Hydraulic Fracturing Chemicals: Structural Classification, Detections in Flowback Water and Analytical Challenges

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Summary

The rapid expansion of unconventional -and in particular shale- gas production has not only increased the number of reported spills and accidents but also the amount of co-occurring wastewaters containing organic contaminants. So far, a comprehensive assessment of the controversially discussed hydraulic fracturing (HF) chemicals has been intricate for several reasons: Commonly, fracturing mixtures are not entirely disclosed, hampering their analysis, assessment and discussion about the used compounds and their influence to the environment. Further, prior to the presented thesis, the insight on the additives' structures and functional groups which are required for HF applications as well as the resulting potential for transformation reactions and possibly harmful metabolites has been limited. This knowledge however, is crucial for its implications for risk assessment and wastewater treatment.

Therefore, the aims of this thesis were to establish a more thorough understanding of the rationale behind the use of hydraulic fracturing chemicals and to overcome analytical challenges for their analysis in complex environmental samples.

In Chapter 2 of this thesis, a comprehensive literature-based review was compiled to surmount the obstacles which were posed by the previously available alphabetic and unstructured lists which were the basis for research work so far: With the application of this environmental chemist's approach to cluster fracturing additives after chemical structures, it was possible to link their purpose in the fracturing process to their functional chemical groups, enabling their assessment, specifically with respect to toxicity, fate, "green" chemistry use and analytical approaches.

In Chapter 3, the organic content of shale gas wastewater samples from the Fayetteville Shale (USA) was investigated with gas chromatography coupled to a mass spectrometer or flame ionization detector as well as comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC-MS, GC-FID and GC×GC-TOF-MS) measurements with strict confidence criteria. Hereby and by using the results of Chapter 2, an unprecedented degree of interpretation could be achieved: Alongside fracturing additives and distinctive geogenic compounds, several compounds were identified to be putative intended byproducts in HF applications, while others were

hypothesized to be unintended byproducts of the fracturing process. Moreover, it could be concluded that fracturing additives are less likely to be disclosed if they feature moieties that are more readily undergoing reaction processes. This is very problematic, as several of the identified compounds pose environmental or health hazards, and non-disclosure of reactive additives is restricting risk assessment of shale gas wastewaters.

To pave the way for using compound-specific isotope analysis (CSIA) at relevant concentrations, a sensitive CSIA analytical method was developed in Chapter 4, making this technique potentially amenable for fingerprinting HF compounds, but also for other micropollutants in environmental water samples. Using the model substance atrazine and its metabolite desethylatrazine, sensitivity, peak shape and matrix effects were improved substantially in comparison to previous approaches by implementing cold-on column injection and a cleanup step by preparative HPLC prior to GC-IRMS. This way, micropollutants at concentrations of sub-µg/L could be analyzed by CSIA in environmental samples for the first time.

Zusammenfassung

In den letzten Jahren fand insbesondere in den USA eine rasante Ausweitung der unkonventionellen Erdgasförderung, zumeist von Schiefergas, statt. Zusammen mit der exponentiell steigenden Fördermenge erhöhten sich sowohl Unfälle z.B. in Form von Leckagen als auch die Menge des anfallenden Abwassers, welches mit organischen Schadstoffen kontaminiert ist und zusammen mit dem Gas zur Oberfläche befördert wird. Eine umfassende Bewertung, aber auch die Analytik der für die Förderung verwendeten, kontrovers diskutierten Hydraulic Fracturing (HF)- Chemikalien war bislang erschwert, da die Zusammensetzung der Fracking-Mixturen nicht vollständig offengelegt ist und somit die Auswahl relevanter Stoffe unmöglich macht. Weiterhin waren vor dem Erscheinen dieser Dissertation die Kenntnis über die chemischen Strukturen im Kontext mit deren Funktion als Additive sowie mögliche Transformationsreaktionen und Metaboliten nie dezidierter Forschungsgegenstand.

Daher war es das Ziel der vorliegenden Dissertation, den theoretischen Kenntnisstand in Bezug auf HF - Chemikalien substanziell und tiefgehend zu verbessern und analytische Herausforderungen für deren Untersuchung in komplexen Umweltproben zu bewältigen.

In Kapitel 2 dieser Arbeit wurde eine umfassende, literaturbasierte Übersicht über Fracking-Additive in Anlehnung an ein umweltchemisches Lehrbuch zusammengestellt, was eine Alternative für die den bisherigen Forschungsarbeiten zugrunde liegenden alphabetischen Chemikalienlisten darstellt. Der gewählte Ansatz, die Chemikalien nach ihrer Struktur und Substanzklasse zu gruppieren, ermöglichte die Verknüpfung ihrer intrinsischen chemischen Charakteristika mit den für das Fracking benötigten Funktionalitäten. Somit wurde eine Diskussions- und Bewertungsgrundlage für die verwendeten Substanzen geschaffen, die auch Aspekte der Toxizität, des Umweltverbleibs, Ansätze für „grüne“ Chemie und mögliche analytische Herangehensweisen beleuchtet.

Die Untersuchung der organischen Substanzen in Schiefergasabwässern aus dem US-amerikanischen Fayetteville Shale mittels GC-MS, GC-FID und GC×GC-TOF-MS ist Gegenstand von Kapitel 3. Durch die gewählte analytische Herangehensweise und das Anwenden von strengen Konfidenzkriterien konnte erstmalig ein detaillierter und spezifischer Einblick in die Probenzusammensetzung gewonnen werden. Die mittlerweile solide Kenntnis der chemischen Strukturen und Funktionsweise von verwendeten

Additiven (Kapitel 2) erwies sich hierbei als ausschlaggebend für die Dateninterpretation: Neben Fracking-Additiven und eindeutig geogenen Substanzen konnten einige Stoffe als mutmaßlich erwünschte Transformationsprodukte des Frack-Prozesses identifiziert werden. Andere hingegen sind vermutlich unerwünschte Nebenprodukte, die keine Funktion im Fracking-Prozess ausüben, jedoch befinden sich darunter auch einige problematische Stoffe. Weiterhin wurde festgestellt, dass die Offenlegungsrate für Chemikalien geringer ist, wenn diese chemisch reaktive funktionelle Gruppen besitzen, was für eine Risikoabschätzung gerade im Hinblick auf Transformationsprodukte bedenklich ist.

In Kapitel 4 wurde eine wegbereitende Methode für die substanz-spezifische Isotopenanalytik (CSIA) von Analyten im Spurenbereich in wässrigen Umweltproben entwickelt. Diese Methode ist potentiell auf HF – Substanzen, etwa für ein Fingerprinting, aber auch auf andere Spurenschadstoffe übertragbar. Durch Etablierung einer On-Column-Injektion und eines präparativen HPLC- Aufreinigungsschrittes wurden für die Modellsubstanzen Atrazin und Desethylatrazin substantielle Verbesserungen in den Bereichen Messsensitivität, Peakform und Matrixeffekten erzielt. Auf diese Weise konnten nun erstmalig Umweltproben mit Spurenschadstoffkonzentrationen unterhalb der µg/L-Schwelle mithilfe von CSIA analysiert werden.

1

General Introduction

1.1 Background

1.1.1 Hydraulic Fracturing and Unconventional Gas: Potentials and Environmental Concerns

Hydraulic Fracturing (HF) is the technical term for stimulation of oil and gas wells in low-permeability reservoirs[1], which has been routinely performed in drilling worldwide since 1947[2]. To enhance conductivity, specially engineered fluids are pumped into the reservoir at high pressure, allowing fluids to escape via the hereby opened fractures[1-4]. Recently, the combination of two technologies, horizontal drilling together with large volume multi-stage hydraulic fracturing, has made it possible to tap unconventional natural gas, which are gas resources trapped in low-permeable coal, sandstone and shale[5.] This way, a whole new dimension of exploration was made economical, with shale holding globally 32% of the total estimated natural gas resources[6]. Technically recoverable plays were found in 137 formations in 41 other countries worldwide[7]. For Germany, these numbers range from 700×10^9 to 2.3×10^{12} m^3 [8], so 70–230 fold of the current annual production[9]. The economical but also political brisance lying in the suddenly new obtainable natural gas resources can be observed very well in the case of the United States of America: For them, the unconventional natural gas development (UNGD) has become a game-changer in terms of energy independence, as they are now the largest natural gas producer worldwide with a shale gas share of 30% and a projected growth for shale gas of 2.6% until 2040[10]. Therefore, also for many other countries worldwide, UNGD poses an attractive domestic source of primary energy.

In contrast to the economic benefits of being able to tap unconventional natural gas reservoirs, environmental concerns associated with the fracturing process have been raised. These range from land coverage[11-13], geohazards[14, 15], greenhouse gas emissions[16, 17], air pollution[18-20], stray gas contamination[21, 22], water demand[23-25], spills or accidents[26-30], water quality changes[31-34] to wastewater disposal[23, 35-40]. For several of these concerns, particular interest has been directed towards the tons of chemicals used as additives, among them harmful substances such as BTEX, Diesel, propargyl alcohol and biocides[41-43]. Within the additives, researchers were recently trying to identify indicator compounds for fracturing applications[44] or pinpoint additive substances of particular concern[45, 46]. However, for preventing risk for water resources and therefore for human and environmental health, it is crucial to have a thorough understanding of the composition of

the fracturing wastewaters not only in terms of additive appearance, but also in terms of potential metabolites stemming from additives or from geogenic compounds.

1.1.2 Principle of the Hydraulic Fracturing Process and Chemical Additive Requirements

From the vertical wellbore, drilling is continued horizontally into the gas-bearing formation, which can be very thin for shale, but needs to be at least 20m thick[47, 48]. After cementing and casing of the well, pressure tests are conducted to ensure its intactness. Then, a fracking perforating gun[3, 49] - a specialized pipe equipped with explosive charges- is introduced into the target area, to perforate casing, cement and the rock, allowing the gas to exit the bedrock. The hereby created primary fractures are hereupon propagated by high-pressure injection of fracturing fluid into the well. Most crucial for gas production is the introduction of proppant particles (mostly sand or bauxite), which keep the new fractures open, to maintain the permeability and this way also the gasflow. The fracking process may be repeated or carried out sequentially on single sections of the wellbore[49]. After the fracturing, a large part of the utilized frack-fluid together with produced water from the bedrock and dissolved gas are flowing to the surface. Here, the gaseous and liquid hydrocarbons are separated from the aqueous residues. The wastewaters are either recycled and (in part) reused or hauled for deep-well injection or treated in wastewater treatment plants[23, 35, 50].

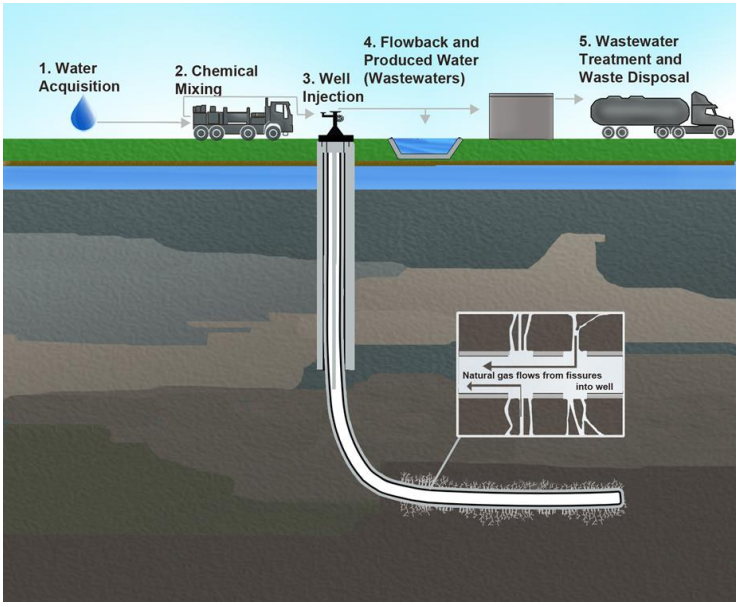


Fig. 1: Scheme of Hydraulic Fracturing principle[51]. The depicted fissures are kept open by proppants, e.g. sand or bauxite grains.

The chemical additives within the fracking fluid are required to ensure an efficient performance of the hydraulic fracturing process. Each additive component serves a specific, engineered purpose[52]: For instance, *biocides* prevent microorganism growth and reduce bio-fouling of the fractures; *oxygen scavengers* prevent corrosion of metal pipes, *acids* are used for pH control or cleanup and *clay stabilizers* prevent migration or swelling of clay layers to ensure wellbore stability.

The fracturing fluids can be composed mostly by water with few additives (*Slickwater Frack*) or rather a more complex designed viscous gel (*Linear* or *Crosslinked Gel Frack*)[53, 54], depending on reservoir depth and temperature[3] as well as on petrophysical parameters like brittleness and fracture behavior[48]. In shallow carbonaceous bedrock, fractures can be etched into the bedrock by so called acid fracturing, and also applications with foamed gels or combinations of the mentioned types are performed, but to a far less extent than the water-based fracks[53].

Every stage in a multi-stage fracturing operation requires around 1,100-2,200 m³ of water, so that the entire multi-stage operation for a single well requires around 9,000-29,000m³ [55, 56] of water and, with chemical additives of between 0.5% and 3% [45, 48, 57] by mass, which translates into 45-870t of chemical additives. Once the fracturing procedure itself is completed, the fluid returns to the surface in a process stage referred to as flowback, together with formation water of the bedrock. Amounts for the total recovered fluids typically average 10% to 25% of the injected volume, however, it may also yield over 70% or exceed the injected volume of hydraulic fracturing fluid[49, 56, 58]. The fluid returning to the surface is carrying the respective amount of additives or possibly metabolites, together with subsurface contaminants that were mobilized during the process, including organic compounds[59, 60], heavy metals[31, 61] and naturally occurring radioactive materials (NORMs)[33, 62].

1.2 State-of-the-Art and Knowledge Gaps

For a solid assessment of Hydraulic Fracturing Chemicals, currently the following aspects are not sufficiently covered: (1) A systematic overview over the chemicals which are applied in fracturing operations, (2) a larger number and more detailed studies on actually detected compounds in residual fluids of unconventional gas production and (3) the appropriate analytical approach to tackle those complex samples for gaining the desired insight. These aspects will be expounded in the following paragraphs.

1.2.1 Systematic Overview over Chemicals used in Hydraulic Fracturing

As explained in section 1.1.2, various fracturing chemicals are utilized to enhance productivity in gas development operations. The applied compounds are mostly disclosed[42, 57, 63, 64], several hundreds of compounds have been published as fracturing additives. However, some substances are subject to non-disclosure as they are either an industrial secret or they do not need to be disclosed if they contribute to less than 0.1% of the additive mixture. Therefore, it can be stated that the listings are not necessarily exhaustive.

For scientists and other stakeholders, it has been cumbersome to gain an overview over all HF additives of their interest. For studying the chemical use in hydraulic fracturing, so far the approach is mostly limited to overviews provided by alphabetic compilations provided by e.g. industrial operators, agencies or associations[57, 63-68]. Unfortunately, these lists are unsuitable for understanding (1) why certain chemicals are used, (2) whether they could possibly be replaced by less hazardous substances or (3) if they are prone to transformation reactions if you consider recycling or wastewater treatment. These aspects are also crucial for risk assessment or for design of experiments and analytical methods related to research on hydraulic fracturing. In short, there is a lack of understanding *which type* of chemical is used *for what purpose* and due to *which inherent property*.

What is so far missing is a comprehensive survey as depicted in Figure 2: A classification of the chemicals in a systematic way would help to understand function, conceptualize properties, appreciate “green chemistry” trends and explain analytical findings, all in one compendium.

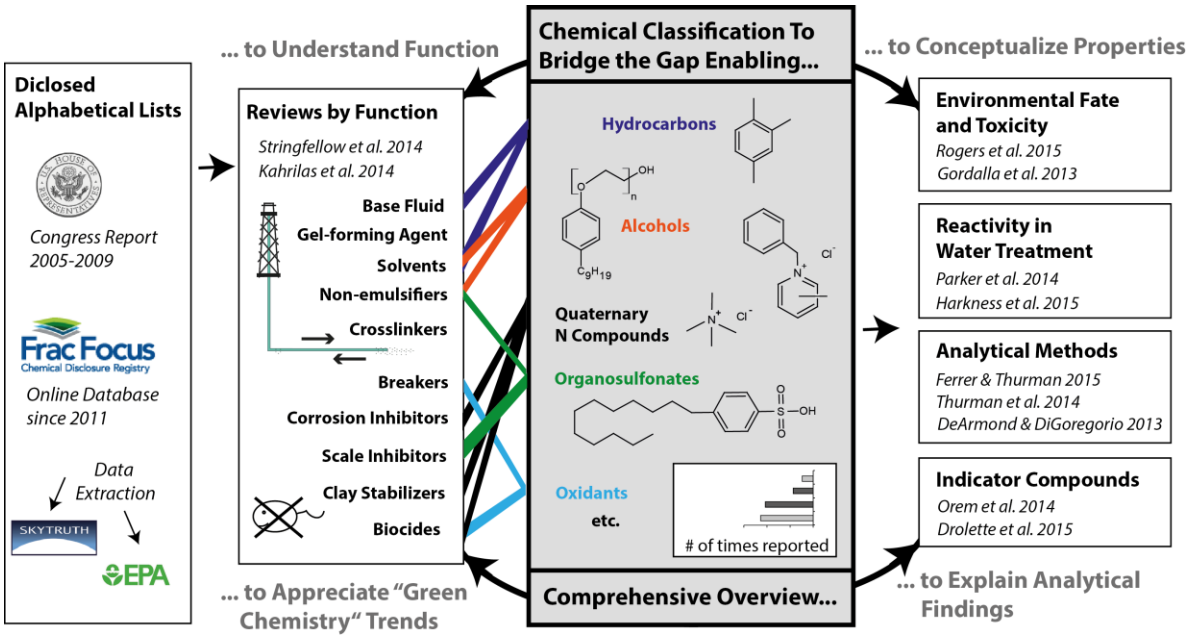


Fig. 2 Depiction of the role of a comprehensive survey (grey background) and how it is linked with existing research (boxes right and second-left) and data compilations provided from companies (left box)[69].

1.2.2 High-Resolved Insight into Complex Samples

There is a clear research need for high-resolved insight into shale gas wastewater including an adequate interpretation, because the more details on its composition are known, the better conclusions regarding environmental fate, toxicity and possible implications for treatment can be derived.

So far, field studies have mostly covered the inorganic content of hydraulic fracturing wastewaters, such as halide and alkaline earth ions, radioactive species and heavy metals[33, 36, 45, 70, 71]. In terms of analyzing organic compounds, field studies are emerging, but they differ in their analytical method and level of detail aimed at identifying specific substances. For instance, compounds likely stemming from fracturing additives, such as phenols, phthalates, or biocides, could be detected by gas chromatography-quadrupole mass spectrometry (GC-qMS)[60, 72-74]. While being a reliable tool for standard applications, GC-qMS is not apposite for non-target analysis, as it has relatively poor mass resolution and cannot uniquely identify molecular formulae in a complex matrix, as it can be expected in shale gas wastewater samples. Even more crucial, however, is the limitation in terms of interpreting compound sources and that potential metabolites are not taken into account, even though reactive conditions are given in the subsurface. A critical assessment of the implications of compound detections will help understanding

processes that geologic and additive compounds may be undergoing in the subsurface and might also have consequences for the design of the additive mixtures or wastewater treatment. In some field studies[29, 30, 59], the use of comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOF-MS) offered enhanced compound and mass resolution. However, only one of those was a wastewater study and most analyte identifications were reported as isomers and not as confirmed individual compounds. Further, no particular substances of anthropogenic origin were identified.[59] High-resolution analysis with unambiguous substance confirmation by standards has been carried out for single compounds (e.g., 2-butoxyethanol or bis(2-ethylhexyl)phthalate) in relatively pure groundwater with suspected hydraulic fracturing influence[29, 30], but not for complex shale gas wastewater samples so far.

1.2.3 Evidence to Trace Compound Origin and Fate

Tracing a compounds' origin is an important issue when it comes to contamination incidents like spills or leakages, for instance, in terms of liability claims. Isotope analysis is a unique tool creating evidence for source discrimination, as isotopic compositions for may be distinct for substances from different sources or manufacturers[75-78], see also paragraph 1.4.2.

Source tracing by isotopes has already been successfully performed following previously contented hydraulic fracturing contamination events: To gain insight on the origin of methane stray gas detections in shallow groundwater, stable isotope analysis was used as thermogenic methane (stemming from geologic processes in the deep subsurface) features a different isotope signature in comparison to biologically derived methane. In the studied region in Pennsylvania, thermogenic methane was confirmed at significantly elevated levels in proximity of active fracturing sites[22, 79], but noble gas isotopy ruled out upward migration from depth, suggesting for instance intermediate-depth gas leakage through failures in borehole annulus cement or faulty production casings[80].

Gaining insight into substances' origin and fate is naturally of high interest for hydraulic fracturing chemicals. For organic compounds, tracing sources has been intricate so far; in recent field studies, evidence for water contamination by hydraulic fracturing were given by carefully ruling out other possible pathways[29, 30]. Promising potential for additional lines of evidence lies in the application of compound specific isotope analysis (CSIA), as

it is an outstanding tool for fingerprinting sources and footprinting compound degradation and fate. Source apportion has for instance successfully been conducted for hydrocarbon mixtures via CSIA in combination with multivariate statistics[81]. Also, source discrimination for emerging micropollutants has been demonstrated[77, 78], making CSIA altogether a desirable approach in the context of hydraulic fracturing chemicals.

1.3 Analytical Challenges

The analysis of chemical compounds in the context of hydraulic fracturing poses several practical challenges. First of all, obtaining samples is difficult, as industrial operators are often not openly welcoming academic research, as they fear competitive disadvantages if proprietary compounds were published. Furthermore, the design or planning of the analyses are hindered by the fact that mixtures for fracturing operations can vary from site to site and that compounds may fall under non-disclosure agreements. Also, the applied additives may be diluted in the flowback due to the mixing with produced water or they can be masked by pronounced occurrences of geogenic compounds. As comprehensive two-dimensional gas chromatography (GC×GC) proved to be a valuable tool in oil- and other petroleum-derived samples[82-85], it was decided to address liquid-liquid-extracts of samples with this comprehensive technique. The fundamentals of GC×GC are explained in section 1.4.1.

Most crucial in compound identification is the fact, that compounds may have undergone transformation reactions, concealing the initially applied additives. As insight into transformation reactions occurring during hydraulic fracturing operations is practically non-existing, not all additives have to be disclosed and no systematic background knowledge of chemical structures was existent previous to the work presented in Chapter 2. Hence, interpretation is even more exacerbated.

For compound-specific isotope analysis (CSIA, see also section 1.4.2), in addition to obstacles mentioned above, instrumentation sensitivity may create an issue for environmental samples. Compared to GC-MS, GC-IRMS is comparatively insensitive, because the rare, heavier isotope (e.g., ^{13}C) needs to be measured with high precision so that relatively high concentrations of the total compound (e.g. around 1 nmol of carbon on-column) are required. Also, preconcentration techniques in combination with GC-IRMS are either not used routinely [86] or are problematic when matrix compounds

interfere, creating an isotope bias[87]. So far, field studies of micropollutants have been only successfully conducted for compounds at concentrations in the µg/L range[88, 89].

For bringing forward CSIA in lower environmental concentrations, field samples containing the pesticide atrazine and its metabolite desethylatrazine at high ng/L range were chosen. This way, a CSIA method for GC-amenable compounds, which are already established model compounds for interpretation of degradation pathways[90, 91], could be developed for concentrations which may be expected in cases of contamination with fracturing chemicals.

In general, environmental samples are often intricate in terms of matrix effects, which can deteriorate instrument performance or hinder the interpretation of results. For this reason, a special focus was set on clean-up and quality control during the analyses.

1.4 Instrumentation

1.4.1 Two-Dimensional Gas-Chromatography (GC×GC)

Comprehensive two-dimensional gas chromatography (GC×GC) provides enhanced peak capacity and resolution, allowing a fast detection and identification of single substances in a complex mixture[92]. In this technique, a modulator periodically collects a portion of effluent from the first column (1D) and rapidly re-injects each into the second column (2D) as a narrow band. The 2D-column typically features a stationary phase of a different polarity than the 1D-column, to reach the ideal of independent retention for an orthogonal separation[93, 94]. Also, the 2D-column is short and of narrow bore to allow complete elution during the subsequent modulation period. The instrumental setup and principle of modulation are illustrated in Figure 3. Effective modulation is mostly carried out by thermal modulation, as first reported by Liu & Phillips[95]; currently cryogenic methods produce the most narrow peaks and minimize breakthrough[96]. Commonly used detectors are FID, ECD or TOF-MS.

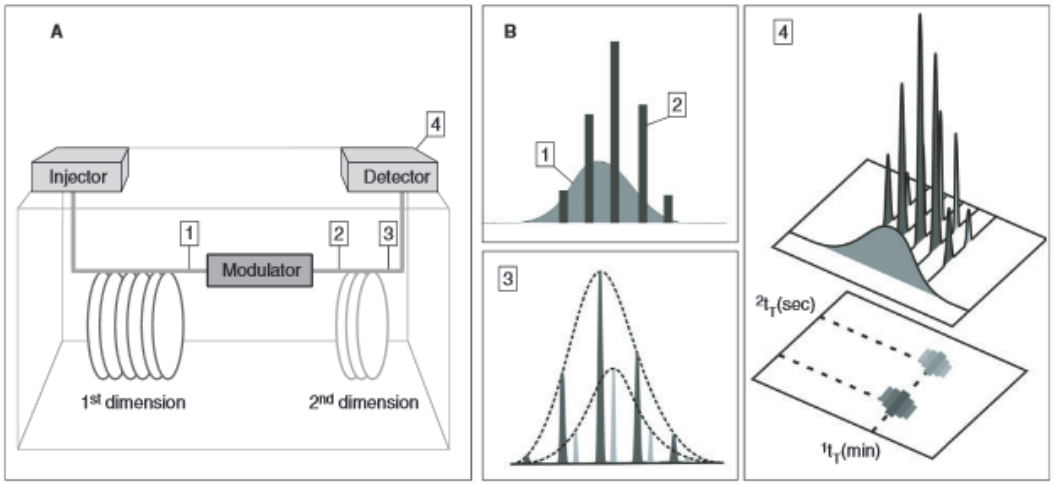


Fig. 3: (A) GC×GC instrumentation, (B) principle of modulation: (1) Peak eluting from first column, (2) Modulator is sampling peak fractions, (3) each of them is focused and reinjected into the second column in quick pulses. Overlapping peaks can be deconvoluted into two series of modulated peaks. (4) The peak signal is sliced according to the modulation period and signals are combined for 2D chromatograms. Modified after Vendeuvre et al. 2007[85].

GC×GC is an ideal technique for the analysis of complex samples, where compounds of similar chemistry can be grouped into patterns in a two-dimensional chromatogram, providing information on both boiling point and polarity. By applying this hyphenated technique, chemical analysis of crude oils and related samples have been carried out successfully[82-85], making it also an ideal tool for approaching shale gas wastewaters: In these, on the one hand a complex mixture of petroleum-derived hydrocarbons can be expected in the samples and on the other hand, a multitude of substances may be masked in case of insufficient resolution and two-dimensional gas-chromatography has the potential to resolve those issues.

1.4.2 Compound-specific isotope analysis (CSIA) via Isotope ratio mass spectrometry (GC-IRMS)

Compound-specific isotope analysis (CSIA) is an elegant tool for investigation and monitoring the fate of organic contaminants in the environment. In principle, it is based on measuring the isotopic composition of stable isotopes (e.g. carbon, nitrogen, oxygen, hydrogen) of a compound at natural abundances. These ratios of the heavier (^{h}E) to the lighter isotope (^{l}E) of the element E (e.g. $^{13}C/^{12}C$, $^{2}H/^{1}H$, $^{15}N/^{14}N$) are expressed in in the δ-notation in per mil (‰) relative to an international reference material (e.g., Vienna PeeDee Belemnite for carbon)[97, 98], see Equation 1.

$$\delta\,{}^{h}E = \frac{\left[\left({}^{h}E/\,{}^{l}E\right)_{sample} - \left({}^{h}E/\,{}^{l}E\right)_{reference}\right]}{\left({}^{h}E/\,{}^{l}E\right)_{reference}} \times 1000 \qquad \text{Eq. 1}$$

Such isotopic compositions may be distinct for compounds from different sources or manufacturers[75-78] and therefore can be used as a fingerprint to distinguish contamination sources in the environment. Further, the technique has been successfully used for the distinction of degradation pathways[99-101]. Most commonly, gas chromatography coupled with an isotope ratio mass spectrometer (GC-IRMS) is used to perform CSIA[102]. After gas chromatographic separation, the compound peaks are combusted online into a gas, e.g. CO_2, which is subsequently transferred to the IRMS (Figure 4). For the analysis of nitrogen isotopes, an additional oven is needed for the reduction of nitrogen oxides (NO_x) to nitrogen (N_2), as well as trapping carbon monoxide by freezing to avoid measurement errors of mass M = 28, which both occurs in $^{14}N^{14}N$ and $^{12}C^{16}O$.

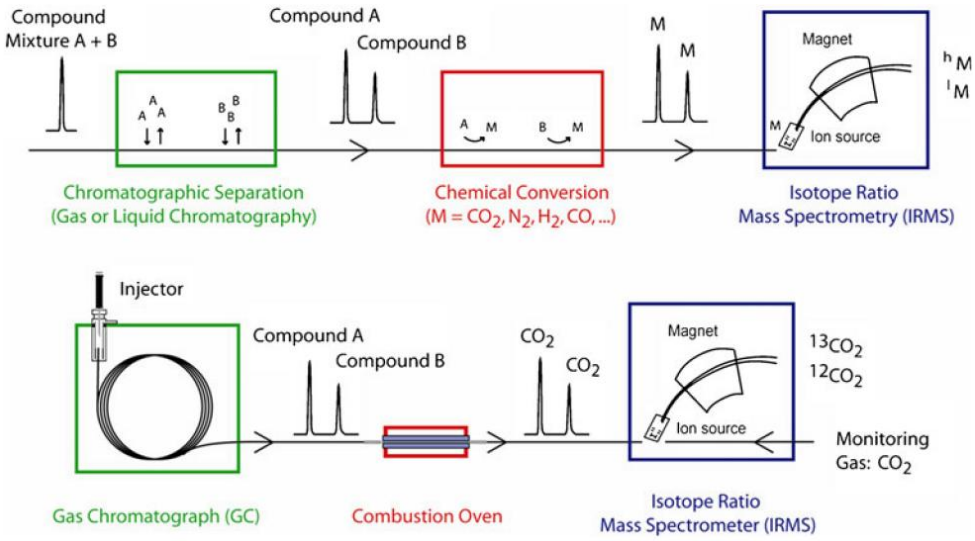


Fig. 4: Depiction of chromatography-IRMS (upper panel) and carbon-isotope analysis by GC-IRMS (lower panel). Compound mixes are baseline separated by chromatography, converted into a measurement gas (M such as CO2) that is suitable for isotope analysis[87].

1.5 Aims & Objectives

The aims of this thesis were to bring forward the knowledge on hydraulic fracturing chemicals and to overcome analytical challenges for their analysis in environmental samples.

To tackle the mentioned prominent gaps hindering process understanding behind the chemical use in fracturing applications, it was aimed to create a literature based approach: In **Chapter 2**, a comprehensive review on hydraulic fracturing chemicals was compiled. Specific targets were to (1) classify compounds according to their chemical structure, (2) link their structure to the desired functionality within the fracturing process and to (3) discuss and assess the chemical use, also with respect to aspects of toxicity, fate and analytical approaches.

In **Chapter 3**, the organic content of five flowback and one produced water sample from the US-American Fayetteville Shale were investigated, to (1) gain more detailed and specific insight into hydraulic fracturing wastewater samples. Alongside GC-MS and GC–FID measurements, resolution was increased by complementing GC×GC-TOF-MS measurements. For the evaluation of the results strict confidence criteria were applied to the detected analytes. Additionally, it was aimed to (2) classify compounds according to their putative origin and to (3) examine whether transformation products could be possibly found and hypothesize their formation.

As a first step towards using compound-specific isotope analysis for pollutants at environmental concentrations, an analytical method was developed for CSIA using atrazine and its metabolite desethylatrazine as model compounds in **Chapter 4**. Specifically, the aims were to (1) yield a high sensitivity to be able to tackle enriched field samples by optimizing injection methods and eliminating matrix effects by preparative HPLC. At the same time, (2) validation of trueness and precision of isotope values was pursued.

2

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

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Environmental Science and Technology, **2016,** DOI: 10.1021/acs.est.5b02818

2.1 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 [103], i.e. gas resources trapped in low-permeable coal, sandstone and shale [5]. For exploitation, vertical drilling to the target formation – in the case of shale, typically between 1000 m and 4000 m deep [58] – 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 [53, 104]. 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 [21] 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 [20, 105-107].

The share of unconventional gas in total gas output is projected to increase from 14% in 2012 to 32% in 2035 [7]. 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 [10] - but also in 41 other countries on different continents where shale gas has been found to reside in a total of 137 formations [6]. 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 [19, 26-28]. Uncertainty about the potential impacts of HF have led to moratoria (Quebec, New Brunswick) or bans (Bulgaria, France, Tunisia, New York State, Vermont)[108, 109].

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 [36, 70, 110]. 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) [45, 48, 57, 58]. Given that a typical fracturing operation requires around 9000 to 29000 m^3 [55] 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 [111]. Knowledge about fracturing chemicals and geogenic substances, however, is warranted for several reasons [112]:

Air emissions are reported to arise from well drilling, the gas itself or condensate tanks [18-20, 105], whereas spills and accidents [26-28, 113] 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 [44, 114-116]. 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 [39, 117]. Knowledge of the most frequently used HF chemicals is further essential for *risk assessment* (environmental behavior, toxicity) [45, 118]. 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 5 (white boxes) illustrates how recent contributions from different ends have aimed to close these knowledge gaps.

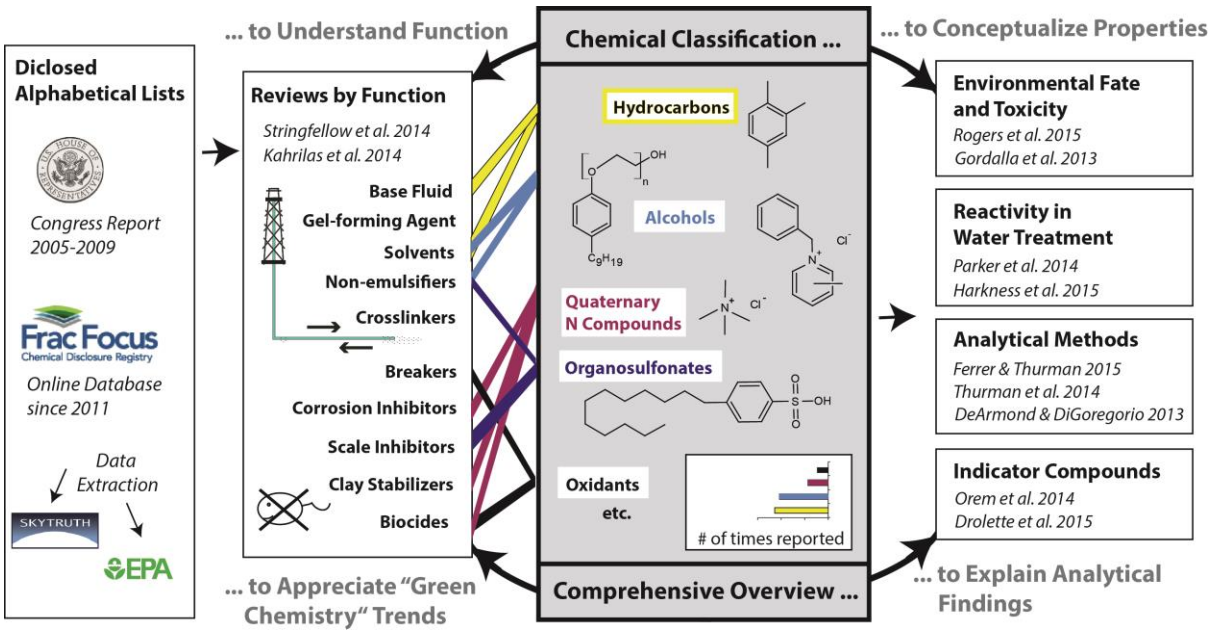


Fig. 5: Information on HF additives disclosed by operators (left-hand side) and explored by scientific publications (right-hand side). The structural classification of the present contribution (grey box) enables understanding of, the chemical purpose in the HF process and may help conceptualize, resultant 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[42, 63, 64] (left-hand side of Figure 5), 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 [63] – 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 [119],

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 [66]. In spring 2015, the U.S. EPA released a dataset extracted independently from FracFocus for essentially the same time period (2011-2013)[49]. A recent publication[65] 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 [42] (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 [67, 68, 120], entries are typically listed according to their function in the HF process (friction reducer, clay stabilizer, etc.) rather than grouped by chemical structure [67, 68, 120].

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 5). This includes reviews of HF chemicals[121, 122], predictions of their environmental lifetime and exposure[65], assessments of toxicity[45, 118, 123], investigations of reactivity in water treatment[38, 39], choice of adequate analytical methods[44, 114-116] and the search for potential indicator compounds[30, 44]. These contributions also typically start from alphabetical / CAS-number lists or classify chemicals by their function in the HF process[121, 122]. 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 5 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 5). 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[122] together with environmental fate and toxicity [118], and this insight is taken to select putative HF indicator substances together with promising analytical methods. Reference is made to expedient recent reviews[65, 122]. In particular, our Supporting Information provides octanol-water and Henry's law coefficients from the U.S. EPA[49] as well as log K_{oc} values, regulatory data and estimated environmental half-lives from Rogers et al.[65] 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.[49, 65, 66]) 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 7) 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.

2.2 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[119] (pages 17, 18) – we made use of three existing data sets from independent data analysis of FracFocus: by the non-profit organization "SkyTruth" [66], by the U.S. EPA[49] and by Rogers et al.[65]. 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.[65]. 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 of Chapter 2.

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 [124, 125] 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.

2.3 Results and Discussion

2.3.1 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 [54, 126]. 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[54]. However, the fluid viscosity of slickwater is typically not sufficient to keep proppants suspended long enough for HF operations in greater depths[54, 126]. For this reason, gel fracks such as outlined in Figure 6 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 [127, 128]. Figure 6 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).

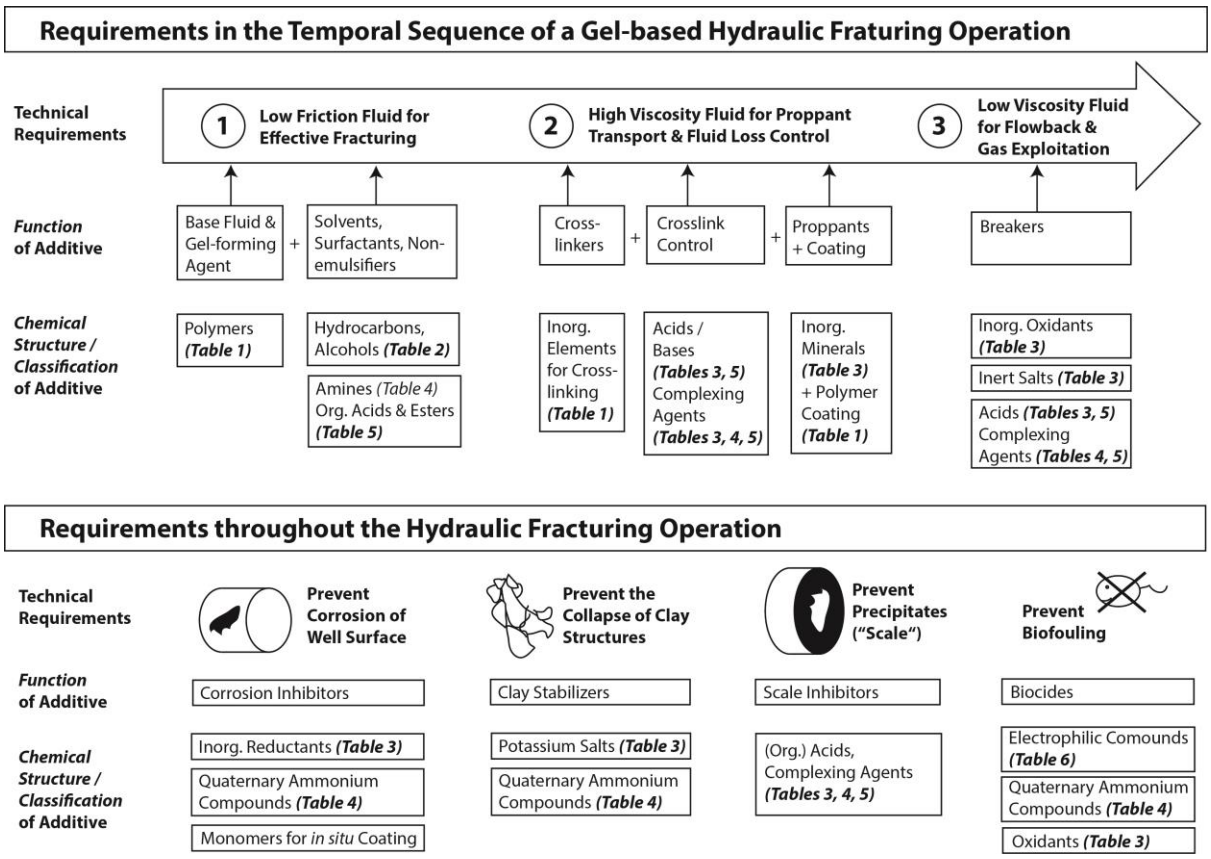


Fig. 6: Requirements of a gel-based HF operation and additives grouped by their *technical function* and their *chemical classification* (corresponding to the Tables in the manuscript).

Figure 6 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 [49, 65, 66]. and on the Waxman List [42]), 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 / $\log K_{ow}$ compiled by the EPA[49] and based on $\log K_{oc}$ data provided in Rogers et al.[65]. All data are included in our comprehensive compilation in the SI. Each chapter ends by discussing which compounds are likely relevant based on toxicity[45, 65] and on environmental persistence[65] (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[54]. 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 [54]. 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[129].

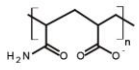
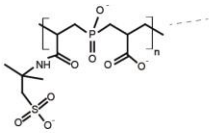
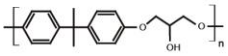
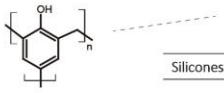
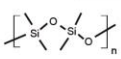
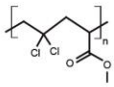
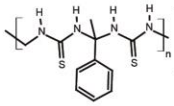
Compared to biopolymers, synthetic polyamide/-acrylate polymers have the advantage that they can be deliberately designed for a spectrum of functionalities. Without crosslinking they act as friction reducers and are, therefore, typical additives in slickwater fracks[54]. If the percentage of acrylate-derived 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).

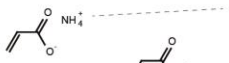
The frequency of reported guar gum versus polyacrylamide / acrylate applications suggests that biopolymers, and therefore gel-based fracks, are at least two to three times preferred over synthetic polymers in putative slickwater fracks. The listing of inorganic elements in Table 1 further suggests that 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. [65]. A more comprehensive list of compounds together with physicochemical properties is provided in the Supporting Information.

Synthetic Polymers

	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-acrylamido-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/ Hexamethylenetetramine);	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/methylacrylate 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

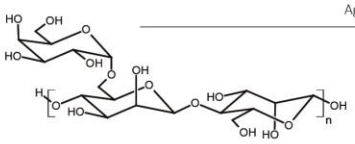
Monomers

	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

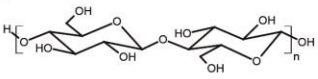
Biopolymers

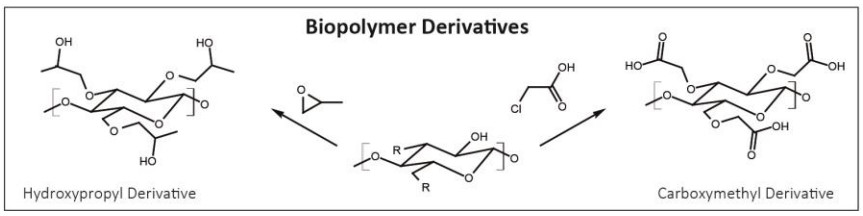
	Biopolymers			**25.1**	**45.5**	**27528**	**123**	
	Guar gum, Guar gum derivatives	Gel Forming Agent	GW-4LDF (Baker Hughes): Gelling Agent (w Petroleum Distillates); WG-36 GELLING AGENT (Halliburton); J580 (Schlumberger): Gelling Agent;	21.1	45.2	23424	53	9000-30-0
	Carboxymethyl Cellulose	Gel Forming 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



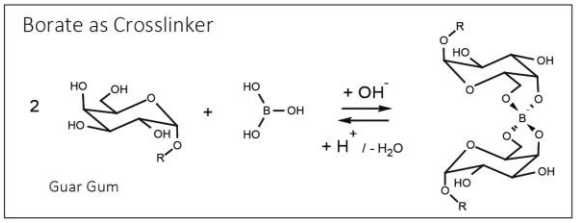
Cellulose

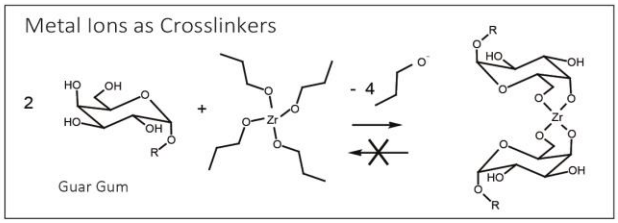




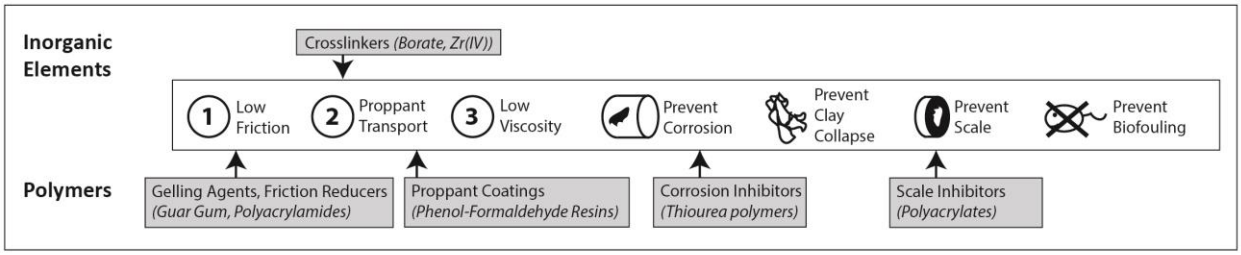
Inorganic Elements Conducive to Condensation / Crosslinking

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

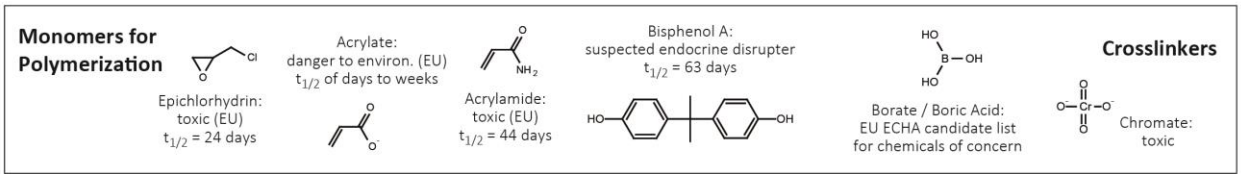




Functions in the Hydraulic Fracturing Process (Summary)



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 [130-133]. 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))[129]. In this context, the polyvinylidene copolymer listed in Table 1 features toxic monomers and is highly resistant to biodegradation or oxidation.[134] Also phenol polymers for proppant coating are potentially problematic, because unreacted phenolic monomers can leach over time and the polymer is barely degradable [135]. Specifically, bisphenol A/epichlorohydrin oligomers are ranked as acutely toxic, long term aquatoxic and carcinogenic[136].

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 [137, 138]. 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[115].

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[139].

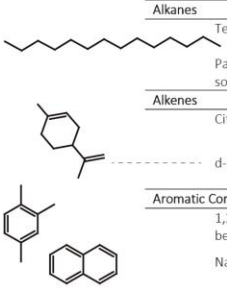
Next to hydrocarbons, alcohols are the most frequently disclosed solvents, in particular methanol and isopropanol (Table 2). The distinguishing feature of alcohols is their -OH group, which makes them miscible with water. Short-chain alcohols, as well as alcohols with numerous alkoxy groups inside their 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 [140]. 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).

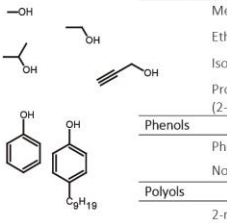
Table 2. Most frequently reported gases, hydrocarbons and alcohols. n.r.: not representative; n.i.: not included. Henry's law constants and log Koc constants are taken from EPI Suite[141],, degradation half-lives from ref. 44, except for 4-nonylphenol [142]. A more comprehensive list of compounds together with physicochemical data is given in the Supporting Information.

Gases and Non-functionalized Hydrocarbons



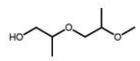
Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Gases			4.0	n.r.	1116	13	
Nitrogen	Fracking Fluid	Nitrogen (Nabors Completion & Production Co.) : Base 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

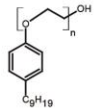
Alcohols, Ethers, Alkoxylated Alcohols



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,

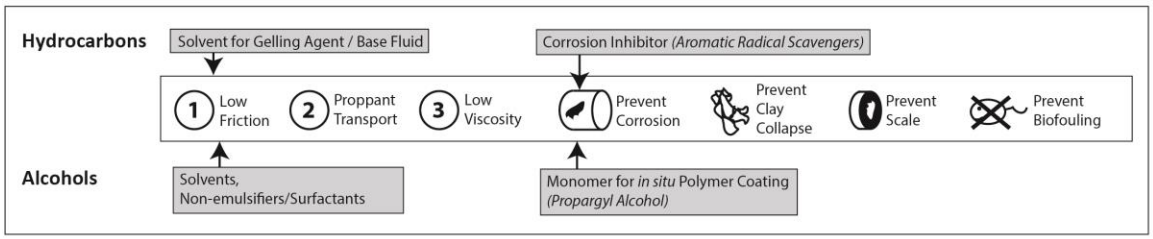
Alcohols, Ethers, Alkoxylated Alcohols (continued)



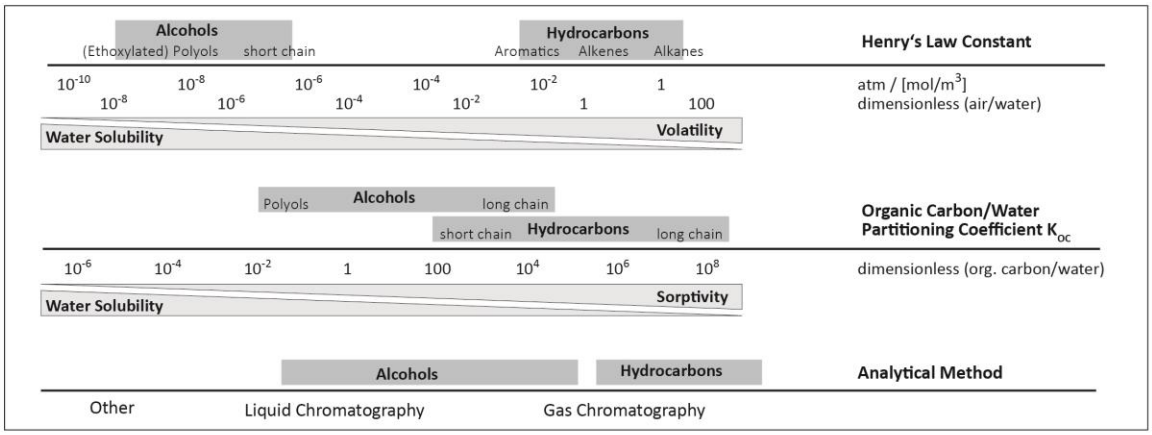


Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Propoxylated Alcohols			2.9	5.0	885	20	
Dipropylene glycol mono-methyl ether (2-methoxymethyl-ethoxy propanol)	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

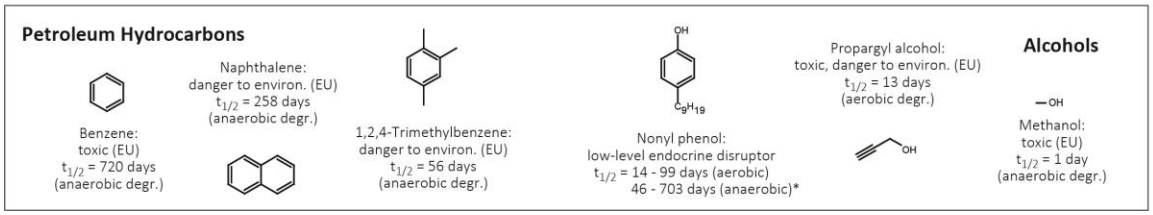
Functions in the Hydraulic Fracturing Process (Summary)



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 [143]. Propargyl alcohol in pure form is

toxic to humans, highly toxic to aquatic organisms [144] and was found to be carcinogenic in rats [145, 146]. However, propargyl alcohol is further transformed in the subsurface (1,3-hydroxyl shift and tautomerization to 1-propenal [147], subsequent polymerization or oxidation) and is readily biodegradable according to OECD criteria [144]. 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 [60, 148, 149]. These compounds are both persistent in the environment and of ecotoxicological concern because they can act as endocrine disruptors [150]. 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[44] 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 [151], 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[152] (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[45, 61, 153]and natural radioactivity[33, 36] into HF wastewater, and formation water may often have a higher salt content than typical HF fluids[154-156]. 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 Supporting Information.

Inert Inorganic Compounds

Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus		No. of Declarations		CAS -Number
			EPA Eval.	Rogers et al.	Sky Truth	Waxman	
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

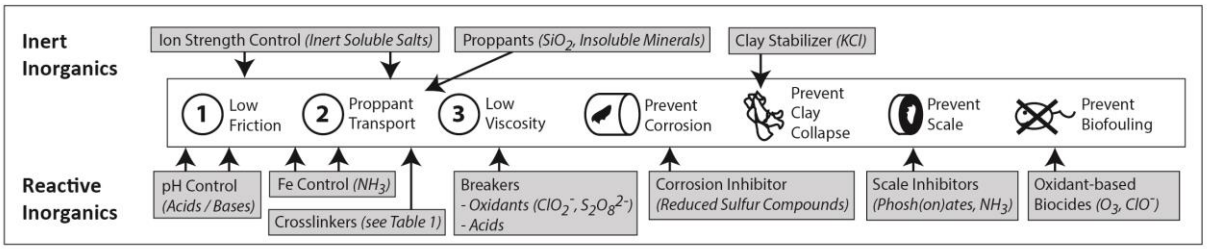
Reactive Inorganic Compounds: Reductants, Oxidants, Acids, Bases, Complexing Agents

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

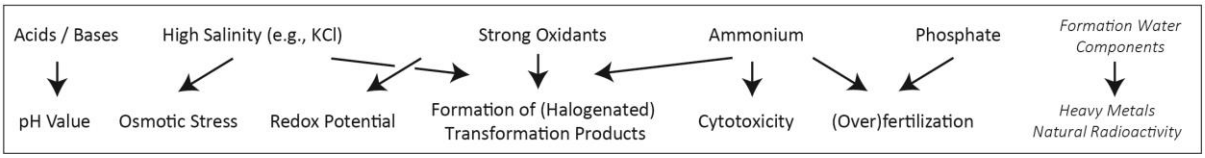
Reactive Inorganic Compounds: Reductants, Oxidants, Acids, Bases, Complexing Agents (continued)

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[157], as reported for plants (Britto[158] and references therein), bacteria[157], humans[159] and fish where acute LC_{50} values can start at 2 mg/L [160]. From a chemical point of view, experience from oxidative water

treatment shows that the application of oxidants in highly saline water [71] – some of them even consisting of reactive chlorine species (NaClO, $NaClO_2$) – can form problematic halogenated organics ("disinfection by-products") [39]. 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

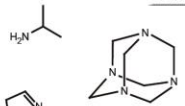
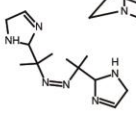
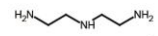
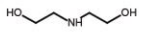
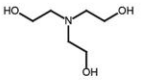
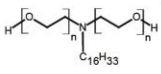
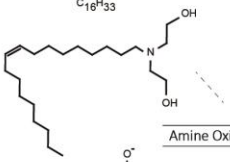
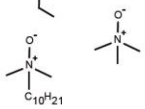
Chemical Properties Relevant in the HF Process. Table 4 shows that, though some amines are used as *solvents* (isopropylamine) and *surfactants* (ethoxylated fatty amines), the main use of amines relates to the *buildup and crosslink control* of polymers. Hexamethylenetetramine (HMT) – the most frequently 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[129]. 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. [161], chapter 8). The second interpretation would be consistent with the disclosure of acrylate and acrylamide monomers in Table 1.

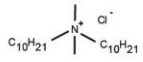
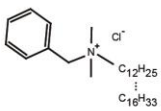
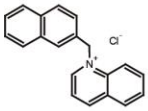
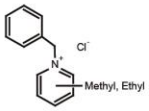
The low number of hits for amine oxides, finally, – which are typical surfactants in VES applications [162-164] – confirms our earlier conclusion that viscoelatic surfactant-based fracks seem to play a minor role in comparison to gel or slickwater fracks.

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[141], degradation half-lives from Rogers et al[65]. A more comprehensive list of compounds together with physicochemical data is given in the Supporting Information.

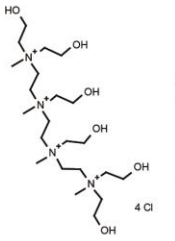
Amines and Alkoxylated Amines

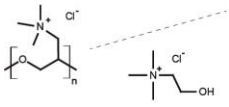
	Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
	Mono- and Polyamines			**16.7**	**22.8**	**12979**	**85**	
	Isopropylamine	Solvent	PAS-C (Reef): Asphaltene/Paraffin 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

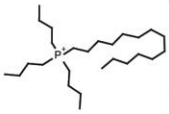
Quaternary Ammonium and Phosphonium Salts

	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)

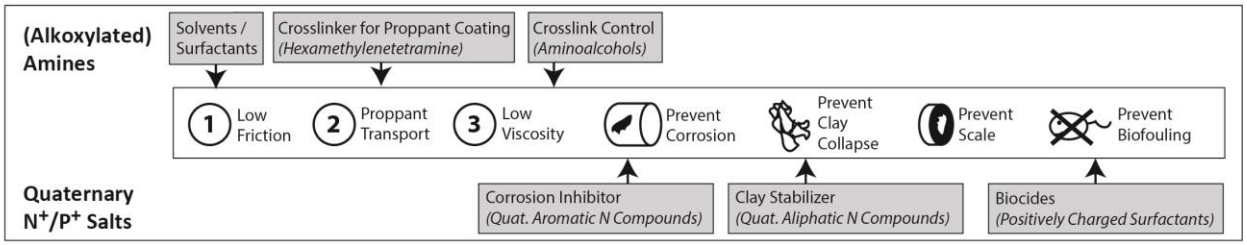




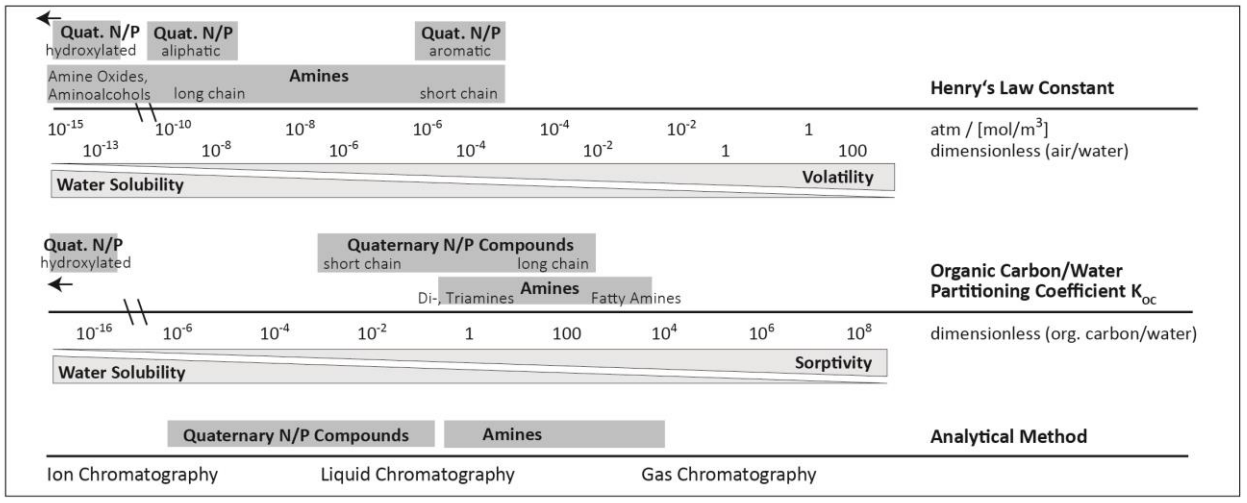


Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Quaternary Ammonium salt - Hydroxyalkylated			16.1	1.6	9035	8	
1,2-Ethanediaminium, (N,N'-bis-[2[bis(2-hydroxyethyl)methylammonio]-ethyl]-N,N'-bis(2-hydroxyethyl)-N,N'-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, trimethylamine 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
Quarternary 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

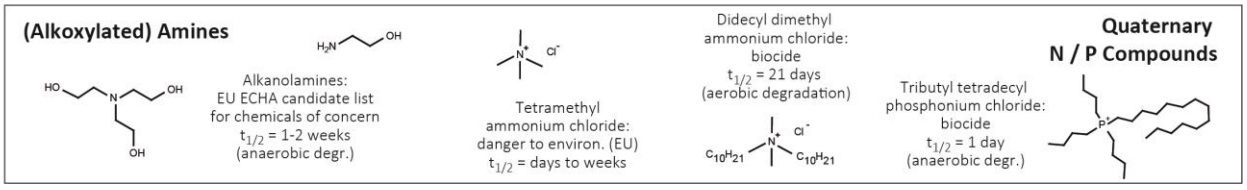
Functions in the Hydraulic Fracturing Process (Summary)



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 [151] (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 [121, 165]. 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 [166] are more biodegradable than diethylenetriamine [167] or tertiary amines [168], and their aquatic toxicity is lower than of diethylenetriamine which is ecotoxic and a suspect teratogen. [169] Nevertheless, alkanolamines are on the ECHA candidate list of chemicals of concern in Europe[137]. *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 [170]. Tetramethyl ammonium chloride is very toxic to aquatic organisms, toxic to humans and not prone to biodegradation [171, 172 173]. In contrast, quaternary ester compounds are less toxic and more easily biodegradable [173]. Quaternium-18 Bentonite is

chemically, physically, and biologically inert with little or no toxic effects [174], and choline is of very low acute toxicity, even occurring naturally in microorganisms, animals and humans [45]. 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 7 [175]. 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")[176] to seal conductivities in order to divert the fluid to other parts of the target zone[177]. These sealers are used to minimize fluid loss into the formation and to enable multi-stage HF[178]. Their common feature is a solid, waxy consistency which poses a physical resistance to the fracking pressure, yet allows their gradual dissolution.

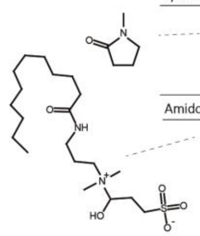
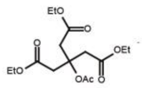
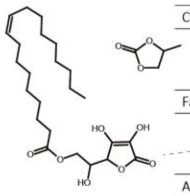
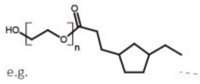
Finally, acids are expected to play a crucial role also as *breakers*, by reversing borate-based crosslinking (see Table 1). Considering that optimized hydraulic fracturing requires an exact timing of crosslinking and breaking, much industry research is reported [129, 179, 180] to focus on *delayed crosslinkers 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 [129] 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 [141]. A more comprehensive list of compounds together with physicochemical data is given in the Supporting Information.

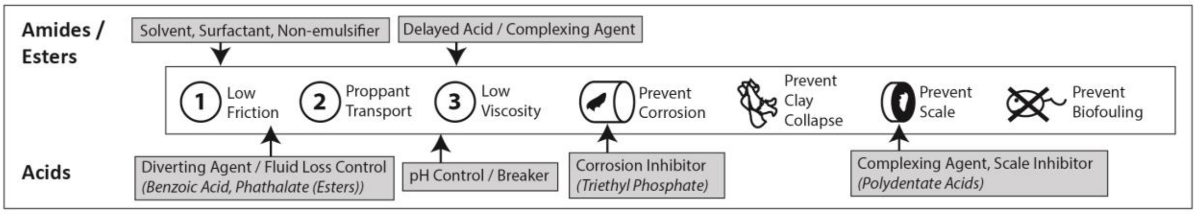
	Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Carboxylic Acids								
Monocarboxylic acids				51.0	75.0	38968	114	
	Formic acid	pH Control	BF-55L (BAKER 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
	Bishexamethylenetriamine penta methylene 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
	Dodecylbenzenesulfonic acid, monoethanolamine 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							

Carboxylic Amides and Esters (continued)

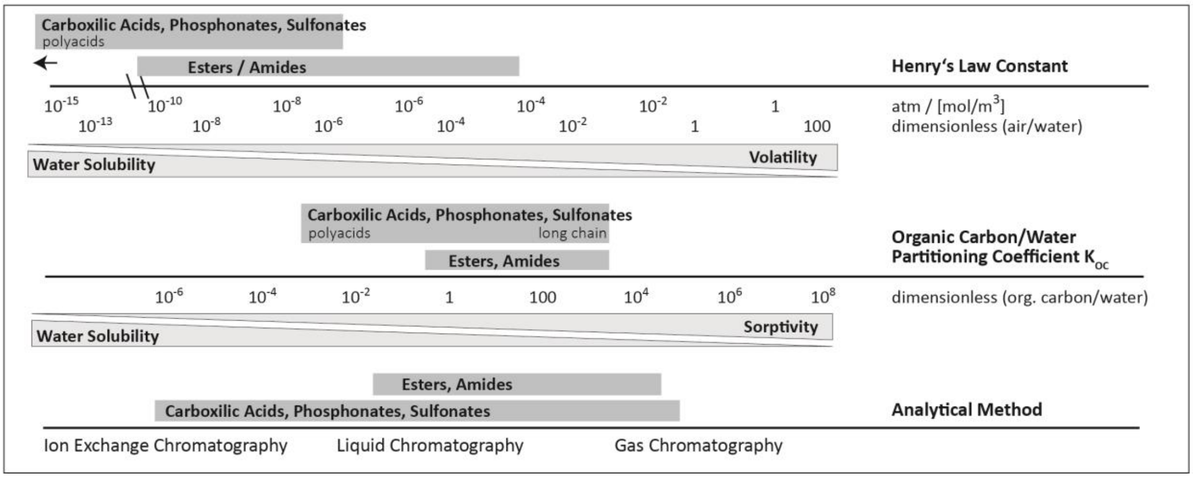





Chemical	Function	Examples of Reported Commercial Products	No. of Declarations Sky Truth	No. of Declarations Waxman	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	CAS -Number
Cyclic Amides			245	2	0.67	0.59	
n-Methylpyrrolidone	Solvent, Surfactant	Super-Flo RPM (Nabors Completion & 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 / Isopropyl 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 [181], 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[182], EDTA is significantly more persistent [183, 184]. Phosphonates are even more persistent, but show strong sorption and, hence, low concentrations in aqueous solution [185]. Sulfonic acids are generally of low toxicity, but poor biodegradability [186]. Among the diverters, finally, phthalate esters have received attention as problematic plasticizers in childrens' toys due to their gonadal toxicity and hormone-active effects [187, 188]. In oligotrophic or low oxygen environments, phthalate esters can remain in the environment up to several months [189]. 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[190], 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 [191].

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 [121]. 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[192]. C-Br bonds in DBNPA undergo rapid reaction with –SH groups of cysteine or glutathione[193] so that

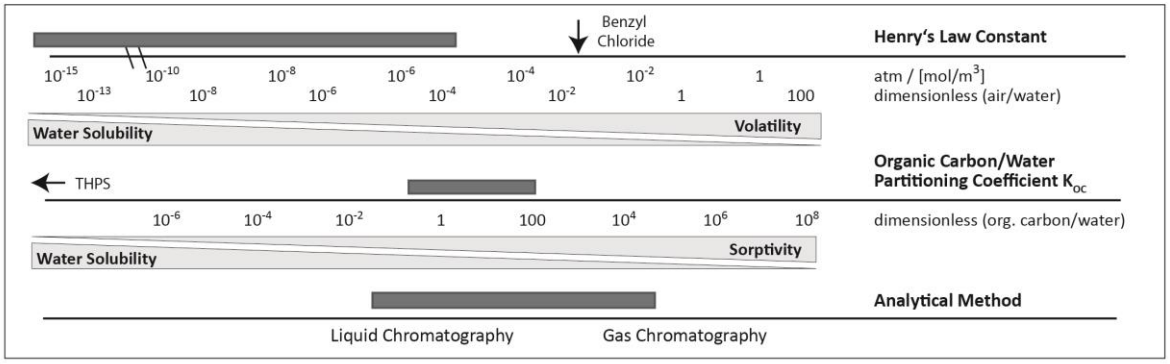
proteins are damaged. The same is true for the P atom in tris(hydroxymethyl)phosphine which is formed from THPS in alkaline solution[193]. These reactions have in common that their toxic action can affect different microorganisms in the same way leading to broad band specificity. In this function compounds 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)[194]. 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[141], degradation half-lives from ref. 44. A more comprehensive list of compounds together with physicochemical data is given in the Supporting Information.

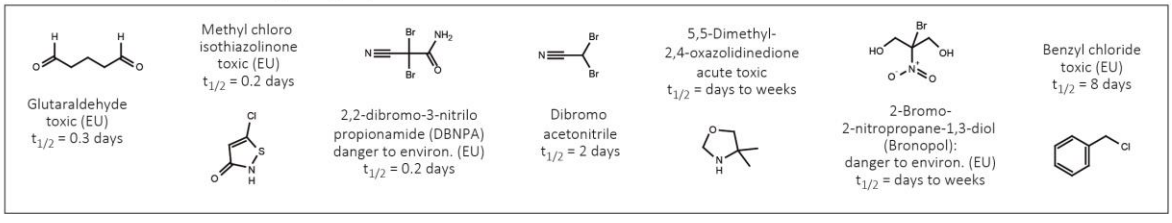
Electrophilic Compounds

	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[194]. 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 [195-198].

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.

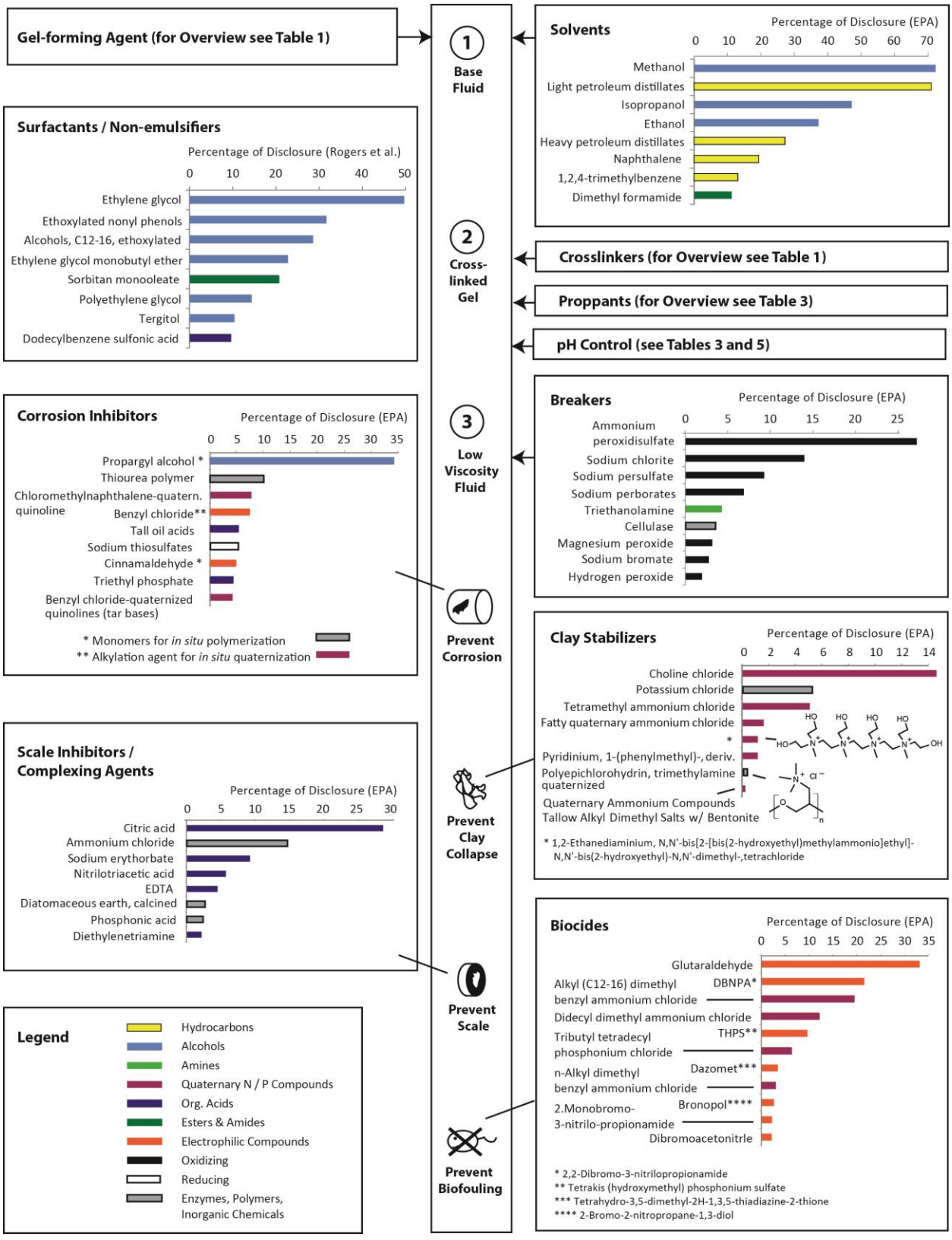


Fig. 7: Ranking of chemicals that may be expected in an average HF operation, based on number of disclosures on FracFocus (as evaluated by EPA[49] and Rogers et al.[65]).

2.3.2 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 7). *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 7 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 7, 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 [199], diesel was still heavily used between 2005 and 2009 [43]. After three congress members put a particular focus on this additive in 2011 [43], 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[194]. 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[49] is easily available for further considerations.

2.4 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 [33, 37, 44, 59, 60, 74, 139, 200], 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.

2.4.1 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 [33, 34, 60, 61, 201, 202] 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 [45]. 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.

2.4.2 Consequences for monitoring schemes / chemical analysis

For air monitoring [105], our survey suggests that volatile hydrocarbons (Table 2) are most relevant, possibly together with volatile halogenated hydrocarbons as potential transformation products [39]. 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 [22, 79, 80]. 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 [117, 203]. 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 [59, 72, 204], produced water [60, 74, 139], residual gas wastewater [35, 37] and contaminated groundwater [29] consistently report detection of aliphatic and aromatic hydrocarbons, further putative detects of (nonyl)phenols [60, 72], fatty acid and amine surfactants [60], phosphate esters [74], polyalkoxylated alcohols [37, 44, 60], butoxyethanol [29], chlorinated hydrocarbons [74, 204] and phthalate esters [60, 72, 74]. 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.

2.4.3 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 6) are applied to organic compounds in the presence of highly saline formation water, as recently demonstrated for oxidative treatment of hydraulic fracturing wastewater [39].

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. [119] and a current Draft Legislation on Fracking in Germany [111] 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.

3

Indications of Transformation Products from Hydraulic Fracturing Additives in Shale Gas Wastewater

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3.1 Introduction

The recent growth in unconventional natural gas development (UNGD) has led to a dramatic increase in related wastewater volumes[23, 37, 40], collectively referred to as flowback and produced waters. For instance, residual fluids from UNGD totaled 570 million liters in 2015's first three quarters in Pennsylvania alone[205]. Field studies have provided preliminary evidence that current wastewater treatment practices are not sufficient[37, 206], and risks to human and ecosystem health are inadequately explored. Furthermore, UNGD-related substances may serve as molecular markers of hydraulic fracturing activities. As a result, much interest is directed at identifying these indicator compounds, recognizing chemicals of particular concern, and considering implications for their adequate disposal.

While flowback fluids and produced water have been analyzed with regard to inorganic composition, such as halides, alkali earth ions, radioactive species, and heavy metals[36, 71, 207, 208], a similar description for organic compounds is only starting to emerge. Several studies have deployed liquid chromatography (LC) with high resolution mass spectrometry (HRMS) to the study of flowback and produced waters[72, 209-212], a technique that targets roughly 90% of the disclosed chemical additives[37]. However, the majority of geogenic compounds and the remaining 10% of additives are expected to be in amenable to gas chromatography (GC), rather than LC. Available GC studies differ in (a) the level of detail aimed at identifying specific chemical substances, (b) the target compound range and resolving power of the analytical methods, and (c) the confidence criteria applied to uniquely identify substances of interest. In all studies that detected substances of

anthropogenic origin, such as phenols, phthalates, or biocides, investigations relied on one-dimensional gas chromatography-quadrupole mass spectrometry (GC-QMS)[60, 72-74]. While useful for many applications, QMS is not ideal for non-target analysis due to its relatively poor mass resolution and slow acquisition time. However, it can be a useful screening tool due to the vast NIST library available. For instance, compound identifications in prior flowback and produced water studies[60, 72-74] were based on the similarity of mass spectra with NIST library matches. These postulated structural assignments could benefit from the application of additional confidence criteria (e.g., use of authentic standard retention times or predictions thereof, or measured retention indices, such as the NIST retention index database)[213, 214], which were not used in most cases. In other studies[59, 215, 216], the use of comprehensive two-dimensional gas chromatography coupled to time-of-flight MS (GCxGC-TOF-MS) offered enhanced chromatographic and mass resolution. However, even the most robust GCxGC-MS study to date[59] grouped identifications according to substance class (e.g., PAHs and aromatics) rather than confirming them as individual compounds. In the absence of such confirmations, we note that enhanced identifications should be possible, as retention index databases, such as the Kovats measured and predicted retention indices, are available from NIST for traditional 1D GC. Lastly, particular substances of anthropogenic origin were not delineated in prior studies.[59] In contrast, two recent studies[215, 216] confirmed chemical identity for single compounds using authentic standards for known UNGD additives (e.g., 2-butoxyethanol and *bis*(2-ethylhexyl)phthalate), but these were in groundwaters with suspected hydraulic fracturing influence, rather than confirmed flowback or produced waters. Perhaps most importantly, the focus of these

previous studies has been on substances that are potentially *applied* as hydraulic fracturing additives; none have searched for compounds that may possibly be *formed* from such additives in subsurface transformations.

A recent review[217] brought forth the possibility of transformation based on the consideration that certain compounds (e.g., strong oxidizers and breakers) are likely designed to react in the subsurface and other compounds may undergo unintended transformations at elevated temperatures, pressure, and salinity. As putative transformation products are not known to regulatory agencies, and perhaps even industrial operators, these compounds could be a primary source of unintended environmental impacts. While their identification is needed, the possibility of transformation product formation has not been investigated in shale gas wastewater samples.

In light of these knowledge gaps, the aims of this study were: (1) to investigate the organic compound composition of shale gas wastewater samples through application of more stringent identification confidence criteria, (2) to classify compounds according to their possible origin and (3) to search for those substances previously untargeted by chemical analysis: those designed to react in the subsurface and those formed as transformation products.

3.2 Experimental Methods

3.2.1 Overarching approach

To identify volatile compounds, we relied on purge and trap (P&T) coupled to GC - flame ionization detection (FID) or GC-MS using authentic standards. Less volatile, hydrophobic substances were targeted by liquid-liquid extraction (LLE) followed by GC-MS, GCxGC-FID, and GCxGC-TOF-MS. Following GCxGC-MS library searching, compound assignment was strengthened according to the following confidence criteria (listed in order of increasing confidence): (i) NIST library agreement with forward and reverse similarity greater than 85% (i.e., 850 out of 999), (ii) plausible retention behavior in accordance with the NIST Kovats retention indices, and (iii) confirmation with authentic standards. Further, we note where a chromatographic feature was detected in multiple samples and assigned the same structural identity. Based on these assignments, we sought to classify each unique detection according to the putative origin of detected compounds by comparison to those commonly found in formation water (classified as of *geogenic origin*) and disclosed additives (classified as *explicitly disclosed UNGD additives*). Compounds that were structurally similar or included in a family of disclosed additives were classified as *implicitly disclosed UNGD additives* (e.g., members of a group of compounds, such as "Alkanes C_{10} - C_{14}"). Note that all disclosure databases were populated on a voluntary basis at the time of this data collection, but as of June 2015, toxic chemicals must be disclosed unless they are deemed as trade secrets (e.g., US EPA Confidential Business Information). Finally, we sought to identify compounds that were likely degradation products (either because of their chemical structure or because of an abundance pattern that cannot be explained by geogenic occurrence) but which were

not likely to be original additives. For these compounds, we postulate reactions by which they may form as transformation products.

3.2.2 Sample collection and storage

Arkansas Oil and Gas Commission personnel collected samples of Fayetteville Shale (1,500-6,500 ft below surface[218]) UNGD wastewater from production wells into 250-mL high-density polyethylene (HDPE) bottles in May 2012. Five of the samples were collected within 3 weeks of the initial fracturing event (i.e., "flowback waters;" samples A-E) and another sample was collected after approximately 50 weeks of the initial hydraulic fracturing (i.e., "produced water;" sample F). The water samples were shipped to Duke University (Durham, NC, USA) where they were immediately transferred to pre-combusted, glass volatile organic analysis (VOA) vials (acidified with 1 ml 50% (v/v) hydrochloric acid (HCl) and kept at 4^{o}C until analysis by P&T-GC-FID or P&T-GC-MS) or to amber jars (without acidification and frozen until analysis by LLE and GCxGC-FID-MS). Note that all extractions and analyses were conducted within 4 weeks of sample receipt, except for the GCxGC analysis. Samples for GCxGC analysis were extracted in November 2012 from samples frozen in precombusted, amber glass jars and analyzed twice: once in November 2012 by 1-D GC and again in October 2013 by GCxGC from preserved extracts.

Critically, we note that HDPE bottles are not ideal for any organic chemical analyses, due to potential losses to the headspace and the polyethylene, in addition to HDPE acting as a potential source of organic chemicals (e.g., phthalates) to the sample. Nevertheless, because access to such samples is rare currently and the qualitative information contained

therein of high value, we performed a thorough and cautious assessment for potential sample contamination (Control Experiments; SI) and estimated the loss of material to the headspace (see SI Table S2). With up to 40% headspace, assuming equilibrium was achieved and ignoring the effect of salts and particles, outgassing of volatile compounds may have resulted in loss of up to 15% for compounds such as benzene and toluene, less than 10% for compounds such as 1,4-dichlorobenzene, and less than 1% for ethylbenzene, xylene, toluene, naphthalene, and representative phthalates. Compounds such as octane would have been almost fully transferred to the air phase (99%) and nearly half of the octadecane (45%) would have partitioned to the air. Of course, we expect some loss of hydrophobic compounds to the HDPE to have occurred, but equilibrating into the HDPE "reservoir" would have been slow (on the order of several weeks for a compound like benzene to years for a phthalate). Therefore, using equilibrium partitioning to estimate losses could be misleading for compounds with low polyethylene diffusivities (i.e., slow transfer into the polyethylene). For example, low-density polyethylene (LDPE)-water partitioning constants (K_{iPEs})[219] are high (log K_{iPEs}>5) for many of the hydrophobic analytes in our study, and more than 99% of the material would have been lost to the HDPE bottles if equilibrium were achieved. For a more polar compound (e.g., phenol, log K_{iPEs} = 2.4)[219], 95% would be in the polyethylene (PE) with 5% in the aqueous phase and a negligible amount in the air at equilibrium. Since results indicate hydrophobic organic compounds persisted in the aqueous phase, the system was either extremely concentrated (i.e., exceeding the uptake capacity of the HDPE) or not at equilibrium. Ultimately, we caution that the results presented here are qualitative.

3.2.3 Analytical methods

Briefly, two approaches were deployed to cover a broad physicochemical spectrum of GC-amenable organic compounds: (1) volatile compounds were analyzed by P&T-GC-FID and P&T-GC-MS (details in SI) and (2) non-purgeable compounds were analyzed by followed by GCxGC-TOF-MS and GCxGC-FID (see SI for LLE method). These analyses were performed at the Woods Hole Oceanographic Institution on a LECO Pegasus 4D (see SI for details).

3.2.4 Confidence assignments

Traditional analytical chemistry classifies compound identifications as either tentative or confirmed. Confirmed identifications require at least two independent pieces of evidence of a compound's identity (e.g., mass spectral library match plus confirmed retention time with an authentic standard, or confirmation of retention time against an authentic standard via the use of two distinct chromatographic columns[84, 220, 221]). In contrast, tentative identifications require only one piece of information, and, in many published organic analyses in flowback water literature[59, 73, 74], this has relied on GC-MS library match assignments. This reliance on single-datum compound assignments largely results because tentatively identified compounds are either not available as authentic standards or too numerous to confirm with standards within a reasonable amount of time and at an attainable cost (e.g., approximately 2,500 compounds at $50 per standard would cost $125,000). Here, we endeavor to provide confirmed identifications when possible and desirable (e.g., for "exotic" compounds beyond the standard alkanes and fatty acids, through the use of available authentic standards) and provide additional confidence

beyond a typical tentative identification. Several degrees of confidence were assigned (ranked from lowest to highest): (i) tentative agreement between measured and NIST library mass spectra (at least 850 forward and reverse match (out of 999), where 800-900 is classified as "good" and >900 is "excellent"[222]), at least eight co-eluting apexing masses, and at least 10x signal-to-noise threshold), (ii) analyte retention index match in the first dimension of GCxGC with a Kovats retention index library, and finally, (iii) authentic standard confirmation. Further, we note where a chromatographic feature (i.e., peak at a given retention time) was assigned the same compound identity in multiple samples (i.e., convergent identifications for a given chromatographic peak).

The NIST Mass Spectral Library with Search Program (Data Version: NIST 14, Software Version: 2.2) was used to collect experimental and estimated retention index data for all available compounds detected in this study. Based on our own n-alkane standards (*n*-C_7 to *n*-C_{36}), we calculated experimental Retention Indices for each of the compound detections that passed the 850 similarity and reverse criteria. Retention Indices from NIST and calculated were both based on the "Kovats Retention Index" for temperature programmed chromatography (see SI) and retention agreements within ± 100 were classified as positive confidence. The wide tolerance threshold was chosen to allow for enough deviation from NIST database (e.g., to account for experimental and configurational variances) while still narrow enough to reject egregious misidentifications. These results were compared to a boiling point prediction model (which was less robust to the broad spectrum of compounds observed here) whose approach and results are available in the SI.

3.3 Results & Discussion

Among the six flowback and produced water samples, there were broad differences in the hydrocarbon chemical distribution reflected in the GCxGC chromatograms (Figure 8), indicating these may potentially serve as chemical fingerprints and carry information about the UNGD process as well as the geologic formation. Despite these differences, there was a remarkable similarity in the total number of compounds detected via GCxGC-FID (2550 ± 140 for *n*=6; 2762, 2565, 2600, 2346, 2490, and 2523 for samples A through F, respectively. Note that not all peaks are visible in Figure 8 due to scaling). Of these nearly 2500 compounds, GCxGC-TOF-MS was able to postulate identifications for 729 unique compounds (using relatively strict MS library match criteria). After application of the Kovats retention index match to reject egregious identifications (described above), the number of confident assignments was reduced to 404, just 55.5% of the original total number of identifications (SI Table S1). This is reasonable compared to the 25% false positive rate that results from MS library match only shown for much smaller data sets (*n*=30, 45, and 87[223]). In the discussion that follows, we refer only to confidently identified chemicals (i.e., those that pass the relatively strict MS criteria and the Kovats retention index match). As a consequence, tentative identifications that did not pass the retention index match were omitted from this discussion, but are nevertheless listed in the SI for completeness (SI Table S1).

3.3.1 Detected substance classes and disclosure rates

Hydrocarbons (i.e., alkanes, alkenes, and aromatic compounds) were most abundant in our detected list of compounds (Figure 9). This is consistent with previous findings [59, 60, 74] and is not surprising since such hydrocarbons are (a) disclosed as additives or solvents

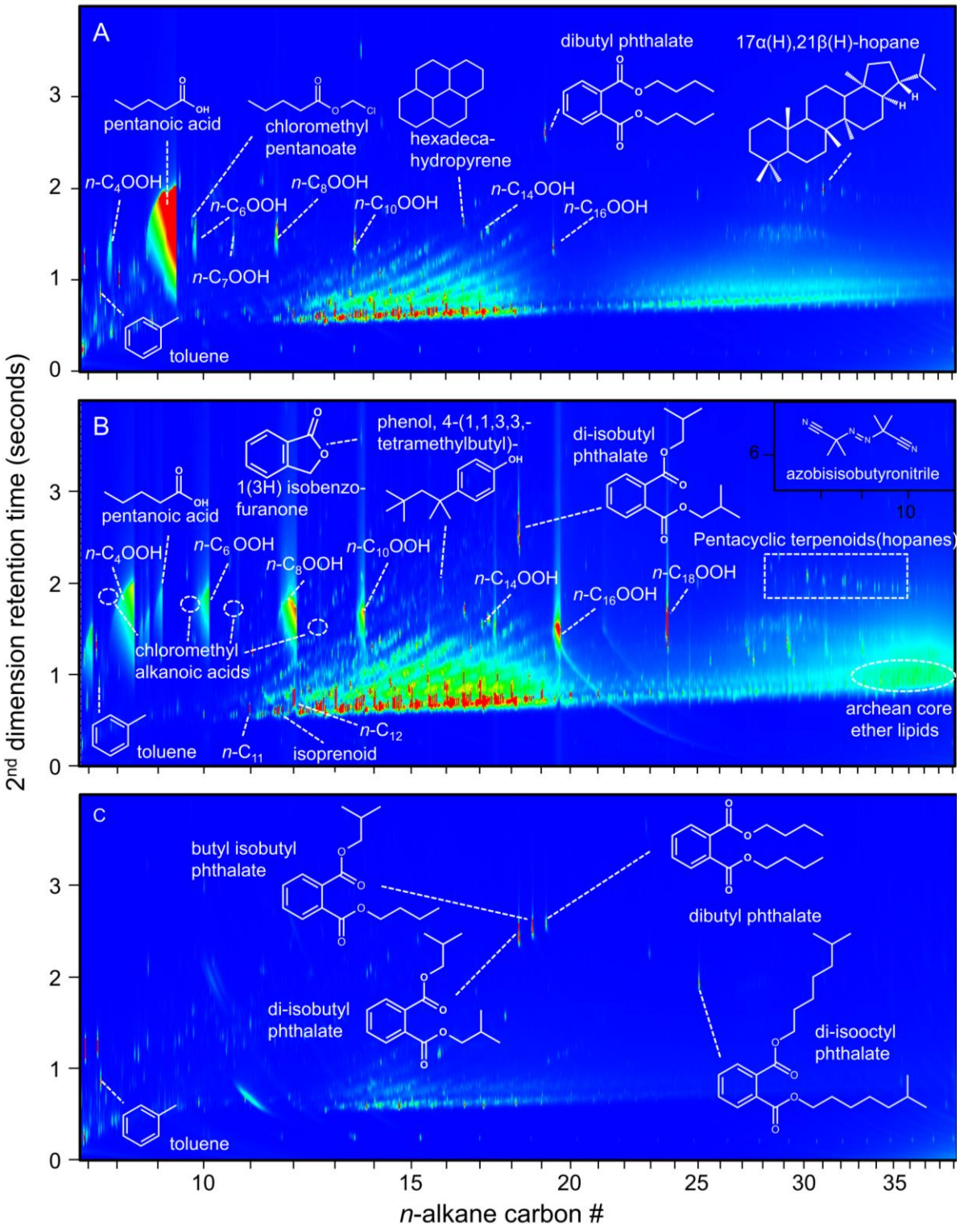


Figure 8 (A-C). GC×GC-FID chromatograms for 6 different UNGD wastewater samples with highlighted compounds and compound groups. The abscissa gives the 1st-dimension retention time (with respect to n-alkane retention time), and the ordinate displays the 2nd-dimension retention time. The heat map reflects signal intensity, increasing from blue to yellow to red. Structures are shown for a subset of compounds identified with a high degree of confidence. Note: Insets in the upper right corners of panels display portions of the chromatograms that would otherwise be outside the selected display range. Samples A-E were collected within three weeks of the initial well fracture (i.e., flowback waters); sample F after approximately 50 weeks of the initial hydraulic fracturing (i.e., produced water).

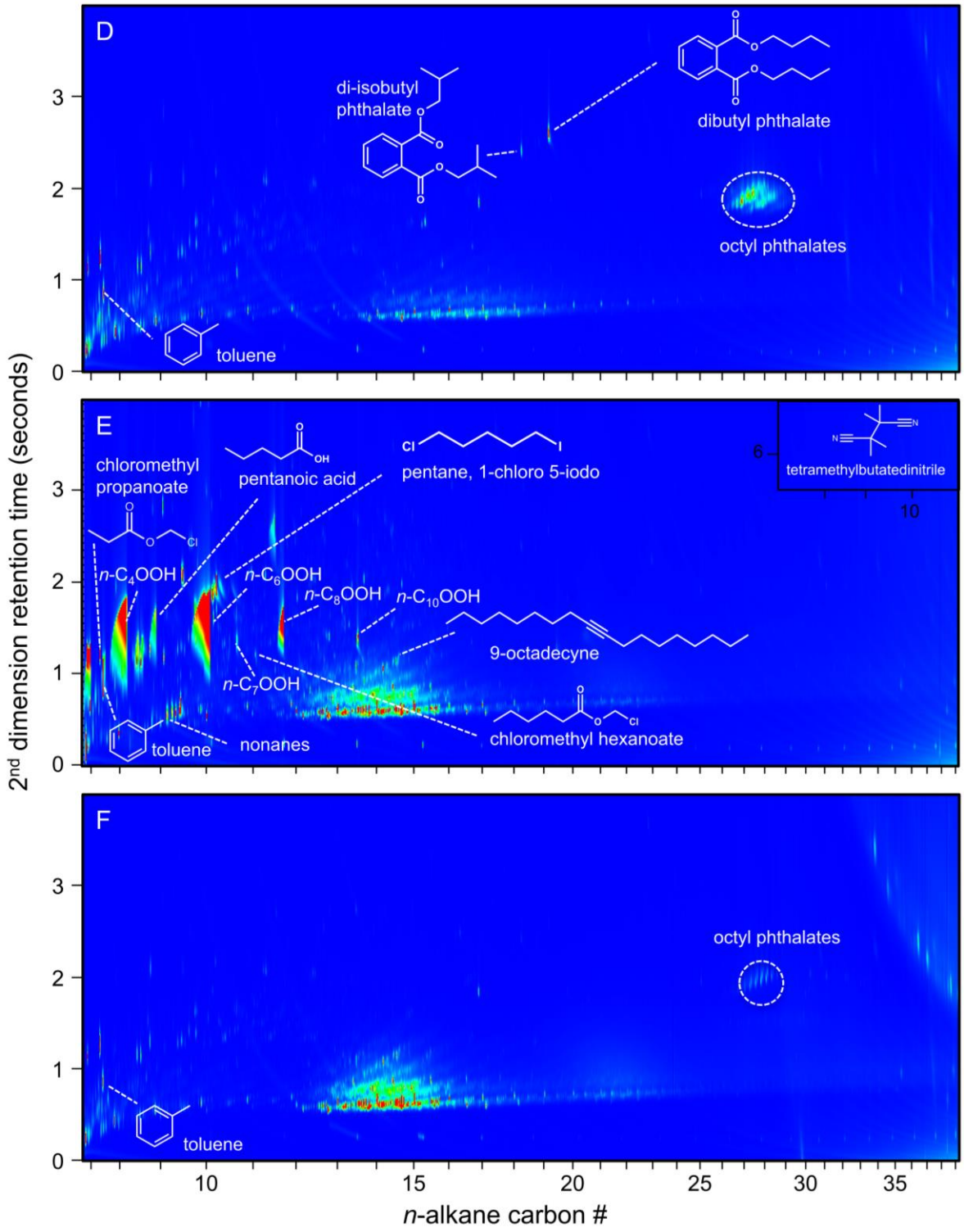


Figure 8 (D-F). GC×GC-FID chromatograms for 6 different UNGD wastewater samples with highlighted compounds and compound groups. The abscissa gives the 1st-dimension retention time (with respect to n-alkane retention time), and the ordinate displays the 2nd-dimension retention time. The heat map reflects signal intensity, increasing from blue to yellow to red. Structures are shown for a subset of compounds identified with a high degree of confidence. Note: Insets in the upper right corners of panels display portions of the chromatograms that would otherwise be outside the selected display range. Samples A-E were collected within three weeks of the initial well fracture (i.e., flowback waters); sample F after approximately 50 weeks of the initial hydraulic fracturing (i.e., produced water).

in practically every UNGD operation[217] and (b) may stem from the geologic target formation[224]. In contrast, substances with functional groups like carbonyl compounds, alcohols, halogenated compounds, carboxylic acids, ethers, epoxides and others (e.g. nitriles and siloxanes; Table 7) were detected in smaller numbers. Typically, many of these compounds are not reported in shale formations[59, 60] or found in crude oil extracts, suggesting an anthropogenic origin. These compounds could be informative, since functional groups and their associated reaction chemistry indicate a putative purpose as fracking additives.

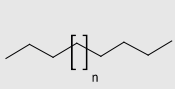
Strikingly, it is precisely these compounds, those potentially performing the critical subsurface chemistry, that are disclosed at a much lower rate compared to alkanes and petroleum hydrocarbons. For example, the disclosure frequency (i.e., number of reports per number of total disclosures) on FracFocus[41] is less than 1% for the organohalogens (other than the biocides, benzyl chloride and dichloromethane), less than 5% for carboxylic acids (other than formic acid, acetic acid, and their salts), and between 2 and 5% for ethers and epoxides[65, 217, 225]. In comparison, petroleum distillates are disclosed in roughly 100% of all UNGD operations reported on FracFocus, with additional disclosure of specific aromatic structures in 30 to 50% of operations[65, 217, 225].

3.3.2 Sample heterogeneity and emerging similarities: Insights from GC×GC

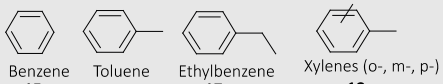
First, we note that all six of the UNGD wastewater samples were derived from a single shale play. While a sample set of six is small and may fail to capture the true heterogeneity of flowback and produced water, this is one of the largest datasets of its kind. Nevertheless, caution should be taken in extending these results to other produced and flowback waters, which could vary between and within a single formation, as a

Table 7: Overview of Selected Compounds and Compound Classes detected in Shale Gas Wastewater Samples.

Chemical	Sample Name A	B	C	D	E	F	analytical method	Stds[3]	MSL[4]	CA[5]	reported detection of this compound class	putative origin/reported function
Hydrocarbons (n=311)												**HF additives or geogenic origin**
n-alkanes	**1-11,[1] 13**	**1-5,7-9 11-13**	**3,9**	**7-12, 14**	**1,3, 5-10**	**3, 6-9**	LLE-GC-MS GCxGC-TOF-MS	x	>850	x	Maguire--Boyle 2014, Orem 2014, Hayes 2009, Strong 2013	Geogenic origin or used as solvent/base fluid (e.g. US Pat 4739834)
BTEX	**15**	**16-18**		**15**			PT-GC-FID[2], PT-GC-MS	x			Hayes 2009; Strong 2013; Maguire-Boyle 2014 , Lester 2015, Thacker 2015	Geogenic origin or used as solvent/base fluid (e.g. US Pat 4739834)

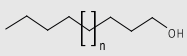


n= 1: Octane **1**
n= 2: Nonane **2**
n= 3: Decane **3**
n= 4: Undecane **4**
n= 5: Dodecane **5**
n= 6: Tridecane **6**
n= 7: Tetradecane **7**
n= 8: Pentadecane **8**
n= 9: Hexadecane **9**
n= 10: Heptadecane **10**
n= 10: Octadecane **11**
n= 11: Nonadecane **12**
n= 12: Eicosane **13**
n= 13: Heneicosane **14**

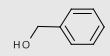


Benzene **15** Toluene **16** Ethylbenzene **17** Xylenes (o-, m-, p-) **18**

Alcohols (n=26)												**Disclosed and suspected HF additives, Transformation products**
primary unsubstituted alcohols	**19,21**	**19-21**			**21**	**22**	PT-GC-MS, GCxGC-TOF-MS	(x)[6]	>850	x	n.a.	HF additives, e.g. US 20120000708 A1
cyclic alcohols		**23**		**23**			GCxGC-TOF-MS	(x)	>850	x	n.a.	Transformation products (hydratization of alkenes or ester hydrolysis) or suspect HF additives
alkyl phenols		**24-27**					GCxGC-TOF-MS		>850	x	Orem 2014	Biogenic or abiotic transformation products from alkylphenol polyethoxylates (see Scheme 1, C2; *Stephanou & Giger,* 1982)

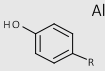


n= 1: Octanol **19**
n= 2: Nonanol **20**
n= 3: Decanol **21**
n= 6: Tridecanol **22**



Benzyl Alcohol **23**

Alkyl phenols



R= methyl **24**
R= p-tert-butyl **25**
R= 1,1,3,3- tetramethylbutyl **26**

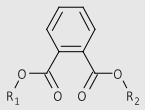


R1 = ethyl, R2 = methyl **27**

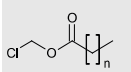
Carboxylic acids, Anhydrides, Chlorides, Chloromethoxy esters (n= 26)												**Transformation products or suspected HF additives**
aliphatic monocarb-oxylic acids	**28,29, 31,32, 34,35**	**28-34, 36, 37**			**28-32, 34**		GCxGC-TOF-MS	(x)	>850	x	Orem 2007,2014, Hayes 2009	Postulated biodegradation products of geopolymeric substances (Orem); but we hypothesize they are transformation products (hydrolysis) of delayed acids
phthalates	**38**	**39,40**	**38, 39**	**39,40**			GCxGC-TOF-MS	x	>850	x	Hayes 2009, Maguire-Boyle 2014, Orem 2014, Lester 2015, Ferrer 2015, Drollette 2015	Phthalates mentioned as suitable organic acids (US Pat 20070125536) or as diverting agents (fracfocus.org, e.g. Nabors Completion and Production Services)
chloro methoxyesters	**42**	**41-44**			**41,43**		GCxGC-TOF-MS		>850	x	n.a.	Putative undisclosed delayed acid (Scheme 1A)
anhydrides and acyl chlorides	**45-47**						GCxGC-TOF-MS		>850	x	n.a.	Carboxylic acid anhydrides are used as delayed acids, e.g. US Pat 8387696. The acyl chloride is either a transformation product of an anhydride (hydrolysis) or is used itself as additive, releasing acid moieties.



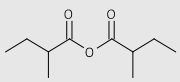
n= 2: Butanoic acid **28**
n= 3: Pentanoic acid **29**
n= 4: Hexanoic acid **30**
n= 5: Heptanoic acid **31**
n= 6: Octanoic acid **32**
n= 7: Nonanoic acid **33**
n= 8: Decanoic acid **34**
n= 9: Undecanoic acid **35**
n= 10: Dodecanoic acid **36**
n= 12: Tetradecanoic acid **37**



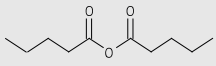
R1, R2 = butyl: Dibutyl phthalate **38**
R1, R2 = isobutyl: Diisobutyl phthalate **39**
R1, R2 = isoocyl: Disooctyl phthalate **40**



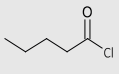
n= 1: Chloromethyl propanoate **41**
n= 3: Chloromethyl pentanoate **42**
n= 4: Chloromethyl hexanoate **43**
n= 6: Chloromethyl octanoate **44**



2-Methylbutanoic anhydride **45**



Pentanoic anhydride **46**

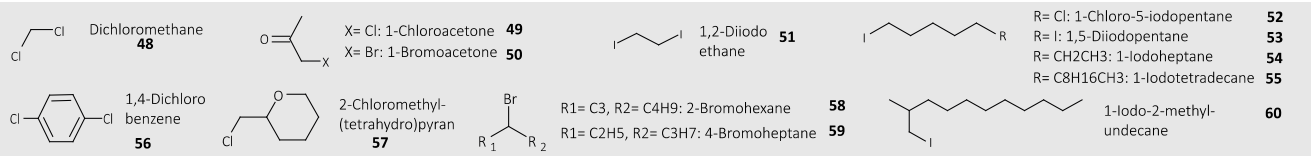


Pentanoyl chloride **47**

[1] Bold-faced numbers indicate compound identity and correspond to their respective structures in the grey boxes.
[2] FID signals were below limit of quantification, but above the limit of detection for several instances.
[3] Stds: x= = Confirmed with authentic standards
[4] MSL: x = Mass Spectra Library forward and reverse similarity (reported as a percent of a total possible match of 999).
[5] CA= Positive confidence assignment via Kovats retention index match
[6] Some of the depicted compounds were confirmed by authentic standards.
[7] Compounds 61 and 62 are displayed in Scheme 1

Table 7 (continued): Overview of Selected Compounds and Compound Classes detected in Shale Gas Wastewater Samples.

Chemical	Sample Name A	B	C	D	E	F	analytical method	Stds[3]	MSL[4]	CA[5]	reported detection of this compound class	putative origin/reported function
Halogenated compounds (n=13)												**Transformation products or suspect HF additives**
halogenated benzenes						**56**	PT-GC-FID,[2] PT-GC-MS	x			Hayes 2009	Other isomers were not detected, therefore unlikely a transformation product; probably biocide additive
halogenated pyran	**57**[1]						GCxGC-TOF-MS		>850	x	n.a.	Electrophilic addition with epoxide intermediate (see Scheme 1, B3)
halomethanes				**48**		**48**	PT-GC-MS		930-960		Hayes 2009, Getzinger 2015, Thacker 2015	Dichloromethane mentioned on SkyTruth (function unclear); could be formed by radical substitution of methane (Scheme 1, B1) or bacteria
halogenated alkanes			**58, 59**		**52**	**55, 60**	GCxGC-TOF-MS		>850	x	Hayes 2009, Maguire-Boyle 2014	Transformation products formed by addition or substitution reactions (Scheme 1B). Precursor compounds: Alkanes, alkenes can be either geogenic or used as solvents (e.g. US Pat 4739834); alcohols or diols are used for scale inhibition or crosslinking (Elsner & Hoelzer)
	51, 54		**51, 53**	**51, 53**	**51**	**51**	LLE-GC-MS		830-960		n.a.	
halogenated acetones	**49**	**49**	**49, 50**	**49, 50**	**49, 50**		PT-GC-MS		>850		n.a.	Halogenation of carbonyl groups of acid or ketone (catalyzed by acid or base)



Nitriles (n=2)		**61**[7]				**62**		(x)[6]	>850	x	Orem 2014	**Chemical transformation products of suspect HF additives:** AIBN is a radical initiator and TMSN a transformation product (Scheme 1, C1)
Other (n=39)												**see Table S1**

[1] Bold-faced numbers indicate compound identity and correspond to their respective structures in the grey boxes.
[2] FID signals were below limit of quantification, but above the limit of detection for several instances.
[3] Stds: x= = Confirmed with authentic standards
[4] MSL: x = Mass Spectra Library forward and reverse similarity (reported as a percent of a total possible match of 999).
[5] CA= Positive confidence assignment via Kovats retention index match
[6] Some of the depicted compounds were confirmed by authentic standards.
[7] Compounds 61 and 62 are displayed in Scheme 1

function of time since spud date, and, of course, due to the variability in additives (i.e., fracturing fluid composition from well-to-well). This work aims to build on the growing body of knowledge that seeks to delineate the possible chemical characters of UNGD waste fluids.

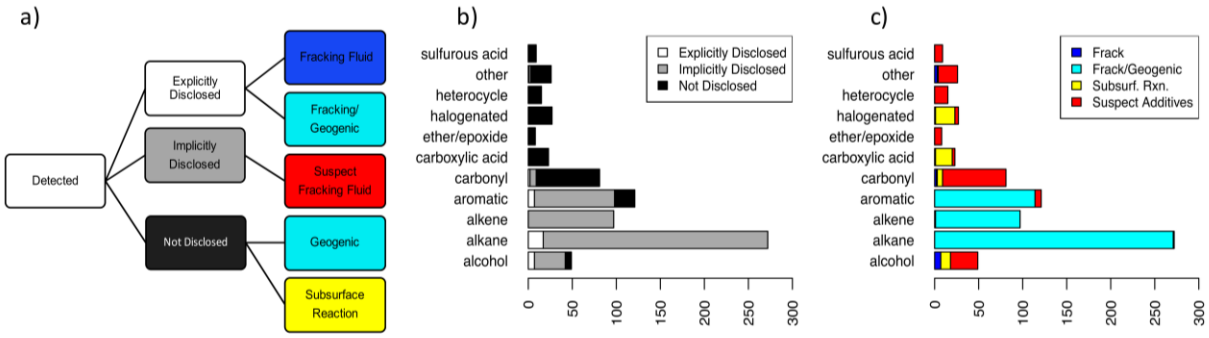


Figure 9. Compound classifications and disclosure..(a) Classification framework for detected compounds. Explicit disclosures were explicitly mentioned by chemical name or synonym on FracFocus, Skytruth, or the "Waxman List". Implicit disclosures included structures that were nonspecific or disclosed as a group of compounds. Undisclosed items had no declarations of use in unconventional natural-gas development (UNGD) activities. Ultimate source classification was assigned using chemical structure, compound class, knowledge of geogenic materials previously reported in oil and gas plays, understanding of potential utility in an UNGD operation (i.e., suspect fracking fluid), and putative transformation pathways with likely precursors. Also shown is the breakdown of disclosure by (b) compound class and (c) source classification by compound class. A detailed list of analytes can be found in the Supporting Information (Table S1).

Comprehensive two-dimensional GC offers enhanced resolution of hydrophobic complex mixtures that has revolutionized the study of oil and gas extracts[82-84, 221, 226] (Figure 8).

Commonly, and in our GCxGC analysis, substances are separated according to vapor pressure in the first dimension (i.e., abscissa or x-axis) and according to polarity in the second dimension (i.e., ordinate or y-axis). Note that samples A-E were collected at the same well age and from the same shale play, yet each exhibits a heterogeneous chemical character visible in GCxGC space.

As expected for shale-derived samples, the majority of the components were detected between *n*-C_{11} and *n*-C_{20} in the first dimension. A higher percentage of lower-boiling, lower-polarity compounds (*n*-C_{12} to *n*-C_{16} and roughly 0.5-1 s in the 2nd dimension) was observed in the samples E (and F, the produced water) compared to the samples A and B, which had a broader distribution in both dimensions (*n*-C_{11} to *n*-C_{20} and roughly 0.5-1.5 s). This difference does not correspond to weathering, in which one would expect losses

of lower-boiling and higher-polarity compounds preferentially.[227] That is, if samples E and F were similar to A and B but had experienced some weathering event (either in the field, during transport, or in lab), then E and F would have some loss in the "front end" (low boiling and high polarity compounds) but not at the "back end" (higher boiling, lower polarity compounds) [227, 228]. Since E and F are lacking both the high and low volatility compounds relative to samples A and B, then the difference is likely due to authentic variations in the chemistry of the source water rather than weathering in the field or a sampling artifact. As all samples were derived from the same shale formation and are of the same age (except for the relatively older F), this suggests that some of the detected hydrocarbons may be hydraulic fracturing additives, contributing to the geogenic hydrocarbons.

Inter-sample differences became even more pronounced in the polar regions of the chromatograms (between 1 and 2 s in the second dimension; Figure 8). Here, carboxylic acid peaks occurred at regular intervals in a ladder-like fashion. An even-over-odd preference is visible in several samples (B, E, and A), which is consistent with Orem et al.'s reporting of C_{12}, $C_{14,}$ and C_{16} carboxylic acids[60] as anaerobic biotic breakdown metabolites of geopolymeric substances[229] and is expected for mixtures of these compounds due to the biological production pathways used to make them (both in the environment and industrially[230-232]). However, in some instances, this pattern of likely geogenic origin is overlain by an overwhelming dominance of a specific alkanoic acid (e.g., pentanoic acid in A, butanoic and hexanoic acid in E). This suggests that these fatty acids derive from UNGD additives through direct addition or through in situ production from an abundant precursor additive. For instance, in sample A, pentanoic acid occurred

together with chloromethyl pentanoate, pentanoyl chloride, and pentanoic acid anhydride, whereas hexanoic acid co-occurred with chloromethylhexanoate in sample E. These chloromethyl alkanoic acids, alkanoyl chlorides, alkanoyl anhydrides, and their potential transformation pathways are described in detail below.

Two classes of compounds emerged that are almost assuredly of geogenic origin: the archean core ether lipids and the pentacyclic terpenoids (i.e., hopanes). These appear in the biomarker region (> *n*-C_{25} and around 2 s in the 2nd dimension) and can be used to trace or fingerprint the shale formation itself, gauge the thermal maturity of the oil hydrocarbons there, and ultimately determine the origin (e.g., kingdom of life) of the organic matter that gave rise to the oil in the source rock[84, 220, 233-235]. Samples A and B showed a clearly defined hopane biomarker region (see SI Figure S3), and thermal maturity indicators, such as the Ts/Tm ratio (where Ts is 18α(H)-22,29,30-trisnorneohopane and Tm is 17α(H)-22,29,30-trisnorhopane), suggested that samples were of the same geological age (see SI). Note that Sample A was much less concentrated than B, but the relative proportions and distribution of hopanes were similar between the two. Other samples had indiscernible levels of hopane biomarkers, and steranes, which can indicate geological formation source information, where not detected. Nevertheless, where available, these biomarkers are powerful for tracing shale wastewaters or in environmental forensics associated with such source apportionment between heterogeneous, complex mixtures.

Sample heterogeneity persisted at higher second dimension retention times (2-3 s), where multiple phthalate esters were detected. While their occurrence clearly indicates an anthropogenic influence, we caution that polymer containers utilized during the initial

sample collection by the Arkansas Oil and Gas Commission raise concern as a potential source of phthalates. However, we do not consider this the prime or only source in our study for the following reasons: (a) the phthalate esters were not detected in all samples, even though all samples utilized the same types of containers over the same timeframe; (b) the specific type of detected phthalate varied among the samples, but would not have varied between the containers; and (c) laboratory control studies in which saline water was equilibrated with the containers over 120 days showed no detectable phthalates at a 7 parts per billion detection limit (see Control Experiments, SI). Thus, while we caution that phthalates are ubiquitous industrial chemicals (i.e., potentially derived from pipe utilized in the field), we expect that these compounds are authentic to the sample and derive from hydraulic fracturing operations. Indeed, *bis*(2-ethylhexyl) phthalate is disclosed as a diverting agent (e.g. from Nabors Completion and Production Services[63]) and di-*n*-octyl phthalate was reported in UNGD wastewater[154]. Undisclosed phthalates, such as diisobutyl, dibutyl, butylisobutyl, dioctyl, and diisooctyl phthalate, were also detected, suggesting that phthalates may have more pervasive uses in hydraulic fracturing than indicated by their disclosure rates[217]. Note that all phthalates were confirmed with authentic standards (and all but dioctyl phthalate passed the Kovats retention index confidence check).

Finally, two additional compounds at very high retention times (around 6 s; Figure 8 insets) are strongly indicative as UNGD additives: azobisisobutyronitrile (AIBN), a disclosed, common radical initiator[236], in sample B, and tetramethylsuccinonitrile (TMSN), its direct transformation product, in sample E (Scheme 1C; discussion below). Radical-initiating azo compounds are occasionally reported in the Waxman List and on

FracFocus, and they do not have geogenic origins. As such, these compounds were categorized as hydraulic fracturing additives and present interesting opportunities for radical-initiated transformation pathways in the subsurface.

3.3.3 Structural classification and quantitative overview of detected compounds

In order to provide an accessible overview, we classified compounds according to their chemical structure (Table 7; Table S1), in a similar way as presented in a recent review of disclosed UNGD additives[217]. Only those compounds that could be confirmed via more rigorous confidence assignment criteria (e.g., 311 hydrocarbons and 27 alcohols, via methods such as authentic standards ("Stds"), mass spectral library agreement score ("MSL"), and retention index confidence assignment ("CA") are presented in the main text (Table 1), whereas a comprehensive overview of all tentative identifications (n=729) are presented in the SI (Table S1). Out of these classes, structures are given for those substances that stand out because of their occurrence in several samples (i.e., columns "A" to "F" in Table 7) and functional groups that indicate a specific reaction chemistry. Identifications are supported by CAS (Chemical Abstracts Services) numbers (where available), putative origin (Table S1), and patent number (where available), as well as by providing references to previous studies which tentatively detected the same chemicals in flowback waters.

Hydrocarbons were the most prominent compound class, and they are both geogenic and utilized as UNGD additives. Among the hydrocarbons, the well-known groundwater contaminants benzene, toluene, ethylbenzene, and xylenes were present in some of the

samples and occurred in concentrations up to 7.3 ± 0.5 µg L^{-1} (SI Table S3; also see Table S2), although we emphasize that up to 15% of the original benzene may have partitioned to the headspace in the non-ideal collection approach (i.e., HDPE containers with headspace). If equilibrium with the HDPE were achieved (> 2 weeks), functionally all of the BTEX would have partitioned into the container itself. In addition, many alcohols were detected and allocated as putative fracturing chemicals (additives) or their transformation products, since (a) long-chain alcohols are occasional UNGD additives commonly used as solvents (e.g., 1-decanol, 2-ethyl-1-hexanol, and isopropyl alcohol, which has a disclosure frequency of 47-50%)[65, 217] and (b) may form by degradation from ethoxylated alcohols, either by abiotic oxidation of the weak C-H bonds next to an either group[237] or in biotic degradation[238]. Such ethoxylated alcohols are disclosed as frequent additives (between 65 and 100%) and have been detected in flowback[44]. (c) Finally, alcohols can be products of chemical hydration of alkenes or of ester hydrolysis[239] and certain alcohols can be biotic fermentation product of sugars. However, since alcohols are typically not prominent in shale gas formation water and due to the structural similarity to disclosed compounds, other detected alcohols were also considered as suspect UNGD additives or transformation products.

Remarkably, there are numerous compounds that are not likely of geogenic origin and are also *not* known reported hydraulic fracturing additives (Table 7). In particular, there was a high abundance of certain carboxylic acids (pentanoic acid in sample A and butanoic and hexanoic acid in sample E) together with the occurrence of hitherto unknown putative fracturing additives (e.g., chloromethyl alkanoates and alkanoic anhydrides). Another example is the rather high occurrence rate of alkyl phenols and benzyl alcohol,

which stands in contrast to the low frequencies at which these compounds are reported as fracturing additives on FracFocus (nonylphenol <0.2%; benzyl alcohol is not disclosed[65, 217, 225]). Additionally, there is strong evidence for halogenated hydrocarbons that were observed in all flowback and produced water samples. With the exception of benzyl chloride (reported on FracFocus in 6-7% of all operations[65, 217, 225]), halogenated hydrocarbons are practically non-existent in lists of reported hydraulic fracturing additives. Specifically, the brominated, iodated, and chlorinated (e.g., bromoacetone, 1-chloro-5-iodopentane, and dicloromethane) substances that were detected in our study were not disclosed as additives in fracturing applications, except for the seldom reported dichloromethane (0.01% frequency[65, 217, 225]). This contrasts strongly with our finding that dichloromethane and 1-iodo-tetradecane were detected in two samples and chloroacetone and/or bromoacetone were detected in five out of six samples. Considering the low disclosure rates, we entertain the hypothesis that these chemicals formed as unintended transformation products in the process of the hydraulic fracturing process. In the subsequent discussion, we postulate putative reaction mechanisms that may lead to formation of these compounds.

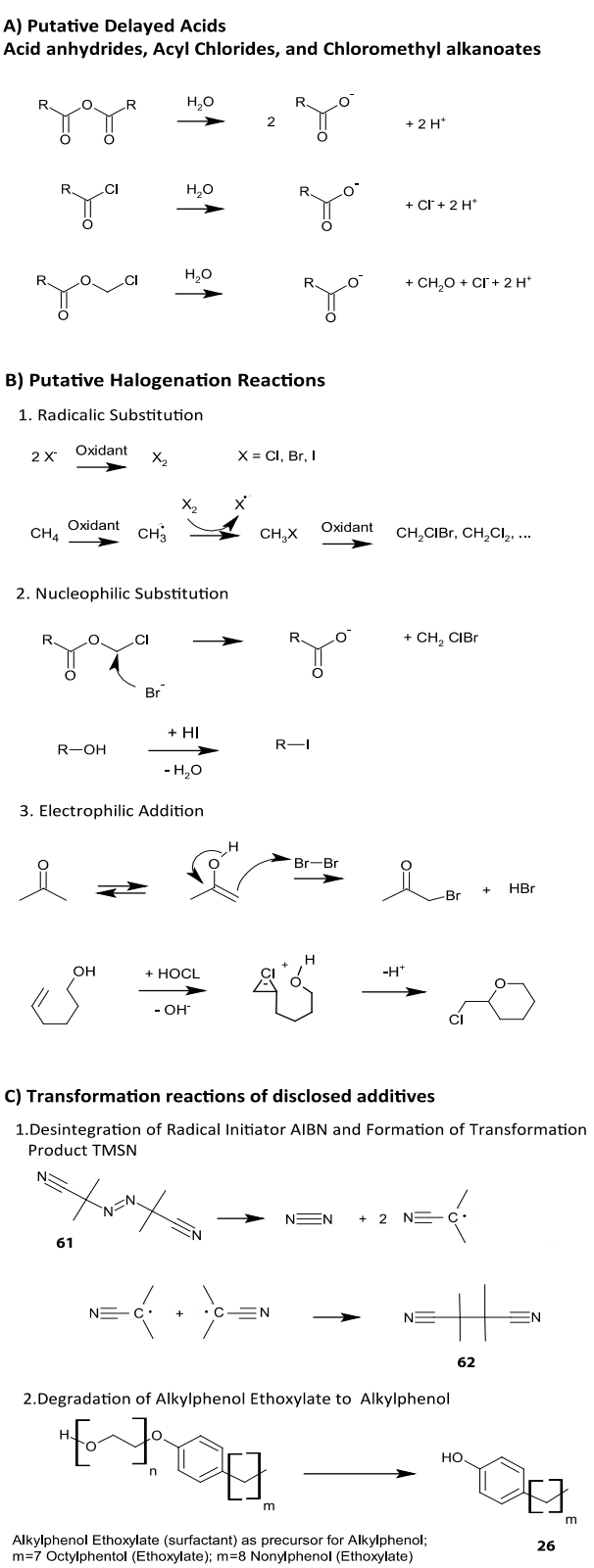
3.3.4 Proposed Reaction Mechanisms Leading to Transformation Products

In general, transformation products can arise in both abiotic and biotic reactions, and very few environments are truly sterile[240]. During the hydraulic fracturing process, conditions are met that are favorable for abiotic processes, such as elevated temperature, pressure, salinity, and the use of strong oxidizing agents and biocides. While the possibility of biological transformations mustn't be ignored, here we consider primarily abiotic transformations to explain products hypothesized to form during the UNGD process (e.g., halogenation reactions are possible in halotolerant organisms, but are generally not considered a broadly distributed, common metabolic capability[241]). In contrast, conditions at the surface for flowback and produced water are quite favorable for biogenic transformation, and we presume degradation was assuredly occurring after the fracturing process.

A. Hydrolysis Reactions of Putative Delayed Acids: Intended Transformations

Detected alkanoyl anhydrides, alkanoyl chlorides, and chloromethyl alkanoates provide an example of likely *intended* abiotic subsurface transformations, as they can function as delayed acids (Scheme 1). In the course of a hydraulic fracturing operation, a base fluid must first be low friction to convey the fracturing pressure underground, then the fluid must become viscous to effectively transport proppants into the formation, and subsequently the fluid must become non-viscous again to facilitate flow back to the surface. To catalyze the last transition, so-called "breakers" are added to destroy the three-dimensional polymer structure of a water-based gel and thereby decrease its viscosity. In the case of guar gum, by far the most commonly applied gel-forming agent in UNGD operations[23], borates are used as cross-linkers to form three-dimensional

polymer structures. Here, acids serve as convenient breakers by shifting the acid-base equilibrium of borate to boric acid. This sequestration of borate ions as cross-linkers causes the three-dimensional gel structure to break[56]. If such a strategy is pursued, the *timing* of acid addition is crucial. If cross-links were broken up too early, proppants could not be transported and the fractures in the formation would close prior to gas recovery. For this reason, alkanoyl anhydrides, alkanoyl chlorides, and chloromethyl alkanoates can be attractive reagents. These first undergo chemical hydrolysis reactions and subsequently release their acid equivalents (Scheme 1A) after the appropriate delay time (i.e., they are *delayed* acids). Potentially, this time could be tuned by choosing different compounds in varying proportions and



Scheme 1: Mechanisms of metabolite formation. (a) Putative delayed acids render acidic protons after a hydrolysis reaction. (b) Putative halogenation reactions can occur via radical-mediated substitution, nucleophilic substitution, or electrophilic addition. (c) Demonstrated transformation pathways of disclosed hydraulic fracturing additives, such as radical initiators (AIBN (azobisisobutyronitrile) degrading to TMSN (tetramethylsuccinonitrile))[46] and alkylphenol ethoxylates degrading to alkylphenols, which can occur biotically and abiotically[48].

by changing the chain length of the alkanoic acid (e.g., C_3, C_4, or C_5), in order to lend the additives different degrees of hydrophilicity.

B. Halogenation Reactions: Unintended Transformations

Halogenation of hydrocarbons provides a potential example of *unintended* transformation reactions that may generate problematic by-products (Scheme 1B). Even though biotic organohalogen production e.g. by marine algae, sponges, and bacteria is known[57], we hypothesize that detected compounds are rather attributable to abiotic transformation (with the possible exception of biotic halomethane formation in the reservoir). Specifically, underlying reaction rates may be enhanced due to the elevated temperatures and high salinity prevailing in the subsurface and many of these reactions could be triggered by the strong oxidants introduced as breakers in the course of the hydraulic fracturing process[23]. For example, in the presence of strong oxidants, halides can form molecular halogens (Cl_2, Br_2, I_2) and, simultaneously, these oxidants can also attack methane, which is present in high concentrations in the formation (Scheme 1B1). Once methyl radicals are formed, they are readily halogenated under these conditions in radical substitution reactions. Alternatively, nucleophilic attack (S_N2) by halide ions (Cl^-, Br^-) may generate dihalomethanes out of the putative chloromethyl alkanoate additives, even in the absence of oxidants (Scheme 1B2). This is an example of how non-disclosed additives may potentially generate unintended by-products, underscoring the importance of disclosing UNGD additives. Finally, molecular halogens and hypohalogenic acids may also facilitate electrophilic addition reactions which can explain the formation of halogenated acetones and a halogenated pyrane observed in this study (Scheme 1B3).

C. Transformation Reactions of Disclosed Additives: Products of Known Additives

Several compounds detected in our study may stem from transformation reactions of disclosed additives (Scheme 1C). One example is the formation of TMSN (**62**) from the radical initiator AIBN (**61**). AIBN (**61**) spontaneously and abiotically releases a molecule of nitrogen gas originating from the azo group to form two 2-cyanoprop-2-yl radicals[58], which can initiate polymer chain reactions or recombine to TMSN (**62**). These compounds were found in two out of six samples in our Fayetteville sampling, suggesting they may serve as UNGD additives to initiate polymerization more often than reflected by the national disclosure rate (0.01%. An alternative source could be leaching from polymers; see Elsner and Hoelzer[23]). Another example of a reaction byproduct of a known additive is benzyl alcohol (**23**), which is not itself reported as UNGD additive[23]. However, benzyl alcohol can form via abiotic hydrolysis of benzyl chloride in an S_N1 reaction. Indeed, benzyl chloride is a rather frequent additive (application frequency of 6% - 7% on FracFocus[23, 33, 34]. Finally, even though phenols are reported as naturally occurring constituents in shale formation water[47, 59] and phenols are also occasionally reported as UNGD additives[23], we hypothesize that at least some of the phenols detected in our study are formed (biotically or abiotically) as transformation products. In particular, (a) the structures of the compounds 4-*tert*-octyl phenol (a precursor in the synthesis of octylphenol polyethoxylates) and p-*tert*-butyl phenol (**26**, **25**) appear too specialized to be of likely natural origin, and (b) the reports of phenols in UNGD databases are greatly outnumbered by the instances at which *alkoxylated* phenols are reported[23]. For this reason, we hypothesize that these phenols are formed as transformation products of the respective alkylphenol ethoxylates[60, 61] (Scheme 1C). Note that alkylphenol ethoxylates can give rise to alkylphenols as metabolites via ϖ-oxidation

or central fission[51, 60, 62, 63] or abiotic oxidation of the weak C-H bond adjacent to ether bonds[50].

3.3.5 Compounds outside the Confidence Assignment

The compounds discussed above passed careful evaluation of data quality by high MS library match scores (>85%), as well as additional confidence assignment criteria, making this study conservative relative to previous investigations. Had we applied less strict proceedings, some other observations would be made, which we want to describe briefly. Beyond our strict confidence assignments, there were indications for more halogenated compounds. For example, 1-chloro-5-iodo-pentane was detected in 5 samples with at least 620 forward and reverse similarity in the MS library (and with greater than 850 and passing the retention index CA in an additional sample) and iodohexane (320 similarity) in 3 samples. Furthermore, a total of nine sulfurous acid alkyl esters were tentatively detected (one passed the Kovats confidence assignment: sulfurous acid, 2-ethylhexyl isohexyl ester). These are not reported as fracturing additives; only inorganic sulfite salts (paired with ammonium or organic ammonium ions) are disclosed to serve for oxygen scavenging or corrosion inhibition. Our findings might indicate their use as additives, although, the purported utility of the sulfurous acid esters is unclear. Nevertheless, the detections are supported by Strong et al.[20], who detected a similar sulfurous acid ester, namely sulfurous acid, dodecyl 2-propyl ester[20].

3.3.6 Implications for Monitoring and the Environment

These data demonstrate that UNGD wastewater not only contains fracturing additives and compounds of geogenic origin, but also intended and unintended transformation products generated during the process. This has the following important consequences: (1) Standard monitoring methods are not sufficient for a proper assessment of UNGD wastewaters. Usually monitored compounds (e.g. via EPA standard methods) will overlook a variety of constituents, especially transformation products. Consequently, more comprehensive monitoring concepts are needed, especially as advanced instrumentation becomes more accessible. For instance, GCxGC TOF-MS (among other advanced techniques) allows detection of undisclosed compounds or transformation products, which could not be observed in targeted analysis. In absence of the broad application of advanced analytical techniques, a primary screen of diesel-range organic compounds would enable one to identify samples for which a more thorough GCxGC analysis was merited.[3, 22] Note that here, we are only describing methods for the hydrophobic organic compounds, and a comprehensive chemical description of these waters is indeed a complex undertaking (i.e., for inorganic materials, naturally occurring radioactive materials (NORMS), and polar organic analytes, which are a large fraction of the disclosed chemical database[3]). In addition, as UNGD expands, heterogeneities between formation waters, injected fracturing fluids, and transformation products must be elucidated and studies pursuant to this should be undertaken whenever possible. (2) Full disclosure of UNGD additives is needed to accurately gauge risk associated with UNGD wastewaters. Current practice (June 2015 to present) maintains that it is sufficient to disclose merely whether an additive is toxic or not, while concealing the chemical

identity due to its proprietary nature. Here, we show that even non-toxic precursors can be converted to problematic products, and disclosing chemical additives could enable enhanced prediction, toxicity screening (see SI for discussion), and mitigation of unintended by-products. Further, because waste treatment practices tend to target biodegradable compounds, it is possible that standard waste treatment practices would not capture many of these non-biodegradable components. In high salinity waters, these could go on to give rise to enhanced disinfection by-product formation in drinking water treatment plants whose intakes are downstream from treated-waste receiving waters. Thus, the information presented in this study could aid in the development of targeted treatment practices that could prevent such unintended consequences. (3) We recommend iodide monitoring[64, 65] alongside chloride and bromide, as well as iodated, chlorinated, and brominated compounds. This is particularly important since iodo-organics' health impacts are often more severe than chlorinated and brominated species[66, 67], and it is not yet clear to what extent they are present in UNGD wastewaters. Furthermore, likely exposure routes of UNGD wastes to the environment should be evaluated and addressed if treatment is deemed necessary[3, 65, 68]. Overall, these considerations illustrate the far-reaching consequences of an adequate identification of transformation products. Here, we present a path for further research in this direction, which must be accompanied by toxicological studies, studies of biological transformation pathways, and ultimately channel into strategies for wastewater treatment (see SI for further discussion).

4

Carbon and Nitrogen Isotope Analysis of Atrazine and Desethylatrazine at Sub-µg/L Concentrations in Groundwater

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4.1 Introduction

Compound specific isotope analysis (CSIA) via gas chromatography-isotope ratio mass spectrometry (GC-IRMS) is a powerful, yet relatively new method to assess organic contaminants in the environment [242]. CSIA can serve for various purposes which are particularly important in environmental studies: Firstly, it may elucidate the source of a compound [243], since isotope ratios at natural abundance (e.g., $^{13}C/^{12}C$, $^{15}N/^{14}N$) may be used as the equivalent of characteristic fingerprints [242]. Secondly, CSIA may prove that a contaminant is naturally degraded [244], because degradation reactions are typically associated with kinetic isotope effects. Heavy isotopes therefore become enriched in the remaining contaminant, $^{13}C/^{12}C$ ratios change and they can consequently serve as a diagnostic tool to detect degradation [244-247]. Thirdly, CSIA can give evidence which reaction pathways have been occurring during compound degradation. The reason is that cleavage of a certain bond often causes characteristic isotope effects of specific elements [248] leading to distinct enrichment trends for different transformation reactions (e.g. in $^{13}C/^{12}C$ versus $^{15}N/^{14}N$). This line of evidence is therefore particularly conclusive when two or more elements can be analyzed by CSIA [90, 249, 250].

For GC-IRMS measurements, target compounds are either evaporated in an injector of a gas chromatograph or, in the case of on-column injection, at the end of a retention gap. Analytes are subsequently separated on an analytical GC column. After elution, the Helium carrier gas transports the compounds into a combustion oven, where they are converted online to CO_2, N_2 and traces of NO_x. When measuring nitrogen, NO_x are subsequently reduced to N_2 via a reduction oven and CO_2 is captured in a cool trap to avoid isobaric interference from CO^+ (m/z =28, same as $^{14}N_2$). The combusted gases are subsequently transferred into an IRMS for isotope ratio measurement [102, 251]. Quality control is usually provided by accompanying measurements of a monitoring (“reference“) gas and by measuring isotope ratios of in-house standards of the target compounds.

Compared to “classic” GC-MS, GC-IRMS is comparatively insensitive, because the rare, heavier isotope (i.e., ^{13}C) needs to be measured with high precision so that relatively high concentrations of total compound (i.e. around 1 nmol of carbon on-column) are required [86]. On this account, preconcentration steps and matrix elimination are crucial particularly when approaching field samples.

Currently, GC-IRMS applications primarily focus on volatilizable, rather small molecules that contain only C, H, O and Cl, for the following reasons. (i) These compounds are

easily analyzed, since the absence of "sticky" atoms like N lends them good chromatographic characteristics (low boiling point, low peak tailing); in addition, it was found that their combustion typically does not introduce an isotopic shift [252, 253]. (ii) In such small compounds only few additional atoms "dilute" the position-specific kinetic isotope effect [248] so that observable compound-specific isotope fractionation is large and indicative of natural degradation (see above). Most importantly, almost all priority pollutants fall into this class, like chlorinated ethenes [254-256], petroleum hydrocarbons [257-259] and fuel oxygenates [260-263]. Since such point-source pollutants typically occur at relatively high concentrations (mg/L to µg/L range) at contaminated sites, (iii) only comparatively small sample amounts (40 mL to 100 mL) are needed for isotope analysis and (iv) matrix interferences are small.

In addition to these „traditional" contaminants, however, more and more attention is directed at micropollutants such as pesticides and pharmaceuticals, which stem from diffuse sources and occur in ng/L concentrations in natural samples. Particularly interesting is the ubiquitous occurrence of these micropollutants in aquatic systems [264] and the fact that they are still present even though their use has been forbidden for decades. Atrazine (Atz) and its major degradation product desethylatrazine (DEA), for example, are still amongst the most frequently detected pesticides in German groundwater surveys [265] – at some sites even in increasing concentrations [266] – despite the fact that Atz use has been forbidden since 1991.

Conventional approaches are for several reasons not comprehensive enough for micropollutant fate assessment. Measuring compound concentrations only cannot distinguish degradation processes from dilution. It can also not be determined whether a contamination will remain in an aquifer for the following decades or whether degradation will occur over longer timescales. While atrazine degradation in soil is well characterized [267-270], it is still insufficiently understood over what time scales atrazine can be degraded in groundwater [271, 272]). In particular, micropollutant assessment is made difficult due to the input from diffuse sources. On the catchment area scale, it is therefore intricate or even impossible to create mass balances so that pure concentration measurements are not informative enough. In an alternative approach, atrazine degradation has therefore been estimated from desethylatrazine-to-atrazine concentration ratios DAR [273, 274]. However, this concept may be biased if DEA is further degraded or if the Atz degradation follows an alternative pathway which does not include DEA formation, but leads to different metabolites such as hydroxyatrazine [275, 276]. Such metabolites of DEA and atrazine have

different physicochemical properties, may be further transformed [277] and are typically not picked up in groundwater monitoring schemes.

Compound specific isotope analysis bears potential to close these research gaps since it can elucidate sources through fingerprinting and identify degradation from changes in isotope values in target compounds. This complementary isotope information therefore allows evaluating the validity of metabolite-to-parent-ratios by independent means. Despite this need for CSIA of micropollutants, however, until now isotope analysis of micropollutants has not yet been reported in natural groundwater samples.

Specifically, pollutants like atrazine were found to be difficult to analyse on GC-IRMS, because the presence of heteroatoms like nitrogen affected chromatographic performance and rendered complete combustion difficult [278, 279]. Recent work has therefore concentrated on the development and testing of reliable combustion ovens and appropriate standardization for CSIA of nitrogen-containing micropollutants [278-280]. In a parallel effort, recent laboratory experiments [90, 281, 282], have demonstrated that similar isotope fractionation can be observed during degradation of atrazine as for other compounds with up to 8 C atoms that dilute position-specific isotope effects in the compound average [258, 283, 284].

Presently, the development is therefore at a stage where isotope analysis of atrazine has been established at higher concentrations (mg/L) and where first lab studies have demonstrated that compound-specific isotope fractionation may indeed be used to characterize atrazine degradation. However, to take the next step and test the feasibility of approaching low atrazine concentrations in groundwater, enrichment methods need to be validated for the absence of isotope fractionation, and strategies are required to eliminate matrix interferences that increase when target compounds and natural organic matter occur in similar concentrations.

The overarching aim of this study was, therefore, to measure isotope ratios of atrazine and desethylatrazine for the first time in natural groundwater samples and to evaluate what insight could be obtained about their natural degradation. Specific objectives were (i) to test enrichment methods in terms of recovery, in order to enrich sufficient amounts of atrazine and desethylatrazine from up to 10 liters of water (ii) to optimize injection methods and test HPLC cleanup as measures to increase sensitivity and to eliminate matrix effects, (iii) to validate the trueness of isotope values during all of these modifications, (iv) to conduct the first measurements of atrazine and desethylatrazine in

natural groundwater samples (v) and to evaluate what may be learned from this independent information about the current use of desethylatrazine-to-atrazine ratios (DAR) to estimate atrazine degradation.

4.2 Materials and Methods

4.2.1 Chemicals

Atrazine (CAS: 1912-24-9, 97.7% purity) was purchased from Oskar Tropitzsch, Marktredwitz, Germany. Desethylatrazine (CAS: 6190-65-4, 99.9%) and desisopropylatrazine (CAS: 1007-28-9, 96.3%) were provided by Riedel de Haën, supplied by Sigma-Aldrich, Seelze, Germany. Methanol (>99%) and acetonitrile (>99.95%) were supplied by Roth (Karlsruhe, Germany), KH_2PO_4 by Alfa Aesar GmbH & Co. KG (Karlsruhe, Germany). Dichloromethane and ethylacetate (99.8%) were produced by Fluka, supplied by Sigma-Aldrich, Taufkirchen, Germany.

4.2.2 Solid Phase Extraction

To two different volumes of tap water (1 and 10 liters) aqueous stock solutions of atrazine, desethylatrazine and desisopropylatrazine were added so that each volume contained the compounds in three concentrations (total amounts of 5 µg, 25 µg and 50 µg per compound, respectively, all in triplicates). The tested concentrations and volumes were chosen to assess whether the typically used ranges of sample volume at concentrations at the upper edge of the expected compound loads were subject to breakthrough. The solutions were solid phase-extracted following the EPA method 502.2: SPE discs (Bakerbond Speedisk H_2O -Philic DBV; J.T. Baker, Phillipsburg, USA) were conditioned with ethylacetate, dichloromethane and methanol each for 90 seconds and with 90 seconds of air dry time. After loading the sample at a flow rate of 0.1 L/min, the drying time was 30 minutes. Elution was carried out once with ethylacetate, followed by two repeats with dichloromethane (again each 90 seconds plus 90 seconds air dry time). The eluate was evaporated entirely and redissolved in 100 µL of ethylacetate. For both extraction volumes of 1 and 10 L, the extracts of the three fortifications gave target concentrations in ethyl acetate of 50 mg/L, 250 mg/L and 500 mg/L. The recoveries were

assessed by quantification via HPLC-UV at UV absorbance at 220 nm: After evaporation of ethylacetate, the analyte extracts were dissolved in methanol and manually injected into a Shimadzu LC-10A series HPLC system. Based on the method described by Berg et al. [285] the column used was an ODS (30) Ultracarb 5 micron (150 x 4.6mm, Phenomenex, Aschaffenburg) with its oven temperature set to 45°C. A binary gradient of 0.001 M KH_2PO_4-buffer (pH 7) and acetonitrile (ACN) was pumped at 0.8 mL/min through the system: In the beginning, ACN was set to 15 % (1 minute), increased linearily to 55 % (7 minutes), then to 75 % (4 minutes). This ratio was maintained for another 2 minutes, then decreased to 15% within 2 minutes again.

4.2.3 Environmental Samples

Water samples from groundwater wells and springs were collected in 5L-Schott bottles (Schott AG, Mainz, Germany) or steel barrels and stored refrigerated (4 -8°C). The initial concentrations of atrazine, desethylatrazine and desisopropylatrazine were calculated from the concentrations measured in the extracts, taking the assessed recovery rates into account.

4.2.4 Isotope Analysis by GC-IRMS

The GC-IRMS system consisted of a TRACE GC Ultra gas chromatograph (GC) (Thermo Fisher Scientific, Milan, Italy) linked to a Finnigan MAT 253 isotope ratio mass spectrometer (IRMS) (Thermo Fisher Scientific, Bremen, Germany) by a Finnigan GC Combustion III Interface (Thermo Fisher Scientific, Bremen, Germany). Emission energy was set to 1.5 mA for carbon isotope analysis and 2 mA for nitrogen isotope analysis. Helium (grade 5.0) was used as carrier gas and the injector was controlled by an Optic 3 device (ATAS GL, distributed by Axel Semrau, Sprockhövel, Germany). The samples were injected using a GC Pal autosampler (DTC, Zwingen, Switzerland) onto a 60m DB-5 (60m x 0.25mm; 1µm film; Restek GmbH, Bad Homburg, Germany) analytical column. For large volume injections, a fritted liner with glassbeads (A 100001-GB; PAS Technologies, Magdala, Germany) was used, whereas for cold on-column (COC) injection, an on-column liner (either A100129; ATAS GL International (Eindhoven, Netherlands) or custom-made by a glassblower) was pressed directly onto a 3m CS-

Fused-Silica FS-Methyl-Sil retention gap (Chromatographie Service GmbH, Langerwehe, Germany).

Isotope values were determined as $\delta^{13}C$ values in per mill (‰) relatively to Vienna PeeDee Belemnite (V-PDB) [286], where $\delta^{13}C$ is expressed as:

$$\partial^{13}C = \frac{^{13}C/^{12}C_{Sample} - ^{13}C/^{12}C_{S\,tan\,dard}}{^{13}C/^{12}C_{S\,tan\,dard}}$$

An analogous equation applies to $\delta^{15}N$, relatively to AIR-N_2 [287]. The $\delta^{13}C$ and $\delta^{15}N$ values were assessed in relation to a monitoring gas (CO_2 and N_2, respectively) which was measured alongside each run at the beginning and the end. In addition, in-house standards of the target compounds - independently characterized by elemental analyzer (EA) (EuroVector, Milano, Italy) IRMS measurements as described in [280] - were included to provide an anchor to the international reference scale. Calibration of monitoring gases was performed in a Finnigan MAT Delta S isotope ratio mass spectrometer with dual inlet system (Thermo Fisher Scientific, Bremen, Germany). The gases were measured against V-PDB and air, respectively by use of international reference materials: the CO_2 gases RM 8562, RM 8563, RM 8564 for CO_2 and N-SVEC ($N_{2\ gas}$) for N_2. Reference standards were provided by the IAEA.

For the LVI, the GC oven was programmed from 150°C (hold 1min), ramp 10°C/min to 190°C (hold 1min), ramp 3°C/min to 230°C (hold 2min), then heated up to 280°C to heat out the column (hold 3min). The Optic 3 initial temperature was set to 30°C, then ramped at 14°C/s to 250°C. Vent time was 15 minutes, the flow was set to 1.4 mL/min. The initial split flow was set to 50 m/min (50 sec), then to 0 mL/min (180 sec) and from then on to 14 mL/min.

For COC, the GC oven started at 35°C (hold 30sec), ramp 5°C/min to 80°C to ensure a complete solvent evaporation during the transfer of the sample from retention gap to analytical column. Then ramp 100°C/min to 160°C, ramp 10°C/min to 220°C, then ramp 2°C/min up to 250°C. Injector temperature for COC was at 40°C at the Optic 3, 300sec hold, then ramp to 250°C at 2°C/sec. The column flow was in the beginning set to 0.3 mL/min (hold 120 sec), then ramped to 1.4 mL/min within 120 sec so that a flow of 1.4 mL/min was established before the GC temperature was raised.

For samples with high matrix interference, the retention gap needed to be exchanged after few injections in carbon mode, since the background (m/z=44) increased strongly and

retention times shifted indicating the formation of reactive zones within the retention gap. Retention times and isotope values were continuously monitored by bracketing each sample with in-house standards of atrazine and desethylatrazine.

4.2.5 Method quantification limits for isotope ratio measurements

To determine the quantification limits for accurate isotope ratio measurements, atrazine and desethylatrazine standards were measured at concentration ranges from 10 mg/L to 50 mg/L in varying injection volumes from 1 µL to 3 µL. The yielded peak intensities were plotted against the resulting isotope value in order to determine threshold peak intensities above which isotope ratio measurements can be carried out with good trueness and precision. Typical values for inaccuracy of measurement (2 sigma) are ± 0.5 ‰ for ^{13}C and ± 1 ‰ for ^{15}N [288].

4.2.6 Correction of Isotope Values

Following the 'identical treatment principle' by Werner et al 2001 [289], we adopted the standard bracketing strategy applied by Reinnicke et al [280] to correct for drifting values: Triplicate sample measurements were bracketed by triplicate measurements of a mixture of compound-specific isotope standards at comparable concentrations to the samples. The sample isotope values were then corrected with the offset of the mean value of standards bracketing the sample in reference to the EA values. As the differences between standards and samples were always smaller than 10 ‰, the correction of isotope values was carried out with one standard only, as it is currently common practice for GC-IRMS[288].

4.2.7 Preparative HPLC Cleanup Step

For the cleanup step, the same HPLC method as described above was used. With this setup, desethylatrazine and atrazine had typical retention times of around 8.7 and 13.4 minutes. The compounds were collected in separate fractions using the Shimadzu Fractionation Collector FRC-10A, discarding all other fractions containing non-target-compounds. For the following GC-IRMS analysis, the methanol in the target fractions

was evaporated and the analytes were redissolved in 20 µL to 200 µL ethylacetate to yield adequate peak heights.

4.3 Results and Discussion

4.3.1 SPE recovery and absence of isotope fractionation

Non-quantitative recovery from solid phase extraction may occur if target compounds break through – either (i) due to high mass loadings which saturate the sorption capacity of the SPE disc or (ii) due to application of large water volumes which wash off compounds that have already adsorbed. Atrazine, desethylatrazine and desisopropylatrazine (DIA) recoveries were therefore (i) determined for mass loads (5 µg, 25 µg and 50 µg of each compound) which slightly exceeded the loads expected in contaminated groundwater, and they were tested (ii) for these loads dissolved in different water volumes (1 L and 10 L, respectively, Table 8). For atrazine and desethylatrazine, no significant difference was observed between different loads or different water volumes. The recovery from 1 L was 88 % ± 8 % (Atz) and 79 % ± 6 % (DEA) as average of all three concentrations; recovery for 10 L was 95 % ± 6 % (Atz) and 76 % ± 4 % (DEA) as average of all concentrations. These results demonstrate that the method was suitable when loads of 50 µg and smaller were extracted out of 10 L of groundwater. In contrast, the extraction efficiency for desisopropylatrazine decreased drastically for larger volume extracted (74.8 % for 1 L in contrast to 40.7 % for 10 L). Since this metabolite was not present in any of the investigated groundwater samples, isotope analysis of DIA was not further in investigated in this study.

Table 8: Overview over recovery and isotope values of solid phase extracted atrazine and metabolites. Diff to EA = Difference in isotopic value of measured SPE extracts compared to values measured in the elemental analyzer. N.a. = not analyzed. The compounds used as bracketing standards were of the same stock as used for spiking the water for SPE.

		Recovery [%]	*$\delta^{13}C$ [‰]*	*$\delta^{13}C$ [‰] diff t EA*	*$\delta^{15}N$ [‰]*	*$\delta^{15}N$ [‰] diff to EA*
Atrazine	extraction from 1 L (5µg, 25µg, 50µg)	**88.0 ± 8.3 (n=18)**	**-28.5 ± 0.2 (n=32)**	0.1 ± 0.2	**-1.7 ± 0.4 (n=23)**	-0.4 ± 0.4
	extraction from 10 L (5µg, 25µg, 50µg)	**94.7 ± 6.3 (n=18)**	**-28.6 ± 0.2 (n=27)**	0.2 ± 0.2	**-1.8 ± 0.5 (n=23)**	-0.5 ± 0.5
	Bracketing Standards		**-28.5 ± 0.2 (n=92)**	0.1 ± 0.2	**-2.1 ± 0.4 (n=115)**	-0.8 ± 0.4
Desethyl atrazine	extraction from 1 L (5µg, 25µg, 50µg)	**79.2 ± 6.3 (n=18)**	**-30.6 ± 0.6 (n=36)**	-0.9 ± 0.6	**-4.3 ± 0.8 (n=23)**	-0.1 ± 0.8
	extraction from 10 L (5µg, 25µg, 50µg)	**75.6 ± 4.0 (n=18)**	**-29.9 ± 0.4 (n=24)**	-0.1 ± 0.4	**-4.7 ± 1.0 (n=23)**	-0.5 ± 1.0
	Bracketing Standards		**-30.0 ± 0.4 (n=92)**	-0.3 ± 0.4	**-4.9 ± 0.3 (n=111)**	-0.7 ± 0.3
Desisopropyl atrazine	extraction from 1 L (5µg, 25µg, 50µg)	**74.8 ± 7.5 (n=18)**	n.a.		n.a.	
	extraction from 10 L (5µg, 25µg, 50µg)	**40.7 ± 4.8 (n=18)**	n.a.		n.a.	

4.3.2 Limits of precise isotope analysis for atrazine and desethylatrazine

Since limits for precise isotope analysis are critical for measurements of low concentrations in field samples, the trueness and precision of measured $\delta^{13}C$ values was systematically evaluated for atrazine and desethylatrazine standards as a function of peak intensity (Figure **Fig.** 10 a/b). For peak intensities down to around 135 mV, isotope abundance values could be measured with a precision of 0.9 ‰ for Atz (n=85, 95 %-confidence = 0.19 ‰). DEA could be measured with a precision of 0.9 ‰ (n=84, 95%-confidence= 0.20 ‰) down to an intensity of 120mV.

Nitrogen isotope measurements could be carried out with a precision of 0.3 ‰ (n=24, 95 %-confidence = 0.11 ‰) for atrazine for peak intensities down to around 125 mV. In a similar way, desethylatrazine could be measured at a precision of 0.4 ‰ (n=26; 95 %-confidence= 0.14 ‰) down to an intensity of 200 mV. Figure 10 a/b also shows that isotope values did not change with signal amplitudes meaning that measurements were

not amount-dependent indicating good linearity. In sample measurements, the concentrations of extracts and standards were therefore adjusted to the linear range of Figure 10, irrespective of the original concentration in groundwater and without correction for signal size.

Panels c and d in Figure 10 further illustrate that while reproducible measurements could be conducted at stable combustion oven performance (e.g., between 130 mV and 200 mV in Figure 10c) the trueness of isotope measurements changed after oxidation events, or when using different combustion ovens, in analogy to observations in previous studies [278, 280]. Therefore, care was taken that sample measurements were only started if the standard deviation of isotopic values in three subsequent standard measurements did not exceed 0.5‰ so that a pronounced short-term drift could be excluded. In addition, sample measurements were always bracketed by triplicate standard measurements, and the average isotope value of these standards (before and after the sample) was used to calibrate the sample value using the EA-IRMS value of the standard [280] (for details see Materials and Methods).

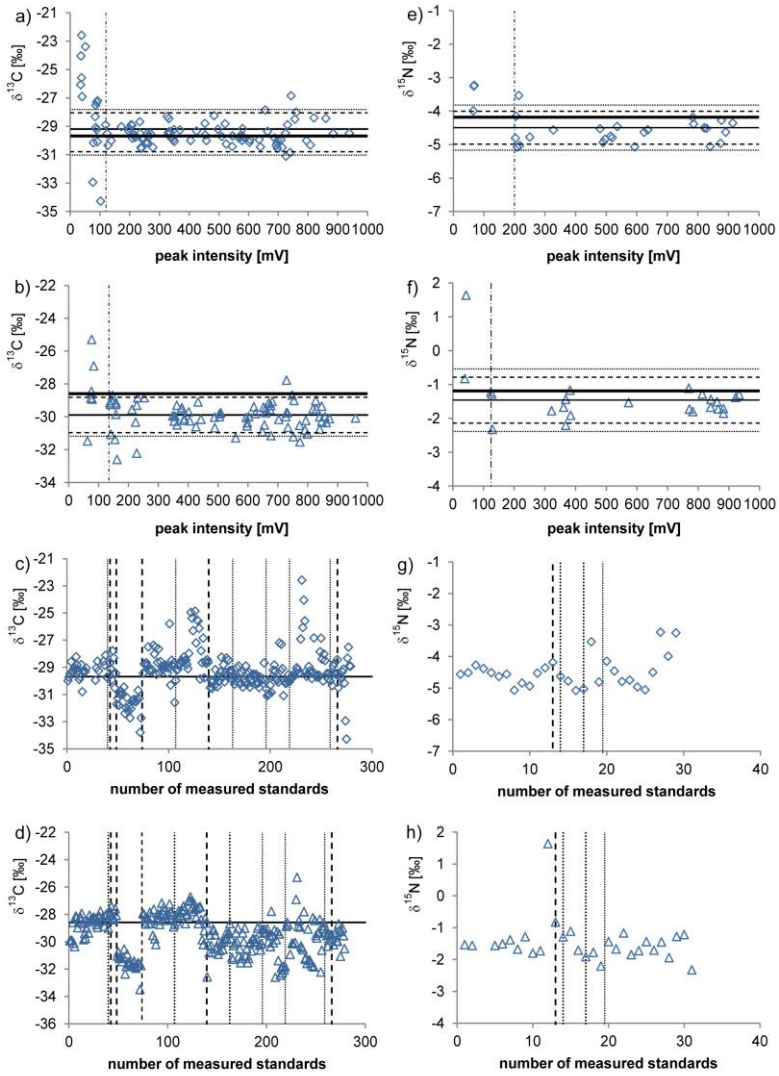


Fig. 10. Panels a and b: $\delta^{13}C$ values versus signal intensity for (a) desethylatrazine (diamonds) and (b) atrazine (triangles). Bold line: Isotopic value of elemental analyzer measurement (-29.7 ‰ and -28.6 ‰, respectively); Solid line: mean value for measured standards. Dashed lines: standard deviation. Dotted lines: 95 % confidence interval. Vertical dashed line: threshold intensity for true values. Measurements were performed with two combustion ovens corresponding to data points in panels c and d between 140 to 280 in an intensity range of up to 1000 mV. Calculated values are given in the text.

Panels c, d, g and h: Variation in $\delta^{13}C$ (c,d) and $\delta^{15}N$ (g,h) values of DEA (c,g) and Atz (d,h) standards over time. Oxidation events (dotted lines) as well as the use of different combustion reactors (reactor change indicated by a dashed line) are indicated.

Panels e and f: $\delta^{15}N$ values versus signal intensity for (e) DEA and (f) Atz. Bold line: Isotopic value of elemental analyzer measurement (-4.2 ‰ and -1.2 ‰, respectively); Solid line: mean value for measured standards. Dashed lines: standard deviation. Dotted lines: 95 % confidence interval. Vertical dashed line: threshold intensity for true values. Plotted measurements were performed on two combustion ovens. Calculated values are given in the text.

4.3.3 Cold-on-column injection versus large-volume-injection: Improved peak width and sensitivity

To increase measurement sensitivity, different injection strategies can be pursued to maximize the amount of substance that is transferred onto the column. Large-volume-injection (LVI) allows introducing a larger aliquot of extract into a programmed-temperature vaporizing (PTV) injector. Solvents are eliminated at low temperature through the split, while analytes are retained in the liner. Subsequently, the split is closed and the injector is heated rapidly to transfer the compounds onto the GC column. Matrix constituents remain in the replaceable liner and do not contaminate the GC (pre)column [290].

In contrast, cold-on-column injection (COC) transfers a smaller, more concentrated sample volume directly into a deactivated capillary pre-column (retention gap) where the liquid forms a thin film. The carrier gas evaporates the liquid film towards the beginning of the analytical GC-column, where analytes are refocused. Compounds of low volatility and high polarity can therefore enter the column directly, without losses or retardation effects [291].

Figure 11 shows chromatograms obtained for standards of target compounds with (a) 9µl of a 20 ppm solution on LVI and (b) on-column injection of 1µl of a 25 ppm solution with our instrumental setup. Although larger volumes, up to 20 µl, were applicable with LVI, the method was found to be associated with rather broad peaks (40-50 seconds width) and peak tailing. In contrast, cold on-column injection led to sharper, narrower peaks (10-20 seconds width) and less peak tailing. Not only did this lead to better peak resolution from interferences and easier integration, also absolute sensitivity was better, because higher peaks were obtained for the same amount of substance applied. Figure 11 shows that COC resulted in comparable peak amplitudes (in Figure 11a: 465 mV and 748 mV, in 2b: 545 mV and 659 mV for each DEA and Atz, respectively) with one ninth of the analyte amount. This improved sensitivity obtained with standards (by a factor of around 6 for atrazine and 8 for desethylatrazine) means that isotope measurements are potentially possible for 12 liters of extracted groundwater, where 70 or even 95 liters would be necessary in the case of LVI. Cold on-column injection was therefore selected as method of choice for samples containing low concentrations of the target analytes.

4.3.4 Elimination of matrix interferences by preparative HPLC-cleanup

Contrasting with the peak separation obtained with a pure standard (Figure 11b), the result obtained with the extraction of a real groundwater sample (Figure 11c) was heavily impaired. Not only did the background increase drastically, atrazine and desethylatrazine peaks were also completely covered by matrix interferences rendering isotope analysis impossible.

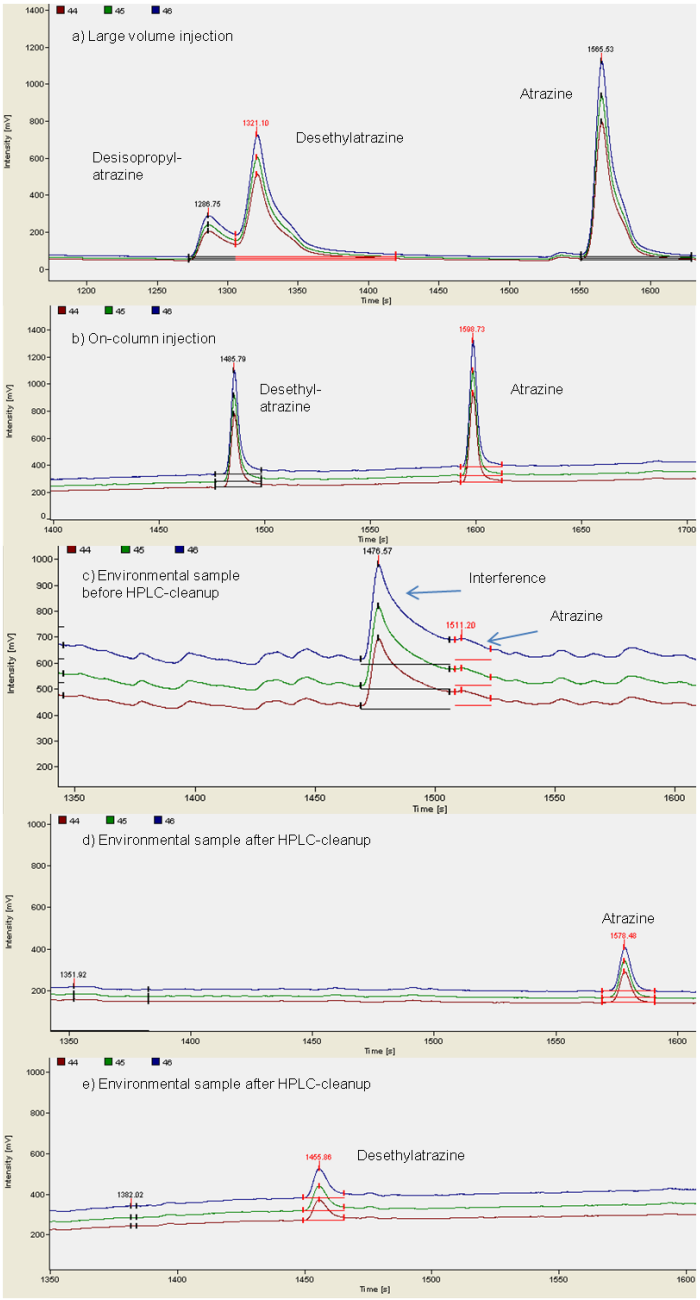


Fig. 11 Panels a,b: Comparison of GC-IRMS chromatograms of large volume injection (20ppm standard, 9µl) vs. on-column injection (25ppm standard, 1µl). Panels c-e: Environmental sample before (c) and after (d,e) preparative HPLC. Note: Variations in retention time are caused either by differences in retention gap length or variations in the temperature ramps during the method development process. Desisopropylatrazine present in panel a was not further investigated since it was not present in any of the investigated groundwater samples.

As shown in Figure 11d and e, background interferences in environmental samples could be greatly reduced through preparative HPLC cleanup. In the displayed samples, the

cleanup step eliminated the large peak covering the atrazine peak (Figure 2c) and enabled detection of the previously masked DEA. For samples with high background, DEA (e) and Atz (d) fractions of the HPLC-cleanup were measured on the IRMS separately to minimize any background interference by impurities.

Validation with standards showed that the HPLC cleanup method did not show significant isotope fractionation within the uncertainty of measurements ($2\sigma = \pm 0.5$ ‰ for ^{13}C and ± 1 ‰ for ^{15}N) [288]: $\delta^{13}C$ values of atrazine and desethylatrazine were -28.1 ‰ ± 0.7 ‰ and -29.5 ‰ ± 0.6 ‰ (each n=3), thus differing by 0.5 ‰ and 0.1 ‰ from EA-IRMS values. $\delta^{15}N$ values of atrazine were -2.0 ‰ ± 0.3 ‰ (n=3) differing by 0.8 ‰ from the EA-IRMS value.

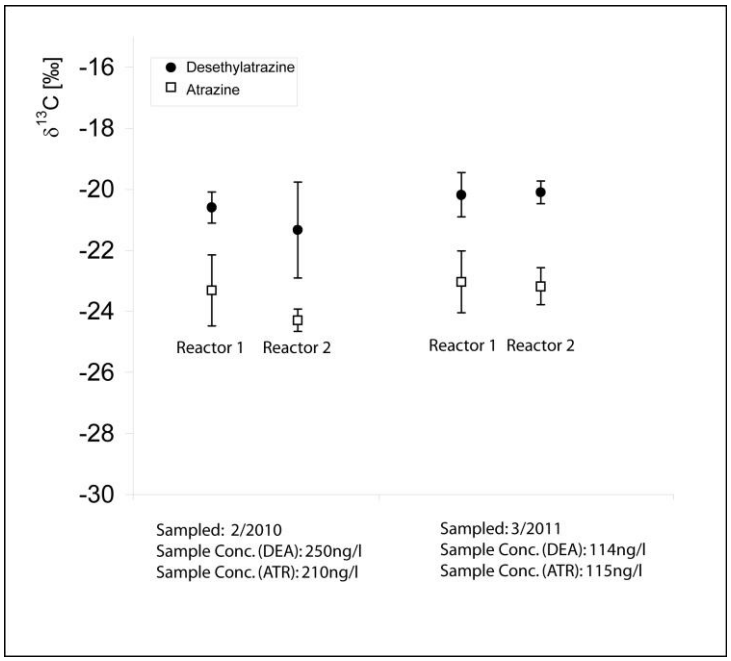


Fig. 12: $\delta^{13}C$ values of a field sample (left: sampled in February 2010, right: sampled in March 2011)**, measured after preparative HPLC cleanup and on-column injection with two Isolink combustion reactors.** Standard deviations are given for three measurement repeats.

4.3.5 Measurements of natural groundwater samples

The optimized method allowed us to measure for the first time carbon and nitrogen isotope values of atrazine and desethylatrazine in natural groundwater samples. In the following, samples from an Austrian site are discussed. Controlled by the federal authorities, no Atz has been deployed at this site since 1995 but still concentrations in the ng/L – range have been prevailing in a groundwater monitoring well. Figure 3 shows

δ^{13}C values of Atz and DEA from this location in two subsequent years, where each sample was analyzed in triplicate with two Isolink combustion reactor tubes ("Reactor 1" and "Reactor 2" data pairs). As illustrated in Figure 3, the agreement between identical samples measured on different dates provides an additional validation of our method.

On the other hand, Figure 12 allows a comparison of δ^{13}C values of atrazine and desethylatrazine over time (2010 and 2011). No significant difference can be observed despite the fact that concentrations of the compounds in groundwater in 2011 were only half as high as the concentrations detected in 2010. Assuming a diffuse atrazine source as a legacy of the past (e.g., leaching out of soil or from a contaminated aquifer), a decrease in concentrations over time can be attributable to two different reasons. (1) Atrazine concentrations decreased due to dilution by non-contaminated groundwater. In this case no changes in isotope values would be expected. (2) Compared to the steady state in 2010, additional atrazine degradation occurred in 2011. In this case, δ^{13}C values of atrazine would be expected to become more positive reflecting the enrichment of ^{13}C induced by additional degradation [90, 282]. Our observation that isotope values did not change over time, therefore, indicates that no additional atrazine degradation took place compared to 2010.

4.3.6 Comparison of atrazine and desethylatrazine isotope ratios

Table 9 summarizes further δ^{13}C and δ^{15}N measurements of atrazine and desethylatrazine in groundwater samples from a wider range of locations in Germany and Austria. The list illustrates that isotope values were not directly correlated with concentrations, or desethylatrazine-to-atrazine ratios (DAR). Even though δ^{13}C values were slightly less negative than typical for petroleum-feedstock [292], both ranges overlap so that this line of evidence alone is not conclusive. The δ^{15}N isotope values alone also do not allow conclusions whether atrazine is further degraded. They are slightly more negative for DEA than for Atz (see Table 9), which is consistent with expectations for a transformation product.

A remarkable observation, however, is that δ^{13}C values of DEA were consistently less negative than those of Atz from the same sample. This observation is in stark contrast to typical trends in isotope ratios where the product normally contains less ^{13}C/^{12}C than the parent compound.

Several reasons may be responsible for the observed trend. (1) The reacting ethyl group of atrazine is cleaved off. The preferential reaction of ^{12}C, which normally lends products more negative $\delta^{13}C$ values, is therefore not observable in DEA.(2) In addition, the loss of the ethyl group may even generate more positive $\delta^{13}C$ values as artefacts. Specifically, if the $^{13}C/^{12}C$ isotope ratio of the ethyl group is much smaller than the compound average of atrazine, $^{13}C/^{13}C$ isotope ratios in DEA would increase, just because the "light" side chain has been cleaved off. (3) Alternatively, if the freshly formed DEA has the same $\delta^{13}C$ isotope values as the atrazine from which it is produced (reflecting the non-reacting positions that are transferred to the product) more positive $\delta^{13}C$ values of DEA would provide a strong indication that the metabolite is itself further degraded. Such a finding would have pronounced implications, since in this case the desethylatrazine-to-atrazine ratio would underestimate the atrazine degradation. Experimental approaches are, therefore, warranted to test for, and rule out, scenario 2 - the presence of an ethyl side chain with a low $^{13}C/^{12}C$ isotope value. To this end, atrazine could be isolated from field samples (e.g., by preparative HPLC) and be selectively decomposed to DEA.

Table 9 $\delta^{13}C$ and $\delta^{15}N$ ratios for atrazine and desethylatrazine in environmental samples. N.m. = not measured.

Sample	extracted volume [L]	DEA (ng/L)	Atz (ng/L)	$\delta^{13}C$ DEA [‰]	$\delta^{13}C$ Atz [‰]	$\delta^{15}N$ DEA [‰]	$\delta^{15}N$ Atz [‰]
Vienna A	11.4	1236	1333	-21.6 ± 0.2	-24.1 ± 0.3	-4.8 ± 0.2	-4.5 ± 0.6
Vienna B	11.3	850	1327	-23.3 ± 0.4	-26.2 ± 0.6	-2.4 ± 0.3	-1.2 ± 0.2
Upper Palatinate A	10.8	1389	648	-21.2 ± 0.2	-24.5 ± 0.2	-4.3 ± 0.1	-2.3 ± 0.2
Upper Palatinate B	10.0	500	500	-18.8 ± 0.4	-24.0 ± 0.9	-4.7 ± 0.1	-3.0 ± 0.9
Upper Palatinate C	11.8	250	158	-22.9 ± 0.3	-27.4 ± 0.3	n.m.	n.m.
Upper Palatinate D	11.9	171	138	-23.3 ± 0.3	-27.3 ± 0.0	n.m.	n.m.

4.4 Conclusion and Outlook

This study presents the first compound-specific isotope measurements of atrazine and desethylatrazine at sub-µg/L concentrations in natural groundwater samples. Critical for this advance has been the combination of solid phase extraction, HPLC cleanup and on-column injection which allowed the extraction of large amounts of water, elimination of matrix interferences and subsequent sensitive isotope analysis. Our method validation therefore opens the way to investigate a question which so far could not be successfully tackled by other methods: whether persistent micropollutants like atrazine may be naturally degraded in groundwater.

First field measurements conducted in this study give an outlook on possible future insight. (i) As a trend, atrazine in the samples of our study contained slightly more $^{13}C/^{12}C$ than the typical average of petroleum feedstock-derived products. If such a trend is observed to continue over time, enrichment of ^{13}C alone can already give unequivocal evidence of atrazine degradation. On the other hand, if isotope values remain invariant over time – as observed in one sampling location of our study – this gives evidence that it was sorption or dilution rather than degradation which attenuated observable concentrations. (ii) If besides carbon, also nitrogen isotope values can be analyzed, this information has the potential to provide even evidence of different degradation pathways occurring at a given location. In our study such insight was not yet possible, because samples represented snapshots from different locations so that a "common history" was missing. (iii) Finally, a particularly intriguing result of our study was the observation that $\delta^{13}C$ values of desethylatrazine were consistently less negative than those of atrazine from the same location. This finding is in contrast to typical trends in isotope ratios, where the products show equal or more negative $\delta^{13}C$ values than the parent compound. Potentially, the presence of an ethyl side chain with a particularly low $^{13}C/^{12}C$ isotope value can create this observation as artefact – future research will be necessary to address this scenario. Alternatively, however, the enrichment of $^{13}C/^{12}C$ may be also be genuine evidence of further DEA degradation - in other words, current assessments based on DEA/Atz ratios would underestimate atrazine degradation. The examples from this study show how isotope analysis of contaminants at trace contaminations has the potential to further our understanding or their fate in groundwater.

5

Conclusions and Outlook

Research on hydraulic fracturing chemicals is crucial for risk assessment of the expanding technology of unconventional natural gas production. In particular, the chemical structure of the numerous additives never played a significant role in relevant literature, despite its important role for understanding the rationale behind their use, implications for chemical conversion and development of analytic approaches. Maybe as a result of this, the generation of transformation products has been neglected in analyses of environmental samples so far, even though their occurrence is of great relevance.

This thesis provides several approaches towards those previously unamenable research gaps. Prior to this work, available compound lists were unsuitable for the development of analytical methods or assessing the link between the used compounds' structure and function.

The review presented in Chapter 2 comprises a substantial step forward: Structure and function are now linked together, enabling the understanding of the chemicals' function by conceptualizing their properties. This allows a deeper insight for analysts and other stakeholders and - very importantly - explaining analytical findings: In a concrete case, the knowledge generated by this compilation was applied to actual flowback and produced water samples in Chapter 3, providing a basis for (a) discerning the detected compounds' origins, (b) revealing that compounds with interesting functional groups are often not disclosed, (c) interpreting functionalities of undisclosed detected compounds, and (d) phrasing metabolite formation hypotheses. After the detection of putative transformation products, the linking of their creation with functionalities towards hydraulic fracturing requirements (e.g., carboxylic acids as byproducts of chloromethyl alkanoates, which decompose as delayed breakers) is also established on this fundamental literature-based, conceptual work.

The analyses in Chapter 3 were carried out with unprecedented strict confidence criteria to be able to discuss putative identifications with high certainty. For the first time, they bring forward evidence that wastewater from fractured shale gas sites does not only contain fracturing additives and compounds of geogenic origin, but also intended and unintended transformation products generated during the process. Consequently, standard monitoring methods are not sufficient for a proper assessment, as simple monitoring of usual suspect compounds as in customary targeted analysis may overlook a variety of

constituents. Among the putative transformation products, iodoalkanes and haloacetones were found. All of them had not been previously reported in pertinent literature. Particularly these findings underline the necessity of an enhanced understanding of chemistry during the fracturing process (Chapter 2) on the one hand and of comprehensive screening approaches (Chapter 3) on the other hand as the mentioned metabolites feature adverse health effects. In the context of iodoalkane detection, iodide monitoring alongside chloride and bromide is recommended as well as monitoring of iodated, chlorinated and brominated compounds. This is particularly important since the health impact of iodo-organics are often more severe than that of chlorinated and brominated species, and it is not yet clear to what extent they are present in unconventional natural gas development (UNGD) wastewaters.

The fact that UNGD wastewater treatment that is often conducted by centralized waste treatment facilities (CWTF) only[37], bears the risk of compound survival and eventually reaching rivers via the effluent. Therefore, aerobic degradation should be mandatorily implemented in wastewater treatment facilities additionally, as it is absolutely necessary to cope with various organic compounds and to avoid environmental exposure.

This precise approach towards complex field samples now encourages going a step further, namely towards elucidation about single compound fate. This approach is often tackled by compound-specific isotope analysis (CSIA), which can go into two directions: (1) Fingerprinting of sources, which has been so far a problem in water contamination related to fracturing activities. Until now, only negative confirmation (i.e., ruling out all other possibilities) has been reported[29, 30], unlike an explicit source pinpointing like it was demonstrated for oil samples via a comprehensive GC approach[83, 293]. Another aspect achieved by CSIA is to (2) elucidate the footprint of degradation pathways.

For CSIA in field samples, the crucial point is to bring sufficient mass of the respective atom on column[86], creating the need for preconcentration techniques, which often entail problems in terms of matrix effects and are therefore deteriorating measurement precision. Stepping into dimensions of environmental sample concentrations, in Chapter 4, precise isotope measurements for organic compounds at concentrations from 0.14 µg/L to 1.39 µg/L from groundwater field samples are demonstrated. As model compounds, the pesticide atrazine and its toxic metabolite desethylatrazine were chosen, as CSIA applications had been already successfully implemented for them on laboratory scale[90, 91], but not suitable for concentration ranges prevalent in environmental samples yet. This

advance was achieved by the combination of solid phase extraction, cleanup by preparative HPLC and on-column injection which allowed the extraction of large amounts of water, elimination of matrix interferences, and subsequent sensitive isotope analysis. This method therefore opens the way to investigate the fate of not only atrazine and metabolites in groundwater (Rieger, unpublished; Melsbach et al. in prep) but was already successfully adapted for the micropollutant diclofenac[77]. Correspondingly, this may be also possible for environmental concentrations of HF-related compounds in future approaches.

Altogether, it can be stated that the mentioned analytical techniques were successfully applied for field samples with complex matrices, like flowback water samples containing a multitude of substances and preconcentration-derived background for environmental concentrations of pesticide samples.

Another promising future application will be the combination of compound-specific isotope analysis with two-dimensional-GC (GC×GC-IRMS), e.g., to pinpoint sources of contamination in incidents of shallow groundwater contamination due to surface spills. Tracking sources on the compound or compound-mixture-level is of particular interest and would add on scientific evidence to the so far chosen approach of ruling out or giving certainty to likely contamination pathways[29, 30].

Alongside these technical developments, it is also crucial to perform background studies[294] to create a baseline for potential fracturing impacts and to gauge the efficiency of the utilized wastewater treatment plants[37], both in order to assess potential environmental impacts of unconventional gas development and the resulting residual waters. Most importantly for a prudent use of this promising technology, farseeing statutory rules taking newest scientific findings and knowledge gaps into account[111] need to be established.

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Abbreviations

% ..... *per centum* (Latin) – percent; parts per hundred; 1% = 1×10^{-2}

‰ ..... *pro mille* (Latin) – per mil; parts per thousand; 1‰ = 1×10^{-3}

°C ..... degree Celsius; 0 °C = 273.15 K

µg ..... microgram; 1 µg = 1×10^{-6} g

µL ..... microliter; 1 µL = 1×10^{-6} L

µm ..... micrometer; 1 µm = 1×10^{-6} m

Atz ..... Atrazine

BTEX ..... Benzene, Toluene, Ethylbenzene, Xylenes

CA ..... Confidence Assignment

CAS ..... Chemical Abstracts Service

COC……...cold on-column

CSIA ..... Compound-specific Stable Isotope Analysis

Dea ..... Desethylatrazine

DNA……...Deoxyribonucleic acid

DOM……...Dissolved organic matter

Dr. rer. nat. ..... *doctor rerum naturalium* (Latin) – Doctor of Natural Sciences

Dr. ..... Doktor (German) – Doctor; equivalent to PhD

e.g. ..... *exempli gratia* (Latin) – for example

EA ..... Elemental Analyzer

ECD ..... Electron Capture Detector

ECHA…….European Chemical Agency

EPA……Environmental Protection Agency

Eq. ..... equation

et al. ..... *et alii* (Latin) – and others

FID ..... flame ionization detector

g ..... gram; 1 g = 1×10^{-3} kg

GC..... Gas Chromatography

GC×GC..... Two-dimensional Gas Chromatography

geb. ..... geboren (German) – born

HDPE……High-density polyethylene

HF……..Hydraulic Fracturing

HPLC ..... High Performance Liquid Chromatography

i.e. ..... *id est* (Latin) – that is; in other words

IAEA..... International Atomic Energy Agency

IRMS ..... Isotope Ratio Mass Spectrometry

L..... liter; 1 L = 1×10^{-3} m^3

LC ..... Liquid Chromatography

LVI ..... Large-Volume-Injection

m ..... meter

M..... molar; 1 M = 1 mol/L = 1×10^{3} mol/m^3

mg ..... milligram; 1 mg = 1×10^{-6} kg

min ..... minute(s); 1 min = 60 s

mL..... milliliter; 1 mL = 1×10^{-3} L

mm ..... millimeter; 1 mm = 1×10^{-3} m

mM ..... millimolar; 1 mM = 1×10^{-3} M

mmol..... millimole; 1 mmol = 1×10^{-3} mol

mol ..... mole

MCL……...Maximum contaminant level

MS ..... Mass Spectrometry

MSL % …….Mass Spectrometry Library Agreement Score

mV ..... millivolt; 1 mV = 1×10^{-3} V

n.d. ..... not determined

ng ..... nanogram; 1 ng = 1×10^{-9} g

nm ..... nanometer; 1 nm = 1×10^{-9} m

NIST……..National Institute of Standards and Technology

NORM……Naturally occurring radioactive materials

N-SVEC ..... N_2; $d^{15}N$ = -2.8‰ ± 0.2‰

OECD……Office of Economic Cooperation and Development

P&T..... Purge and trap

PAH ..... Polycyclic Aromatic Hydrocarbon

UNGD……Unconventional natural gas development

PD ..... Privatdozent (German) – academic title for PhDs denoting the ability to teach on university level

pH..... *potentia Hydrogenii* (Latin) – decimal logarithm of the reciprocal of the hydrogen ion activity in solution

PhD ..... Doctor of Philosophy

pK_a..... logarithmic form of the acid dissociation constant K_a; pK_a = $-\log_{10} K_a$

ppm ..... parts per million; 1 ppm = 1×10^{-6}

Prof..... Professor

PTV……programmed-temperature vaporizing

ref. ..... reference

s..... second(s)

SI……...Supporting Information

SPE..... Solid Phase Extraction

t……..ton; 1t = 1000kg

UV..... ultraviolet

VES..... Viscoelastic Surfactant

V-PDB ..... Vienna PeeDee Belemnite

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Curriculum Vitae

Juni 2011- Feb 2016	Doctoral candidate at Helmholtz Zentrum München, German Research Center for Environmental Health. Institute of Groundwater Ecology, Research Unit Environmental organic Isotope Chemistry. Installation of research collaboration with 5 months Lab and Field Research stay at Duke University, NC, USA with DAAD scholarship.
May 2014 – Dec 2014	Maternal leave
April/May 2011	Research associate at Helmholtz Zentrum München, German Research Center for Environmental Health. Institute of Groundwater Ecology, Research Unit Environmental organic Isotope Chemistry.
Oct 2005 – Jan 2011	5-year University programme (Diplom) Geoecology/Ecosystem management at Eberhard-Karls-Universität Tübingen. Majors in Soil/Water, Environmental Management and Environmental Law.
	Research assistant at the Institute of Geomicrobiology (2007-2009) and at the Division for International Affairs (2009-2010).
Jul 2008 – Jul 2009	Research assistant at PE INTERNATIONAL (Software and Consulting for Sustainability, CSR, Life Cycle Assessment), Echterdingen, Germany.
Apr – May 2008	Intern in Porto Alegre, Brazil, at GOPA Consulting-Office, development cooperation with SEMA (Environmental Agency of Rio Grande do Sul).
Feb – Apr 2006	Intern at the Federal Environmental Agency (UBA), Berlin, Germany, Section IV/2.6 „Analysis and assessment of substances hazardous to water”.
Oct 2003-June 2005	Biochemistry studies at Universität Regensburg, Germany.
June 2003	Abitur (A-levels) at Gymnasium Eschenbach, Germany.

Publications

Note: Some articles were published under birth name Schreglmann

- Hoelzer, Sumner, Karatum, Nelson, Drollette, O'Connor, D'Ambro, Getzinger, Ferguson, Reddy, Elsner, Plata: *"Indications of Transformation Products from Hydraulic Fracturing Additives in Shale Gas Wastewater"*. Environmental Science and Technology, 2016
- Elsner & Hoelzer: *"Quantitative Survey and Structural Classification of Hydraulic Fracturing Chemicals Reported in Unconventional Gas Production"*. Environmental Science & Technology, 2016
- Drollette, Hoelzer, Warner, Darrah, Karatum, O'Connor, Nelson, Fernandez, Reddy, Vengosh, Jackson, Elsner, Plata : *"Elevated levels of diesel range organic compounds in groundwater near Marcellus gas operations are derived from surface activities"*. Proceedings of the National Academy of Sciences, 2015
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Supporting Information

A.1.1 Supporting Information of Chapter 2

45 pages including Table S1 and Table S2

A.1.2 Supporting Information of Chapter 3

Additional details on analytical details, confidence assignment, control experiments, quantitative results and corrections for potential losses, hopane biomarkers, toxicology and water treatment implications, and references. Tables showing a full list of mass spectral library matching derived tentative identifications and putative compound origins, potential losses to the air phase, and the quantitative outcome of volatile organic compound analysis. Figures showing a retention index verification confidence assignment plot, boiling point versus 1D retention model confidenc e assignment plots, effect of retention index verification filter, and hopane biomarker patterns and representative ratios.

Supporting Information

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

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Table S1: Complete list of all HF fracturing chemicals extracted from the Waxman List and the FracFocus databas. (39 Pages). The same document is provided as an Excel file in electronic form.

Table S2: Information on the sources of the quantitative data used (4 Pages)

Table S1: Comprehensive Overview over chemical compounds with their substance classes, function and CAS number.
Reported amount or frequency are displayed as well as fundamental physicochemical parameters and information on fate and toxicity.

Frequency Shading	
generally	> 100000
very frequently	10000-100000
frequently	1000-10000
occasionally	100-1000
seldomly	10-100
very seldomly	1-10

MCL/ HAI	**Maximum concentration levels (MCL) or health assessment information (HAI) available**
RfD	**Oral reference dose (EPA IRIS database)**
OSF	**Carcinogenic oral risk slope factors (EPA IRIS database)**
RfC	**Inhalation reference concentration (EPA IRIS database)**
Koc	**Organic Carbon-Water Partitioning Coefficient**
pka	**Logarithmic acid dissociation constant**
Kd (L kg-1)	**Sorption distribution coefficient, K d , calculated according to equation in SI of Rogers et al (Kd=an*Koc*foc+ac*Kdex)**

For source information see Table S2

Number of reported applications					Substance Classification and Function			Patent	Physicochem. Information (from EPI Suite™ version 4.1)			Rogers et al.		
FracFocus (SkyTruth)	Waxman	FracFocus (EPA)	FracFocus (EPA)	FracFocus (Rogers et al.)	Chemical Abstract Service Number (CAS)	Chemical Component	Function	Patent Number	Log K ow estimated	Water Solubility Estimate from log K_{ow} (mg/L at 25°C)	Henry's law constant (atm-m^3/mol at 25°C)	t1/2 (d)	MCL/ HAI	log Koc est.
(Total count)	(Total count)	(Total count)	(Frequency)	(Frequency)							(Bond method)	or estimated primary degr. timeframe		
1116	**13**		**4.0**	**0.0**		**Gases (Table 2 in Manuscript)**								
77	4	96	0.57		124-38-9	Carbon dioxide	fracking fluid	US 6729409; US 5551516; US7049436B2	0.83	$2.57 \times 10_{4}$	$1.52 \times 10_{-2}$			
1039	9	580	3.42		7727-37-9	Nitrogen	fracking fluid	US 6729409; US 5551516						
						Non-functionalized Hydrocarbons (Table 2 in the Manuscript)								
1692	**30**		**1.3**	**5.0**		**alkanes**								
3	0	n.s.		0.004	74-82-8	Methane	fracking fluid		0.78	2610	$4.14 \times 10_{-1}$	70		0.9
5	0	n.s.		0.006	74-84-0	Ethane	fracking fluid		1.32	938.6	$5.50 \times 10_{-1}$	33		1.6
22	0	6	0.04	0.064	74-98-6	Propane	fracking fluid		1.81	368.9	$7.30 \times 10_{-1}$	99		2
12	0	5	0.03	0.028	106-97-8	n-Butane	fracking fluid		2.31	135.6	$9.69 \times 10_{-1}$	5		2.5
17	0	2	0.01	0.054	75-28-5	Butane(s)	fracking fluid		2.23	175.1	$9.69 \times 10_{-1}$	26		2.4
2	0	n.s.		0.01	78-78-4	Isopentane	fracking fluid		2.72	184.6	1.29	3		2.4
4	0	n.s.		0.038	109-66-0	Pentane(s)	fracking fluid		2.8	49.76	1.29	5		2.9
5	1			0.014	*, 110-54-3	Hexane(s) (C6+)	fracking fluid	US 4739834				2	Y	3.4
1	1	n.s.		0.002	110-82-7	Cyclohexane	solvent, fracking fluid	US 4739834	3.18	43.02	$2.55 \times 10_{-1}$	10	Y	3
0	1	n.s.		0	108-87-2	Methylcyclohexane	solvent, fracking fluid	US 4739834	3.59	28.4	$3.39 \times 10_{-1}$	4		3.1
0	1	n.s.		0	142-82-5	N-heptane	solvent, fracking fluid	US 4739834	3.78	3.554	2.27	4		4
	1	n.s.			*	Nonane, all isomers	solvent, fracking fluid	US 4739834						
368	0	48	0.28	0.99	112-40-3	Dodecane	solvent, fracking fluid		6.23	0.1099	9.35	4		5.3
354	0	48	0.28	0.88	629-50-5	Tridecane	solvent, fracking fluid		6.73	0.02746	$1.24 \times 10_{1}$	3		5.8
306	0	48	0.28	0.91	629-59-4	Tetradecane	solvent, fracking fluid		7.22	0.009192	$1.65 \times 10_{1}$	8		6.2
0	0			0.002	68476-44-8	Hydrocarbons, C>3	solvent, fracking fluid					3		1.6
3	0				90622-53-0	C9 to C21 Alkanes, Linear and Branched	solvent, fracking fluid							
0	2	n.s.			93924-07-3	Alkanes, C10-14	solvent, fracking fluid	US 4739834						
0	0	n.s.		0.11	73138-29-1	n-Alkanes,C10-C18	solvent, fracking fluid					9		4.3
514	1	48 (CAS 1120-21-4)	0.28	1.7	1120-21-4, 112-40-3	C-11 TO C-14 N-ALKANES, MIXED	solvent, fracking fluid	US 4739834	5.74 - 6.23	0.0199 - 0.2571	7.04 - 9.35	104		5

2	0	n.s.		0.004	68551-19-9	C12-C14 Isoalkanes	solvent, fracking fluid		6.65	0.03173	$1.24 \times 10_{1}$	12		5.8
34	2	11	0.06	0.036	68551-20-2	Alkanes, C13-16-iso	solvent, fracking fluid	US 4739834	7.63	0.003311	$2.19 \times 10_{1}$	102		5.8
0	1	n.s.			*	Cyclic alkanes	solvent, fracking fluid	US 4739834	3.17	142.1	$5.26 \times 10_{-4}$			
0	10	n.s.			*	Iso-alkanes/n-alkanes	solvent, fracking fluid	US 4739834						
0	1	n.s.			*	Modified alkane	solvent, fracking fluid	US 4739834						
18	8			0.14	8002-74-2, *,*,*,	Paraffins/Parrafinic solvent/Paraffinic naphthenic	diverting agent					12		8.8
22	0	n.s.		0.044	8012-95-1	Acyclic Paraffin and Olefin Oils C11 to C14						12		5.3
7406	**37**		**21.3**	**17.2**		**alkenes**								
1	0	n.s.		0.002	74-85-1	Ethylene	fracking fluid		1.27	3449	$9.78 \times 10_{-2}$	3		1
6	0	n.s.		0.026	115-07-1	Propylene	fracking fluid		1.68	1162	$1.53 \times 10_{-1}$	56		1.5
4	0	n.s.		0.006	25167-67-3	1-Butene	fracking fluid		2.17	354.8	$2.03 \times 10_{-1}$	3		2.1
4	0	n.s.		0.006	106-99-0	1,3-butadiene	fracking fluid		2.03	792.3	$7.79 \times 10_{-2}$	28	Y	1.7
0	0			0.068	112-41-4	1-Dodecene						9		5.3
88	0			0.25	1120-36-1	1-Tetradecene	fracking fluid					13		6.1
88	0			0.25	629-73-2	1-Hexadecene	fracking fluid					17		7
88	0			0.25	112-88-9	1-Octadecene	fracking fluid		7.08-9.04	1.256× 10-4 - 0.01191	3.46-10.7	33		7.8
0	0	n.s.		0.25	3452-07-1	1-Eicosene						32		8.7
2	0	n.s.		0.004	115-11-7	C4 Olefins	fracking fluid		2.23	399.2	$2.40 \times 10_{-1}$	2		2
2609	**7**	1321 (CAS 64743-02-8)	7.79	6.7	*, 64743-02-8, 68411-00-7, *	Alkenes: Alkenes, C>10 alpha- alkenes, C>8-alkenes, Olefins	solvent, fracking fluid	US 5674816				7		4.9
0	1	n.s.			*	Substituted alkene	solvent, fracking fluid	US 5674816						
0	0			0.002	7756-94-7	Triisobutylene						9		5.2
40	1	n.s.			68526-88-5	Heptene, hydroformylation products, high-boiling	solvent							
1911	11	840 (CAS 94266-47-4)	4.95	5.7	94266-47-4, 94266474686 47-72-3	Citrus terpenes	solvent					17		3.8
1903	2	1124 (CAS 68647-72-3), 1 (CAS 8028-48-6)	6.63	0.22	68647-72-3, 8028-48-6	Orange Terpenes, Terpenes and terpenoids, sweet orange-oil	solvent	WO2013028307 A1; 4594378				0.8		3.8

0	1	n.s.			*	Terpenes	solvent	WO2013028307 A1; 4594378						
6	3	n.s.		0.45	68956-56-9	Terpene hydrocarbon byproducts	solvent	WO2013028307 A1				3		3.2
656	11	323	1.90	3	5989-27-5	d-Limonene	solvent	US 7334635B2	4.83	4.581	3.80×10^{-1}	1		3.8
16485	**188**		**33.9**	**46.5**		**aromatic compounds**								
2	3	n.s.		0.03	71-43-2	Benzene	solvent, fracking fluid	US 4739834	1.99	2000	5.39×10^{-3}	720	Y	1.8
248	29	2	0.01	0.97	108-88-3	Toluene	solvent, fracking fluid	US 4739834	2.54	573.1	5.95×10^{-3}	15	Y	2.4
150	28	10	0.06	0.3	100-41-4	Ethylbenzene	solvent, fracking fluid	US 4739834	3.03	228.6	7.89×10^{-3}	228	Y	2.7
724	44	48	0.28	2.3	1330-20-7	Xylene	solvent, fracking fluid	US 4739834	3.09	207.2	6.56×10^{-3}	360	Y	2.8
20	0	n.s.			95-47-6	o-Xylene			3.09	224.1	6.56×10^{-3}			
0	1	n.s.			106-42-3	p-Xylene	solvent, fracking fluid	US 4739834	3.09	228.6	6.56×10^{-3}			
0	1	34	0.20	0.064	25340-17-4	Diethylbenzene	solvent, fracking fluid	US 4739834	4.07	58.86	1.16×10^{-2}	347		4
3	5	n.s.		0	25551-13-7	Trimethylbenzene	solvent, fracking fluid	US 4739834				4		3
144	1	7	0.04	0.69	526-73-8	1,2,3-trimethylbenzene	solvent, fracking fluid	US 4739834	3.63	75.03	7.24×10^{-3}	4		3.2
5980	21	2.229	13.14	16.9	95-63-6	1,2,4-trimethylbenzene	solvent, fracking fluid	US 4739834	3.63	79.59	7.24×10^{-3}	56	Y	3.2
180	3	41	0.24	0.75	108-67-8	1,3,5-trimethylbenzene	solvent, fracking fluid	US 4739834	3.63	120.3	7.24×10^{-3}	180	Y	3
171	6	34	0.20	0.37	98-82-8	Cumene = Isopropylbenzene	solvent, fracking fluid		3.45	75.03	1.05×10^{-2}	16	Y	3.2
0	0			0.052	98-83-9	alpha-Methylstyrene						3		3

8557	44	3294 (CAS 91-20-3)	19.41	22	91-20-3	Naphthalene	solvent	US 4739834				258	Y	2.9
2	0	n.s.		0.004	38640-62-9	Disopropylnaphthalene	solvent		6.08	0.2421	1.99×10^{-3}	46		5.3
0	1	n.s.			*	Naphthalene derivatives	solvent	US 4739834						
293	1	47	0.28	2	68648-87-3	Benzene, C10-16, alkyl derivatives	solvent	US 4739834	8.43	0.0002099	1.78×10^{-1}	23		7.5
8	0			0.018	70693-06-0	Aromatic hydrocarbons, C9-11	solvent					7		3.8
1	0	n.s.		0	123-01-3	Dodecylbenzene (impurity)	solvent		7.94	0.001015	1.34×10^{-1}	10		7.5
2	0	n.s.		0.008	64742-89-8	Alkanes, Xylene, Ethyl Benzene, Napthalene, Trimethylbenzene	solvent					39		4
75394	**321**		**107.4**	**111.6**		**petroleum distillates/products**								
4	0			0.006	68919-39-1	Natural Gas Condensate	fracking fluid					39		2.5
0	0			0.002	8006-61-9	Gasoline, natural	fracking fluid					39		2.4
214	**51**	32 (CAS 68476-34-6)	0.19	0.054	68476-34-6, 68476-30-2, 68334-30-5, *	Diesel	solvent, fracking fluid	US 20080202744A1, US 4541935, WO 2008057892				21 - 22		2.9 to 6.2
424	**16**	270 (CAS 8008-20-6), 36 (CAS 64742-81-0)	1.8	0.184	64742-81-0, 8008-20-6, 6742-81-0	Kerosene	solvent, fracking fluid, defoamer	US 4541935				12 to 22		5.3
47923	**103**	11897 (CAS 64742-47-8), 115 (CAS 64742-95-6), 27 (CAS 6742-47-8)	70.95	71.6	64742-47-8, 68333-25-5, 64742-95-6, 6742-47-8	Light petroleum distillates, unspecified ("naphtha")	solvent	US 5488083				25 to 231		2.9 to 7.5
96	0	n.s.			8032-32-4	Ligroine	solvent							
801	**20**	68 (CAS 64741-44-2), 4 (CAS 64742-88-7), 65 (CAS 64742-46-7)	0.8	1.48	64742-80-9, 64742-46-7, 64742-88-7, 64741-86-2, 64741-44-2	Middle petroleum distillates, unspecified ("naphtha")	solvent, fracking fluid, defoamer	US 5488083				9 to 77		4.3 to 6.7
0	0			0.024	64742-30-9	Distillates (petroleum), chemically neutralized middle	solvent, fracking fluid, defoamer					19		6.7

20705	**68**	3287 (CAS 64742-94-5), 1129 (CAS 64742-48-9), 238 (CAS 64742-96-7), 12 (CAS 64742-54-7), 34 (CAS 64741-68-0)	27.69	28.542	68132-00-3, 64742-94-5, 64741-68-0, 64742-52-5, 64742-54-7, 64742-48-9, 64741-96-4, 64742-96-7	Heavy petroleum distillates, Solvent naphtha, (Petroleum) heavy aliphatic	solvent, fracking fluid	US 5488083				6 to 422		2.9 to 9
0	0			0.002	68410-00-4	Distillates (petroleum), crude oil	solvent, fracking fluid					10		5
1141	**52**	173 (CAS 64741-67-9), 167 (CAS 64741-85-1), 26 (CAS 64742-65-0), 28 (CAS 68477-31-6)	2.32	2.85	64742-65-0,*, 64742-97-5, 68477-31-6,*, 64741-43-1, 64741-85-1, 64741-67-9, 68131-87-3, 64742-91-2	Petroleum products: Distillates,Cracked Distillates,Gas Oils, Raffinates, Residues,	solvent, fracking fluid	US 20080202744 A1				6 to 77		2.9 to 7.5
2348	0	153 (CAS 64742-55-8)	0.90	0.006	64742-55-8, 64741-88-4	Parffinic Petroleum Distillate						145		13
2	1	n.s.			12002-43-6	Natural asphalt								
1584	8	366 (CAS 8042-47-5), 50 (CAS 64742-53-6)	2.45	6.59	8042-47-5, 64742-53-6	White mineral oil	solvent, fracking fluid	US 20080202744 A1				6 to 77		4.5
152	2	50	0.29	0.22	8052-41-3	Mineral spirits (stoddard solvent)	solvent, fracking fluid	US 20080202744				9		4.3
0	0			0.006	68915-97-9	Gas oils (petroleum), straight-run, high-boiling						539		16
0	0			0.002	64742-60-5	Hydrocarbon waxes (petroleum), hydrotreated microcryst.						88		11
0	0			0.004	64741-92-0	Naphtha (petroleum), solvent-refined heavy						39		4.9
						unspecified or other								
5	0				267-56-1	Benzo[1,2-b:5,4-b']difuran								
1	0				75-20-7	Calcium carbide (CaC2)								
0	5			0.19	8002-05-9, *,*	Hydrocarbon mixtures	solvent, fracking fluid					62		9.7
0	0			0.12	64743-01-7	Petrolatum (petroleum), oxidized	solvent, fracking fluid					weeks		3.1
0	2	n.s.			*	Hydrotreated and hydrocracked base oil	solvent, fracking fluid							
0	1	n.s.			*	Low toxicity base oils								

						Alcohols (Table 2 in the Manuscript)								
155916	**769**		**206.1**	**212.1**		**primary and secondary alcohols**								
72806	342	12.269	72.31	76.5	67-56-1	Methanol (Methyl alcohol)	solvent	US 7334635 (co-solvent)	−0.63	1.00×10^{6}	4.27×10^{-6}	1	Y	0.1
22749	36	6.325	37.28	34.2	64-17-5	Ethanol (Ethyl alcohol)	solvent	US 4477360	−0.14	7.92×10^{5}	5.67×10^{-6}	2		0.3
2673	18	1.185	6.98	4.9	71-23-8	Propanol (Propyl alcohol)	solvent, surfactant	US 20120000708 A1	0.35	2.72×10^{5}	7.52×10^{-6}	7		0.7
33819	274	8.008	47.19	50.1	67-63-0	Isopropanol (Isopropyl alcohol, Propan-2-ol)	solvent, surfactant	US 20120000708 A1; US 7334635B2 (solvent)	0.28	4.02×10^{5}	7.52×10^{-6}	14		0.5
913	3	5	0.03	2.1	71-36-3	Butanol	solvent, surfactant	US 20120000708 A1;US 7049436 B2	0.84	7.67×10^{4}	9.99×10^{-6}	54	Y	1
113	4	13	0.08	0.27	78-83-1	Isobutanol (Isobutyl alcohol), Amyl Alcohol	solvent, surfactant	US 20120000708 A1	0.77	9.71×10^{4}	9.99×10^{-6}	14	Y	0.9
5	0	5	0.03	0.01	71-41-0	1-Pentanol	solvent, surfactant		1.33	2.09×10^{4}	1.33×10^{-5}	11		1.3
2	3	n.s.		0.008	107-98-2	1-methoxy-2-propanol	solvent, surfactant	US 20120000708 A1	−0.49	1.00×10^{6}	5.56×10^{-8}	17		0.2
0	1	n.s.		0	123-51-3	Iso amyl alcohol	solvent	US 4739834	1.26	4.16×10^{4}	1.33×10^{-5}	15		1.2
2	3	n.s.		0	108-11-2	Methyl isobutyl carbinol (Methyl amyl alcohol)	solvent	US 4739834	1.68	1.38×10^{4}	1.76×10^{-5}	0.71		1.4
7	1	7	0.04	0.012	111-27-3	1-hexanol	solvent, surfactant	US 20120000708 A1	1.82	6885	1.76×10^{-5}	4		1.6
3006	18	537	3.16	7.2	104-76-7	Ethylhexanol (2-ethylhexanol)	solvent, surfactant	US 20120000708 A1	2.73	1379	3.10×10^{-5}	284		2
2	0	n.s.		0.004	108-93-0	Cyclohexanol	solvent		1.64	3.37×10^{4}	4.90×10^{-6}	1		1.2
784	2	344	2.03	1.9	111-87-5	Octanol	solvent, surfactant	US 20120000708 A1	2.81	814	3.10×10^{-5}	0.9		2.2
21	2	4	0.02	0.024	26952-21-6	Isooctanol	solvent, surfactant	US 20120000708 A1	2.73	1379	3.10×10^{-5}	days		2
808	2	344	2.03	2	112-30-1	Decanol	solvent, surfactant	US 20120000708 A1	3.79	28.21	5.47×10^{-5}	145		3
3	0	n.s.			128973-77-3	Undecanol, branched and linear (impurity)	solvent							
0	0			0.002	112-53-8	1-Dodecanol	solvent					9		3.4
20	0	13	0.08	0.018	123-17-1	2,6,8-Trimethyl-4-nonanol	solvent		4.48	24.97	9.63×10^{-5}	days to weeks		3
0	1	n.s.		0	112-70-9	Tridecyl alcohol	solvent	US 4739834	5.26	4.533	1.28×10^{-4}	6		3.4
10	0	6	0.04	0.048	85566-12-7	C8-C10 Alcohol	solvent					days		2.2
19	4	11	0.06		126950-60-5	Alcohols, C12-14-secondary	solvent	US 4739834	5.19	5.237	1.28×10^{-4}			
0	1	n.s.			8000-41-7	Terpineol	solvent	US 20130029884						
0	0				106-22-9	Citronellol						18		2.7
0	0				106-24-1	Geraniol						53		2.4
0	0				78-70-6	Linalool						12		2.2

0	3	n.s.		0.072	98-00-0	Furfuryl alcohol	solvent, monomer for coating	US 4477360	0.45	2.21×10^{5}	2.17×10^{-7}	1		0.7
124	5	91	0.54	0.03	5877-42-9	Ethyl octynol (1-octyn-3-ol,4-ethyl-)	corrosion inhibitor	US 4739834	2.87	833.9	4.27×10^{-6}	days		2.1
18030	46	5.811	34.25	32.7	107-19-7	Propargyl alcohol (2-propyn-1-ol)	corrosion inhibitor		−0.42	9.36×10^{5}	5.88×10^{-7}	13	Y	0.3
374	**9**		**0.69**	**0.78**		**phenols**								
263	5	109	0.64	0.63	108-95-2	Phenol		US 20120000708 A1	1.51	2.62×10^{4}	5.61×10^{-7}	7	Y	1.9
0	3				53964-94-6	Di-secondary-butylphenol	surfactant	US 20120000708 A1						
0	0			0.002	106-25-2	2,6-Di-tert-butyl-4-methoxyphenol						4		2.4
111	1	9 (CAS 104-40-5)	0.05	0.144	104-40-5, 25154-52-3	Nonylphenol	surfactant		5.99	1.57	5.97×10^{-6}	6 to 20		4.3
41638	**166**		**41.3**	**75.6**		**polyols**								
9	0			0.028	80-05-7	4,4'-Isopropylidenediphenol						63	Y	3.1
3613	13	106	0.62	8.7	60-24-2	2-mercaptoethanol (Thioglycol)	corrosion inhibitor	US 4655287	−0.2	1.94×10^{5}	1.27×10^{-7}	113		0.4
30061	119	5493 (CAS 107-21-1)	32.37	49.7	107-21-1, 76-31-3	Ethylene glycol (1,2-ethanediol)	crosslinker, scale inhibitor, surfactant	US 20120000708 A1	−1.2	1.00×10^{6}	1.31×10^{-7}	24	Y	-0.7
3623	18	435	2.56	7.1	57-55-6	Propylene glycol (1,2-propanediol)	scale inhibitor, surfactant	US 20120000708 A1	-0.78	8.11×10^{5}	1.74×10^{-7}	10		-0.4
4014	16	973	5.73	10.1	56-81-5	Glycerol (1,2,3-Propanetriol, Glycerine)	crosslinker	US 4477360	−1.65	1.00×10^{6}	6.35×10^{-9}	2		-0.9
226	0	n.s.		0.004	486-66-8	Soy Isoflavone (Daidzein)			2.55	568.4	3.91×10^{-16}	days to weeks		2.9
92	0	n.s.			8043-29-6	Polyol								
						unspecified/other								
226	0			0.004	67-03-8	Thiamine-HCl						weeks		-1.6
0	1					Acetylenic alcohol								
0	9					Alcohols								
0	1					Alcohols, C9-C22								
0	7					Secondary alcohol								
0	2					Substituted alcohol								
1999	**25**		**1.9**	**4.6**		**Ethers**								
329	1	1	0.01	1.1	75-21-8	Ethylene oxide			−0.05	2.37×10^{5}	1.20×10^{-4}	14	Y	0.7
0	1	n.s.		0.12	75-56-9	Propylene oxide			0.37	1.29×10^{5}	1.60×10^{-4}	5	Y	0.9
877	5	4 (CAS 106-89-8), 28 (CAS 25085-99-8)	0.19	0.43	25085-99-8, 106-89-8	Epichlorohydrin	proppant coating		0.63	5.06×10^{4}	5.62×10^{-5}	24	Y	1.1
0	0			0.008	30499-70-8	Trimethylolpropane triglycidyl ether						weeks		1

0	5	91 (CAS 2426-08-6)	0.54	0.93	2426-08-65	Butyl glycidyl ether	proppant coating					232		1.1
373	0	n.s.		1.2	123-91-1	Dioxane			−0.32	2.14×10^{5}	5.91×10^{-6}	360	Y	0.6
0	1	n.s.			*	Alkyl hexanol								
419	0	196 (CAS 112-34-5)	1.16	0.84	1-52-5, 112-34-5	Short chained glycol ether						0.1		0.6
0	**3**	n.s.			*	Aromatic alcohol glycol ethers								
1	9				*, 1589-47-5	Glycol ethers								
						Alkoxylated Alcohols (Table 2 in the Manuscript)								
61668	**219**		**65.7**	**123.5**		**ethoxylated alcohols**								
14605	126	3.325	19.60	22.8	111-76-2	Ethylene glycol monobutyl ether (2-butoxyethanol)	surfactant, solvent	US 7334635 (11), US 20120000708 A1 (7)	0.57	6.45×10^{4}	9.79×10^{-8}	56	Y	0.9
1267	0	97	0.57	1.1	5131-66-8	1-Butoxy-2-Propanol	solvent		0.98	4.21×10^{4}	1.30×10^{-7}	days		1
1112	0	n.s.		0.81	15821-83-7	2-Butoxy-1-Propanol			0.98	4.21×10^{4}	1.30×10^{-7}	days		1
1	0	1	0.01		57018-52-7	1-Tert-Butoxy 2-Propanol	solvent		0.87	5.24×10^{4}	1.30×10^{-7}			
1	0	n.s.			150-76-5	Hydroquinone monomethyl ether			1.59	1.65×10^{4}	3.32×10^{-8}			
3895	8	762	4.49	8.1	111-46-6	Diethylene glycol	scale inhibitor, solvent, surfactant	US 20120000708 A1	−1.47	1.00×10^{6}	2.03×10^{-9}	9		-0.8
12	4	8	0.05	0.008	111-77-3	Diethylene glycol monomethyl ether	solvent		−1.18	1.00×10^{6}	6.50×10^{-10}	16		-0.3
1025	3	360	2.12	2.7	112-27-6	Triethylene glycol	surfactant	US 20120000708 A1	−1.75	1.00×10^{6}	3.16×10^{-11}	9		-1
1	1	1	0.01	0.002	112-60-7	Tetraethylene glycol	surfactant, solvent	US 7723272	−2.02	1.00×10^{6}	4.91×10^{-13}	53		-1.3
6900	20	1969 (CAS 25322-68-3)	10.0	14.4	25322-68-3, 65545-80-4	Polyethylene glycol = Poly(oxy-1,2-ethanediyl), alpha-hydro-omega-hydroxy	surfactant, solvent	US 20120000708 A1				days to weeks		-1.5
112	4	1	0.01	0.5	9004-77-7	Polyethylene glycol monobutyl ether	surfactant					days		-0.2
1298	0	511	3.01	4.3	31726-34-8	Polyethylene glycol monohexyl ether						days to weeks		0.3
8	5	7	0.04	0.004	107-41-5	Hexylene glycol	surfactant	US 20120000708 A1	0.58	3.26×10^{4}	4.06×10^{-7}	8		0.4
422	0	4	0.02	2.8	61827-42-7	Polyethylene glycol isodecyl ether = Poly(oxy-1,2-ethanediyl), alpha-isodecyl-omega-hydroxy						days to weeks		1.2
3	0	n.s.		0.018	9002-92-0	Polyethylene glycol monododecyl ether			4.5	14.19	9.45×10^{-7}	14		1.9
252	8	50 (CAS 34398-01-1)	0.29		127036-24-2, 34398-01-1	Polyethylene glycol undecyl ether = Ethoxylated undecyl alcohol = Polyethylene glycol monoundecyl ether = Poly-(oxy-1,2-ethanediyl)-alpha-undecyl-omega-hydroxy	surfactant, solvent							
32	0	18	0.11	0.036	60828-78-6	Polyethylene glycol trimethylnonyl ether, synonym "2-[(2,6,8-Trimethylnonan-4-yl)oxy]ethanol")						days to weeks		1.8
5937	1	281 (CAS 9043-30-5)	1.66	7.8	24938-91-8, 9043-30-5	Polyethyleneglycol isotridecyl ether = Isotridecanol, ethoxylated = Poly(oxy-1,2-ethanediyl), a-isotridecyl-w-hydroxy	surfactant, solvent	US 20120000708 A1				days to weeks		2 to 2.2
0	0			0.05	9004-98-2	Polyethylene glycol monooleyl ether	surfactant					days to weeks		3.5

1	0	n.s.			92046-34-9	Surfactant (Triton X-405, reduced = 23-{[4-(2,4,4-Trimethyl-2-pentanyl)cyclohexyl]oxy}-3,6,9,12,15,18,21-heptaoxatricosan-1-ol)	surfactant							
467	2	101	0.60	0.84	68439-45-2	Alkyl (C6-C12) alcohol, ethoxylated = polyethylene glycol C6-C12 ether	surfactant	US 20120000708 A1	4.49	8.832	1.10×10^{-2}	days to weeks		0.9
1338	5	356	2.10	2.4	78330-19-5	EO-C7-9-iso-, C8-rich alcohols			2.46	1513	3.04×10^{-7}	days to weeks		0.8
0	0			0.016	26183-52-8	Polyethyleneglycol 300 monodecylether						days to weeks		1.4
0	0			0.002	71060-57-6	Alcohols, C8-10, ethoxylated	surfactant					days		3
743	1	185	1.09	1.2	68439-46-3	Alkyl (C9-11) alcohol, ethoxylated	surfactant	US 20120000708 A1	4.98	2.874	1.47×10^{-2}	12		1.4
1284	4	352	2.07	2.3	78330-20-8	Alcohols, C9-11-iso-, C10-rich, ethoxylated	surfactant, solvent	US 8338340	4.9	3.321	1.47×10^{-2}	days		3.5
2353	7	389	2.29	6.4	68002-97-1	C10-C16 alcohol, ethoxylated	surfactant, solvent	US20100190666 A1 (as co-surfactants)	4.99	4.532	1.25×10^{-6}	days to weeks		1.6
2	0			0.006	78330-23-1	Alcohols, C11-14-iso-, C-13-rich, ethoxylated propoxylated						days		4.3
0	0			0.012	69227-21-0	Alcohols, C12-18, ethoxylated propoxylated	surfactant					days		4.1
1944	20 (1,19)	79 (CAS 84133-50-6), 35 (CAS 68131-40-8)	0.68	5.84	68131-40-8, 84133-50-6	Alcohols, C11-15-secondary, ethoxylated	surfactant	US 8338340				days to weeks		1.6 to 1.9
148	0	15	0.09	0.21	66455-14-9	Alcohols, C12-13, ethoxylated			5.96	0.2995	2.58×10^{-2}	days to weeks		4.1
1501	0	366	2.16	3.9	68439-50-9	C12-C14 Alcohols Ethoxylated						days		4.1
12848	11	1321 (CAS 68951-67-7), 662 (CAS 68551-12-2), 1 (CAS 68131-39-5)	11.7	28.6	68131-39-5, 103331-86-8, 68551-12-2, 68951-67-7	Alcohols, C12-16, ethoxylated	surfactant, solvent	US20100190666 A1 (as co-surfactants)	6.45	0.09603	3.43×10^{-2}	days to weeks		1.9 to 4.7
0	1					Fatty alcohol alkoxylate								
2156	8	165 (CAS 78330-21-9)	0.97	6.4	78330-21-9, 104780-82-7, 66455-15-0, 64425-86-1, *	Ethoxylated alcohols	surfactant, solvent	US 20120000708 A1				23		3.6 to 4.3
885	**20**		**2.9**	**5.0**		**propoxylated alcohols**								
13	1	n.s.		0.01	25265-71-8	Dipropylene glycol	surfactant, solvent	US 20120000708 A1	−0.64	3.11×10^{5}	3.58×10^{-9}	16		-0.3
608	12	255	1.50	2	34590-94-8	Dipropylene glycol monomethyl ether (2-methoxymethylethoxy propanol)	surfactant, solvent	US 20120000708 A1	−0.27	4.27×10^{5}	1.15×10^{-9}	days to weeks		0.1
203	1	42	0.25	0.39	25322-69-4	Polypropylene glycol	surfactant, solvent	US 20120000708 A1				days to weeks		-0.4
0	5	181 (CAS 9003-11-6)	1.07	2.6	9003-11-6	Polyethylene-polypropylene glycol	surfactant, solvent					days to weeks		-1.4

0	1			0	20324-33-8	Propanol, [2(2-methoxy-methylethoxy) methylethoxyl]	surfactant, solvent	US 20120000708 A1				days to weeks		0.1
44	0	10	0.06		37251-67-5	Oxirane, 2-methyl-, polymer with oxirane, monodecyl ether								
17	0	n.s.			64366-70-7	Oxirane, methyl-, polymer with oxirane, mono(2-ethylhexyl) ether	surfactant							
9	26	3 (CAS 68015-67-8), 4 (CAS 228414-35-5)	0.04	0.016	*, 228414-35-5, 68015-67-8, *,*,*,*	Alcohol alkoxylate, Alkyl alkoxylate, Oxyalkylated alcohol	surfactant, solvent					days		3.02
25318	**81**		**31.4**	**42.2**		**alkoxylated phenols**								
20201	73	964 (CAS 9016-45-9), 2455 (CAS 127087-87-0), 819 (CAS 68412-54-4), 430 (CAS 26027-38-3)	27.51	31.7	127087-87-0, 26027-38-3,*, 68412-54-4, 9016-45-9,*, 9016-45-6, 9018-45-9	Ethoxylated nonyl phenols = Polyethyleneglycol p-nonylphenyl ether = Polyethylene glycol mono(branched p-nonylphenyl) ether [Poly(oxy-1,2-ethanediyl), alpha-(4-nonylphenyl)-omega-hydroxy-, branched (Nonylphenol ethoxylate)]	surfactant, solvent	US 4552673				25 to 43		2.6 to 2.7
50	0	26	0.15	0.08	9014-93-1	DINONYPHENYL (should be "α-(2,3-Dinonylphenyl)-ω-hydroxypoly(oxyethylene)"						days to weeks		5.2
0	1	n.s.			9081-17-8	Nonylphenol, ethoxylated and sulfated	surfactant							
15	5	1 (CAS 9036-19-5), 1 (CAS 9002-93-1)	0.02	0.026	9036-19-5, 68987-90-6, 9002-93-1	Ethoxylated octyl phenol	surfactant, solvent	US 4552673	5.01	3.998	1.24×10^{-7}	50		2.3 to 3.3
5052	1	624	3.68	10.4	68439-51-0	Tergitol	surfactant, solvent	nonionic tenside (type nonylphenol ethoxylate)	6.67	0.02971	7.08×10^{-4}	days		4.1
0	1	n.s.			*	Alkylphenol ethoxylates	surfactant, solvent		4.91	5.237	1.25×10^{-6}			
683	**17**					**unspecified/other**								
0	1					Oxylated alcohol								
0	1	n.s.			*	Ethoxylated nonionic surfactant								
0	1	n.s.			*	Dispersing agent								
0	13	n.s.			*	Surfactants								
0	1	n.s.			*	Nonionic surfactant								
337	0	n.s.			67254-71-1	Surfactant Mixture			5.47	0.9301	1.95×10^{-2}			
338	0	n.s.			56449-46-8	Surfactant Mixture								
8	0				154518-36-2	Surfactant								
						Amines (Table 4 in the Manuscript)								
12978	**78**		**16.7**	**22.8**		**mono- and polyamines**								
282	1	n.s.		0.64	75-31-0	Isopropylamine	solvent	US 4739834	0.27	8.38×10^{5}	1.34×10^{-5}	16		1
0	0			0.12	108-09-8	1,3-Dimethylbutylamine						days to weeks		1.8
0	0			0.086	2190-04-7	1-Octadecanamine, acetate (1:1)						days		5.2
2	0	n.s.			19834-02-7	Cyclohexanamine, Sulfate (1:1)			1.63	6.40×10^{4}	1.38×10^{-5}			
15	0	8	0.05	0.034	62-53-3	Aniline			1.08	2.08×10^{4}	1.90×10^{-6}	349	Y	1.4
543	0	n.s.		1.5	75-50-3	Trimethylamine			0.04	1.00×10^{6}	3.65×10^{-5}	0.8		0.9
547	1	11	0.06	1.5	593-81-7	Trimethylammonium chloride			0.04	1.00×10^{6}	3.65×10^{-5}	days to weeks		-0.65
394	0	14	0.08	0.7	1120-24-7	Decyldimethyl amine (impurity)			4.46	82.23	4.68×10^{-4}	days to weeks		3.3
0	5	n.s.		0	124-28-7, 1613-17-8	N,N-dimethyloctadecylamine			8.39	0.008882	4.51×10^{-3}	15		4 to 5.5
202	0	37 (CAS 61790-60-1)	0.22	0.394	61790-33-8, 61790-60-1	Amines, Tallow Alkyl						16		3.9 to 5.1
55	0	n.s.		0.11	61790-85-0	Fatty Alkyl Amine Salt						weeks		7.9
242	0	n.s.		1.7	61788-62-3	Amines, dicoco alkylmethyl - TS						11		6.9

63	0	n.s.		0.1	61788-46-3	AMINES, COCO ALKYL						22		3.5
63	0	n.s.		0.1	61789-76-2	Amines, Dicoco Alkyl						147		6.8
0	0			0.004	61791-63-7	Amines, N-coco alkyltrimethylenedi-						days		6.7
4	0	n.s.		0.17	61788-90-7	Di(cocoalkyl)methyl amine hydrochloride						days		3.4
0	3	n.s.		0	61790-57-6	Amines, coco alkyl, acetate	surfactant					days		2.4
8203	37	2.134	12.58	11.8	100-97-0	Hexamethylenetetramine	crosslinker (for polymer coating)		−4.15	1.00×10^{6}	1.63×10^{-1}	1		-1.6
2	0			0.006	68607-19-2	Pyridine, alkyl derivatives, hydrochlorides						days to weeks		0.6
8	2	n.s.		0.008	110-91-8	Morpholine	surfactant, anti-sludge agent		−0.56	1.00×10^{6}	1.14×10^{-7}	10		0.3
99	0	99	0.58		68909-77-3	Morpholine process residue								
10	0	6	0.04	0.048	91-22-5	Quinoline			2.14	1711	6.88×10^{-7}	5	Y	1.8
29	0	24	0.14	0.012	119-65-3	Isoquinoline			2.14	1551	6.88×10^{-7}	days to weeks		1.8
39	0	30	0.18	0.06	91-63-4	Quinaldine			2.69	498.5	7.60×10^{-7}	days to weeks		2.2
1	0	1	0.01		290-87-9	1,3,5-Triazine			−0.2	1.03×10^{5}	1.21×10^{-6}			
0	1	n.s.		0	2997-92-4	2,2`-azobis (2-amidopropane) dihydrochloride (should be 2,2'-azobis(2-amidinopropane) dihydrochloride)	radical initiator		−3.28	1.00×10^{6}	1.21×10^{-14}	weeks		-2.3
2	0	n.s.		0.002	27776-21-2	2,2`-Azobis-2-(imidazolin-2-yl)propane-di hydrochloride (= 2,2'-(Azobis(1-methylethylidene))bis(4,5-dihydro-1H-imidazole) dihydrochloride)	radical initiator		2.12	193.3	3.11×10^{-14}	days to weeks		2.8
351	0	n.s.		0.55	107-15-3	Ethylenediamine			−1.62	1.00×10^{6}	1.03×10^{-9}	22		-0.2
1466	2	372	2.19	2.8	111-40-0	Diethylenetriamine	complexing agent, enhancer (gel formation)	US 6342468	−2.13	1.00×10^{6}	3.10×10^{-13}	37		-0.3
6	0	n.s.		0.068	112-24-3	Triethylenetetramine			−2.65	1.00×10^{6}	9.30×10^{-17}	days		-0.7
6	2	n.s.		0.068	112-57-2	Tetraethylenepentamine	complexing agent		−3.16	1.00×10^{6}	2.79×10^{-20}	days		-1
6	0	n.s.		0.068	4067-16-7	Pentaethylenehexamine			−3.67	1.00×10^{6}	8.36×10^{-24}	days		-1.3
111	0	51	0.30		68155-37-3	(C12-C18) N-Alkylpropylenediamine			4.74	23.71	6.81×10^{-8}			
138	0	21	0.12	0.022	109-55-7	N,N- Dimethyl-1,3-Propanediamine			−0.45	1.00×10^{6}	6.62×10^{-9}	days to weeks		0.6
0	2	n.s.		0	124-09-4, 6055-52-3	Hexanediamine; 1,6-hexanediamine dihydrochloride	crosslinker	US 229009	0.35	5.34×10^{5}	3.21×10^{-9}	12		0.1 to 1.1
0	0			0.006	68647-57-4	Fatty acids, C18-unsatd., dimers, compds. With diethylenetriamine-tall-oil fatty acid reaction products						days		10
0	1	n.s.			*	N-tallowalkyltrimethylenediamines								
0	0			0.038	1760-24-3	N-[3-(Trimethoxysilyl) propyl]ethylenediamine						28		-0.1
0	0			0.02	71011-03-5	Amines, ditallow alkyl, acetates						days to weeks		8.7
0	1	n.s.		0	61790-69-0	Diethylenetriamine, tall oil fatty acids reaction product	complexing agent, enhancer (gel formation)	US 6342468				days to weeks		2.8
0	2	n.s.			68603-67-8	Polyethylene polyammonium salt	clay stabilizer							
0	2	n.s.			*	Polyamine								
24	0	24	0.14	0.002	61788-93-0	Cocodimethylamine						17		3.9
						amine - unspecified								
16	0	8	0.05	0.088	2002-24-6	Ethanolamine hydrochloride			−1.61	1.00×10^{6}	3.68×10^{-10}	days		-2.2
0	1	n.s.			*	Amino compounds								
0	2	n.s.			*	Alkyl amine		US 4739834						
0	2				*	Substituted alkylamine								
0	1	n.s.			*	Alkyl amine blend in a metal salt solution								
0	3	n.s.			*	Modified cycloaliphatic amine adduct								
0	2	n.s.			*	Amine salt								
0	1	n.s.			*	Fatty alkyl amine salt			8.55	0.0003941	8.09			
0	1	n.s.		0	61789-39-7	Amphoteric alkyl amine						days		-1.7
0	2	n.s.			*	Inner salt of alkyl amines								
0	1	n.s.			*	Organo-metallic ammonium complex								
49	0				68139-75-3	Fatty Acid Amine Salt Mixture								
7280	**75**		**8.9**	**15.4**		**amine - aminoalcohol**								

1574	17	402 (CAS 141-43-5)	2.37	2.3	141-43-5, 9007-33-4	Monoethanolamine (Ethanolamine)	crosslinker		−1.61	1.00×10^{6}	3.68×10^{-10}	days	-0.2
103	0				68425-67-2	Ethanolamine Borate							
2318	14	97	0.57	5.2	111-42-2	Diethanolamine (2,2-iminodiethanol)	surfactant, crosslinker, breaker	US 4524829	−1.71	1.00×10^{6}	3.92×10^{-11}	14	-0.7
161		n.s.		0.32	61791-44-4	Ethanol, 2,2'-Iminobis-,N-Tallow Alkyl Deriviatives						27	3.7
2479	21	714	4.21	5.6	102-71-6	Triethanolamine (2,2,2-nitrilotriethanol)	crosslinker, breaker	US 4524829	−2.48	1.00×10^{6}	4.18×10^{-12}	6	-0.5
157	0	n.s.		1.1	637-39-8	Triethanolamine Hydrochloride			−2.48	1.00×10^{6}	4.18×10^{-12}	days	-2.9
3	0	1	0.01		68299-02-5	Triethanolamine hydroxyacetate			−2.97	1.00×10^{6}	6.28×10^{-11}		
19	0	7	0.04	0.062	78-96-6	Isopropanolamine			−1.19	1.00×10^{6}	4.88×10^{-10}	68	0
1	7			0.002	110-97-4	2-Propanol, 1,1'-iminobis-						28	-0.4
457	5	281	1.66	0.82	122-20-3	Triisopropanolamine	crosslinker		−1.22	1.00×10^{6}	9.77×10^{-12}	14	-0.6
0	4	n.s.		0	102-81-8	Dibutylaminoethanol (2-dibutylaminoethanol)	surfactant	US 20120000708 A1	2.01	3297	9.70×10^{-9}	days	1.9
0	1	n.s.		0	34375-28-5	Ethanol, 2-(hydroxymethylamino)-		US 4739834	−1.53	1.00×10^{6}	1.62×10^{-12}	days	-1.2
0	1	n.s.		0	10213-78-2	Ethanol, 2, 2'-(Octadecylamino) bis-		US 4739834	6.85	0.08076	1.06×10^{-8}	days to weeks	3.8
0	1	n.s.		0	135-37-5	Ethanoldiglycine disodium salt			−3.04	1.90×10^{5}	3.90×10^{-17}	days	-4.9
0	1	n.s.			77-86-1	Tris(hydroxymethyl)aminomethane			−1.56	1.00×10^{6}	8.67×10^{-13}		
8	3	n.s.		0.004	150-25-4	Alkanolamine			−3.27	3.52×10^{5}	1.28×10^{-14}	days	-2.5
4608	**19**		**0.63**	**5.64**		**amine- alkoxylated**							
8	0	3	0.02	0.01	5332-73-0	MOPA--Methoxypropylamine			−0.42	1.00×10^{6}	1.56×10^{-7}	days	0.6
1976	2	3 (CAS 61791-26-2)	0.02	3.602	61791-26-2, 61790-82-7	Ethoxylated hydrogenated tallow alkylamines = Amines, tallow alkyl, ethoxylated	surfactant	US 20120000708 A1				days to weeks	3.4 to 3.5
21	0	n.s.		0.024	61790-59-8	Amines, hydrogenated tallow alkyl, acetates						days to weeks	4.1
1969	0	n.s.		2	61791-14-8	Amines, coco alkyl, ethoxylated	surfactant					days to weeks	1.9
551	3	99 (CAS 26635-93-8)	0.58	0	13127-82-7, 26635-93-8	Ethoxylated oleyl amine	surfactant	US 20120000708 A1	6.63	0.1268	9.35×10^{-9}	days to weeks	3.7
0	7			0	*,68551-33-7	Alkoxylated amines; Salts of oxyalkylated fatty amines	surfactant					days to weeks	2.3
0	1	n.s.		0	68155-39-5	Amines, C14-18; C16-18-unsaturated, alkyl, ethoxylated	surfactant	US 20120000708 A1				days to weeks	4.3
81	1	n.s.			68966-36-9	Amines, polyethylenepoly-, ethoxylated, phosphonomethylated	surfactant	US 20120000708 A1					
0	1	n.s.		0	929-59-9	1,8-diamino-3,6-dioxaoctane			−2.17	1.00×10^{6}	2.50×10^{-13}	days to weeks	-0.5
2	0	2	0.01		25214-63-5	1,2-Ethanediamine, polymer with methyloxirane	surfactant						
0	1	n.s.			*	Oxyalkylated polyamine	surfactant						
0	3	n.s.		0	9046-10-0	Polyetheramine	surfactant					days to weeks	0.2
1250	**11**		**0.08**	**1.47**		**amine oxides**							
452	0	n.s.		0.52	1184-78-7	Trimethylamine, N-oxide	surfactant		−3.02	1.00×10^{6}	3.81×10^{-15}	days to weeks	0.5
18	0	n.s.		0.042	70592-80-2	Amine- (C10-C16- Alcyldimethyl) Oxides	surfactant		2.87	89.63	1.14×10^{-13}	days	2.9
768	4	14	0.08	0.88	2605-79-0	Decyl-dimethyl amine oxide	surfactant	US 20120000708 A1	1.4	2722	4.88×10^{-14}	days	2.9
0	0			0.032	100545-50-4	Didecyl-methyl-oxido-azanium						days	5.3
1	1	n.s.		0	68155-09-9	Cocamidopropylamine oxide	surfactant,	US 5551516				days	1.6

0	1	n.s.		0	61791-47-7	Coco bis-(2-hydroxyethyl) amine oxide	surfactant	US 20120000708 A1				days		1.8
11	4	n.s.			68647-77-8	Amides, tallow, n-[3-(dimethylamino)propyl],n-oxides	surfactant							
	1	n.s.			*	Amine oxides	surfactant	US 20120000708 A1	1.22	2816	9.42×10^{-11}			
						Cationic Surfactants (N / P Quaternary Compounds) (Table 4 in the Manuscript)								
28274	**65**		**49.4**	**43.3**		**quarternary aliphatic ammonium salts**								
4349	14	858	5.06	8.2	75-57-0	Tetramethyl ammonium chloride	clay stabilizer	US 5099923, US 7012044	−4.18	1.00×10^{6}	4.17×10^{-12}	days to weeks		-1.5
52	0	n.s.		0.77	7398-69-8	Dimethyldiallyammonium chloride	surfactant		−2.49	1.00×10^{6}	7.20×10^{-12}	days to weeks		-0.5
8	0	2	0.01	0.024	26062-79-3	Polydimethyl dially ammonium chloride	surfactant					days to weeks		-0.5
0	1	n.s.		0	57-09-0	Octyltrimethylammonium bromide	surfactant	US 6875728	3.18	28.77	2.93×10^{-10}	days to weeks		2.6
0	0			0.068	1941-30-6	Tetrapropylammonium bromide	surfactant					days to weeks		0.7
49	6	45	0.27	0	112-03-8	Trimethyloctadecylammonium (1-octadecanaminium, N,N,N-trimethyl-, chloride)	surfactant	US 6875728	4.17	2.862	5.16×10^{-10}	0.4		3.1
645	0	306	1.80	1.8	68607-28-3	Dimethylcocoamine, bis(chloroethyl) ether, diquaternary ammonium salt	surfactant					days to weeks		2.4
22	4	22	0.13	0	*, 61789-18-2	Quaternary amine compounds	surfactant					days to weeks		1.5
4109	1	2.063	12.16	9.3	7173-51-5	Didecyl dimethyl ammonium chloride	biocide	US20100190666 A1	4.66	0.9	6.85×10^{-10}	21		3.4
4165	0	46	0.27		68953-58-2	Quaternary Ammonium Compounds bisHydrogenated Tallow Alkyl Dimethyl Salts With Bentonite	clay stabilizer							
2427	0	n.s.			121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex	clay stabilizer							
1645	20	151 (CAS 68989-00-4), 127 (CAS 61789-77-3)	1.64	4.7	*, 19277-88-4, 68989-00-4, 8030-78-2, 61789-77-3,61789-68-2,*,*,*	Fatty quaternary ammonium chloride	clay stabilizer, Surfactant	US 5099923; 20120000708 A1				39 to 181		0.8 to 4.5
26	0	n.s.		0.47	56-93-9	Benzenemethanaminium, NNN-trimethyl, chloride	clay stabilizer		−2.47	1.00×10^{6}	3.37×10^{-13}	days to weeks		-0.4
6882	7	3.259	19.21	13.2	68424-85-1	Alkyl (C12-16) dimethyl benzyl ammonium chloride	biocide	US20100190666 A1				10		3
491	0	330 (CAS 68391-01-5), 1 (CAS 68956-79-6)	1.95	0.07	68391-01-5, 68956-79-6	Alkyl (C12-18) dimethyl ethylbenzyl ammonium chloride = Quaternary ammonium compounds, benzyl-C12-18-alkyldimethyl, chlorides			4.95	0.3172	1.96×10^{-11}	days to weeks		3
1655	1	516	3.04	2.8	139-08-2	n-alkyl dimethyl benzyl ammonium chloride	biocide	US20100190666 A1	3.91	3.608	1.34×10^{-11}	4		3

624	0	305	1.80		85409-23-0	Alkyl dimethyl ethylbenzyl ammonium chloride (68 C12, 32 C14)								
0	9				*, *	Alkyl quaternary ammonium chlorides = Alkylated quaternary ammonium chloride								
353	0			0.83	34004-36-9	(2,3-dihydroxypropyl)trimethylammonium chloride	clay stabilizer					days		-3.2
0	0			0.002	68334-55-4	[2-hydroxy-3-(tridecyloxy)propyl] trimethylammonium chloride						days to weeks		1.2
354				0.83	3327-22-8	3-Chloro-2-hydroxypropyltrimethyl ammonium chloride						days to weeks		-2.1
0	0			0.002	139-07-1	Benzyldimethyldodecylammonium chloride						days to weeks		2.5
355		351	2.07	0.026	122-18-9	Benzyldimethylhexadecylammonium chloride						days to weeks		3.5
8		4	0.02	0.008	100765-57-9	Pyridinium, 1-(phenylmethyl)-, alkyl derivs., chlorides						days to weeks		0.1
3		3	0.02	0.17	61789-71-7	Quaternary ammonium compounds, benzylcoco alkyldimethyl, chlorides						days to weeks		2.5
0				0.002	8001-54-5	Benzalkonium chloride						183		2.5
52					177149-89-2, 61789-71-7	Quaternary Amine, Quaternary ammonium compounds, Quaternary Ammonium Chloride								
0	2	n.s.			68391-11-7	Quaternized alkyl nitrogenated compound								
5101	**26**		**14.0**	**7.0**		**quaternary N-heterocyclic ammonium salt**								
2434	3	1.326	7.81	4.6	15619-48-4	Chloromethylnaphthalene quinoline quaternary amine	corrosion inhibitor		4.4	6.02	1.19×10^{-6}	days to weeks		-1.3
1797	5	723	4.26		72480-70-7	Tar bases, quinoline derivatives, benzyl chloride-quaternized	corrosion inhibitor							
0	6	n.s.			*	Haloalkyl heteropolycycle salt								
390	9	202	1.19	0.9	68909-18-2	Pyridinium, 1-(phenylmethyl)-, ethyl methyl derivatives, chlorides	corrosion inhibitor, clay stabilizer		4.1	14.13	1.78×10^{-5}	days to weeks		0.4
130	0				689096-18-2	Benzyl alcyl pyridinium choride								
124	1	113	0.67	0.1	65322-65-8	1-(1-naphthylmethyl)quinolinium chloride			5.57	0.02454	1.16×10^{-7}	days to weeks		-0.3
0	0			0.002	62763-89-7	2-Methylquinoline hydrochloride						days to weeks		-0.9
0	0			0.002	35674-56-7	2-Benzylisoquinolinium chloride						days to weeks		-1.3
0	1	n.s.			*	Isomeric aromatic ammonium salt								
0	1	n.s.			*	2-substituted aromatic amine salt			-5.8 - 4.89	$0.35 - 1.00 \times 10^{6}$	$9.84 \times 10^{-18} - 2.36 \times 10^{-11}$			
226	0	17	0.10	1.4	78-21-7	Cetylethylmorpholinium ethyl sulfate = 4-Ethyl-4-hexadecylmorpholin-4-ium ethyl sulfate			4.54	0.9381	2.66×10^{-12}	days to weeks		4.3

9035	**8**		**16.1**	**1.6**		**quaternary ammonium salt - hydroxyalkylated**								
1112	2	204	1.20	0.76	138879-94-4	1,2-ethanediaminium, N, N'-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N,N'-bis(2-hydroxyethyl)-N,N'-dimethyl-,tetrachloride	clay stabilizer		−23.19	1.00×10^{6}	2.33×10^{-35}	days		-13.1
31	0	n.s.			27103-90-8	Ethanaminium, N,N,N-trimethyl-2-(2-methyl-1-oxo-2-propenyl)oxy-, methyl sulfate,								
147	0	n.s.		0.88	7006-59-9	2-hydroxy-N,N-bis(2-hydroxyethyl)-N-methylethanaminium chloride			−6.7	1.00×10^{6}	4.78×10^{-19}	days		-3.7
1	2	n.s.			120086-58-0	Aliphatic amine derivative ((z)-13 docosenyl-n,n-bis(2-hydroxyethyl)-n-methyl ammonium chloride)			4.38	0.3827	3.32×10^{-15}			
962	1	50	0.29		51838-31-4	Polyepichlorohydrin, trimethylamine quaternized	clay stabilizer							
6723	3	2.477	14.60		67-48-1	Choline chloride	clay stabilizer		−5.16	1.00×10^{6}	2.03×10^{-16}			
59	0	2	0.01		78-73-9	CHOLINE BICARBONATE			−5.16	1.00×10^{6}	2.03×10^{-16}			
						quarternary organic phosphonium salt								
5473	5	1.079	6.36	7.7	81741-28-8	Tributyl tetradecyl phosphonium chloride	surfactant, biocide	US 6875728	11.22	7.90×10^{-7}	2.61×10^{-1}	days		3.4
						Organic Acids (Table 5 in the Manuscript)								
38969	**114**		**51.0**	**75.0**		**carboxylic acids**								
5671	24	2.118	12.48	12.4	64-18-6	Formic acid	pH control	US 4462917	−0.46	9.55×10^{5}	7.50×10^{-7}	14		-0.1
381	0	n.s.		0.89	141-53-7	Sodium Formate			−0.46	9.55×10^{5}	7.50×10^{-7}	6		-2.2
2946	3	367	2.16	5.4	590-29-4	Potassium formate	pH control		−0.46	9.55×10^{5}	7.50×10^{-7}	days		-2.2
17788	56	3.563	21.00	31.7	64-19-7	Acetic acid	pH control	US 4846277	0.09	4.76×10^{5}	5.48×10^{-7}	7		0.1
5612	4	1.042	6.14	10	631-61-8	Ammonium acetate	pH control		0.09	4.76×10^{5}	5.48×10^{-7}	7		-0.8
853	6	217	1.28	2	127-09-3	Sodium acetate	pH control		0.09	4.76×10^{5}	5.48×10^{-7}	2		-1.9
5	2	2	0.01	0.026	126-96-5	Sodium diacetate			0.09	4.76×10^{5}	5.48×10^{-7}	days		-1.9
763	1	140	0.83	2.5	127-08-2	Potassium acetate	pH control		0.09	4.76×10^{5}	5.48×10^{-7}	7		-1.9

4325	7	1.185	6.98	5.8	108-24-7	Acetic anhydride	pH control	US 8387696	−0.58	3.59×10^{5}	3.57×10^{-5}	3E-		0.1
1	0				79-10-7	Acrylic acid						3		
291	0	12	0.07	2.1	10604-69-0	Ammonium Acrylate			0.44	1.68×10^{5}	2.89×10^{-7}	days to weeks		-0.6
213	0	n.s.		0.41	18016-19-8	Sodium Carboxylate (should be sodium carboxyacrylate)			0.05	1.04×10^{5}	1.35×10^{-12}	hours to days		-1.6
0	0			0.018	24634-61-5	2,4-Hexadienoic acid, potassium salt (1:1), (2E,4E)-						hours to days		-1.1
51	11	7	0.04	0.27	65-85-0	Benzoic acid	diverting agent		1.87	2493	1.08×10^{-7}	0.8	Y	1.2
68	0	n.s.		0.088	532-32-1	Sodium Benzoate			1.87	2493	1.08×10^{-7}	days to weeks		-1.1
0	0			0.002	56-40-6	Glycine						days		-1.6
0	0			1.4	625-45-6	Methoxyacetic acid						days		-0.3
0	0			0.004	56-85-9	Glutamine						53		-1.9
1	0				992-98-3	Carboxylic Acid								
8901	**27**		**10.4**	**20.2**		**alpha-hydroxy / thio, alpha-keto carboxylic acids**								
13	2	1	0.01	0.006	89-65-6	Erythorbic acid		US 4784694	−1.88	1.00×10^{6}	4.07×10^{-8}	hours to days		-1
3783	4	1.558	9.18	7.2	6381-77-7	Sodium erythorbate	complexing agent		−1.88	1.00×10^{6}	4.07×10^{-8}	hours to days		-3.9
30	1	15	0.09	0.032	526-95-4	Gluconic acid	retarding agent (crosslinking)	US 4470915	−1.87	1.00×10^{6}	4.74×10^{-13}	hours to days		-1.7
24		n.s.		0.068	110-44-1	Sorbic Acid			1.62	1.94×10^{4}	5.72×10^{-7}	5		0.9
725	6	48 (CAS 79-14-1)	0.29	1.506	79-14-1, 35249-89-9	Hydroxyacetic acid (Glycolic acid)	crosslinker	US 4524829, US 4657081	−1.07	1.00×10^{6}	8.54×10^{-8}	2		-2.1 to -0.9
855	6	49	0.29	1.9	68-11-1	Thioglycolic acid	complexing agent	US 5669447				17		0.2
654	0	n.s.			5421-46-5	Ammonium mercaptoacetate			0.03	2.56×10^{5}	1.94×10^{-8}			
0	1	n.s.		0	298-12-4	Glyoxylic acid			−1.4	1.00×10^{6}	2.98×10^{-9}	hours to days		-0.8
2321	2	45	0.27	7.4	2836-32-0	Sodium glycolate	complexing agent		−1.07	1.00×10^{6}	8.54×10^{-8}	hours to days		-3.1
242	4	48 (CAS 50-21-5)	0.29	1.3	10326-41-7, 50-21-5, 79-33-4	Lactic acid	crosslinker	4524829	−0.65	1.00×10^{6}	1.13×10^{-7}	13		-0.7
124	0	n.s.		0.35	515-98-0	Ammonium Lactate			−0.65	1.00×10^{6}	1.13×10^{-7}	days		-1.8
130	0	n.s.		0.396	867-56-1, 72-17-3	Sodium Lactate			−0.65	1.00×10^{6}	1.13×10^{-7}	days		-0.7, -2.9 (?)
0	1	n.s.		0	54-21-7	Sodium salicylate			2.24	3808	1.42×10^{-8}	days to weeks		-0.5
4211	**14**		**7.7**	**11.8**		**fatty acids**								
281	0	n.s.		1.6	112-80-1	Oleic Acid			7.73	0.01151	4.48×10^{-5}	0.7		4.4
281	0	n.s.		1.6	143-18-0	Potassium Oleate			7.73	0.01151	4.48×10^{-5}	days		2.3
106	5	378 (CAS 8002-09-3)	2.23	0.92	8002-09-3, 2228-95-7	Pine oil	corrosion inhibitor					days to weeks		2
3520	4	923	5.44	7	61790-12-3	Tall oil acids	corrosion inhibitor					24		4.4
0	0			0.71	68188-40-9	Fatty acids, tall oil reaction products w/acetophenone, formaldehyde & thiourea						days to weeks		4.9
23	0				9-89-2	Ethoxylated oleic acid								
0	2				*	Tallow soap								
0	2	n.s.			68608-68-4	Sodium cocaminopropionate	surfactant	US 6875728						

0	1	n.s.			*	Fatty acids			4.49 - 4.71	0.8126 - 1.254	6.27×10^{-8}			
73	**0**		**0.02**	**0.26**		**amino acids**								
7	0	4	0.02	0.014	70161-44-3	Glycine^ N-(Hydroxymethyl)-^ Monosodium Salt			−3.41	7.82×10^{5}	1.80×10^{-12}	hours to days		-3.7
57	0	n.s.		0.16	56-86-0	L-Glutamic acid			−3.83	9.42×10^{5}	1.47×10^{-14}	hours to days		-1.9
9	0			0.088	17593-73-6	Iminodiacetate disodium salt	complexing agent/iron control					days to weeks		0.2
						unspecified								
0	5	n.s.			*	Organic acids, unspecified								
0	1	n.s.			*	Organic salt								
23214	**82**		**39.7**	**34.4**		**polycarboxylic acids**								
677	8	73	0.43	1.4	110-17-8	Fumaric acid	pH control, complexing agent	US 4784694 (12), US 4477360 (8)	0.05	1.04×10^{5}	1.35×10^{-12}	15		0.4
511	6	40	0.24	0.8	124-04-9	Adipic acid	pH control (gel formation, friction reduction)	US 4477360	0.23	1.67×10^{5}	9.53×10^{-12}	4		0.2
0	1	n.s.			*	Dicarboxylic acid								
0	0			0.002	88-99-3	Phthalic acid						17		0.6
0	2	n.s.		0.004	85-44-9	Phthalic anhydride	pH control, diverting agent	US 8387696	2.07	3326	6.35×10^{-6}	2.00E-03	Y	1.4
0	1			0	6132-04-31	1,2,3-propanetricarboxylic acid, 2-hydroxy-, trisodium salt, dihydrate	complexing agent					hours to days		-1.2
13392	29	4.832	28.48	23.4	77-92-9	Citric acid (2-hydroxy-1,2,3 propanetricarboxylic acid)	complexing agent, pH control	US 4784694	−1.67	1.00×10^{6}	8.33×10^{-18}	0.4		-1.2
20		7 (CAS 3012-65-5)	0.04	0.106	3012-65-5, 7632-50-0	Ammonium Citrate			−1.67	1.00×10^{6}	8.33×10^{-18}	days		-2.3 to -3.2
222	3	21 (CAS 93858-78-7), 42 (CAS 37971-36-1)	0.37	0.46	37971-36-1, 93858-78-7	2-phosphonobutane-1,2,4-tricarboxylic acid (+salt)	scale inhibitor	US 4784774	−1.66	1.00×10^{6}	1.17×10^{-26}	hours to days		-0.7 (salt - 2.8)
0	0			0.002	10543-57-4	Tetraacetylethylenediamine						days to weeks		-0.4
0	1	n.s.		0	139-89-9	Hydroxyethylethylenediaminetriacetic acid, trisodium salt	complexing agent	US 6267979 B1,	−4.09	4.31×10^{5}	3.81×10^{-24}	days		-6.7
3441	23	796 (CAS 5064-31-3), 163 (CAS 18662-53-8)	5.65	0.816	139-13-9, 18662-53-8, 5064-31-3	Nitrilotriacetic acid (sodium salts)	complexing agent	US 6267979 B1, US 4784694	−3.81	7.39×10^{5}	1.19×10^{-16}	17		-5.5 to -2
4268	6	673 (CAS 64-02-8), 45 (CAS 150-38-9), 44 (CAS 139-33-3)	4.5	5.9	139-33-3, 6381-92-6, *, 60-00-4, 150-38-9, 19019-43-3, 64-02-8	EDTA (ethylenediamine tetra acetic acid + sodium salts)	complexing agent, scale inhibitor	US 6267979 B1, (US 4784694)				hours to days		-5.8 to -7.2
341	1			1.5	38011-25-5	Disodium ethylenediaminediacetate						hours to days		-2.6
342	1	1	0.01		19019-43-3	Trisodium ethylenediaminetriacetate								
0	0			0.01	140-01-2	Glycine, N,N-bis[2-[bis(carboxymethyl)amino]ethyl]-,sodium salt (1:5)								
						Carboxylic Acid Esters (Table 5 in the Manuscript)								
1056	**25**		**0.38**	**2.1**		**ester - alkyl ester**								
130	4	n.s.		0.35	141-78-6	Ethyl acetate	solvent		0.86	2.99×10^{4}	2.33×10^{-4}	4	Y	1.3

0	1	n.s.		0	141-97-9	Ethyl acetoacetate	solvent		−0.2	5.62×10^{4}	1.57×10^{-7}	days		1.2
41	1	24	0.14	0.028	1119-40-0	Dimethyl glutarate			0.9	2.02×10^{4}	7.36×10^{-7}	5		1.1
15	0	3	0.02	0.028	106-65-0	Succinic acid, dimethyl ester			0.4	3.96×10^{4}	5.54×10^{-7}	0.7		1
15	0	3	0.02	0.028	627-93-0	Adipic acid, dimethyl ester			1.39	7749	9.77×10^{-7}	5		1.4
418	4	34	0.20	0.58	138-22-7	Butyl lactate	solvent	US 7334635B2	0.8	5.30×10^{4}	8.49×10^{-5}	17		0.9
0	0				9004-99-3	Polyoxyethylene stearate						days to weeks		3.5
0	1	n.s.		0	77-93-0	Triethyl citrate			0.33	2.82×10^{4}	6.39×10^{-10}	days		0.6
352	1	n.s.		0.67	77-89-4	Acetyltriethyl citrate	solvent		1.34	688.2	6.91×10^{-11}	days		1.5
22		n.s.		0.058	82469-79-2	n-Butyryl tri-n-hexyl citrate	breaker		8.21	5.56×10^{-5}	3.65×10^{-9}	hours to days		5.3
62	6	n.s.		0.39	119-36-8	Methyl salicylate			2.6	1875	4.55×10^{-6}	4		2.4
0	3	n.s.			*	Alkyl esters								
1	0	n.s.			13533-05-6	Diethyleneglycol acrylate			−0.52	3.99×10^{5}	6.98×10^{-11}			
0	3	n.s.		0.004	117-81-7	Di (2-ethylhexyl) phthalate	diverting agent		8.39	0.001132	1.18×10^{-5}	389	Y	5
0	1				*	Plasticizer								
1469	**3**		**0.08**	**3.7**		**ester - cyclic ester**								
1469	2	13	0.08	3.7	108-32-7	Propylene carbonate (1,3-dioxolan-2-one, methyl-)	solvent	US 7334635B2	0.08	2.58×10^{5}	3.63×10^{-4}	4		0.5
0	1	n.s.		0	4511-42-6	L-Dilactide		US 20120000708 A1	1.65	3165	1.22×10^{-5}	days		1.7
8736	**8**		**3.9**	**23.1**		**ester - fatty acid ester**								
7393	1	627	3.70	20.7	1338-43-8	Sorbitan monooleate	surfactant, friction reducer	US 20120000708 A1	5.89	0.01914	1.42×10^{-12}	20		3.2
282	0	n.s.		0.64	26266-58-0	Sorbitan Trioleate			22.56	1.12×10^{-19}	4.02×10^{-11}	hours to days		21
391	0	12	0.07		61723-83-9	Sorbitol Tetraoleate								
153	0	9	0.05	0.99	1338-41-6	Sorbitan stearate			6.1	0.01218	1.61×10^{-12}	14		3.3
377	1				67701-32-0, *	Fatty acid ester								
1	0	1	0.01		68334-28-1	HYDROGENATED VEGETABLE OILS								
6	0	4	0.02	0.008	8001-31-8	Coconut oil (Ventura)	surfactant					hours to days		9.7
1	0	n.s.		0.004	120962-03-0	Canola Oil						days		13
0	0			0.1	67784-80-9	Soybean oil, methyl esters						days		4.6
0	6				*	Essential oils								
9	0	4	0.02		68607-07-8	Complex Ester								
103	0	11	0.06	0.7	8001-79-4	Castor Oil						hours to days		10
20	0	n.s.			8002-26-4	Tall Oil								
10209	**11**		**1.44**	**26.08**		**ester - alkoxylated**								
2181		n.s.		3.9	68410-62-8	Naphthenic acid ethoxylate			3.41	112.5	3.62×10^{-8}	days to weeks		1.3
310	4	26	0.15	0.34	112-15-2	Di (ethylene glycol) ethyl ether acetate			0.32	3.09×10^{4}	5.62×10^{-8}	5		0.9
221	0	17	0.10	1.4	9005-64-5	Polyethylene glycol sorbitan monolaurate						24		-1.7
723	0	151	0.89	0.93	9005-67-8	Poly(oxyethylene) sorbitol monostearate						weeks		-0.1
5077	0	9	0.05	12.6	9005-65-6	Sorbitan monooleate polyoxyethylene derivative						71		-0.2
0	1	n.s.			*	Ethoxylated sorbitol esters	surfactant, friction reducer							
32	1	n.s.			61790-90-7	Fatty acid, tall oil, hexaesters with sorbitol, ethoxylated	surfactant, friction reducer							
331	1	n.s.		1.8	61791-12-6	Polyoxyethylene castor oil	surfactant, friction reducer	US 20120000708 A1				days to weeks		1.3
28	0				90049-80-2	Polyoxyethylene (2) oleyl ether	surfactant							

419	0	29	0.17	2.3	9004-96-0	Polyethelene glycol monooleate						days to weeks		3.4
153	0	9	0.05	0.99	68308-89-4	Fatty acids, C18-unsatd., dimers, ethoxylated propoxylated						days to weeks		6.6
2	0				61791-00-2	Fatty acids, tall-oil, ethoxylated								
226	0	3	0.02		65071-95-6	Ethoxylated Tall Oil								
377	2				*, 70142-34-6	Oxyalkylated fatty acid = Fatty Acid Oxyalkylate	surfactant, friction reducer	US 20120000708 A1						
129	1			1.82	*, 61791-29-5, 61791-08-0	Ethoxylated fatty acid ester = Ethoxylated Fatty Acid	surfactant, friction reducer					days to weeks		-0.7 to 1.9
0	1				" 9005-02-1"	Polyethylene glycol ester with tall oil fatty acid	surfactant, friction reducer							
						Amides (Table 5 in the Manuscript)								
14136	**36**		**15.9**	**24.9**		**Amides (Inorganic and Short- & Long-chain Alkyl)**								
164	9	7	0.04	0.15	62-56-6	Thiourea	corrosion inhibitor, complexing agent	US 4784694	−1.31	5.54×10^{5}	1.58×10^{-7}	19		0.6
	1	n.s.		0.002	109-46-6	n,n-dibutylthiourea			2.57	2287	4.17×10^{-6}	hours to days		2.7
0	1			0.002	13547-17-6	N,N"-methylenebis(urea)						days to weeks		-0.8
606	5	370	2.18	1.4	75-12-7	Formamide	solvent, corrosion inhibitor	US 4739834				days		-0.1
4705	5	1.892	11.15	9.1	68-12-2	Dimethyl formamide	solvent, corrosion inhibitor	US 7334635B2				238	Y	0.1
658	2	88	0.52	3.2	79-06-1	Acrylamide						41	Y	0.6
909	6	249	1.47		5329-14-6	Sulfamic acid (amidosulfonic acid)	friction reducer							
151		16	0.09		1004542-84-0	Sulfamic acid, N-Bromo, Sodium Salt	scale inhibitor?							
0	4	n.s.		0	4862-18-4	Nitrilotriacetamide			−4.75	1.00×10^{6}	1.61×10^{-18}	days		-1.8
0	1	n.s.		0	110-26-9	n,n'-Methylenebisacrylamide	crosslinker	US 6169058 B1	−1.52	7.01×10^{4}	1.14×10^{-9}	days		0
1274	1	75	0.44	4.6	68603-42-9	Coconut fatty acid diethanolamide (Cocamide Diethanolamine Salt)	surfactant					23		1.7
4933	1	n.s.		5.8	68155-20-4, 68092-28-4	Tall oil acid diethanolamide; Tall oil, compound with diethanolamine	surfactant					days		2.3 to 3.2
16	0			0.32	93-83-4	Oleamide DEA						days		3.2
137	0	n.s.		0.29	70851-08-0	Fatty Amide Derivative						days to weeks		-0.3
583	0	n.s.			68442-77-3	Modified Amide								
245	**2**		**0.67**	**0.59**		**cyclic amides**								
101	1	n.s.		0.32	872-50-4	n-Methylpyrrolidone	solvent, surfactant	temperature resistant solvent for polymers	−0.11	2.48×10^{5}	3.16×10^{-8}	2		0.7
144	1	114	0.67	0.27	2687-96-9	n-dodecyl-2-pyrrolidone	solvent, surfactant		5.3	5.862	7.12×10^{-7}	days		3.2
572	**13**		**0.49**	**0.76**		**quaternary amidoamines**								
245	1	55	0.32	0.63	68139-30-0	n-cocoamidopropyl-n,n-dimethyl-n-2-hydroxypropylsulfobetaine	surfactant, corrosion inhibitor	US 20120000708 A1				days		-0.9
0	1	n.s.		0	*	Hydroxysultaine			7.72	0.002229	2.49×10^{-12}	days		-0.3

49	3	3 (CAS 61789-40-0)	0.02	0.08	70851-07-9, 61789-40-0	Cocoamidopropyl betaine	surfactant	US 20120000708 A1				6 to 10	0.4
7	0	n.s.		0.018	73772-46-0	CAPRYLAMIDOPROPYL BETAINE						hours to days	-0.7
7	3	3	0.02	0.008	149879-98-1	Erucic amidopropyl dimethyl betaine		US 20120000708 A1				days	2.7
138	1	21	0.12	0.022	68140-01-2	Cocomidopropyl dimethylamine	surfactant					days to weeks	3.3
0	2			0	143106-84-7,*	Complex substituted keto-amine	surfactant					weeks to months	4
0	1	n.s.			*	Fatty amine carboxylates	surfactant	US 20120000708 A1	-4.79 to - 3.86	2.28 x 10^{5} to 1 x 10^{6}	1.17 × 10^{-23} to 1.10 x 10^{-16}		
125	1				68990-47-6, *	(Modified) Amidoamine	surfactant						
1	0	1	0.01	0.002	68604-75-1	Fatty acids, coco, reaction products with diethylenetriamine and soya fatty acids, ethoxylated, chlo						weeks	4.5
						Organophosphorous Compounds (Table 5 in the Manuscript)							
						phosphine oxides							
2	0				1067-12-5	Phosphinylidynetrimethanol							
1496	**20**		**1.07**	**2.83**		**organo phosphonates**							
232	1	n.s.		1.2	35657-77-3, 34690-00-1	Bishexamethylenetriamine penta methylene phosphonic acid	complexing agent, scale inhibitor	US 6767868 B2	−5.79	1.00 × 10^{6}	--	months	-4
68	1	47	0.28	0.16	15827-60-8	Diethylene triaminepenta (methylene phosphonic acid)	complexing agent	US 6767868 B2	−9.72	1.00 × 10^{6}	--	months	-4.5
1122	3	133 (CAS 6419-19-8)	0.78	1.41	6419-19-8, 2235-43-0	Amino trimethylene phosphonic acid + salts (e.g., Phosphonic acid, [nitrilotris(methylene)]tris-, pentasodium salt)	complexing agent, scale inhibitor	US 6767868 B2	−5.45	1.00 × 10^{6}	1.65 × 10^{-34}	weeks	-1, -6.5
0	0			0.004	27794-93-0	Aminotrimethylenephosphonic acid potassium salt						weeks	-3.7
0	1	n.s.		0	3794-83-0	Tetrasodium 1-hydroxyethylidene-1,1-diphosphonic acid *	complexing agent, scale inhibitor	US 6767868 B2	−0.01	1.34 × 10^{5}	9.79 × 10^{-26}	days to weeks	-6.3
0	1	n.s.		0	29712-30-9	Phosphonic acid (dimethlamino(methylene))	complexing agent	US 6767868 B2	−1.9	1.00 × 10^{6}	1.00 × 10^{-24}	weeks	-0.1
0	3	n.s.			*	Amine phosphonate	complexing agent						
0	1	n.s.			*	Amino methylene phosphonic acid salt	complexing agent	US 6767868 B2					
8	0	n.s.			68132-59-2	Phosphonomethylated polyamine	scale inhibitor						
0	1	n.s.			*	Salt of phosphono-methylated diamine	complexing agent						
2	0				68920-95-6	Amines, polyethylenepoly-, ethoxylated, phosphonomethylated, compounds with alkylpyridine derivative							
64	8	2 (CAS 68649-44-5)	0.01	0.054	*,*,*, 68649-44-5, 70714-66-8	Organophosphonate, Organic phosphonates (and salts)						months	-6.2
												days to weeks	-0.4
2811	**26**		**4.7**	**4.2**		**organo phosphate - esters**							
1634	1	742	4.37	3	78-40-0	Triethyl phosphate	corrosion inhibitor, solvent	US 4739834	0.87	1.12 × 10^{4}	5.83 × 10^{-7}	days	1.5

0	3	n.s.		0	68412-60-2	Phosphoric acid, mixed decyl, octyl and ethyl esters						hours to days		5.3
0	0			0.002	39322-78-6	Phosphoric acid, dodecyl ester, potassium salt						days to weeks		1.9
0	4	n.s.			*	Alkyl (ortho)phosphate ester	corrosion inhibitor, solvent, viscosity control, delayed acid	US 8387696B2, US 6169058						
127	1	5	0.03		68131-72-6	Polyphosphoric acid, esters with triethanolamine, sodium salts	scale inhibitor							
3	0	n.s.		0.022	68171-29-9	Triethanolamine triphosphate ester, sodium salt			−3.13	1.00×10^{6}	3.08×10^{-36}	weeks		-2.5
757	3	n.s.			68131-71-5	Triethanolamine polyphosphate ester	scale inhibitor							
213	0	n.s.		0.3	8002-43-5	1,2-Dimyristoyl-sn-glycero-3-phosphocholine						days to weeks		8.2
0	1	n.s.			68412-53-3	Phosphate esters of alkyl phenyl ethoxylate								
0	2	34	0.20	0.89	9046-01-9	Ethoxylated tridecyl alcohol phosphate	corrosion inhibitor					days to weeks		2.7
0	1	n.s.			51811-79-1	Polyethylene glycol monononylphenyl ether phosphate; Poly(oxy-1,2-ethanediyl),a-(nonylphenyl)-w-hydroxy-, phosphate								
43	1	3	0.02		68649-29-6	Oxirane, methyl-, polymer with oxirane, mono-C10-16-alkyl ethers, phosphates	pH control							
6	0	4	0.02		68130-47-2	POLY(OXY-1,2-ETHANEDIYL), .ALPHA.-HYDRO-.OMEGA.-HYDROXY- , MONO-C8-10-ALKYL ETHERS, PHOSPHATES								
28	0	2	0.01		68585-36-4	Phophate Esters of Alcohol Ethoxylate								
0	9	n.s.			*	Phosphate ester (salts)	delayed acid	US 8387696						
						Organosulfonates and -sulfates (Table 5 in the Manuscript)								
7840	**62**		**4.8**	**21.3**		**organosulfonates**								
10	0	n.s.		0.02	68584-25-8	Benzenesulfonic Acid, Triethanolamine			5.2	0.255	8.32×10^{-8}	days to weeks		2.4
3435	24	505 (CAS 27176-87-0), 3 (CAS 90218-35-2), 6 (CAS 42615-29-2)	3.04	9.558	27176-87-0, 42615-29-2, 68648-81-7, 90218-35-2, 26264-06-2	Dodecylbenzene sulfonic acid (salts)	surfactant	US 20080108522A1, US 20120000708 A1, US 6436154				17		3.4 to 9.1
0	0			0.002	25155-30-0	Sodium dodecylbenzenesulfonate	surfactant					39		2
0	0			0.068	128824-30-6	1-Dodecanesulfonic acid, hydroxy-, sodium salt						days		0.2
0	0			0.068	30965-85-6	Dodecene-1-sulfonic acid, sodium salt						days		1.5
725	1	162	0.95	1.5	26836-07-7	Dodecylbenzenesulfonic acid, monoethanolamine salt	surfactant, scale inhibitor	US 6436154	4.71	0.8126	6.27×10^{-8}	days to weeks		3.6
6	1	n.s.		0.006	12068-08-5	Dodecylbenzenesulphonic acid, morpholine salt	surfactant, scale inhibitor	US 6436154	4.71	0.8126	6.27×10^{-8}	days to weeks		4
12	1	7	0.04		42504-46-1	Dodecylbenzenesulfonate isopropanolamine	surfactant	US 6875728	7.94	0.001015	1.34×10^{-1}			
0	0			0.34	26264-05-1	Dodecylbenzenesulfonate isopropanolamine	surfactant	US 6875728				16		4.5

178	1	n.s.		0.3	68584-27-0	Benzenesulfonic acid, C10-16-alkyl derivs., potassium salts	surfactant	US 6035936	5.2	0.255	8.32×10^{-8}	days to weeks	2.6
63	3	47	0.28	0.024	1300-72-7	Sodium xylene sulfonate	surfactant	US 6468945; US 20120000708 A1	−0.07	5.89×10^{4}	3.06×10^{-9}	days to weeks	-0.1
5	0	5	0.03	0.002	28348-53-0	Sodium Cumene Sulfonate			0.29	2.46×10^{4}	4.89×10^{-9}	days to weeks	1.2
473	3	6	0.04	1.2	68584-22-5, *	Alkyl benzenesulfonic acid	surfactant	US6035936				1	3
0	0			0.004	68411-30-3	Sodium alkylbenzene sulfonate	surfactant					8	2
50	0	n.s.		0.91	68081-81-2	Linear alkyl benzene sulfonate			4.22	2.584	4.72×10^{-8}	days to weeks	2
0	2	n.s.		0	28757-00-8	Diisopropylnaphthalenesulfonic acid	surfactant		2.92	43.36	9.29×10^{-10}	days to weeks	2.5
0	1	n.s.			99811-86-6	Naphthalenesulphonic acid, bis (1-methylethyl)-methyl derivatives	surfactant		4.02	3.45	1.13×10^{-9}		
2	1	n.s.		0.004	68425-61-6	Bis(1-methylethyl)naphthalenesulfonic acid, cyclohexylamine salt	surfactant		2.92	43.36	9.29×10^{-10}	weeks	3.9
681	0	n.s.		1.3	119345-04-9	Sodium Aryl Sulfonate						82	5.3
0	3				*, *, 27176-93-9	Alkyaryl sulfonate	surfactant	US 20120000708 A1					
409	0	n.s.		1.2	40139-72-8	Diethylenetriamine Alkylbenzene Sulfate			4.78	0.7032	6.27×10^{-8}	days to weeks	3.1
0	1				255043-08-04	Alkyl aryl amine sulfonate	surfactant	US 20120000708 A1					
411	0	n.s.		1.2	119345-03-8	Benzene, 1,1'-oxybis-, tetrapropylene derivs., sulfonated, sodium salts						22	6.8
23	0	n.s.			147732-60-3	benzene, 1,1-oxybis-, sec-hexyl derivatives, sulfonated sodium salts	surfactant						
4	1	n.s.			25704-18-1	Poly(sodium-p-styrenesulfonate)	surfactant, gel forming agent	US 20120000708 A1; 4018286					
181	1	n.s.		1	577-11-7	Dioctyl sodium sulfosuccinate	surfactant	US 20120000708 A1	6.1	0.001227	5.00×10^{-12}	25	3
403	0	n.s.		1.1	2673-22-5	Diester of Sulfosuccinic Acid Sodium Salt			11.15	7.46×10^{-9}	8.51×10^{-11}	days	5.8
0	4	n.s.		0.04	2373-38-8	Butanedioic acid (Butanedioic Acid,Sulfo-,1,4-Bis(1,3-Dimethylbutyl))	surfactant		3.98	0.1733	1.61×10^{-12}	110	1.8
0	1	n.s.		0	28519-02-0	Sodium alkyl diphenyl oxide sulfonate	surfactant	US 20120000708 A1	5.05	0.0353	6.40×10^{-16}	days to weeks	2.8
0	1	n.s.			*	Modified lignosulfonate	surfactant	US 20120000708 A1	−6.73	1.00×10^{6}	5.29×10^{-42}		
342	4	60	0.35	0.52	68439-57-6	Sodium (C14-16) olefin sulfonate	surfactant	US 20120000708 A1	4.36	2.651	4.95×10^{-7}	days	2.2
0	5			0	*,*,*,*, 61789-85-3	Sulfonates (sulfonate acids, olefinic sulfonate)	surfactant	US 20120000708 A1				days to weeks	6.1
15	3	3	0.02	0.028	80-08-0	4,4'-diaminodiphenyl sulfone, 4,4'-Sulfonyldianiline	crosslinker (hardener)	US 5331068	0.77	3589	3.11×10^{-14}	days to weeks	1.4
226	0	n.s.		0.004	119616-38-5	D-Biotin ,USP (Sodium 2,5-dioxo-1-({5-[(3aS,4S,6aR)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl]pentanoyl}oxy)-3-pyrrolidinesulfonate)						days to weeks	-1
186	0	n.s.		0.88	870-72-4	Sodium Sulfonate			−3.85	1.00×10^{6}	4.60×10^{-13}	days	-2.8
0	0	n.s.		0.008	15214-89-8	1-Propanesulfonic acid, 2-methyl-2- [(1-oxo-2	monomer					289	-0.3
452	**10**		**0.92**	**1.17**		**alkyl sulfates**							
37	0	37	0.22		308074-31-9	Quaternary ammonium compounds (2-ethylhexyl) hydrogenated tallow alkyl)dimethyl, Mesulfates	corrosion inhibitor?						

119	0			0.21	2207-98-9	1-hexyl sulfate						days		0.4
80	1	62	0.37	0.35	126-92-1	Sodium 2-ethylhexyl sulfate	surfactant		0.38	$1.82 \times 10_{4}$	$5.91 \times 10_{-8}$	days		0.9
119	4	n.s.		0.21, 0.26	142-87-0, 142-31-4	Sulfuric acid, alkyl ester, sodium salt	surfactant		0.46 - 1.44	1617 to 1.58 × 104	$5.91 \times 10-8$ to $1.04 \times 10_{-7}$	days		0.9, 1.5
93	2	55	0.32		32612-48-9	Dodecyl alcohol ammonium sulfate	surfactant							
1	0			0.61	68081-98-1	Primary C14-15 Alcohol Sulfate	surfactant					days to weeks		2.8
3	3	2 (CAS 151-21-3)	0.01	0.002	68891-38-3, 151-21-3	Sodium lauryl-ether sulfate	surfactant	US 20120000708 A1	2.42	163.7	$1.84 \times 10_{-7}$	8		2
385	**16**		**0.19**	**0.38**		**alkoxylated sulfates**								
45	2	14	0.08	0.078	25446-78-0	Ethanol, 2-2-2-(tridecyloxy)ethoxyethoxy-, hydrogen sulfate, sodium salt		US 20120000708 A1	2.09	42	$9.15 \times 10_{-13}$	days to weeks		1.6
46	4	13	0.08		68891-29-2	Ammonium C8-C10 alkyl ether sulfate	surfactant	US 20120000708 A1						
135	4	2	0.01	0.3	68187-17-7	Ammonium C6-C10 alcohol ethoxysulfate	surfactant	US 6875728	0.46	$1.58 \times 10_{4}$	$5.91 \times 10_{-8}$	days		1.9
3	3	n.s.			63428-86-4	Polyethylene glycol hexyl ether sulfate, ammonium salt; [Poly(oxy-1,2-ethanediyl), alpha-sulfo-omega-(hexyloxy)-, ammonium salt]	surfactant							
0	1	n.s.			*	Ammonium salt of ethoxylated alcohol sulfate	surfactant							
6	1	4	0.02		68037-05-8	Ammonium alcohol ether sulfate	surfactant							
0	1	n.s.			*	Alkylethoxyammonium sulfates	surfactant							
150	0	n.s.			68585-34-2	Alcohol Ether Sulfate	surfactant							
						unspecified/other								
0	1	n.s.			*	Sulfate								
0	2	n.s.			*	Organic sulfur compound			−0.88	$1.00 \times 10_{6}$	$6.91 \times 10_{-11}$			
0	1	n.s.			*	Sulfur compound			3.29	17.24	1.71			
0	1				61790-29-8	a-organic surfactants								
						Electrophilic Compounds (Table 6 in the Manuscript)								
25753	**60**		**41.3**	**52.5**		**Aldehydes and Ketones**								
3625	12	368 (CAS 50-00-0), 1 (CAS 30525-89-4)	2.18	9	50-00-0, 30525-89-4	Formaldehyde, Paraformaldehyde	gel forming agent, biocide	US 5402846; US 20100190666A1	0.35	$5.70 \times 10_{4}$	$9.29 \times 10_{-5}$	14	Y	0.9
366	1	n.s.		0.91	75-07-0	Acetaldehyde	gel forming agent	US 5402846	−0.17	$2.57 \times 10_{5}$	$6.78 \times 10_{-5}$	4	Y	0.5
320	3	22	0.13	0.26	107-22-2	Glyoxal	gel forming agent, crosslinker	US 5402846	−1.66	$1.00 \times 10_{6}$	$3.70 \times 10_{-7}$	days		-0.5
44	1	n.s.		0	107-89-1	Aldol	solvent, corrosion inhibitor	US 4739834	−0.72	$1.00 \times 10_{6}$	$4.37 \times 10_{-9}$	days		-0.1
44	1	n.s.			123-73-9	Crotonaldehyde	corrosion inhibitor	US 5402846	0.6	$4.15 \times 10_{4}$	$5.61 \times 10_{-5}$			
1	1			0	98-01-1	Furfural						6	Y	0.9

17196	20	5.635	33.21	33.3	111-30-8	Glutaraldehyde	biocide	US20100190666 A1	−0.18	1.67×10^{5}	1.10×10^{-7}	0.3		0.4
2280	5	874	5.15	4.8	104-55-2	Cinnamaldehyde (3-phenyl-2-propenal)	corrosion inhibitor		1.82	2150	1.60×10^{-6}	4		1.7
0	6	n.s.			*	Aldehydes								
249	3	41	0.24	1.4	67-64-1	Acetone	solvent		−0.24	2.20×10^{5}	4.96×10^{-5}	7	Y	1
1531	0	n.s.		2.6	108-10-1	METHYL ISOBUTYL KETONE			1.16	8888	1.16×10^{-4}	24	Y	1.8
39	0	27	0.16	0.03	108-83-8	Diisobutyl ketone			2.56	528.8	2.71×10^{-4}	7		2.5
39	0	27	0.16	0.03	19549-80-5	2-Heptanone, 4,6-dimethyl			2.56	528.8	2.71×10^{-4}	days to weeks		2.5
0	2	n.s.		0	78-94-4	Methyl vinyl ketone	monomer		0.41	6.06×10^{4}	2.61×10^{-5}	days to weeks		1.3
0	1	n.s.		0	108-94-1	Cyclohexanone			1.13	2.41×10^{4}	5.11×10^{-5}	6	Y	1.6
13	1	6	0.04	0.15	98-86-2	Acetophenone	solvent, corrosion inhibitor		1.67	4484	9.81×10^{-6}	32	Y	2
6	2	2	0.01		224635-63-6	Aromatic ketones (Reaction product of acetophenone, formaldehyde, cyclohexylamine, methanol and acetic acid)								
0	1	n.s.		0	96-29-7	2-butanone oxime			1.69	3.66×10^{4}	1.04×10^{-5}	days to weeks		0.5
7383	**27**		**8.3**	**15.7**		**N-heterocycles**								
751	1	9	0.05	2.4	2634-33-5	1,2-benzisothiazol-3	biocide	US 5024276	0.64	2.14×10^{4}	6.92×10^{-9}	days to weeks		1
1412	4	90	0.53	1.2	2682-20-4	2-methyl-4-isothiazolin-3-one	biocide	US 5024276, US20100190666 A1 http://www.dow.com/assets/attachments/business/pcare/kathon_for_personal_care/kathon_cg/tds/kathon_cg.pdf	−0.83	5.37×10^{5}	4.96×10^{-8}	0.2		0.4
1410	5	89	0.52	1.2	26172-55-4	5-chloro-2-methyl-4-isothiazolin-3-one	biocide	US 5024276, US20100190666 A1 http://www.dow.com/assets/attachments/business/pcare/kathon_for_personal_care/kathon_cg/tds/kathon_cg.pdf	−0.34	1.49×10^{5}	3.57×10^{-8}	0.2		0.7
12	0	n.s.		0.53	55965-84-9	Mixture, contaning 5-Chloro-2-methyl-2H-isothiazol-3-one and 2-methyl-2H-isothiazol-3-one (3:1)	biocide					days to weeks		0.4
761	0	310	1.83	1.9	51200-87-4	4,4-Dimethyloxazolidine	biocide		−0.08	1.00×10^{6}	3.02×10^{-6}	days to weeks		0.7
761	0	310	1.83	1.9	75673-43-7	3,4,4-Trimethyloxazolodine	biocide		0.13	8.22×10^{5}	6.63×10^{-6}	weeks		0.8
2268	13	586	3.45	6.1	533-74-4	Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione (Dazomet)	biocide	US20100190666 A1, US 20120157356	0.94	1.94×10^{4}	2.84×10^{-3}	0.1		2.4
2	0	2	0.01	0.006	21564-17-0	2-(Thiocyanomethylthio)benzothiazole	biocide		3.12	41.67	6.49×10^{-12}	1		3.1
0	4			0.43	"4719-04-4"	Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine (Actane)	biocide					weeks		-2.7

6	0	6	0.04	0.014	4080-31-3	3,5,7-Triaza-1-azoniatricyclo3.3.1.13,7 decane,1-(3-chloro-2-propenyl)-, chloride (CTAC)	biocide		−5.92	1.00×10^{6}	1.76×10^{-8}	1		0.6
0	0			0.042	57116-45-7	Pentaerythritol tris[3-(1-aziridinyl)propionate]						weeks		-0.6
12051	**33**		**26.2**	**24.5**		**nitriles**								
9181	27	3.668	21.62	18.3	10222-01-2	2,2-dibromo-3-nitrilopropionamide (DBNPA)	biocide	Patent WO2007081988 A3 http://www.epa.gov/oppsrrd1/REDs/factsheets/3056fact.pdf	1.01	2841	6.16×10^{-14}	0.2		1.8
1528	1	388	2.29	2.1	1113-55-9	2-monobromo-3-nitrilopropionamide	biocide		−0.31	3274	5.35×10^{-13}	days		1.1
0	1	n.s.		0	35691-65-7	1,2-dibromo-2,4-dicyanobutane (**iupac**: 2-bromo-2-(bromomethyl)-pentanedinitrile)	biocide		1.63	424	3.94×10^{-10}	0.9		2.6
0	0	n.s.		0.078	73003-80-2	2,2-Dibromopropanediamide			0.37	1.00×10^{4}	3.58×10^{-14}	days		1.1
0	3	n.s.		0	7327-60-8	Nitrilotriacetonitrile			−1.39	1.00×10^{6}	2.61×10^{-15}	weeks		0.9
1342	1	382	2.25	4	3252-43-5	Dibromoacetonitrile	biocide		0.47	9600	4.06×10^{-7}	2		1.6
0	0	0		0.008	107-13-1	Acrylonitrile	monomer					37		1.5
						quarternary organic phosphonium salt								
5408	12	1.645	9.69	9.5	55566-30-8	Tetrakis (hydroxymethyl) phosphonium sulfate (THPS)	biocide	US20100190666 A1	−5.03	1.00×10^{6}	9.17×10^{-13}	23		-11
2983	**4**		**4.56**	**3.90**		**substituted propanols**								
2220	4	463	2.73	2	52-51-7	2-bromo-2-nitropropane-1,3-diol , Bronopol	biocide	US20100190666 A1 http://www.dow.com/productsafety/pdfs/233-00698.pdf	−1.51	8.37×10^{5}	6.35×10^{-21}	days to weeks		0
0	0	0		0.002	77-49-6	2-Methyl-2-nitropropane-1,3-diol						days		-0.3
763	0	310	1.83	1.9	124-68-5	2-Amino-2-methyl-1-propanol	biocide		−0.74	1.00×10^{6}	6.48×10^{-10}	38		0.1
						non-specified / others								
2	0	2	0.01	0.006	6317-18-6	Methylene bis(thiocyanates)	biocide, corrosion inhibitor		0.62	2.72×10^{4}	2.61×10^{-8}	0.1		2.1
0	4				*,*	Antifoulant, Biocide component	biocide							
695	0				56652-26-7	Formaldehyde Amine	biocide							
4	0			0.1	69-53-4	Ampicillin	biocide					days		0.8
						other nitroorganic compounds								
0	0	0	0	0.002	75-52-5	Nitromethane	solvent					184		1
3185	**9**		**7.45**	**7.40**		**other halogenated hydrocarbons**								
108	0			1.2	74-87-3	Methyl chloride						11	Y	0.8
6	0	6	0.04	0.012	75-09-2	Dichloromethane (methylene chloride)						108	Y	1.1
6	0	6	0.04	0.012	542-75-6	1,3-Dichloropropene			2.29	1994	2.45×10^{-2}	25	Y	1.8
2785	8	1.252	7.38	5.8	100-44-7	Benzyl chloride	corrosion inhibitor		2.79	1030	2.09×10^{-3}	8	Y	2
259	0	n.s.		0.37	111-44-4	Dichloroethyl ether (DCEE)			1.56	6435	1.89×10^{-4}	30		1.5
4	0	n.s.		0.006	3926-62-3	Sodium chloroacetate			0.34	1.95×10^{5}	1.93×10^{-7}	days		-1.8
0	1	n.s.		0	650-51-1	Sodium trichloroacetate			1.44	1.20×10^{4}	2.39×10^{-8}	days to weeks		-1.2
0	0	n.s.		0.002	64-69-7	Acetic acid, 2-iodo-						days		0.6
17	0				82030-84-0	Fluoroaliphatic Amine Oxide								

						Dyes (not included in a Table in the Manuscript)								
2754	**0**			**4.45**		**diazo dyes**								
1109	0	n.s.		2.3	915-67-3	2,7-Naphthalenedisulfonic acid, 3-hydroxy-4-(4-sulfor-1-naphthalenyl) azo -, trisodium salt	dye tracer		1.63	1.789	1.49×10^{-30}	5		-1.3
267	0	n.s.		0.36	6625-46-3	2,7-Naphthalenedisulfonic acid, 5-(acetylamino) -4-hydroxy-3-(2-methoxyphenyl) azo -, disodium salt	dye tracer		0.59	3.379	2.21×10^{-30}	days to weeks		0.5
266	0	n.s.		0.39	2783-94-0	2-Naphthalenesulfonic acid, 6-hydroxy-5-(4-sulfophenyl)azo-, disodium salt	dye tracer		1.4	242.7	3.26×10^{-23}	days to weeks		0.9
4	0	n.s.		0.002	3567-66-6	2,7-Naphthalenedisulfonic acid, 5-amino-4-hydroxy-3-(phenylazo)-, disodium salt	dye tracer		0.48	11.87	1.15×10^{-26}	weeks		0.3
317	0	n.s.			1934-21-0	Tartrazine / DYE-ACID YELLOW 23	dye tracer		−1.82	7.388	1.31×10^{-28}			
268	0	n.s.		0.36	3734-67-6	Food red 10 (Disodium 5-acetamido-4-hydroxy-3-(phenyldiazenyl)naphthalene-2,7-disulfonate)	dye tracer		0.51	6.157	3.73×10^{-29}	days to weeks		0.4
523	0	n.s.		0.88	6410-41-9	C.I. Pigment Red 5 (N-(5-Chloro-2,4-dimethoxyphenyl)-4-{[5-(diethylsulfamoyl)-2-methoxyphenyl]diazenyl}-3-hydroxy-2-naphthamide)	dye tracer		7.65	4.38×10^{-5}	4.36×10^{-21}	weeks		5.7
0	0	n.s.		0.16	2610-11-9	Direct Red 81	dye tracer					weeks		2.6
330	**1**		**0.06**	**0.49**		**triphenylmethane dyes**								
41	0	n.s.		0.04	18472-87-2	Acid Red 92 (Disodium 2,3,4,5-tetrachloro-6-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl)benzoate)	dye tracer		9.62	1.64×10^{-8}	6.37×10^{-21}	recalcitrant		4.4
20	0	11	0.06	0.056	129-17-9	Acid Blue 1 Mixture (Sodium 4-{[4-(diethylamino)phenyl][4-(diethyliminio)-2,5-cyclohexadien-1-ylidene]methyl}-1,3-benzenedisulfonate)	dye tracer		−1.34	50.67	1.31×10^{-26}	weeks		-2.1
266	1	n.s.		0.39	3844-45-9	Benzenemethanaminium (should be Brilliant Blue FCF = Disodium 2-[(Z)-{4-[ethyl(3-sulfonatobenzyl)amino]phenyl}{(4Z)-4-[ethyl(3-sulfonatobenzyl)iminio]-2,5-cyclohexadien-1-ylidene}methyl]benzenesulfonate)	dye tracer		−0.15	0.2205	2.25×10^{-35}	weeks to months		-1.9
3	0	n.s.		0.008	81-88-9	C.I. basic violet 010 (Rhodamine B = 9-(2-Carboxyphenyl)-6-(diethylamino)-N,N-diethyl-3H-xanthen-3-iminium chloride)	dye tracer		6.03	0.0116	--	weeks		1.2
1183	**2**		**0.77**	**2.51**		**Carbohydrates (not included in a Table in the Manuscript)**								
145	1	9	0.05	0.3	50-70-4	D-Glucitol (sorbitol)	crosslinker	US 4477360	−3.01	1.00×10^{6}	7.26×10^{-13}	hours to days		-1.6
327	1	114	0.67	0.64	57-50-1	Sucrose		US 7431087	−4.27	1.00×10^{6}	4.47×10^{-22}	days		-2.2
213	0	n.s.		0.3	5989-81-1	Lactose			−5.12	1.00×10^{6}	4.47×10^{-22}	hours to days		-3
491	0	7	0.04	1.2	8007-43-0	Sorbitan			14.32	2.31×10^{-11}	7.55×10^{-12}	days		7.5
7	0			0.066	87246-72-8	Carbohydrates						hours to days		0.9
27528	**123**		**25.07**	**45.46**		**Biopolymers (Table 1 in the Manuscript)**								
23424	53	3.586	21.13	45.2	9000-30-0, *	Guar gum, Guar gum derivative	gel forming agent	US 6454008 B1, 5460226				0.1		2.5

797	6	100	0.59		11138-66-2	Xanthan gum	gel forming agent, friction reducer	US 6454008 B1, US 4500437						
652	7	323	1.90		39346-76-4	Carboxymethyl guar gum, sodium salt	gel forming agent	US 6454008 B1						
6					51198-15-3	Guar gum, carboxymethyl ether	gel forming agent							
528	11	199	1.17		68130-15-4	Carboxymethyl hydroxypropyl guar	gel forming agent	US 6454008 B1						
4	2	2	0.01		39421-75-5	Hydroxypropyl guar gum	gel forming agent, friction reducer	US 6454008 B1, US 4500437						
0	20	n.s.			*	Polysaccharide	gel forming agent	US 6454008 B1, 5460226						
141	5	n.s.		0.26	9005-25-8	Starch	fluid loss control agent, gel forming agent	US 6016871				hours to days		1
1782	0	19	0.11		9004-32-4	Carboxymethyl cellulose	gel forming agent							
0	2				*	Polyanionic cellulose	gel forming agent	US 4018286						
4	3				9004-34-6; *	Cellulose, Cellulose derivative	gel forming agent	US 6454008 B1						
78	0	3	0.02		9004-67-5	Methylcellulose	gel forming agent							
4	1	n.s.			9004-62-0	Hydroxyethylcellulose	gel forming agent, friction reducer	US 6454008 B1, US 4500437						
0	2	n.s.			9005-81-6	Cellophane								
0	1	n.s.		0	50-99-7	Dextrose monohydrate			−2.89	1.00×10^{6}	9.72×10^{-15}	days		-1.8
0	1	n.s.			430439-54-6	Inulin, carboxymethyl ether, sodium salt								
0	3	n.s.			*	Carbohydrates								
82	6	23	0.14		9000-70-8	Collagen (Gelatin)	diverting agent							
26	0	n.s.			34345-47-6	L-Aspartic Acid, Homopolymer, Sodium Salt	scale inhibitor							
						Synthetic Polymers (Table 1 in the Manuscript)								
7238	**31**		**8.83**	**0.00**		**acrylamides/acrylates**								
195	3	40 (CAS '9003-05-8)	0.24		910644-97-2, '9003-05-8, *	Polypropenamide = Polyacrylamides	gel forming agent, friction reducer	US 4500437, US 6454008 B1, US 3938594						
22	0	1	0.01		35429-19-7	Ethanaminium,n,n,n-trimethyl-methyl-oxo, chloride, polymer with propenamide								
335	4	24	0.14		69418-26-4	Ethanaminium, n,n,n-trimethyl-2-[(1-oxo-2-propenyl)oxy]-,chloride, polymer with 2-propenamide	friction reducer							
0	1				40623-75-4	2-acrylamido-2-methylpropanesulphonic acid sodium salt polymer								
1954	1	697	4.11		25987-30-8	Copolymer of acrylamide and sodium acrylate	gel forming agent, friction reducer	US 3938594						
455	0	75	0.44		26100-47-0	Acrylamide P/W acrylic acid, ammonium	friction reducer							
644	0	173	1.02		25085-02-3	Acrylamide sodium acrylate copolymer	gel forming agent	US 6844296						
29	0				699-00-3	Poly Acrylamide - co-Acrylic Acid								
596	0	1	0.01		62649-23-4	Polyacrylamide (2-Propenamide w/ propenoic acid and sodium propenoate								
62	0	26	0.15		136793-29-8	Polymer of 2-acrylamido-2-methylpropanesulfonic acid sodium salt and methyl acrylate								

0	1	n.s.			37350-42-8	Acrylic acid/2-acrylamido-methylpropylsulfonic acid copolymer	scale inhibitor, gel forming agent, friction reducer	US 4500437						
752	0	103 (CAS 110224-99-2), 3 (CAS 129898-01-7), 21 (CAS 71050-62-9)	0.75		110224-99-2, 129898-01-7, 71050-62-9	Acrylic Acid, with (Sodium-2-acrylamido-2-methyl-1-propanesulfonate and sodium phosphinate); 2-Propenoic acid, polymer with sodium phosphinate, sodium salt	scale inhibitor		−2.19	1.00×10^{6}	5.18×10^{-15}			
213	6	197 (CAS 9003-04-7)	1.16	0	*,*,9003-04-7,*, *, 111560-38-4	Polyacrylate	gel forming agent	US 6844296				hours		0.6
3	0				27401-06-5	Polymer (2-Methylacrylic acid - octadecyl 2-methylacrylate (1:1))								
153	0	9	0.05		36089-45-9	2-Propenoic acid, 2-ethylhexyl ester, polymer with 2-hydroxyethyl 2-propenoate								
0	1	n.s.		0	818-61-1	Acrylic acid, 2-hydroxyethyl ester	friction reducer	US 4500437	−0.25	5.07×10^{5}	4.49×10^{-9}	days		0.3
21	0	14	0.08		28208-80-2	2-Propenoic acid, polymer with ethene, zinc salt								
1	0	n.s.			54076-97-0	Modified acrylate polymer								
63	7				*, 9002-98-6	Cured acrylic resin	proppant coating	US 7334635						
569	3	41 (CAS 38193-60-1)	0.24		*, 38193-60-1,*, 108388-79-0	Acrylamide (copolymer)	gel forming agent, friction reducer	US 4500437						
941	4	66 (CAS 26006-22-4), 5 (CAS 28205-96-1)	0.42		403730-32-5, *, 26006-22-4, 28205-96-1	Acrylic (co)polymer	gel forming agent, friction reducer, scale inhibitor	US 4500437						
3	0	1	0.01		25038-45-3	Anionic Copolymer of Acrylamide								
1	0				153568-80-0	Modified acrylamide copolymer								
0	0			0.002	7446-81-3	Sodium acrylate						days		-1.7
1	0				26006224647 42-47-8	Acrylic Polymers Distillates Petroleum Hydrotreated middle	gel forming agent							
225	0	n.s.			397256-50-7	Polymer containing phosphonate, sulphonate, and carboxyl functional groups, sodium salt								
1990	**11**		**0.60**	**0.02**		**other vinyl polymers**								
213	0	n.s.			113221-69-5	Maleic Anhydride Terpolymer								
150	1	n.s.			24937-78-8	Ethylene-vinyl acetate copolymer								
8	6			0	25213-24-5,*,9002-89-5, 304443-60-5	Polyvinyl alcohol/polyvinylacetate copolymer = Polyvinyl alcohol (Acetic acid ethenyl ester, polymer with ethenol) = Polyvinyl acetate, partially hydrolyzed	gel forming agent	US 7571767				hours to days		-2.8
21	0	13	0.08	0.018	9003-39-8	Polyvinylpyrrolidone						days		0.9
1574	1	78	0.46		15220-87-8	Propylene pentamer	gel forming agent		6.28	0.05601	3.92×10^{-1}			
2	0			0.006	9003-29-6	Polybutene (Isobutylene/Butene copolymer)						days to weeks		15
1	0	n.s.			68648-89-5	Ethenylbenzene polymer w/ 2-methyl-1,3-butadiene								
21	0	10	0.06		25085-34-1	Styrene acrylic copolymer								
0	3				*	Anionic copolymer								
11184	**54**		**13.33**			**phenol /formaldehyde / epoxy polymers**								
498	5	139	0.82		25068-38-6	Bisphenol A/Epichlorohydrin resin	proppant coating	US 7334635						
0	1	n.s.			28906-96-9	Bisphenol A/Novolac epoxy resin	proppant coating	US 7334635						
0	5	n.s.			*	Epoxy resin	proppant coating	US 7334635						

8087	32	1.852	10.91		9003-35-4	Phenol-formaldehyde resin	proppant coating; gel forming agent	US 7334635, US 5402846						
30	0	n.s.			40404-63-5	Formaldehyde, polymer with 4-nonylphenol and phenol								
637	1	n.s.			63428-92-2	Alkoxylated phenol formaldehyde resin		US 7334635						
28	0	n.s.			25085-75-0	Formaldehyde-4,4'-isopropylidene diphenol								
181	0	n.s.			68123-18-2	Crosslinked PO/EO-block polymer								
6	0	n.s.			68036-95-3	RX Prod of EO - PO & EPON (i.e., epoxide resin: reaction product of 2-(chloromethyl)oxirane; 4-[1-(4-hydroxyphenyl)-1-methyl-ethyl]phenol; 2-methyloxirane; oxirane)								
22	3	7	0.04		30704-64-4	Formaldehyde, polymer with 4-(1,1-dimethyl)phenol, methyloxirane and oxirane								
855	1	152	0.90		30846-35-6	Formaldehyde, polymer with 4-nonylphenol and oxirane								
490	0	n.s.			29316-47-0	Formaldehyde polymer with 4,1,1-dimethylethyl phenolmethyl oxirane								
10	0	n.s.			68188-99-8	Formaldehyde, polymer with 4-(1,1-dimethylethyl)phenol, 2-methyloxirane, 4-nonylphenol and oxirane								
3	0	n.s.			55845-06-2	Ethylene oxide-formaldehyde nonyl phenol polymer								
0	1				*	Ethylene oxide-nonylphenol polymer								
0	0	n.s.		0.002	9063-06-3	Oxirane, methyl-, polymer with oxirane, monomethyl ether							days to weeks	-0.6
0	2	n.s.			35297-54-2	Formaldehyde, polymer with ammonia and phenol								
0	1				*	Alkanolamine/aldehyde condensate								
337	0	112	0.66		70750-07-1	Formaldehyde, polymer with N1-(2-aminoethyl)-1,2-ethanediamine, benzylated								
0	2				*	Formaldehyde polymer								
1628	**7**		**0.98**	**3.47**		**silicones**								
86	0	24	0.14	0.14	556-67-2	Octamethylcyclotetrasiloxane							days to weeks	5.8
66	0	23	0.14	0.11	541-02-6	Decamethyl cyclopentasiloxane							days to weeks	7
67	0	23	0.14	0.1	540-97-6	Dodecamethylcyclohexasiloxane							378	7.9
339	0	n.s.		0.53	63148-52-7	Siloxanes and silicones, dimethyl,							weeks	9.2
153	0	9	0.05	0.99	68937-55-3	Siloxanes and Silicones, di-Me, 3-hydroxypropyl Me, ethoxylated propoxylated							weeks	3.2
1	0	1	0.01		68037-59-2	Siloxanes and silicones, dimethyl, methyl hydrogen								
35	0				1760-24-3	n-Beta-(aminoethyl)-gamma-aminopropyl trimethoxysilane								
12	0	n.s.			68037-74-1	Siloxanes and silicones, di-Me, polymers with Me silsesquioxanes								
389	1	43	0.25	1.6	63148-62-9	Cured silicone rubber-polydimethylsiloxane	defoamer						days to weeks	7.13
479	1	43	0.25		67762-90-7	Silica (silixanes and silicones - hydrophobic surfaces)	defoamer							
0	2				*	Dimethyl silicone								
0	1				*	Silicone emulsion								
0	1	n.s.		0	681-84-5	Silicon carboxylate							2	-1.7
1	1	n.s.			27306-78-1	Polyether-modified trisiloxane								
1058	**1**		**0.67**			**halogenated polymers**								
0	1				*	Fluoroaliphatic polymeric esters								

26	0	6	0.04		9002-84-0	Poly(tetrafluoroethylene)								
104	0	9	0.05		9002-85-1	Polyvinylidene chloride								
928	0	99	0.58		25038-72-6	Vinylidene chloride/methylacrylate copolymer								
7648	**20**		**11.21**			**others**								
26	2	17	0.10		25038-54-4	Nylon fibers	proppant coating	US 4462917, US 4470915						
0	3				*	Cured urethane resin	proppant coating	US 7334635						
7101	3	1.702	10.03		68527-49-1	Thiourea polymer	corrosion inhibitor							
1	0				76470106852 7-49-1	Hydrochloric Acid Modified Thiorea Polymer								
0	3				*	Polylactide resin		US 7334635						
128	0	117 (CAS 31974-35-3)	0.69		31974-35-3, 25988-97-0	Epiamine polymer, Aziridine Polymer								
0	1				*	Polyoxyalkylenes								
0	0	n.s	0	0.002	9016-88-0	Terephthalic acid ethylene glycol polyethylene glycol polymer							days to weeks		1.3
0	4				*	Cured resin		US 7334635						
0	2	12	0.07	0.04	8050-09-7	Resin							50		3.7
392	2	54	0.32		9051-89-2	Synthetic organic polymer	diverting agent								
0	0	0	0.00	0.008	68131-73-7	Polyethylene Polyamine-							days		-1.3
4022	**10**		**5.39**	**1.33**		**Enzymes (not included in a Table in the Manuscript)**								
1698	8	594 (CAS 9012-54-8)	3.5		9012-54-8, *	Cellulase	breaker	US 4477360						
2056	2	274	1.61		9025-56-3	Hemicellulase	breaker	US 4462917						
268	0	46	0.27	0.48	73049-73-7	Tryptone (Dimethyl (3-ethyl-3-methylpentyl)malonate)	breaker						days		2.8
0	0	n.s.			37288-54-3	Mannan Endo-1,4-B-Mannosidase								
0	1	n.s.		0.85	9014-01-1	Alkaline protease							0.2		0.1
1541	**7**		**2.60**	**3.43**		**Organic - oxidizing (not included in a Table in the Manuscript)**								
1	1	1	0.01	0	614-45-9	Benzenecarboperoxoic acid, 1,1-dimethylethyl ester; tert-Butyl peroxybenzoate	radical initiator		2.89	159.2	2.06×10^{-4}		days to weeks		2.3
1239	6	218	1.28	3.4	75-91-2	Tert-butyl hydroperoxide	breaker, biocide?	US 20100190666A1	0.94	1.97×10^{4}	1.60×10^{-5}		days to weeks		0.8
301	0	222	1.31	0.026	79-21-0	Peroxyacetic Acid			−1.07	1.00×10^{6}	1.39×10^{-6}		0.3		0.1
						Inorganic Chemicals (Tables 1 and 3 in the Manuscript)								
						elements conducive to condensation / crosslinking (Table 1 in the Manuscript)								
30693	**95**		**32.51**			**Borates and Zirconium**								
25919	**67**		**21.55**			**borates**								

4898	31	1048 (CAS 10043-35-3), 2 (CAS 20786-60-1), 4 (CAS 1333-73-9)	6.21		*,*, 10043-35-3, 20786-60-1, 1333-73-9, *	Boric acid/Borate salts (with Potassium or Sodium)	crosslinker	US 5460226, US 7334635										
1027	1	98	0.58		1303-86-2	Boric oxide	crosslinker	US 5460226, US 7334635										
19	0	18	0.11		7440-42-8	Boron (as Boron Trioxide, B2O3)												
1909	1	150	0.88		26038-87-9	Monoethanolamine borate	crosslinker											
137	0	n.s.			12045-78-2	Potassium Borate												
6377	6	620 (CAS 13709-94-9)	3.65		13709-94-9,16481-66-6	Potassium metaborate	crosslinker											
1018	0	61	0.36		1332-77-0	Potassium Tetraborate Tetrahydrate												
0	1				*	Potassium pentaborate	crosslinker											
478	0				13840-56-7	Boric Acid, sodium salt												
1385	8	234 (CAS 10555-76-7), 3 (CAS 35585-58-1), 21 (CAS 7775-19-1)	1.52		7775-19-1, 35585-58-1, 10555-76-7	Sodium metaborate (tetrahydrate)	crosslinker											
7295	17	812 (CAS 1330-43-4), 437 (CAS 1303-96-4), 14 (CAS 12179-04-3)	7.45		1330-43-4, 1303-96-4, 12179-04-3	Sodium tetraborate (decahydrate)	crosslinker											
1164	1	133	0.78		1319-33-1	Ulexite	crosslinker											
31	1	1	0.01		12008-41-2	Disodium octaborate tetrahydrate	crosslinker											
181	0	n.s.			7440-67-7, 92908-33-3, 12280-03-4	BORATE, Borate salts	crosslinker											
4774	**28**		**10.96**	**8.51**		**Zirconium-based**												
2007	23	518 (CAS 101033-44-7), 263 (CAS 113184-20-6)	4.6	2.8	*,101033-44-7, *,*,113184-20-6, 7699-43-6, 62010-10-0	Zirconium oxides; Zirconium complex (lactate, triethanolamine, n-propyl)	crosslinker	US5460226,US 7334635								weeks to months		-6.8
68	1	n.s.			174206-15-6	Sodium zirconium lactate	crosslinker	US 5460226,US 7334635										
2206	0	673	3.97	4.6	68909-34-2	Zirconium, acetate lactate oxo ammonium complexes	crosslinker									days to weeks		-2.2
466	0	399	2.35	1.1	23519-77-9	n-Propyl Zirconate	crosslinker									days to weeks		0.5
27	4	8	0.05		197980-53-3	Alkanolamine chelate of zirconium alkoxide (Zirconium complex)	crosslinker	US 5460226,US 7334635										
0	0	0	0.00	0.006	68309-95-5	Diammonium bis[carbonato-O]dihydroxyzirc	crosslinker									days to weeks		-1.6
1358	**33**		**1.42**	**0.48**		**Others**												
0	7			0.002	*,*,*, 74665-17-1, 36673-16-2	Titanium complex; Titanium triethanolaminate	crosslinker	US 5460226,US 7334635, WO 2008057892								weeks		-2.7
361	3	n.s.			7705-08-0	Ferric chloride	crosslinker	US 5065822										
21	7	7	0.04		10028-22-5	Ferric sulfate	crosslinker	US 5065822										
2	0				13478-10-9	Iron (II) Chloride Tetrahydrate												

64	4	31	0.18		7782-63-0	Ferrous sulfate, heptahydrate								
2	0				7646-79-9	Cobalt (II) Chloride								
162	1	37	0.22	0.48	71-48-7	Cobalt acetate	crosslinker						days to weeks	0.1
0	1	n.s.		0	1066-30-4	Chromium (iii) acetate	crosslinker	US20080058229, US 3938594					days to weeks	-0.1
0	1				*	Chromates	crosslinker, corrosion inhibitor	US 3938594						
226	0	n.s.			7631-95-0	Sodium Molybdate								
1	0	n.s.			7440-38-2	Arsenic								
0	1				*	Antimonate salt	crosslinker	US 5460226, US 7334635						
130	2	n.s.			1314-60-9	Antimony pentoxide	crosslinker	US 5460226, US 7334635						
389	4	166	0.98		29638-69-5	Antimony potassium oxide	crosslinker, corrosion inhibitor	US 5460226, US 7334635						
0	2	n.s.			10025-91-9	Antimony trichloride	crosslinker, corrosion inhibitor	US 5460226,US 7334635						
9	**10**		**0.02**			**aluminum-based**								
0	1	n.s.			1302-42-7	Sodium aluminate	crosslinker	US 7334635						
3	1	1	0.01		10043-01-3	Aluminum sulfate hydrate	crosslinker	US 5460226						
3	5	1 (CAS 1327-41-9)	0.01		*, 1327-41-9	Aluminum chloride	crosslinker	US 5460226						
1	0	n.s.			39290-78-3	Aluminum chloride hydroxide sulfate								
2	0				7360-44-3	Aluminum - acetic acid (1:1) dihydrate								
0	1	n.s.		0	555-31-7	Aluminium isopropoxide	crosslinker	US 5460226					days to weeks	0.8
0	2				*	Complex aluminum salt	crosslinker	US 5460226						
4469	**32**		**0.81**			**other metal salts**								
98	1	n.s.			7758-89-6	Cuprous chloride								
1382	10	40	0.24		7447-39-4	Cupric chloride	iron control agent							
1974	7	94	0.55		10125-13-0	Cupric chloride dihydrate	iron control agent							
238	0	n.s.			7758-99-8	Cupric Sulfate 5 H2O, ACS								
2	1	1	0.01		7681-65-4	Copper iodide								
15	3	2	0.01		7758-98-7	Copper sulfate								
0	1	n.s.			7646-85-7	Zinc chloride	anti-sludge agent							
226		n.s.			7446-19-7	Zinc Sulfate Heptahydrate								
528	7	13 (CAS 10025-69-1)	0.08		7772-99-8, 10025-69-1	Stannous chloride	iron control agent							
2	0				13446-34-9	Manganese (II) Chloride								
0	2	n.s.			10101-97-0	Nickel sulfate hexahydrate								
4	0	n.s.			7786-81-4	Nickel Chelate Catalyst								
5279	**39**		**5.41**			**inorganic reducing (Table 3 in the Manuscript)**								

2387	13	824 (CAS 7772-98-7), 1 (CAS 10102-17-7)	4.87		7772-98-7, 10102-17-7	Sodium thiosulfates	temperature stabilizer	US20100190666 A1							
635	0	1	0.01		7757-83-7	Sodium sulfite									
1092	6	6	0.04		7631-90-5	Sodium bisulfite		US 3996135							
488	1	4	0.02		7681-57-4	Sodium metabisulfite		J605 Schlumberger: Breaker acid							
0	1	n.s.			13427-63-9	Amine bisulfite		US 3976593	−1.61	$1.00 \times 10_{6}$	$3.68 \times 10_{-10}$				
458	15	81	0.48		10192-30-0	Ammonium bisulfite	oxygen scavenger	US 3996135							
0	1				"7783-06-4"	Hydrogen sulfide									
0	1	n.s.		0	7803-51-2	Phosphine						days	Y	-0.2	
0	1	n.s.			12057-74-8	Magnesium phosphide									
214	0	n.s.			13446-12-3	Ammonium phosphite									
5	0	n.s.			13492-26-7	DIPOTASSIUM PHOSPHITE									
58328	**110**		**77.00**			**inorganic oxidizing (Table 3 in the Manuscript)**									
211	0	211	1.24		10028-15-6	Ozone	biocide								
1158	4	339	2.00		7722-84-1	Hydrogen peroxide	breaker	US 6861394							
1551	6	536 (CAS 14452-57-4)	3.16		1335-26-8, 14452-57-4	Magnesium peroxide	breaker	US 6861394							
934	5	119	0.70		1305-79-9	Calcium peroxide	breaker	US 6861394							
2	0				76320-44-0	Perboric acid	breaker								
5379	6	1152 (CAS 10486-00-7), 1 (CAS 10332-33-9), 21 (CAS 7632-04-4)	6.92		1113-47-9, '7632-04-4, 10486-00-7, 447-63-2, 10332-33-9	Sodium perborates	breaker	US 5460226							
26456	37	4.618	27.22		7727-54-0	Ammonium persulfate (Diammonium peroxidisulfate)	breaker	US 5460226							
8073	6	1.574	9.28		7775-27-1	Sodium persulfate	breaker	US 5460226, US7049436B2							
85	9	14	0.08		7727-21-1	Potassium persulfate	breaker	US 5460226, US7049436B2							
1	0	1	0.01		7790-92-3	Hypochlorous Acid	biocide								

3983	14	1.439	8.48		7681-52-9	Sodium hypochlorite	breaker, biocide	US 5460226 (breaker); US20100190666 A1 (oxidizing biocide)						
3	1	1	0.01		7778-54-3	Calcium hypochlorite	breaker, biocide	US 5460226 (breaker); US20100190666 A1 (oxidizing biocide)						
8486	8	2.372	13.98		7758-19-2	Sodium chlorite	breaker	US 20120000708 A1						
0	2				*	Chlorous ion solution								
0	1				7775-09-9	Sodium chlorate	biocide							
555	1	186	1.10		10049-04-4	Stabilized aqueous chlorine dioxide	biocide	US 20100190666A1						
1451	10	481	2.83		7789-38-0	Sodium bromate	breaker	US 20120000708 A1						
47457	**99**		**80.22**			**inorganic acids (Table 3 in the Manuscript)**								
41020	42	12351 (CAS 7647-01-0)	72.79		7647-01-0, 6747-01-0	Hydrogen chloride (Hydrochloric acid)	pH control	US 4817717						
210	2	127	0.75		7664-39-3	Hydrogen fluoride (Hydrofluoric acid)	corroding acid	US 4817717						
136	9	89	0.52		12125-01-8	Ammonium fluoride	corroding acid, fluoride source							
165	10	104	0.61		1341-49-7	Ammonium bifluoride (Ammonium hydrogen difluoride)	corroding acid, temperature stabilizer	US 6491099 B1						
1742	9	13 (CAS 7664-38-2), 24 (CAS 22042-96-2)	1.22	0.068	7664-38-2, 10294-56-1, *, 10361-65-6, 22042-96-2	Phosphoric acid (+salts)	pH control, scale inhibitor	US 6904972					months	-9.7
508	5	136 (CAS 7601-54-9), 57 (CAS 7758-29-4)	1.14		68915-31-1, 7758-29-4, 7601-54-9, 10101-89-0	(Poly)phosphate sodium salts	scale inhibitor							
0	5	n.s.			7758-16-9	Sodium acid pyrophosphate	scale inhibitor							
0	2				*	Sodium phosphate	scale inhibitor							
0	1	n.s.			7785-88-8	Sodium aluminum phosphate	corrosion inhibitor	US20120094130						
2938	5	406 (CAS 13598-36-2)	2.39		*, 129828-36-0, 13598-36-2	Phosphonic acid	scale inhibitor							
694	9	86	0.51		7664-93-9	Sulfuric acid	pH control	US 6904972						
8	0		0.29		7446-09-5	Sulfur Dioxide								
2	0	n.s.			7646-93-7	Sulfuric Acid, Monopotassium Salt								
29	0	n.s.			7681-38-1	Sodium bisulfate								
5	0	n.s.			10039-54-0	Sulfuric Acid Salt								
56760	**193**		**64.40**			**inorganic base (Table 3 in the Manuscript)**								
25435	80	4656 (CAS 1310-73-2)	27.44		1310-73-2, 95077-05-7	Sodium hydroxide (Caustic soda)	pH control	US 8387696						
3	1	n.s.			1313-59-3	Sodium oxide (Na2O)	pH control	US 7067459						

1303	10	21	0.12		144-55-8	Sodium bicarbonate (Sodium hydrogen carbonate)	pH control	US 7007757	−0.46	8.42×10^{5}	6.05×10^{-9}			
901	14	146	0.86		497-19-8	Sodium carbonate	pH control	US 7007757	−0.46	8.42×10^{5}	6.05×10^{-9}			
2	0	1	0.01		7722-88-5	Tetrasodium Pyrophosphate (TSPP)								
2	0	1	0.01		7785-84-4	Sodium Trimetaphosphate								
18562	25	2.843	16.76		1310-58-3	Potassium hydroxide	pH control	US 8387696						
2	1	n.s.			12136-45-7	Potassium oxide	pH control	US 7067459						
7428	12	2.154	12.69		584-08-7	Potassium carbonate	pH control	US 7007757	−0.46	8.42×10^{5}	6.05×10^{-9}			
56	0	n.s.			7778-53-2	Potassium Phosphate	pH control, scale inhibitor							
1268	18	562	3.31		1309-48-4	Magnesium oxide	pH control	US 8387696; US 20120000708 A1						
652	4	160	0.94		1309-42-8	Magnesium hydroxide	pH control	US 7007757						
174	1	n.s.			546-93-0, 7757-69-9	Magnesium carbonate	pH control	US 7007757						
369	9	113	0.67		1305-62-0	Calcium hydroxide	pH control	US 8387696						
6	6	1	0.01		1305-78-8	Calcium oxide	pH control	WO 2008057892						
596	10	181 (CAS 471-34-1), 88 (CAS 1317-65-3)	1.59		471-34-1 (calcite), 1317-65-3 (calcium carbonate)	Calcium carbonate	pH control	US 20120000708 A1, US 484846						
0	2	n.s.			1314-13-2	Zinc oxide	pH control	US 8387696						
1	0	n.s.			1313-82-2	Sodium Sulfide								
18375	**49**		**19.68**			**inorganic - ammonia and derivatives (Table 3 in the Manuscript)**								
1	0	1	0.01		302-01-2	Hydrazine								
540	0	35	0.21	0.91	57-13-6	Urea			−1.56	4.26×10^{5}	3.65×10^{-10}	3		-0.3
0	0	0	0.00	0.002	108-19-0	Biuret	probable impurity					0.3		0.1
671	0	152	0.90		1762-95-4	Thiocyanic acid, ammonium salt			0.58	4.36×10^{4}	1.46×10^{-4}			

11832	30	2483	14.63		12125-02-9	Ammonium chloride	pH control, complexing agent	US 4846277						
533	7	266	1.57		7664-41-7	Ammonia	scale inhibitor							
4	0	4	0.02		8013-59-0	Ammonium								
0	1	21	0.12	0.53	5470-11-1	Hydroxylamine hydrochloride	reducing agent, complexing agent					days to weeks		-2.3
1519	4	194	1.14		1336-21-6	Ammonium hydroxide	pH control, complexing agent	US 4846277						
0	1	n.s.			1066-33-7	Ammonium bicarbonate	pH control, complexing agent	US 7007757	−0.46	8.42×10^{5}	6.05×10^{-9}			
0	2	n.s.			6484-52-2	Ammonium nitrate								
1190	0	184	1.08		7783-20-2	Ammonium Sulfate	friction reducer							
0	3	n.s.			7803-63-6	Ammonium bisulfate	oxygen scavenger	US20100190666 A1						
68	0	n.s.			7783-18-8	Ammonium Salt (Ammonium Sulfate)								
2017	0	n.s.			7722-76-1, 10124-31-9	Ammonium phosphate								
0	1				*	Ammonium salt	pH control, complexing agent							
48290	**122**		**36.84**			**inorganic salt (Table 3 in the Manuscript)**								
27503	48	3608 (CAS 7647-14-5)	21.26		7647-14-5, 76471-41-5	Sodium chloride	ionic strength control	US 20120000708 A1						
385	1	145	0.85		7647-15-6	Sodium bromide		US 20100190666A1						
2081	0	9	0.05		7681-82-5	Sodium iodide								
0	1	n.s.			540-72-7	Thiocyanate sodium			0.58	4.36×10^{4}	1.46×10^{-4}			
153	1	9	0.05		7632-00-0	Sodium nitrite		US 20100190666A1; US 4846277						
33	0	7	0.04		7631-99-4	Sodium Nitrate								
6066	7	410	2.42		7757-82-6	Sodium sulfate	ion strength control							
232	0	n.s.			7778-80-5	Potassium Sulfate								
3626	29	874	5.15		7447-40-7	Potassium chloride	clay stabilizer	US 2012/0157356 A1						
0	2				*	Alkaline bromide salts								
233	6	n.s.			7681-11-0	Potassium iodide								

6	0	n.s.			10476-85-4	Strontium chloride								
1579	4	131	0.77		7786-30-3	Magnesium chloride	ion strength control	US 4623021						
118	0	n.s.			7791-18-6	Magnesium chloride hexahydrate								
1435	5	90	0.53		10377-60-3	Magnesium nitrate	ion strenght control?							
226	0	n.s.			7487-88-9	Magnesium Sulfate								
3556	17	382	2.25		10043-52-4	Calcium chloride	ion strength control	US 20120000708 A1						
3	1	n.s.			10035-04-8	Calcium chloride, dihydrate	ion strength control							
2	0	n.s.			7778-18-9	Calcium sulfate								
1053	0	587	3.46		16887-00-6	Various chlorides								
						radioactive tracer								
9	0	9	0.05		12030-49-8	Iridium Oxide	radioactive tracer							
8	0	8	0.05		12060-08-1	Scandium Oxide	radioactive tracer							
5	0	5	0.03		1309-64-4	Antimony Oxide	radioactive tracer							
						other/unspecified								
0	2				*	Complex organometallic salt								
0	1				*	Inorganic salt								
0	1	n.s.			533-96-0	Inorganic salt			−0.46	8.42 × 10^{5}	6.05 × 10^{-9}			
148	1	n.s.			7446-70-0	Inorganic salt								
0	2				*	Metal salt								
0	1				*	Metal salt solution								
0	1				*	Non-hazardous salt								
						Insoluble inorganic materials (Table 3 in the Manuscript)								
116904	**443**		**23.61**			**pure oxides**								
2727	25				1332-37-2, 1309-37-1, 76774-74-8, *, *	Iron oxides	proppant							
266	0	156	0.92		1310-14-1	Goethite								
41	0	n.s.			1309-38-2	Magnetite								
40	5				*, 1317-60-8	Hematite	proppant	US 20120000708 A1						
3869	77				*, 1344-28-1, 1302-74-5, 90669-62-8, 1302-44-56	Aluminum oxides	proppant	US 7334635						
2593	21	n.s.			1317-80-2, 13463-67-7, 98084-96-9	Titanium oxides	proppant	US 7334635						

5719	47	n.s.			7631-86-9, 148-60-7	Silica (Silicon dioxide), Silica Sand	proppant													
3670	44	92 (CAS 14464-46-1)	0.54		14464-46-1, 14464-46-4	Crystalline silica - cristobalite	proppant													
95200	207	3758 (CAS 14808-60-7)	22.15		14808-60-7, 308075-07-2, 75-20-7	Crystalline silica - quartz (SiO2)	proppant													
121	2	n.s.			15468-32-3	Crystalline silica, tridymite	proppant													
2604	1	n.s.			1317-95-9, 112926-00-8	Microcrystalline silica, silica gel	proppant													
6	1	n.s.			99439-28-8	Amorphous silica	proppant													
4	3	n.s.			112945-52-5, 69012-64-2	Pyrogenic silica, Fumed silica	proppant													
0	3				*	Silica, amorphous	proppant													
44	7	n.s.			60676-86-0	Silicon dioxide (Fused silica)	proppant													
12624	**131**		**3.78**			**silicates & clay minerals**														
4060	93	2 (CAS 1327-36-2)	0.01		1302-76-7, 1302-93-8, 1327-36-2, 839-20-3, 1305-75-5	Aluminum silicate (mullite)	proppant													
0	3	n.s.			12001-26-2	Mica	proppant	US 7334635B2												
266	0				1302-27-8	Biotite														
204	4	n.s.			1332-58-7	Hydrated aluminum silicate (Kaolin)	proppant	US 7334635												
10	2	n.s.			1302-78-9	Bentonite	proppant													
3	0				488-16-4	Modified Bentonite														
896	2	101	0.60		14807-96-6	Magnesium silicate hydrate (talc)	proppant	US 7334635												
0	1	n.s.			1302-62-1	Almandite and pyrope garnet	proppant													
0	1	n.s.			12068-56-3	Aluminum oxide silicate	proppant													
64	3	n.s.			1317-71-1	Magnesium iron silicate	proppant													
69	3	n.s.			1343-88-0	Magnesium silicate	proppant													
0	1	n.s.			93763-70-3	Perlite	proppant													
84	0	38	0.22		12173-60-3	Illite														
84	0	38	0.22		98072-94-7	Ilmenite														
29	0	n.s.			8031-18-3	Attapulgite														
5640	7	453	2.67		91053-39-3	Diatomaceous earth, calcined	scale inhibitor component													
255	3	1	0.01		61790-53-2	Diatomaceous earth														
0	2	n.s.			1344-09-8	Sodium silicate	pH control	US 7007757												
0	2	n.s.			6834-92-0	Sodium metasilicate, anhydrous														
0	1	n.s.			10034-77-2	Di-calcium silicate														
0	1	n.s.			12168-85-3	Tri-calcium silicate														
41	2				*, 68539-58-2	Organophilic clay														

919	0	9	0.05		12174-11-7	Clay									
						others / not specified									
36	2	12	0.07		7789-75-5	Calcium fluoride									
0	3	n.s.			7727-43-7	Barium sulfate		US 20120000708 A1							
69	1	36	0.21		7758-87-4	b-tricalcium phosphate									
266	0				64476-38-6	Apatite									
1036	3	7	0.04		65997-17-3	Glass fiber ("Glassy calcium magnesium phosphate")									
716	16	n.s.			1318-16-7, 13181-60-7	Bauxite	proppant	EP 136606A2, US 7334635B2							
0	1	n.s.			12068-35-8	Tetra-calcium-alumino-ferrite									
119	0	n.s.			65997-18-4	Calcium magnesium sodium phosphate frit									
0	1				*	Inorganic particulate									
94	0	n.s.			63800-37-3	Inorganic mineral									
662	0	n.s.			66402-68-4	Ceramic materials and wares, chemicals									
0	1				*	Mineral									
0	1				*	Mineral Filler									
166	**4**					**metals**									
2	2	n.s.			7429-90-5	Aluminum									
0	1	n.s.			7440-50-8	Copper									
0	1	n.s.			7439-92-1	Lead									
164	0	n.s.			7439-89-6	Iron									
						Unclassified/ other									
0	1				*	Instant coffee purchased off the shelf									
0	2				*	Nuisance particulates									
0	1				*	Wall material									
0	1	n.s.			50815-10-6	Coal, granular									
0	2				*	Walnut hulls		EP 136606A2, US 7334635B2							
299	0	13	0.08	0.004	8001-26-1	Linseed Meal							119		13

Table S2. Sources of quantitative data

FracFocus (SkyTruth)	Excel Columns B, O
Source	Website of the non-profit organization "SkyTruth" (http://frack.skytruth.org/fracking-chemical-database/frack-chemical-data-download)
Original Source	FracFocus Chemical Disclosure Registry 1.0 (https://fracfocus.org/) Analysis of data provided by the FracFocus 1.0 website between January 2011 and July 2013
Data for chemical "i"	Counts over the products containing chemical "i" in their material data sheet (MDS), multiplied by the number of times the products were reported in hydraulic fracturing events.
Comments	- only chemicals with a valid CAS number were considered from the database - chemical "i" may be counted several times for the same HF event if it is listed in the MDS of several products of this event - counts only reflect how often a chemical was applied, not in what concentrations - compounds that are considered proprietary may not be included in FracFocus reports

FracFocus (EPA)	Excel Column G
Source	Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0 (FracFocus 1.0 Data Analysis; EPA/601/R-14/003), March 2015 (http://frack.skytruth.org/fracking-chemical-database/frack-chemical-data-download)
Original Source	FracFocus Chemical Disclosure Registry 1.0 (https://fracfocus.org/) Analysis of 39,136 disclosures in PDF format submitted to the FracFocus 1.0 website prior to March 1, 2013.
Data for chemical "i"	Counts over all hydraulic fracturing events for which chemical "i" was reported.
Comments	- only chemicals with a valid CAS number were considered from the database - chemical "i" is counted only once per HF event, even if contained in several products - database contains information about concentrations in applications, which, however, was not considered here. - compounds that are considered proprietary may not be included in FracFocus reports

FracFocus (Rogers et al.)	Excel Columns J, W-AG
Source	Rogers et al., "Framework for Identifying Organic Compounds of Concern in Hydraulic Fracturing Fluids Based on Their Mobility and Persistence in Groundwater", Environ. Sci. Technol. Lett., 2015, 2 (6), pp 158–164; DOI: 10.1021/acs.estlett.5b00090
Original Source	- FracFocus Chemical Disclosure Registry 1.0 and 2.0 (https://fracfocus.org/) Analysis of FracFocus reports acquired for Colorado (7,772 reports), North Dakota (5,662 reports), Pennsylvania (4,312 reports), and Texas (32,278 reports) as of November 2014. - Sources for physicochemical and toxicological properties - U.S. Environmental Protection Agency. Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources; EPA 601/R-12/011; U.S. Environmental Protection Agency Office of Research and Development: Washington, D.C, 2011. Groundwater Protection Council; Interstate Oil & Gas Conservation Commission. - FracFocus Chemical Disclosure Registry. http://fracfocus.org/ (accessed Febuary 2015).

	- Chemicals Used in Hydraulic Fracturing; U.S. House of Representatives, Committee on Energy and Commerce, Minority Staff: Washington, D.C., 2011. - American Chemical Society. SciFinder. http://scifinder.cas.org (accessed Febuary 2015). - Richardson, N.; Gottlieb, M.; Krupnick, A.; Wiseman, H. The State of State Shale Gas Regulation; Resources for the Future Report: Washington, D.C., 2013. - U.S. Environmental Protection Agency; Syracuse Research Corporation (SRC). Estimation Programs Interface Suite for Microsoft Windows, v 4.11; U.S. Environmental Protection Agency: Washington, D.C, and Syracuse, NY, 2012. - Royal Society of Chemistry. ChemSpider. http://www.chemspider.com/ (accessed Febuary 2014). - U.S. Environmental Protection Agency. ChemView. http://java.epa.gov/chemview (accessed Febuary 2015). - Mackay, D. Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals; 2nd ed.; CRC/Taylor & Francis: Boca Raton, FL, 2006. - Howard, P. H. Handbook of Environmental Degradation Rates; Lewis Publishers: Chelsea, MI, 1991. - U.S. National Library of Medicine. Toxicology Data Network (TOXNET) Hazardous Substances Data Bank (HSDB). http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB (accessed Febuary 2015). - U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS). http://www.epa.gov/IRIS/ (accessed February 2015)
Data for chemical “i”	Counts over all hydraulic fracturing events for which chemical “i” was reported.
Comments	- only chemicals with a valid CAS number were considered from the database - chemical “i” is counted only once per HF event, even if contained in several products - only a subselection - counts only reflect how often a chemical was applied, not in what concentrations - compounds that are considered proprietary may not be included in FracFocus reports

Waxman List	Excel Column E
Source	House of Representatives (U.S. House of Representatives). (2011). Chemicals used in hydraulic fracturing. Washington, D.C.: http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic-Fracturing-Chemicals-2011-4-18.pdf
Original Source	Voluntary disclosure by companies what chemicals are contained in the products commonly applied in hydraulic fracturing.
Data for chemical “i”	Numbers state in how many products a certain chemical “i” was reported.
Comments	- chemicals with and without valid CAS number are considered - counts only reflect the number of products in which a chemical “i” is disclosed, not how often this product was applied. - counts only reflect how often a chemical was applied, not in what concentrations - compounds that are considered proprietary may not be disclosed

Lists without quantitative data

EPA List (2012)	
Source	U.S. Environmental Protection Agency. Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources; EPA 601/R-12/011; U.S. Environmental Protection Agency Office of Research and Development: Washington, D.C, 2012.
Original Sources	- US House of Representatives 2011. Chemicals Used in Hydraulic Fracturing. Available at http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic%20Fracturing%20Report%204.18.11.pdf. Accessed November 27, 2012. (see Waxman List) - Colborn, T; Kwiatkowski, C; Schultz, K; Bachran, M. (2011). Natural gas operations from a public health perspective. Hum Ecol Risk Assess 17: 1039-1056. http://dx.doi.org/10.1080/10807039.2011.605662 - NYSDEC (New York State Department of Environmental Conservation). (2011). Revised draft supplemental generic environmental impact statement (SGEIS) on the oil, gas and solution mining regulatory program: Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus shale and other low-permeability gas reservoirs. Albany, NY: NY SDEC. http://www.dec.ny.gov/energy/75370.html Accessed September 1, 2011. - US Environmental Protection Agency. 2011. Data Received from Hydraulic Fracturing Service Companies. Non-confidential business information located in Federal Docket ID: EPA-HQ-ORD-2010-674.. - Material Safety Data Sheets. (a) Encana/Halliburton Energy Services, Inc.: Duncan, Oklahoma. Provided by Halliburton Energy Services during an onsite visit by the EPA on May 10, 2010; (b) Encana Oil and Gas (USA), Inc.: Denver, Colorado. Provided to US EPA Region 8. - US Environmental Protection Agency, Office of Water. 2004. Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed MethaneReservoirs. EPA 816-R-04-003. Available at http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/wells_coalbedmethanestudy.cfm. Accessed November 27, 2012. - Pennsylvania Department of Environmental Protection. 2010. Chemicals Used by Hydraulic Fracturing Companies in Pennsylvania for Surface and Hydraulic Fracturing Activities.Available at http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/MarcellusShale/Frac%20list%206-30-2010.pdf. Accessed November 27, 2012. - Ground Water Protection Council. 2012b. FracFocus well records: January 1, 2011, through February 27, 2012. Available at http://www.fracfocus.org/. - Hayes, T. 2009. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas. Gas Technology Institute for Marcellus Shale Coalition. Available at http://eidmarcellus.org/wp-content/uploads/2012/11/MSCommission-Report.pdf. Accessed November 30, 2012. - US Environmental Protection Agency. 2011. Sampling Data for Flowback and Produced Water Provided to EPA by Nine Oil and Gas Well Operators (Non-Confidential Business Information). Available at http://www.regulations.gov/#!docketDetail;rpp=100;so=DESC;sb=docId;po=0;D=EPA-HQ-ORD-2010-0674 Accessed November 27, 2012.
Comments	- list of chemicals with source of information, without quantitative information

EPA List (2015)	Excel Columns H, Q-V
Source	U.S. Environmental Protection Agency. Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources (External Review Draft). EPA/600/R-15/047; Appendix A, U.S. Environmental Protection Agency Office of Research and Development: Washington, D.C, 2015.
Original Sources	- US House of Representatives 2011. Chemicals Used in Hydraulic Fracturing. Available at http://democrats.energycommerce.house.gov/sites/default/files/documents/Hydraulic%20Fracturing%20Report%204.18.11.pdf.. (see Waxman List) - Colborn, T; Kwiatkowski, C; Schultz, K; Bachran, M. (2011). Natural gas operations from a public health perspective. Hum Ecol Risk Assess 17: 1039-1056. http://dx.doi.org/10.1080/10807039.2011.605662 - NYSDEC (New York State Department of Environmental Conservation). (2011). Revised draft supplemental generic environmental impact statement (SGEIS) on the oil, gas and solution mining regulatory program: Well permit issuance for horizontal drilling and high-volume hydraulic fracturing to develop the Marcellus shale and other low-permeability gas reservoirs. Albany, NY: NY SDEC. http://www.dec.ny.gov/energy/75370.html - US Environmental Protection Agency. 2013. Data received from oil and gas exploration and production companies, including hydraulic fracturing service companies 2011 to 2013. Non-confidential business information source documents are located in Federal Docket ID: EPA-HQ-ORD2010-0674. Available at http://www.regulations.gov. -- Material Safety Data Sheets. (a) Encana/Halliburton Energy Services, Inc.: Duncan, Oklahoma. Provided by Halliburton Energy Services during an onsite visit by the EPA on May 10, 2010; (b) Encana Oil and Gas (USA), Inc.: Denver, Colorado. Provided to US EPA Region 8. - US Environmental Protection Agency, Office of Water. 2004. Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed MethaneReservoirs. EPA 816-R-04-003. Available at http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/wells_coalbedmethanestudy.cfm. - Pennsylvania Department of Environmental Protection. 2010. Chemicals Used by Hydraulic Fracturing Companies in Pennsylvania for Surface and Hydraulic Fracturing Activities.Available at http://files.dep.state.pa.us/OilGas/BOGM/BOGMPortalFiles/MarcellusShale/Frac%20list%206-30-2010.pdf. - Hayes, T. 2009. Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas. Gas Technology Institute for Marcellus Shale Coalition. Available at http://eidmarcellus.org/wp-content/uploads/2012/11/MSCommission-Report.pdf. - US Environmental Protection Agency. 2011. Sampling Data for Flowback and Produced Water Provided to EPA by Nine Oil and Gas Well Operators (Non-Confidential Business Information). Available at http://www.regulations.gov/#!docketDetail;rpp=100;so=DESC;sb=docId;po=0;D=EPA-HQ-ORD-2010-0674. Physicochemical Properties were taken (when available) from EPI Suite™ version 4.1 (U.S. EPA). http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm
Comments	- list of chemicals with source of information, without quantitative information

Supporting Information for:

Indications of Transformation Products from Hydraulic Fracturing Additives in Shale Gas Wastewater

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Analytical details for volatile compound analysis.

All glassware was combusted in a muffle furnace for 8 hr at 450°C. Glass syringes with metal needles and plungers were used for sample transfer and preparation of standards and rinsed with high purity solvents (hexane, dichloromethane (DCM), acetone, methanol) and HPLC-grade water prior to use.

Purge-and-trap (P&T): Following a modified EPA 624 method, 5-mL aliquots of the water sample were manually injected with a glass micro-mate syringe (Cadence Science Inc., RI, USA) into a 5-mL Tekmar glass sparger on a Teledyne Tekmar Stratum Purge& Trap (Mason, OH, USA). At ambient temperature, the samples were purged for 4 min with purified Helium (Agilent Big Universal Trap Superior Helium Purifier (RMSH2)) at a purge flow of 40 mL min-1. Dry Purge time was 1.0 min at 40°C at a dry purge flow of 100 mL min-1. Measurements were carried out in triplicate.

GC: Wide-bore, thick phase columns were employed to achieve maximum separation of volatile compounds (DB-624 (60m x 320 um x 1.8 µm; flow: 6mL min-1; T 40°C, 2 min hold, ramp 4°C min-1to 150°C, then ramp 8°C min-1 to 200°C) or Restek-502.2 (105 m x 320um x 3µm; flow: 20 mL min-1; T 40°C, 6 min hold, ramp 6°C min-1to 200°C).

FID: The FID was set to a temperature of 300°C and operated with a H2 flow of 30 mL min-1, an air flow of 400mL min-1, and a makeup gas flow (He) of 25 mL min-1. VOCs were identified and quantified by comparison with standard reference compounds (502.2 CAL 2000 Mega-Mix (no. 30431), 624 Calibration Mix #1 (no. 30020), 624 Calibration Mix #2 (no. 30021), 624 Calibration Mix #3 (no. 30022), all by Restek, Bellefonte, PA, USA).

MS: Before analysis, perdeuterated n-Pentadecane (Cambridge Isotope Laboratories, Inc., Andover, MA, USA) was added as internal standard. The actual volume of the sample extract was taken into account to yield an internal standard concentration of 1 µg L-1. MS scan-mode parameters were 72 - 472 amu at a sampling rate of 50 Hz.

Confidence assignment: Boiling point ladder construction and approach.

First, the CAS number (Chemical Abstracts Services) of the best NIST library match (i.e., with the highest forward and reverse similarity) was used to populate an inventory of theoretical and experimental boiling points. Then, a simple linear regression model of boiling point versus 1D retention time was developed using an n-alkane standard ladder ($R2 = 0.9998$). Boiling points of the tentative mass spectral assignments were run through the algorithm, calculating a predicted 1D retention time. This predicted value was compared to the actual 1D retention time of the detected peak. Agreements within a tolerance of 500 seconds of the predicted retention time (derived from either the theoretical or experimental boiling points) were classified as positive confirmation assignments (CA). The wide tolerance threshold was chosen to allow for enough

deviation from the n-alkane ladder (e.g., as should be the case for distinct compound classes) while still narrow enough to reject misidentifications and outliers.

When possible, we constructed similar standard ladders composed of additional chemical compound classes: specifically, for alcohols, aldehydes, carboxylic acids, and sulfurous acid esters. Tentative identifications were divided manually into chemical classes and run through their respective standard ladder linear models. Note that compounds that did not fall under one of the listed classes deferred to the original n-alkane ladder. As expected, deviations in chemical behavior led to differing relationships between boiling point and 1D retention time. However, most of the observed deviations were not large, with the notable exception being the carboxylic acid ladder. This was not surprising, since the hydrogen bonding within carboxylic acids leads to enhanced intermolecular interactions relative to n-alkanes, affecting compound's ability to transit the column. Thus, the carboxylic acid ladder was retained in the final linear model and applied to all carboxylic acids, aldehydes, and sulfurous acid esters to better capture these compounds' behaviors; the n-alkane ladder was used for all remaining compounds.

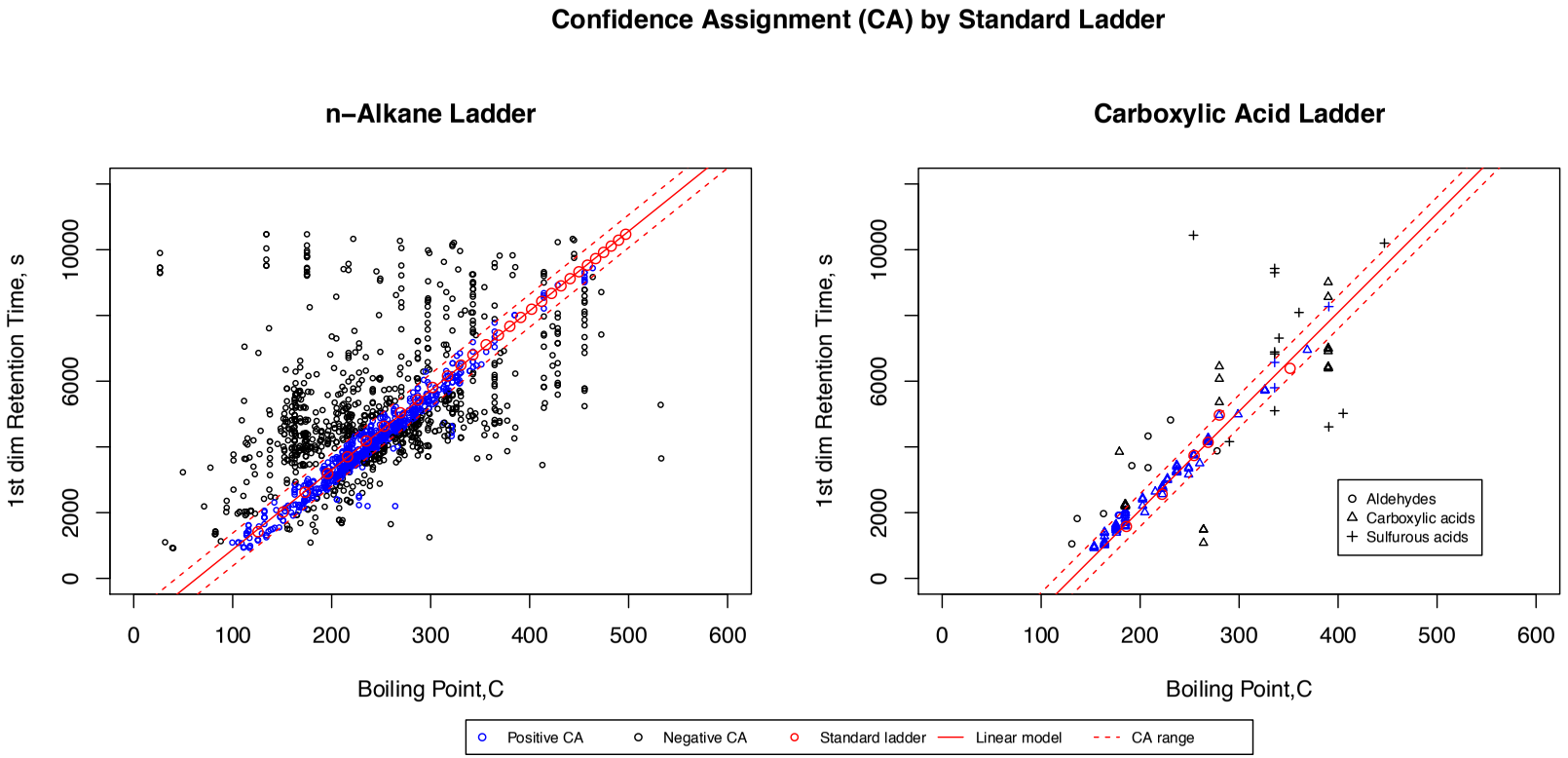


Figure S1. Confidence assignment plots. Confidence assignments (CA) were made by applying a predictive linear model relating boiling point and retention time (solid line), constructed using a standard ladder of known compounds. Positive assignments showed agreement between the top NIST library hit from TOF-MS spectral matching and the predicted retention time (± 500 s, tolerance shown by "CA range" dashed lines). Unique standard ladders were chosen to help reflect the types of chemical interactions available to each compound class.

Control experiments.

Experiments to exclude compound formation or leaching during sample storage. In addition to using standard blank procedures, we conducted three sets of control experiments to ensure that sample collection and storage methods were not a source of analytes. In particular, we probed the potential generation of halogenated or volatile organic compounds in (a) the presence and absence of highly saline water and a model organic compound (acetone) in VOA vials, (b) the presence and absence of actual flowback water samples and a model organic compound (acetone) in an all-glass volumetric flask system, and (c) in the presence of low and high salinity water in representative HDPE bottles similar to the ones initially used by the Arkansas Oil and Gas commission. Synthetic brines (for (a) and (c)) were generated using a recipe of 5.96 g NaHCO3, 7.54 g CaCl2, 34.07 g NaCl, 2.21 g MgCl2, and 1.30 g MgBr2 in 4.0 L of HPLC-grade water. ("Low salt" samples were generated from a 50% dilution of this stock solution). Samples associated with (a) and (b) were acidified with 1 mL of 50% v/v HCl. All experiments were conducted from 0-30 days and analyzed via GC-MS for non-target screening ((a) and (b)) or GC-FID for a target subset of analytes (c). In all analyses, no unexpected halogenated compounds formed.

Experiments to investigate mass loss over time in VOA vials. EPA standard compounds (see SI; high molecular weight compounds simulated using 502.2 CAL 2000 Mega-Mix (no. 30431); low molecular weight compounds using 624 Calibration Mix #1 (no. 30020); Restek, Bellefonte, PA, USA) were spiked to HPLC grade water in the VOA vials and measured quantitatively on the GC-FID over 28 days. Losses were less than 5% for low molecular weight compounds and negligible for high molecular weight compounds.

Table S1: Full list of mass spectral library matching-derived tentative identifications and putative compound origins. In columns labeled Sample A-F, a non-zero entry corresponds to detection in the respective sample. Y (yes) or N (no) indicates whether a positive confidence assignment (conf) could be made based on T (theoretical) or E (experimental) boiling points (bp). An entry of "N/A" represents a detection without available boiling point information. Note: Compounds are sorted according to confidence assignment (Y on top; i.e., those compounds that passed the retention time prediction) and alphabetical order of compound class.

***Note**: Table S1 appears at the end of this document, due to its large size.*

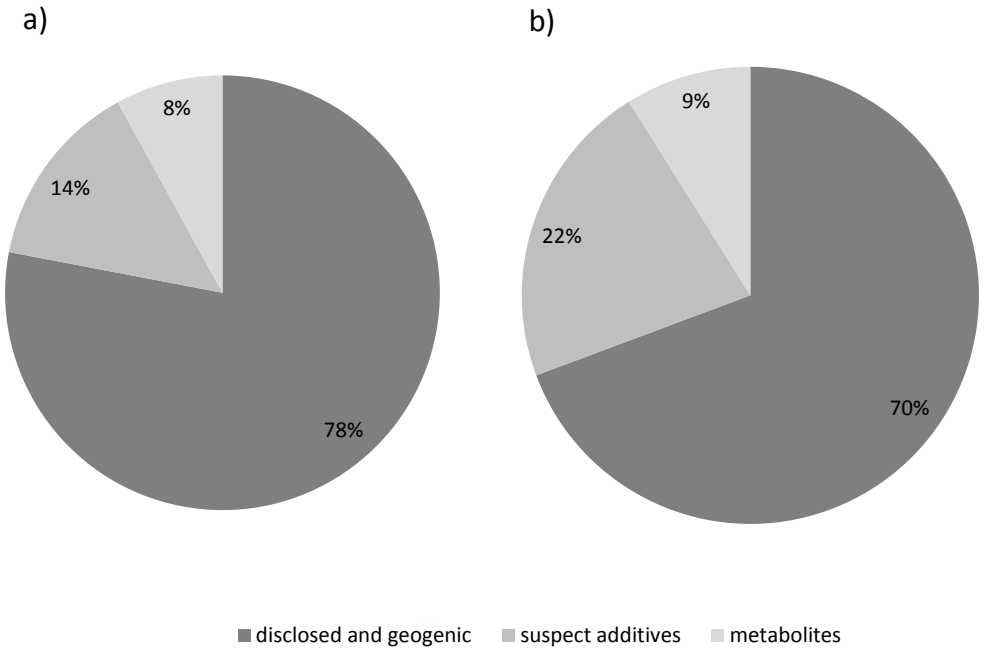


Figure S2: Effect of boiling-point-prediction filter for more stringent confidence assignments as a function of putative source of compound. (a) All TOF-detected compounds with 85% library matching that passed the additional confidence assignment filter (i.e., boiling point prediction; *n*= 412). (b) All TOF-detected compounds with 85% library matching, prior to applying the boiling point prediction algorithm (*n* = 727). Dark gray: Disclosed additives and geogenic compounds. Medium gray: suspect additives. Light gray: metabolites. Suspect additives (e.g. ketones and esters) were preferentially filtered out during application of confidence assignments, as there were no compounds that could be used to construct an appropriate ladder for that family (e.g., there were no or few compounds within that family confirmed with authentic standards inherently present in the sample).

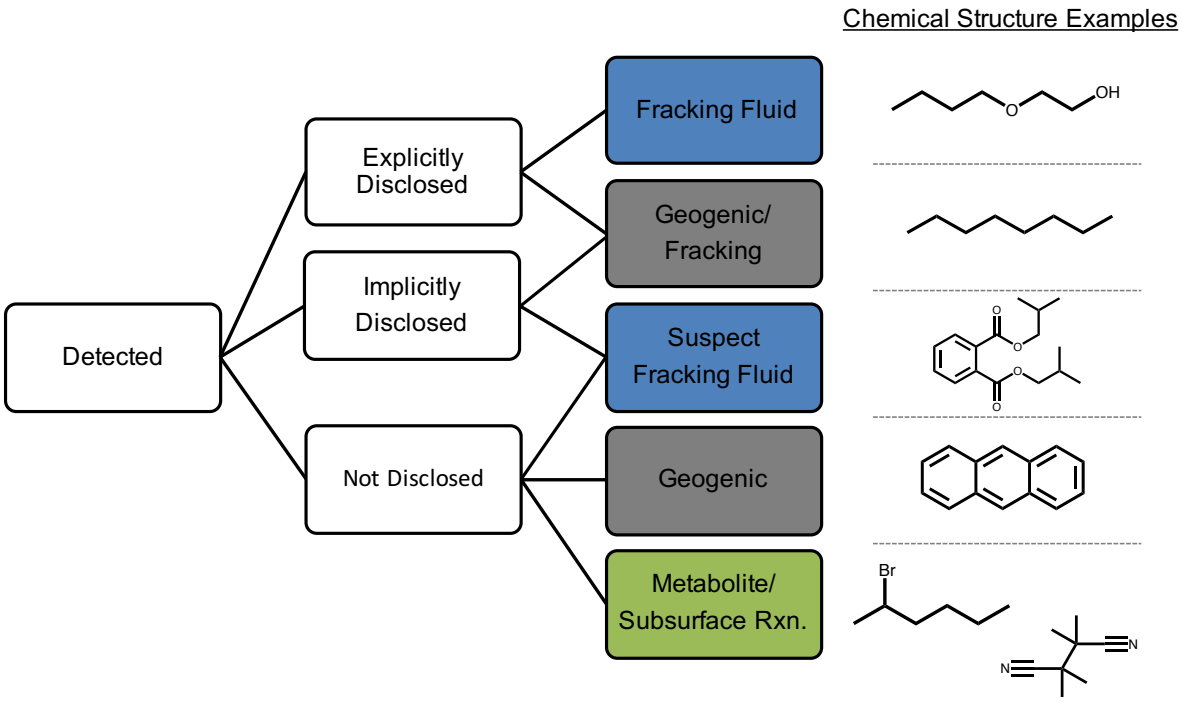


Figure S3. Framework for assignment of detected compound disclosure and source classification. Explicit disclosures were explicitly mentioned by chemical name or synonym on FracFocus, Skytruth, or the Waxman list. Implicit disclosures included structures that were non-specific or disclosed as a group of compounds. Not disclosed items had no declarations of use in unconventional natural gas development (UNGD) activities. Ultimate source classification was assigned using chemical structure, compound class, knowledge of geogenic materials previously reported in oil and gas plays, understanding of potential utility in an UNGD operation (i.e., suspect fracking fluid), and putative transformation pathways with likely precursors (for metabolites).

Table S2. Quantitative outcome of volatile organic compound analysis. Analysis performed using a modified EPA Method 624 (see page S2). Italicized values are below the limit of quantification, but above the limit of detection. Sample names (A-F)

correspond to those used in Table S1 and Table 1 in the main text.

Target analyte	LOQ (µg/L)	A	B	C	D	E	F
1,1,1,2-Tetrachloroethane	0.4						
1,1,1-trichloroethane	4						
1,1,2,2-Tetrachloroethane	0.4						
1,1,2-Trichloroethane	2						
1,1-Dichloroethane	2						
1,1-Dichloroethene	2						
1,1-Dichloropropene	4						
1,2,3-Trichlorobenzene	2						
1,2,3-Trichloropropane	10						
1,2,4-Trichlorobenzene	1						
1,2,4-Trimethylbenzene	1		26.8 ± 1.8		0.9 ± 1.1		
1,2-Dibromo-3-chloropropane	20						
1,2-Dibromoethane (EDB)	4						
1,2-Dichlorobenzene	1						
1,2-Dichloroethane	0.8						
1,2-Dichloropropane	1						
1,3-Dichlorobenzene	1						
1,3-Dichloropropane	2						
1,4-Dichlorobenzene	0.4						4.3 ± 0.4
2,2-Dichloropropane	4						
2-Chlorotoluene	0.4						
4-Chlorotoluene	0.4						
4-Isopropyltoluene (p-Cymene)	1						
Benzene	0.8	*0.3 ± 0.1*			*0.1 ± 0.1*		
Bromobenzene	0.4						
Bromochloromethane	4						
bromodichloromethane	10						
bromoform	0.4						
carbon tetrachloride	40						
Chlorobenzene	0.8						
Chloroform	10						
cis-1,2-Dichloroethene	4						
cis-1,3-Dichloropropene	2						
dibromochloromethane	10						
Dibromomethane	10						
Ethylbenzene	0.8		7.3 ± 0.5				
Hexachlorobutadiene	10						
Isopropylbenzene (Cumene)	2		8.6 ± 0.8				
Methylene chloride	2						
m-Xylene,p-Xylene	0.4		2.6 ± 0.1				
Napthalene	1						
n-Butylbenzene	0.4						
n-Propylbenzene	4						
tert-Butylbenzene	1						
Tetrachloroethene	4						
Toluene	0.4		6.2 ± 0.2				
trans-1,2-Dichloroethene	2						
trans-1,3-Dichloropropene	4						
Trichloroethene	4						
sum GRO [µg/L]		5 ± 2 x 10^2	9 ± 1 x 10^2	4.1 ± 7.2	2.3 ± 2.6	1 ± 1 x 10^2	3.8 ± 0.3
sum DRO [mg/L] of LLE extracts		5.9 ± 1.8	13.8 ± 5.6	0.5 ± 0.1	0.3 ± 0.1	1.8 ± 1.0	1.9 ± 0.2

Toxicology and water treatment: Implications

In terms of toxicology and water treatment, the following can be stated: (1) Alcohols and carboxylic acids can be assumed to degrade quickly with exception of phenolic compounds: alkyl phenols are toxic and endocrine disrupting [1, 2] degradation product of alkylphenol polyethoxylates [3]. (2) Phthalates are non- to moderately persistent but may be problematic due to their sorption to soils with consequent partitioning into water[4].

Dibutyl phthalate, which was detected in two samples, is listed on the 2005 Priority List of Hazardous Substances for the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)[5]. (3) It is precarious that a nitrile serving as a radical initiator could still be detected because it entails the risk of ongoing and unwanted reactivity, leading to further halogenated compound formation. (4) Halogenated hydrocarbons are much more toxic than their parent compounds [6], particularly bromo-and chloroacetones are toxic, irritating gases, which exhibit their effects probably by alkylation of sulfhydryl (SH) -groups of enzymes [7]. Dihalomethanes are mutagenic and reactive [8], dichloromethane is even a suspect human carcinogen[9, 10]. One may presume that the general concentrations of iodoalkanes in UNGD wastewaters are very low up to not detectable. However, due to the substances' adverse health effects and low level of scientific examination so far, their occurrence should be investigated more in detail in future studies. (5) UNGD wastewater treatment that is often done by centralized waste treatment facilities (CWTF) only[11], bears the risk of compound survival, hence reaching rivers via effluent. Therefore, aerobic degradation should be implemented additionally, as it is necessary to cope with various organic compounds and to reduce environmental exposure scenarios.

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Table S1 appears on the following pages.

Table S1: Full list of mass spectral library matching-derived tentative identifications and putative compound origins. In columns labeled Sample A-F, a non-zero entry corresponds to detection in the respective sample. Y (yes) or N (no) indicates whether a positive confidence assignment (conf) could be made based on T (theoretical) or E (experimental) boiling points (bp). An entry of "N/A" represents a detection without available boiling point information. Note: Compounds are sorted according to confidence assignment (Y on top; i.e., those compounds that passed the retention time prediction) and alphabetical order of compound class.

CAS	Name	bp	type	conf	std ladder	disclosed	compound class	source	Sample A	Sample B	Sample C	Sample D	Sample E	Sample F
638-29-9	Pentanoyl chloride	109	E	y	n.alkanes	no	acyl chloride	Suspect Frack	y E	0	0	0	0	0
112-30-1	1-Decanol	231	E	y	n.alkanes	explicit	alcohol	Frack	y E	y E	0	0	y E	0
104-76-7	1-Hexanol, 2-ethyl-	185	E	y	n.alkanes	explicit	alcohol	Frack	y E	y E	y E, n E	0	0	0
68603-15-6	1-Octanol	195.1	E	y	n.alkanes	explicit	alcohol	Frack	y E	y E	0	0	0	0
112-70-9	1-Tridecanol	272.1	T	y	n.alkanes	explicit	alcohol	Frack	n T	n T	0	0	0	n T, y T
99328-46-8	5-Methyl-1-hepten-4-ol	172.7	T	y	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	y T	0	y T	0	y T	0
1131587-94-4	Cycloheptanemethanol	215.1	T	y	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	0	y T	0	0	0	0
1124-63-6	Cyclohexanepropanol-	218	T	y	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	y T	0	0	0	0	0
	Cyclopentane, 1-hydroxymethyl-1,3-dimethyl-	173.7	T	y	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	n T	y T, n T	n T	0	0	n T
6750-34-1	1-Dodecanol, 3,7,11-trimethyl-	279.2	T	y	n.alkanes	implicit	alcohol	Suspect Frack	y T	0	y T	0	0	n T, y T
143-08-8	1-Nonanol	213.3	E	y	n.alkanes	implicit	alcohol	Suspect Frack	0	y E	0	0	0	0
106-21-8	1-Octanol, 3,7-dimethyl-	213	E	y	n.alkanes	implicit	alcohol	Suspect Frack	0	y E	0	0	0	0
	1-Tridecyn-4-ol	297.4	T	y	n.alkanes	implicit	alcohol	Suspect Frack	0	0	0	0	0	y T
10522-26-6	2-Methyl-1-undecanol	245.5	T	y	n.alkanes	implicit	alcohol	Suspect Frack	0	0	0	0	0	y T
58175-57-8	2-Propyl-1-pentanol	179.2	T	y	n.alkanes	implicit	alcohol	Suspect Frack	0	0	0	y T	0	0
13432-25-2	3-Hexanol, 2,4-dimethyl-	163.5	T	y	n.alkanes	implicit	alcohol	Suspect Frack	0	0	0	0	y T	0
623-55-2	3-Hexanol, 5-methyl-	152.7	T	y	n.alkanes	implicit	alcohol	Suspect Frack	0	0	0	y T	0	0
589-98-0	3-Octanol	171	E	y	n.alkanes	implicit	alcohol	Suspect Frack	0	y E	0	0	0	0
584-02-1	3-Pentanol	114	E	y	n.alkanes	implicit	alcohol	Suspect Frack	0	0	y E	0	y E	0
565-67-3	3-Pentanol, 2-methyl-	126.5	E	y	n.alkanes	implicit	alcohol	Suspect Frack	0	y E	0	0	0	0
597-49-9	3-Pentanol, 3-ethyl-	142	E	y	n.alkanes	implicit	alcohol	Suspect Frack	0	0	y E	0	0	0
625-31-0	4-Penten-2-ol	116	E	y	n.alkanes	implicit	alcohol	Suspect Frack	0	0	0	0	y E	0
100-51-6	Benzyl Alcohol	205.3	E	y	n.alkanes	no	alcohol	Suspect Frack	0	y E	0	0	y E	0
1687-64-5	Phenol, 2-ethyl-6-methyl-	232.4	E	y	n.alkanes	no	alcohol	Suspect Frack	0	n E, y E	0	0	0	0
1138-52-9	Phenol, 3,5-bis(1,1-dimethylethyl)-	276.7	T	y	n.alkanes	no	alcohol	Suspect Frack	0	y T	0	0	0	0
140-66-9	Phenol, 4-(1,1,3,3-tetramethylbutyl)-	282.3	T	y	n.alkanes	no	alcohol	Suspect Frack	0	y T	0	0	0	0
98-54-4	Phenol, p-tert-butyl-	237	E	y	n.alkanes	no	alcohol	Suspect Frack	0	y E	0	0	0	0
100-52-7	Benzaldehyde	178	E	y	carbacids	no	aldehyde	Suspect Frack	y E	0	0	0	y E	0
1560-89-0	2-methylheptadecane (Chiron)	304.9	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
6418-44-6	3-methylheptadecane (Chiron)	313.4	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	n T	0	0	0	0
	Aromadendran ('2')	256.5	T	y	n.alkanes	no	alkane	Frack/Geogenic	0	y T	0	0	0	0
3891-98-3	C15 Isoprenoid Alkane (Farnesane)	249.1		y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y	y	y T	0	n T
3892-00-0	C18 Isoprenoid Alkane (Norpristane)	298.2	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T, y T	0	n T, y T	y T	y T	y T
1921-70-6	C19 Isoprenoid Alkane (Pristane)	296	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	y E	0	y E	y E	y E	y E
638-36-8	C20 Isoprenoid Alkane (Phytane)	322	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T, y T	n T	y T	0	0	y T
124-18-5	Decane	173	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	y E, n E	y E	y E	0	y E	y E
13151-73-0	Decane, 2-cyclohexyl-	293.1	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
6975-98-0	Decane, 2-methyl-	189.3	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E	n E	0	0	0
17312-54-8	Decane, 3,7-dimethyl-	203	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T, n T	0	0	0	0	0
62108-21-8	Decane, 6-ethyl-2-methyl-	217	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	0	0	0	y T, n T
112-40-3	Dodecane	216	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	y E	y E	0	0	y E	0
3891-98-3	Dodecane, 2,6,10-trimethyl-	249.1	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T, y T	n T	0	0	y T	y T
31295-56-4	Dodecane, 2,6,11-trimethyl-	247.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	n T	0	0	y T, n T
74645-98-0	Dodecane, 2,7,10-trimethyl-	249.1	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	n T	n T	0	0	y T, n T
1560-97-0	Dodecane, 2-methyl-	227.7	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T	n T	0	0	y T	y T, n T
17312-57-1	Dodecane, 3-methyl-	229.3	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	0	0	y T	y T	0
6117-97-1	Dodecane, 4-methyl-	227.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	y T
6044-71-9	Dodecane, 6-methyl-	224.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	y T
112-95-8	Eicosane	343	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	n E	y E, n E	0	0	0	n E
593-49-7	Heptacosane	463.8	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E, n E	0	0	0	0
629-78-7	Heptadecane	302	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	y E	0	0	y E	y E	0
26429-11-8	Heptadecane, 4-methyl-	312.6	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	0	0	0	0	0
20959-33-5	Heptadecane, 7-methyl-	308.7	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
13287-23-5	Heptadecane, 8-methyl-	306.2	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
4032-93-3	Heptane, 2,3,6-trimethyl-	156	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E	0	0	0	0
592-27-8	Heptane, 2-methyl-	117.6	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E	0	0	0	0
	Heptane, 3-ethyl-5-methylene-	161	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	y T	0	0	0
544-76-3	Hexadecane	287	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	n E, y E	y E, n E	n E, y E	y E	y E	y E, n E
1560-92-5	Hexadecane, 2-methyl-	291.4	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	y T	0	0	0	0
26730-20-1	Hexadecane, 7-methyl-	292.1	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
	n-C13	235	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	0	y E	0	0	0	0
	n-C14	253	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	0	y E	0	0	0	0
	n-C16	287	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	n E	n E, y E	0	0	0	0
	n-C18	317	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	y E	n E	0	0	0	0
	n-C19	330.5	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	n E	n E, y E	0	0	0	0
	n-C20	342.7	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	y E	n E, y E	0	0	0	0
	n-C21	356.1	T	y	n.alkanes	explicit	alkane	Frack/Geogenic	0	0	0	y T	0	0
	n-Nonylcyclohexane	282.6	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	y T	0	0	0	y T
629-92-5	Nonadecane	330.5	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E, n E	0	y E	0	0
1560-86-7	Nonadecane, 2-methyl-	329.7	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
111-84-2	Nonane	151	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	y E	y E	0	0	0	0
17302-28-2	Nonane, 2,6-dimethyl-	180.6	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	n T
871-83-0	Nonane, 2-methyl-	167.1	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E	0	0	0	0
17302-32-8	Nonane, 3,7-dimethyl-	183.3	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
	Nonane, 3-methyl-	167.9	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
6006-33-3	n-Tridecylcyclohexane	345.7	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	n T, y E	0	0	0	0
593-45-3	Octadecane	317	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E, n E	0	y E	0	0
1560-88-9	Octadecane, 2-methyl-	317.7	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
10544-95-3	Octadecane, 4-methyl-	325.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
25117-35-5	Octadecane, 5-methyl-	325.2	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
111-65-9	Octane	125.5	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	y E	y E	0	0	y E	0
62016-28-8	Octane, 2,2,6-trimethyl-	172.3	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	y T	0
62016-37-9	Octane, 2,4,6-trimethyl-	172.2	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
	Octane, 2-cyclohexyl-	256.9	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T, y T	0	0	0	0	y T
62183-55-5	Octane, 3-ethyl-2,7-dimethyl-	198.6	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T, n T	0	0	0	0	0
2216-34-4	Octane, 4-methyl-	142.4	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E	0	0	0	0
62016-19-7	Octane, 6-ethyl-2-methyl-	181.2	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
629-62-9	Pentadecane	269.5	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	y E	y E, n E	0	y E	y E	y E
3892-00-0	Pentadecane, 2,6,10-trimethyl-	298.2	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
1560-93-6	Pentadecane, 2-methyl-	282	E	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y E	0	0	0	0
2882-96-4	Pentadecane, 3-methyl-	282.7	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	y T
629-59-4	Tetradecane	253	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	n E, y E	n E, y E	0	y E	n E, y E	y E
1560-95-8	Tetradecane, 2-methyl-	261.6	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	0	0	0	0	y T
18435-22-8	Tetradecane, 3-methyl-	265.1	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	y T	0	0	y T	y T
25117-24-2	Tetradecane, 4-methyl-	263.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	n T, y T
25117-32-2	Tetradecane, 5-methyl-	262.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	y T
629-50-5	Tridecane	234.5	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	y E	n E	n E	0	y E	y E
1560-96-9	Tridecane, 2-methyl-	245.2	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T, n T	y T	0	0	y T	y T
13286-73-2	Tridecane, 3-ethyl-	265.6	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	0	0	0	0	0
6418-41-3	Tridecane, 3-methyl-	248.7	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	y T	y T	y T	y T
55030-62-1	Tridecane, 4,8-dimethyl-	256.1	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	y T	0
26730-12-1	Tridecane, 4-methyl-	247.4	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	n T	y T	0	0	0	y T
25117-31-1	Tridecane, 5-methyl-	246.3	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	y T	0	0	0	0
13287-21-3	Tridecane, 6-methyl-	244.6	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	y T
1120-21-4	Undecane	196	E	y	n.alkanes	explicit	alkane	Frack/Geogenic	y E, n E	n E, y E	0	0	0	n E
17301-23-4	Undecane, 2,6-dimethyl-	218.9	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	y T	0	y T	y T
17301-26-7	Undecane, 2,9-dimethyl-	223.3	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
7045-71-8	Undecane, 2-methyl-	208.9	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	y T	n T	0	0	0
17312-81-1	Undecane, 3,5-dimethyl-	219.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	y T
1002-43-3	Undecane, 3-methyl-	210.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	n T	n T	0	0	n T
2980-69-0	Undecane, 4-methyl-	209.2	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	y T	0	0	0	0	0
17453-94-0	Undecane, 5-ethyl-	223.8	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	y T
632-70-8	Undecane, 5-methyl-	207.9	T	y	n.alkanes	implicit	alkane	Frack/Geogenic	0	y T	0	0	0	0
544-25-2	1,3,5-Cycloheptatriene	117	E	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	y E	0	0	y E
	1,3,5-Cycloheptatriene, 2,4-diethyl-7,7-dimethyl-	232	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	0
21195-59-5	1,3,8-p-Menthatriene	196.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	0
	1,6,9-Tetradecatriene	256.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	0
	1,9-Tetradecadiene	248.8	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	0
	1,E-8,Z-10-Pentadecatriene	278.3	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	0
1599-67-3	1-Docosene	364.6	E	y	n.alkanes	implicit	alkene	Frack/Geogenic	n E	n E, y E	n E	0	0	n E
18435-45-5	1-Nonadecene	329	E	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y E, n E	0	y E	0	0
74630-38-9	1-Undecene, 5-methyl-	205	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	y T, n T	0	0	0	0	n T

700000-97-1	2,3,3-Trimethyl-1-hexene	132	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	y T	0	y T	0
51174-12-0	2,4,4-Trimethyl-1-hexene	132	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	y T	0	0	0
51655-65-3	2-Butyl-1-decene	249.1	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	y T	0	0	0	0	0
41446-59-7	2-Tridecene, (Z)-	235.3	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	0	0	0	y T
28980-74-7	3,5-Dodecadiene, 2-methyl-	235.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	0
7206-14-6	3-Dodecene, (E)-	212.2	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	0
19781-34-1	3-Ethyl-3-phenyl-1-pentene	229.7	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T, n T	0	0	0	0
34303-81-6	3-Hexadecene, (Z)-	288.1	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	y T	0	0	0	0	0
7206-19-1	3-Octadecene, (E)-	322.2	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	0	y T	0	n T
41446-68-8	3-Tetradecene, (E)-	251.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	n T, y T	y T	0	0	0	y T
41446-57-5	3-Tridecene, (E)-	232.3	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	y T	0	0	0	0	y T
	3-Undecene, 9-methyl-, (E)-	207.4	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	n T
41446-78-0	4-Tetradecene, (E)-	251.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	y T	0	0	0
41446-65-5	4-Tetradecene, (Z)-	251.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	y T	0	0	0	0	y T
41446-66-6	5-Tetradecene, (E)-	251.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	0	0	0	y T
23051-84-5	5-Tridecene, (E)-	232.3	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	n T, y T	y T	0	0	0	0
25524-42-9	5-Tridecene, (Z)-	232.3	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	y T	0	0	0	0	n T
764-96-5	5-Undecene, (Z)-	192.3	E	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y E	0	0	0	0
10374-74-0	7-Tetradecene	251.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	y T	0	0	0
41446-60-0	7-Tetradecene, (Z)-	251.6	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	0	y T
54290-12-9	8-Heptadecene	305.4	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	y T	0	0	0	0	0
7206-25-9	9-Octadecene, (E)-	322.2	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	y T	0	0	n T
1501-82-2	Cyclododecene	240	E	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y E	0	0	0	0
	Cyclohexane, (2-ethyl-1-methyl-1-butenyl)-	238.9	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	y T	0	0	0	0	0
	Cyclohexane, (2-ethyl-1-methylbutylidene)-	237.5	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	0	y T	0	0	0	0
24524-53-6	Hexane, 1-(isopropylidenecyclopropyl)-	211.3	T	y	n.alkanes	implicit	alkene	Frack/Geogenic	n T	y T	0	0	0	0
629-89-0	1-Octadecyne	313	E	y	n.alkanes	implicit	alkyne	Frack/Geogenic	0	0	0	0	0	y E
638-60-8	2-Tetradecyne	252.5	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	y T	0	0	0	0	0
61886-62-2	3-Hexadecyne	287	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	y T	n T	0	0	0	0
61886-64-4	3-Octadecyne	315.4	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	0	y T	0	0	0	0
60212-33-1	4-Tetradecyne	255.4	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	0	y T	0	0	0	y T
	7-Pentadecyne	272.7	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	0	n T, y T	0	0	0	0
35216-11-6	7-Tetradecyne	255.4	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	y T, n T	y T	0	0	0	0
19781-86-3	8-Hexadecyne	289.3	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	n T	n T, y T	0	0	0	0
71899-38-2	9-Eicosyne	351.3	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	0	y T	0	0	0	0
35365-59-4	9-Octadecyne	321.2	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	y T	0	0	0	y T	y T
1129-90-4	Cyclododecyne	247.7	T	y	n.alkanes	implicit	alkyne	Frack/Geogenic	0	n T, y T	0	0	0	0
	N,N,O-Triacetylhydroxylamine	211.1	T	y	n.alkanes	implicit	amine	Frack	0	0	n T, y T	0	0	0
1538-75-6	2,2-Dimethylpropanoic anhydride	193	E	y	n.alkanes	no	anhydride	Suspect Frack	y E	0	0	0	n E	0
1468-39-9	2-Methylbutanoic anhydride	215	E	y	n.alkanes	no	anhydride	Suspect Frack	y E	0	0	0	0	0
2082-59-9	Valeric anhydride	227	E	y	n.alkanes	no	anhydride	Suspect Frack	y E	0	0	0	0	0
7383-90-6	1,1'-Biphenyl, 3,4'-dimethyl-	289	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
643-93-6	1,1'-Biphenyl, 3-methyl-	272.7	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
	1,4,6,7-Tetramethyl1,2,3,4-tetrahydronaphthaler	278	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
2471-83-2	1H-Indene, 1-ethylidene-	237.2	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T	0	0	0	0
	1H-Indene, 1-methyl-3-propyl-	265.7	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T	0	0	0	0
40650-41-7	1H-Indene, 2,3-dihydro-1,1,5-trimethyl-	217.2	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T, n T	0	0	0	0
14276-95-0	1H-Indene, 2,3-dihydro-1,1,6-trimethyl-	212.8	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T	0	0	0	0
4912-92-9	1H-Indene, 2,3-dihydro-1,1-dimethyl-	191	E	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y E	0	0	0	0
4175-53-5	1H-Indene, 2,3-dihydro-1,3-dimethyl-	208.7	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T	0	0	0	0
17059-48-2	1H-Indene, 2,3-dihydro-1,6-dimethyl-	213.5	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T	0	0	0	0
6682-71-9	1H-Indene, 2,3-dihydro-4,7-dimethyl-	226.6	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T	0	0	0	0
	1H-Indene, 2,3-dihydro-4-propyl-	234.5	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T	0	0	0	0
874-35-1	1H-Indene, 2,3-dihydro-5-methyl-	202	E	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y E	0	0	0	0
54832-83-6	1H-Indene, octahydro-2,2,4,4,7,7-hexamethyl-, tr	239.4	T	y	n.alkanes	no	aromatic	Frack/Geogenic	y T	0	y T	0	y T	y T
1595-10-4	1-Methyl-2-n-hexylbenzene	247.5	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
605-39-0	2,2'-Dimethylbiphenyl	259	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	n E, y E	0	0	0	0
2234-20-0	2,4-Dimethylstyrene	206	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
	9-Methyl-S-octahydrophenanathracene	314	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
480-72-8	Acenaphthylene, 1,2,2a,3,4,5-hexahydro-	249	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
1079-71-6	Anthracene, 1,2,3,4,5,6,7,8-octahydro-	305.6	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
	Anthracene, 1,2,3,4,5,6,7,8-octahydro-1-methyl-	317.1	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	n T, y T	0	0	0	0
2049-95-8	Benzene, (1,1-dimethylpropyl)-	192.4	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
19219-84-2	Benzene, (1,3-dimethylbutyl)-	207.7	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T, n T	0	0	0	0
4413-16-5	Benzene, (1-cyclohexylethyl)-	265	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
1985-97-3	Benzene, (1-ethyl-1-methylpropyl)-	205	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
4701-36-4	Benzene, (1-ethyl-1-propenyl)-	204	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
98-82-8	Benzene, (1-methylethyl)-	153	E	y	n.alkanes	explicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
135-98-8	Benzene, (1-methylpropyl)-	173.5	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
	Benzene, (2,4-dimethylcyclopentyl)-	244.5	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
4410-75-7	Benzene, (cyclohexylmethyl)-	255.6	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
538-86-3	Benzene, (methoxymethyl)-	170	E	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y E	0	0	0	0
1746-23-2	Benzene, 1-(1,1-dimethylethyl)-4-ethenyl-	219	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
	Benzene, 1-(1-formylethyl)-4-(1-buten-3-yl)-	269.8	T	y	n.alkanes	no	aromatic	Frack/Geogenic	0	y T	0	0	0	0
	Benzene, 1-(1-methyl-2-propenyl)-4-(2-methylpr	250.3	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
5557-93-7	Benzene, 1-(1-methylethenyl)-2-(1-methylethyl)-	223	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
1129-29-9	Benzene, 1-(1-methylethenyl)-3-(1-methylethyl)-	219.9	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
526-73-8	Benzene, 1,2,3-trimethyl-	176.1	E	y	n.alkanes	explicit	aromatic	Frack/Geogenic	0	y E, n E	0	0	0	0
95-93-2	Benzene, 1,2,4,5-tetramethyl-	196.8	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
877-44-1	Benzene, 1,2,4-triethyl-	218	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
10222-95-4	Benzene, 1,2,4-trimethyl-5-(1-methylethyl)-	221	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
	Benzene, 1,3,5-trimethyl-2-propyl-	232.1	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
4706-90-5	Benzene, 1,3-dimethyl-5-(1-methylethyl)-	193.9	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
13632-94-5	Benzene, 1,4-diethyl-2-methyl-	206.7	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
4132-72-3	Benzene, 1,4-dimethyl-2-(1-methylethyl)-	196.2	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
55669-88-0	Benzene, 1,4-dimethyl-2-(2-methylpropyl)-	222.5	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
4575-46-6	Benzene, 1-cyclohexyl-3-methyl-	262.6	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
4920-99-4	Benzene, 1-ethyl-3-(1-methylethyl)-	192.5	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
620-14-4	Benzene, 1-ethyl-3-methyl-	161.3	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
4218-48-8	Benzene, 1-ethyl-4-(1-methylethyl)-	197.1	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
54410-74-1	Benzene, 1-methyl-2-(1-ethylpropyl)-	217.4	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
535-77-3	Benzene, 1-methyl-3-(1-methylethyl)-	175.1	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
1595-03-5	Benzene, 1-methyl-3-hexyl-	245.1	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
99-87-6	Benzene, 1-methyl-4-(1-methylethyl)-	177.1	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
1595-16-0	Benzene, 1-methyl-4-(1-methylpropyl)-	195.9	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T, n T	0	0	0	0
	Benzene, 1-methyl-4-(2-methylpropyl)-	196	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
826-18-6	Benzene, 1-pentenyl-	217	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
1758-88-9	Benzene, 2-ethyl-1,4-dimethyl-	186.9	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
104-51-8	Benzene, butyl-	183.3	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
827-52-1	Benzene, cyclohexyl-	240.1	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
1077-16-3	Benzene, hexyl-	226.1	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
1081-77-2	Benzene, nonyl-	280.5	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
2189-60-8	Benzene, octyl-	264.5	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
700-12-9	Benzene, pentamethyl-	232	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
538-68-1	Benzene, pentyl-	205.4	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
103-65-1	Benzene, propyl-	159.2	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
101-81-5	Diphenylmethane	265	E	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
100-41-4	Ethylbenzene	136.1	E	y	n.alkanes	explicit	aromatic	Frack/Geogenic	0	y E	0	0	0	0
767-58-8 and	Indan, 1-methyl-	193.4	T	y	n.alkanes	implicit	aromatic	Frack/Geogenic	0	y T	0	0	0	0
106-42-3	p-Xylene	137.5	E	y	n.alkanes	explicit	aromatic	Frack/Geogenic	0	n E, y E	0	0	0	0
108-88-3	Toluene	111	E	y	n.alkanes	explicit	aromatic	Frack/Geogenic	y E	y E	0	0	y E	0
	(R)-(-)-4-Methylhexanoic acid	215.3	T	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y T	0	0	0	0
1871-67-6	2-Octenoic acid	260.2	T	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y T	0	0	0	0
626-98-2	2-Pentenoic acid	204.7	T	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y T	0	0	0	0	0
65-85-0	Benzoic acid	249	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E	y E	0	0	0	0
107-92-6	Butanoic acid	164	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E	y E	0	0	y E	0
116-53-0	Butanoic acid, 2-methyl-	175.5	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E	y E	0	0	y E	0
503-74-2	Butanoic acid, 3-methyl-	176	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E	y E	0	0	y E	0
143-07-7	Dodecanoic acid	298.9	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y E	0	0	0	0
111-14-8	Heptanoic acid	222.5	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E	y E	0	0	y E	0
2416-20-8	Hexadecenoic acid, Z-11-	368.9	T	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y T	0	0	0	0
142-62-1	Hexanoic acid	202.5	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y E	0	0	y E	0
149-57-5	Hexanoic acid, 2-ethyl-	227.5	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y E	0	0	0	0

334-48-5	n-Decanoic acid	268.7	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E	y E	0	0	y E	0
112-05-0	Nonanoic acid	254	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y E	0	0	0	0
124-07-2	Octanoic Acid	237	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E	y E	0	0	y E	0
109-52-4	Pentanoic acid	185	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E, n E	y E, n E	0	0	y E	0
79-31-2	Propanoic acid, 2-methyl-	153.5	T	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y T	0	0	0	0
544-63-8	Tetradecanoic acid	326	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	y E	0	0	0	0
112-37-8	Undecanoic acid	280	E	y	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	y E	n E	0	0	0	0
54105-77-0	(2-Methylbutyl)cyclohexane	197.2	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	1,1,6,6-Tetramethylspiro[4.4]nonane	220	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
92-51-3	1,1'-Bicyclohexyl	227	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y E	y E	0	0	0	0
50991-12-3	1,1'-Bicyclohexyl, 2-ethyl-, cis-	264.1	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
50991-13-4	1,1'-Bicyclohexyl, 2-ethyl-, trans-	264.1	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	0
50991-08-7	1,1'-Bicyclohexyl, 2-methyl-, cis-	245	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	y T
50991-09-8	1,1'-Bicyclohexyl, 2-methyl-, trans-	245	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T, n T	y T, n T	0	0	0	y T
54823-98-3	1,1'-Bicyclohexyl, 4,4'-dimethyl-	257.6	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	y T
	1,1'-Bicyclohexyl, 4-methyl-4'-propyl-	294	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	1,3,4-Trimethyladamantane	214.1	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
707-35-7	1,3,5-Trimethyladamantane	207.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
645-10-3	1,7-Dimethyl-4-(1-methylethyl)cyclodecane	270.4	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T, y T	n T, y T	n T, y T	0	0	n T
	1H-Fluorene, dodecahydro-	253.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T, y T	0	0	0	0
1687-34-9	1-Methyl-3-ethyladamantane	220.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	9-Methyltetracyclo[7.3.1.0(2.7).1(7.11)]tetradeca	280.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
702-79-4	Adamantane, 1,3-dimethyl-	201	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y E	0	0	0	0
	Bicyclo[4.1.0]heptane, 3-methyl-7-pentyl-	233.2	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
41977-45-1	Bicyclo[4.1.0]heptane, 7-pentyl-	219.7	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	0	0	0	0	0
1618-23-1	cis, cis-3-Ethylbicyclo[4.4.0]decane	225.4	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	cis,cis,cis-1-Isobutyl-2,5-dimethylcyclohexane	205.8	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	cis-anti-trans-Tricyclo[7.3.0.0(2,6)]dodecane	232.4	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
14398-71-1	cis-Decalin, 2-syn-methyl-	204.6	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T, y T	0	0	0	0
	Cyclohexane, (1,3-dimethylbutyl)-	212.8	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
61142-38-9	Cyclohexane, (3-methylpentyl)-	218.1	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	y T, n T	0	0	0	y T
4431-89-4	Cyclohexane, (cyclopentylmethyl)-	231.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
29799-19-7	Cyclohexane, 1-(1,5-dimethylhexyl)-4-methyl-	265.3	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	0	0	0	0	y T
54823-95-9	Cyclohexane, 1-(cyclohexylmethyl)-3-methyl-, tra	264.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T, y T	y T	0	0	0	0
54823-97-1	Cyclohexane, 1-(cyclohexylmethyl)-4-methyl-, cis	264.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	0
6165-44-2	Cyclohexane, 1,1'-(1,4-butanediyl)bis-	305	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y E	0	0	0	0
41851-35-8	Cyclohexane, 1,1'-(1-methyl-1,3-propanediyl)bis-	302.3	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
54965-05-8	Cyclohexane, 1,1,3-trimethyl-2-(3-methylpentyl)-	255.3	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
3178-23-2	Cyclohexane, 1,1'-methylenebis-	252.7	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T, y T	n T, y T	0	0	0	y T
	Cyclohexane, 1,5-diisopropyl-2,3-dimethyl-	235.4	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	0	0	0	0	0
	Cyclohexane, 1-ethyl-1,3-dimethyl-, cis-	162.6	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	y T, n T	0	0	0	n T
	Cyclohexane, 1-ethyl-1,3-dimethyl-, trans-	162.6	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	y T, n T	n T	0	0	n T
62238-33-9	Cyclohexane, 1-ethyl-2-propyl-	196.3	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
16580-26-0	Cyclohexane, 1-isopropyl-1-methyl-	163.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	y T, n T	n T	0	0	0
16580-24-8	Cyclohexane, 1-isopropyl-3-methyl-, trans-	166.5	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y E	0	0	y E	0
54411-01-7	Cyclohexane, 1-methyl-2-pentyl-	216.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T, n T	y T, n T	n T	0	0	n T
4291-79-6	Cyclohexane, 1-methyl-2-propyl-	176	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	y E, n E	0	0	0	n E
	Cyclohexane, 1-methyl-3-pentyl-	216.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	0
54411-00-6	Cyclohexane, 1-methyl-4-(1-methylbutyl)-	211.6	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T, n T	y T, n T	0	0	0	n T
54676-39-0	Cyclohexane, 2-butyl-1,1,3-trimethyl-	221	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	Cyclohexane, 3-ethyl-5-methyl-1-propyl-	211	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	y T
1678-93-9	Cyclohexane, butyl-	180.9	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y E	0	0	0	0
1795-16-0	Cyclohexane, decyl-	299	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y E	0	0	n E	0
4292-75-5	Cyclohexane, hexyl-	224	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y E	y E	0	0	0	0
1795-15-9	Cyclohexane, octyl-	264	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y E, n E	0	y E, n E	0	0	y E
4292-92-6	Cyclohexane, pentyl-	203.7	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y E	0	0	0	0
54105-66-7	Cyclohexane, undecyl-	315.8	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	n T	0	0	n T	0
15232-85-6	Cyclohexene, 1-pentyl-	203.6	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
15232-86-7	Cyclohexene,1-heptyl-	243.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
21524-26-5	Cyclohexene,4-butyl-	178.2	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
16538-89-9	Cyclooctane, (1-methylpropyl)-	221.3	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T, n T	n T	0	0	0	y T, n T
23609-46-3	Cyclooctane, 1,2-diethyl-	220.6	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	0
	Cyclopentadecanone, 2-methyl-	329.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
4413-21-2	Cyclopentane, 1,1'-ethylidenebis-	223.7	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T, n T	0	0	0	0
62199-52-4	Cyclopentane, 1,2-dibutyl-	235.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	0	0	0	0	0
61142-68-5%	Cyclopentane, 1-hexyl-3-methyl-	215.2	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	n T	n T	0	0	n T
62199-51-3	Cyclopentane, 1-pentyl-2-propyl-	235.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T, n T	0	0	0	0
4457-00-5	Cyclopentane, hexyl-	203	E	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y E, n E	n E, y E	0	0	0	n E
	Cyclopentene, 5-hexyl-3,3-dimethyl-	222.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	0
1606-08-2	Cyclopentylcyclohexane	215.1	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
295-17-0	Cyclotetradecane	280.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	n T	0	0	0	0
80655-44-3	Decahydro-4,4,8,9,10-pentamethylnaphthalene	248.9	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
14398-67-5	Decalin, syn-1-methyl-, cis-	210	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T, y T	0	0	0	0
	Dispiro[4.2.4.2]tetradecane	284.7	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T, y T	0	0	0	0
2292-79-7	Pentacyclo[7.3.1.1.(4,12).0(2,7).0(6,11)]tetradeca	269.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
5743-97-5	Phenanthrene, tetradecahydro-	273.7	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	y T	0	0	0	0
2435-85-0	Pyrene, hexadecahydro-	318.5	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T, y T	0	0	0	0
	Tetradecahydro-1-methylphenanthrene	284.8	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	y T	n T, y T	0	0	0	0
28071-99-0	trans-anti-trans-Tetra-decahydroanthracene	273.7	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	Tricyclo[4.4.1.0(1,6)]undecane	223.2	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
53485-49-7	Tricyclo[6.4.0.0(2,7)]dodecane	232.4	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	Tricyclo[7.3.0.0(2,6)]dodecane, trans-anti-trans-	232.4	T	y	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	y T	0	0	0	0
	Bicyclo[10.1.0]tridec-1-ene	268.3	T	y	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	y T	n T	0	0	0	0
156747-45-4	Isolongifolene, 4,5,9,10-dehydro-	281.8	T	y	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	0	y T	0	0	0	0
	Neoisolongifolene, 8,9-dehydro-	271.4	T	y	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	0	y T	0	0	0	0
	Tetracyclo[3.3.1.0(2,8).0(4,6)]-non-2-ene	181	T	y	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	0	y T	0	0	0	0
	Tetracyclo[4.2.1.0(3,7).0(2,9)]non-4-ene, 4-butyl-	237.7	T	y	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	0	y T	0	0	0	0
	Tricyclo[4.2.2.0(2,5)]dec-7-ene, 7-butyl-	261.5	T	y	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	0	y T	0	0	0	0
286-20-4	7-Oxabicyclo[4.1.0]heptane	129.5	E	y	n.alkanes	no	epoxide	Suspect Frack	0	0	y E	0	0	0
706-14-9	2(3H)-Furanone, 5-hexyldihydro-	304.4	E	y	n.alkanes	no	ester	Suspect Frack	n E	n E, y E	0	0	0	0
104-61-0	2(3H)-Furanone, dihydro-5-pentyl-	266.6	T	y	n.alkanes	no	ester	Suspect Frack	0	y T	0	0	0	0
705-86-2	2H-Pyran-2-one, tetrahydro-6-pentyl-	267.2	T	y	n.alkanes	no	ester	Suspect Frack	0	y T	0	0	0	0
72218-58-7	3-Methylheptyl acetate	195.7	T	y	n.alkanes	no	ester	Suspect Frack	0	0	y T	0	0	0
	Acetic acid, trifluoro-, 3,7-dimethyloctyl ester	233.7	T	y	n.alkanes	no	ester	Suspect Frack	n T	0	0	0	0	y T, n T
124-10-7	Methyl tetradecanoate	295	E	y	n.alkanes	no	ester	Suspect Frack	0	y E	0	0	0	0
	Oxalic acid, allyl hexadecyl ester	428.4	T	y	n.alkanes	no	ester	Suspect Frack	n T	n T, y T	n T	0	0	n T
	Oxalic acid, allyl octadecyl ester	455.5	T	y	n.alkanes	no	ester	Suspect Frack	n T, y T	n T, y T	n T	0	0	n T
	Oxalic acid, allyl pentadecyl ester	414.4	T	y	n.alkanes	no	ester	Suspect Frack	n T, y T	y T	n T	0	0	0
	Oxalic acid, butyl cyclohexylmethyl ester	317.3	T	y	n.alkanes	no	ester	Suspect Frack	n T	y T, n T	n T	0	0	0
	Valeric acid, 4-tridecyl ester	326.5	T	y	n.alkanes	no	ester	Suspect Frack	0	y T	0	0	0	0
123-20-6	Vinyl butyrate	116	E	y	n.alkanes	no	ester	Suspect Frack	0	0	y E	0	y E	0
4359-46-0	1,3-Dioxolane, 2-ethyl-4-methyl-	117	E	y	n.alkanes	no	ether	Suspect Frack	0	0	0	0	y E	0
73105-67-6%	1-Iodo-2-methylundecane	297	T	y	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	y T, n T	0	0	0	0	y T, n T
18420-41-2	2-(Chloromethyl)tetrahydropyran	181.6	E	y	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	y E	0	0	0	0	0
998-93-6	4-Bromoheptane	178.6	E	y	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	y E	0	0	0
56325-56-5	Cyclodecene, 3-bromo-	241.5	T	y	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	y T, n T	n T, y T	0	0	0	0
3377-86-4	Hexane, 2-bromo-	144	E	y	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	y E	0	0	0
60274-60-4	Pentane, 1-chloro-5-iodo-	227.6	T	y	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	0	0	y T	0
19218-94-1	Tetradecane, 1-iodo-	329.7	T	y	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	n T	0	n T	0	0	y T
66542-51-6	Chloromethyl hexanoate	178.8	T	y	n.alkanes	no	halogenated	Suspect Frack	0	y T	0	0	y T	0
61413-70-5	Chloromethyl octanoate	221.3	T	y	n.alkanes	no	halogenated	Suspect Frack	0	y T	0	0	0	0
77877-94-2	Chloromethyl pentanoate	155.9	T	y	n.alkanes	no	halogenated	Suspect Frack	y T	y T	0	0	0	0
5402-53-9	Chloromethyl propanoate	105.7	T	y	n.alkanes	no	halogenated	Suspect Frack	0	y T	0	0	y T	0
95-16-9	Benzothiazole	231	E	y	n.alkanes	no	heterocycle	Frack/Geogenic	0	y E	0	0	0	0
3777-69-3	Furan, 2-pentyl-	167	E	y	n.alkanes	no	heterocycle	Frack/Geogenic	0	y E	0	0	0	0
	Furan, tetrahydro-2,2-dimethyl-5-(1-methylethyl	148	T	y	n.alkanes	no	heterocycle	Frack/Geogenic	0	0	y T	0	0	0
10317-17-6	Oxetane, 3-(1-methylethyl)-	99.6	T	y	n.alkanes	no	heterocycle	Frack/Geogenic	y T	0	0	0	0	0
	1,1,3a-Trimethyl-1a,3a,5,6-tetrahydro-1H-cyclop	243.2	T	y	n.alkanes	no	ketone	Suspect Frack	0	y T	0	0	0	0
	1,2,3,5,6,7-Hexahydro-inden-4-one	254.3	T	y	n.alkanes	no	ketone	Suspect Frack	0	y T	0	0	0	0
1660-04-4	1-Adamantyl methyl ketone	262.3	T	y	n.alkanes	no	ketone	Suspect Frack	0	y T	0	0	0	0
93-55-0	1-Propanone, 1-phenyl-	217.5	E	y	n.alkanes	no	ketone	Suspect Frack	0	0	y E	0	0	0
17429-36-6	2-Cyclohexen-1-one, 4-methyl-4-phenyl-	254.1	T	y	n.alkanes	no	ketone	Suspect Frack	0	y T, n T	0	0	0	0
821-55-6	2-Nonanone	195	E	y	n.alkanes	no	ketone	Suspect Frack	0	y E	n E	0	0	0

106-35-4	3-Heptanone	147	E	y	n.alkanes	no	ketone	Suspect Frack	0	0	y E	0	0	0
115-22-0	3-Hydroxy-3-methyl-2-butanone	140.5	E	y	n.alkanes	no	ketone	Suspect Frack	0	0	0	0	y E	0
1075-06-5	Ethanone, 2,2-dihydroxy-1-phenyl-	212.8	E	y	n.alkanes	no	ketone	Suspect Frack	y E	y E	0	0	0	0
	Spiro[2.3]hexan-5-one, 4,4-diethyl-	209.8	T	y	n.alkanes	no	ketone	Suspect Frack	0	y T	0	0	0	0
119-64-2	Naphthalene, 1,2,3,4-tetrahydro-	207.6	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E	0	0	0	0
475-03-6	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	240	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E, n E	0	0	0	0
1985-59-7	Naphthalene, 1,2,3,4-tetrahydro-1,1-dimethyl-	221.5	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
4175-54-6	Naphthalene, 1,2,3,4-tetrahydro-1,4-dimethyl-	234.4	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
25419-33-4	Naphthalene, 1,2,3,4-tetrahydro-1,8-dimethyl-	241.7	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n T, y T	0	0	0	0
1559-81-5	Naphthalene, 1,2,3,4-tetrahydro-1-methyl-	220.6	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E	0	0	0	0
23342-25-8	Naphthalene, 1,2,3,4-tetrahydro-2,2,5,7-tetrame	266.6	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
30316-17-7	Naphthalene, 1,2,3,4-tetrahydro-2,5,8-trimethyl-	261.9	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
3877-19-8	Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	221	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E	0	0	0	0
21693-54-9	Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	250	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
2809-64-5	Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	234	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E	0	0	0	0
42775-77-9	Naphthalene, 1,2,3,4-tetrahydro-6-propyl-	264.8	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n T, y T	0	0	0	0
2245-38-7	Naphthalene, 1,6,7-trimethyl-	285	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E, n E	0	0	0	0
490-65-3	Naphthalene, 1-methyl-7-(1-methylethyl)-	284.2	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
2027-17-0	Naphthalene, 2-(1-methylethyl)-	268	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E	0	0	0	0
6305-52-8	Naphthalene, 2-butyldecahydro-	263.9	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	y T	y T	0	0	0	y T
939-27-5	Naphthalene, 2-ethyl-	258	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E	0	0	0	0
32367-54-7	Naphthalene, 2-ethyl-1,2,3,4-tetrahydro-	235	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E	0	0	0	0
1618-23-1	Naphthalene, 2-ethyldecahydro-	225.4	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	y T	y T	0	0	0	0
55682-81-0	Naphthalene, 3-(1,1-dimethylethyl)-1,2-dihydro-	262.9	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
42775-75-7	Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-	245	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E, n E	0	0	0	0
30654-45-6	Naphthalene, 6-butyl-1,2,3,4-tetrahydro-	282.5	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n T, y T	0	0	0	0
22531-20-0	Naphthalene, 6-ethyl-1,2,3,4-tetrahydro-	244	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E, n E	0	0	0	0
493-02-7	Naphthalene, decahydro-, trans-	187.3	E	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y E	0	0	0	0
66552-62-3	Naphthalene, decahydro-1,5-dimethyl-	218.3	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
1750-51-2	Naphthalene, decahydro-1,6-dimethyl-	218.3	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	y T	y T	0	0	0	0
29788-41-8	Naphthalene, decahydro-1,6-dimethyl-4-(1-meth	265.1	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n T	0	0	0	y T
	Naphthalene, decahydro-2,3-dimethyl-	213.6	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
1618-22-0	Naphthalene, decahydro-2,6-dimethyl-	218.3	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
2958-76-1	Naphthalene, decahydro-2-methyl-	204.6	T	y	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	y T	0	0	0	0
3333-52-6	Tetramethylbutanedinitrile	264.2	T	y	n.alkanes	no	nitrile	Metab./Subsurf. Rxn.	0	0	0	0	y T	0
78-67-1	Propanenitrile, 2,2'-azobis[2-methyl-	236.3	T	y	n.alkanes	no	nitrile	Suspect Frack	0	y T	0	0	0	0
84-69-5	1,2-Benzenedicarboxylic acid, bis(2-methylpropy	327	E	y	n.alkanes	no	phthalate	Suspect Frack	0	y E	y E	y E	0	0
17851-53-5	1,2-Benzenedicarboxylic acid, butyl 2-methylproj	315.7	T	y	n.alkanes	no	phthalate	Suspect Frack	0	0	0	y T	0	0
27554-26-3	1,2-Benzenedicarboxylic acid, diisooctyl ester	384.9	T	y	n.alkanes	no	phthalate	Suspect Frack	0	y T	y T	0	0	0
84-74-2	Dibutyl phthalate	339.5	E	y	n.alkanes	no	phthalate	Suspect Frack	y E	0	y E	0	0	0
556-67-2	Cyclotetrasiloxane, octamethyl-	175	E	y	n.alkanes	explicit	silicone	Frack	n E	0	n E, y E	0	0	0
541-05-9	Cyclotrisiloxane, hexamethyl-	134	E	y	n.alkanes	no	silicone	Suspect Frack	y E, n E	0	y E, n E	0	0	0
	Sulfurous acid, 2-ethylhexyl isohexyl ester	335.9	T	y	carbacids	no	sulfurous acid	Suspect Frack	n T	0	y T, n T	0	0	y T
	Sulfurous acid, dodecyl pentyl ester	390.6	T	y	carbacids	no	sulfurous acid	Suspect Frack	0	y T	0	0	0	n T
111-27-3	1-Hexanol	157.6	E	n	n.alkanes	explicit	alcohol	Frack	0	n E	0	0	0	0
111-76-2	Ethanol, 2-butoxy-	168.4	E	n	n.alkanes	explicit	alcohol	Frack	0	0	n E	0	0	0
67-63-0	Isopropyl Alcohol	82.5	E	n	n.alkanes	explicit	alcohol	Frack	0	n E	n E	0	n E	0
	5-Nonadecen-1-ol	384.6	T	n	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	0	n T	0	0	0	0
506-43-4	9,12-Octadecadien-1-ol, (Z,Z)-	374	T	n	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	0	n T	0	0	0	0
35153-15-2	cis-9-Tetradecen-1-ol	307.1	T	n	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	0	n T	0	0	0	0
1892-12-2	Cyclododecanemethanol	298.7	T	n	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	n T	n T	0	0	0	0
100-49-2	Cyclohexanemethanol	183	E	n	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	0	0	0	0	0	n E
	Dodeca-1,6-dien-12-ol, 6,10-dimethyl-	292.5	T	n	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	0	n T	0	0	0	0
64437-47-4	Hexadecen-1-ol, trans-9-	340	T	n	n.alkanes	implicit	alcohol	Metab./Subsurf. Rxn.	n T	0	0	0	0	0
	(2,4,6-Trimethylcyclohexyl) methanol	216	T	n	n.alkanes	implicit	alcohol	Suspect Frack	0	0	0	0	0	n T
65686-49-9	11-Hexadecyn-1-ol	340.1	T	n	n.alkanes	implicit	alcohol	Suspect Frack	0	n T	0	0	0	0
818-81-5	1-Octanol, 2-methyl-	196.6	T	n	n.alkanes	implicit	alcohol	Suspect Frack	n T	0	0	0	0	0
616-25-1	1-Penten-3-ol	115	E	n	n.alkanes	implicit	alcohol	Suspect Frack	n E	0	0	0	0	0
594-60-5	2-Butanol, 2,3-dimethyl-	118.4	E	n	n.alkanes	implicit	alcohol	Suspect Frack	n E	0	n E	0	n E	n E
625-23-0	2-Hexanol, 2-methyl-	143	E	n	n.alkanes	implicit	alcohol	Suspect Frack	0	0	n E	0	0	0
4911-70-0	2-Pentanol, 2,3-dimethyl-	138.3	T	n	n.alkanes	implicit	alcohol	Suspect Frack	0	0	n T	0	0	0
108-11-2	2-Pentanol, 4-methyl-	131.6	E	n	n.alkanes	implicit	alcohol	Suspect Frack	n E	0	0	0	0	0
	2š, 4aš, 8aš-Decahydro-2-naphthalenol	NA		N/A		no	alcohol	Suspect Frack	0	N/A	0	0	0	0
5842-53-5	3-Penten-1-ol, 2,2,4-trimethyl-	114	E	n	n.alkanes	implicit	alcohol	Suspect Frack	0	n E	n E	0	0	0
6982-25-8	DL-2,3-Butanediol	183.5	E	n	n.alkanes	no	alcohol	Suspect Frack	n E	0	n E	0	0	0
53535-33-4	Heptanol	175.5	E	n	n.alkanes	implicit	alcohol	Suspect Frack	0	n E	0	0	0	0
106-44-5	Phenol, 4-methyl-	201.9	E	n	n.alkanes	no	alcohol	Suspect Frack	0	n E	0	0	0	0
	2,3,4-Trimethyl-hex-3-enal	191.6	T	n	carbacids	implicit	aldehyde	Frack/Geogenic	n T	0	0	0	0	0
2363-88-4	2,4-Decadienal	277.7	E	n	carbacids	implicit	aldehyde	Metab./Subsurf. Rxn.	0	n E	0	0	0	0
112-31-2	Decanal	208	E	n	carbacids	implicit	aldehyde	Metab./Subsurf. Rxn.	n E	0	0	0	0	0
66-25-1	Hexanal	131	E	n	carbacids	implicit	aldehyde	Metab./Subsurf. Rxn.	0	n E	0	0	0	0
123-05-7	Hexanal, 2-ethyl-	163	E	n	carbacids	implicit	aldehyde	Metab./Subsurf. Rxn.	0	0	n E	0	0	0
	Hexanal, 3-(hydroxymethyl)-4-methyl-	230.7	T	n	carbacids	implicit	aldehyde	Metab./Subsurf. Rxn.	0	n T	0	0	0	0
14250-88-5	Pentanal, 2,2-dimethyl-	136.4	T	n	carbacids	implicit	aldehyde	Metab./Subsurf. Rxn.	0	0	n T	0	0	0
	Benzeneacetaldehyde, š,2,5-trimethyl-	NA		N/A		no	aldehyde	Suspect Frack	0	N/A	0	0	0	0
93-53-8	Benzeneacetaldehyde, š-methyl-	203.5	E	n	n.alkanes	no	aldehyde	suspect frack	0	n E	0	0	0	0
75-83-2	Butane, 2,2-dimethyl-	49.7	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n E	0	0	0
	C14 Isoprenoid Alkane	NA		N/A		explicit	alkane	Frack/Geogenic	0	N/A	0	0	N/A	N/A
	C16 Isoprenoid Alkane	NA		N/A		implicit	alkane	Frack/Geogenic	0	N/A	0	0	0	0
	C21 Isoprenoid Alkane	NA		N/A		implicit	alkane	Frack/Geogenic	N/A	0	0	0	0	0
	C29-Ts	NA		N/A		explicit	alkane	Frack/Geogenic	N/A	0	0	0	0	0
192823-15-7	Decane, 2,3,5,8-tetramethyl-	230.5	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	0	0	0	0
62238-11-3	Decane, 2,3,5-trimethyl-	217.4	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	0
2801-84-5	Decane, 2,4-dimethyl-	204.7	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	n T	0	0
62108-22-9	Decane, 2,5,9-trimethyl-	212.2	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	0
1002-17-1	Decane, 2,9-dimethyl-	202.4	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	n T
17312-55-9	Decane, 3,8-dimethyl-	204.6	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	0	0	0	0
13151-34-3	Decane, 3-methyl-	188.1	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	n E	0	0	0	0
17312-62-8	Decane, 5-propyl-	218.2	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	n T
17453-93-9	Dodecane, 5-methyl-	226.6	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	n T
18344-37-1	Heptadecane, 2,6,10,14-tetramethyl-	356.9	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	0
54105-67-8	Heptadecane, 2,6-dimethyl-	318.1	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	n T	0
1560-89-0	Heptadecane, 2-methyl-	311	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	n E	0	0
589-43-5	Hexane, 2,4-dimethyl-	109.2	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	n T	0	0	0	0
563-16-6	Hexane, 3,3-dimethyl-	111.9	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	n E	0	0	0	0	n E
31081-18-2	Nonane, 3-methyl-5-propyl-	213.1	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	n T
62016-34-6	Octane, 2,3,7-trimethyl-	179.3	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	0
54166-32-4	Octane, 2,6,6-trimethyl-	176.1	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	0
1072-16-8	Octane, 2,7-dimethyl-	159.9	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	n E	0	0
	Octane, 4-bromo-	190.8	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	n T	0	0	0
15869-86-0	Octane, 4-ethyl-	163.7	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	n E	0	0	0	0	0
6165-40-8	Pentadecane, 7-methyl-	277.1	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	0	0	0	0
71005-15-7	Pentadecane, 8-heptyl-	382.8	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	n T	0	0	0	0
565-75-3	Pentane, 2,3,4-trimethyl-	113.5	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	n E	0	0	0	0
617-78-7	Pentane, 3-ethyl-	93.5	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	n E
1068-87-7	Pentane, 3-ethyl-2,4-dimethyl-	136.7	E	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	n E	0	0	0	0
17312-80-0	Undecane, 2,4-dimethyl-	220.3	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	n T	0	0	0
17301-25-6	Undecane, 2,8-dimethyl-	221.8	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	0	0	0	0	n T
17301-29-0	Undecane, 3,7-dimethyl-	221.8	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	0	n T	0	0	0	0
17301-30-3	Undecane, 3,8-dimethyl-	223	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	0	0	0	0
17301-32-5	Undecane, 4,7-dimethyl-	220.3	T	n	n.alkanes	implicit	alkane	Frack/Geogenic	n T	0	0	0	0	0
2153-66-4	Santolina triene	166.6	T	n	n.alkanes	implicit	alkene	Frack	0	n T	0	0	0	0
35365-53-8	1,2-Diheptylcyclopropene	308.6	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	0	0
3479-89-8	1,3,5-Cycloheptatriene, 3,7,7-trimethyl-	172.8	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	0	0
	1,5-Hexadiene, 2,5-dipropyl-	206.5	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	0	0	0	0
95008-11-0	10-Heneicosene (c,t)	369.7	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	n T	n T	0	0	n T
872-05-9	1-Decene	170.5	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	0	0	0	n E
61142-79-8	1-Decene, 8-methyl-	183.7	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	0	0	0	n T
13151-05-8	1-Heptene, 4-methyl-	112.8	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n E	0	0	0	0
5026-76-6	1-Heptene, 6-methyl-	113.2	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	n E	0	0	0
629-73-2	1-Hexadecene	284.9	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n E	0	0	0	0
13427-43-5	1-Hexene, 3,3,5-trimethyl-	127.1	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	0	0	0	n T
16106-59-5	1-Hexene, 4,5-dimethyl-	106.9	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	n T	0	0	0	0

54410-98-9	1-Nonene, 4,6,8-trimethyl-	195.7	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	0	0
	1-Octene, 3,7-dimethyl-	156.2	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	0	0	0	n T
13151-12-7	1-Octene, 4-methyl-	137.6	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	0	0	0	0
13151-10-5	1-Octene, 6-methyl-	137.6	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	n T	0	0	0	n T
3404-73-7	1-Pentene, 3,3-dimethyl-	77.5	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	n E	0	0	0	0	0
2437-56-1	1-Tridecene	232.8	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n E	0	0	0	0
74630-42-5	1-Undecene, 7-methyl-	205	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	0	0	0	0
55771-40-9	2,4,6-Trimethyl-1-nonene	200.1	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	n T	0	0	0
7206-13-5	2-Dodecene, (E)-	216.2	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	n T	0	0	0
	2-Hexene, 4-ethyl-2,3-dimethyl-	164.9	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	n T	0
107-40-4	2-Pentene, 2,4,4-trimethyl-	104.9	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n E	0	0	0	0
598-96-9	2-Pentene, 3,4,4-trimethyl-	112	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	n E	0	0	0
74685-33-9	3-Eicosene, (E)-	354.3	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	0	n T
	3-Undecene, 7-methyl-, (Z)-	207.4	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	0	0	0	0
	4-Nonene, 3-methyl-, (Z)-	163.9	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	0	0	0	0	n T
	4-Octene, 2,3,7-trimethyl-, [S-(E)]-	176.5	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	0	0	0	0
60186-79-0	4-Tridecene	232.3	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	0	0	0	0
	4-Undecene, 10-methyl-, (E)-	NA		N/A		implicit	alkene	Frack/Geogenic	0	0	N/A	0	0	0
74685-30-6	5-Eicosene, (E)-	354.3	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	0	n T
7206-21-5	5-Octadecene, (E)-	322.2	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	n T	0	0	0
41446-64-4	6-Tetradecene, (E)-	251.6	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	0	0
35507-09-6	7-Hexadecene, (Z)-	288.1	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	n T	0	0	n T
31035-07-1	9-Nonadecene	338.5	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n T	0	0	0	0
1486-75-5	Cyclododecene, (E)-	240	E	n	n.alkanes	implicit	alkene	Frack/Geogenic	0	n E	0	0	0	0
	Hexylidencyclohexane	226.9	T	n	n.alkanes	implicit	alkene	Frack/Geogenic	n T	0	0	0	0	0
37050-06-9	3-Octyne, 7-methyl-	145.3	T	n	n.alkanes	implicit	alkyne	Frack/Geogenic	n T	0	0	0	0	0
6975-99-1	6-Dodecyne	281.2	E	n	n.alkanes	implicit	alkyne	Frack/Geogenic	n E	0	0	0	0	0
35354-38-2	7-Octadecyne, 2-methyl-	327.8	T	n	n.alkanes	implicit	alkyne	Frack/Geogenic	0	n T	0	0	0	0
33582-68-2	Cyclobutane-1,1-dicarboxamide, N,N'-di-benzoyl	NA		N/A		no	amide	Suspect Frack	0	N/A	0	0	0	0
2516-34-9	Cyclobutylamine	82	E	n	n.alkanes	implicit	amine	Frack	0	0	0	0	n E	0
97-72-3	Propanoic acid, 2-methyl-, anhydride	183	E	n	carbacids	no	anhydride	Suspect Frack	n E	0	0	0	0	0
2717-39-7	1,4,5,8-Tetramethylnaphthalene	314.9	T	n	n.alkanes	implicit	aromatic	Frack/Geogenic	0	n T	0	0	0	0
2177-48-2	1H-Indene, 1,3-dimethyl-	228.9	T	n	n.alkanes	no	aromatic	Frack/Geogenic	0	n T	0	0	0	0
869682-25-7	1H-Indene, 1-ethylideneoctahydro-7a-methyl-, c	214.2	T	n	n.alkanes	no	aromatic	Frack/Geogenic	0	n T	0	0	0	0
	1H-Indene, 3-ethenyl-2,3-dihydro-1,1-dimethyl-	231.5	T	n	n.alkanes	no	aromatic	Frack/Geogenic	0	n T	0	0	0	0
613-33-2	4,4'-Dimethylbiphenyl	295	E	n	n.alkanes	implicit	aromatic	Frack/Geogenic	0	n E	0	0	0	0
620-83-7	Benzene, 1-methyl-4-(phenylmethyl)-	286	E	n	n.alkanes	implicit	aromatic	Frack/Geogenic	0	n E	0	0	0	0
	Benzeneethanol, ˚-methyl-	NA		N/A		no	aromatic	Frack/Geogenic	0	N/A	0	0	0	0
	Benzeneethanol, š,˚-dimethyl-	NA		N/A		no	aromatic	Frack/Geogenic	0	N/A	0	0	0	0
	Benzenemethanol, š,š-dimethyl-	NA		N/A		no	aromatic	Frack/Geogenic	0	N/A	0	0	0	0
	Benzenemethanol, š-methyl-, (S)-	NA		N/A		no	aromatic	Frack/Geogenic	0	N/A	0	0	0	0
91-20-3	Naphthalene	217.9	E	n	n.alkanes	explicit	aromatic	Frack/Geogenic	0	n E	0	0	0	0
108-95-2	Phenol	181.8	E	n	n.alkanes	explicit	aromatic	Frack/Geogenic	0	n E	0	0	0	0
	4a(2H)-Naphthalenemethanol, octahydro-	258	T	n	n.alkanes	no	aromatic	Suspect Frack	n T	n T	0	0	0	0
946-80-5	Benzene, (phenoxymethyl)-	286.5	E	n	n.alkanes	no	aromatic	Suspect Frack	0	n E	0	0	0	0
	Benzoic acid, 2-(benzoylthio)thiazol-4-yl ester	533	T	n	n.alkanes	no	aromatic	Suspect Frack	0	0	n T	0	0	0
112-80-1	Oleic Acid	390	E	n	carbacids	explicit	carboxylic acid	Frack/Geogenic	0	n E	0	0	0	0
1821-02-9	2-Oxo-n-valeric acid	179	E	n	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	0	n E	0	0	0
57-10-3	n-Hexadecanoic acid	390	E	n	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	n E	n E	0	0	0	0
594-61-6	Propanoic acid, 2-hydroxy-2-methyl-	264	E	n	carbacids	no	carboxylic acid	Metab./Subsurf. Rxn.	0	0	n E	0	0	n E
23183-11-1	1,1'-Bicycloheptyl	273.7	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	n T
54934-89-3	1,1'-Bicyclohexyl, 2-propyl-, trans-	282.3	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	0
6708-17-4	1,1'-Bicyclooctyl	312	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
	1,3-Dimethyl-(3,7-dimethyloctyl)cyclohexane	309.6	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
	17a(H),21B(H)-30-Norhopane	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	17a(H)-22,29,30-Trinorhopane	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
1161-11-1¾	1-Cyclohexyl-1-(4-methylcyclohexyl)ethane	277.9	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
99-82-1	1-Methyl-4-(1-methylethyl)-cyclohexane	168	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	0	0	0	0	n E
	1-Methylbicyclo[3.2.1]octane	148.4	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
766-70-1	2-Methylbicyclo[3.2.1]octane	156	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	0
	4,8-dimethyl-1-cyclohexane (Chiron AS 0827.17 (	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	N/A	0	0	0	0	N/A
281-23-2	Adamantane	187.1	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
5617-41-4	alkylcyclohexane (ChC07 mw 182)	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	N/A	N/A	0	0	N/A	N/A
1795-15-9	alkylcyclohexane (ChC08 mw 196)	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	alkylcyclohexane (ChC09 mw 210)	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	alkylcyclohexane (ChC18 mw 336)	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	N/A	0	0	0	0	0
5634-30-0	alkylcyclopentane (acp C12 C17H34 mw 238)	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
6006-34-4	Alkylcyclopentane (CpC13 mw 252)	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	Benzocyclodecene, tetradecahydro-	277	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
473-55-2	Bicyclo[3.1.1]heptane, 2,6,6-trimethyl-	169	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	0	0	0	0	n E
	Bicyclo[4.1.0]heptane, 3,7,7-trimethyl-, [1S-(1š,3	NA		N/A		no	cyclic alkane	Frack/Geogenic	N/A	0	0	0	0	0
294-62-2	Cyclododecane	247	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n E	0	0	0	0
295-65-8	Cyclohexadecane	318.7	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
61208-94-4	Cyclohexane, (1-methylbutyl)-	154.8	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n E	0	0	0	0
696-29-7	Cyclohexane, (1-methylethyl)-	154.8	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n E	0	0	0	n E
	Cyclohexane, (1-methylpropyl)-	179.3	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	0
1678-98-4	Cyclohexane, (2-methylpropyl)-	171.3	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	n E	0	0	0	n E
55401-72-4	Cyclohexane, [6-cyclopentyl-3-(3-cyclopentylpro	444.9	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
74663-71-1	Cyclohexane, 1,1'-(1,2-dimethyl-1,2-ethanediyl)b	297.3	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	0
3178-24-3	Cyclohexane, 1,1'-(1,3-propanediyl)bis-	291.5	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n E	0	0	0	0
6783-92-2	Cyclohexane, 1,1,2,3-tetramethyl-	155.8	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	0	0	0	0	n T
	Cyclohexane, 1,1,4,4-tetramethyl-	151.3	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	n T
3642-13-5¾	Cyclohexane, 1,2-diethyl-, cis-	174.3	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	0
62376-17-4	Cyclohexane, 1,2-dimethyl-3-pentyl-4-propyl-	281.9	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
	Cyclohexane, 1,4-dimethyl-2-(2-methylpropyl)-, (	NA		N/A		no	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	Cyclohexane, 1-ethyl-1,4-dimethyl-, cis-	162.6	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	n T
	Cyclohexane, 1-ethyl-1,4-dimethyl-, trans-	162.6	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	0
4926-90-3	Cyclohexane, 1-ethyl-1-methyl-	152.2	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	n E	n E	0	0	n E
16580-24-8	Cyclohexane, 1-methyl-3-(1-methylethyl)-	168.2	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	n T
4291-80-9	Cyclohexane, 1-methyl-3-propyl-	164.5	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	0	n E	0	0	n E
6069-98-3	Cyclohexane, 1-methyl-4-(1-methylethyl)-, cis-	172	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	n E	0	0	0	n E
1678-82-6	Cyclohexane, 1-methyl-4-(1-methylethyl)-, trans-	170.6	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	n E	0	0	0	0
61142-70-9	Cyclohexane, 2,4-diethyl-1-methyl-	189.8	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	n T	n T
5617-41-4	Cyclohexane, heptyl-	244	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	0	0	0	n E	0
	Cyclohexane, nonyl-	282.6	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	0	0	0	n T	0
1453-24-3	Cyclohexene, 1-ethyl-	137	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n E	0	0	0	0
	Cyclohexene, 4-(4-ethylcyclohexyl)-1-pentyl-	345.2	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
13151-94-5	Cyclooctane, 1,2-dimethyl-	177.6	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
13151-98-9	Cyclooctane, 1,4-dimethyl-, trans-	177.6	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
	Cyclooctane, cyclohexyl-	273.7	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	n T
13152-02-8	Cyclooctane, ethyl-	184.8	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	0
1502-38-1	Cyclooctane, methyl-	161.9	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	0
295-48-7	Cyclopentadecane	300.1	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	0
53366-38-4	Cyclopentane, (2-methylbutyl)-	173.4	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	0	0	0	0	n T
1005-68-1	Cyclopentane, (3-methylbutyl)-	173.4	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	0
2980-70-3	Cyclopentane, 1,1'-(1,4-butandiyl)bis-	268.7	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
74421-09-3	Cyclopentane, 1,1,3-trimethyl-3-(2-methyl-2-pro	189.2	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	n T
55429-35-1	Cyclopentane, 1,1'-[4-(3-cyclopentylpropyl)-1,7-h	443.5	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
489-20-3	Cyclopentane, 1,2-dimethyl-3-(1-methylethyl)-	159.8	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	n T
	Cyclopentane, 1,3-dimethyl-2-(1-methylethenyl)-	159.8	T	n	n.alkanes	no	cyclic alkane	Frack/geogenic	0	n T	0	0	0	0
72993-32-9	Cyclopentane, 1-butyl-2-ethyl-	194.5	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	0	0	0	0	n T
62199-50-3	Cyclopentane, 1-butyl-2-propyl-	215.4	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	n T	0	0	0
2613-65-2	Cyclopentane, 1-ethyl-3-methyl-, trans-	121	E	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n E	0	0	0	0	0
3728-57-2	Cyclopentane, 1-methyl-2-propyl-	148.9	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	0
29053-04-1	Cyclopentane, 1-methyl-3-(2-methylpropyl)-	166.7	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	0	0	0	0
32281-85-9	Cyclopentane, 2-isopropyl-1,3-dimethyl-	159.8	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	n T	n T	0	0	n T
6703-82-8	Cyclopentane, heneicosyl-	423.2	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
	Cyclopropane, 1,2-dimethyl-, trans-	31.7	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	0	n T	0	0	0
62238-04-4	Cyclopropane, 1,2-dimethyl-1-pentyl-	157.2	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	0
62238-07-7	Cyclopropane, 1-methyl-2-(3-methylpentyl)-	163	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	n T
74663-85-7	Cyclopropane, nonyl-	219.8	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	n T	0	0	0	0	0
88828-82-4	Cycloundecene, 1-methyl-	233.1	T	n	n.alkanes	implicit	cyclic alkane	Frack/Geogenic	0	n T	0	0	0	0
	Dia(Ba)C27(R): 13B(H),17a(H)-20R-24-Ethyl-Chol	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0

	Perhydrophenalene, (3aš, 6aš, 9aš, 9b˚)-	NA		N/A		no	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	tricyclic terpane C21H38 mass 290	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	tricyclic terpane C25H46 mass 346	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	tricyclic terpane C26H48b mass 360	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	0	N/A	0	0	0	0
	tricyclic terpane C28H52b mass 388	NA		N/A		implicit	cyclic alkane	Frack/Geogenic	N/A	0	0	0	0	0
	1,2-Dipentylcyclopropene	235.7	T	n	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	0	n T	0	0	0	0
	7-Octylidenebicyclo[4.1.0]heptane	280.7	T	n	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	0	n T	0	0	0	0
56666-90-1	Bicyclo[6.1.0]nonane, 9-(1-methylethylidene)-	223.5	T	n	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	0	n T	0	0	0	0
	Bicyclo[7.7.0]hexadec-1(9)-ene	325.8	T	n	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	n T	n T	0	0	0	0
2114-42-3	Cyclohexane, 2-propenyl-	153.5	E	n	n.alkanes	implicit	cyclic alkene	Frack/Geogenic	n E	n E	0	0	0	n E
1073-91-2	1,2,4,5-Tetroxane, 3,3,6,6-tetramethyl-	100.8	T	n	n.alkanes	no	diperoxide	Suspect Frack	0	0	n T	0	0	0
	2,7-Ethanonaphth[2.3-b]oxirene, 1a,2,7,7a-tetrał	NA		N/A		no	epoxide	Suspect Frack	0	N/A	0	0	0	0
264628-23-1	7-Methylene-9-oxabicyclo[6.1.0]non-2-ene	201.1	T	n	n.alkanes	no	epoxide	Suspect Frack	n T	0	0	0	0	0
42328-43-8	Oxirane, 2-methyl-2-(1-methylpropyl)-	110.8	T	n	n.alkanes	no	epoxide	Suspect Frack	0	0	0	0	n T	0
7320-37-8	Oxirane, tetradecyl-	323.5	T	n	n.alkanes	no	epoxide	Suspect Frack	0	n T	0	0	0	0
	Santolina epoxide	183.9	T	n	n.alkanes	no	epoxide	Suspect Frack	0	n T	0	0	0	0
	1,2-Dimethyl-4-trifluoroacetoxycyclohexane	200	T	n	n.alkanes	no	ester	Suspect Frack	0	0	0	0	0	n T
104-50-7	2(3H)-Furanone, 5-butyldihydro-	234	E	n	n.alkanes	no	ester	Suspect Frack	0	n E	0	0	0	0
695-06-7	2(3H)-Furanone, 5-ethyldihydro-	215.5	E	n	n.alkanes	no	ester	Suspect Frack	0	n E	n E	0	0	0
104-67-6	2(3H)-Furanone, 5-heptyldihydro-	286	E	n	n.alkanes	no	ester	Suspect Frack	0	n E	0	0	0	0
108-29-2	2(3H)-Furanone, dihydro-5-methyl-	207.5	E	n	n.alkanes	no	ester	Suspect Frack	n E	n E	0	0	0	0
105-21-5	2(3H)-Furanone, dihydro-5-propyl-	226.3	T	n	n.alkanes	no	ester	Suspect Frack	0	n T	0	0	0	0
591-11-7	2(5H)-Furanone, 5-methyl-	210	T	n	n.alkanes	no	ester	Suspect Frack	n T	0	0	0	0	0
5343-96-4	2-Butanol, 3-methyl-, acetate	122.4	E	n	n.alkanes	no	ester	Suspect Frack	0	0	0	0	n E	0
713-95-1	2H-Pyran-2-one, 6-heptyltetrahydro-	126	E	n	n.alkanes	no	ester	Suspect Frack	0	n E	0	0	0	0
542-28-9	2H-Pyran-2-one, tetrahydro-	219	E	n	n.alkanes	no	ester	Suspect Frack	n E	n E	0	0	0	0
823-22-3	2H-Pyran-2-one, tetrahydro-6-methyl-	231	E	n	n.alkanes	no	ester	Suspect Frack	0	0	0	0	n E	0
698-76-0	2H-Pyran-2-one, tetrahydro-6-propyl-	238	E	n	n.alkanes	no	ester	Suspect Frack	0	n E	0	0	0	0
25719-55-5	2-Propenoic acid, 2-methyl-, ethenyl ester	111.5	E	n	n.alkanes	no	ester	Suspect Frack	0	0	0	0	0	n E
	2-Propylhept-3-enoic acid, phenylthio ester	359	T	n	n.alkanes	no	ester	Suspect Frack	0	n T	0	0	0	0
33467-74-2	3-Hexen-1-ol, propanoate, (Z)-	210.9	T	n	n.alkanes	no	ester	Suspect Frack	0	0	n T	0	0	0
	Acetic acid, trifluoro-, tetradecyl ester	248.8	T	n	n.alkanes	no	ester	Suspect Frack	0	n T	0	0	0	0
2306-92-5	Decanoic acid, octyl ester	334.7	T	n	n.alkanes	no	ester	Suspect Frack	0	n T	0	0	0	0
13632-94-5	m-Toluic acid, 4-cyanophenyl ester	412.9	T	n	n.alkanes	no	ester	Suspect Frack	0	n T	0	0	0	0
112-66-3	n-Dodecyl acetate	265	E	n	n.alkanes	no	ester	Suspect Frack	0	n E	0	0	0	0
124-07-2	Octanoic acid, methyl ester	239	E	n	n.alkanes	no	ester	Suspect Frack	0	n E	0	0	0	0
	Oxalic acid, allyl dodecyl ester	370.6	T	n	n.alkanes	no	ester	Suspect Frack	0	0	0	n T	0	0
	Oxalic acid, allyl tridecyl ester	385.5	T	n	n.alkanes	no	ester	Suspect Frack	n T	0	n T	0	0	n T
	Oxalic acid, butyl propyl ester	231.9	T	n	n.alkanes	no	ester	Suspect Frack	0	0	n T	0	0	0
	Oxalic acid, cyclobutyl octadecyl ester	472.4	T	n	n.alkanes	no	ester	Suspect Frack	n T	n T	0	0	0	0
	Oxalic acid, di(cyclohexylmethyl) ester	377.4	T	n	n.alkanes	no	ester	Suspect Frack	0	n T	0	0	0	n T
	Oxalic acid, isobutyl nonyl ester	333.4	T	n	n.alkanes	no	ester	Suspect Frack	0	0	0	n T	0	0
109-52-4	Pentanoic acid, 10-undecenyl ester	314	T	n	n.alkanes	no	ester	Suspect Frack	n T	0	0	0	0	n T
5426-43-7	Pentyl glycolate	197.4	T	n	n.alkanes	no	ester	Suspect Frack	n T	0	0	0	0	0
2445-69-4	Propanoic acid, 2-methyl-, 2-methylbutyl ester	165.2	T	n	carbacids	no	ester	Suspect Frack	0	0	0	0	0	n T
74367-34-3	Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trime	249	T	n	carbacids	no	ester	Suspect Frack	n T	0	0	0	0	0
100666-89-5	Tetrahydrofurfuryl acrylate	238.6	E	n	n.alkanes	no	ester	Suspect Frack	0	0	n E	0	0	0
818-44-0	Vinyl caprylate	212	T	n	n.alkanes	no	ester	Suspect Frack	0	n T	0	0	0	0
53042-79-8	Z,E-7,11-Hexadecadien-1-yl acetate	365.7	T	n	n.alkanes	no	ester	Suspect Frack	0	n T	0	0	0	0
75-09-2	Methylene Chloride	39	E	n	n.alkanes	explicit	halogenated	Frack	n E	0	n E	0	0	0
1985-88-2	1,1-Dimethyl-3-chloropropanol	178.6	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	0	0	n T	0
	1,3-Dioxolane, 2-(3-bromo-5,5,5-trichloro-2,2-dir	341.9	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	n T	0	0	0
1561-86-0	2-Chlorocyclohexanol	218.3	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	n T	0	0	0
	2-Piperidinone, N-[4-bromo-n-butyl]-	341.1	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	n T	0	0	0	0
	5-Iodopentan-2-one	207.6	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	n T	0	n T	0
	Butane, 1-chloro-3,3-dimethyl-	117	E	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	n E	0	0	0	0	0
18295-27-7	Butane, 2-iodo-3-methyl-	136.9	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	n T	0	0	0
6294-39-9	Cyclohexane, 1-bromo-2-methyl-	174.6	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	n T	0	0	0	0
	Cyclopropane, 3-chloro-1,1,2,2-tetramethyl-	122.6	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	0	0	n T	0
	Decane, 4,5-dibromo-, (R*,R*)-	281.9	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	n T	0	0	0	0	0
75-27-4	Methane, bromodichloro-	88	E	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	n E	0	0	0
4282-42-2	Nonane, 1-iodo-	269	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	0	0	0	n T
	Pentadec-7-ene, 7-bromomethyl-	342	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	n T	0	0	0	0	0
141-76-4	Propanoic acid, 3-iodo-	259.7	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	0	0	0	n T	0
7314-85-4	Tricyclo[3.3.1.1(3,7)]decane, 2-bromo-	248.6	T	n	n.alkanes	no	halogenated	Metab./Subsurf. Rxn.	0	n T	0	0	0	0
87-41-2	1(3H)-Isobenzofuranone	290	E	n	n.alkanes	no	heterocycle	Suspect Frack	0	n E	0	0	0	0
	1,3-Benzodioxol-2-one, hexahydro-, trans-	298.8	T	n	n.alkanes	no	heterocycle	Suspect Frack	0	0	n T	0	0	0
	1,4-Methano-1H-cyclohepta[d]pyridazine, 4,4a,5	252.7	T	n	n.alkanes	no	heterocycle	Suspect Frack	0	n T	0	0	0	0
	1,4-Methanophthalazine, 1,4,4a,5,6,7,8,8a-octah	NA		N/A		no	heterocycle	Suspect Frack	0	N/A	0	0	0	0
	1,4-Methanophthalazine, 1,4,4a,5,6,7,8,8a-octah	NA		N/A		no	heterocycle	Suspect Frack	0	N/A	0	0	0	0
288-94-8	1H-Tetrazole	220.2	T	n	n.alkanes	no	heterocycle	Suspect Frack	n T	0	0	0	0	0
4879-95-2	2-Azetidinone, 3,3-dimethyl-	212.1	T	n	n.alkanes	no	heterocycle	Suspect Frack	0	n T	0	0	0	0
7326-46-7	2-Furanol, tetrahydro-2-methyl-	155.1	T	n	n.alkanes	no	heterocycle	Suspect Frack	0	0	0	0	n T	0
5628-99-9	Aziridine, 1-vinyl-	71.1	T	n	n.alkanes	no	heterocycle	Suspect Frack	0	0	n T	0	0	0
	Carbamic acid, N-(3-oxo-4-isoxazolidinyl)-, benzy	415.41	T	n	n.alkanes	no	heterocycle	Suspect Frack	0	0	0	0	0	n T
98-86-2	Acetophenone	202	E	n	n.alkanes	explicit	ketone	Frack	0	n E	0	0	0	0
108-94-1	Cyclohexanone	155.4	E	n	n.alkanes	explicit	ketone	Frack	0	0	n E	0	0	0
529-34-0	1(2H)-Naphthalenone, 3,4-dihydro-	115	E	n	n.alkanes	no	ketone	Suspect Frack	0	n E	0	0	0	0
83-33-0	1H-Inden-1-one, 2,3-dihydro-	243	E	n	n.alkanes	no	ketone	Suspect Frack	0	n E	0	0	0	0
	2-Ethyl-3-methylene-indan-1-one	279.8	T	n	n.alkanes	no	ketone	Suspect Frack	0	n T	0	0	0	0
	2H-Benzocyclohepten-2-one, 3,4,4a,5,6,7,8,9-oct	287.9	T	n	n.alkanes	no	ketone	Suspect Frack	0	n T	0	0	0	0
	2-Nonanone, 9-hydroxy-	268.9	T	n	n.alkanes	no	ketone	Suspect Frack	0	n T	0	0	0	0
20633-03-8	3,4-Hexanedione, 2,2,5-trimethyl-	177.8	T	n	n.alkanes	no	ketone	Suspect Frack	0	0	0	0	0	n T
1703-51-1	3,6-Heptanedione	208.3	T	n	n.alkanes	no	ketone	Suspect Frack	0	n T	0	0	0	0
13891-87-7	4-Penten-2-one	93.9	T	n	n.alkanes	no	ketone	Suspect Frack	0	0	n T	0	n T	0
96-04-8	Acetyl valeryl	183.9	E	n	n.alkanes	no	ketone	Suspect Frack	n E	0	0	0	0	0
4480-47-1¼	Butanal, 3,3-dimethyl-2-oxo-, hemihydrate	128.2	T	n	n.alkanes	no	ketone	Suspect Frack	n T	0	0	0	0	0
1011-12-7	Cyclohexanone, 2-cyclohexylidene-	295	E	n	n.alkanes	no	ketone	Suspect Frack	0	n E	0	0	0	0
98-53-3	Cyclohexanone, 4-(1,1-dimethylethyl)-	114	E	n	n.alkanes	no	ketone	Suspect Frack	0	0	n E	0	0	0
134-81-6	Ethanedione, diphenyl-	347	E	n	n.alkanes	no	ketone	Suspect Frack	0	0	0	0	0	n E
	Spiro[3.6]deca-5,7-dien-1-one,5,9,9-trimethyl	283.5	T	n	n.alkanes	no	ketone	Suspect Frack	0	n T	0	0	0	0
75-24-1	Trimethylaluminum	NA		N/A		no	metal	Suspect Frack	N/A	0	0	0	0	0
3031-15-0	Naphthalene, 1,2,3,4-tetramethyl-	314	T	n	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n T	0	0	0	0
2131-41-1	Naphthalene, 1,4,5-trimethyl-	290.3	T	n	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n T	0	0	0	0
581-40-8	Naphthalene, 2,3-dimethyl-	268	E	n	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n E	0	0	0	0
581-42-0	Naphthalene, 2,6-dimethyl-	262	E	n	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n E	0	0	0	0
91-57-6	Naphthalene, 2-methyl-	241.1	E	n	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	0	n E	0	0	0	0
	Naphthalene, decahydro-2,2-dimethyl-	213.6	T	n	n.alkanes	implicit	naphthalene derivative	Frack/Geogenic	n T	0	0	0	0	0
19212-27-2	3-Oxo-4-phenylbutyronitrile	267.8	T	n	n.alkanes	no	nitrile	Suspect Frack	0	n T	0	0	0	0
52805-36-4	4-Benzyloxybenzonitrile	532.4	E	n	n.alkanes	no	nitrile	Suspect Frack	0	0	0	0	0	n E
	1-Hexyl-1-nitrocyclohexane	297.4	T	n	n.alkanes	no	nitro alkane	Suspect Frack	n T	0	0	0	0	0
	1-Hexyl-2-nitrocyclohexane	297.4	T	n	n.alkanes	no	nitro alkane	Suspect Frack	n T	n T	0	0	0	n T
	Bicyclo[3.3.1]nonan-9-one, 1,2,4-trimethyl-3-nitr	330.5	T	n	n.alkanes	no	nitro alkane	Suspect Frack	n T	n T	0	0	0	n T
14255-44-8	Hexane, 2-nitro-	174.1	T	n	n.alkanes	no	nitro alkane	Suspect Frack	n T	0	0	0	0	0
75-76-3	Silane, tetramethyl-	26.5	E	n	n.alkanes	no	silicone	Suspect Frack	n E	0	n E	0	0	0
	Sulfurous acid, 2-ethylhexyl hexyl ester	340.3	T	n	carbacids	no	sulfurous acid	Suspect Frack	n T	0	0	0	0	0
	Sulfurous acid, 2-ethylhexyl isobutyl ester	335.9	T	n	carbacids	no	sulfurous acid	Suspect Frack	0	0	n T	0	0	0
	Sulfurous acid, butyl undecyl ester	360.5	T	n	carbacids	no	sulfurous acid	Suspect Frack	n T	0	0	0	0	0
	Sulfurous acid, hexadecyl pentyl ester	446.8	T	n	carbacids	no	sulfurous acid	Suspect Frack	0	n T	0	0	0	0
	Sulfurous acid, isobutyl pentyl ester	253.9	T	n	carbacids	no	sulfurous acid	Suspect Frack	0	0	0	0	0	n T
	Sulfurous acid, octyl 2-propyl ester	290.2	T	n	carbacids	no	sulfurous acid	Suspect Frack	0	0	n T	0	0	0
	Sulfurous acid, pentyl tridecyl ester	405.1	T	n	carbacids	no	sulfurous acid	Suspect Frack	n T	0	0	0	0	0
69078-80-4	Ethanethioic acid, S-(2-methylbutyl) ester	180.8	T	n	n.alkanes	no	thioacetate	Suspect Frack	0	0	n T	0	0	0