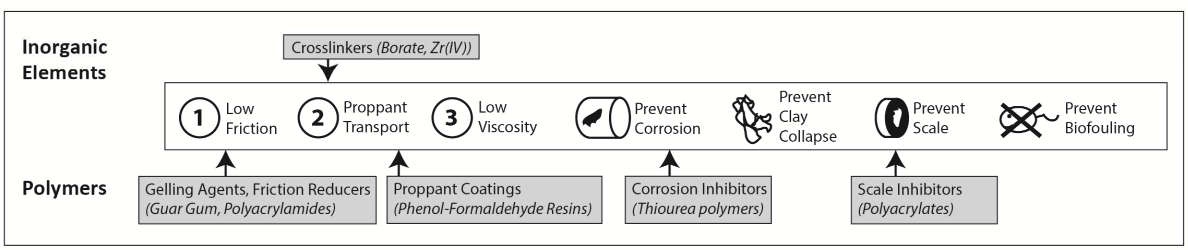
Inorganic Elements Conducive to Condensation / Crosslinking

Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Borates and Zirconium			32.5	n.r.	30693	95	
Borates	Crosslinker	XL-8 (Nabors Completion and Production Services): Cross-linkers (with ethylene glycol); XLW-32 (Baker Hughes): Crosslinker (with Methanol/methyl borate); WXL-105L (WFT): Crosslink Control (with ethylene glycol / monoethanolamine)	21.6	n.i.	25919	67	10043-35-3, 20786-60-1, 1333-73-9, 1303-86-2, 7440-42-8, 26038-87-9, 12045-78-2, 13709-94-9,16481-66-6, 1332-77-0, 13840-56-7, 7775-19-1, 35585-58-1, 10555-76-7, 1330-43-4, 1303-96-4, 12179-04-3, 1319-33-1, 12008-41-2, 7440-67-7, 92908-33-3, 12280-03-4
Zirconium complexes (triethanolamine, n-propanoyl, lactate, etc.)	Crosslinker	CL-37 CROSSLINKER (Halliburton): Crosslinker (with Propanol/Glycerine); XL-4 (Nabors Completion and Production Services): Cross-linkers (with Water/ Propanol/ Isopropanol);	11.0	8.5	4774	28	101033-44-7, 113184-20-6, 7699-43-6, 62010-10-0, 68909-34-2, 23519-77-9
Others			1.4	0.48	1358	33	
Ferric chloride / Ferric sulfate	Crosslinker	XL-1 (Halliburton): Crosslinker;	0.04	n.i.	382	10	7705-08-0, 10028-22-5
Cobalt acetate	Crosslinker	CAT-OS-1 (Halliburton): Activator (w/ Ammonium acetate);	0.22	0.48	162	1	71-48-7

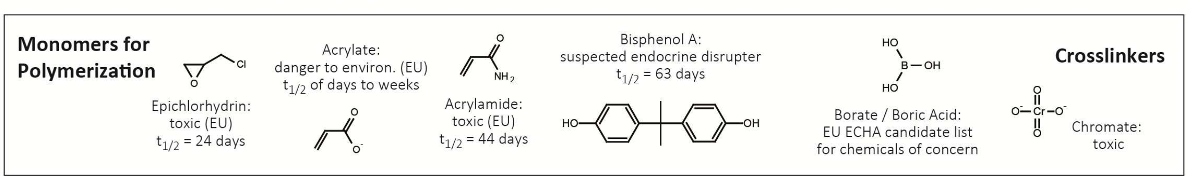




Functions in the Hydraulic Fracturing Process (Summary)



Potential Substances of Concern (Examples)



Substances of Concern / Consequences for Environmental Monitoring. Biopolymers, the listed acrylamides/acrylate and silicone polymers are all of low toxicity where biodegradability is better for acrylamides than for silicones [60-63]. In water treatment, the main relevance of these structures is likely their high oxygen demand. Instead, potential substances of concern are monomers such as acrylate, acrylamide, epichlorohydrin or Bisphenol A (see

Table 1). These monomers may either leach out of the polymer, or they are, potentially, even applied deliberately to conduct polymerization *in situ* during the HF process which is a known practice to enable slow gel formation at elevated temperatures (see, e.g., chapter 8 in Fink (2011))[59] . In this context, the polyvinylidene copolymer listed in Table 1 features toxic monomers and is highly resistant to biodegradation or oxidation.[64] Also phenol polymers for proppant coating are potentially problematic, because unreacted phenolic monomers can leach over time and the polymer is barely degradable [65]. Specifically, bisphenol A/epichlorohydrin oligomers are ranked as acutely toxic, long term aquatoxic and carcinogenic[66].

Of the crosslinkers, finally, borate is of greatest concern. Although not regulated in North America, this substance is on the European Chemicals Agency Candidate List of Substances of Very High Concern because of its reproductive toxicity [67, 68]. Chromate has been of concern in the past, but is disclosed only once in the Waxman List, and not on FracFocus, indicating that its use has been discontinued.

To capture the potential influence of polymers and crosslinkers on the environment, monitoring efforts should, therefore, focus on dissolved organic carbon and borate, ideally complemented by analysis for inorganic metals such as Zr or Cr. In addition, routine monitoring by gas chromatography or liquid chromatography is recommended for organic monomers of particular concern such as bisphenols, acrylamide and acrylate[33].

2. Hydrocarbons, Alcohols

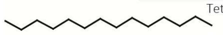
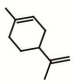
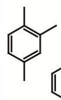
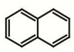
Chemical Properties Relevant in the HF Process. Gases and hydrocarbon structures of Table 2 are largely void of chemical functional groups, which makes them suitable as either *hydraulic fracturing base fluids* or as *solvents*. The high disclosure frequency of water-based polymers (see previous chapter), however, indicates that oil-based fracks or foam fracks are rare and that hydrocarbons are primarily applied as solvents for the gelling agent in water-based fracks. The use of petroleum hydrocarbons likely reflects the necessity of supplying the gel forming agent (guar gum, etc.) and additional additives (e.g. organic zirconium complexes) in a medium that dissolves them in high concentrations, yet is to some extent miscible with water so that the gel ends up in a homogeneous water-based hydraulic fracturing fluid. In addition, these hydrocarbons may also be present in the formation and come up in the HF wastewater as geogenic substances[69] .

Next to hydrocarbons, alcohols are the most frequently disclosed solvents, in particular methanol and isopropanol (Table 2). The distinguishing feature of alcohols is their -OH group, which makes them miscible with water. Short-chain alcohols, as well as alcohols with numerous alkoxy groups inside their structure ("polyethyleneglycol", "alkoxylated alcohol", "Poly(oxy-1,2-ethanediyl)") make for very polar organic solvents to keep water, polymers and less polar hydrocarbons together in homogeneous solution ("non-emulsifiers"). Polyols with numerous –OH groups can act as complexing agents to keep metal ions for crosslinking dissolved ("*crosslinker*", "*crosslink control*") or to prevent geogenic precipitates ("*scale inhibitor*"). Propargyl alcohol serves as *corrosion inhibitor* because of its unsaturated bond which allows *in situ* polymerization to form a protective polymer coating at the well surface [70]. Alkoxylated nonylphenols, finally, are used as *solvents, surfactants and non-emulsifiers* (Table 2).

Substances of Concern / Consequences for Environmental Fate and Monitoring. Of the disclosed petroleum hydrocarbons, many are notorious groundwater contaminants from oils spills or leaking underground storage tanks at gasoline stations. These compounds are both of concern because of their acute toxicity – in the case of occupational exposure of workers and residents – and because of their persistence in the environment. For example, benzene is classified as toxic in the EU. It is regulated as water pollutant with a maximum contaminant level (MCL) of 5 μg/L by the US-EPA and is known to be rather persistent in the absence of oxygen. (For degradation scenarios, we assume here that anaerobic degradation and anoxic conditions are a likely scenario for compounds in HF fluids, because the high organic carbon load is expected to quickly use up any available oxygen.) Similar concerns exist for BTEX (benzene, toluene, ethylbenzene, xylenes), naphthalene or other alkylated aromatic and polyaromatic hydrocarbons (PAH).

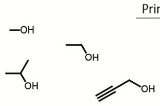
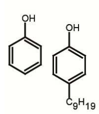
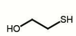
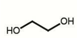
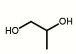
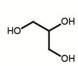
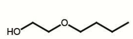
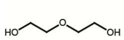
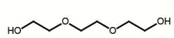
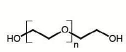
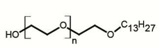
Table 2. Most frequently reported gases, hydrocarbons and alcohols. n.r.: not representative; n.i.: not included. Henry's law constants and log Koc constants are taken from EPI Suite[71], , degradation half-lives from ref. 44, except for 4-nonylphenol [72]. A more comprehensive list of compounds together with physicochemical data is given in the S.I.

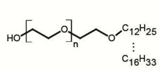
Gases and Non-functionalized Hydrocarbons

Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Gases			4.0	n.r.	1116	13	
Nitrogen	Fracking Fluid	Nitrogen (Nabors Completion & Production Co.) : Base Fluid; NITROGEN LIQUEFIED (Halliburton): Fluid;	3.4	n.i.	1039	9	7727-37-9
Alkanes			1.3	5.0	1692	30	
Tetradecane	Solvent	Plexgel 907l-EB (Chemplex): Viscosifier for water (with guar gum)	0.28	0.91	306	0	629-59-4
Paraffins/Paraffinic solvent	Diverting Agent	Wax diverter (RSI): Diverter;	n.i.	0.14	18	8	8002-74-2
Alkenes			21.3	17.2	7230	37	
Citrus terpenes	Solvent	WT-603 (Frac Specialists): Wetting Agent (with Alcohol ether sulfate/ Alkyl benzene sulfonate/NaCO3)	5.0	5.7	1911	11	94266-47-4, 9426647468647-72-3
d-Limonene	Solvent	EcoFlow NE (Independence): Non Emulsifier (with Water/Surfactants/Methanol/proprietary);	1.9	3.0	656	11	5989-27-5
Aromatic Compounds			33.9	46.5	16581	188	
1,2,4-Trimethyl-benzene	Solvent	LoSurf-300D Halliburton Non-ionic Surfactant (w Heavy naphtha/Nonylphenyl-branched/Ethanol/Naphthalene);	13.1	16.9	5980	21	95-63-6
Naphthalene	Solvent	SCS P762 (Smart Chemical Services): Process Corrosion Inhibitor (with Ethylbenzene/Xylene/Cumene/Aromatic hydrocarbons); SandChem500 (EES): Inhibitor	19.4	22.0	8653	44	91-20-3, 8032-32-4
Petroleum Distillates			107.4	111.6	75298	321	
Diesel	Solvent	LGC-VI (Halliburton) Liquid Gel Concentrate (with Guar derivative proprietary);	0.19	0.05	214	51	68476-34-6, 68476-30-2, 68334-30-5
Light petroleum distillates ("naphtha")	Solvent	NE-6 (EES): CATIONIC NON-EMULSIFIER (with other tri-methylbenzenes/xylene/2-ethylhexanol); 64742-47-8: SCS P762 (Smart Chemical Services): Process Corrosion Inhibitor (w ethylbenzene/xylene/cumene/naphthalene).	71.0	71.6	47923	103	64742-47-8, 68333-25-5, 64742-95-6, 6742-47-8
Heavy petroleum distillates, Solvent naphtha, heavy aliphatic	Solvent	SCS P762 (Smart Chemical Services): Process Corrosion Inhibitor (with ethylbenzene/ xylene/ cumene/ naphtha-lene); SandWedge® WF (Halliburton): Conductivity Enhancer (with Isoprop/Methanol); LGC-36 UC (Halliburton): Liquid Gel Concentrate (with Guar Gum); GA-15L Standard Guar Slurry (Frac-Chem): Gelling Agent	27.7	28.5	20705	68	68132-00-3, 64742-94-5, 64741-68-0, 64742-52-5, 64742-54-7, 64742-48-9, 64741-96-4, 64742-96-7
Paraffinic Petroleum Distillate					2348		64742-55-8, 64741-88-4
White mineral oil	Solvent	GBW-23L (Baker Hughes): Breaker; FGA-15L (Frac Specialists): Water Gelling Agent (w Guar Powder); BR-37 (CJES): Gel Breaker	2.5	6.6	1584	8	8042-47-5, 64742-53-6

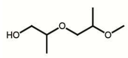
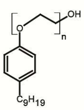
Alcohols, Ethers, Alkoxylated Alcohols

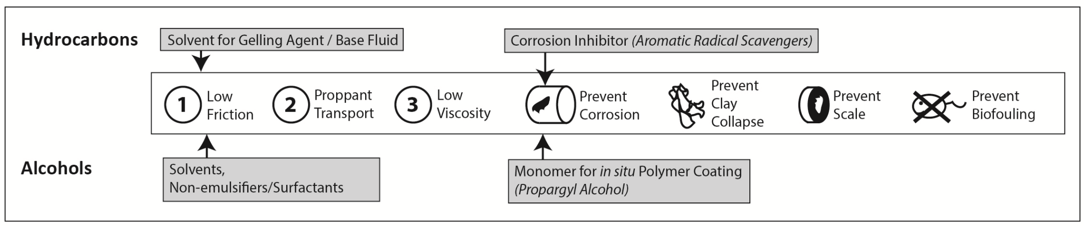


Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Primary and Secondary Alcohols			206.1	212.1	155960	769	
Methanol	Solvent		72.3	76.5	72810	342	67-56-1, 267-56-1
Ethanol	Solvent		37.3	34.2	22749	36	64-17-5
Isopropanol	Solvent		47.2	50.1	33819	274	67-63-0
Propargyl alcohol (2-propyn-1-ol)	Corrosion Inhibitor	HAI-OS ACID INHIBITOR (Halliburton): Corrosion Inhibitor; CI-14 (Baker Hughes): Corrosion Inhibitor	34.3	32.7	18030	46	107-19-7
Phenols			0.67	0.78	374	9	
Phenol			0.64	0.63	263	5	108-95-2
Nonylphenol	Surfactant		0.05	0.14	111	1	104-40-5, 25154-52-3
Polyols			41.3	75.6	41638	166	
2-mercaptoetha-nol (Thioglycol)			0.62	8.7	3613	13	60-24-2
Ethylene glycol (1,2-ethanediol)	Crosslinker, Scale Inhibi-tor, Solvent	BC-140 (Halliburton): Crosslinker (with ethanolamine borate); Scaletrol 7208 (BHI): Scale Inhibitor (with diethylene glycol); CX-9 (Universal): Crosslinkers and Delayers (with metaborate and OH⁻);	32.4	49.7	30061	119	107-21-1, 76-31-3
Propylene glycol (1,2-propanediol)	Scale Inhibitor, Solvent	Super TSC (Nabors Completion and Production Services): Paraffin & Scale Additives (with anionic polymer and 2 Phosphobutane 1,2,4 tricarboxylic acic); NE-35 (Baker Hughes): Non-emulsifier (surfactant)	2.6	7.1	3623	18	57-55-6
Glycerol			5.7	10.1	4014	16	56-81-5
Ethoxylated Alcohols			65.7	123.5	61668	219	
Ethylene glycol monobutyl ether	Solvent	MUSOL SOLVENT (Halliburton): Solvent; NE-212 (Chemplex, L.C.): Non-emulsifier (with Methanol/ Quats/ Isopropanol/etc);	19.0	22.8	14605	126	111-76-2
Diethylene glycol	Solvent, Scale Inhibitor	Scaletrol 7208 (BHI): Scale Inhibitor (with ethylene glycol); CI-150 (FTSI) Acid Corrosion Inhibitor (in mix with quaternary ammonium salts, surfactant, etc.)	4.5	8.1	3895	8	111-46-6
Triethylene glycol	Solvent	Ecopol-ME100 (RockPile Energy): Surfactant; Ecopol-NE601 (RockPile Energy): Non-emulsifying Agent (with Water/Methanol/Coconut Diethanolamide);	2.1	2.7	1025	3	112-27-6
Polyethylene-glycol	Solvent, Surfactant	TPC-F-031 (Sanjel): Non-emulsifier; Bioclear 5000 (Trican): Biocide (with 2,2-dibromo-3-nitrilopropion-amide); Plexflow RTS (Chemplex): Oil field Surfactant; Synonym: [Poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy]	10.0	14.4	6900	20	25322-68-3,65545-80-4
Polyethylene-glycol isotridecyl ether	Surfactant	HVG-1 (FTSI): Surfactant; Synonyms: [Isotridecanol, ethoxylated], [Poly(oxy-1,2-ethanediyl),α-isotridecyl-ω-hydroxy],	1.7	7.8	5937	1	24938-91-8, 9043-30-5
Alcohols, C12-16, ethoxylated	Surfactant	Plexsurf 240-E (Consolidated): Surfactant; Plexhib 256 (Chemplex): Corrosion inhibitor for HCl (with Olefins/ Methyl Alcohol/ Propargyl Alcohol/ Thiourea/ Formalde-hyde Copolymer);	11.7	28.6	12848	11	68131-39-5, 68951-67-7, 103331-86-8, 68551-12-2,

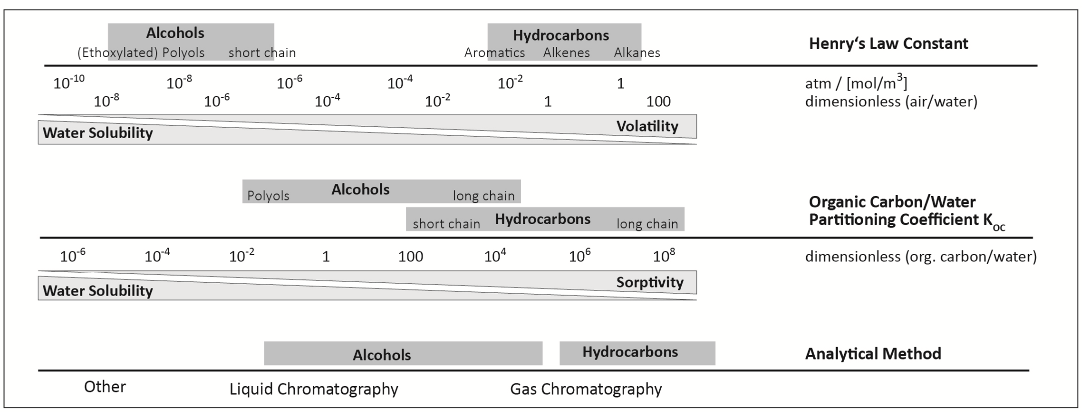
Alcohols, Ethers, Alkoxylated Alcohols (continued)

Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Propoxylated Alcohols			2.9	5.0	885	20	
 Dipropylene glycol mono-methyl ether (2-methoxymethyl-ethoxy propanol)	Solvent	SandWedge® NT (Halliburton): Conductivity Enhancer (with Naphtha); Super Stim-Oil (Nabors): Surfactants & Foamers (with Water/Citrus Terpenes/ Isopropanol/ Proprietary polymer/ Organic Polyol/Proprietary Castor Oil);	1.5	2.0	608	12	34590-94-8
Alkoxylated Phenols			31.4	42.2	25318	81	
 Polyethylene-glycol p-nonyl-phenyl ether [= Ethoxylated nonyl phenols] [= Nonylphenol ethoxylate]	Surfactant, Solvent	OilPerm A Halliburton Non-ionic Surfactant (with Ethanol/Naphtha/Naphthalene); NE-900, tote (Baker Hughes): Non-emulsifier (with Methanol); Stim 802ACT Catalyst Resin Activator (with Methyl Alcohol/C12-14 Secondary Ethoxylated Alcohol); Synonym: [Poly(oxy-1,2-ethanediyl), α- (4-nonylphenyl)-ω- hydroxy]	27.5	31.7	20201	73	127087-87-0, 26027-38-3, 68412-54-4, 9016-45-9, 9016-45-6, 9018-45-9
Tergitol	Surfactant, Solvent	LSG-100 (Nabors Completion and Production Services): Gelling Agents (w Petroleum Distillates/Guar Gum); HVG-1 (FTS): Gel (w Petroleum Distillates/Guar Gum/Clay);	3.7	10.4	5052	1	68439-51-0

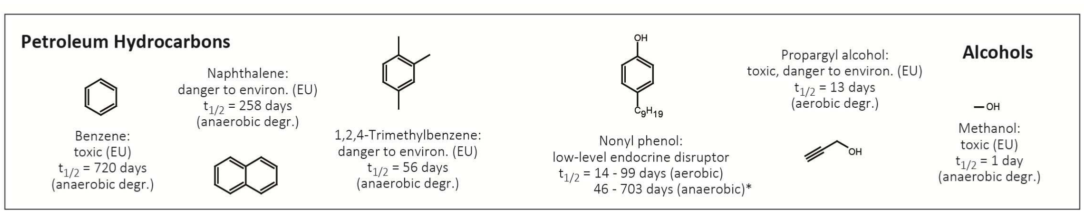
Functions in the Hydraulic Fracturing Process (Summary)



Physicochemical Properties and Analytical Methods (Overview)



Potential Substances of Concern (Examples)



Many alcohols are primarily of concern because of their acute toxicity during exposure. In contrast, they are more quickly biodegraded in the environment. For example, methanol is classified as toxic in the EU, but it is rapidly metabolized and not expected to persist in the environment over longer time scales [73]. Propargyl alcohol in pure form is toxic to humans, highly toxic to aquatic organisms [74] and was found to be carcinogenic in rats [75, 76]. However, propargyl alcohol is further transformed in the subsurface (1,3-hydroxyl shift and tautomerization to 1-propenal [77], subsequent polymerization or oxidation) and is readily biodegradable according to OECD criteria [74]. It is, therefore, expected to persist in the environment for weeks rather than months after application, similar to other reactive monomers (see acrylamide, epichlorhydrin, etc., in Table 1). Alkoxylated alcohols (= polyglycol alkyl ethers) are not harmful and their alkoxylated side chain tends to be readily biodegraded. However, in the case of alkoxylated nonylphenols – which, together with Tergitol, are disclosed in 50% of all operations – such degradation leads to octyl- or nonylphenols [78, 79, 80]. These compounds are both persistent in the environment and of ecotoxicological concern because they can act as endocrine disruptors [81]. Therefore, even though nonylphenols are seldom directly reported as hydraulic fracturing additives (Table 2) they are nonetheless likely to form as a result of HF operations.

The abundant disclosure of BTEX hydrocarbons and nonylphenol-based alcohols raises ecotoxicological concerns. Also, these compounds may serve as potential tracers of fracturing operations. Both aspects put a focus on their partitioning in the environment and on adequate analytical methods. Table 2 illustrates that, because of their high organic carbon / water constants, hydrocarbons are expected to be retained to some extent in the case of groundwater contaminations. Also, Table 2 illustrates that most petroleum hydrocarbons, as well as some (short chain) alcohols are distinguished by their high volatility. Of all HF additives, these compounds are therefore of greatest concern as air pollutants for workers and nearby residents, and they should be target compounds for air monitoring. Because of their high volatility, these compounds can also be easily targeted by gas chromatography-based analytical methods in both air and groundwater monitoring. Liquid chromatography-based analyses are the method of choice for alkoxy- and polyalcohols[32] which are highly water soluble, difficult to extract and have low volatility, but whose limited half-life can make them convenient short term tracers for recent impacts of HF operations.

3. Inorganic Compounds

Chemical Properties Relevant in the HF Process. Table 3 distinguishes between inorganic compounds with an obvious chemical function (oxidants, reductants, acids, bases) and those that are non-reactive / inert. Among the *inert insoluble minerals,* SiO_2 stands out by the number in which its various forms – quartz, cristobalite, in microcrystalline form or as sand – are reported as *proppants*. Less frequent proppants are silicates, aluminum oxides, titanium oxides and iron oxides. These proppants are in addition often coated by a synthetic phenol/formaldehyde epoxy polymer (Table 1). Inert soluble salts (mostly alkali chlorides) serve mostly for *ionic strength control* and, in small part, for *clay stabilization* (by K^+ exchange into clay interlayers [82], see section below). Of the *reactive inorganic chemicals*, finally, most frequent listings are *pH control* reagents (HCl and other acids / NaOH, KOH and other bases) as well as *oxidants* ($(NH_4)_2(S_2O_8)$, Na_2SO_5, NaClO, $NaClO_2$). Both pH control and oxidation capability are crucial properties of *breakers*. Strong oxidizing agents ($(NH_4)_2(S_2O_8)$, Na_2SO_5, NaClO, $NaClO_2$) effectuate oxidative breakdown of the sugar backbone of biopolymer structures (Table 1). Acids can remove borate-based crosslinks by shifting the equilibrium from borate to boric acid (Table 1). An additional benefit of acids is the dissolution of precipitates (*scale inhibition*), and oxidants may in addition serve as *biocides*. Ammonia, finally, can complex iron and, thereby, avoid precipitation of iron oxides and prevent uncontrolled crosslinking[83] (see role of Fe^{III} as crosslinker in Table 1).

Potential Substances of Concern / Consequences for Environmental Fate and Monitoring. Table 3 illustrates that elements with long-term toxicity such as heavy metals are not reported in disclosed HF additives. The greatest concern deriving from additives can, therefore, be expected to lay in their short-term reactivity, as well as in the change that these inorganic additives induce in environmental conditions such as salinity, redox potential and pH value. In contrast, inorganic species that are *naturally* present in the formation water of many shales are reported to bring heavy metals[24, 84, 85]and natural radioactivity[21, 86] into HF wastewater, and formation water may often have a higher salt content than typical HF fluids[87-89]. With regard to inorganic species, formation waters can, therefore, be expected to be of equal or even greater concern compared to the HF fluid itself.

Table 3. Most frequently reported inorganic compounds (inert, reactive, insoluble, soluble). n.r.: not representative; n.i.: not included. A more comprehensive list of compounds together with physicochemical data is given in the S.I.

Inert Inorganic Compounds

Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Inorganic Soluble Salts			36.8	n.r.	48290	122	
Sodium chloride	Breaker	HpH BREAKER (Halliburton): Breaker; FR-3 (Nalco): Friction Reducer (with distillates/Acrylamide/ethoxylated alcohols); VICON NF BREAKER (Halliburton): Breaker (w/ Sodium chlorite); BXL-3 (FTSI): Crosslinker (mix includes borate)	21.3	n.i.	27503	48	7647-14-5, 76471-41-5
Sodium iodide			0.05	n.i.	2081	0	7681-82-5
Sodium sulfate	Ion Strength Control	Borate XL Delayed High Temp (BXL03) (FTSI): Crosslinker Agent (with Borate/Potassium Formate/NaCl/Silica); GST 530 Green Field Energy Services): Gel Stabilizer (with water/Sodium Sulfite/Thiosulfate)	2.4	n.i.	6066	7	7757-82-6
Potassium chloride	Ion Strength Control, Clay Stabilizer	WBK-143L (WFT): Breaker (with Sodium chlorite); pHaserFrac (Halliburton): Carrier (no mix); CS-03 (Agri-Emppresa): Clay Stabilizer (no mix);	5.2	n.i.	3626	29	7447-40-7
Magnesium chloride	Ion Strength Control	X-Cide 207 (Baker Hughes): Biocide (with isothiazolinones/quartz/MgNO3); CS-12 (Shrieve Chem Prod): Clay Control (with Choline Chloride/ NaCl/ KCl/ water)	0.77	n.i.	1579	4	7786-30-3
Magnesium nitrate		X-Cide 207 (Baker Hughes): Biocide (with isothiazolinones/quartz/MgCl); X-Cide 207 (BHI) Biocide (same mix);	0.53	n.i.	1435	5	10377-60-3
Calcium chloride	Ion Strength Control	Scaletrol 720 (Baker Hughes): Scale Inhibitor (with ethylene glycol); Lease Water (Operator): Base Fluid (with water/NaCl); Calcium Chloride (Baker Hughes): Salts (with KCl/NaCl);	2.3	n.i.	3556	17	10043-52-4
Insoluble Oxides			n.r.	n.r.	116904	443	
Iron oxides	Proppant	Super LC 20/40 (2.51 sg) (WFT): Proppant (Phenol/Formaldehyde Resin with Quartz/Silica/Iron Oxide/Hexamethylenetetramine); Frac Sand (Lewis): Proppant (Same Mix); Pacific MidProp (Sanjel): Proppant	n.i.	n.i.	2727	25	1332-37-2, 1309-37-1, 76774-74-8,
Aluminum oxides	Proppant	PREMIUM PROP PLUS (Halliburton): Proppant (w/ Crystallline silica); Frac Sand Lewis Proppant (with Quartz/Iron Oxide/Titanium Oxide); Sand (Proppant) (CWS): Propping Agent (in Corundum form (CAS 1302-74-5) with Mullite);	n.i	n.i.	3869	77	1344-28-1, 1302-74-5, 90669-62-8, 1302-44-56
Titanium oxides	Proppant	Ceramic Proppant (Sanjel): Proppant (Rutile); Ceramic Proppant (OWS) Proppant Ceramic (with other minerals: Cristobalite SiO2;Corundum Al2O3, Mullite); Pacific MidProp (Sanjel): Proppant	n.i	n.i.	2593	21	1317-80-2, 13463-67-7, 98084-96-9
SiO_2 (Quartz, Cristobalite, Silica Sand, partly microcrystalline)	Proppant	Sand, Tempered, H 30/50 (FTSI): Proppant; Ceramic Proppant (Sanjel): Proppant; CERAMIC PROP (Halliburton): Proppant (with Mullite); Ceramic Proppant (OWS): Proppant Ceramic (with Mullite); ValuProp (proppant); Sand (Proppant) (Carmeuse): Proppant, 30/50 Brown (Unim): Proppant; Econoprop, 20/40 Baker Hughes Proppant (with Mullite)	22.7 (only partly included)	n.i.	107370	315	7631-86-9, 148-60-7, 14464-46-1, 14464-46-4, 14808-60-7, 308075-07-2, 75-20-7, 15468-32-3, 1317-95-9, 112926-00-8, 99439-28-8, 112945-52-5, 69012-64-2, 60676-86-0
Silicates And Clay Minerals			3.8	n.r.	12624	131	
Aluminum silicate (mullite)	Proppant	CERAMIC PROP (Halliburton): Proppant (with Cristobalite); Versalite (Halliburton): Proppant; ShaleProp Imerys Proppant (with Cristobalite/Amorphous silica); VersaLite (Saint-Gobain): Proppant;	0.01	n.i.	4060	93	1302-76-7, 1302-93-8, 1327-36-2, 839-20-3, 1305-75-5

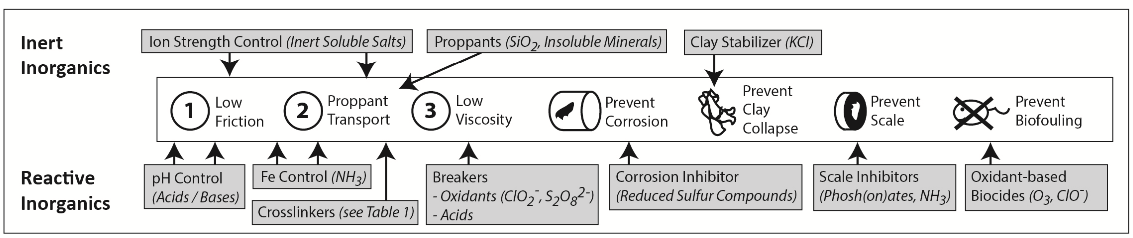
Reactive Inorganic Compounds: Reductants, Oxidants, Acids, Bases, Complexing Agents

Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Inorganic Reducing			5.4	n.i.	5279	39	
Sodium thiosulfates	Temp. Stabilizer	GEL-STA L STABILIZER (Halliburton): Stabilizer (no mix); Ecopol-HTSL (RockPile Energy): Temperature Stabilizer (with water); GST 530 Green Field Energy Services): Gel Stabilizer (with water/Sodium Sulfite/Sodium Sulfate)	4.9	n.i.	2387	13	7772-98-7, 10102-17-7
Sodium bisulfite & metabisulfite		ScaleSorb 7 (Baker Hughes): Defoamers (w/ Organophosphorous salts/ Quartz/ NaCl/Sodium Formaldehyde Bisulfite); ScaleSorb 7 (50lb) (Baker Hughes): Scale Inhibitor (w/ water/Sodium Sulfonate); Super 100 NE (NCPS): Surfactants & Foamers (w/ Epichlorohydrin/Monoethanolamine/Glycol Ether/Ethoxylated Alcohols/ Ammonium salts/Naphthalene/etc);	0.06	n.i.	1580	7	7631-90-5, 7681-57-4
Ammonium bisulfite	Oxygen Scavenger	SS-5075 (Multi-Chem): Oxygen Savenger (no mix); Techni-Hib 604 (Baker Hughes): Oxygen Scavenger (with water/nickel chelate catalyst proprietary)	0.48	n.i.	458	15	10192-30-0
Inorganic Oxidizing			77.0	n.i.	58328	110	
Hydrogen peroxide	Breaker	FBK-XPA Frac Specialists Polymer Breaker (with Phosphoric Acid/ Water/ Solvent/Dye Direct Red 2610-11-9); Plexgel XPA (Chemplex): Breaker (no mix);	2.0	n.i.	1158	4	7722-84-1
Magnesium peroxide Calcium peroxide	Breaker	GBW-23L (Baker Hughes): Breaker (with distillates, MgO); BR-37 (CJES): Gel Breaker (with CaCO3, CaOH, Mineral Oil); Plexgel Breaker: HTC Chemplex Breaker (with Alcohol Ethoxylate/Clay/Distillates);	3.2	n.i.	2485	11	1335-26-8, 14452-57-4, 1305-79-9
Sodium perborates	Breaker	FRB-704 (FRAC-CHEM): Friction Reducer Breaker (with Sodium metaborate); GBO-1 (Trican): Breaker; Optikleen (Halliburton): Breaker;	6.9	n.i.	5379	6	1113-47-9, 7632 -04-4, 10486-00-7, 447-63-2, 10332-33-9
Ammonium peroxidisulfate	Breaker	OPTIFLO-II DELAYED RELEASE BREAKER (Halliburton): Breaker (w quartz); EGB-16LT (Fritz Industries, Inc.): Breaker (w quartz);	27.2	n.i.	26456	37	7727-54-0
Sodium persulfate	Breaker	SP BREAKER (Halliburton): Breaker; WBO 2 (Trican Well Service Ltd.): Breaker;	9.3	n.i.	8073	6	7775-27-1
Sodium hypochlorite	Breaker, Biocide	BE-7™ (Halliburton): Biocide (with NaOH); Sodium Hypochlorite (Universal): BIOCIDES (no mix);	0.08	n.i.	3983	14	7681-52-9
Sodium chlorite	Breaker	WBK-143L (WFT): Breaker (with KCl); VICON NF BREAKER (Halliburton): Breaker (with NaCl);	14.0	n.i.	8486	8	7758-19-2
Stabilized aqueous chlorine dioxide	Biocide	3rd Party Biocide (Bosque) Biocide (no mix); Bosque ClO2 (Bosque Systems, LLC): Biocide (no mix); C102 (Bosque Disposal Systems, LLC): Oxidizer (no mix)	1.1	n.i.	555	1	10049-04-4
Sodium bromate	Breaker	OB-3 (Pro-Stim): Oxidizing breaker; Breaker J481 (Schlumberger): Breaker;	2.8	n.i.	1451	10	7789-38-0
Ozone	Biocide	Ozone (Ecosphere): Microbial Control	1.4	n.i.	211	0	10028-15-6

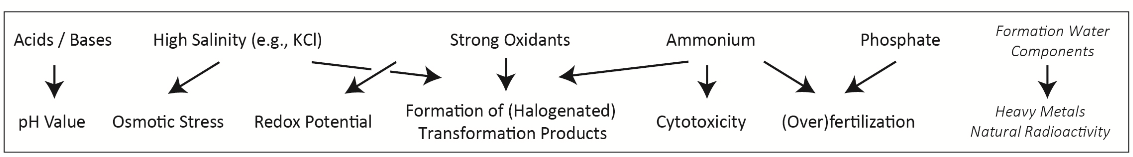
Reactive Inorganic Compounds: Reductants, Oxidants, Acids, Bases, Complexing Agents (continued)

Chemical	Function	Examples of Reported Commercial Products	No. of Declarations Sky Truth	No. of Declarations Waxman	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	CAS -Number
Inorganic Acids			**47457**	**99**	**80.2**	**n.r.**	
Hydrogen chloride (Hydrochloric acid)	pH Control	Payzone 214 SI (Catalyst Oilfield Services): Scale Inhibitor; Acid, Hydrochloric 15pct (SCHLUMBERGER): Acid	41020	42	72.8	n.i.	7647-01-0, 6747-01-0, 7732-18-5
Hydrogen fluoride	Corrosive acid		210	2	0.75	n.i.	7664-39-3
Phosphoric acid + salts	Scale Inhibitor	S-644 (Aegis Chem.): Scale Inhibitor (with HCl); SI-115 (Clearwater): Scale Inhibitor	1742	9	1.2	0.07	7664-38-2, 10294-56-1, 10361-65-6, 22042-96-2
Phosphonic acid	Scale inhibitor	ScaleSorb 3, (25# pail)(Baker Hughes): Scale Inhibitor (with Amino Alkyl Phosphonic Acid proprietary / SiO2/Diatomaceous Earth);	2938	5	2.4	n.i.	129828-36-0, 13598-36-2
Inorganic Bases			**56760**	**193**	**64.4**	**n.i.**	
Sodium hydroxide (Caustic soda)	pH Control	MO-67 (Halliburton): pH Control Additive; XLW-10A Baker Hughes Crosslinker (with Sodium Tetraborate/Ethylene Glycol);	25435	80	27.4	n.i.	1310-73-2, 95077-05-7
Sodium bicarbonate	pH Control		1303	10	0.12	n.i.	144-55-8
Potassium hydroxide	pH Control	BF-9L (Baker Hughes): Buffer (w/ K2CO3); CL-31 CROSSLINKER (Halliburton): Crosslinker (w/ metaborate), WPB-584L (WFT): ph Adjust. Agents (w/ K2CO3)	18562	25	16.8	n.i.	1310-58-3
Potassium carbonate	pH Control	BF-9L (Baker Hughes): Buffer (with KOH); BA-40L BUFFERING AGENT (Halliburton): Buffer	7428	12	12.7	n.i.	584-08-7
Magnesium oxide	pH Control, Breaker	TBK-53 (Economy Polymers): Breaker (w/ Mineral Oil/MgOH/MgPeroxide/ Sorbitan Trioleate/Propylene Carbonate)	1268	18	3.3	n.i.	1309-48-4
Ammonia and Ammonium Salts			**18375**	**49**	**19.7**	**n.r.**	
Ammonium chloride	pH Control, Complexing Agent	FERCHEK A REDUCING AGENT (Halliburton): Iron Reducing Agent; FRW-200 (FTSI) Friction reducer (with acrylamide/ ethoxylated alcohols); CL-23 (Halliburton): Crosslinker (with Zirconium-Acetat-Lactat-Komplex);	11832	30	14.6	n.i.	12125-02-9
Ammonia, Ammonium hydroxide	Complexing Agent, Scale Inhibitor,	WSI-3601 (Sabre): Scale Inhibitor; AS-290 (Reef) Anti-Sludge Additive; ISIW-302 (Impact): Scale Inhibitor; Ferrotrol 280L (Baker Hughes): Iron Control (with Mercaptoethanol/Cupric Chloride)	2052	11	1.6	n.i.	7664-41-7, 1336-21-6
Ammonium Sulfate	Friction Reducer	ASP 900 (Nalco): Friction Reducer	1190	0	1.1	n.i.	7783-20-2

Functions in the Hydraulic Fracturing Process (Summary)



Potential Concerns (Examples)



Besides the concerns of high salinity, heavy metals and radioactivity, the expected processes when components of HF fluids and substances from the formation are brought together is an important consideration. From a biological point of view, microbial communities are affected by strong oxidants, while the simultaneous presence of ammonium, phosphate and high DOM may cause eutrophic conditions in the HF wastewater. In addition, ammonium features cytotoxic effects[90], as reported for plants (Britto[91] and references therein), bacteria[90], humans[92] and fish where acute LC_{50} values can start at 2 mg/L [93]. From a chemical point of view, experience from oxidative water treatment shows that the application of oxidants in highly saline water [94] – some of them even consisting of reactive chlorine species (NaClO, $NaClO_2$) – can form problematic halogenated organics ("disinfection by-products") [35]. Considering that most formation waters are highly saline, and that, on average, four out of five HF operations apply strong oxidants (see Table 3) the possibility of similar by-product formation must also be considered in the course of HF operations.

Since many of the inorganic HF additives are either inert solids (proppants) or chemicals of immediate reactivity (acids, bases), not many of them are likely candidates as tracers for hydraulic fracturing activities. However, the effect of salinity, acids / bases and oxidants / reductants can easily be captured by inexpensive monitoring for hydraulic conductivity, pH and redox potential. Such basic measurements are, therefore, attractive as an early indicator of potential HF impacts on groundwater. To further confirm the presence of formation water, additional measurements may target radioactivity, organic compounds by GC / LC-based methods, and screens for geogenic heavy metals by ICP-MS (inductively coupled plasma-mass spectrometry).

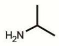
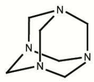
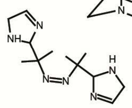
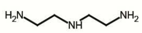
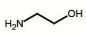
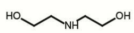
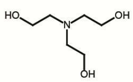
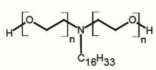
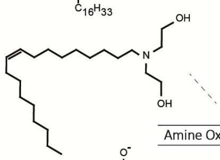
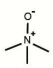
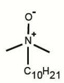
4. Amines and Quaternary Ammonium / Phosphonium Salts

Chemical Properties Relevant in the HF Process. Table 4 shows that, though some amines are used as *solvents* (isopropylamine) and *surfactants* (ethoxylated fatty amines), the main use of amines relates to the *buildup and crosslink control* of polymers. Hexamethylenetetramine (HMT) – the most frequently reported compound – is used as crosslinker in phenolic resins for proppant coating (see "Phenol / Formaldehyde / Epoxy Polymers" entry in Table 1) and it greatly enhances the performance of propargyl alcohol as corrosion inhibitor[59]. Diethylenetriamine, as well as mono-, di- and triethanolamine, are reported as crosslink control and activators of crosslinking. This indicates that they are used as complexing agents of Zr^{IV} in order to control the rate and timing of guar gum crosslinking. Since they are also reported as breakers, ethanolamines appear to be able to shift the crosslinking equilibrium in *both* directions, thereby enabling a reversibility in the scheme “Metal Ions as Crosslinkers” in Table 1 that would otherwise not be possible and which lends these substances their property as breakers. Table 4 further includes 2,2’-azobis-2-(imidazolin-2-yl)-propane dihydrochloride, a radical initiator for polymerization, even though this compound was reported only twice. This substance may either be an impurity of applied polymers, left as a radical initiator of the polymerization process, or used to initiate *in situ* radical polymerization directly in the HF process, for example to enable slow gel formation at elevated temperatures (see, e.g. [95], chapter 8). The second interpretation would be consistent with the disclosure of acrylate and acrylamide monomers in Table 1.

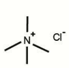
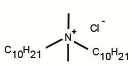
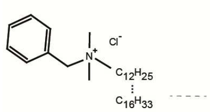
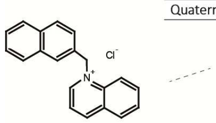
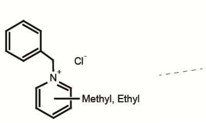
The low number of hits for amine oxides, finally, – which are typical surfactants in VES applications [96-98] – confirms our earlier conclusion that viscoelatic surfactant-based fracks seem to play a minor role in comparison to gel or slickwater fracks.

Table 4. Most frequently reported amines and quaternary ammonium and phosphonium salts. Henry’s law constants and log Koc constants are taken from EPI Suite[71], degradation half-lives from ref. 44. A more comprehensive list of compounds together with physicochemical data is given in the S.I.

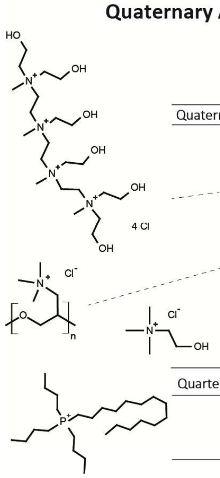
Amines and Alkoxylated Amines

Structure	Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
	Mono- and Polyamines			16.7	22.8	12979	85	
	Isopropylamine	Solvent	PAS-C (Reef): Asphaltene/Paraffin Solvent	n.i.	0.64	282	1	75-31-0
	Hexamethylene-tetramine	Crosslinker (for Coating)	CRS PP, 40/70 mesh (Baker Hughes): Proppant (with quartz and phenolic resin); hardener (forms methylene and dimethylene amino bridges in Novolac resins)	12.6	11.8	8203	37	100-97-0
	2,2`-Azobis-2-(imidazolin-2-yl)-propane dihydro-chloride	Radical Initiator	Synonym: 2,2'-(Azobis(1-methylethylidene))bis(4,5-dihydro-1H-imidazole) dihydrochloride)	n.i.	0.002	2	0	27776-21-2
	Diethylenetri-amine	Complexing Agent, En-hancer (Gel Formation)	CAT-4 (Halliburton): Activator;	2.2	2.8	1466	2	111-40-0
	Aminoalcohols			8.9	15.4	7279	68	
	Monoethanol-amine	Crosslinker	WXL-105L (WFT): Crosslink Control, CL-142 (CESI): Crosslinker	2.4	2.3	1574	17	141-43-5, 9007-33-4
	Diethanolamine (2,2-imino-diethanol)	Surfactant, Crosslinker, Breaker	NE-1 (Universal): De-Emulsifier; BC-1 (Benchmark): Breaker; WRS-3 (Universal): Surfactants	0.57	5.2	2318	14	111-42-2
	Triethanolamine (2,2,2-nitrilotriethanol)	Crosslinker, Breaker	XLW-14 (Baker Hughes): Crosslinker (with n-propyl zirconate and propyl alcohol; BC-1 (Benchmark): Breaker (with diethanolamine)	4.2	5.6	2479	21	102-71-6
	Alkoxylated Amines			0.63	5.6	4608	9	
	Ethoxylated hydrogenated tallow alkylamines	Surfactant	Synonym: Amines, tallow alkyl, ethoxylated	0.02	3.8	1976	2	61791-26-2, 61790-82-7
	Amines, coco alkyl, ethoxylated	Surfactant		n.i.	2.0	1969	0	61791-14-8
	Ethoxylated oleyl amine	Surfactant	WFR-3B (Nabors Completion and Production Services): Friction Reducer (with Distillates/Ethoxylated alcohols);	0.58	n.i.	551	3	13127-82-7, 26635-93-8
	Amine Oxides			0.08	1.5	1250	11	
	Trimethylamine, N-oxide	Surfactant		n.i.	0.52	452	0	1184-78-7
	Decyldimethyl amine oxide	Surfactant	Slickwater, YF125FlexD (Schlumberger)	n.i.	0.03	768	4	2605-79-0

Quaternary Ammonium and Phosphonium Salts

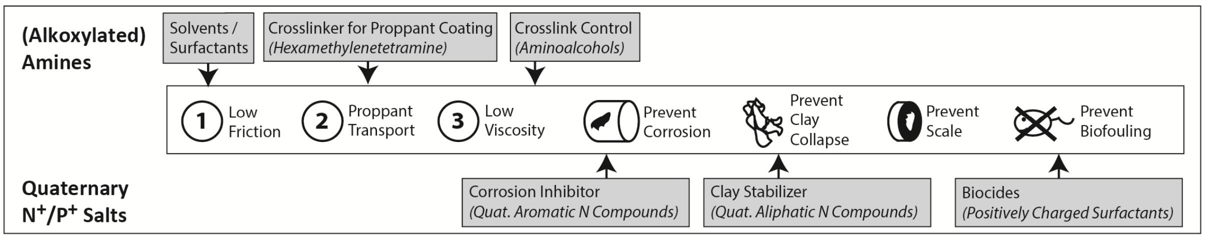
Structure	Chemical	Function	Examples of Reported Commercial Products	EPA Eval.	Rogers et al.	Sky Truth	Waxman	CAS -Number
	Quarternary Aliphatic Ammonium Salts			49.4	43.3	28287	65	
	Tetramethyl ammonium chloride	Clay Stabilizer	CS-16 Benchmark Energy Products, L.P.): Clay Control/ Stabilizers (with water); CT1206 F&L Blend (Pioneer Natural Resources Pumping Services LLC): Non-Emulsifier (with Oxyalkylated alcohols proprietary);	5.1	8.2	4349	14	75-57-0
	Didecyl dimethyl ammonium chloride	Biocide	ALPHA 1427 Baker Petrolite Biocide (with Glutaraldehyde/Ethanol/Quaternary ammonium com-pound); MC B-8626 Multi-Chem Biocide (similar mix);	12.2	9.3	4109	1	7173-51-5
	Bis Hydrogenated Tallow Alkyl Dimethyl Salts with Bentonite	Clay Stabilizer	e.g., Bentonite, benzyl (hydrogenated tallow alkyl) dimethylammonium stearate complex (CAS-No. 121888-68-4, 2327 hits)	0.30	n,i.	4165	0	68953-58-2
	Alkyl (C12-16) dimethyl benzyl ammonium chloride	Biocide	Alpha 114, 260 gl tote (Baker Hughes): Biocide (with Glutaraldehyde); Antimicrobial 220 (Frac-Chem): Bacteria Control (with Glutaraldehyde/Ethanol/Didecyl dimethyl ammonium chloride);	19.5	13.2	6882	7	68424-85-1
	Quaternary N-heterocyclic Ammonium Salt			14.0	7.0	5101	26	
	Chloromethyl-naphthalene qui-noline quaternary amine	Corrosion Inhibitor	HAI-404M™ Halliburton Corrosion Inhibitor (with Methanol/Aldehyde proprietary/Isopropanol/Quat proprietary);	7.8	4.6	2434	3	15619-48-4
	Tar bases, quino-line derivatives, benzyl chloride-quaternized	Corrosion Inhibitor	WAI-251LC (WFT): Acid Corrosion Inhibitor (w Ethylene Glycol/ N,N-Dimethylformamide/ Cinnamaldehyde/2-Butoxyethanol/ 1-Decanol/ 1-Octanol/ Isopropanol/ Poly(oxy-1,2-ethanediyl),α-(4-nonylphenyl)-ω-hydroxy)	4.3	n.i.	1797	5	72480-70-7
	Pyridinium, 1-(phenylmethyl)-, ethyl methyl, chlorides	Corrosion Inhibitor, Clay Stabilizer	Acid Inhibitor 445 (RSI): Acid Corrosion Inhibitor; Shale Guard 469 (Smart Chemical Services): Clay Stabilizer (with Methanol); TCA-6038 (SWN Well Services): Corrosion Inhibitor (Methyl alcohol);	1.2	0.9	390	9	68909-18-2

Quaternary Ammonium and Phosphonium Salts (continued)

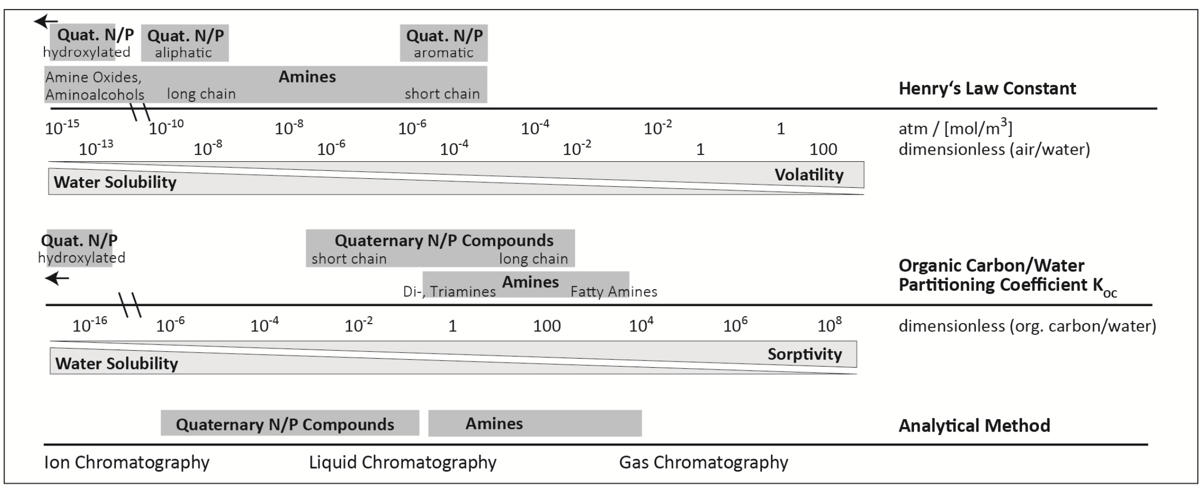


Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Quaternary Ammonium salt - Hydroxyalkylated			16.1	1.6	9035	8	
1,2-Ethanediaminium, (N,N'-bis-[2[bis(2-hydroxy-ethyl)methylammonio]-ethyl] -N,N'-bis (2-hydroxyethyl)-N,N'-dimethyl-) tetrachloride	Clay Stabilizer	Clay Master-5C (Baker Hughes): Clay Control; CLAY MASTER-5C (BAKER HUGHES): Clay Stabilizer;	1.2	0.76	1112	2	138879-94-4
Polyepichlorohydrin, trimethyl-amine quaternized	Clay Stabilizer	CLA-STA XP Additive (Halliburton): Clay Stabilizer;	0.3	n.i.	962	1	51838-31-4
Choline chloride	Clay Stabilizer	TCS-302 (Economy Polymers): Clay Control (with water); ClayCare, tote (Baker Hughes): Clay Control;	14.6	n.i.	6723	3	67-48-1
Quaternary Organic Phosphonium Salt							
Tributyl tetradecyl phosphonium chloride	Surfactant, Biocide	BE-9 (Halliburton): Biocide; PH 355-G (Performance): Biocide;	6.4	7.7	5473	5	81741-28-8

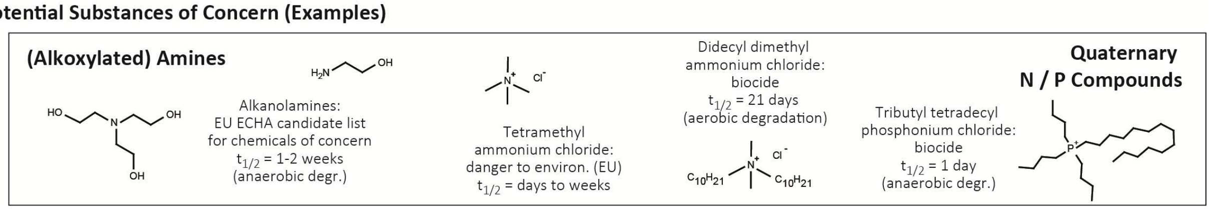
Functions in the Hydraulic Fracturing Process (Summary)



Physicochemical Properties and Analytical Methods (Overview)



Potential Substances of Concern (Examples)



In contrast to amines, quaternary ammonium salts are used as *clay stabilizers, biocides or corrosion inhibitors* (see Table 1). Clay stabilizers are necessary, because hydraulic fracturing can lead to swelling of clays resulting in the collapse of permeabilities. Short-chain quaternary ammonium salts (tetramethylammonium chloride, choline chloride) - also in oligomeric or polymeric form or as fatty acid quaternary ammonium compounds - can intercalate into clay interlayers because of their positive charge and stabilize the clay in the formation [82] (see entries in Table 4). Further, quaternary ammonium compounds with long-chain hydrophobic alkyl chains (e.g., didecyl dimethyl ammonium chloride, DDAC) are lipophilic cations. In this property, they may disrupt lipid bilayers and act as a broad spectrum biocide to prevent microbial growth [48, 99]. Finally, aromatic N-heterocyclic ammonium compounds (pyridine or quinolone-based) sorb to surfaces forming a protective layer on the well surface against strong acids in the fracturing process.

Potential Substances of Concern / Consequences for Environmental Fate and Monitoring. The substances of Table 4 are of concern either because of their acute toxicity (alkyl amines) or because of their lipophilic / cationic character that lends them biocidal properties (quaternary ammonium compounds). Of the *alkylamines*, alkanolamines [100] are more biodegradable than diethylenetriamine [101] or tertiary amines [102], and their aquatic toxicity is lower than of diethylenetriamine which is ecotoxic and a suspect teratogen. [103] Nevertheless, alkanolamines are on the ECHA candidate list of chemicals of concern in Europe[67]. *Quaternary ammonium compounds* in general can be toxic to susceptible species and moderately persistent in the environment; despite their tendency to sorption they are known to exit wastewater treatment plants and reenter the environment [104]. Tetramethyl ammonium chloride is very toxic to aquatic organisms, toxic to humans and not prone to biodegradation [105, 106 107]. In contrast, quaternary ester compounds are less toxic and more easily biodegradable [107]. Quaternium-18 Bentonite is chemically, physically, and biologically inert with little or no toxic effects [108], and choline is of very low acute toxicity, even occurring naturally in microorganisms, animals and humans [24]. These differences in toxicity indicate further potential of present-day HF operations to reduce potential environmental impacts.

Essentially all chemicals of Table 4 are not volatile. They are positively charged and, thus, water-soluble at circumneutral pH. Further, practically all compounds show a potential for sorption to organic matter (long chain amines / quaternary compounds) or into clay minerals (long and short chain quaternary compounds). If released into the environment, these compounds are, therefore, expected to stay in receiving waters where some of them may strongly sorb to sediments. Based on these properties, liquid chromatography / ion chromatography-based methods are most promising for chemical analysis. For monitoring, compounds should be targeted that are indicative, relevant, potentially persistent and not strongly retained. Based on these criteria, tetramethylammonium and short-chain akyl/alkanol amines are likely candidates.

5. Organic Acids, Esters and Amides

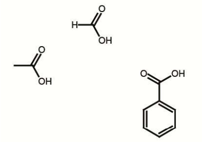
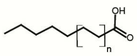
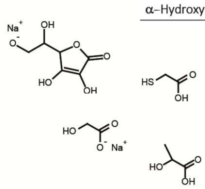
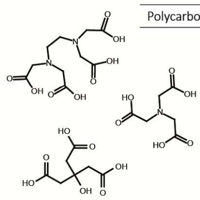
Chemical Properties Relevant in the HF Process. Table 5 lists frequently reported organic acids (carboxylic, sulfonic/sulfuric, phosphonic/phosphoric) including esters and amides. While the distinguishing feature of carboxylic acids is their -COOH group, the rest of the molecule determines their function in the HF process. Short-chain carboxylic acids like formic and acetic acid are reported to serve as *pH control*, while the hydrophobic tail of long-chain fatty acids or sulfonates enables them to form protective surface layers as *corrosion inhibitors* on surfaces and lends them properties as negatively charged surfactants. Also carboxylic amides and esters are primarily reported as *solvents and surfactants* (fatty acid esters and diethanolamides) and *friction reducers* (sulfamic acid). Specifically, even though formamide and dimethylformamide are reported in corrosion inhibitor products, they actually represent inert solvents for the contained active additives of Figure 3 [109]. Cocamidopropyl betaines - typical viscoelastic surfactants – are reported in only relatively small number. Table 5 further illustrates that the presence of additional –OH, –COOH or $–PO_3H$ groups in compounds such as erythorbic acid, lactic acid, glycolic acid, citric acid, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) or aminotrimethylenephosphonic acid lends these substances properties as *complexing agents*. On the one hand, they can bind Zr^{IV} and Fe^{III} to avoid premature crosslinking, ("crosslinker", "iron control"), on the other hand they form complexes with Ca^{2+} or other geogenic cations to prevent precipitates ("*scale inhibitors*").

A less obvious function of organic acids and esters is indicated for benzoic acid, which is reported to serve as *diverting agent*, alongside with such different chemical substances as phthalate esters (Table 5), paraffin (Table 2) or collagen (Table 1). These diverting agents are used as *water-soluble plugs* ("perf ball = perforation ball sealers")[110] to seal conductivities in order to divert the fluid to other parts of the target zone[111]. These sealers are used to minimize fluid loss into the formation and to enable multi-stage HF[112]. Their common feature is a solid, waxy consistency which poses a physical resistance to the fracking pressure, yet allows their gradual dissolution.

Finally, acids are expected to play a crucial role also as *breakers*, by reversing borate-based crosslinking (see Table 1). Considering that optimized hydraulic fracturing requires an exact timing of crosslinking and breaking, much industry research is reported [59, 113, 114] to focus on *delayed crosslinkers and breakers* - substances that are added to the original hydraulic fracturing fluid, but develop their action only at a given time after injection. Since such information is likely proprietary, Table 5 may not give the full picture of available acids. In this context, the following compounds of Table 5 are interesting even though they do not rank among most frequently reported additives: acetyltriethyl citrate ("breaker"), di-(2-ethylhexyl)phthalate ("diverter"), diesters of sulfosuccinic acid ("scale inhibitors") and triethyl phosphate ("corrosion inhibitor"). These substances have in common that hydrolysis of their ester bonds converts them into active compounds. The importance of such "masked" additives becomes clear when considering that the effect of breakers can be a mixed blessing in the course of the HF process. Citrate is beneficial when it complexes metal ions in order to break crosslinks (see Scheme in Table 1), but it may be detrimental if the breaking occurs too early so that fluid loss occurs into the formation and proppants are not well transported. Elsewhere, in a similar strategy, polyglycolic acid is reported to serve as a retarded acid [59] for delayed breakage of borate crosslinks.

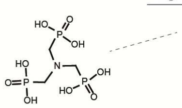
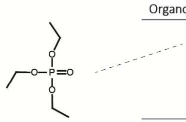
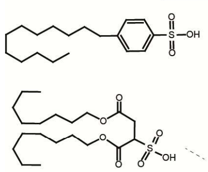
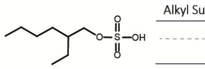
Table 5. Most frequently reported organic acids, amides and esters. Henry's law constants and log Koc constants are taken from EPI Suite [71]. A more comprehensive list of compounds together with physicochemical data is given in the S.I.

Carboxylic Acids

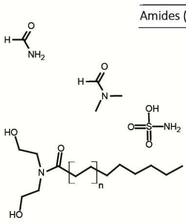
Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Monocarboxylic acids			51.0	75.0	38968	114	
Formic acid	pH Control	BF-55L (BAKER HUGHES): BUFFER; applied for (e.g.): XLBHT-2 (Nabors Completion and Production Services): Cross-linkers; DAP-925 (CalFrac): Corrosion Inhibitor;	12.5	12.4	5671	24	64-18-6
Acetic acid	pH Control	BA-20 BUFFERING AGENT (Halliburton): Buffer (w acetate); Acetic Anhydride Blend, (BAKER HUGHES): ACIDIZING; AIC (Archer): Liquid Acid Iron Control;	21.0	31.7	17788	56	64-19-7
Benzoic acid	Diverting Agent	TLC-80 (Halliburton): Diverter; Benzoic Acid Flakes (Eastman): Diverter; WDA-220 (WFT): Diverting Agents;	0.04	0.27	51	11	65-85-0
Fatty Acids			7.7	11.8	4211	14	
Tall oil acids	Corrosion Inhibitor	CI-27 (Baker Hughes): Corrosion Inhibitor	5.4	7.0	3520	4	61790-12-3
α–Hydroxy / α-Thio / α-Keto Monocarboxylic acids			10.4	20.2	8901	27	
Sodium erythorbate	Complexing Agent	L058 (Schlumberger): Iron Stabilizer; FERCHEK FERRIC IRON INHIBITOR (Halliburton): Iron Reducing Agent;	9.2	7.2	3783	4	6381-77-7
Thioglycolic acid	Corrosion Inhibitor Component	Acid Inhibtor 445 (RSI): Acid Corrosion Inhibitor; MSA-III US (Halliburton): Corrosion Inhibitor (with isopropanol, ethoxylated alkyl amines)	0.29	1.9	855	6	68-11-1
Sodium glycolate	Complexing Agent	VERSENE* Powder Chelating Agent (Pioneer Natural Resources Pumping Services LLC): Scale Inhibitor (with EDTA and other polyacetates, NaOH);	0.27	7.4	2321	2	2836-32-0
Lactic acid	Crosslink Control	CL-41 (Halliburton): Crosslinker (with inorganic salt)	0.29	2.0	242	4	10326-41-7, 50-21-5
Polycarboxylic Acids			39.7	34.4	23214	82	
EDTA + sodium salts	Complexing Agent, Scale Inhibitor	Versene * Powder Chelating Agent (Pioneer Natural Resources): Scale Inhibitor; EDTA-ACID (Univar): Iron Control;	4.5	5.9	4268	6	139-33-3, 6381-92-6, 60-00-4, 150-38-9, 64-02-8
Nitrilotriacetic acid + sodium salts	Complexing Agent	TIC-608 (Economy Polymers): Iron Control; FE-11 (Chemplex): Sequesterant; VERSENE* Powder Chelating Agent (Pioneer Natural Resources Pumping Services LLC): Scale Inhibitor (with EDTA);	5.7	0.82	3441	23	139-13-9, 18662-53-8, 5064-31-3
Citric acid	Complexing Agent	Ferriplex 66 (Chemplex): Iron Control ; FEAC-20 (Trican Well Service): Iron Control (with Acetic Acid);	28.5	23.4	13392	29	77-92-9

Organo Phosph(on)ates and Sulf(on)ates

Organo Phosphonates			1.1	2.8	1496	20	
Amino trimethylene phosphonic acid (+ salts)	Complexing Agent, Scale Inhibitor	Pro-Hib 312 (Performance Chemicals): Scale Inhibitor; TSC-6755 (Xchem): Scale Inhibitor	0.78	1.4	1122	3	6419-19-8, 2235-43-0
Bishexamethylenetri-amine penta methy-lene phosphonic acid	Complexing Agent, Scale Inhibitor	SI-1 (Universal): scale converters, solvents, and inhibitors	n.i.	1.2	232	1	35657-77-3, 34690-00-1
Organo Phosphates			4.7	4.2	2811	26	
Triethyl phosphate	Corrosion Inhibitor, Solvent	Acid Inhibitor 3M (AI-3M) (Nabors Completion and Production Services): Acid Corrosion Inhibitors; WAI-251LC (WFT) Inhibitor	4.4	3.0	1634	1	78-40-0
Triethanolamine polyphosphate ester	Scale Inhibitor	KSIW-624 (Pioneer Natural Resources Pumping Services LLC): Scale Inhibitor;	n.i.	n.i.	757	3	68131-71-5
Organo Sulfonates			4.8	21.3	7840	62	
Dodecylbenzene sulfonic acid	Surfactant, Scale Inhibitor	NE-100 (FRAC TECH): NON-EMULSIFIER; NE-100 (FTSI INC.): Non-emulsifier (with 2-Butoxyethanol /2-Propanol); PLEXSURF WRS-A (CHEMPLEX): SURFACTANT (w methanol / nonionic fluorosurfactant)	3.0	9.6	3435	24	27176-87-0, 42615-29-2, 68648-81-7, 90218-35-2, 26264-06-2
Dodecylbenzenesul-fonic acid, mono-ethanolamine salt	Surfactant, Scale Inhibitor	WNE-363L (WFT): Surfactant (with Ethylene Propylene Oxide Polymer/ 2-Ethylhexanol/Poly-(oxy-1,2-ethanediyl), α-isotridecyl-ω-hydroxy-)	0.95	1.5	725	1	26836-07-7
Diester of Sulfosuccinic Acid, Sodium Salt		e.g., Dioctyl sodium sulfosuccinate (CAS-No. 577-11-7, 181 hits)	n.i.	1.1	403	0	2673-22-5
Alkyl Sulfates			0.92	1.17	452	10	
Sodium 2-ethylhexyl sulfate	surfactant	D-2 (Sanjel): Surfactant; OWS-DMF-A (WST): Demulsifier (with water/2-Ethylhexanol);	0.37	0.35	80	1	126-92-1

Carboxylic Amides and Esters



Amides (Inorganic, Short- & Long-chain Alkyl)			14136	36	15.9	24.9	
Formamide	Solvent	CI-350 HT (FTSI): Corrosion Inhibitor (with quaternary ammonium salts, alkoxylated phenol, etc.)	606	5	2.2	1.4	75-12-7
Dimethyl formamide	Solvent	Acid Corrosion Inhibitor - Mid Temp to High (Cationic) (Weatherford): Corrosion Inhibitor; Acid Inhibitor;	4705	5	11.2	9.1	68-12-2
Sulfamic acid	Friction Reducer	SURF 660 (ChemRock Technologies): Flow Aid	909	6	1.6	n.i.	5329-14-6
Coconut fatty acid diethanolamide	Surfactant	NE-1 (Universal): Non-Emulsifier and De-Emulsifiers;	1274	1	0.44	4.6	68603-42-9
Tall oil acid diethanolamide			4933	1	n.i.	5.8	68155-20-4, 68092-28-4
Acrylamide: see Table 1							

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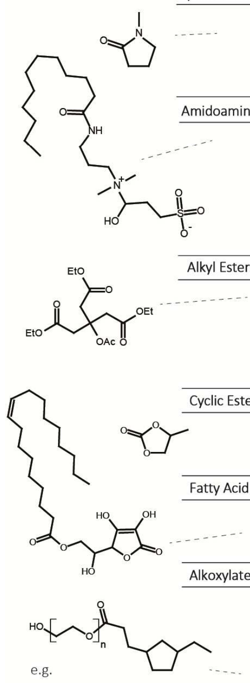
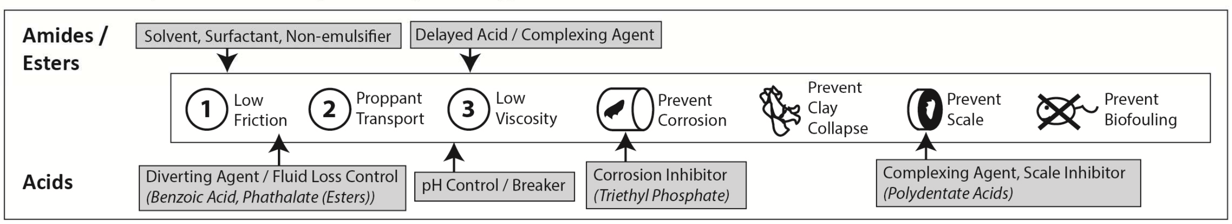
Carboxylic Amides and Esters (continued)

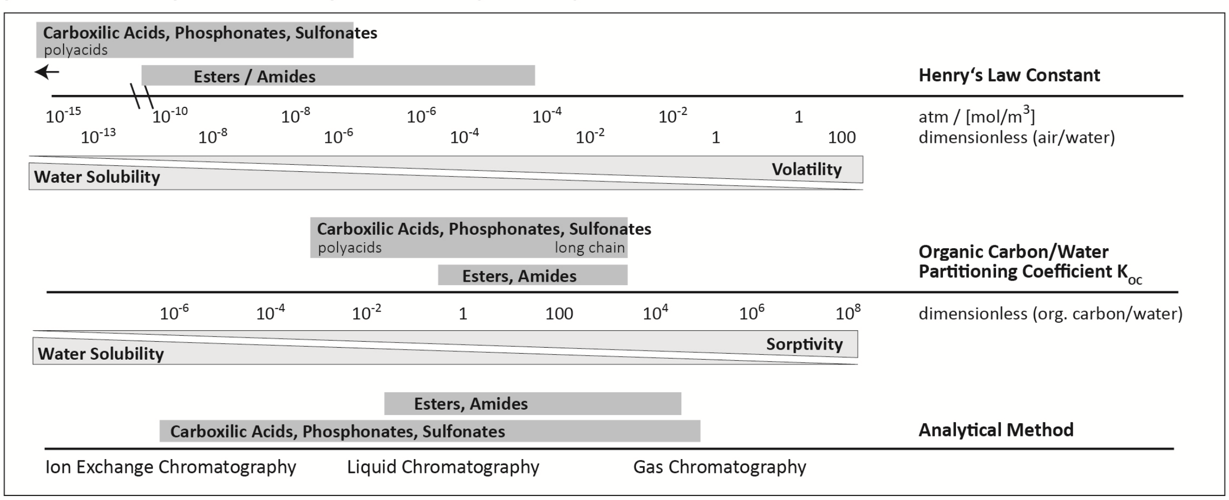


Chemical	Function	Examples of Reported Commercial Products	No. of Declarations Sky Truth	No. of Declarations Waxman	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	CAS -Number
Cyclic Amides			245	2	0.67	0.59	
n-Methylpyrrolidone	Solvent, Surfactant	Super-Flo RPM (Nabors Completion & Production Services Co.): Solvent-Surfactant	101	1	n.i.	0.32	872-50-4
N-dodecyl-2-pyrrolidone	Solvent, Surfactant	FRS 51 (Weatherford): Non-Emulsifier	144	1	0.67	0.27	2687-96-9
Amidoamines			572	13	0.49	0.76	
N-cocoamidopropyl-N,N-dimethyl-N-2-hydroxypropyl sulfobetaine	Surfactant, Corrosion Inhibitor	CAS-1 (Sanjel): Surfactant - Acid Inhibitor; WFM-463LZ (WFT): Foaming Agent (with 2-Butoxyethanol / Isoproyl alcohol/Cocoamidopropyl betaine);	245	1	0.32	0.63	68139-30-0
Cocamidopropyl dimethylamine	Surfactant		138	1	0.12	0.02	68140-01-2
Alkyl Esters			1056	25	0.38	2.1	
Acetyltriethyl citrate	Solvent, Breaker	Enzyme G-1 and BC-3 (Baker Hughes): Breaker and Catalyst	352	1	n.i.	0.67	77-89-4
Di (2-ethylhexyl) phthalate	Diverter	Perf Balls RCN 7/8 inch 1.3 SG (Nabors Completion and Production Services): Diverting Agents (with Phthalic Anhydride/Zinc Oxide);	3	3	n.i.	0.004	117-81-7
Cyclic Esters			1469	3	0.08	3.7	
Propylene carbonate	Solvent	Synonym: 1,3-dioxolan-2-one, methyl-	1469	2	0.08	3.7	108-32-7
Fatty Acid Esters			8736	8	3.9	23.1	
Sorbitan monooleate	Surfactant, Friction Reducer	FRW-15A, tote (Baker Hughes) Friction Reducer;	7393	1	3.7	20.7	1338-43-8
Alkoxylated Esters			10209	11	1.4	26.1	
Sorbitan monooleate polyoxyethylene derivative			5077	0	0.05	12.6	9005-65-6
Diethylene glycol ethyl ether acetate		Superset-U, tote (Baker Hughes): Activator;	310	4	0.15	0.34	112-15-2
Naphthenic acid ethoxylate			2181	0	n.i.	3.9	68410-62-8

Functions in the Hydraulic Fracturing Process (Summary)



Physicochemical Properties and Analytical Methods (Overview)



Potential Substances of Concern / Consequences for Environmental Fate and Monitoring. Most substances of Table 5 are not primarily of concern because of their inherent toxicity, but they may become problematic because their molecular design allows them to undergo specific reactions. Complexing agents are of concern due to their potential persistence and chelating effect which may cause mobilization of metals [115], among them potentially geogenic radioactive elements. Table 5 shows a variety of substances with different environmental persistence. Whereas erythorbic acid, citric acid, lactic acid or NTA are non-toxic and readily biodegradable[116], EDTA is significantly more persistent [117, 118]. Phosphonates are even more persistent, but show strong sorption and, hence, low concentrations in aqueous solution [119]. Sulfonic acids are generally of low toxicity, but poor biodegradability [120]. Among the diverters, finally, phthalate esters have received attention as problematic plasticizers in childrens' toys due to their gonadal toxicity and hormone-active effects [121, 122]. In oligotrophic or low oxygen environments, phthalate esters can remain in the environment up to several months [123]. In addition to these disclosed substances, proprietary substances of presently unknown structure potentially serve as retarded acids, bases or complexing agents, as discussed above. These substances are likely important for environmental assessments because, by definition, they are *designed* to be transformed in the subsurface, bringing about a potential for as yet unknown transformation products.

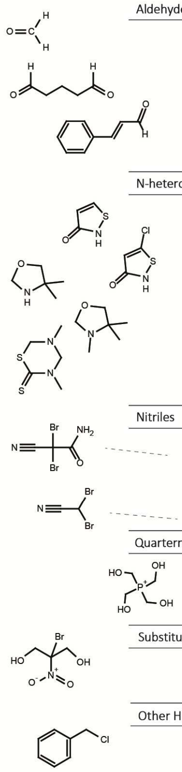
Table 5 illustrates that most disclosed organic acids, esters and amides have low volatility, but high water-solubility. With the exception of phosph(on)ates, which strongly sorb to mineral surfaces[124], these compounds are, hence, expected to be mobile when present in groundwater. They are, therefore, of interest both because of their environmental fate and because they may be potential indicator substances of hydraulic fracturing activities. While esters, amides and monocarboxylic acids may be analyzed by either gas chromatography or liquid chromatography-based methods, polycarboxilic acids are less volatile so that liquid chromatography or ion exchange chromatography are preferable. In addition, because polydentate acids can complex heavy metals, analysis by LC-MS/MS (liquid chromatography-tandem mass spectrometry) may be complemented by inorganic analysis by LC-ICP-MS (liquid chromatography-inductively coupled plasma-mass spectrometry). Finally, as discussed above, the possibility exists that some ester structures are proprietary, because they represent "hidden" delayed acids or complexing agents. This raises a particular need for non-target analysis: to detect, on the one hand, relevant non-disclosed compounds and to discover, on the other hand, potential transformation products of environmental relevance [125].

6. Electrophilic Compounds

Chemical Properties Relevant in the HF Process. Electrophilic compounds can form covalent bonds to nucleophiles like sulfur, nitrogen or oxygen-based species. They, therefore, act as alkylating agents. Besides the electrophiles in Table 6, some monomers listed in Tables 1 and 2, such as acrylamide, acrylate, epichlorohydrin or propargyl alcohol, also belong to this compound class. Table 6 illustrates that electrophilic properties are used in different ways. Benzyl chloride is used as *in situ* alkylation agent to ensure complete quaternization of N-heterocyclic compounds for improved corrosion inhibition (see Table 4). Cinnamaldehyde and other monomers of Tables 1 and 2 serve as monomers for polymerization. The majority of disclosed electrophilic compounds in Table 6, however, are applied as biocides. Their use, environmental fate and toxicity have recently been treated in an excellent comprehensive review [48]. The toxicity of electrophilic biocides relies on their reaction with –SH or $–NH_2$ groups in amino acids. Specifically, the C=O double bond in aldehydes (glutaraldehyde) reacts with $–NH_2$ groups to form diamine crosslinks which lead to protein coagulation[126]. C-Br bonds in DBNPA undergo rapid reaction with –SH groups of cysteine or glutathione[127] so that proteins are damaged. The same is true for the P atom in tris(hydroxymethyl)phosphine which is formed from THPS in alkaline solution[127]. These reactions have in common that their toxic action can affect different microorganisms in the same way leading to broad band specificity. In this function compounds are tailored to meet both the need for sufficient reactivity and rapid (bio)degradation, and the need for a sufficient persistence to support their toxic action. Short-lived biocides are suitable to kill sulfate-reducing bacteria during the HF process and, thus, to avoid corrosion by hydrogen sulfide (biofouling). In contrast, more persistent biocides are needed to sustainably prevent the growth of microorganisms so that pipes are not clogged during gas production (bioclogging)[128]. This different design is reflected in the half-lives of the different compounds as illustrated in the selection of compounds of potential concern at the bottom of Table 6.

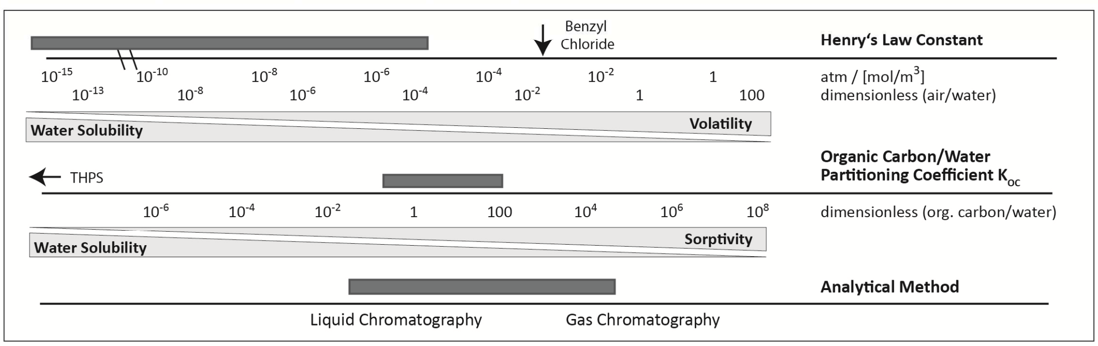
Table 6. Most frequently reported electrophilic compounds. Henry's law constants and log Koc constants are taken from EPI Suite[71], degradation half-lives from ref. 44. A more comprehensive list of compounds together with physicochemical data is given in the S.I.

Electrophilic Compounds

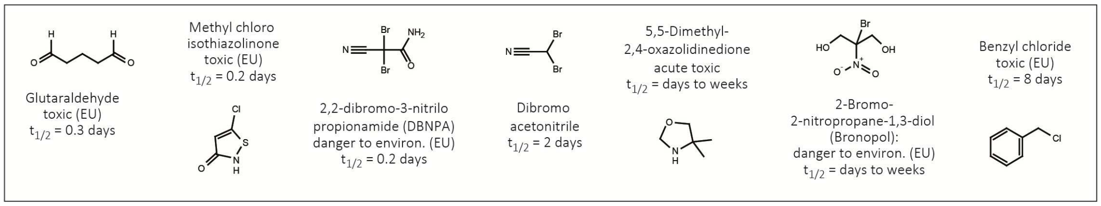


Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations SkyTruth	No. of Declarations Waxman	CAS -Number
Aldehydes and Ketones			41.3	52.5	25753	60	
Formaldehyde, Paraformaldehyde	Gel Forming Agent, Biocide	TCI-653LC (Economy Polymers): Corrosion Inhibitor (w Methanol/ Fatty Acids/ Polyoxyalkylenes/ Modified thiourea polymer/ Propargyl alcohol/ Olefin/ NaCl);	2.2	9.0	3625	12	50-00-0, 30525-89-4
Glutaraldehyde	Biocide	Alpha 1427 (BHI): Biocide; K-139 Biocide (Champion): Biocide; MC B-8642 (MULTI-CHEM): BIOCIDE;	33.2	33.3	17196	20	111-30-8
Cinnamaldehyde	Corrosion Inhibitor	Acid Inhibitor 3M (AI-3M) (Nabors Completion and Production): Acid Inhibitor	5.2	4.8	2280	5	104-55-2
N-heterocycles			8.3	15.7	7383	27	
2-methyl-4-isothiazolin-3-one	Biocide	X-Cide 207 (Baker Hughes): Biocide	0.53	1.2	1412	4	2682-20-4
5-chloro-2-methyl-4-isothiazolin-3-one	Biocide	X-Cide 207 (Baker Hughes): Biocide	0.52	1.2	1410	5	26172-55-4
4,4-Dimethyloxazolidine	Biocide	MC B-8520 (Multichem): Antibacterial Agent	1.8	1.9	761	0	51200-87-4
3,4,4-Trimethyloxazolodine	Biocide	MC B-8520 (Multichem): Antibacterial Agent	1.8	1.9	761	0	75673-43-7
Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione	Biocide	BIO-8 (Universal): Biocides	3.5	6.1	2268	13	533-74-4
Nitriles			26.2	24.4	12051	33	
2,2-dibromo-3-nitrilopropionamide	Biocide	Frac-Cide 1000 (BHI): Biocide Synonym: DBNPA	21.6	18.3	9181	27	10222-01-2
2-monobromo-3-nitrilopropionamide	Biocide	BE-3S BACTERICIDE (Halliburton): Biocide	3.3	2.1	1528	1	1113-55-9
Dibromoacetonitrile	Biocide	AQUCAR DB 20 (Dow): Biocide	2.3	4.0	1342	1	3252-43-5
Quarternary Organic Phosphonium Salt							
Tetrakis (hydroxymethyl) phosphonium sulfate (THPS)	Biocide	Alpha 452 (Baker Hughes): Biocide;	9.7	9.5	5408	12	55566-30-8
Substituted Propanols			4.6	3.9	2983	4	
2-Bromo-2-nitropropane-1,3-diol	Biocide	BE-6 MICROBIOCIDE (Halliburton): Biocide Synonym: Bronopol	2.7	2.0	2220	4	52-51-7
Other Halogenated Hydrocarbons			7.5	7.4	3185	9	
Benzyl chloride	Corrosion Inhibitor	AS-52C (CESI) ANTI-SLUDGE (Mix); CI-31 (Baker Hughes) Corrosion Inhibitor	7.4	5.8	2785	8	100-44-7

Physicochemical Properties and Analytical Methods (Overview)



Potential Substances of Concern (Examples)



Substances of Concern / Consequences for Environmental Fate and Monitoring.

Electrophiles are, by definition, of potential concern because they may serve as alkylating agents of proteins and DNA and are, therefore, *designed* to have an adverse effect on organisms. Whether they are problematic in the long run is determined by their persistence. For example, even though glutaraldehyde (to the left in the box of Table 6) is highly toxic, it is highly biodegradable so that it is commonly considered an environmentally friendly biocide[128]. In contrast, compounds with longer half-lives (to the right of the box in Table 6) are more persistent. However, even if parent compounds are broken down, the properties of transformation products must also be considered. For example, 2,2-dibromo, 3-nitrilo propionamide (DBNPA) can form dibromoacetonitrile, which is a more toxic and more persistent biocide than DBNPA itself [129-132].

With the exception of benzyl chloride, the compounds of Table 6 are not volatile and they are all water soluble. Because of their toxicity they are also relevant for environmental monitoring, even though some are short-lived and may not be detected long after a HF operation. Based on their physicochemical parameters, they can be targeted by a combination of liquid chromatography and gas chromatography.

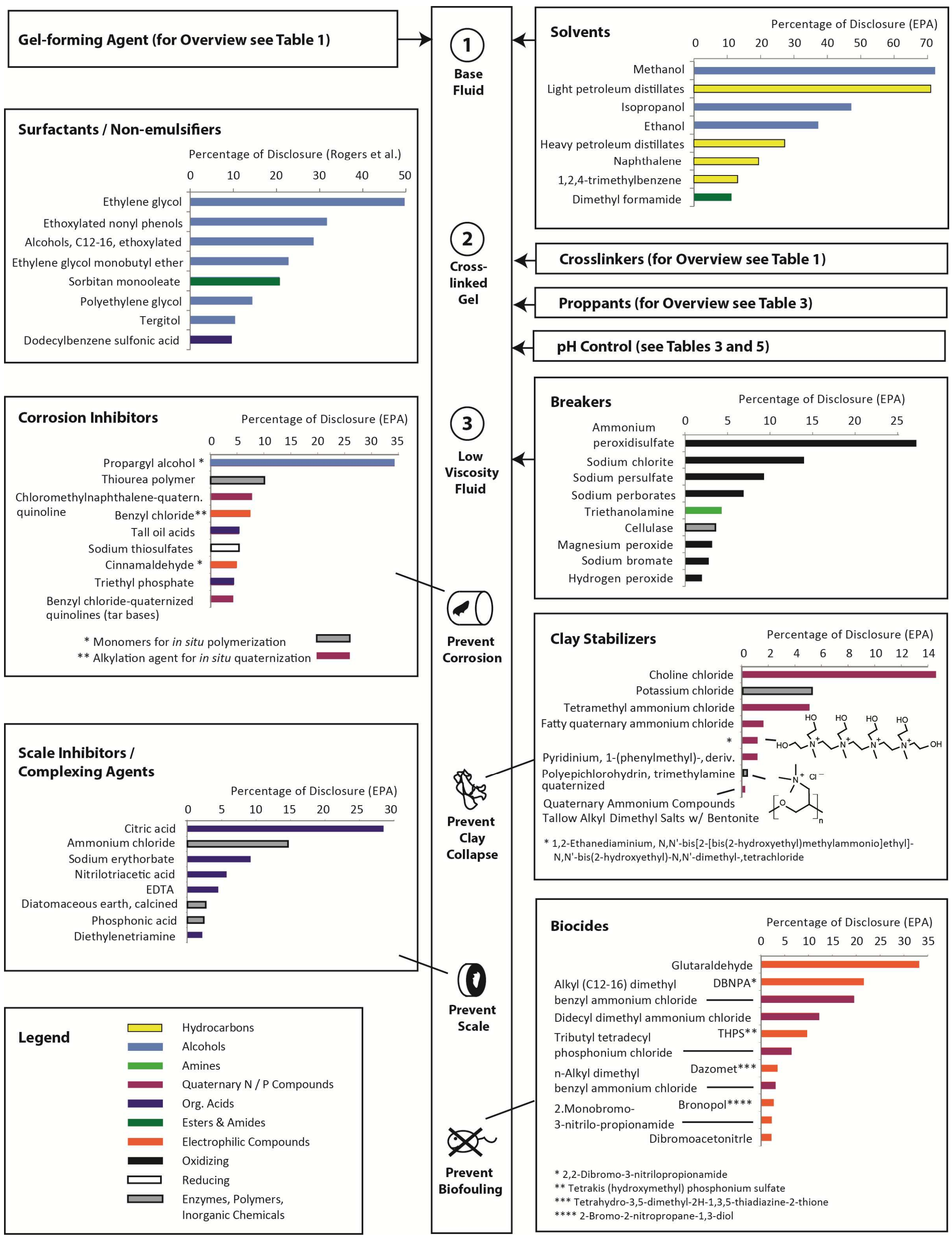


Figure 3. Ranking of chemicals that may be expected in an average HF operation, based on number of disclosures on FracFocus (as evaluated by EPA (ref. 43) and Rogers et al. (ref. 44))

Typical Chemicals of an "Average" HF Operation

Even though it is frequently stated that hundreds of HF chemicals exist, and that general conclusions are difficult because the choice of substances is site-dependent, our overview shows that some general patterns nevertheless emerge with regard to the use and chemical structure of additives. We may, therefore, consider what chemicals are disclosed in an "average" HF operation (Figure 3). *Gel-forming Agents.* One fourth to 50% of all operations relies on guar gum, whereas specific acrylamides / -acrylates are disclosed in only 10% of the cases (Table 1). *Solvents.* Practically every operation relies on a combination of methanol, isopropanol, ethanol and petroleum distillates to bring gel and crosslinkers into solution. *Surfactants/Non-emulsifiers.* Most frequently disclosed compounds are ethylene glycol derivatives, whereas the share of disclosed fatty acid derivatives (sorbitan monooleate, about 20%) and sulfonic acids (about 10%) is minor. Ethoxylated nonylphenols and Tergitol, which may be degraded to problematic nonlyphenol, are disclosed in a remarkable 50% of all operations. *Crosslinkers.* Borate and Zr are reported in 30% or all operations, in a proportion of about 2:1. Other compounds are marginal. *Breakers.* On average, more than 50% of all operations report oxidation agents as breakers such as peroxodisulfate, persulfate, perborate or chlorite. Acids may also function as breakers, but do not show up in this ranking, since they are typically reported as pH control. Disclosures of other substances (triethanolamine, cellulase) are below 5% for each additive. *Corrosion Inhibitors.* The vast majority of disclosures – i.e., every third operation - relies on toxic and highly reactive propargyl alcohol, followed by thiourea polymer and quaternized N-heterocyclic (quinoline-based) derivatives (each about 10%). Tall oil acids, inorganic thiosulfate and triethyl phosphate account for about 5% each. *Clay Stabilizers.* This functional class is reported in only a fraction of operations. Non-problematic choline chloride dominates (about 15% of all operations), followed by KCl and toxic tetramethylammonium chloride (each 5%). *Scale Inhibitors/Complexing Agents.* Biodegradable agents dominate: citric acid (30% of all operations), ammonia (15%), erythorbate (10%) and nitrilotriacetic acid (5%). Persistent EDTA was disclosed in only about 5%, and inorganic phosphonic acid in about 3% of all operations. *Biocides.* Electrophilic biocides (orange bars) are more frequently disclosed than quaternary N/P compounds (pink bars) and oxidants (see chlorite under "Breakers"). Biodegradable glutaraldehyde (over 30%) dominates, but also more persistent DBNPA (about 20%) and quaternary ammonium compounds such as didecyl dimethyl ammonium chloride (about 10%) are frequent.

The ranking of Figure 3 may now be compared to a summary of HF chemicals that is provided on the FracFocus website itself (https://fracfocus.org/chemical-use/what-chemicals-are-used, accessed on 17th of Dec 2015). The summary there does not provide quantitative information in terms of disclosures, but claims to contain the chemicals used most often, and it provides an alphabetical list where chemicals are grouped by function. While many compounds agree, several important (and most frequent) chemicals are missing, among them some of the most problematic substances: ethoxylated nonylphenols, propargyl alcohol, DBNPA, sodium chlorite, potassium chloride and ammonium. The critical evaluation of Figure 3, therefore, illustrates the importance of this present overview, since available lists may not be complete, and it suggests that the use of HF chemicals may presently not yet be optimized for potential environmental impacts. Potentially problematic compounds continue to be used, even though environmentally friendly alternatives may exist. Aromatic hydrocarbons and petroleum distillates may serve as example. They are substances of toxicological concern, but are nonetheless used in practically every HF operation. The question arises whether these compounds are truly indispensable and represent the best choice of solvent. (For example, guar gum likely dissolves equally well in more polar, less toxic organic solvents.) A possible explanation is that these substances may have been developed for HF of oil reservoirs – where their use seems intuitive, given that the same aromatic hydrocarbons are already present in the formation – and that these blends may simply have been adapted to the exploitation of gas resources without looking for alternatives. A telling indication is the fact that even though diesel was the one explicit additive that still required an underground injection control (UIC) permit when the US congress exempted all other additives from the Safe Drinking Water Act ("SDWA"), in 2005 [133], diesel was still heavily used between 2005 and 2009 [134]. After three congress members put a particular focus on this additive in 2011 [134], the use of diesel was discontinued in subsequent years: Table 2 shows that the Waxman List discloses that no less than 51 HF products with diesel before 2009, whereas less than 0.2% of all operations used this additive after 2011. An open, constructive discussion about HF additives and equally effective alternatives may, therefore, play a catalytic role in steering industry design towards more environmentally friendly HF additives[128]. Such a discussion must in addition not only consider *how often* a HF chemical was used (as discussed here) but also *in what quantities / concentrations*. This aspect is not covered by this review, but a comprehensive survey in a recent EPA report[43] is easily available for further considerations.

Environmental Significance

Our review offers a systematic overview of what has been a daunting number of reported hydraulic fracturing chemicals. By classifying compounds according to their chemical structure, meaningful subsets were obtained which allow extracting recurrent features, critically assessing hydraulic fracturing chemical use and discussing alternatives. Combining this information with first insight on flowback composition [32, 69, 78, 86, 135-138], we can attempt to summarize potential impacts on human and ecosystem health and derive consequences for monitoring schemes. Further, we attempt to consider what chemicals may be of relevance that are *not* yet contained in disclosed lists, what consequences this has for future disclosure by operators and what research needs this brings about in environmental chemistry.

Impacts on human and ecosystem health. To assess toxicological impacts in the course of HF operations, two exposure scenarios are particularly relevant: occupational exposure of workers and long-term exposure in the environment. For occupational safety our review identifies a number of substances of particular concern based on their acute toxicity. Electrophilic monomers that are used for polymerization such as propargyl alcohol are expected to have the highest acute toxicity and carcinogenicity. Also biocides may show effects even at low concentrations. Microcrystalline silica is carcinogenic on inhalation (Table 3). Petroleum hydrocarbons, citrus terpenes, alcohols (methanol, isopropanol, Table 2) or alkylamines (Table 4) are toxic and volatile so that their exposure may also be relevant for nearby residents. Strong oxidants (Table 3), borate (Table 1) tetramethyl ammonium chloride (Table 4) or sodium metabisulfite (Table 3) can also become hazardous when handled inappropriately.

For environmental exposure, on the other hand, our review identifies relevant chemicals based on their ecotoxicity and persistence. Biocides stand out, because they are designed to have an adverse effect on organisms. N-heterocyclic corrosion inhibitors (Table 4) have a structure related to some biocides and are expected to show a similar toxicity and persistence. Tetramethyl ammonium chloride and alkyl amines are additional problematic N-containing compounds (Table 4), whereas petroleum hydrocarbons (Table 2) are well-known, notorious groundwater pollutants. Nonylphenols are endocrine disruptors which can be formed by degradation of ethoxylated nonylphenols (Table 2). Finally, recent publications on geogenic substances [78, 85, 86, 139-141] suggest that aromatic hydrocarbons, mercury, arsenic, heavy metals and radioactive elements can surface with the formation water and that they may be more toxic than the actual HF additives themselves [24]. Together with the elevated salinity of formation water, they pose as yet unresolved challenges to wastewater treatment. Even though much interest is currently directed at HF additives, it is therefore essential that also such geogenic substances are considered, since they will play a crucial role in research efforts to minimize environmental impacts of hydraulic fracturing.

Consequences for monitoring schemes / chemical analysis. For air monitoring [7], our survey suggests that volatile hydrocarbons (Table 2) are most relevant, possibly together with volatile halogenated hydrocarbons as potential transformation products [35]. Practically all other reported HF additives are highly water soluble and / or non-volatile. For water monitoring, analyses of methane concentrations and $^{13}C/^{12}C$ ratios – in combination with ethane and propane concentrations and noble gas isotope ratios – have previously been brought forward as strategy to characterize sources of abiogenic methane close to fracturing operations [142-144]. To detect not only gases, but to also trace fracturing fluids and formation water, additional measurements of salinity, lithium and boron isotope values have been recommended [36, 145]. Our survey suggests that such monitoring schemes could be complemented with organic indicator substances, which – when detected together – may provide a chemical fingerprint of HF activities: (aromatic) hydrocarbons (Table 2), (nonyl)phenols, (polyalkoxylated) alcohols (Table 2), (polyalkoxylated) amines (Table 4), quaternary ammonium compounds (Table 4), complexes of metal ions with complexing agents (Table 5), biocides (Table 6) and different sorts of surfactants (Tables 2, 4, 5). In particular, analysis of the relative proportion of easily degradable compounds (polyalkoxylated alcohols and amines, certain complexing agents and surfactants) versus persistent substances (certain hydrocarbons, nonylphenols, tetramethylammonium, EDTA) may give information about the age of the flowback fluid, and the potential for natural attenuation. Indeed, first investigations of flowback [135, 146, 147], produced water [69, 78, 136], residual gas wastewater [138, 148] and contaminated groundwater [149] consistently report detection of aliphatic and aromatic hydrocarbons, further putative detects of (nonyl)phenols [78, 147], fatty acid and amine surfactants [78], phosphate esters [136], polyalkoxylated alcohols [32, 78, 138], butoxyethanol [149], chlorinated hydrocarbons [136, 146] and phthalate esters [78, 136, 147]. These initial reports give a promising glimpse on the potential of chemical fingerprints as tracers of HF activities. Further careful investigations will be necessary to confirm these findings in a larger number of studies including more locations, and applying high resolution analytical methods (regarding both, peak resolution and mass resolution) with confidence assignments to pinpoint the chemical identity of putative detections.

Potential for additional chemicals of relevance. Based on our assessment we furthermore postulate that the lists of compounds from FracFocus and the Waxman report are not sufficient for environmental assessments. Instead, additional compounds may be relevant which are presently not disclosed or even known. *(i) Not disclosed.* As discussed above, some of the substances which are currently claimed proprietary are likely designed to form active agents *in situ* by deprotection reactions. Because of this built-in reactivity the substances are by definition relevant for environmental assessments, even if they are not toxic in the first place. *(ii) Not known.* In particular, substances of significant abiotic and biotic reactivity in the subsurface bring about the potential for new transformation products. In the case of some highly reactive and toxic monomers (propargyl alcohol, Table 2; acrylate, epichlorhydrin, Table 1) or alkylation agents (benzyl chloride, Table 6) transformations are expected to be beneficial and to result in products of lower toxicity. In contrast, degradation of alkoxylated nonylphenols (Table 2) may yield nonylphenols as persistent, problematic metabolites. Of particular concern is the possibility that halogenated hydrocarbons may be formed, because they are known as notorious groundwater contaminants from applications of high-volume industrial organohalogens such as chlorinated solvents, brominated flame retardants, etc. Our survey shows that hardly any organohalogens are reported for use in HF operations (See SI). However, halogenated hydrocarbons may be formed when strong oxidants (Figure 2) are applied to organic compounds in the presence of highly saline formation water, as recently demonstrated for oxidative treatment of hydraulic fracturing wastewater [35].

These considerations illustrate the need for two kinds of future actions. On the one hand, there is the need for environmental chemists to perform further research into the possibility of subsurface transformation reactions. Knowledge about potentially problematic substances is important for environmental assessments as well as for wastewater treatment, and the possibility exists that these compounds presently constitute a blind spot in assessments. Monitoring schemes should therefore involve non-target analysis to screen for such substances, and mechanistic hypotheses of product formation should be further investigated in laboratory experiments.

On the other hand, since reaction of proprietary compounds can form new substances of unknown structure and toxicity, a full disclosure of all HF additives is the prerequisite of this much-needed research. Indeed, initiatives in this direction are on the way – both the Secretary of Energy Advisory Board Task Force Report on FracFocus 2.0 in the U.S. [41] and a current Draft Legislation on Fracking in Germany [27] advocate the establishment of professionally maintained and easily accessible databases with *full disclosure of all* chemical hydraulic fracturing components. The present review supports these initiatives and emphasizes the need to set up a registry which facilitates a quick overview as provided in this review: what chemicals are used in what frequency, in what quantity, for what reason and what alternatives exist. Such a complete set of easily accessible information is crucial to adequately inform the public, to assess fate and toxicity of the compounds in environmental impact assessments and to initiate academic research to close urgent research gaps. As advocated in the Energy Advisory Board Task Force Report on FracFocus 2.0, the benefits of full disclosure – i.e., the possibility of raising societal acceptance by making the use of chemicals better and more transparent – may outweigh, in the long run, any intellectual property value.

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SUPPORTING INFORMATION PARAGRAPH

A complete classification of all hydraulic fracturing chemicals together with physicochemical parameters (log K_{ow}, log K_{oc}, water solubility, Henry's law constants, estimated environmental half-lives, regulatory data) and references to patents is provided as a pdf and an Excel document in the Supporting Information (Table S1). Additional information about the original sources is also provided (Table S2).

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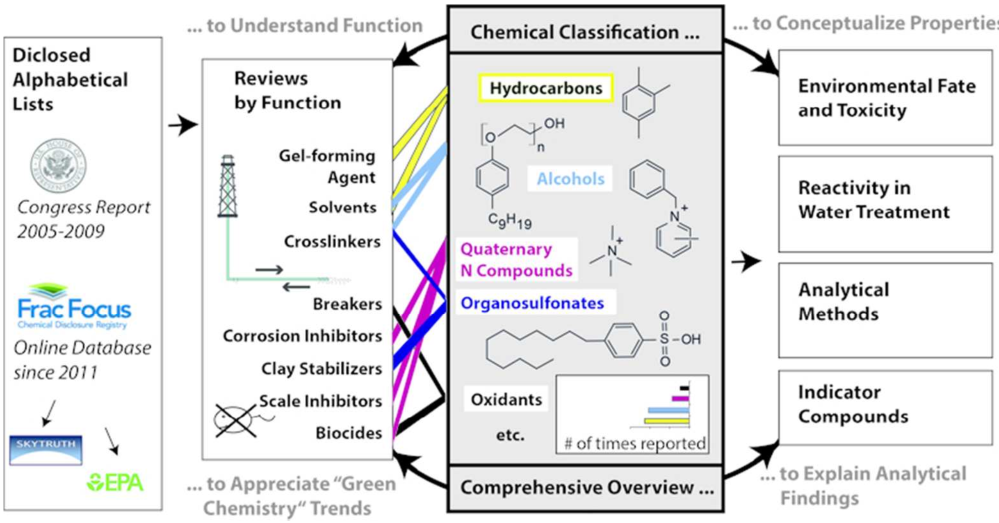

Graphical Abstract
68x35mm (300 x 300 DPI)