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Authors

Stringfellow, William T
Camarillo, Mary Kay
Domen, Jeremy K
[et al.](#)

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Identifying chemicals of concern in hydraulic fracturing fluids used for oil production[☆]



William T. Stringfellow^{a, b, *}, Mary Kay Camarillo^b, Jeremy K. Domen^b,
Whitney L. Sandelin^b, Charuleka Varadharajan^a, Preston D. Jordan^a,
Matthew T. Reagan^a, Heather Cooley^c, Matthew G. Heberger^c, Jens T. Birkholzer^a

^a Earth & Environmental Sciences Area, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

^b Ecological Engineering Research Program, School of Engineering & Computer Science, University of the Pacific, 3601 Pacific Avenue, Stockton, CA 95211, USA

^c Pacific Institute, 654 13th Street, Preservation Park, Oakland, CA 94612, USA

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ABSTRACT

Chemical additives used for hydraulic fracturing and matrix acidizing of oil reservoirs were reviewed and priority chemicals of concern needing further environmental risk assessment, treatment demonstration, or evaluation of occupational hazards were identified. We evaluated chemical additives used for well stimulation in California, the third largest oil producing state in the USA, by the mass and frequency of use, as well as toxicity. The most frequently used chemical additives in oil development were gelling agents, cross-linkers, breakers, clay control agents, iron and scale control agents, corrosion inhibitors, biocides, and various impurities and product stabilizers used as part of commercial mixtures. Hydrochloric and hydrofluoric acids, used for matrix acidizing and other purposes, were reported infrequently. A large number and mass of solvents and surface active agents were used, including quaternary ammonia compounds (QACs) and nonionic surfactants. Acute toxicity was evaluated and many chemicals with low hazard to mammals were identified as potentially hazardous to aquatic environments. Based on an analysis of quantities used, toxicity, and lack of adequate hazard evaluation, QACs, biocides, and corrosion inhibitors were identified as priority chemicals of concern that deserve further investigation.

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1. Introduction

Hydraulic fracturing and other types of well stimulation treatments, such as acid stimulation and acid fracturing, are being used extensively throughout the U.S. and globally to increase oil and gas production and extract resources that would otherwise be inaccessible (Clark et al., 2013; King, 2012; Long et al., 2015a). These well stimulation treatments, collectively referred to as unconventional oil and gas development, use a wide variety of chemical additives (King, 2012; Stringfellow et al., 2014; Elsner and Hoelzer, 2016) and can cause both direct and indirect impacts on the environment and human health (Long et al., 2015b; Long, 2014; Jain,

2015; Gregory and Mohan, 2015). Potential direct impacts may include a hydraulic fracture extending into protected groundwater, accidental spills of fluids containing hydraulic fracturing chemicals, or inappropriate disposal or reuse of produced water containing hydraulic fracturing chemicals (Burton et al., 2016; Vengosh et al., 2014). Indirect impacts are impacts not specific to the activity of well stimulation, but are impacts associated with all oil and gas production that also occur at production sites enabled by unconventional methods. Impacts that are independent of well stimulation, such as long-term emissions of volatile hydrocarbon air pollutants, fugitive methane emissions, groundwater contamination from produced water spills or casing failures, etc., will occur as part of all oil and gas development and can occur whether or not a well was completed using stimulation technology (Long et al., 2015b). Most of the direct impacts of unconventional oil and gas development can be attributed to chemical use during well stimulation (Long et al., 2015b).

In order to understand the direct impacts of unconventional oil

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* Corresponding author. Earth & Environmental Sciences Area, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA.

E-mail address: wstringfellow@lbl.gov (W.T. Stringfellow).

and gas development, it is therefore necessary to understand and evaluate the types and amounts of chemicals used during well stimulation. Hydraulic fracturing practices and chemical-use varies by region of the USA and hydraulic fracturing is most frequently used for production of natural-gas from shale and similar source rock formations (Long et al., 2015a; U.S. EPA, 2015a; California Council on Science and Technology (CCST), 2014). Previous studies have evaluated and characterized chemical additives in fracturing fluids based on use nationally (Stringfellow et al., 2014; Elsner and Hoelzer, 2016; U.S. EPA, 2015a; SCAQMD, 2013; Long et al., 2015c; U.S. Environmental Protection Agency (U.S. EPA), 2013a) and these analyses of chemical use are therefore weighted toward chemical use for natural gas development.

In this review we examine the use of chemicals for hydraulic fracturing in the context of oil development. In California, hydraulic fracturing is exclusively used for oil production and it is estimated that approximately 20% of oil production in California is dependent on unconventional oil recovery, predominately acidizing and hydraulic fracturing in diatomite formations (Long et al., 2015a). California is the third largest producer of oil in the USA and hydraulic fracturing has occurred in both onshore and offshore oil fields (Long et al., 2015a; Houseworth and Stringfellow, 2015; US EIA, 2014). We evaluate chemical additives used for hydraulic fracturing and acidizing of oil reservoirs in California, with the objective of obtaining a better understanding of the types and amounts of chemicals used in oil production. In an effort to demystify the often confusing use of chemicals in well stimulation, we evaluate mass and frequency of use by both functionality and chemical classification. Our goal is to understand the significance of individual chemicals and chemical mixtures, the amounts at which they are being used, the purpose of their use, the class of chemical to which they belong, and other distinguishing characteristics. We use a rational approach, identifying the chemicals used most frequently and in the highest mass and cross reference these materials with toxicity analysis, to create a priority chemical list for further investigation and regulation.

2. Materials and methods

Data on chemicals, concentrations, and water volumes used in hydraulic fracturing were obtained from the FracFocus database (versions 1 and 2) for hydraulic fracturing operations conducted in California between January 30, 2011 and May 19, 2014 (FracFocus, 2013a). The FracFocus database was started in 2011 and contains voluntarily disclosed data on hydraulic fracturing treatments. Entries in the FracFocus database were edited to standardize chemical names and to validate the assigned Chemical Abstracts Services Registry Number (CASRN). Masses of chemicals per treatment were only calculated for complete records where both volume and concentrations data were provided and where the sum of reported mass percentages was between 95% and 105%.

Data on acidizing treatments, including matrix acidizing, were compiled from data collected by the South Coast Air Quality Management District (SCAQMD) for treatments conducted between June 2013 and June 2014 (SCAQMD, 2013). The SCAQMD includes the counties of San Bernardino, Orange, Riverside, and Los Angeles, including the City of Los Angeles. The SCAQMD does not include the San Joaquin Valley nor Kern County, where the majority of hydraulic fracturing takes place in California (Long et al., 2015a, 2015c). Operators and chemical suppliers working in the SCAQMD must disclose chemical and materials used for drilling, hydraulic fracturing, and acidizing in that district. The SCAQMD data started being collected in 2013 (SCAQMD, 2013).

Toxicity data were collected from chemical databases and references (U.S. Environmental Protection Agency (U.S. EPA), 2013a;

Service, 2014; National Library of Medicine, 2013a; U.S. Environmental Protection Agency (U.S. EPA), 2014; European Chemicals Agency (ECHA), 2000; Lewis and Sax, 1996; U.S. Environmental Protection Agency (U.S. EPA), 2013b; National Library of Medicine, 2013b; Organization for Economic Cooperation and Development (OECD), 2007). Rat and mouse oral toxicity data were collected to represent mammalian toxicity. Environmental toxicity data were collected for water flea (*Daphnia magna*), fathead minnow (*Pimephales promelas*), and trout (Rainbow Trout, *Oncorhynchus mykiss* and Brook Trout, *Salvelinus fontinalis*). Data on median lethal dose (LD50) were compiled for mammals, while data on median lethal concentration (LC50) and median effective concentration (EC50) were compiled for aquatic species. Toxicity ratings for chemical additives were assigned using the United Nations Globally Harmonized System (GHS) of Classification and Labelling of Chemicals (United Nations, 2013). In the GHS system, lower numbers indicate higher toxicity, with a designation of “1” indicating the most toxic category. Chemicals for which the LD50 or EC50 exceeded the least toxic GHS category were classified as non-toxic.

3. Results and discussion

3.1. Chemicals used in hydraulic fracturing and matrix acidizing

Using data collected from FracFocus, we identified 1623 individual hydraulic fracturing operations conducted in California between January 30, 2011 and May 19, 2014. During this time period, there were an estimated 5000 to 7000 hydraulic fracturing treatments in California (Long et al., 2015a), suggesting that the voluntary dataset represents one-third to one-fifth of the total hydraulic fracturing treatments. From these 1623 treatments, we identified 338 unique additives based on name and CASRN combinations, of which 228 were reported with a CASRN and 110 were identified by chemical or common name only or had proprietary designations. The additives included chemicals, mineral proppants and carriers, and base fluids consisting of water, salt, and brine solutions. There were 326 unique additive names in the database. Some additives—e.g. hemicellulose enzyme—had multiple CASRN and/or were identified by CASRN in some entries and proprietary designations in other entries. Of the 45,058 entries for additives, 3071 entries did not report CASRN under various claims for proprietary information (e.g. trade secret, confidential business information).

Matrix acidizing treatments applied in California involve the use of strong acids, including hydrochloric and hydrofluoric acid (Long et al., 2015a; Abdullah et al., 2016). Information concerning chemical use during matrix acidizing is not generally available, but the SCAQMD requires operators to report chemical use during acid treatments, which includes both routine well maintenance and matrix acidizing treatments. We analyzed the use of chemicals in conjunction with all acid treatments in the SCAQMD reporting area, which is limited to parts of Southern California (see methods). In the SCAQMD, we only examined chemicals reported with a valid CASRN. There were 78 chemicals identified as being used during acid treatments, of which 24 were not reported to the FracFocus disclosure registry (Table S1). Although this data is restricted to one region, the SCAQMD data was, to our knowledge, the only public source of high quality data on acid treatments available during this study.

The results of this analysis indicate that well over 300 chemicals have been used for hydraulic fracturing in California and that, based on reporting in only one region of California, an additional two dozen chemical additives are also used during matrix acidizing treatments (Table S1). Since common names were sometimes used for chemical additives on the disclosures (e.g., surfactant mixture,

salt), reporting before January 2014 was voluntary, and chemical names are not definitive identifiers of chemical additives, any enumeration of the total number of chemicals used in well stimulation should be considered approximate.

The dependence of data from voluntary reporting, the bias of that reporting for hydraulic fracturing operations, and the limited data available on matrix acidizing treatments means that the list of chemicals used for well stimulation in California is incomplete; however, the list of chemicals is believed to be representative of well stimulation practices in California. The disclosures we examined include the major producers and service companies operating in California, including Baker Hughes, Schlumberger, and Halliburton. The chemical additives listed in the voluntary disclosures were consistent with additives described in information available from mandatory reporting, industry literature, patents, scientific publications, and other sources, such as government reports [e.g. Stringfellow et al., 2014; Gadberry et al., 1999; U.S. EPA, 2004; Baker Hughes Oilfield Operations Inc., 2014].

3.2. Functions of chemical additives

Given the large number of chemicals that have been used for well stimulation in California, it is useful to evaluate the chemical additives by function. Unfortunately, although chemical function is often reported, the assigned function for a chemical is frequently inaccurate. For example, solvents, such as methanol, and surfactants used for formulating corrosion inhibitor mixtures (Finsgar and Jackson, 2014; Schmitt, 1984) are frequently reported as being corrosion inhibitors. Another common example is the reporting of magnesium nitrate and magnesium chloride as biocides, where in fact these chemicals are residuals from the manufacturing of isothiazolone biocides (Miller and Weiler, 1978; Scientific Committee on Consumer Safety, 2009). Using a combination of patent literature, manufacturing information, and journal articles, we were able to positively identify function for the majority of the chemical additives (Table 1). Some chemicals had multiple functions and were assigned to more than one category.

Many of the chemicals on the list were so-called “impurities” and product-stabilizers found in chemical additive formulations. Product-stabilizers and impurities include solvents, surfactants, carriers, and salts that are added to chemical blends to improve their handling characteristics, provide product stability, enhance the effectiveness of the primary ingredients, or are residuals of manufacturing processes. For example, sulfate and phosphate salts

can be added as allosteric effectors for enzymatic breakers (Armstrong et al., 2014) and thiosulfate can be added as a stabilizing agent to guar gum mixtures (Pakulski and Gupta, 1994; Halliburton Energy Services, 2010). Carriers include ingredients added as solid sorbents to biocides, corrosion inhibitors, and other products that improve stability or effect dissolution kinetics, allowing the active ingredient to be released in the formation or at other appropriate times and locations (Gupta and Kirk, 2009; Greene and Lu, 2010). Carriers include diatomaceous earth and other silicates (Gupta and Kirk, 2009; Greene and Lu, 2010; Bri-Chem Supply Ltd., 2013), which are often misidentified as proppants. These compounds are typically added in small percentages, but can still occur in significant mass (see below).

3.3. Frequency of use of chemical additives

Although over 300 chemicals were identified as being used in California for hydraulic fracturing between 2011 and 2014, many of these compounds were reported as used only infrequently. In the 1623 treatments, 152 of the compounds were reported as used 10 times or less, 282 compounds were used less than 100 times, and 304 compounds were used less than 163 times (or 10% of applications). Breakers, proppants, gelling agents, biocides, carriers, and crosslinkers were added to more than 90% of the 1623 total treatments (Table 1). Friction reducers, diverting agents, and antifoam agents appear to be used infrequently (identified in less than 3% of all treatments, Table 1).

In Table S2, we report the chemical additives used in more than 10% of the reported hydraulic fracturing treatments. Table S2 does not include mineral proppants, mineral solids identified as carriers, and base fluids. The most commonly reported chemical additives are typical of gel-based treatments (King, 2012; Stringfellow et al., 2014). Guar gum is a gelling agent to increase viscosity; boron compounds are used as crosslinkers to further increase viscosity; enzymes and ammonium persulfate are breakers used to reduce viscosity after treatment (Tables 1 and S2). The frequent use of guar gum supports previous reports that hydraulic fracturing in California is primarily conducted using gelled treatments as opposed to other parts of the U.S., where slick-water treatments are common (Long et al., 2015a; U.S. EPA, 2015a; U.S. EPA, 2015b).

The most commonly used biocide in California is the combination of 2-methyl-3(2H)-isothiazolone and 5-chloro-2-methyl-3(2H)-isothiazolone (Table S2). The use of isothiazolones as biocides is characteristic of hydraulic fracturing in California, as these biocides are applied less frequently in other states (U.S. EPA, 2015a; U.S. EPA, 2015b; Kahrilas et al., 2015). Other biocides used in California include glutaraldehyde, DBNPA (2,2-dibromo-3-nitropropionamide), and tetrakis hydroxymethyl-phosphonium sulfate. The chemical 1,2-ethanediaminium, N1,N2-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N1,N2-bis(2-hydroxyethyl)-N1,N2-dimethyl-chloride (1:4) is a polymeric quaternary ammonium compound that is used as a clay control agent (Poelker et al., 2010; Baker Hughes, 2011). Two phosphonic acids are listed in Table S2, which are used as scale inhibitors (Gupta and Kirk, 2009; Fink, 2012; FracFocus, 2013b). Petroleum distillates and the additives ethylene glycol, 2-butoxypropan-1-ol, 1-butoxypropan-2-ol, and ethoxylated isotridecanol are used to formulate guar gum and other mixtures (Gupta and Carman, 2011; Baker Hughes, 2008). Sodium hydroxide is also one of the most commonly used additives, presumably for pH adjustment (Fink, 2012). Phenol polymer with formaldehyde is a resin used to coat sand proppant to increase hardness (Santral Proppants, 2011; Halliburton Energy Services, 2011; Zoveidavianpoor and Gharibi, 2015).

The number of unique hydraulic fracturing fluid components applied per treatment—using complete records—varied from 8 to

Table 1
Hydraulic fracturing chemical use in California by function, where function was positively identified.^a

Function	Chemicals in each function	Chemical categories represented ^b	Treatments using chemicals with this function
Breaker	11	4	1599
Proppant	19	1	1598
Gelling agent	2	1	1593
Biocide	10	6	1516
Carrier	23	5	1515
Crosslinker	13	5	1503
Clay control	7	4	1184
Scale inhibitor	19	6	971
Iron control	8	4	262
Corrosion inhibitor	10	5	102
Friction reducer	3	3	43
Diverting agent	3	3	10
Antifoam	1	1	6

^a Based on all records (N = 45,058), consisting of 1623 treatments.

^b Chemical categories are listed in Table 2.

69 with a median value of 23 (Fig. 1). The median number of components used is slightly higher in this study than in a recent US EPA survey (U.S. EPA, 2015a), which reported a median of 19 chemicals per treatment in California, because the US EPA analysis did not include base fluids and proppants and a smaller data set was reviewed in that study. Since proppants such as quartz sand, impurities such as methanol and nitrate, and carriers such as diatomaceous earth, may have environmental or human health importance, these components were included in our analysis. Base fluids may be brines, salt solutions, or produced water, but are most frequently fresh water. Water use ranged from 23 to 16,666 m³ per treatment with a median value of 280 m³ per treatment (Fig. 2). This analysis confirms previous studies indicating hydraulic fracturing operations in California requires less water than in other regions (King, 2012; U.S. EPA, 2015b; NYS DEC, 2011; NYS DPH, 2014).

3.4. Characterization by chemical class

We grouped the chemicals by chemical class (Table 2) to gain a better understanding of the general hazards associated with the chemicals used for hydraulic fracturing in California. Some categories consist of only a few types of chemicals (e.g., five types of enzymes were used). Other categories were populated with many chemical types, for example 50 solvents and 84 surfactants were identified (Tables 3 and 4). Of the 338 additives evaluated, most (304) could be placed in one primary category, but 34 fell into in two categories. For example, QACs (16 compounds) are categorized as both ammonium compounds and surfactants, eight chelating agents are also categorized as amine/amides (5) or carboxylic acids (3) and three compounds were both phosphonic acids and amine/amides. Twelve classes of components were used in over 80% of all treatments: mineral solids, solvents, carbohydrates, water, surfactants, ammonium compounds, boron compounds, oxidizing agents, amines and amides, strong bases, mineral salts, and enzymes (Table 2).

The number of chemical additives used, as characterized by chemical type, per treatment varies (Fig. 3). For example, typically only one ammonium compound is added per treatment, while four to five different mineral solids and solvents are added. Up to 22

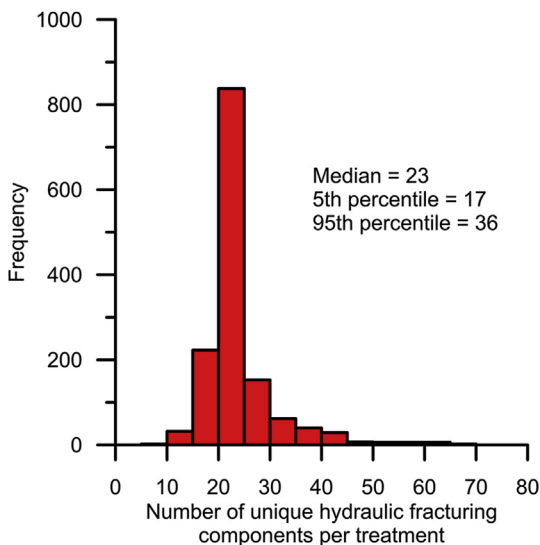


Fig. 1. Frequency distribution of the number of unique components used per hydraulic fracturing operation in California. Based on complete records (N = 39,669), consisting of 1406 treatments.

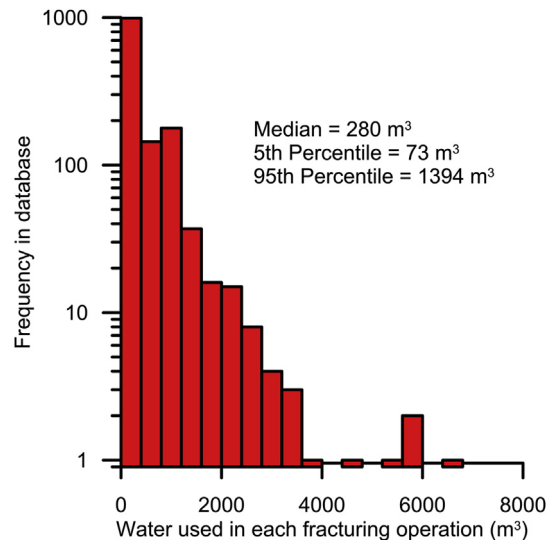


Fig. 2. Frequency distribution of the quantity of water used per hydraulic fracturing operation in California. Based on complete records (N = 39,669), consisting of 1406 treatments.

different types of surfactants are added in a single treatment. Notable results from this analysis include the occurrence of a large number of ammonium compounds, which are predominantly QACs, but including some poly-quaternary ammonium clay control agents; the large number of solvents, which includes both hydrocarbon and alcohol solvents (Table 3); and the large number of surfactants (Table 4), which includes some cationic surfactant QACs. A further analysis by category shows that most applications use an oxidizing agent, phosphorous compounds, only one surfactant, but a variety of solvents per treatment or application (Fig. 3).

Many of the environmental and health hazards associated with oil field chemical additives are due to the physical and chemical properties of solvents, surfactants, and QACs (Konnecker et al., 2011; Lewis, 1992; Ying, 2006; Hutchinson et al., 2006; Kreuzinger et al., 2007). QACs are difficult to categorize as they are used for a variety of purposes on oil fields and often the functional use is not reported by the operator. When a specific use was reported, the most commonly reported functions for QACs were for surfactants and clay control, followed by use as biocides and corrosion inhibitors. QACs in particular are known to pose environmental hazards (García et al., 2001). Approximately half of the QACs were reported without a corresponding CASRN, but the entries “oxyalkylated amine quat,” “oxyalkylated amine,” “quaternary amine,” and “quaternary ammonium compound,” all indicate that these additives are unspecified QACs. Similarly, many of the general names suggest that the proprietary additives are surfactants (e.g. “ethoxylated alcohol,” “surfactant mixture,” etc.) that are widely used in the industry (Fink, 2012). The chemical additives not identified by CASRN were not included in the toxicity analysis (below), but many solvents, surfactants, and QACs have similar mechanisms of toxicity, especially to aquatic organisms, and are presumed to be toxic to aquatic life.

3.5. Masses of chemical additives used per treatment

Analysis of chemical mass applied per treatment is an important criterion for evaluating hazard and can identify major ingredients from impurities, which can occur frequently but in small quantities. As expected, proppant, typically sand, and the carrier fluid,

Table 2
Hydraulic fracturing chemical use in California by class.^a

Category	Chemicals in each category ^b	Treatments reporting using chemicals in this category
Mineral solids	28	1611
Solvents	50	1604
Carbohydrates	7	1599
Water	6	1579
Surfactants	84	1546
Ammonium compounds	25	1552
Boron compounds	10	1488
Oxidizing agents	6	1481
Amines and amides	32	1182
Strong bases	2	1428
Mineral salts	10	1409
Enzymes	5	1368
Isothiazolones	2	1187
Phosphorus compounds	12	990
Polymers	21	310
Carbonate compounds	4	282
Chelating agents	8	264
Carboxylic compounds	5	251
Resins	8	227
Unknown	15	192
Aldehydes	4	136
Nutrient mixtures	3	115
Organic compounds, misc.	3	103
Reducing agents	9	60
Strong acids	4	44
Organosilicons	9	18

^a Based on all records (N = 45,058), consisting of 1623 treatments.

^b Of 338 unique components, 304 were placed in one category and 34 were placed in two categories.

Table 3
Types of solvents used for hydraulic fracturing in California.^a

Category	Chemicals in each category	Treatments using chemicals in this category
Hydrocarbons	11	1404
Glycols	4	1292
Glycol ethers	9	1284
Alcohols	8	518
Aromatic hydrocarbons	12	127
Esters	3	90
Cyclic hydrocarbons	2	7
Ethers	1	1

^a Based on all records (N = 45,058), consisting of 1623 treatments.

typically fresh-water, are applied in large quantities (see above). Approximately 87% of the records (1406 treatments) reported sufficient information to calculate the chemical mass used for materials in addition to proppants and carrier fluids (see [methods](#)). The additives used in the largest masses per treatment were in many cases used infrequently ([Table S3](#)). Of the top twenty chemicals ranked by mass used per treatment, these chemicals were typically used in less than 250 out of 1406 treatments ([Table S3](#)). Notably, of the chemical additives used in the largest masses per

treatment, eight were reported without a CASRN and therefore could not be definitively identified. The chemical additive used in the largest mass per treatment was a proprietary phosphonate compound used for scale control. Hydrochloric acid was used in large quantities when it was used and, to a lesser extent, so was hydrofluoric acid ([Table S3](#)). Some of the chemical additives used in the largest quantities ([Table S3](#)) are also those used most frequently ([Table S2](#)). There are several petroleum products, salts, and carbohydrates on both lists. Prominently present on the list of chemicals used in the largest quantities are surfactants, while one of the chemicals used in the largest quantity was unidentified and labeled “unknown” in the database. Large mass applications of undefined chemicals raise concerns, especially in the absence of mandatory reporting.

3.6. Toxicity of chemical additives

Acute toxicity is a fundamental parameter for the classification of chemical hazards. Typically, data on acute toxicity are collected before analysis of chronic toxicity or other long-term effects are conducted ([European Chemicals Agency \(ECHA\), 2000](#); [Kreuzinger et al., 2007](#); [U.S. Environmental Protection Agency, 2011](#)). In this study we examined what was known about the acute aquatic and mammalian toxicity of compounds used for hydraulic fracturing in California. As was found in previous studies, there are significant data gaps concerning what is known about the acute toxicity of chemicals used in the oil and gas industry ([Stringfellow et al., 2014](#); [Abdullah et al., 2016](#); [U.S. EPA, 2015b](#); [NYS DPH, 2014](#); [Wattenberg et al., 2015](#); [Rogers et al., 2015](#)). Toxicity data were not found for five of the most frequently used chemicals, and in many cases, a complete set of mammalian and aquatic acute toxicity measurements were not available ([Table S2](#)). In this study, we only assigned toxicity results to chemicals identified by CASRN, so many of the 20 the chemicals used in highest mass, which were reported by name only, are of unknown toxicity ([Table S3](#)). In other studies that were not limited to chemicals identified by CASRN, it was still found that significant data gaps concerning the understanding of chemical toxicity remained ([U.S. EPA, 2015b](#); [Shonkoff et al., 2015](#)).

Of the compounds for which CASRN and publically-available acute mammalian oral toxicity data were available, no compounds were identified as GHS category 1, which indicate the most toxic compounds. However, four compounds were identified as having a GHS category ranking of 2 and 18 compounds were identified as having a GHS category ranking of 3 for at least one mammalian species ([Table S4](#)). [Table S4](#) includes aldehydes, acids, bases, amines, and amides. Many of the additives in [Table S4](#), including 2,2-dibromo-3-nitrilopropionamide and formaldehyde, are specifically added as biocides ([Kahrilas et al., 2015](#)) and are therefore required to have toxicity testing under current regulation. Tetrakis hydroxymethyl-phosphonium sulfate is used to control sulfur reducing bacteria that induce production of corrosive hydrogen sulfide gas ([Kahrilas et al., 2015](#); [Struchtemeyer et al., 2012](#)). Propargyl alcohol is widely used in oil and gas development as a corrosion inhibitor ([Finsgar and Jackson, 2014](#); [Schmitt,](#)

Table 4
Types of surfactants used for hydraulic fracturing in California.^a

Category	Chemicals in each category	Treatments using chemicals in this category	Chemicals identified as biodegradable (%)	Chemicals missing toxicity data (%)
Nonionic	38	1495	22	76
Cationic	16	354	6	94
Anionic	20	210	33	67
Unspecified	6	168	0	100
Amphoteric	4	53	33	67

^a Based on all records (N = 45,058), consisting of 1623 treatments.

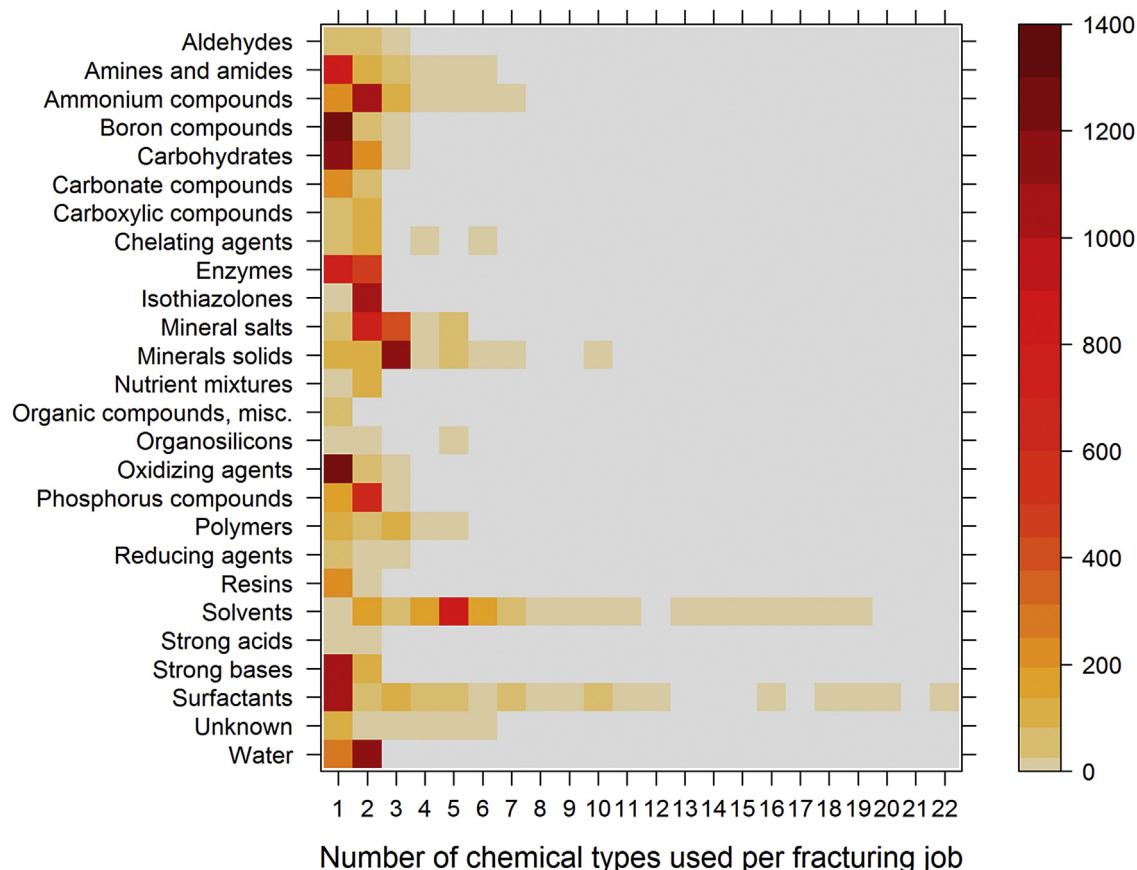


Fig. 3. Number of hydraulic fracturing treatments reported in California that used a specified number of uniquely identified components, as classified by chemical category. Based on complete records ($N = 39,669$), consisting of 1406 treatments.

1984; Perry et al., 1987). The majority of chemicals for which there were data fall into categories greater than GHS category 4 for acute oral toxicity to mammals, suggesting they are of lower priority for hazard and risk evaluation than the more toxic chemicals in Table S4.

The list of chemical additives most toxic to aquatic organisms (Table S5) differs from the list for mammalian toxicity (Table S4). Fourteen chemicals were identified as having a GHS category ranking of 1 and 23 were identified as having a GHS category ranking of 2 for at least one aquatic species (Table S5). The isothiazolone compounds—used as biocides—appear on this list as does the biocide 2,2-dibromo-3-nitropropionamide, however, many of the chemical additives most toxic to aquatic life are ethoxylated alcohol surfactants. There are several hydrocarbon products listed, which also have well-established toxicity profiles.

Important chemical additives that have CASRN, but were still missing toxicity data included 1,2-ethanediaminium, N1,N2-bis[2-bis(2-hydroxyethyl)methylammonio]ethyl]-N1,N2-bis(2-hydroxyethyl)-N1,N2-dimethyl-,chloride (1:4), 2-Butoxypropan-1-ol, phenol polymer with formaldehyde, and 2-acrylamido-2-methylpropane sulfonate. Given the prevalent use of these chemical additives, toxicity data—including both mammalian and aquatic toxicity—should be obtained.

3.7. Environmental implications of chemical use

The use of large numbers of poorly characterized chemicals has raised public concerns about the environmental and human health impacts of oil and gas development using hydraulic fracturing

(Wattenberg et al., 2015; Rogers et al., 2015; Hurley et al., 2016). In this paper we identified chemicals of concern based on the frequency of use, amounts used, and toxicological properties. This analysis indicates that biocides, corrosion inhibitors, and QACs are potential chemicals of concern and deserve further investigation. Biocides are subject to more regulation than other chemicals used in hydraulic fracturing and are typically more completely characterized than other industrial chemicals, but still further deserve scrutiny due to their designed toxicity, especially in the context of water treatment and reuse (Camarillo et al., 2016). Corrosion inhibitors are widely used in oil and gas fields and corrosion inhibitors are known to have poor environmental profiles (Finsgar and Jackson, 2014; Kahrilas et al., 2015). QACs as a class should be further investigated based on their wide-spread and frequent use, potential aquatic toxicity, and poor characterization for properties related to environmental transport and persistence. QACs are important components of hydraulic fracturing fluid formulations. Sixteen unique QACs were identified that were used in 349 treatments. Of the 16 reported QACs, only nine were identified by CASRN.

Many other chemical additives used consist of nitrogen-containing compounds (QACs, amines, amides, ammonium salts, etc.). Twenty-four percent of the compounds reported contained nitrogen. The prevalence of nitrogen-containing compounds suggests that elevated nitrogen levels may be present in environmental waters that are impacted by hydraulic fracturing waste streams.

It is not known if chemicals injected during well stimulation will return to the surface with produced water, are bound in the

subsurface, or are degraded (Stringfellow et al., 2015). Since techniques for analysis of these chemicals in water samples are still under development (Esser et al., 2015; Ferrer and Thurman, 2015a, 2015b; Thurman et al., 2014), there is very little direct information of the presence of fracturing chemicals or their degradation products in fluids returning to the surface. Most studies examining organic chemicals in produced water from wells that have been hydraulically fractured have found hydrocarbons naturally present in oil and gas formations (Ferrer and Thurman, 2015b; Maguire-Boyle and Barron, 2014; Orem et al., 2014; Lester et al., 2015; Strong et al., 2014) and some studies have found ethoxylated surfactants or their residuals (Thurman et al., 2014; Lester et al., 2015). Understanding the fate of these material in the subsurface and in produced water will be critical for understanding the environmental impact of chemical use during oil and gas development.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.09.082>.

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SUPPLEMENTAL MATERIALS

Identifying Chemicals of Concern in Hydraulic Fracturing Fluids Used for Oil Production

by:

William T. Stringfellow^{a,b,*}, Mary Kay Camarillo^b, Jeremy K. Domen^b, Whitney L. Sandelin^b, Charuleka Varadharajan^a, Preston D. Jordan^a, Matthew T. Reagan^a, Heather Cooley^c, Matthew G. Heberger^c, and Jens T. Birkholzer^a

^aEarth & Environmental Sciences Area, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA.

^bEcological Engineering Research Program, School of Engineering & Computer Science, University of the Pacific, 3601 Pacific Avenue, Stockton, CA 95211, USA.

^cPacific Institute, 654 13th Street, Preservation Park, Oakland, CA 94612, USA.

* corresponding author: wstringfellow@lbl.gov, (510) 486-7903

Environmental Pollution

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Table S1. Compounds submitted to South Coast Air Quality Management District (SCAQMD) from acidizing operations that were not found in voluntary notices reported for hydraulic fracturing to the FracFocus Chemical Disclosure Registry.

Chemical Name	CASRN
1-Eicosene	3452-07-1
Pine oil	8002-09-3
Toluene	108-88-3
Morpholine	110-91-8
1-Tetradecene	1120-36-1
1-Octadecene	112-88-9
Isoquinoline	119-65-3
Ammonium fluoride ((NH ₄)F)	12125-01-8
D-Limonene	138-86-3
Nitrilotriacetic acid	139-13-9
Acrylic polymer	26006-22-4
Etidronic acid	2809-21-4
1-Octyn-3-ol, 4-ethyl-	5877-42-9
Amines, hydrogenated tallow alkyl, acetates	61790-59-8
1-Hexadecene	629-73-2
Benzenesulfonic acid, C10-16-alkyl derivs., compds. with 2-propanamine	68584-24-7
Benzenesulfonic acid, C10-16-alkyl derivs., compds. with triethanolamine	68584-25-8
Hydrocarbons, terpene processing byproducts	68956-56-9
Petroleum naphtha	68990-35-2
Potassium iodide	7681-11-0
Phosphoric acid, calcium salt (2:3)	7758-87-4
Calcium bromide	7789-41-5
Quinaldine	91-63-4
Acetophenone	98-86-2

Table S2. Hydraulic fracturing additives used in more than 10% of treatments reported in California, excluding base fluids (e.g. water and brines) and inert mineral proppants and carriers.^a

Chemical	CASRN	Treatments using this chemical	Toxicity data available^{b,c}
Guar gum	9000-30-0	1,572	RMDT
Ammonium persulfate	7727-54-0	1,373	RDT
Sodium hydroxide	1310-73-2	1,338	RT
Ethylene glycol	107-21-1	1,227	RMDFT
2-Methyl-3(2H)-isothiazolone	2682-20-4	1,187	DT
Magnesium chloride	7786-30-3	1,187	RMDF
Magnesium nitrate	10377-60-3	1,187	R
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4	1,184	RDT
Isotridecanol, ethoxylated	9043-30-5	1,171	RD
Hydrotreated light petroleum distillate	64742-47-8	1,167	RFT
Distillates, petroleum, hydrotreated light paraffinic	64742-55-8	1,129	RDT
2-Butoxypropan-1-ol	15821-83-7	1,119	--
Hemicellulase enzyme	9025-56-3	1,098	--
1,2-Ethanediaminium, N1,N2-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N1,N2-bis(2-hydroxyethyl)-N1,N2-dimethyl-, chloride (1:4)	138879-94-4	1076	--
1-Butoxypropan-2-ol	5131-66-8	973	R
Phosphonic acid	13598-36-2	790	RM
Amino alkyl phosphonic acid	Proprietary	668	--
Boron sodium oxide	1330-43-4	666	RD
Sodium tetraborate decahydrate	1303-96-4	520	RMDT
Enzyme G	Proprietary	480	--
Sodium chloride	7647-14-5	437	RMDFT
Methanol	67-56-1	424	RMDFT
Potassium carbonate	584-08-7	279	RMDF
Glycerol	56-81-5	247	RMDT
Potassium hydroxide	1310-58-3	226	R
Phenol, polymer with formaldehyde	9003-35-4	225	R
Acetic acid	64-19-7	191	RMDFT
Isopropanol	67-63-0	170	RMDF

^aBased on all records (N=45,058), consisting of 1,623 treatments.

^bRat=R, mouse=M, *Daphnia magna*=D, fathead minnow=F, trout=T.

^cToxicity data could only be positively identified for chemicals with a CASRN.

Table S3. Twenty reported hydraulic fracturing chemicals in California used in the largest masses per treatment, excluding base fluids (e.g. water and brines) and inert mineral proppants and carriers.^a

Chemical	CASRN	Treatments using this chemical	Median mass per treatment (kg)	Median concentration by mass (%)	Toxicity data available^{b,c}
Organic phosphonate	Proprietary	6	7,687	0.47	--
Alkanes / alkenes	Proprietary	33	5,803	0.30	--
Hydrochloric acid	7647-01-0	42	5,267	0.25	MDT
Petroleum distillate blend	Proprietary	146	4,236	0.33	--
Monoethanolamine	141-43-5	13	3,662	0.19	RMDFT
Biovert CF	Proprietary	6	3,102	0.21	--
Sodium carbonate	497-19-8	1	2,542	0.11	RDF
Lactose	63-42-3	6	2,002	0.16	--
GS-1L (sodium thiosulfate)	Proprietary	1	1,650	0.15	--
Phenol, polymer with formaldehyde	9003-35-4	202	1,605	0.32	--
2-Acrylamido-2-methylpropane sulfonate	38193-60-1	3	1,318	0.05	--
Naphtha, hydrotreated heavy	64742-48-9	1	1,250	0.46	RF
Ethylbenzene	100-41-4	5	1,241	0.12	RMDFT
Potassium carbonate	584-08-7	253	1,212	0.09	RMDF
Mixture of surfactants	Proprietary	62	1,136	0.09	--
Sodium bicarbonate	144-55-8	31	1,067	0.07	RMDT
Hydrofluoric acid	7664-39-3	11	1,022	0.08	DT
Glyoxal	107-22-2	83	1,021	0.06	RMDF
Polyquaternary amine salt	Proprietary	5	956	0.06	--
Unknown	Proprietary	11	876	0.07	--

^aBased on complete records (N=39,581), consisting of 1,406 treatments.

^bRat=R, mouse=M, *Daphnia magna*=D, fathead minnow=F, trout=T

^cToxicity data could not be positively identified for chemicals without a CASRN. Other missing toxicity data were not located in the references consulted.

Table S4. Most toxic hydraulic fracturing chemicals used in California with respect to acute oral mammalian toxicity, based on the United Nations Globally Harmonized System (GHS) of Classification and Labelling of Chemicals system. Lower numbers indicate higher toxicity, with a designation of “1” indicating the most toxic compounds. Results are shown for chemicals with GHS ratings 2 and 3; no chemicals were identified that had a GHS rating of 1. Only compounds identified by CASRN are included in this analysis.

Chemical	CASRN	GHS rating^a	Animal model^{b,c}
Formaldehyde	50-00-0	2	RM
Propargyl alcohol	107-19-7	2	RM
Tetramethyl ammonium chloride	75-57-0	2	RM
Tetrasodium ethylenediaminetetraacetate	64-02-8	2	RM
2-Mercaptoethyl alcohol	60-24-2	3	RM
4,4'-Diaminodiphenyl sulfone	80-08-0	3	RM
Acrylamide	79-06-1	3	RM
Ammonium bifluoride	1341-49-7	3	R
Chlorous acid, sodium salt (1:1)	7758-19-2	3	RM
DBNPA (2,2-dibromo-3-nitrilopropionamide)	10222-01-2	3	R
Ethaneperoxoic acid	79-21-0	3	RM
Glutaraldehyde	111-30-8	3	RM
Glyoxal	107-22-2	3	R
Hydrochloric acid	7647-01-0	3	R
Linear/branched alcohol ethoxylate (11eo)	127036-24-2	3	R
Potassium hydroxide	1310-58-3	3	R
Quaternary ammonium chloride, benzylcoco alkyldimethyl, chlorides	61789-71-7	3	R
Sodium hydroxide	1310-73-2	3	R
Sodium sulfate	7757-82-6	3	RM
Sodium thiosulfate	7772-98-7	3	R
Tetrakis hydroxymethyl-phosphonium sulfate	55566-30-8	3	R
Thioglycolic acid	68-11-1	3	RM

^aGHS rating determined by the mammal model yielding the lowest rating.

^bMammal model defining the lowest GHS rating.

^cRat=R, mouse=M.

Table S5. Most toxic hydraulic fracturing chemicals used in California with respect to acute aquatic toxicity, based on the United Nations Globally Harmonized System (GHS) of Classification and Labelling of Chemicals system. Lower numbers indicate higher toxicity, with a designation of “1” indicating the most toxic compounds. Results are shown for chemicals with GHS ratings 1 and 2. Only compounds identified by CASRN are included in this analysis.

Chemical	CASRN	GHS rating ^a	Aquatic model ^{b,c}
2-Propenoic acid, ammonium salt (1:1), polymer with 2-propenamide	26100-47-0	1	D
2-Methyl-3(2H)-isothiazolone	2682-20-4	1	DT
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4	1	DT
Alcohols, C10-16, ethoxylated	68002-97-1	1	D
Alcohols, C12-13, ethoxylated	66455-14-9	1	DM
Alkyl dimethylbenzyl ammonium chloride	68424-85-1	1	DMT
Chlorous acid, sodium salt (1:1)	7758-19-2	1	D
DBNPA (2,2-dibromo-3-nitrilopropionamide)	10222-01-2	1	DMT
Ethoxylated C14-15 alcohols	68951-67-7	1	DMT
Glutaraldehyde	111-30-8	1	DMT
Hydrochloric acid	7647-01-0	1	DT
Naphthalene	91-20-3	1	DMT
Quaternary ammonium chloride, benzylcoco alkyldimethyl, chlorides	61789-71-7	1	D
Solvent naphtha, petroleum, heavy arom.	64742-94-5	1	DMT
1,2,4-Trimethylbenzene	95-63-6	2	DM
1,3,5-Trimethylbenzene	108-67-8	2	D
2-Mercaptoethyl alcohol	60-24-2	2	D
Alcohols, C11 linear, ethoxylated	34398-01-1	2	DM
Alcohols, C9-C11, ethoxylated	68439-46-3	2	DM
Ammonium chloride	12125-02-9	2	DMT
Benzyl chloride	100-44-7	2	M
Butyl glycidyl ether	2426-08-6	2	D
Cocamidopropyl betaine	61789-40-0	2	D
Dodecylbenzene sulfonic acid	27176-87-0	2	DT
Ethaneperoxy acid	79-21-0	2	D
Ethoxylated hexanol	68439-45-2	2	DT
Ethylbenzene	100-41-4	2	DMT
Ethylenediamine	107-15-3	2	DMT
Hydrogen peroxide	7722-84-1	2	DMT
Hydrotreated light petroleum distillate	64742-47-8	2	MT
Isopropylbenzene	98-82-8	2	DMT
Isotridecanol, ethoxylated	9043-30-5	2	D
Poly(oxy-1,2-ethandiyl), a-(nonylphenyl)-w-hydroxy-	9016-45-9	2	DT
Propargyl alcohol	107-19-7	2	M

Chemical	CASRN	GHS rating^a	Aquatic model^{b,c}
Sodium perborate tetrahydrate	10486-00-7	2	D
Solvent naphtha, petroleum, light arom.	64742-95-6	2	DT
Xylenes	1330-20-7	2	MT

^aGHS rating determined by the aquatic model yielding the lowest rating. ^bAquatic model defining the lowest GHS rating. ^c*Daphnia magna*=D, fathead minnow=F, trout=T.