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Toxins found in fracking fluids and wastewater, study shows

Date: January 6, 2016

Source: Yale University

Summary: In an analysis of more than 1,000 chemicals in fluids used in and created by hydraulic fracturing (fracking), researchers found that many of the substances have been linked to reproductive and developmental health problems, and the majority had undetermined toxicity due to insufficient information.

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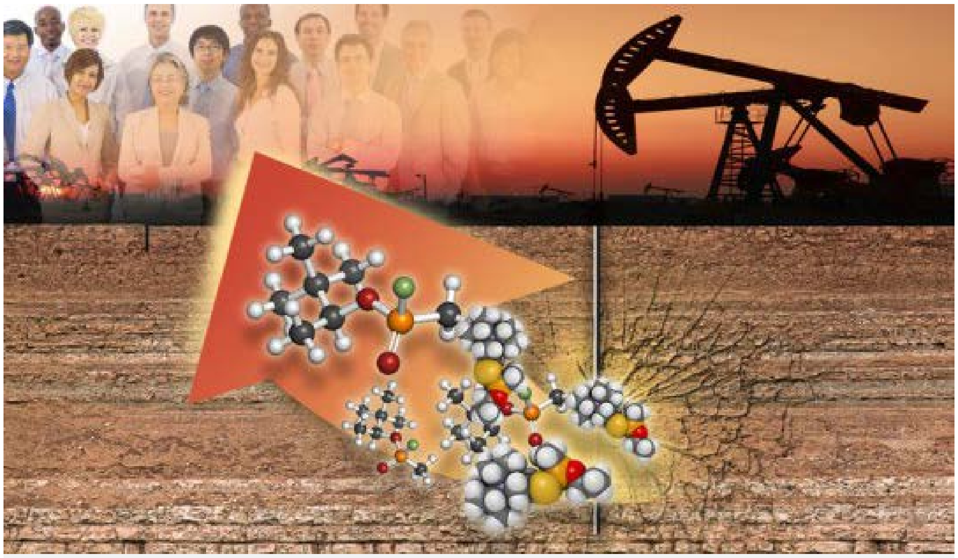

Fracking has increased dramatically in recent years and the practice is expected to grow in the future. It involves drilling into the earth -- as deep

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as two miles -- and releasing a high-pressure mixture of water, sand, and chemicals that fracture the rock and release the gas trapped inside.

Credit: Illustration by Pat Lynch / Yale University

In an analysis of more than 1,000 chemicals in fluids used in and created by hydraulic fracturing (fracking), Yale School of Public Health researchers found that many of the substances have been linked to reproductive and developmental health problems, and the majority had undetermined toxicity due to insufficient information.

Further exposure and epidemiological studies are urgently needed to evaluate potential threats to human health from chemicals found in fracking fluids and wastewater created by fracking, said the research team in their paper, published Jan. 6 in the *Journal of Exposure Science and Environmental and Epidemiology*.

The research team evaluated available data on 1,021 chemicals used in fracking, a process that recovers oil and natural gas from deep within the ground by using a mixture of hydraulic-fracturing fluids that can contain hundreds of chemicals. The process creates significant amounts of wastewater and fractures the bedrock, posing a potential threat to both surface water and underground aquifers that supply drinking water, note the researchers.

While they lacked definitive information on the toxicity of the majority of the chemicals, the team members analyzed 240 substances and concluded that 157 of them -- chemicals such as arsenic, benzene, cadmium, lead, formaldehyde, chlorine, and mercury -- were associated with either developmental or reproductive toxicity. Of these, 67 chemicals were of particular concern because they had an existing federal health-based standard or guideline, said the scientists, adding that data on whether levels of chemicals exceeded the guidelines were too limited to assess.

"This evaluation is a first step to prioritize the vast array of potential environmental contaminants from hydraulic fracturing for future exposure and health studies," said Nicole Deziel, senior author and assistant professor of public health. "Quantification of the potential exposure to these chemicals, such as by monitoring drinking water in people's homes, is vital for understanding the public health impact of hydraulic fracturing."

Some previous studies have observed associations between proximity to hydraulic fracturing sites and reproductive and developmental problems, but they did not investigate specific chemicals. This latest evaluation could inform the design of future studies by highlighting which chemicals could have the highest probability of health impact, note the researchers.

Fracking has increased dramatically in recent years and the practice is

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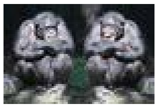
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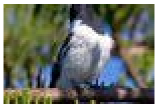
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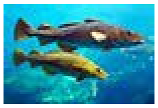
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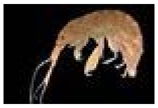
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expected to grow in the future. It involves drilling into Earth -- as deep as two miles -- and releasing a high-pressure mixture of water, sand, and chemicals that fracture the rock and release the gas trapped inside. Fracking is now commonly used in the United States and has significantly boosted domestic natural gas production and driven down prices.

However, the practice may come with a significant public health consequences, warn critics of fracking, noting that the process has the potential to contaminate drinking water supplies with toxic chemicals. Air pollution, greenhouse gas emissions, and small earth tremors from the drilling and waste disposal processes are also cited as concerns.

"We focused on reproductive and developmental toxicity because these effects may be early indicators of environmental hazards. Gaps in our knowledge highlight the need to improve our understanding of the potential adverse effects associated with these compounds," said Elise Elliott, a public health doctoral student and the paper's first author.

The researchers determined that wastewater produced by fracking may be even more toxic than the fracking fluids themselves. This led the researchers to conclude that more focus is needed to study not just what goes into the well, but what chemicals and by-products are generated during the fracking process.

The researchers also noted that the 781 chemicals for which information is currently lacking need to be rigorously analyzed to determine if they pose health threats.

Story Source:

Materials provided by **Yale University**. Original written by Michael Greenwood. *Note: Content may be edited for style and length.*

Journal Reference:

1. Elise G Elliott, Adrienne S Ettinger, Brian P Leaderer, Michael B Bracken, Nicole C Deziel. **A systematic evaluation of chemicals in hydraulic-fracturing fluids and wastewater for reproductive and developmental toxicity**. *Journal of Exposure Science and Environmental Epidemiology*, 2016; DOI: 10.1038/jes.2015.81

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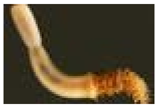
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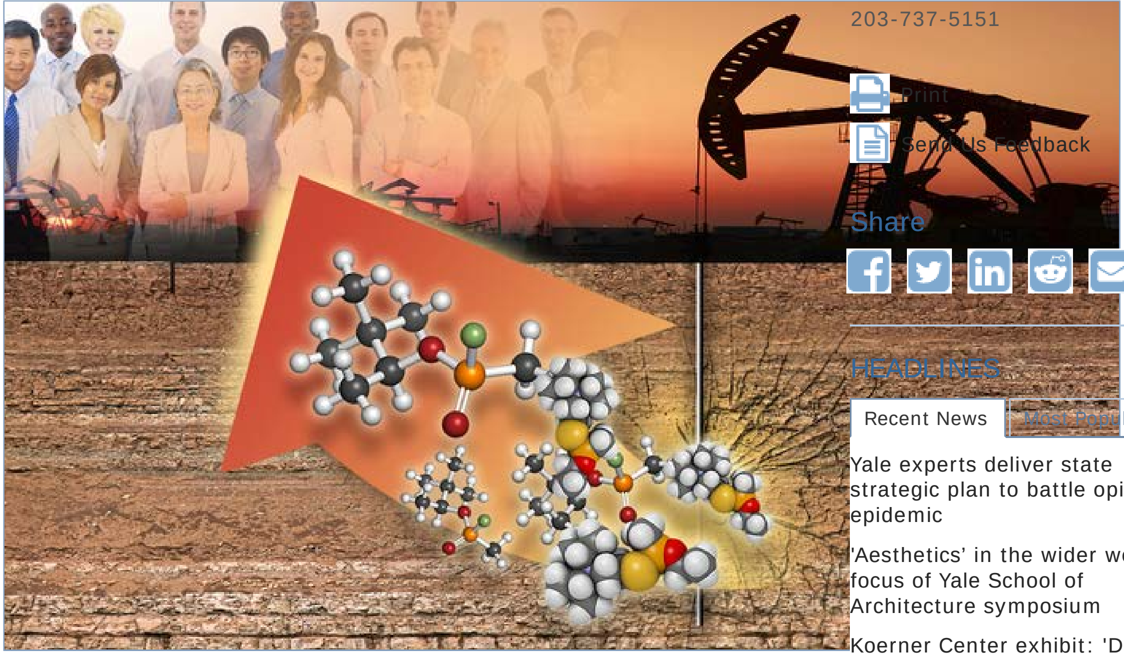
Toxins found in fracking fluids and wastewater, study shows

By Michael Greenwood

January 6, 2016



(Illustration by Pat Lynch / Yale University)

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Some previous studies have observed associations between proximity to hydraulic fracturing sites

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The researchers also noted that the 781 chemicals for which information is currently lacking need to be rigorously analyzed to determine if they pose health threats.

In addition to Deziel and Elliott, the research team included Yale School of Public Health Deputy Dean Brian Leaderer; Michael Bracken, the Susan Dwight Bliss Professor of Epidemiology (chronic diseases); and Adrienne Ettinger, an assistant professor at the school when the research was conducted.

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What happens to hydraulic fracturing wastewater on cropland

Date: June 1, 2016

Source: American Chemical Society

Summary: The use of hydraulic fracturing, or 'fracking,' has grown rapidly in the US over the past 15 years -- but concerns persist that the oil and gas extraction method could harm the environment and people's health. To better understand its potential effects, scientists simulated what would happen to the wastewater produced by the technique after a spill.

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FULL STORY

The use of hydraulic fracturing, or "fracking," has grown rapidly in the U.S. over the past 15 years -- but concerns persist that the oil and gas extraction method could harm the environment and people's health. To better understand its potential effects, scientists simulated what would happen to the wastewater produced by the technique after a spill. They published their findings in the ACS journal *Environmental Science & Technology*.

This spring, the U.S. Energy Information Administration estimated that hydraulic fracturing accounts for two-thirds of the country's natural gas production. Customers have benefited from lower gas bills, but the technique's growth comes with some risks. The Colorado Oil and Gas Conservation Commission received reports of 838 spills that released a total

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Apr. 7, 2016 — Unconventional oil and gas operations combine directional drilling and hydraulic fracturing, or 'fracking,' to release natural gas and oil from underground rock. Studies have centered on ... **read more**

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Mar. 29, 2016 — A survey of a major oil and natural gas-producing region in Western Canada suggests a link between hydraulic fracturing or 'fracking' and induced earthquakes in the ... **read more**

Fracking Plays Active Role in Generating Toxic Metal Wastewater, Study Finds

Dec. 15, 2015 — The production of hazardous wastewater in hydraulic fracturing is assumed to be partly due to chemicals introduced into injected freshwater when it mixes with highly saline brine naturally present in ... **read more** of more than 660,000 gallons of fluids associated with fracking in 2014. Since hydraulic fracturing and, potentially, any associated spills often occur near agricultural land, Jens Blotevogel, Thomas Borch and colleagues wanted to find out whether compounds in the wastewater biodegrade or stick around in the soil where they might be taken up by crops.

The researchers tested the fates of three common hydraulic fracturing additives in agricultural topsoil. The surfactant polyethylene glycol completely degraded within 42 to 71 days. But the surfactant did not break down when combined with another hydraulic fracturing additive called a biocide at a salt concentration typical for wastewater produced during oil and gas extraction. The researchers say their findings highlight the need for further testing to better understand spills' potential effects on crops and the environment.

Story Source:

Materials provided by **American Chemical Society**. *Note: Content may be edited for style and length.*

Journal Reference:

1. Molly C. McLaughlin, Thomas Borch, Jens Blotevogel. **Spills of Hydraulic Fracturing Chemicals on Agricultural Topsoil: Biodegradation, Sorption, and Co-contaminant Interactions**. *Environmental Science & Technology*, 2016; DOI: 10.1021/acs.est.6b00240

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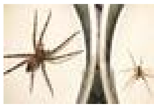

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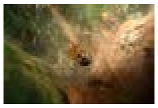

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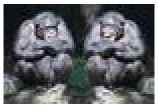

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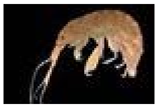

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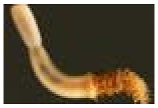

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Oil and gas wastewater disposal may harm West Virginia waterways

Scientists draw conclusions after study at natural gas, oil extraction wastewater disposal facility

Date: April 7, 2016

Source: University of Missouri-Columbia

Summary: Unconventional oil and gas operations combine directional drilling and hydraulic fracturing, or 'fracking,' to release natural gas and oil from underground rock. Studies have centered on potential water pollution from this process that may increase endocrine disrupting chemicals in surface and ground water. Now, researchers report high levels of EDC activity in the surface water near a hydraulic fracturing wastewater disposal facility in West Virginia.

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FULL STORY

Unconventional oil and gas (UOG) operations combine directional drilling and hydraulic fracturing, or "fracking," to release natural gas and oil from underground rock. Recent studies have centered on potential water pollution from this process that may increase endocrine disrupting chemicals (EDCs) in surface and ground water and whether populations living near these operations have an increased risk of disease. Now, researchers from the University of Missouri (MU) report high levels of EDC activity in the

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Jan. 14, 2015 — High levels of two potentially hazardous contaminants, ammonium and iodide, have been documented in wastewater being discharged into streams and rivers from oil and gas operations in Pennsylvania. ... **read more**

Fracking Chemicals Disrupt Hormone Function

surface water near a hydraulic fracturing wastewater disposal facility in West Virginia. Scientists warn that this level of activity may be associated with negative health effects in aquatic organisms, other animals and humans.

"Surface water samples collected on the disposal facility site and immediately downstream exhibited considerably greater EDC activity than surface water samples collected immediately upstream and in a nearby reference stream" said Susan C. Nagel, director of the study and an associate professor in the Department of Obstetrics, Gynecology and Women's Health in the School of Medicine, and an adjunct associate professor of biological sciences in the MU College of Arts and Science. "The level of EDC activity was within the range or higher than the level known to impact the health of aquatic organisms."

Dozens of chemicals may be used in fracturing at one site and approximately 1,000 different chemicals are reportedly used across the industry; more than 100 of these chemicals are known as or suspected to be EDCs. Large volumes of wastewater are produced in the process of fracking. Fracking wastewater is laden with chemicals used to drill and frack the well and may also contain radioactive compounds and heavy metals released from deep underground.

Disposal wells, like the one in the current study, are used only to dispose of fluids associated with oil and natural gas production, according to the U.S. Environmental Protection Agency.

"Approximately 36,000 of these disposal wells are currently in operation across the U.S., and little work has been done to evaluate their potential impacts on nearby surface water," said Christopher Kassotis, a former graduate student in Nagel's laboratory and a current postdoctoral fellow at Duke University. "Given the large number of disposal wells in the U.S., it is critical for further investigation into the potential human and environmental health impacts."

Story Source:

Materials provided by **University of Missouri-Columbia**. *Note: Content may be edited for style and length.*

Journal Reference:

1. Susan C. Nagel et al. **Endocrine Disrupting Activity in Surface Water Associated with a West Virginia Oil and Gas Industry Wastewater Injection Disposal Site**. *Science of the Total Environment*, April 2016

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Dec. 16, 2013 — A controversial oil and natural gas drilling technique called hydraulic fracturing, or fracking, uses many chemicals that can disrupt the body's hormones, according to new ... **read more**

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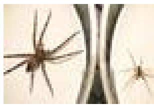
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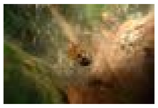
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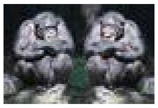
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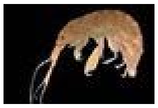
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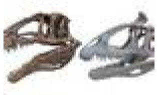

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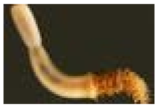

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Fracking -- not wastewater disposal -- linked to most induced earthquakes in Western Canada

Date: March 29, 2016

Source: Seismological Society of America

Summary: A survey of a major oil and natural gas-producing region in Western Canada suggests a link between hydraulic fracturing or 'fracking' and induced earthquakes in the region.

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FULL STORY

A survey of a major oil and natural gas-producing region in Western Canada suggests a link between hydraulic fracturing or "fracking" and induced earthquakes in the region, according to a new report published online in the journal *Seismological Research Letters*.

The study's findings differ from those reported from oil and gas fields in the central United States, where fracking is not considered to be the main cause of a sharp rise in induced seismicity in the region. Instead, the proliferation of hundreds of small earthquakes in that part of the U.S. is thought to be caused primarily by massive amounts of wastewater injected back into the ground after oil and gas recovery.

The SRL study does not examine why induced seismicity would be linked to different processes in the central U.S. and western Canada. However, some oil and gas fields in the U.S., especially Oklahoma, use "very large amounts of water" in their operations, leading to much more wastewater disposal than

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in Canadian operations, said Gail M. Atkinson of Western University.

It is possible that massive wastewater disposal in the U.S. is "masking another signal" of induced seismicity caused by fracking, Atkinson said. "So we're not entirely sure that there isn't more seismicity in the central U.S. from hydraulic fracturing than is widely recognized."

The fracking process uses high-pressure injections of fluid to break apart rock and release trapped oil and natural gas. Both fracking and wastewater injections can increase the fluid pressure in the natural pores and fractures in rock, or change the state of stress on existing faults, to produce earthquakes.

The Western Canada Sedimentary Basin (WCSB) contains one of the world's largest oil and gas reserves, and is dotted with thousands of fracking wells drilled in multi-stage horizontal operations. Atkinson and her colleagues compared the relationship of 12,289 fracking wells and 1236 wastewater disposal wells to magnitude 3 or larger earthquakes in an area of 454,000 square kilometers near the border between Alberta and British Columbia, between 1985 and 2015.

The researchers performed statistical analyses to determine which earthquakes were most likely to be related to hydraulic fracturing, given their location and timing. The analyses identified earthquakes as being related to fracking if they took place close to a well and within a time window spanning the start of fracking to three months after its completion, and if other causes, such as wastewater disposal, were not involved.

Atkinson and colleagues found 39 hydraulic fracturing wells (0.3% of the total of fracking wells studied), and 17 wastewater disposal wells (1% of the disposal wells studied) that could be linked to earthquakes of magnitude 3 or larger.

While these percentages sound small, Atkinson pointed out that thousands of hydraulic fracturing wells are being drilled every year in the WCSB, increasing the likelihood of earthquake activity. "We haven't had a large earthquake near vulnerable infrastructure yet," she said, "but I think it's really just a matter of time before we start seeing damage coming out of this."

The study also confirmed that in the last few years nearly all the region's overall seismicity of magnitude 3 or larger has been induced by human activity. More than 60% of these quakes are linked to hydraulic fracture, about 30-35% come from disposal wells, and only 5 to 10% of the earthquakes have a natural tectonic origin, Atkinson said.

Atkinson said the new numbers could be used to recalculate the seismic hazard for the region, which could impact everything from building codes to safety assessments of critical infrastructure such as dams and bridges. "Everything has been designed and assessed in terms of earthquake hazard in the past, considering the natural hazard," she said. "And now we've fundamentally changed that, and so our seismic hazard picture has changed."

across the US, people are hearing more and more about a controversial oil and gas extraction technique called hydraulic fracturing – aka, hydro-fracking. Controversies pivot on some ... **read more**

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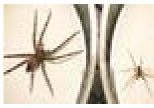
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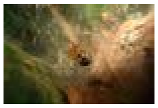
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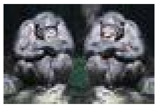
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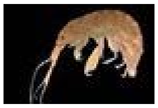
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The researchers were also surprised to find that their data showed no relationship between the volume of fluid injected at a hydraulic fracturing well site and the maximum magnitude of its induced earthquake.

"It had previously been believed that hydraulic fracturing couldn't trigger larger earthquakes because the fluid volumes were so small compared to that of a disposal well," Atkinson explained. "But if there isn't any relationship between the maximum magnitude and the fluid disposal, then potentially one could trigger larger events if the fluid pressures find their way to a suitably stressed fault."

Atkinson and her colleagues hope to refine their analyses to include other variables, such as information about extraction processes and the geology at individual well sites, "to help us understand why some areas seem much more prone to induced seismicity than others."

The scientists say the seismic risks associated with hydraulic fracturing could increase as oil and gas companies expand fracking's use in developing countries, which often contain dense populations and earthquake-vulnerable infrastructure.

Story Source:

Materials provided by **Seismological Society of America**. *Note: Content may be edited for style and length.*

Journal Reference:

1. Gail M. Atkinson, David W. Eaton, Hadi Ghofrani, Dan Walker, Burns Cheadle, Ryan Schultz, Robert Shcherbakov, Kristy Tiampo, Jeff Gu, Rebecca M. Harrington, Yajing Liu, Mirko van der Baan, and Honn Kao. **Hydraulic Fracturing and Seismicity in the Western Canada Sedimentary Basin**. *Seismological Research Letters*, May/June 2016 DOI: 10.1785/0220150263

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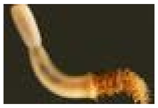

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Hydraulic fracturing linked to earthquakes in Ohio

Date: October 14, 2014

Source: Seismological Society of America

Summary: Hydraulic fracturing triggered a series of small earthquakes in 2013 on a previously unmapped fault in Harrison County, Ohio, according to a new study.

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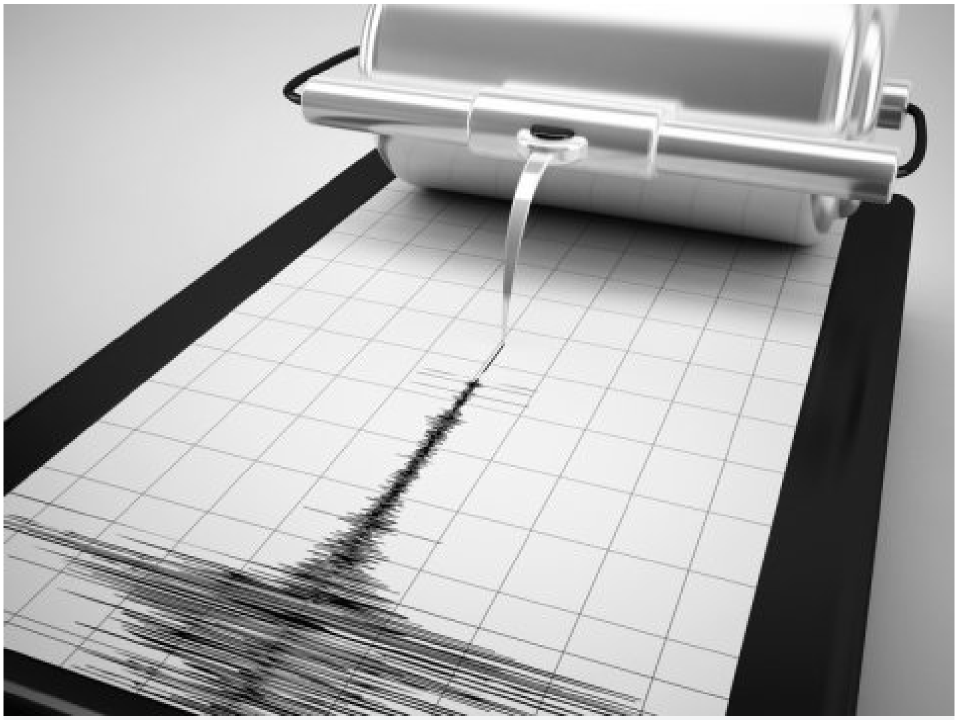

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Aug. 19, 2013 — Since records began in 1776, the people of Youngstown, Ohio had never experienced an earthquake. However, from January 2011, 109 tremors were recorded and new research reveals how this may be the ... **read more** small earthquakes in 2013 on a previously unmapped fault in Harrison County, Ohio, according to a study.

Credit: © hakandogu / Fotolia

Hydraulic fracturing triggered a series of small earthquakes in 2013 on a previously unmapped fault in Harrison County, Ohio, according to a study published in the journal *Seismological Research Letters (SRL)*.

Nearly 400 small earthquakes occurred between Oct. 1 and Dec. 13, 2013, including 10 "positive" magnitude earthquake, none of which were reported felt by the public. The 10 positive magnitude earthquakes, which ranged from magnitude 1.7 to 2.2, occurred between Oct. 2 and 19, coinciding with hydraulic fracturing operations at nearby wells.

This series of earthquakes is the first known instance of seismicity in the area.

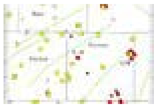
Hydraulic fracturing, or fracking, is a method for extracting gas and oil from shale rock by injecting a high-pressure water mixture directed at the rock to release the gas inside. The process of hydraulic fracturing involves injecting water, sand and chemicals into the rock under high pressure to create cracks. The process of cracking rocks results in micro-earthquakes. Hydraulic fracturing usually creates only small earthquakes, ones that have magnitude in the range of negative 3 (−3) to negative 1 (-1).

"Hydraulic fracturing has the potential to trigger earthquakes, and in this case, small ones that could not be felt, however the earthquakes were three orders of magnitude larger than normally expected," said Paul Friberg, a seismologist with Instrumental Software Technologies, Inc. (ISTI) and a co-author of the study.

The earthquakes revealed an east-west trending fault that lies in the basement formation at approximately two miles deep and directly below the three horizontal gas wells. The EarthScope Transportable Array Network Facility identified the first earthquakes on Oct. 2, 2013, locating them south of Clendening Lake near the town of Uhrichsville, Ohio. A subsequent analysis identified 190 earthquakes during a 39-hour period on Oct. 1 and 2, just hours after hydraulic fracturing began on one of the wells.

The micro-seismicity varied, corresponding with the fracturing activity at the wells. The timing of the earthquakes, along with their tight linear clustering and similar waveform signals, suggest a unique source for the cause of the earthquakes -- the hydraulic fracturing operation. The fracturing likely triggered slip on a pre-existing fault, though one that is located below the formation expected to confine the fracturing, according to the authors.

"As hydraulic fracturing operations explore new regions, more seismic monitoring will be needed since many faults remain unmapped." Friberg co-



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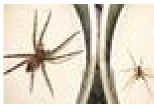

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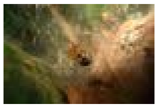

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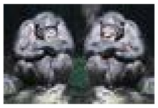

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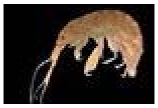

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authored the paper with Ilya Dricker, also with ISTI, and Glenda Besana-Ostman originally with Ohio Department of Natural Resources, and now with the Bureau of Reclamation at the U.S. Department of Interior.

Story Source:

Materials provided by **Seismological Society of America**. *Note: Content may be edited for style and length.*

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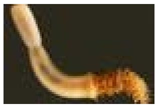

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Hydro-fracking: Fact vs. fiction

Date: November 5, 2012

Source: Geological Society of America

Summary: In communities across the US, people are hearing more and more about a controversial oil and gas extraction technique called hydraulic fracturing – aka, hydro-fracking. Controversies pivot on some basic questions: Can hydro-fracking contaminate domestic wells? Does it cause earthquakes? How can we know? What can be done about these things if they are true?

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FULL STORY

In communities across the U.S., people are hearing more and more about a controversial oil and gas extraction technique called hydraulic fracturing -- aka, hydro-fracking. Controversies pivot on some basic questions: Can hydro-fracking contaminate domestic wells? Does it cause earthquakes? How can we know? What can be done about these things if they are true?

"When people talk about contamination from hydraulic fracturing, for instance, they can mean a lot of different things," says hydrogeologist Harvey Cohen of S.S. Papadopulos & Associates in Bethesda, Maryland. "When it's what's happening near their homes, they can mean trucks, drilling machinery, noise." These activities can potentially lead to surface water or groundwater contamination if there are, for example, accidental fuel spills.

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People also worry about fracking fluids leaking into the aquifers they tap for domestic or municipal water.

On the other hand, when petroleum companies talk about risks to groundwater from hydro-fracking, they are often specifically referring to the process of injecting fluids into geologic units deep underground and fracturing the rock to free the oil and gas it contains, says Cohen. This is a much smaller, much more isolated part of the whole hydraulic fracturing operation. It does not include the surface operations -- or the re-injection of the fracking waste fluids at depth in other wells, which is itself another source of concern for many.

But all of these concerns can be addressed, says Cohen, who will be presenting his talk on groundwater contamination and fracking on the morning of Nov. 7. For instance, it has been proposed that drillers put non-toxic chemical tracers into their fracking fluids so that if a nearby domestic well is contaminated, that tracer will show up in the well water. That would sort out whether the well is contaminated from the hydro-fracking operations or perhaps from some other source, like a leaking underground storage tank or surface contaminants getting into the groundwater.

"That would be the 100 percent confident solution," says Cohen of the tracers.

Another important strategy is for concerned citizens, cities, and even oil companies to gather baseline data on water quality from wells before hydro-fracking begins. Baseline data would have been very helpful, for example, in the case of the Pavillion gas field the Wind River Formation of Wyoming, according to Cohen, because there are multiple potential sources of contaminants that have been found in domestic wells there. The Pavillion field is just one of multiple sites now being studied by the U.S. Environmental Protection Agency (EPA) to learn about past and future effects of hydro-fracking on groundwater.

The same pre-fracking science approach is being taken in some areas to evaluate the seismic effects of disposing of fracking fluids by injecting them deep underground. In Ohio and Texas, this disposal method has been the prime suspect in the recent activation of old, dormant faults that have generated clusters of low intensity earthquakes. So in North Carolina, as well as other places where fracking has been proposed, some scientists are scrambling to gather as much pre-fracking seismic data as possible.

Story Source:

Materials provided by **Geological Society of America**. *Note: Content may be edited for style and length.*

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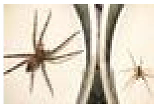

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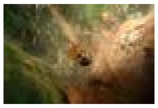

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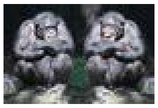

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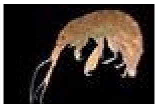

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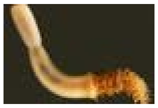

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Fracking in Ohio confirmed as cause of rare earthquake strong enough to be felt

Date: January 5, 2015

Source: Seismological Society of America

Summary: A new study links the March 2014 earthquakes in Poland Township, Ohio, to hydraulic fracturing that activated a previously unknown fault. The induced seismic sequence included a rare felt earthquake of magnitude 3.0, according to new research.

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A new study links the March 2014 earthquakes in Poland Township, Ohio to hydraulic fracturing that activated a previously unknown fault. The induced seismic sequence included a rare felt earthquake of magnitude 3.0, according to research published online by the *Bulletin of the Seismological Society of America* (*BSSA*).

In March 2014, a series of five recorded earthquakes, ranging from magnitude 2.1 to 3.0, occurred within one kilometer (0.6 miles) of a group of oil and gas wells operated by Hilcorp Energy, which was conducting active hydraulic fracturing operations at the time. Due to the proximity of a magnitude 3.0 event near a well, the Ohio Department of Natural Resources (ODNR) halted operations at the Hilcorp well on March 10, 2014.

Hydraulic fracturing, or fracking, is a method for extracting gas and oil from shale rock by injecting a high-pressure water mixture directed at the rock to

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How Shale Fracking Led to an Ohio Town's First 100 Earthquakes release the oil and gas trapped inside. The process of fracturing the rocks normally results in micro-earthquakes much smaller than humans can feel.

It remains rare for hydraulic fracturing to cause larger earthquakes that are felt by humans. However, due to seismic monitoring advances and the increasing popularity of hydraulic fracturing to recover hydrocarbons, the number of earthquakes -- felt and unfelt -- associated with hydraulic fracturing has increased in the past decade.

"These earthquakes near Poland Township occurred in the Precambrian basement, a very old layer of rock where there are likely to be many pre-existing faults," said Robert Skoumal who co-authored the study with Michael Brudzinski and Brian Currie at Miami University in Ohio. "This activity did not create a new fault, rather it activated one that we didn't know about prior to the seismic activity."

Using a technique called template matching, the researchers sifted through seismic data recorded by the Earthscope Transportable Array, a network of seismic stations, looking for repeating signals similar to the known Poland Township earthquakes, which were treated like seismic "fingerprints." They identified 77 earthquakes with magnitudes from 1.0 and 3.0 that occurred between March 4 and 12 in the Poland Township area. The local community reported feeling only one earthquake, the magnitude 3.0, on March 10.

Skoumal and his colleagues compared the identified earthquakes to well stimulation reports, released in August 2014 by the ODNR, and found the earthquakes coincided temporally and spatially with hydraulic fracturing at specific stages of the stimulation. The seismic activity outlined a roughly vertical, east-west oriented fault within one kilometer of the well. Industry activities at other nearby wells produced no seismicity, suggesting to the authors that the fault is limited in extent.

"Because earthquakes were identified at only the northeastern extent of the operation, it appears that a relatively small portion of the operation is responsible for the events," said Skoumal, who suggests the template matching technique offers a cost-effective and reliable means to monitor seismicity induced by hydraulic fracturing operations.

"We just don't know where all the faults are located," said Skoumal. "It makes sense to have close cooperation among government, industry and the scientific community as hydraulic fracturing operations expand in areas where there's the potential for unknown pre-existing faults."

Story Source:

Materials provided by **Seismological Society of America**. *Note: Content may be edited for style and length.*

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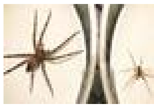
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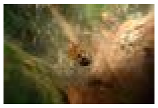
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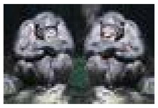
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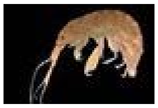
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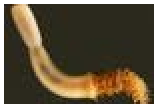

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Toxicologists outline key health and environmental concerns associated with hydraulic fracturing

Date:	May 9, 2014
Source:	Society of Toxicology
Summary:	Since the rise in the use of hydraulic fracturing of shale to produce natural gas and oil, many have debated the merits and detractions of the practice. Scientists outline how toxicological sciences can be used to determine what risks may or may not be associated with fracking.
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FULL STORY

Since the rise in the use of hydraulic fracturing of shale to produce natural gas and oil, scientists, politicians, industrialists, and others have debated the merits and detractions of the practice. In a newly published paper in *Toxicological Sciences*, members of the Society of Toxicology (SOT), alongside other experts, outline how toxicological sciences can be used to determine what risks may or may not be associated with hydraulic fracturing.

"Toxicology is the study of the effects of chemical, physical, or biological agents on living organisms and the environment. As such, toxicologists should be at the forefront of discussions of hydraulic fracturing," says Society of Toxicology President Norbert E. Kaminski, PhD. "We can provide information on the potential toxicity of the chemical and physical agents

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June 1, 2016 — The use of hydraulic fracturing, or 'fracking,' has grown rapidly in the US over the past 15 years -- but concerns persist that the oil and gas extraction method could harm the environment ... **read more**

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Dec. 15, 2015 — The production of hazardous wastewater in hydraulic fracturing is assumed to be partly due to chemicals introduced into injected freshwater when it mixes with highly saline brine naturally present in ... **read more**

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Oct. 14, 2014 — Hydraulic fracturing triggered a series of small earthquakes in 2013 on a previously unmapped fault in Harrison County, Ohio, according to a new ...
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associated with the process, individually and in combination."

In "The Role of Toxicological Science in Meeting the Challenges and Opportunities of Hydraulic Fracturing" Bernard D. Goldstein, et al, identify a series of potential pathways of contamination and toxicological effects associated with hydraulic fracturing that should and are being explored by researchers:

- **Water pollution**: There is a potential for surface or groundwater contamination by hydraulic fracturing fluids and their constituents. The authors found that there are few confirmed cases of groundwater contamination, but that there is little research available on the chemical baselines of drinking and surface waters prior to hydraulic fracturing practices to determine contamination with toxicologically significant levels of chemicals as a result of routine hydraulic fracturing.
- **Air Pollution**: The authors write, "A single hydraulic fracturing site is unlikely to produce significant increments of ozone precursors. However, there is concern that in aggregate hydraulic fracturing activities in regions with thousands of wells, and which already have ozone levels close to the allowable health-based standard, such as the Northeast, may be tipped into nonattainment of the standard." Potential contaminants that are being studied include methane gas, diesel emissions, volatile organic compounds, and benzene, among others.
- **Occupational Exposure**: Workers at hydraulic fracturing sites are exposed to a series of potential hazards to their health. These potential hazards range from inhalation of gases and particulate matter to dermal exposure to these same elements. Evaluating exposure amounts, types of exposure, and lengths of exposure to various individual chemicals and the chemicals in combination is necessary to determine potential risks to hydraulic fracturing workers.

Story Source:

Materials provided by **Society of Toxicology**. *Note: Content may be edited for style and length.*

Journal Reference:

1. B. D. Goldstein, B. W. Brooks, S. D. Cohen, A. E. Gates, M. E. Honeycutt, J. B. Morris, J. Orme-Zavaleta, T. M. Penning, J. Snawder. **The Role of Toxicological Science in Meeting the Challenges and Opportunities of Hydraulic Fracturing**. *Toxicological Sciences*, 2014; 139 (2): 271 DOI: 10.1093/toxsci/kfu061

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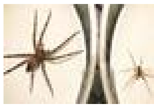
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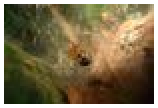
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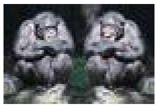
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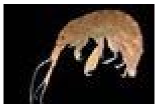
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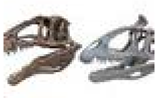

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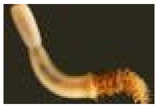

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How shale fracking led to an Ohio town's first 100 earthquakes

Date:	August 19, 2013
Source:	Wiley
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The study authors analyzed the Youngstown earthquakes, finding that their onset, cessation, and even temporary dips in activity were all tied to the activity at the Northstar 1 well. The first earthquake recorded in the city occurred 13 days after pumping began, and the tremors ceased shortly after the Ohio Department of Natural Resources shut down the well in December

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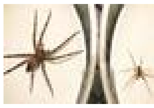
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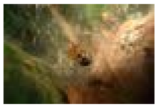
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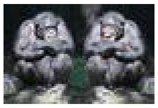
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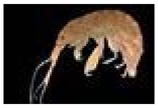
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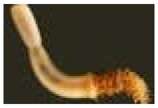

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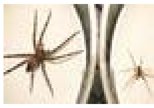
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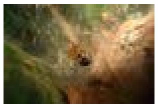
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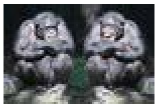
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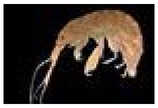
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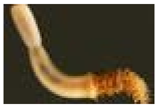
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How to get a handle on potential risks posed by fracking fluids

Date: March 9, 2016

Source: American Chemical Society

Summary: The latest skirmishes over hydraulic fracturing in Florida and California are, at their core, about water. Many fracking-related spills have been recorded, and opponents say that such incidents pose unacceptable threats to water supplies. But the issue is fraught with uncertainties. Scientists review what's known about the fluids and conclude that a comprehensive assessment of potential risks requires full disclosure of fracking fluid contents.

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The expansion of fracking in recent years has lowered energy costs for customers and is expected to continue its growth for the next several years,

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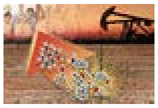

Toxins Found in Fracking Fluids and Wastewater, Study Shows

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Nov. 5, 2012 — In communities across the US, people are hearing more and more about a controversial oil and gas extraction technique called hydraulic fracturing – aka, hydro-fracking. Controversies pivot on some ... **read more**

Hydraulic Fracturing Poses Substantial Water Pollution Risks, industry experts have reported. But the compounds used to crack shale formations to release their gas and oil reserves are under increasing scrutiny. While many are considered harmless, others are known toxins or carcinogens. And there are substances that oil and gas companies use in fracking operations that they don't disclose publicly. But in a recent review article, Martin Elsner and Kathrin Hoelzer note several reasons why these companies should list all the compounds involved.

The researchers say transparency could go a long way toward improving these operations. Among other benefits, full disclosure could allow for better monitoring of waterways for potential contamination. It also could help in assessing what new compounds might form from underground chemical reactions. Although some fluid additives might be non-toxic to start, they could react with other substances once injected into a well and form new potentially harmful products, the team explains. A complete listing could also contribute to improving the treatment of wastewater from fracking operations to remove potential toxins before they can contaminate aquifers, rivers and lakes. In addition to knowing the starting materials, the researchers say cataloging naturally occurring compounds that seep into the fluids from underground deposits is critical.

Story Source:

Materials provided by **American Chemical Society**. *Note: Content may be edited for style and length.*

Journal Reference:

1. Martin Elsner, Kathrin Hoelzer. **Quantitative Survey and Structural Classification of Hydraulic Fracturing Chemicals Reported in Unconventional Gas Production**. *Environmental Science & Technology*, 2016; DOI: 10.1021/acs.est.5b02818

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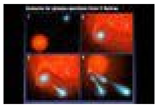

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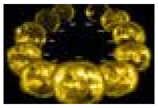

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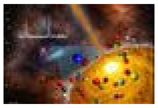

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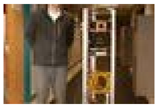

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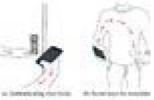

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Critical Review

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

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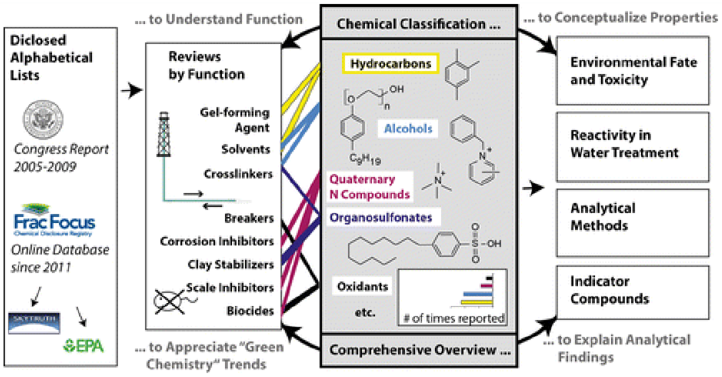

Much interest is directed at the chemical structure of hydraulic fracturing (HF) additives in unconventional gas exploitation. To bridge the gap between existing alphabetical disclosures by function/CAS number and emerging scientific contributions on fate and toxicity, we review the structural properties which motivate HF applications, and which determine environmental fate and toxicity. Our quantitative overview relied on voluntary U.S. disclosures evaluated from the FracFocus registry by different sources and on a House of Representatives ("Waxman") list. Out of over 1000 reported substances, classification by chemistry yielded succinct subsets able to illustrate the rationale of their use, and physicochemical properties relevant for environmental fate, toxicity and chemical analysis. While many substances were nontoxic, frequent disclosures also included notorious groundwater contaminants like petroleum hydrocarbons (solvents), precursors of endocrine disruptors like nonylphenols (nonemulsifiers), toxic propargyl alcohol (corrosion inhibitor), tetramethylammonium (clay stabilizer), biocides or strong oxidants. Application of highly oxidizing chemicals, together with occasional disclosures of putative delayed acids and complexing agents (i.e., compounds *designed* to react in the subsurface) suggests that relevant transformation products may be formed. To adequately investigate such reactions, available information is not sufficient, but instead a full disclosure of HF additives is necessary.

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Kathrin Hoelzer, Andrew J. Sumner, Osman Karatum, Robert K. Nelson, Brian D. Drollette, Megan P. O'Connor, Emma L. D'Ambro, Gordon J. Getzinger, P. Lee Ferguson, Christopher M. Reddy, Martin Elsner, and Desiree L. Plata

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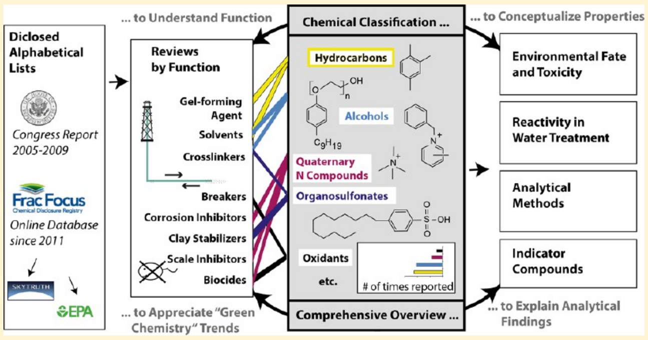
Quantitative Survey and Structural Classification of Hydraulic Fracturing Chemicals Reported in Unconventional Gas Production

Martin Elsner* and Kathrin Hoelzer

Helmholtz Zentrum München, Institute of Groundwater Ecology, Ingolstädter Landstr. 1, D-85764 Neuherberg, Germany

S Supporting Information

ABSTRACT: Much interest is directed at the chemical structure of hydraulic fracturing (HF) additives in unconventional gas exploitation. To bridge the gap between existing alphabetical disclosures by function/CAS number and emerging scientific contributions on fate and toxicity, we review the structural properties which motivate HF applications, and which determine environmental fate and toxicity. Our quantitative overview relied on voluntary U.S. disclosures evaluated from the FracFocus registry by different sources and on a House of Representatives ("Waxman") list. Out of over 1000 reported substances, classification by chemistry yielded succinct subsets able to illustrate the rationale of their use, and physicochemical properties relevant for environmental fate, toxicity and chemical analysis. While many substances were nontoxic, frequent disclosures also included notorious groundwater contaminants like petroleum hydrocarbons (solvents), precursors of endocrine disruptors like nonylphenols (nonemulsifiers), toxic propargyl alcohol (corrosion inhibitor), tetramethylammonium (clay stabilizer), biocides or strong oxidants. Application of highly oxidizing chemicals, together with occasional disclosures of putative delayed acids and complexing agents (i.e., compounds *designed* to react in the subsurface) suggests that relevant transformation products may be formed. To adequately investigate such reactions, available information is not sufficient, but instead a full disclosure of HF additives is necessary.



INTRODUCTION

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

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

Particular concern surrounds the chemicals that may return to the surface as a result of hydraulic fracturing. Both "fracking chemicals"—substances that are injected together with the HF fluid to optimize the fracturing performance—and geogenic substances are of relevance. These compounds can emerge in the flowback (the part of the injected HF fluid that returns to the surface), in the produced water (the water that emerges during gas production and originates from the target formation) or in a mixture of both.[20−22] The concentrations of additives

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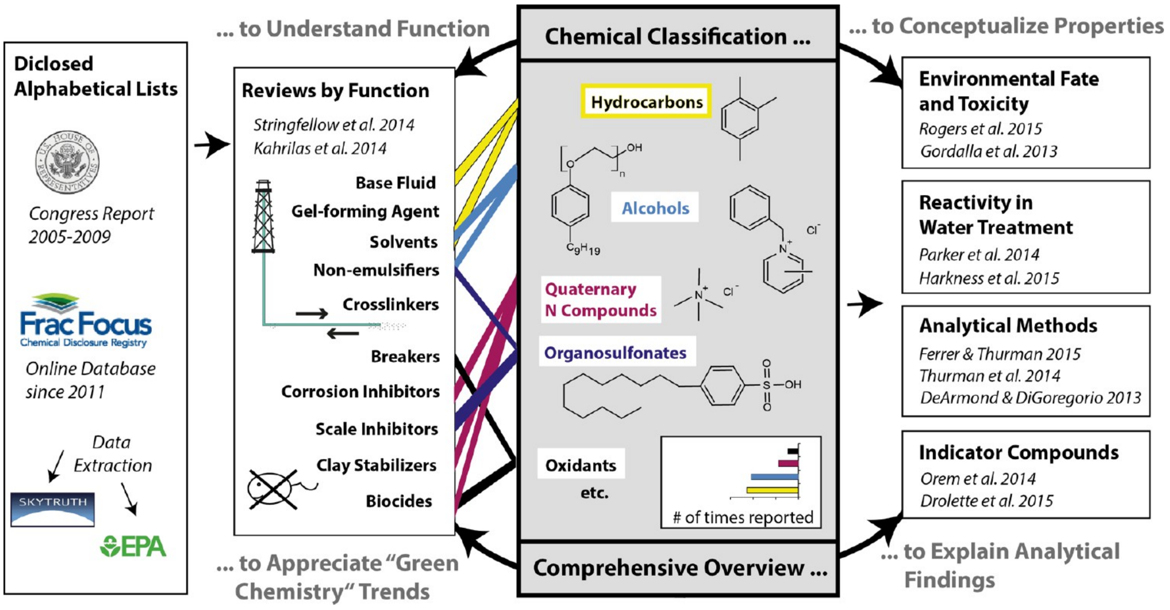


Figure 1. Information on HF additives disclosed by operators (left-hand side) and explored by scientific publications (right-hand side). The structural classification of the present contribution (gray box) enables understanding of, the chemical purpose in the HF process and may help conceptualize, resultant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

typically make up between 0.5% and 3% of an injected gel-based fluid (reported by mass or volume of the fluid, depending on the source).[3,23−25] Given that a typical fracturing operation requires around 9000 to 29 000 m^3 [26] of water, this translates into kilograms to tens of tons of the respective compounds. In 2005, underground injections of these substances for HF operations related to oil and gas were exempted from all U.S. federal regulations aiming to protect the environment (Clean Water Act, Save Drinking Water Act, Clean Air Act, Super Fund Law, Resource Recovery and Conservation Act, Toxic Release Inventory); in Germany, HF operations have been regulated by the Federal Law of Mining which currently does not require Environmental Impact Assessments including public disclosure of these chemicals.[27] Knowledge about fracturing chemicals and geogenic substances, however, is warranted for several reasons:[28]

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

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

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

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

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

■ MATERIALS AND METHODS

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

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 sublists according to substance classes: "Gases and Non-functionalized Hydrocarbons", "Alcohols, Ethers, Alkoxylated Alcohols", "Carboxylic Acids" etc. These sublists correspond to the classification typically found in textbooks[53,54] and they allow for an overview of the chemical functional groups used and why−even if the same functionality serves different purposes in the HF process.

■ RESULTS AND DISCUSSION

Types of Hydraulic Fracturing Fluids and Required Properties. All hydraulic fracturing operations require a base

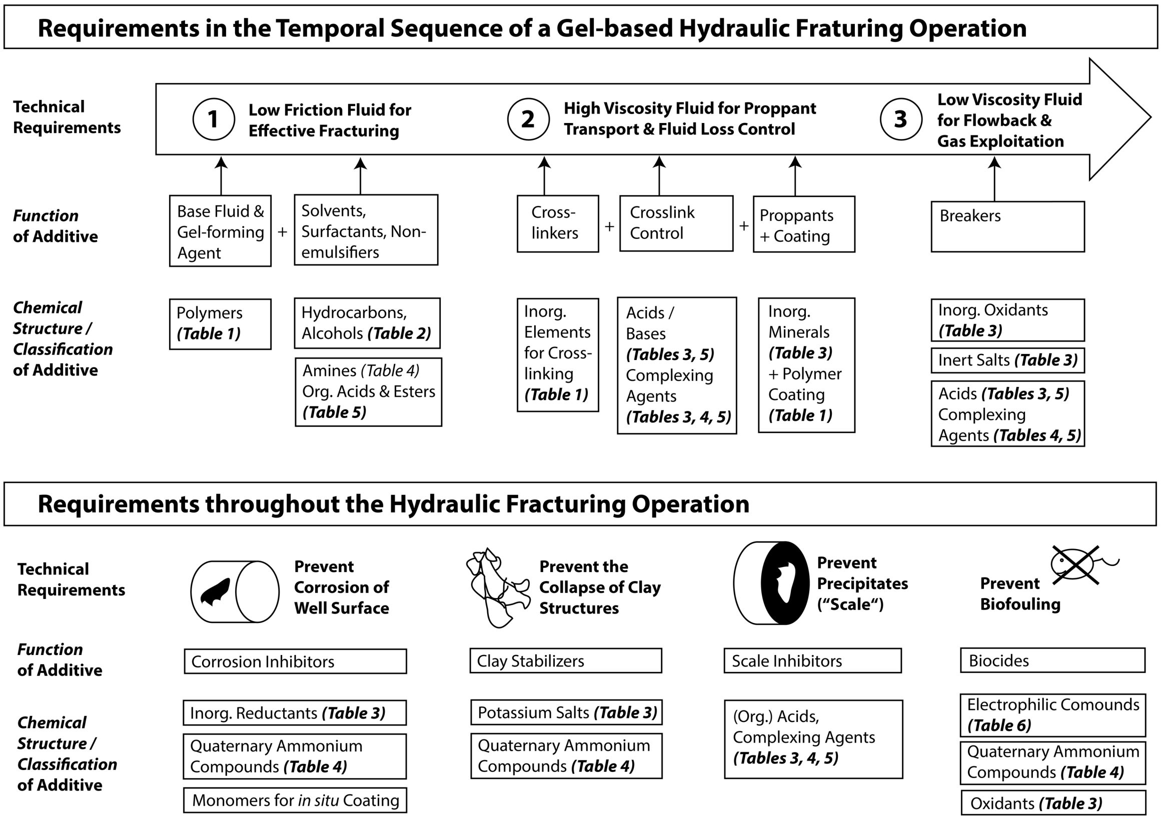


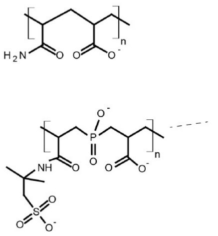
Figure 2. Requirements of a gel-based HF operation and additives grouped by their *technical function* and their *chemical classification* (corresponding to the Tables in the manuscript).

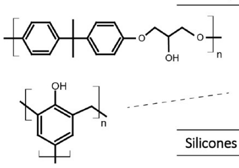
fluid (carrier medium) which must be of sufficiently low friction to convey a high hydraulic pressure into the target formation so that fissures are generated. In the process it must further acquire sufficient viscosity to prevent loss of the base fluid into the formation, and to transport proppants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

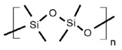
Figure 2 illustrates how such *functional* requirements are related to chemical *substance classes* and, therefore, provides a roadmap through this review. Each substance class is treated in a dedicated chapter. An associated Table links chemical properties with functionalities in the HF process by listing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

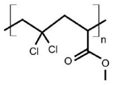
Table 1. Most Frequently Reported Synthetic Polymers, Biopolymers and Inorganic Cross-Linkers, Together with Corresponding Reaction Schemes[a]

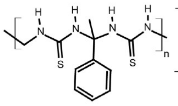
Synthetic Polymers





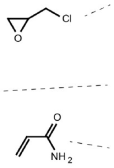






Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus		No. of Declarations		CAS -Number
			EPA Eval.	Rogers et al.	Sky Truth	Waxman	
Acrylamides / Acrylates			**8.8**	**n.r.**	**7238**	**31**	
Copolymer of acrylamide and sodium acrylate	Gel Forming Agent, Friction Reducer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

Monomers

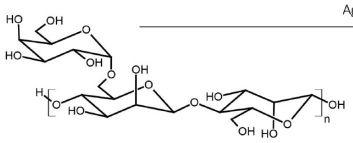


Epichlorohydrin	Proppant Coating	Superior EXP-PCH 20/50 (Nabors Completion and Production Services): Proppants (with Quartz); HyperProp G2, 20/40 Baker Hughes: Proppant	0.19	0.43	877	5	25085-99-8, 106-89-8
Bisphenol A			0	0.028	9	0	80-05-7
Ammonium Acrylate			0.07	2.1	291	0	10604-69-0
Acrylamide			0.52	3.2	658	2	79-06-1

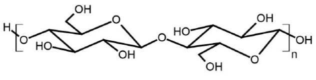
Biopolymers

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



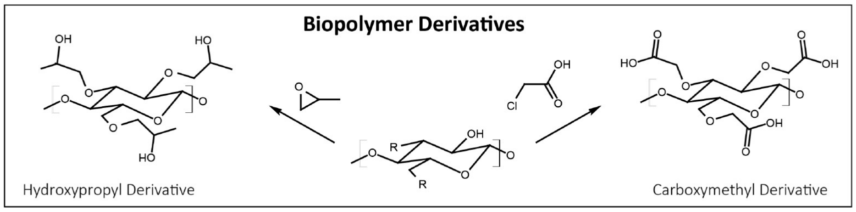
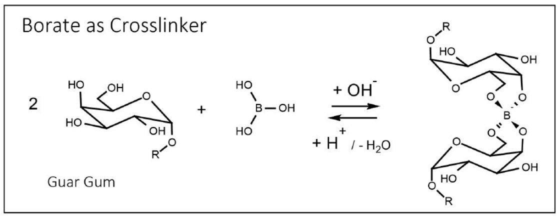
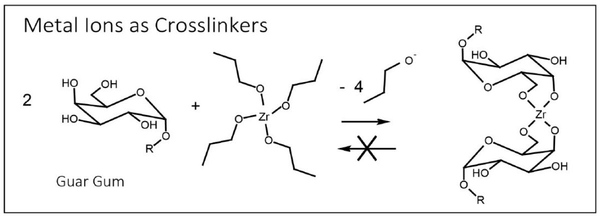


Table 1. continued

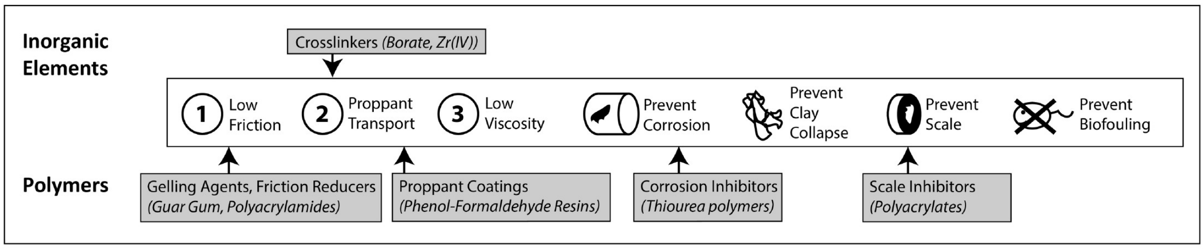
Inorganic Elements Conducive to Condensation / Crosslinking

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

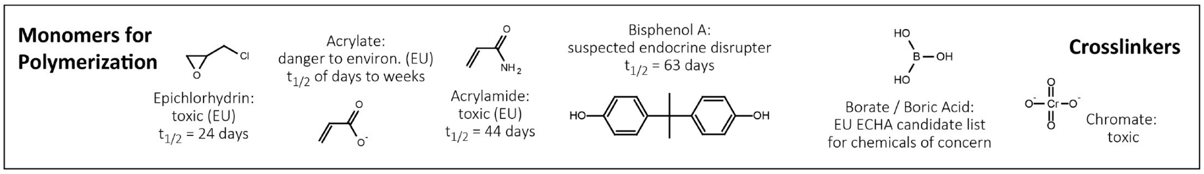




Functions in the Hydraulic Fracturing Process (Summary)



Potential Substances of Concern (Examples)



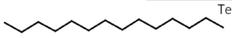
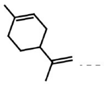
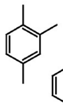
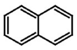
[a]Degradation half-lives are from ref 44. A more comprehensive list of compounds together with physicochemical properties is provided in the SI. n.r.: not representative; n.i.: not included.

1. Polymers and Cross-Linkers. *Chemical Properties Relevant in the HF Process.* Table 1 lists disclosed synthetic polymers and biopolymers together with inorganic elements that are conducive to condensation/cross-linking. As illustrated by the functions and the frequency of disclosure, polymer properties—that is, 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 cross-linked 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 cross-linking 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 cross-linking. To establish cross-links, complexation of −OH groups can be achieved with either borate or metal ions. Borate has the

Table 2. Most Frequently Reported Gases, Hydrocarbons and Alcohols[a]

Gases and Non-functionalized Hydrocarbons

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

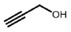
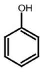
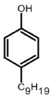
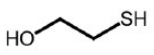
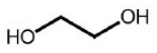
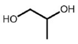
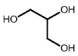
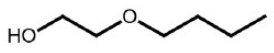
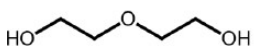
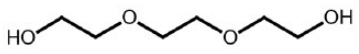
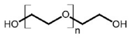
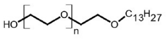
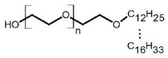
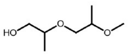
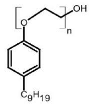
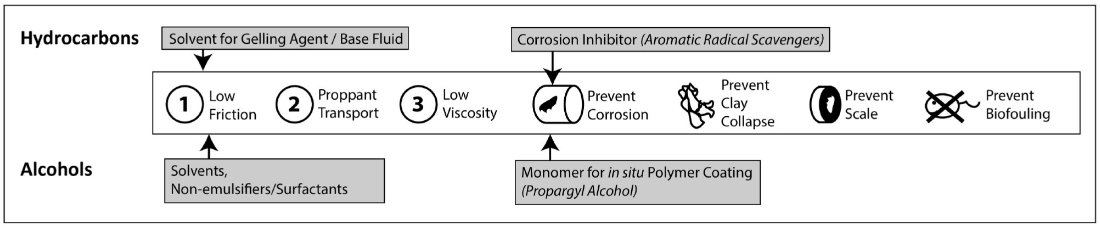
Primary and Secondary Alcohols				**206.1**	**212.1**	**155960**	**769**	
	Methanol	Solvent		72.3	76.5	72810	342	67-56-1, 267-56-1
	Ethanol	Solvent		37.3	34.2	22749	36	64-17-5
	Isopropanol	Solvent		47.2	50.1	33819	274	67-63-0
	Propargyl alcohol (2-propyn-1-ol)	Corrosion Inhibitor	HAI-OS ACID INHIBITOR (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-mercaptoethanol (Thioglycol)			0.62	8.7	3613	13	60-24-2
	Ethylene glycol (1,2-ethanediol)	Crosslinker, Scale Inhibitor, 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-nitrilopropionamide); 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/ Formaldehyde Copolymer);	11.7	28.6	12848	11	68131-39-5, 68951-67-7, 103331-86-8, 68551-12-2,

Table 2. continued

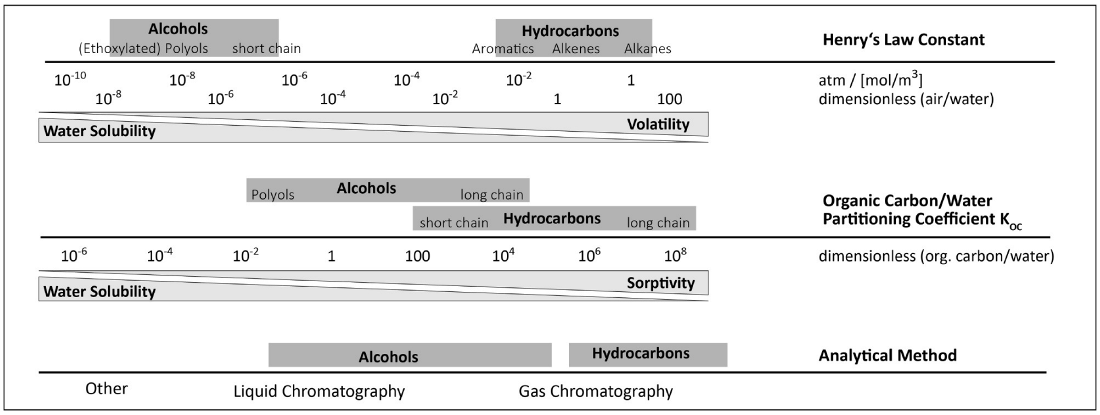
Alcohols, Ethers, Alkoxylated Alcohols (continued)

	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

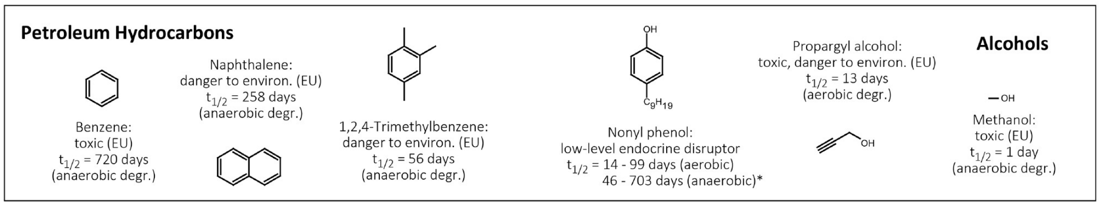
Functions in the Hydraulic Fracturing Process (Summary)



Physicochemical Properties and Analytical Methods (Overview)



Potential Substances of Concern (Examples)



[a]Henry's law constants and log K_{oc} constants are taken from EPI Suite,[71] degradation half-lives from ref 44, except for 4-nonylphenol.[72] A more comprehensive list of compounds together with physicochemical data is given in the SI. n.r.: not representative; n.i.: not included.

advantage that the complexation can be reversed by adding acid as a breaker (left scheme in Table 1), but it has the disadvantage that linkages are not stable at high temperatures.[56] Metal ions have the advantage of temperature stability, but the cross-linking is not as easily reversed and some metal ions (e.g., Zr^{IV}) form precipitates when brought into contact with water.[56] Until cross-linking, 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 cross-linking.[59]

Compared to biopolymers, synthetic polyamide/-acrylate polymers have the advantage that they can be deliberately designed for a spectrum of functionalities. Without cross-linking they act as friction reducers and are, therefore, typical additives in slickwater fracks.[56] If the percentage of acrylate-derived carboxyl groups is increased, these groups can be cross-linked 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).

Substances of Concern/Consequences for Environmental Monitoring. Biopolymers, the listed acrylamides/acrylate and silicone polymers are all of low toxicity where biodegradability is better for acrylamides than for silicones.[60−63] In water treatment, the main relevance of these structures is likely their high oxygen demand. Instead, potential substances of concern are monomers such as acrylate, acrylamide, epichlorohydrin or Bisphenol A (see Table 1). These monomers may either leach out of the polymer, or they are, potentially, even applied deliberately to conduct polymerization in situ during the HF process which is a known practice to enable slow gel formation at elevated temperatures (see, e.g., chapter 8 in Fink (2011)).[59] In this context, the polyvinylidene copolymer listed in Table 1 features toxic monomers and is highly resistant to biodegradation or oxidation.[64] Also phenol polymers for proppant coating are potentially problematic, because unreacted phenolic monomers can leach over time and the polymer is barely degradable.[65] Specifically, bisphenol A/epichlorohydrin oligomers are ranked as acutely toxic, long-term aquatoxic and carcinogenic.[66]

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

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

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

Next to hydrocarbons, alcohols are the most frequently disclosed solvents, in particular methanol and isopropanol (Table 2). The distinguishing feature of alcohols is their −OH group, which makes them miscible with water. Short-chain alcohols, as well as alcohols with numerous alkoxy groups inside their structure ("polyethylene glycol", "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 cross-linking dissolved ("*crosslinker*", "*crosslink control*") or to prevent geogenic precipitates ("*scale inhibitor*"). Propargyl alcohol serves as *corrosion inhibitor* because of its unsaturated bond which allows in situ polymerization to form a protective polymer coating at the well surface.[70] Alkoxylated nonylphenols, finally, are used as *solvents*, *surfactants*, and *nonemulsifiers* (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).

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

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Table 3. Most Frequently Reported Inorganic Compounds (Inert, Reactive, Insoluble, Soluble)[a]

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

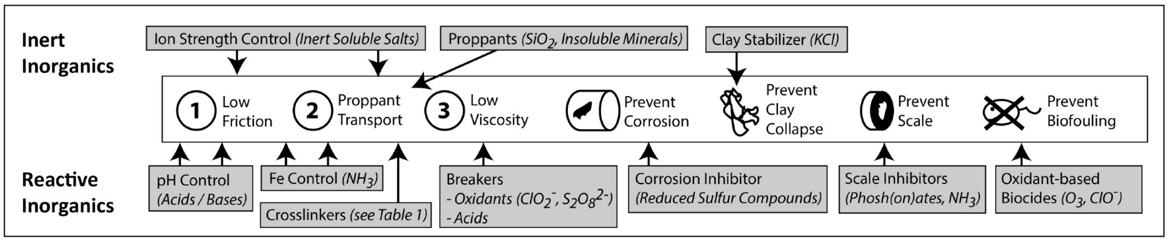
Inorganic Reducing			**5.4**	**n.i.**	**5279**	**39**	
Sodium thiosulfates	Temp. Stabilizer	GEL-STA L STABILIZER (Halliburton): Stabilizer (no mix); Ecopol-HTSL (RockPile Energy): Temperature Stabilizer (with water); GST 530 Green Field Energy Services): Gel Stabilizer (with water/Sodium Sulfite/Sodium 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

Table 3. continued

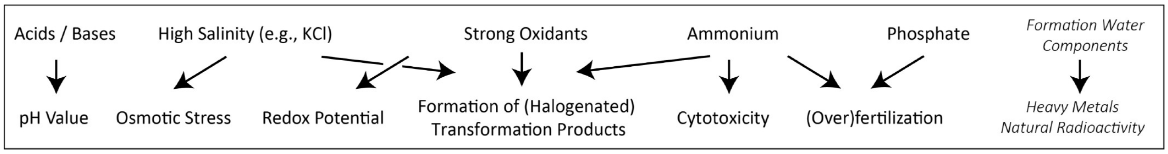
Reactive Inorganic Compounds: Reductants, Oxidants, Acids, Bases, Complexing Agents (continued)

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



[a] A more comprehensive list of compounds together with physicochemical data is given in the SI. n.r.: not representative; n.i.: not included.

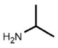
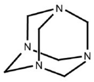
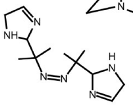
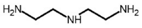
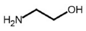
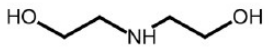
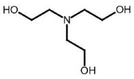
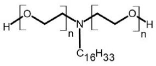
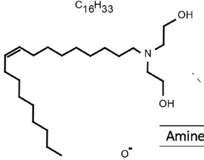
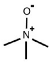
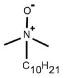
directly reported as hydraulic fracturing additives (Table 2) they are nonetheless likely to form as a result of HF operations.

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

3. Inorganic Compounds. *Chemical Properties Relevant in the HF Process.* Table 3 distinguishes between inorganic compounds with an obvious chemical function (oxidants, reductants, acids, bases) and those that are nonreactive/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 metal chlorides) serve mostly for *ionic strength control* and, in small part, for *clay stabilization* (by K^+ exchange into clay interlayers,[82] see section below). Of the *reactive inorganic chemicals*, finally, most frequent listings are *pH control* reagents (HCl and other acids/NaOH,

Table 4. Most frequently reported amines and quaternary ammonium and phosphonium salts[a]

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

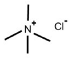
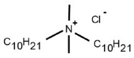
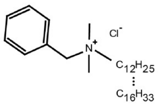
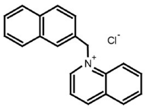
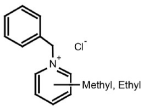
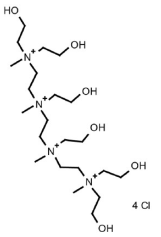
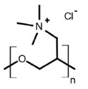
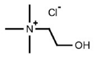
	Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
	Quarternary Aliphatic Ammonium Salts			49.4	43.3	28287	65	
	Tetramethyl ammonium chloride	Clay Stabilizer	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

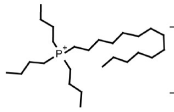
Table 4. continued

Quaternary Ammonium and Phosphonium Salts (continued)



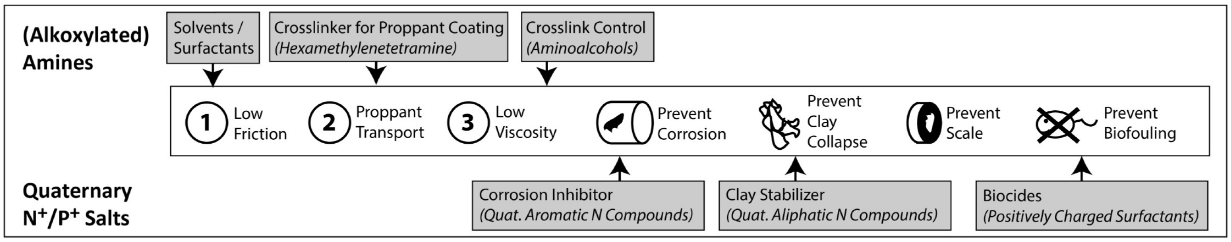




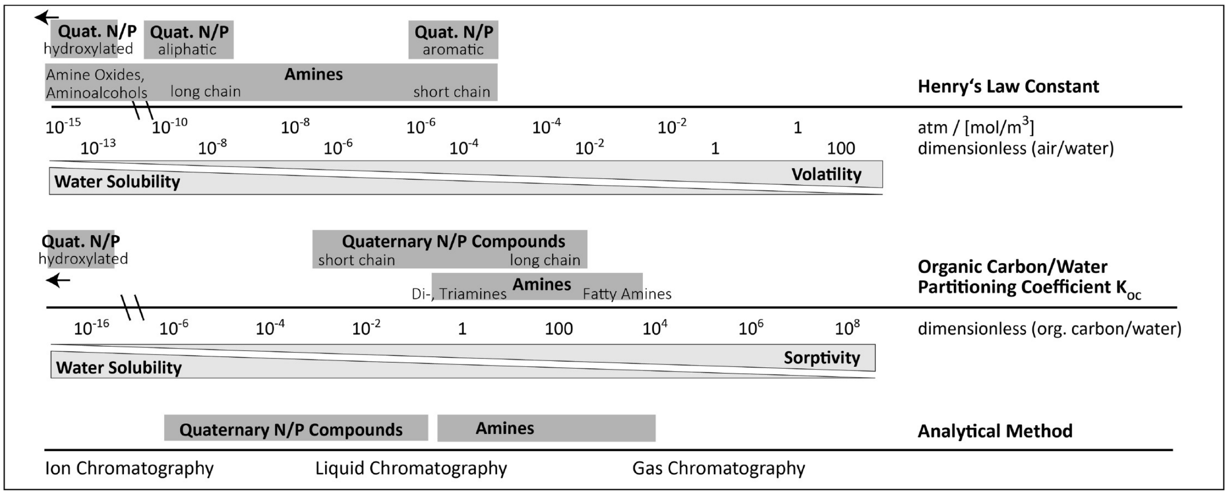


Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus EPA Eval.	Freq. (%) in FracFocus Rogers et al.	No. of Declarations Sky Truth	No. of Declarations Waxman	CAS -Number
Quaternary Ammonium salt - Hydroxyalkylated			16.1	1.6	9035	8	
1,2-Ethanediaminium, (N,N'-bis-[2[bis(2-hydroxyethyl)methylammonio]-ethyl]-N,N'-bis(2-hydroxyethyl)-N,N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

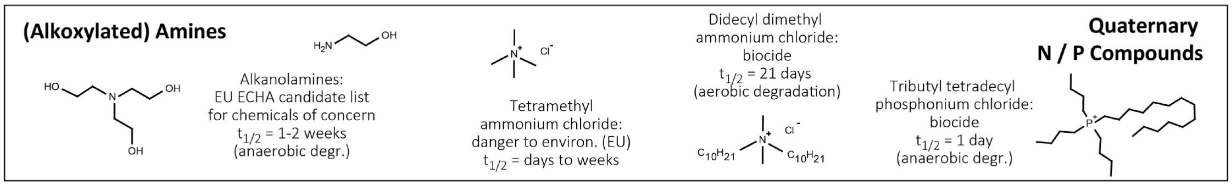
Functions in the Hydraulic Fracturing Process (Summary)



Physicochemical Properties and Analytical Methods (Overview)



Potential Substances of Concern (Examples)



[a] Henry's law constants and log K_{oc} constants are taken from EPI Suite,[71] degradation half-lives from ref 44. A more comprehensive list of compounds together with physicochemical data is given in the SI. n.i.: not included.

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 cross-links 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 cross-linking[83] (see role of Fe^{III} as cross-linker in Table 1).

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

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, whereas the simultaneous presence of ammonium, phosphate, and high DOM may cause eutrophic conditions in the HF wastewater. In addition, ammonium features cytotoxic effects,[90] as reported for plants (Britto[91] and references therein), bacteria,[90] humans,[92] and fish where acute LC_{50} values can start at 2 mg/L.[93] From a chemical point of view, experience from oxidative water treatment shows that the application of oxidants in highly saline water[94]—some of them even consisting of reactive chlorine species (NaClO, $NaClO_2$)—can form problematic halogenated organics ("disinfection by-products").[35] Considering that most formation waters are highly saline, and that, on average, four out of five HF operations apply strong oxidants (see Table 3) the possibility of similar byproduct 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 cross-link control* of polymers. Hexamethylenetetramine (HMT)—the most frequently reported compound—is used as cross-linker in phenolic resins for proppant coating (see "Phenol/Formaldehyde/Epoxy Polymers" entry in Table 1) and it greatly enhances the performance of propargyl alcohol as corrosion inhibitor.[59] Diethylenetriamine, as well as mono-, di-, and triethanolamine, are reported as cross-link control and activators of cross-linking. This indicates that they are used as complexing agents of Zr^{IV} in order to control the rate and timing of guar gum cross-linking. Since they are also reported as breakers, ethanolamines appear to be able to shift the cross-linking 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., ref 95 chapter 8). The second interpretation would be consistent with the disclosure of acrylate and acrylamide monomers in Table 1.

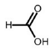
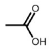
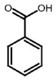
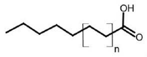
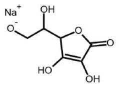
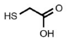
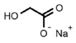
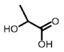
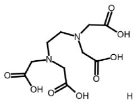
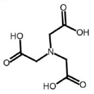
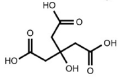
The low number of hits for amine oxides, finally—which are typical surfactants in VES applications[96−98]—confirms our earlier conclusion that viscoelatic surfactant-based fracks seem to play a minor role in comparison to gel or slickwater fracks.

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

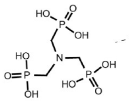
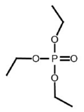
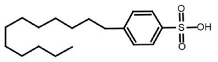
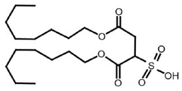
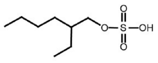
Potential Substances of Concern/Consequences for Environmental Fate and Monitoring. The substances of Table 4 are of concern either because of their acute toxicity (alkyl amines) or because of their lipophilic/cationic character that lends them biocidal properties (quaternary ammonium compounds). Of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

Table 5. Most Frequently Reported Organic Acids, Amides and Esters[a]

Carboxylic Acids

	Chemical	Function	Examples of Reported Commercial Products	Freq. (%) in FracFocus		No. of Declarations		CAS -Number
				EPA Eval.	Rogers et al.	Sky Truth	Waxman	
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 Inhbitor 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, mono-ethanolamine salt	Surfactant, Scale Inhibitor	WNE-363L (WFT): Surfactant (with Ethylene Propylene Oxide Polymer/ 2-Ethylhexanol/Poly-(oxy-1,2-ethanediyl), α-isotridecyl-ω-hydroxy-)	0.95	1.5	725	1	26836-07-7
	Diester of Sulfosuccinic Acid, Sodium Salt		e.g., Dioctyl sodium sulfosuccinate (CAS-No. 577-11-7, 181 hits)	n.i.	1.1	403	0	2673-22-5
Alkyl Sulfates				0.92	1.17	452	10	
	Sodium 2-ethylhexyl sulfate	surfactant	D-2 (Sanjel): Surfactant; OWS-DMF-A (WST): Demulsifier (with water/2-Ethylhexanol);	0.37	0.35	80	1	126-92-1

Carboxylic Amides and Esters

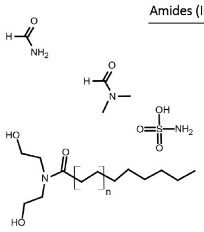
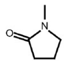
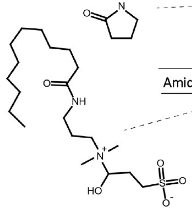
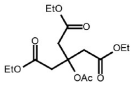
Amides (Inorganic, Short- & Long-chain Alkyl)				14136	36	15.9	24.9	
	Formamide	Solvent	CI-350 HT (FTSI): Corrosion Inhibitor (with quaternary ammonium salts, alkoxylated phenol, etc.)	606	5	2.2	1.4	75-12-7
	Dimethyl formamide	Solvent	Acid Corrosion Inhibitor - Mid Temp to High (Cationic) (Weatherford):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

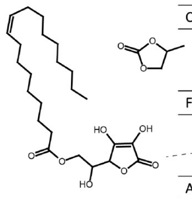
Table 5. continued

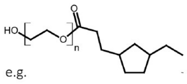
Carboxylic Amides and Esters (continued)







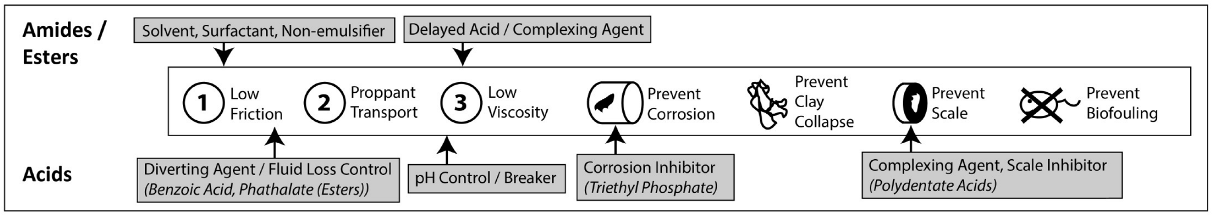




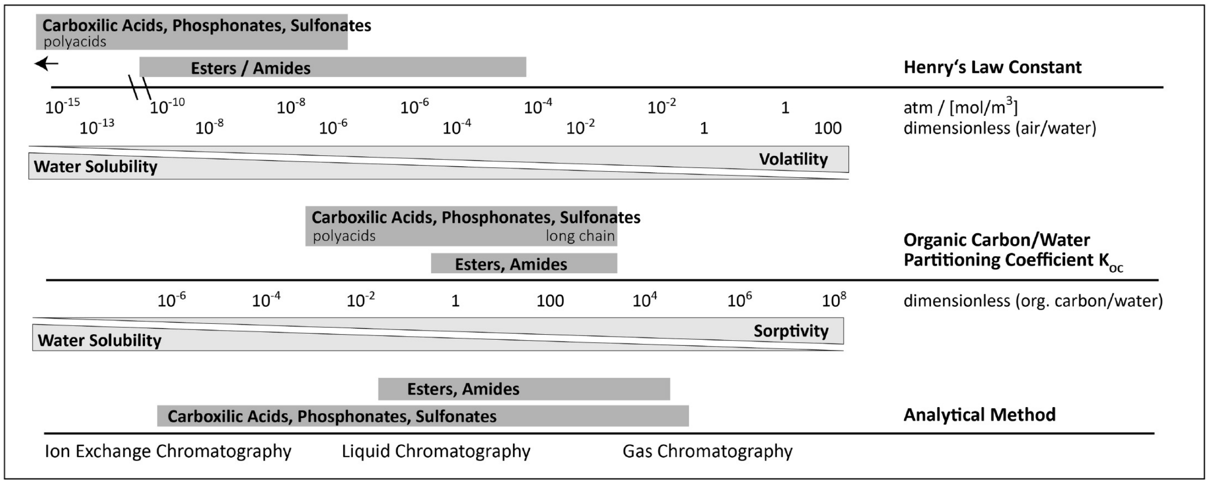
e.g.

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

Functions in the Hydraulic Fracturing Process (Summary)



Physicochemical Properties and Analytical Methods (Overview)



[a] Henry’s law constants and log K_{oc} constants are taken from EPI Suite.[71] A more comprehensive list of compounds together with physicochemical data is given in the SI. n.i.: not included.

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*, whereas the hydrophobic tail of long-chain fatty acids or sulfonates enables them to form protective surface layers as *corrosion inhibitors* on surfaces and lends them properties as negatively charged surfactants. Also carboxylic amides and esters are primarily reported as *solvents and surfactants* (fatty acid esters and diethanolamides) and *friction reducers* (sulfamic acid). Specifically, even though formamide and dimethylformamide are reported in corrosion inhibitor products, they actually represent inert solvents for the contained active additives of Figure 3.[109] Cocamidopropyl betaines—typical viscoelastic surfactants—are reported in only relatively small number. Table 5 further illustrates that the presence of additional −OH, −COOH, or $-PO_3H$ groups in compounds such as erythorbic acid, lactic acid, glycolic acid, citric acid, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or aminotrimethylenephosphonic acid lends these substances properties as *complexing agents*. On the one hand, they can bind Zr^{IV} and Fe^{III} to avoid premature cross-linking, ("crosslinker", "iron control"), on the other hand they form complexes with Ca^{2+} or other geogenic cations to prevent precipitates ("*scale inhibitors*").

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

Finally, acids are expected to play a crucial role also as *breakers*, by reversing borate-based cross-linking (see Table 1). Considering that optimized hydraulic fracturing requires an exact timing of cross-linking and breaking, much industry research is reported[59,113,114] to focus on *delayed cross-linkers 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 cross-links (see Scheme in Table 1), but it may be detrimental if the breaking occurs too early so that fluid loss occurs into the formation and proppants are not well transported. Elsewhere, in a similar strategy, polyglycolic acid is reported to serve as a retarded acid[59] for delayed breakage of borate cross-links.

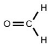
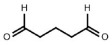
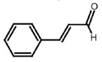
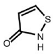
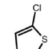
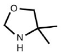
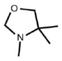
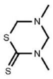
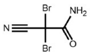
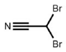
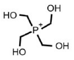
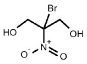
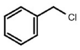
Potential Substances of Concern/Consequences for Environmental Fate and Monitoring. Most substances of Table 5 are not primarily of concern because of their inherent toxicity, but they may become problematic because their molecular design allows them to undergo specific reactions. Complexing agents are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

Table 5 illustrates that most disclosed organic acids, esters and amides have low volatility, but high water-solubility. With the exception of phosph(on)ates, which strongly sorb to mineral surfaces,[124] these compounds are, hence, expected to be mobile when present in groundwater. They are, therefore, of interest both because of their environmental fate and because they may be potential indicator substances of hydraulic fracturing activities. While esters, amides and monocarboxylic acids may be analyzed by either gas chromatography or liquid chromatography-based methods, (poly)carboxylic 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 nontarget analysis: to detect, on the one hand, relevant nondisclosed compounds and to discover, on the other hand, potential transformation products of environmental relevance.[125]

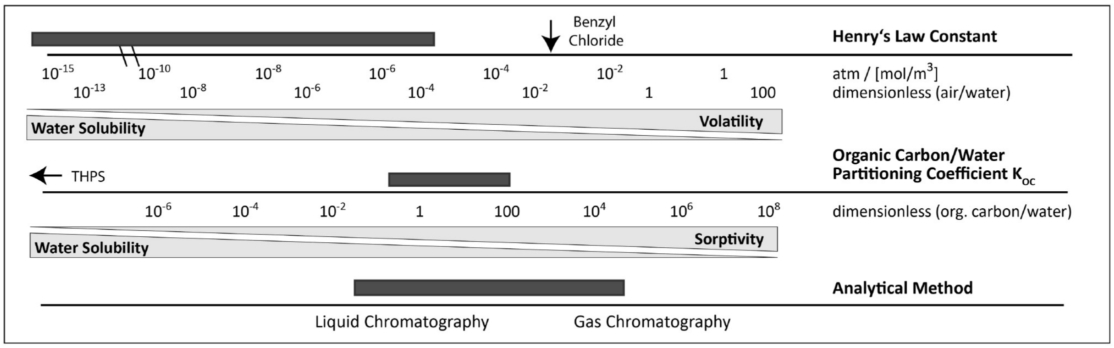
6. Electrophilic Compounds. *Chemical Properties Relevant in the HF Process.* Electrophilic compounds can form covalent bonds to nucleophiles like sulfur, nitrogen or oxygen-based species. They, therefore, act as alkylating agents.

Table 6. Most Frequently Reported Electrophilic Compounds[a]

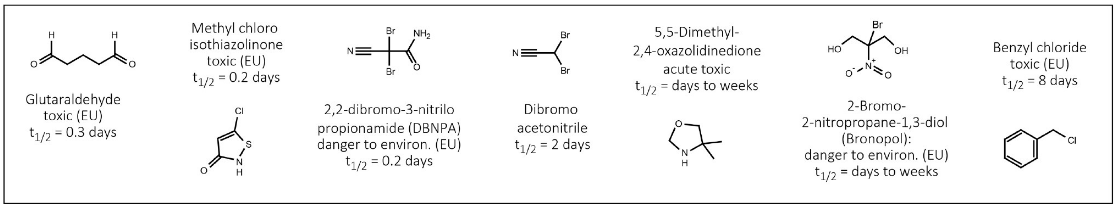
Electrophilic Compounds

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



[a] Henry's law constants and log K_{oc} constants are taken from EPI Suite,[71] degradation half-lives from ref 44. A more comprehensive list of compounds together with physicochemical data is given in the SI.

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

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

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

Typical Chemicals of an "Average" HF Operation. Even though it is frequently stated that hundreds of HF chemicals exist, and that general conclusions are difficult because the choice of substances is site-dependent, our overview shows that some general patterns nevertheless emerge with regard to the use and chemical structure of additives. We may, therefore, consider what chemicals are disclosed in an "average" HF operation (Figure 3). *Gel-forming Agents.* One fourth to 50% of all operations relies on guar gum, whereas specific acrylamides/-acrylates are disclosed in only 10% of the cases (Table 1). *Solvents.* Practically every operation relies on a combination of methanol, isopropanol, ethanol, and petroleum distillates to bring gel and cross-linkers 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. *Cross-linkers.* 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—that is, 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. Nonproblematic 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 dimethylammonium chloride (about 10%) are frequent.

The ranking of Figure 3 may now be compared to a summary of HF chemicals that is provided on the FracFocus Web site itself (https://fracfocus.org/chemical-use/what-chemicals-are-used, accessed on December 17, 2015). The summary there does not provide quantitative information in terms of disclosures, but claims to contain the chemicals used most often, and it provides an alphabetical list where chemicals are grouped by function. While many compounds agree, several important (and most frequent) chemicals are missing, among them some of the most problematic substances: ethoxylated nonylphenols, propargyl alcohol, DBNPA, sodium chlorite, potassium chloride, and ammonium. The critical evaluation of Figure 3, therefore, illustrates the importance of this present overview, since available lists may not be complete, and it suggests that the use of HF chemicals may presently not yet be optimized for potential environmental impacts. Potentially problematic compounds continue to be used, even though environmentally friendly alternatives may exist. Aromatic hydrocarbons and petroleum distillates may serve as example. They are substances of toxicological concern, but are nonetheless used in practically every HF operation. The question arises whether these compounds are truly indispensable and represent the best choice of solvent. (For example, guar gum likely dissolves equally well in more polar, less toxic organic solvents.) A possible explanation is that these substances may have been developed for HF of oil reservoirs—where their use seems intuitive, given that the same aromatic hydrocarbons are already present in the formation—and that these blends may simply have been adapted to the exploitation of gas resources without looking for alternatives. A telling indication is the fact that even though diesel was the one explicit additive that still required an underground injection control (UIC) permit when the US

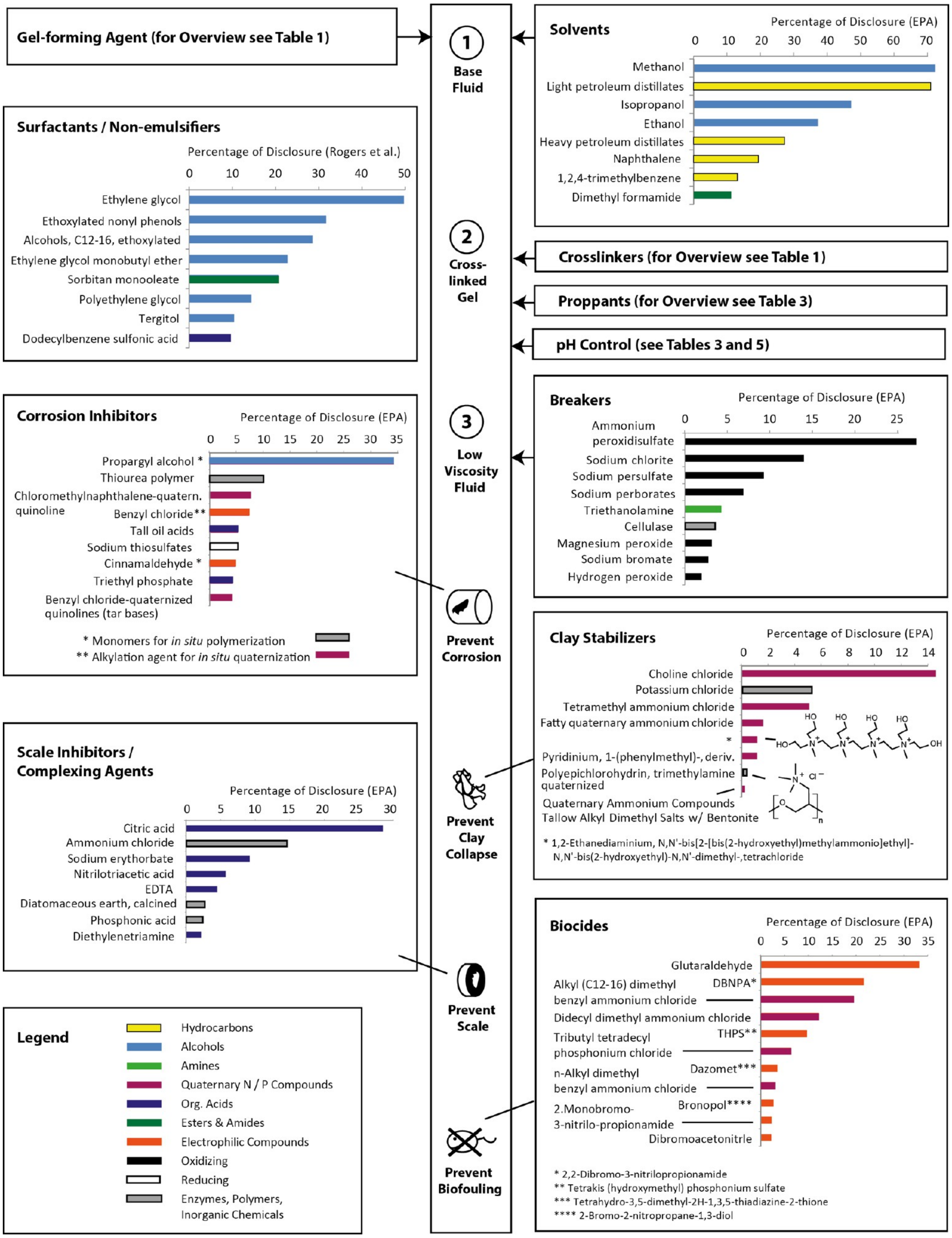


Figure 3. Ranking of chemicals that may be expected in an average HF operation, based on number of disclosures on FracFocus (as evaluated by EPA (ref 43) and Rogers et al. (ref 44)).

congress exempted all other additives from the Safe Drinking Water Act ("SDWA"), in 2005,[133] diesel was still heavily used between 2005 and 2009.[134] After three congress members put a particular focus on this additive in 2011,[134] the use of diesel was discontinued in subsequent years: Table 2 shows that the Waxman List discloses that no less than 51 HF products with diesel before 2009, whereas less than 0.2% of all operations used this additive after 2011. An open, constructive discussion about HF additives and equally effective alternatives may, therefore, play a catalytic role in steering industry design toward more environmentally friendly HF additives.[128] Such a discussion must in addition not only consider *how often* a HF chemical was used (as discussed here) but also *in what quantities/concentrations*. This aspect is not covered by this review, but a comprehensive survey in a recent EPA report[43] is easily available for further considerations.

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

Impacts on Human and Ecosystem Health. To assess toxicological impacts in the course of HF operations, two exposure scenarios are particularly relevant: occupational exposure of workers and long-term exposure in the environment. For occupational safety our review identifies a number of substances of particular concern based on their acute toxicity. Electrophilic monomers that are used for polymerization such as propargyl alcohol are expected to have the highest acute toxicity and carcinogenicity. Also biocides may show effects even at low concentrations. Microcrystalline silica is carcinogenic on inhalation (Table 3). Petroleum hydrocarbons, citrus terpenes, alcohols (methanol, isopropanol, Table 2) or alkylamines (Table 4) are toxic and volatile so that their exposure may also be relevant for nearby residents. Strong oxidants (Table 3), borate (Table 1) tetramethylammonium 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. Tetramethylammonium chloride and alkyl amines are additional problematic *N*-containing compounds (Table 4), whereas petroleum hydrocarbons (Table 2) are well-known, notorious groundwater pollutants. Nonylphenols are endocrine disruptors which can be formed by degradation of ethoxylated nonylphenols (Table 2). Finally, recent publications on geogenic substances[78,85,86,139−141] suggest that aromatic hydrocarbons, mercury, arsenic, heavy metals and radioactive elements can surface with the formation water and that they may be more toxic than the actual HF additives themselves.[24] Together with the elevated salinity of formation water, they pose as yet unresolved challenges to wastewater treatment. Even though much interest is currently directed at HF additives, it is therefore essential that also such geogenic substances are considered, since they will play a crucial role in research efforts to minimize environmental impacts of hydraulic fracturing.

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

Potential for Additional Chemicals of Relevance. Based on our assessment we furthermore postulate that the lists of compounds from FracFocus and the Waxman report are not sufficient for environmental assessments. Instead, additional compounds may be relevant which are presently not disclosed or even known. (i) *Not disclosed.* As discussed above, some of the substances which are currently claimed proprietary are likely designed to form active agents in situ by deprotection reactions. Because of this built-in reactivity the substances are by definition relevant for environmental assessments, even if they are not toxic in the first place. (ii) *Not known.* In particular, substances of significant abiotic and biotic reactivity in the subsurface bring about the potential for new transformation products. In the case of some highly reactive and toxic monomers (propargyl alcohol, Table 2; acrylate, epichlorhydrin, Table 1) or alkylation agents (benzyl chloride, Table 6) transformations are expected to be beneficial and to result in products of lower toxicity. In contrast, degradation of alkoxylated nonylphenols (Table 2) may yield nonylphenols as persistent, problematic metabolites. Of particular concern is the possibility that halogenated hydrocarbons may be formed, because they are known as notorious groundwater contaminants from applications of high-volume industrial organohalogens such as chlorinated solvents, brominated flame retardants, etc. Our survey shows that hardly any organohalogens are reported for use in HF operations (see SI). However, halogenated hydrocarbons may be formed when strong oxidants (Table 3) are applied to organic compounds in the presence of highly saline formation water, as recently demonstrated for oxidative treatment of hydraulic fracturing wastewater.[35]

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

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

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02818.

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

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Notes

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'Fracking' wastewater that is treated for drinking downstream produces potentially harmful compounds

Date: September 24, 2014

Source: American Chemical Society

Summary: Concerns that fluids from hydraulic fracturing, or 'fracking,' are contaminating drinking water abound. Now, scientists are bringing to light another angle that adds to the controversy. A new study has found that discharge of fracking wastewaters to rivers, even after passage through wastewater treatment plants, could be putting the drinking water supplies of downstream cities at risk.

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Concerns that fluids from hydraulic fracturing, or "fracking," are contaminating drinking water abound. Now, scientists are bringing to light another angle that adds to the controversy. A new study, appearing in the ACS journal *Environmental Science & Technology*, has found that discharge of fracking wastewaters to rivers, even after passage through wastewater treatment plants, could be putting the drinking water supplies of downstream cities at risk.

William A. Mitch, Avner Vengosh and colleagues point out that the disposal

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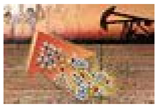

Toxins Found in Fracking Fluids and Wastewater, Study Shows

Jan. 6, 2016 — In an analysis of more than 1,000 chemicals in fluids used in and created by hydraulic fracturing (fracking), researchers found that many of the substances have been linked to reproductive and ... **read more**

Fracking Plays Active Role in Generating Toxic Metal Wastewater, Study Finds

Dec. 15, 2015 — The production of hazardous wastewater in hydraulic fracturing is assumed to be partly due to chemicals introduced into injected freshwater when it mixes with highly saline brine naturally of fracking wastewater poses a major challenge for the companies that use the technique, which involves injecting millions of gallons of fluids into shale rock formations to release oil and gas. The resulting wastewater is highly radioactive and contains high levels of heavy metals and salts called halides (bromide, chloride and iodide). One approach to dealing with this wastewater is to treat it in municipal or commercial treatment plants and then release it into rivers and other surface waters.

The problem is these plants don't do a good job at removing halides. Researchers have raised concern that halide-contaminated surface water subsequently treated for drinking purposes with conventional methods, such as chlorination or ozonation, could lead to the formation of toxic byproducts. Mitch's team set out to see if that was indeed the case.

The researchers diluted river-water samples of fracking wastewater discharged from operations in Pennsylvania and Arkansas, simulating real-world conditions when wastewater gets into the environment. In the lab, they then used current drinking-water disinfection methods on the samples. They found that even at concentrations as low as 0.01 percent up to 0.1 percent by volume of fracking wastewater, an array of toxic compounds formed. Based on their findings, the researchers recommend either that fracking wastewater should not be discharged at all into surface waters or that future water treatment include specific halide-removal techniques.

Story Source:

Materials provided by **American Chemical Society**. *Note: Content may be edited for style and length.*

Journal Reference:

1. Kimberly M. Parker, Teng Zeng, Jennifer Harkness, Avner Vengosh, William A. Mitch. **Enhanced Formation of Disinfection Byproducts in Shale Gas Wastewater-Impacted Drinking Water Supplies**. *Environmental Science & Technology*, 2014; 140924125647003 DOI: 10.1021/es5028184

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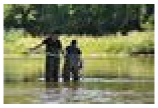

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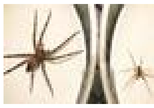

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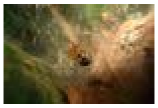

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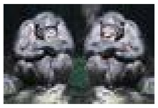

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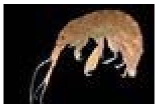

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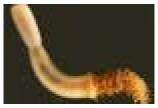
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Science News *from research organizations*

Fracking plays active role in generating toxic metal wastewater, study finds

Date:	December 15, 2015
Source:	Dartmouth College
Summary:	The production of hazardous wastewater in hydraulic fracturing is assumed to be partly due to chemicals introduced into injected freshwater when it mixes with highly saline brine naturally present in the rock. But a new study investigating the toxic metal barium in fracking wastewater finds that chemical reactions between injected freshwater and the fractured shale itself could play a major role.
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'Fracking' Wastewater That Is Treated for Drinking Downstream Produces Potentially Harmful Compounds

Sep. 24, 2014 — Concerns that fluids from hydraulic fracturing, or 'fracking,' are contaminating drinking water abound. Now, scientists are bringing to light another angle that adds to the controversy. A ... **read more**

Acid Mine Drainage Reduces Radioactivity

Dartmouth Professor Mukul Sharma and his colleagues find that chemical reactions between injected freshwater and hydraulically fractured shale could play a major role in generating toxic metal barium in fracking wastewater.

Credit: Dartmouth College

The production of hazardous wastewater in hydraulic fracturing is assumed to be partly due to chemicals introduced into injected freshwater when it mixes with highly saline brine naturally present in the rock. But a Dartmouth study investigating the toxic metal barium in fracking wastewater finds that chemical reactions between injected freshwater and the fractured shale itself could play a major role.

The findings, which are published in the journal *Applied Geochemistry*, show that transformation of freshwater used for fracking to a highly saline liquid with abundant toxic metals is a natural consequence of water-rock reactions occurring at depth during or following fracking. Fracking wastewater poses a hazard to drinking water supplies if improperly disposed.

The researchers examined samples from three drill cores from the Marcellus Shale in Pennsylvania and New York to determine the possible water-rock reactions that release barium and other toxic metals during hydraulic fracturing. The Marcellus Shale in the eastern United States contains large natural gas reserves, which have been extensively exploited in recent years using hydraulic fracturing. A mile below Earth's surface where fracturing takes place, chemical reactions occur between water and fractured rock at elevated pressure and temperature and in the absence of oxygen.

in Fracking Waste

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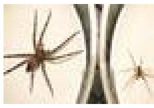

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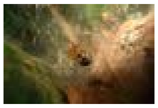

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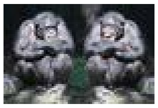

Apes Understand That Some Things Are All in Your Head

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Methane Muted: How Did Early Earth Stay Warm?

Climate Change Will

Hydraulic fracturing is an important technological advance in the extraction of natural gas and petroleum from black shales, but produced wastewater, or water that is produced along with shale gas and petroleum following fracking, is extremely saline and contains extraordinarily high concentrations of barium. It has been assumed that the peculiar composition of the produced wastewater results from mixing of freshwater used for fracking with high salinity water already underground that also contains barium. But the Dartmouth team found that a large amount of barium in the shale is tied to clay minerals, and this barium is readily released into the injected water as the water becomes more saline over time.

"Based on barium yields determined from laboratory leaching experiments of the Marcellus Shale and a reasonable estimate of the water/rock mass ratio during hydraulic fracturing, we suggest that all of the barium in produced water can be reconciled with leaching directly from the fractured rock," says senior author Mukul Sharma, a professor of Earth Sciences. "Importantly, barium behavior allows us to understand the behavior of radium, which is very abundant in produced water and is a very real environmental concern. There has been much discussion about injection of water with lots of toxic compounds during fracking. What is less known is that produced water is hazardous waste and chemical reactions between water and the rock are likely playing a role in its formation, not simply a mixing of freshwater with natural brines in the rock."

Story Source:

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1. Devon Renock, Joshua D. Landis, Mukul Sharma. **Reductive weathering of black shale and release of barium during hydraulic fracturing**. *Applied Geochemistry*, 2016; 65: 73 DOI: 10.1016/j.apgeochem.2015.11.001

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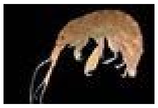
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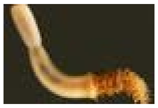
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‘Fracking’ wastewater that is treated for drinking produces potentially harmful compounds

"Enhanced Formation of Disinfection By-Products in Shale Gas Wastewater-Impacted Drinking Water Supplies"
Environmental Science & Technology

Treating fracking wastewater doesn’t do enough to ensure clean drinking water for downstream cities, according to a new study. Credit: antikainen/iStock/Thinkstock

Concerns that fluids from hydraulic fracturing, or “fracking,” are contaminating drinking water abound. Now, scientists are bringing to light another angle that adds to the controversy. A new study, appearing in the ACS journal *Environmental Science & Technology*, has found that discharge of fracking wastewaters to rivers, even after passage through wastewater treatment plants, could be putting the drinking water supplies of downstream cities at risk.

Cutting-Edge Chemistry

William A. Mitch, Avner Vengosh and colleagues point out that the disposal of fracking wastewater poses a major challenge for the companies that use the technique, which involves injecting millions of gallons of fluids into shale rock formations to release oil and gas. The resulting wastewater is highly radioactive and contains high levels of heavy metals and salts called halides (bromide, chloride and iodide). One approach to dealing with this wastewater is to treat it in municipal or commercial treatment plants and then release it into rivers and other surface waters. The problem is these plants don't do a good job at removing halides. Researchers have raised concern that halide-contaminated surface water subsequently treated for drinking purposes with conventional methods, such as chlorination or ozonation, could lead to the formation of toxic byproducts. Mitch's team set out to see if that was indeed the case.

The researchers diluted river-water samples of fracking wastewater discharged from operations in Pennsylvania and Arkansas, simulating real-world conditions when wastewater gets into the environment. In the lab, they then used current drinking-water disinfection methods on the samples. They found that even at concentrations as low as 0.01 percent up to 0.1 percent by volume of fracking wastewater, an array of toxic compounds formed. Based on their findings, the researchers recommend either that fracking wastewater should not be discharged at all into surface waters or that future water treatment include specific halide-removal techniques.

The authors acknowledge funding from the National Science Foundation.

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Enhanced Formation of Disinfection Byproducts in Shale Gas Wastewater-Impacted Drinking Water Supplies

Kimberly M. Parker[†], **Teng Zeng**[†], **Jennifer Harkness**[‡], **Avner Vengosh**[‡], and **William A. Mitch**[*†]
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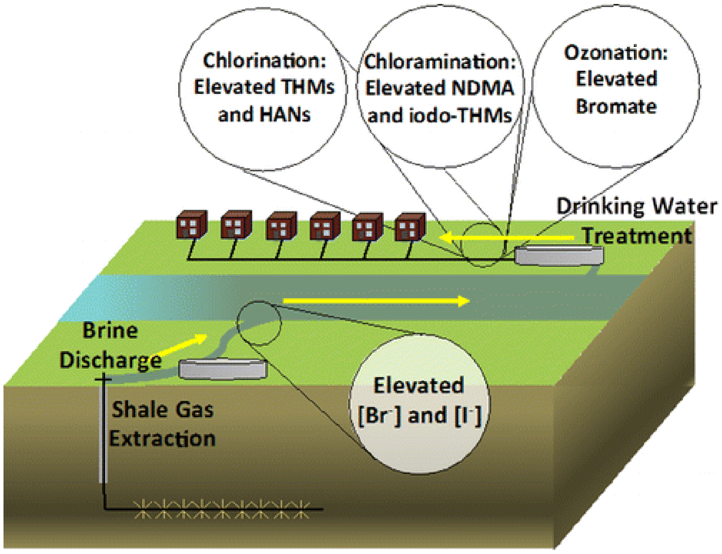

The disposal and leaks of hydraulic fracturing wastewater (HFW) to the environment pose human health risks. Since HFW is typically characterized by elevated salinity, concerns have been raised whether the high bromide and iodide in HFW may promote the formation of disinfection byproducts (DBPs) and alter their speciation to more toxic brominated and iodinated analogues. This study evaluated the minimum volume percentage of two Marcellus Shale and one Fayetteville Shale HFWs diluted by fresh water collected from the Ohio and Allegheny Rivers that would generate and/or alter the formation and speciation of DBPs following chlorination, chloramination, and ozonation treatments of the blended solutions. During chlorination, dilutions as low as 0.01% HFW altered the speciation toward formation of brominated and iodinated trihalomethanes (THMs) and brominated haloacetonitriles (HANs), and dilutions as low as 0.03% increased the overall formation of both compound classes. The increase in bromide concentration associated with 0.01–0.03% contribution of Marcellus HFW (a range of 70–200 μg/L for HFW with bromide = 600 mg/L) mimics the increased bromide levels observed in western Pennsylvanian surface waters following the Marcellus Shale gas production boom. Chloramination reduced HAN and regulated THM formation; however, iodinated trihalomethane formation was observed at lower pH. For municipal wastewater-impacted river water, the presence of 0.1% HFW increased the formation of *N*-nitrosodimethylamine (NDMA) during chloramination, particularly for the high iodide (54 ppm) Fayetteville Shale HFW. Finally, ozonation of 0.01–0.03% HFW-impacted river water resulted in significant increases in bromate formation. The results suggest that total elimination of HFW discharge and/or installation of halide-specific removal techniques in centralized brine treatment facilities may be a better strategy to mitigate impacts on downstream drinking water treatment plants than altering disinfection strategies. The potential formation of multiple DBPs in drinking water utilities in areas of shale gas development requires comprehensive monitoring plans beyond the common regulated DBPs.

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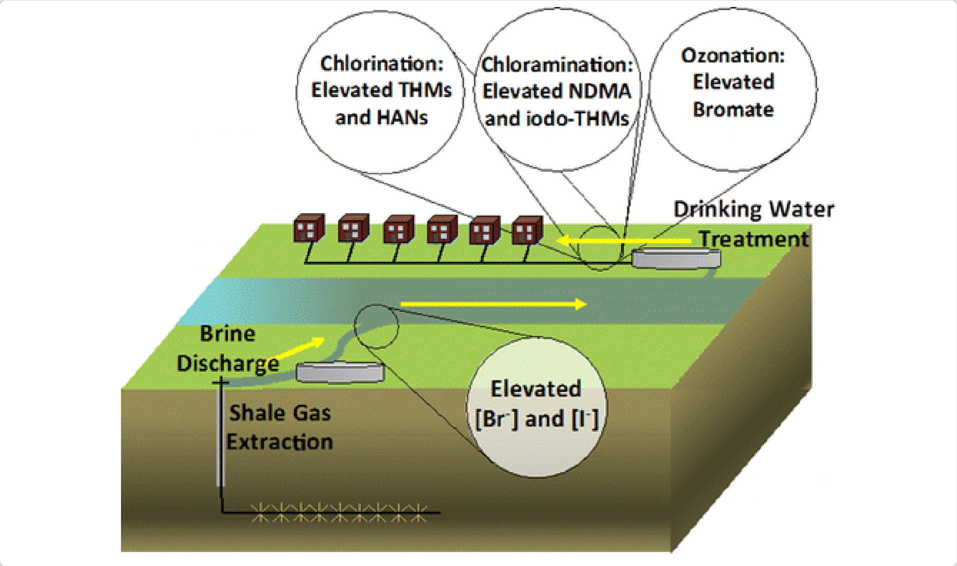

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