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Toxicity of acidization fluids used in California oil exploration

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ABSTRACT

There has been considerable public interest regarding the toxicity of chemicals used in hydraulic fracturing, but little is known about its sister technique, acidizing. Little to no research has been done on what the chemicals of acidization are and what impact they could have on humans and the environment. This paper discusses the differences between three acidizing techniques (acid maintenance, matrix acidization, and acid fracturing) and quantifies the amounts of the chemicals used for each. Washington State's Quick Chemical Assessment Tool is used to identify F-graded toxins, which are known carcinogens, mutagens, reproductive toxins, developmental toxins, endocrine disruptors, or high acute toxicity chemicals. The analysis of the present data shows that there have been over 600 instances of acidizing in urbanized Southern and Central California from April 2013 to August 2015. Although most of the chemicals of acidizing are similar to hydraulic fracturing, those used most frequently are different. There are close to 200 specific chemicals used in acidization, with at least 28 of them being F-graded hazardous chemicals. Some are used frequently in the range of 100−1000 kg per treatment, such as hydrofluoric acid, xylene, diethylene glycol, and ethyl benzene. Close to 90 more chemicals are identified using non-specific names as trade secrets or reported with no quantity. Unlike hydraulic fracturing the chemical concentrations in acidizing are high, ranging from 6% to 18%, and the waste returns can be highly acidic, in the range of pH 0−3. With this paper it is hoped that acidization becomes part of the larger discussion on concerns with oil exploration and be evaluated by appropriate authorities.

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Toxicity; acidizing; oil exploration; hydraulic fracturing; hazard assessment

1. Introduction

Unconventional oil exploration has led to greater energy independence for the USA. It has also raised concerns among the public, NGOs, and policymakers regarding harmful impacts. While researchers have begun exploring the potential impacts of hydraulic fracturing more seriously, impacts from acidizing are not being examined as closely. It is important that acidizing be a bigger part of the discussion to protect the public and environment from potential harm.

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The overall objective of this paper is to identify potential human health risks and environmental hazards associated with acidizing that require further evaluation for responsible decision-making. This paper discusses the differences between three acidizing techniques (acid maintenance, matrix acidization, and acid fracturing) and quantifies the type and amounts of the chemicals used in them. Washington State's Quick Chemical Assessment Tool (QCAT) is used to identify F-graded toxins, which are known carcinogens, mutagens, reproductive toxins, developmental toxins, endocrine disruptors, or high acute toxicity chemicals. QCAT is based on methodology developed by the United States Environmental Protection Agency's (EPA) Design for the Environment program. It looks at various toxicological endpoints (i.e. carcinogenicity, neurotoxicity, etc.) to assign chemicals a hazard grade.

Recently, the California Council on Science and Technology published chemical information for matrix acidization. This chemical information was gathered primarily from the California Department of Conservation's Division of Oil, Gas, and Geothermal Resources (DOGGR). Here, we will use the chemical information from DOGGR as well as the South Coast Air Quality Monitoring District (SCAQMD) to discuss all the acidizing treatment types as well as look at different toxicological endpoints to assign a QCAT hazard grade.

1.1. Description of acidizing techniques

The first use of acids in oil exploration was in 1895, but because of acid attack on metal in the wellbore it was not used much (Putman 1933). The modern-day use of acid in oil stimulation began in the 1930s when it was discovered that corrosion inhibitors could stop acid attack on metal. Commercial use of acids finally began in the 1950s (Williams, Gidley, and Schechter 1979). The idea of using acids for oil stimulation or cleaning a wellbore is an old concept, but the chemicals, volumes, and techniques used in acidizing have evolved.

Acid is used in oil wells as part of three different techniques: acid maintenance, matrix acidization, and acid fracturing. Acid maintenance is a routine procedure used to remove deposits formed on well surfaces, also known as scale. In acid maintenance, operators inject acid solutions at a specific location in the wellbore to react with the scale. The scale is thus cleaned off the surfaces of the wellbore and equipment without any acid penetrating into the formation (Robertson, Chilingarian, and Kumar 1989).

The second technique, matrix acidization, is used to remove formation damage (i.e. blocked oil/gas pathways) around the wellbore and/or increase reservoir rock permeability. Permeability is a characteristic that allows oil and gas to flow through the rock rather than be stuck in pores. Operators inject acid solutions into the well to etch away at the reservoir rock, creating channels for oil and gas to flow through. Matrix acidization does not fracture the formation. Solutions are injected at pressures below the pressure required to fracture the rock, also known as fracture pressure (Robertson, Chilingarian, and Kumar 1989). Matrix acidizing in carbonate formations can nonetheless create small channels or tubes called wormholes that can propagate as much as 6.1 m (20 feet) into the formation, as carbonates are easily dissolved by acids. This is similar to the result of a small hydraulic fracturing treatment (CCST 2014). However, in sandstone, acid dissolution is limited to a much smaller distance of 0.3−0.6 m (1−2 feet) into the formation because the silica

matrix is harder to dissolve. Matrix acidizing in sandstone is therefore primarily used to remove damaging solids that have reduced the near-well permeability of the reservoir. There are some instances of matrix acidizing using HF/HCl reported in the Monterey Formation in California that may have had greater penetration because of the presence of natural fractures (CCST 2014). In California, matrix acidizing is done at depths ranging from 2000 to 11,000 feet. The wells at the lower end of this range come close to drinking water aquifers.

The last acidizing technique is acid fracturing. Acid fracturing, like matrix acidization, uses acids to etch the reservoir. The main difference is the injection rate. Injection rates with pressures below the pressure needed to fracture are termed matrix acidizing, while those above fracture pressure are termed acid fracturing (Mcleod 1986). Acid fracturing is similar to hydraulic fracturing in that a solution is injected into the wellbore at a high pressure to fracture the formation. The difference between acid fracturing and hydraulic fracturing is the composition of the stimulation fluids. Hydraulic fracturing uses a solution consisting of 99.5% water and sand and 0.5% chemicals (US DOE 2009), whereas, as determined from this research, in both matrix acidization and acid fracturing, the concentration of the solution used is 6%−18% chemicals. For acid fracturing to be able to etch channels in the fracture walls, the rock has to be soluble in acid, and the acid should not excessively leak off into the formation without reacting. Thus this technique is mainly used in carbonate formations (Williams, Gidley, and Schechter 1979).

1.2. Acidization fluid make up

Acidizing fluid includes water, acids, and additives. Water is the main solvent and conduit of the chemicals to the wellbore and/or reservoir. Acids are used to dissolve minerals and mobilize mineral grains by decomposing the rock structure. Many other chemicals are added for various purposes that are discussed in the appendix.

The most commonly used acids are listed in Table 1. In California, oil stimulations occur primarily in sandstone and some carbonate formations. Hydrofluoric acid (HF) in combination with other acids is used to dissolve silicates in sandstone. Hydrochloric acid (HCl) and other acids are used to dissolve carbonate minerals, such as limestone. See the supplemental section for more details on which acids are used for different minerals.

Table 1. Acids used in acidizing (Scheiber 2013).

Inorganic	Organic	Mixtures
Hydrochloric acid (HCl)	Acetic acid (CH_3COOH)	Organic acids/HBF_4
Hydrofluoric acid (HF)	Formic acid (HCOOH)	
Mud acid (HCl/HF)	Citric acid ($C_6H_8O_7$)	
Tetrafluoroboric acid (HBF_4)	Biodegradable acids	

1.3. Chemical exposure pathways

There are many different types of chemicals used in acidizing, and the risk of each is dependent on the chemical's exposure, toxicity, fate and transport, transformation, and cumulative and synergistic effects with other chemicals. Many of these factors have not been studied. Here, we focus on the chemicals' human exposure pathways through water.

Table 2. Surface and subsurface chemical release mechanisms into waterways.

Surface	Subsurface
Percolation from unlined pit	Fractured/acid wormhole pathway
Siting of disposal well into aquifer	Deteriorated abandoned well
Inadequately treated wastewater for reuse or disposal	Failure of production or disposal well
Spills, leaks, and accidents	Fault pathway

Table 2 lists the surface and subsurface chemical release mechanisms into waterways from oil stimulation, production, and wastewater management and disposal activities in California. For a diagram of the surface and subsurface release mechanisms see the supplemental section.

The most likely source of water contamination comes from improper handling of wastewater at the surface. Surface release mechanisms include percolation from unlined pits, siting of a disposal well into an aquifer, reuse or disposal of inadequately treated wastewater, and spills, leaks, and accidents. More than half of the wastewater from fractured oil wells in California is disposed of in open, unlined pits and could contaminate groundwater. More than 900 such pits, many without proper permits from the state, lie in the oil fields of the San Joaquin Valley, and some atop usable aquifers (CCST 2015). Wastewater from the surface can also be directly injected into Underground Sources of Drinking Water and "Usable" Water defined under EPA and Bureau of Land Management regulations. The California State Water Board confirmed that at least nine wastewater disposal wells have been injecting waste into aquifers that contain high-quality water protected under federal and state law (Bishop 2014). This becomes a serious issue in drought-stricken places with a high water demand, like the Central Valley of California. Another surface exposure route is reusing or disposing inadequately treated wastewater. In California, about 25% of wastewater was injected into disposal wells or reused for oil/gas extraction. Some wastewater has also been permitted for irrigation in California (CCST 2015). Surface spills, another surface release mechanism, have contaminated both groundwater and surface water. According to the available data between January 2009 and February 2014, 423 surface spills at oil and gas fields in California released nearly 2.8 million gallons of wastewater, or an average of 6500 gallons per incident. Of these, 34 spills released a total of 88,000 gallons of wastewater into California waterways (CCST 2014).

Subsurface release mechanisms include acid wormhole pathways in the rock formation leading to aquifers, fault pathways leading to aquifers, deteriorated abandoned wells leaking into the subsurface, and the failure of production or disposal wells. Modeling work suggests that hydraulic fracturing stimulation fluid contaminating aquifers by connecting pathways is highly unlikely, happening on a 1000−100,000 year scale (Kissinger et al. 2013; Gassiat et al. 2013; Flewelling and Sharma 2014). It is even more unlikely for wormhole pathways to reach an aquifer, because they do not extend very far. However, it becomes a greater threat in California, where unconventional oil stimulation is occurring at relatively shallow depths closer to aquifers with usable water. Matrix acid stimulation has occurred in many fields at depths around 2000 feet (CCST 2014). In both the San Joaquin Valley and the densely populated Los Angeles Basin, oil stimulation has happened at depths less than 1000 feet (CCST 2015). Pathways created by the compromised or failed structural integrity of cement in oil and gas wells and wellbores are considered the most likely potential pathway for groundwater contamination.

2. Methods

2.1. Information sources

Information about the geographical location of acidizing sites in California, volume of water used per treatment, chemical names and chemical abstracts service (CAS) registry numbers, chemical purpose, and chemical amounts were collected, sorted, and analyzed from two California government databases: the Division of Oil, Gas, and Geothermal Resource's (DOGGR) Interim Senate Bill 4 (Interim SB 4) self-reporting portal (DOGGR 2015) and the South Coast Air Quality Monitoring District's (SCAQMD) Rule 1148.2 self-reporting portal (SCAQMD 2015). The data are inclusive of dates from the inception of the Interim SB 4 on 1 January 2014 and SCAQMD's Rule 1148.2 on 5 April 2013 to mid-August 2015.

The data from DOGGR's portal from January 2014 to June 2014 only included information on what operators are required by law to report what they considered as acid fracturing or matrix acidizing; it was not based on a generally applicable regulatory definition. Furthermore, it did not include treatments that used acid concentrations of 7% or less (DOGGR, 2014). After June 2014, operators self-reported matrix acidization or acid fracking based on a uniform regulatory definition with no acid concentration exemption (DOGGR, 2014). As for SCAQMD's data, all chemical information on what operators considered as acidizing was collected. From April 2013 to March 2014 there was no way to determine whether what was reported was acid maintenance, matrix acidizing, or acid fracturing (SCAQMD, 2015), and the chemicals in use during this period could have been representative of any of the techniques. After March 2014, operators reported which acidizing techniques they were using. Information on acid maintenance and matrix acidization was collected from SCAQMD.

There are some clear limitations. Although information is required to be reported, self-reporting reduces transparency; there is no real-time way to validate information or that all information is being reported. Sometimes information is withheld because of trade secrets. Thus, the information may not be representative of consistent and transparent data collection. Furthermore, what was reported to SCAQMD as matrix acidization or acid fracturing should in theory also have been reported to DOGGR because SCAQMD is collecting information for Southern California and DOGGR for the whole state, but there is a lack of expected overlap. The data collected from DOGGR's portal came from only four operators for 100 wells, whereas SCAQMD received information from over 20 different operators for about 500 different wells.

2.2. Hazard assessment

Washington State's Ecology Department's QCAT was used to evaluate hazards associated with acidizing chemicals. The QCAT evaluation is a two-step process that assigns a grade to each chemical.

QCAT examines nine hazard endpoints; carcinogenicity, mutagenicity and genotoxicity, reproductive toxicity, developmental toxicity, endocrine toxicity, acute mammalian toxicity, acute aquatic toxicity, persistence, and bioaccumulation.

Step 1 uses authoritative sources to rank each chemical's hazard endpoints as very high, high, moderate, or low. The authoritative sources for Step 1 are toxicity characteristics

lists and databases generated by internationally recognized authoritative bodies or appropriate government agencies (US NIH, EC-REACH SVHS, IARC, Cal/EPA Prop 65, New Zealand HSNO, Lancet-Grandjean and Landrigan list, etc.). The chemical is ranked in accordance with the strength of the authority and the nature of the classification (Category 1, Priority list, etc.). Once each endpoint is ranked, a grade can be assigned. The grade is assigned on the basis of hazard endpoint-ranking combinations (see supplementary section for the process of assigning an initial grade). For example, a rank of high in carcinogenicity or reproductive toxicity automatically earns the chemical an F-grade.

If the hazard endpoints are found in Step 1 sources they are sufficient for assigning a grade. If however not all the hazard endpoints are found in Step 1 sources, one proceeds to the Step 2 sources. In some instances not all hazard endpoints are needed to assign an F-grade. For example, if a chemical is carcinogenic it is given an F-grade and no information from a Step 2 sources could give it a lower grade. Once the chemical is identified as an F-grade chemical in Step 1 there is no need to look further into Step 2 sources.

Step 2 requires more technical expertize. Its sources could include measured data from publicly available risk assessments and databases such as the Registry of Toxic Effects of Chemical Substances (RTECS) and the Hazardous Substances Data Bank (HSDB), or estimated data from PBT Profiler or other modeling tools. For the purposes of this paper only Step 1 sources were used. All F-graded chemicals have been identified only using Step 1 sources. More F-graded chemicals could be identified through Step 2 sources. Table 3 explains the meanings of the grade levels assigned by the QCAT assessment.

Table 3. Grade levels from the QCAT assessment process.

Grade A	Few concerns (i.e. relatively safe)	Preferable
Grade B	Slight concern	Improvement possible
Grade C	Moderate concern	Use but search for safer alternative
Grade F	High concern	Avoid

Because a QCAT assessment only looks at selected endpoints, chemicals of concerns could be missed during the evaluation process. The QCAT assessment is not as thorough an evaluation of the hazards posed by a chemical as other screening methods, like the GreenScreen® method. However, based on the level of technical expertize required to use it, it is a good starting point to identify hazardous chemicals (Washington State Department of Ecology 2015).

3. Results and discussion

3.1. Acidizing events

Well operators submitted chemical reports to DOGGR for matrix acidizing and acid fracturing only. DOGGR does not require acid maintenance activities to be reported. To SCAQMD, operators submitted chemical reports for acid maintenance and matrix acidizing only. There were no reported instances of acid fracturing to SCAQMD. However, it should be noted that these reports were submitted prior to the actual treatment, and it is not possible to distinguish matrix acidizing from acid fracturing without reviewing well completion reports to determine whether the fracture pressure was exceeded. Operators typically do not distinguish matrix acidizing from acid fracturing. From April 2013 to

March 2014, operators did not distinguish the type of acidizing to SCAQMD. After this time period, operators were required to identify which acidizing technique they would perform. But as stated before the distinction can only be made once an operation is completed. March 2014 onwards there were hundreds of reported instances of acid maintenance and only a handful of cases for matrix acidizing. It is thus likely that the instances of acidizing in the early time period were also mainly acid maintenance cases.

DOGGR acidizing events were primarily in Elk Hills Oil Field in Kern County, California, 40 miles east of Bakersfield, California. They represent 5% of the total unconventional oil stimulation techniques reported to DOGGR; 95% were hydraulic fracturing or listed as other stimulations.

SCAQMD acidizing events were in highly urbanized city centers of Southern California. They represent 65% of the total events reported to SCAQMD. A breakdown of the reported acidizing events can be seen in Table 4. Surprisingly, the SCAQMD matrix acidizing events did not show up in DOGGR's database, though based upon legal jurisdiction they should have. The way local and state authorities define matrix acidizing or an issue of enforcement could explain this discrepancy. There were few acid fracturing events reported to DOGGR and none to SCAQMD. This is probably due to the geology of the region. Acid fracturing is most effective in carbonate formations, whereas most of the oil-bearing formations in California are sandstone. Given the lack of oversight and enforcement and broad range of discretion afforded operators, it is possible that the acidizing events are under-reported.

Table 4. Reported acidizing events in California.

Treatment type	Submitted proposals as of mid-August 2015
SCAQMD acid maintenance	474
SCAQMD acid matrix	6
DOGGR acid matrix	90
DOGGR acid fracturing	10

3.2. Acidizing chemicals

There are many chemicals used in acidizing with data gaps. Many chemicals are listed as trade secrets; others have no toxicological or even basic chemical property information available. As for chemicals with known hazardous endpoints, the amounts used are substantial and create high toxic loads per treatment. The high acidity creates uncertainties as to how chemicals will transform or how much heavy metal will leach out.

This section details the composition and amount of chemicals in acidizing fluids and compares it with hydraulic fracturing. It also details the amounts of F-graded chemicals used in acidizing and what the toxicological load per treatment is – meaning what mass of carcinogens or reproductive toxins, for example, are used per treatment. Finally, it looks at the potential impacts of the acidic fluid.

3.2.1. Composition of acidizing fluids

There are about 200 different chemicals and around 90 chemical families, trade secrets, or chemicals of undefined amount used in acidizing in California. A list of all the chemicals and their amounts reported to DOGGR and SCAQMD, grouped by acidizing technique, is set out in the supplemental materials.

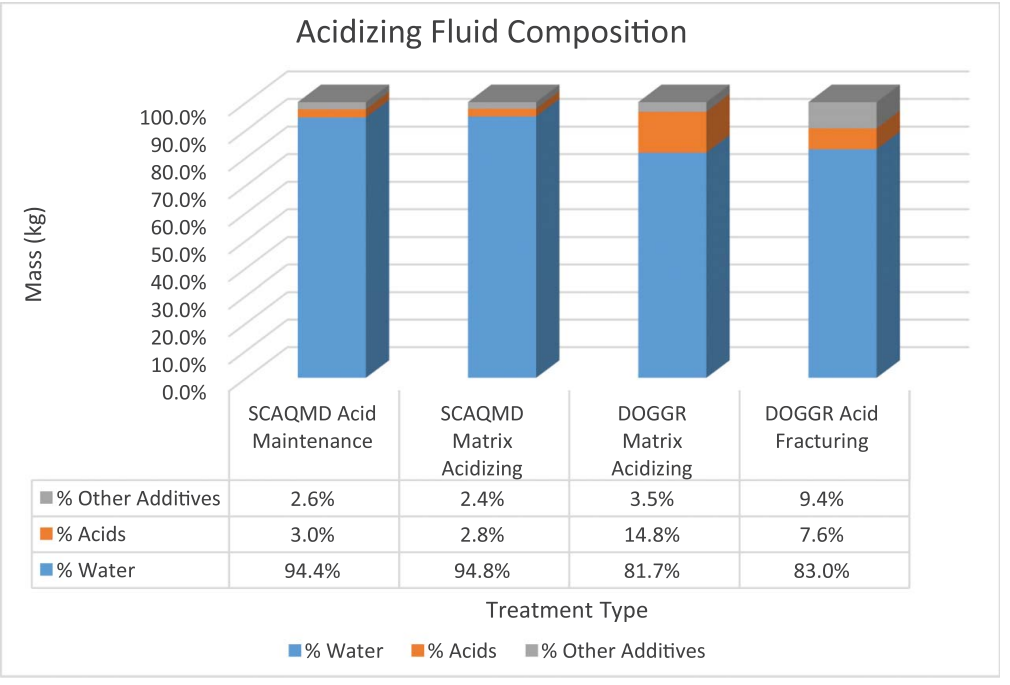

Figure 1. Acidizing fluid composition in California.

Unlike hydraulic fracturing fluid, where chemicals make up only 0.5% of the fluid (US DOE 2009), acidizing chemicals (acids and other chemicals, not including silica in acid fracturing) can make up 17% (acid fracturing), 5%−18% (matrix acidizing), or 6% (acid maintenance) of the fluid. Figure 1 shows a graphical representation of these percentages. Matrix acidizing as reported to DOGGR on average is the most concentrated with at least 81.7% being water and up to 18.3% other chemicals, of which 15% is acid. Acid fracturing as reported to DOGGR is about 8% acid and 9% other additives. In general, acidizing reported to SCAQMD had acids making up 3% of the fluid and other additives around 2.5% of the fluid.

These concentrated fluids have a greater impact than diluted hydraulic fracturing fluid. Microbes are not as effective at breaking down organic chemicals at higher concentrations, making them more persistent in the environment (Kekacs et al. 2015). Furthermore, new research is beginning to show that biocides that are used in unconventional oil stimulation techniques are also not effective at higher concentrations, possibly contributing to bacterial resistance to antibiotics (Kahrilas et al. 2015; Vikram, Bomberger, and Bibby 2015).

Although overall most of the chemicals used in acidizing are similar to the chemicals used in hydraulic fracturing (Stringfellow et al. 2014), those used most frequently in the two operations are different. If we compare the top 20 chemicals in Table 8 of the US EPA Report (2015) (20 most frequently reported additive ingredients in oil disclosures, ranked by frequency of occurrence) to the top 20 frequently used chemicals of acidizing techniques (Tables S4−S7), we see that only 10 of the most frequently used hydraulic fracturing chemicals are those that are used in acidizing treatments (the 10 most frequently used chemicals that are not among the most frequently used chemicals of hydraulic

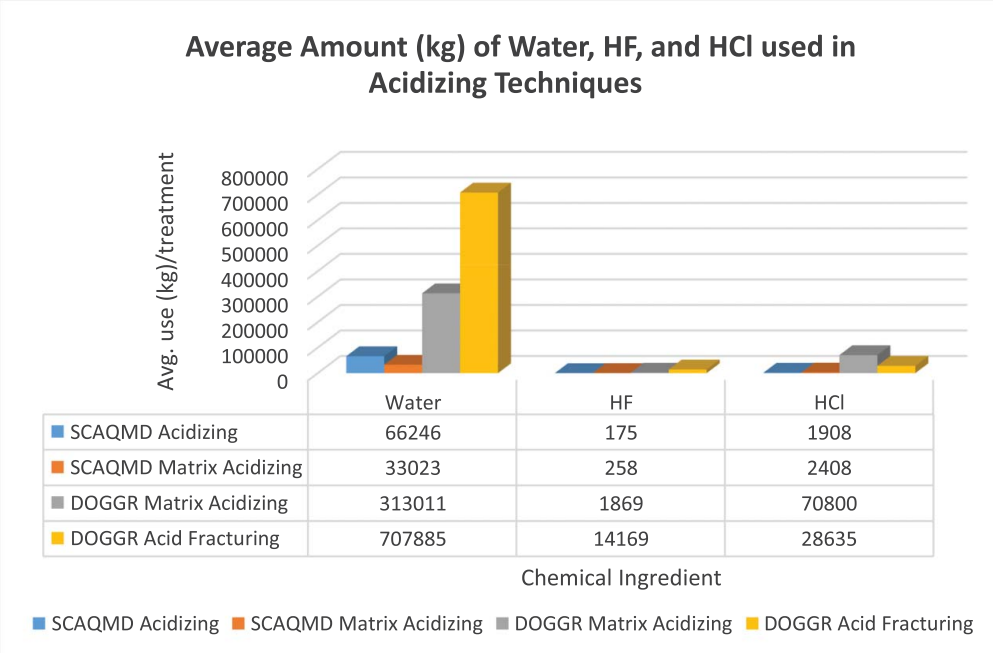

Figure 2. Average amount of water, HF, and HCl used in acidizing techniques.

fracturing are marked with an asterisks in the Tables S4−S7). In other words, 50% of the most frequently used chemicals of acidizing are different from the most frequently used chemicals of hydraulic fracturing, highlighting the need for increased research regarding the effects of acidizing.

Taking a closer look at water and acid use, Figure 2 shows the average amount of water, HF, and HCl used in acidizing.

The treatments reported to DOGGR, whether acid fracturing or matrix acidizing, used more water and acid. Acid fracturing used the most water, close to 700,000 kg/treatment. Acidizing is not as water intensive as hydraulic fracturing, and in general, California oil well stimulations use less water compared to other states. In other states hydraulic fracturing uses 4−12 million kg/well (CCST 2014), whereas in California the average use of water for the various acidizing techniques is between 60,000−700,000 kg/treatment.

Acid fracturing also used the most HF (~14,000 kg/treatment) of the treatments. Matrix acidizing as reported to DOGGR used the most HCl (~71,000 kg/treatment). The acidizing treatments reported to SCAQMD used the least HF (~200 kg/treatment) and HCl (~2300 kg/treatment).

HF is one of the more concerning chemicals, and is used in some of the largest quantities. HF is typically used in a combination with HCl and called mud acid (HF + HCl) to dissolve sandstone as well as remaining drilling mud. In Central California there is a greater use of mud acid. The average concentration by mass percentage (%w/w) of HF and HCl used in mud acid treatments is 0.5%−3% and 4%−15%, respectively (Scheiber 2013). Figure 2 shows that acid fracturing uses the most HF, more than 14,000 kg/treatment, followed by matrix acidizing (reported to DOGGR) at 1870 kg/treatment. All the treatments use more than the minimum reportable quantity of 45.4 kg, as set out by the

Emergency Planning and Notification Act, 40 CFR part 355. Even though acid maintenance uses on average 175 kg/treatment, it is such a common and routine procedure used in wells that the total accumulated load of HF in a region becomes significant. As for matrix acidization, more HF and HCl are used per treatment in Central California (reported to DOGGR) as opposed to Southern California (reported to SCAQMD). This difference could be because of geology or the scale of the activity in these regions. HF is primarily used to dissolve silicates and HCl for carbonates.

HF is of great concern because of its very high acute mammalian toxicity and neurotoxicity. Exposure to fumes or very short-term contact with liquid HF may cause severe and painful burns; it penetrates the skin to cause deep-seated ulceration that may lead to gangrene (National Center for Biotechnology Information 2015). Transport and storage of such large quantities of HF prior to use are serious concerns.

In addition, HF use in wells leaves fluoride behind which can also have detrimental impacts. Fluoride is beneficial in limited quantities for the mineralization of bones and formation of dental enamel. However, excessive fluoride is detrimental; 1.5−4 mg/L results in dental fluorosis, 4−10 mg/L results in skeletal fluorosis, and > 10 mg/L results in crippling fluorosis (Dissanayake 1991). If this excessive fluoride reaches drinking water sources, exposure becomes a serious concern.

The amount of HCl used also creates some concern. Individual reports show that HCl can be up to 270,000 kg/treatment. The %w/w of HCl reported in treatments other than mud acid mixtures is 15%−28%. HCl is corrosive to the eyes, skin, and mucous membranes. Chronic (long-term) occupational exposure to HCl has been reported to cause gastritis, chronic bronchitis, dermatitis, and photosensitization in workers. Prolonged exposure to low concentrations may also cause dental discoloration and erosion (US EPA 1999). Markey et al. (2014) also discuss the health and safety concerns of using HCl in oil drilling, as well as its corrosive impact on flow lines and equipment and environmental effects of the produced HCl.

3.2.2. F-graded chemicals

A main goal of this report was to identify the most toxic acidizing chemicals against a standard criterion. Table 5 lists the QCAT F-graded chemicals that are used in acidizing in California. They are listed in decreasing frequency of use. The primary hazardous toxicological endpoints of these chemicals are noted. These endpoints are detailed with references in the supplemental section.

There are at least 28 F-graded chemicals. The frequency of use and average amount per treatment gives an idea of exposure. However, information about the fate and transport of the chemicals, their transformations, synergistic and cumulative effects, as well as routes of exposure, are vital to understanding their true risk. The most commonly used F-graded chemicals in all acidizing treatments that were used on average in the 100's−1000's kg/treatment are methanol, HF, xylene, and diethylene glycol. These four chemicals are all neurotoxins and in some cases are also developmental or reproductive toxins. Methanol was used in almost all the treatments. HCl, although not listed as an F-rated chemical was also used in most treatments. HF, polyethylene glycol nonylphenyl ether, ethylene glycol, and formaldehyde were used in about half of the treatments. The amount used per treatment and how often a treatment is done are important in understanding the toxicological load put on a certain area.

Table 5. QCAT F-graded chemicals used in acidizing in California (ordered in decreasing frequency of use).

Chemical	CAS #	Maximum (kg)/ treatment	Average (kg)/ treatment)	Frequency of use	Acid maintenance	Matrix acidizing	Acid fracturing	Purpose*	Primary QCAT l ow grade reason**
Methanol	67-56-1	32,062.42	261.86	505	✓	✓	✓	Corrosion inhibitor, non-emulsifier, anti-sludging agents, wetting surfactant, clay stabilizer, solvent	Developmental toxin, neurotoxin, persistent
Hydrofluoric acid	7664-39-3	24,974.71	850.50	290	✓	✓	✓	Acidizing, well stimulation	Acute mammalian toxicity, persistent, neurotoxin
Polyethylene glycol nonylphenyl ether; poly (oxy-1,2-ethandiyl), A-(nonylphenyl)-W-hydroxy	9016-45-9	147.32	30.29	256	✓	✓	✓	Non-emulsifier, surfactant	Developmental toxin, endocrine disruptor, persistent
Ethylene glycol	107-21-1	404.31	11.90	201	✓	✓	✓	Cleaner	Developmental toxin, neurotoxin
Formaldehyde	50-00-0	32.06	0.22	191	✓	✓	✓	Corrosion inhibitor	Carcinogen
Xylene	1330-20-7	11,509.90	361.70	169	✓	✓	✓	Surfactant, solvent, asphaltene dispersant, paraffin inhibitor, demulsifier, cleaner	Reproductive toxin, neurotoxin
Naphthalene	91-20-3	28.08	1.79	169	✓	✓	✓	Surfactant, non-emulsifier, solvent	Carcinogen, acute aquatic toxicity
Ethylbenzene	100-41-4	2578.80	52.40	160	✓	✓	✓	Surfactant, solvent, cleaner	Carcinogen, reproductive toxin, persistent
Cumene	98-82-8	1.39	0.33	146	✓	✓	✓	Demulsifier, surfactant	Carcinogen, neurotoxin
Diethylene glycol	111-46-6	5013.96	1667.81	141	✓	✓	✓	Corrosion inhibitor	Neurotoxin
Ethylene oxide	75-21-8	0.50	0.01	105	✓	✓			Carcinogen, mutagen, developmental toxin, reproductive toxin, neurotoxin, persistent
Silica, amorphous-fumed	7631-86-9	31,895.35	395.51	81	✓	✓	✓	Proppant, friction reducer	Occupational carcinogen, persistent
Crystalline silica	14808-60-7	6769.86	537.70	28	✓	✓	✓	Sand control, proppant	Carcinogen, very high acute mammalian toxicity, persistent
Nitrilotriacetic acid	139-13-9	3206.24	282.67	27	✓	✓		Iron control	Carcinogen, mutagen
Ethanol	64-17-5	857.11	84.12	26	✓	✓	✓	Wellbore cleaner, clay control, iron control	Carcinogen, reproductive toxin, mutagen, persistent
Light aromatic naphtha	64742-95-6	62.23	12.98	21	✓	✓	✓	Non-emulsifier	Carcinogen, mutagen
Cristobalite	14464-46-1	31,895.35	1993.54	16		✓	✓	Proppant, friction reducer	Carcinogen, occupational carcinogen, persistent
Diisopropylnaphthalene/bis (isopropyl) naphthalene	38640-62-9	2.50	1.90	14	✓			Non-emulsifier	Carcinogen, persistent
Toluene	108-88-3	660.11	144.98	13	✓	✓		Solvent, asphaltene dispersant	Reproductive toxin, developmental toxin, persistent

(*continued*)

Table 5. (*Continued*)

Chemical	CAS #	Maximum (kg)/ treatment	Average (kg)/ treatment)	Frequency of use	Acid maintenance	Matrix acidizing	Acid fracturing	Purpose*	Primary QCAT l ow grade reason**
Paraffinic petroleum distillate	64742-55-8	34.51	14.23	12		✓	✓		Carcinogen, persistent
Diethanolamine	111-42-2	27.43	5.30	9		✓	✓	Corrosion inhibitor, surfactant	Carcinogen
Methyl isobutyl ketone	108-10-1	27.43	5.30	9		✓	✓	Solvent	Carcinogen, developmental toxin, neurotoxin
Oxyalkylated alkylphenol; polyethylene glycol mono (branched P-nonylphenyl) ether	127087-87-0	12.23	7.45	6		✓	✓	Surfactant, wellbore cleaner, emulsifier, wetting agent	Developmental toxin, reproductive toxin, endocrine disruptor, persistent
Oxyalkylated alkylphenol; polyethylene glycol nonylphenyl ether; poly (oxy-1,2-ethandiyl), A-(nonylphenyl)-W-hydroxy	26027-38-3	12.23	6.90	5		✓	✓		Developmental toxin, reproductive toxin, endocrine disruptor, persistent
Boric acid (H3B03)	10043-35-3	487.63	299.07	4		✓	✓		Developmental toxin, reproductive toxin, persistent
Cyclotetrasiloxane, 2,2,4,4,6,6,8,8-octamethyl-	556-67-2	0.02	0.02	2	✓			Friction reducer	Reproductive toxin, endocrine disruptor, very persistent
Acrylamide	79-06-1	0.06	0.06	1		✓			Carcinogen, mutagen, developmental toxin, reproductive toxin, neurotoxin
Acrylonitrile	107-13-1	0.0004	0.0004	1			✓		Carcinogen, persistent

*Chemical purposes listed are what the oil operator identifies.
**See the appendix for references for the toxicological endpoints.

The maximum reported use is also listed in Table 5. Some values are far above the average amounts used and may have been mis-reported. Methanol is reported to be used in up to 32,000 kg/treatment, HF up to 25,000 kg/treatment, xylene up to 12,000 kg/treatment, ethylbenzene up to 2600 kg/treatment, diethylene glycol up to 5000 kg/, and silica and cristobalite up to 32,000 kg/treatment. Their various toxicological endpoints can be seen in Table 5.

3.2.3. Toxicological load

In addition to identifying the F-rated chemicals, it is important to understand the toxicological load, or amount of carcinogens or reproductive toxins, for example, per acidizing treatment (see Figure 3).

In acid maintenance there is a high reproductive toxin load from xylene, ethylbenzene, and toluene. The high neurotoxin load is primarily from xylene and HF. Crystalline silica, ethylbenzene, and nitriloacetic acid are the main contributing carcinogens. HF and crystalline silica cause the high acute mammalian toxicity load.

In matrix acidizing as reported to SCAQMD there is a higher reproductive toxin load from xylene and ethylbenzene as well as a neurotoxin load from xylene, methanol, and HF. In matrix acidization reported to DOGGR the high developmental toxin and neurotoxin load are primarily from methanol. HF, xylene, and diethylene glycol also add substantially to the neurotoxin load. The acute mammalian toxicity is primarily from HF. Nitrotriacetic acid is the main carcinogen accounting for the high load.

The acid fracturing treatments have the largest carcinogen load from silica use. The high neurotoxicity and high acute mammalian toxicity in acid fracturing are from HF.

There are between 7000−90,000 kg/treatment of these seven toxicological endpoint chemicals listed in any one acidizing treatment at one time. The actual amounts used in the treatment can be found in the supplemental section (Tables S4−S7). The weighted toxicological impact of these chemicals do not take into account any transformation, or

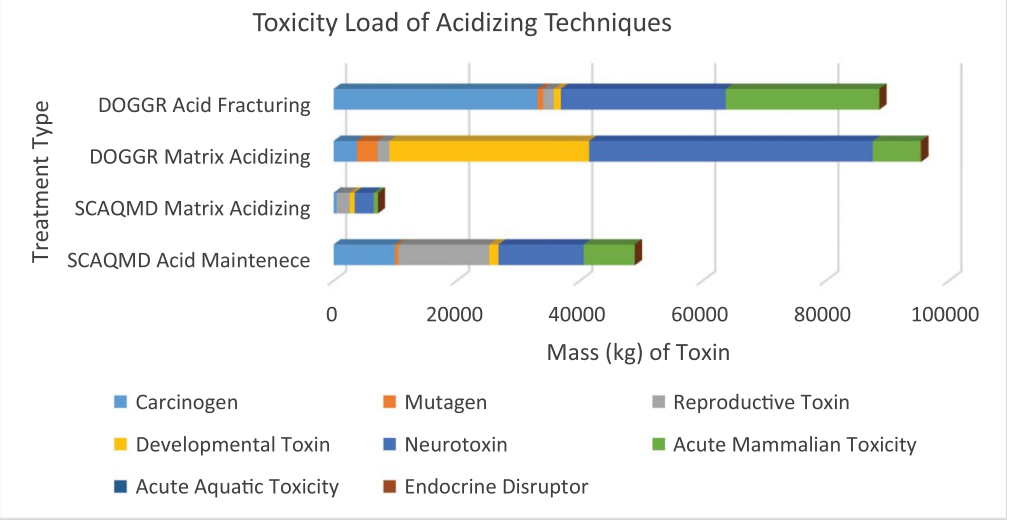

Figure 3. Toxicity load of acidizing techniques in California.

Table 6. Range of pH of matrix acidizing flowback water.

Treatment type	Range of pH of flowback	Time period or volume amount measured over	Reference
HCl/HF (5 diff. treatments)	0.5−3.5 (2.2−3.2)	200 min 500−700 bbl	Schuchart (1995)
15% HCl/1.5% HF	0−3	600 bbl	Gdanski and Peavy (1986)
15% HCl	0.2−5	5 h	Taylor, Nasr-El-Din, and Dajani (1999)

*bbl − oil barrel = 42 US gallon.

synergistic or cumulative impacts. In a highly acidic environment the stability and reactivity of the chemicals are unknown. The potential environmental impact of these chemicals and their byproducts is also unknown. Another problem of acidic solutions is the dissolution and mobilization of naturally occurring heavy metals and other pollutants from the oil-bearing formation, the extent of which is also unknown (CCST 2015).

It should be noted that not only is the acidizing fluid acidic, but the "flowback," in the case of matrix acidization for example, can also be acidic. A few industry reports show that the pH of returning waste is mainly between 0 and 3 for the first few hours (see Table 6). It is unknown how much of the chemicals returns to the surface for acidizing, but recent data submitted to DOGGR by operators show that the volume of recovered fluids collected after matrix acidization is 50%−60% (CCST 2015)

4. Conclusions

The analysis of the present data shows that there have been 474 reported acid maintenance events in Southern California, 96 reported matrix acidization events in Central and Southern California, and 10 reported acid fracturing events in Central California from April 2013 to mid-August 2015. In Southern California, acidization events are occurring in highly urban areas around Los Angeles County. There are about 200 chemicals used in acidization, and 50% of the most commonly used acidizing chemicals are most commonly used hydraulic fracturing treatment chemicals. Unlike hydraulic fracturing, the chemical concentrations in the fluids for acidization are high, ranging from 6% to 18% chemicals, and the waste that returns can also be highly acidic.

The amounts of chemical used per treatment are anywhere between 100's of milligrams and 100,000's of kilograms. Some of the chemicals are known to be of concern for both human health and the environment. An initial hazard assessment was done, and 28 QCAT F-graded chemicals of concern have been identified. It should be noted that close to 90 other chemicals are identified by non-specific names, family classes, or chemicals of undefined amount.

Furthermore, the flowback conditions, pH of the fluid and what chemicals are returning are unknown. The toxicity, the chemical fate and transport, and exposure potential of all these chemicals should be understood, and if a hazard is noted then substitute chemicals should be suggested. Understanding where these chemicals are likely to end up in our environment is critical in predicting how vulnerable populations will be affected. Understanding the toxicity will help us to identify possible impacts we might see in the near to distant future on humans and other living organisms. The stability and reactivity of these chemicals under such strong acid conditions is also unknown. The potential hazard of these chemicals and their byproducts have unknown environmental impacts.

The aim of this paper was to present potential problems of acidizing that need to be investigated so that scientists and legislators can evaluate the environmental impact of acidization. There is a need for the most up-to-date information on what chemicals and quantities are being used and the specific uses of these chemicals. The information in this paper only includes self-reported information, which is limited. There needs to be a transparent way to gather information from industry. Even more important is the need for monitoring and reporting of what is returning as wastewater.

Future research should include identifying appropriate stable indicator chemicals or stable byproduct chemicals from the process that can be monitored in groundwater to track any leakage from wellbores or disposal wells and pits. Possible treatment techniques for chemicals of concern in the wastewater as well as the water remaining in the ground that can contaminate groundwater should also be researched. The feasibility of treatment needs to consider cost effectiveness. If acidization is to be used in oil exploration we need to be aware of the possible impacts and ways to prevent them, including appropriate treatment of residual water at the surface and in the ground.Finally, understanding the current regulatory framework and jurisdiction that is in place to regulate acidization effectively, as well as identifying the gaps that exist, are important in moving forward to safely regulate acidization.

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