UNIVERSITY OF CALIFORNIA

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Acidizing Oil Wells, a Sister-Technology to Hydraulic Fracturing:
Risks, Chemicals, and Regulations

A dissertation submitted in partial satisfaction of the requirements for the degree

Doctorate in Environmental Science and Engineering

by

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ABSTRACT OF THE DISSERTATION

Acidizing Oil Wells, a Sister-Technology to Hydraulic Fracturing:
Risks, Chemicals, and Regulations

by

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The United States has seen resurgence in petroleum production, mainly driven by technology improvements in unconventional oil and gas stimulation from shale formations. Hydraulic fracturing, one of the unconventional oil and gas stimulation technologies, has caught a lot of public attention that has led to more research on it and its impacts as well increased debate over more regulatory oversight. Other unconventional oil stimulation techniques have more or less been left out of the discussion. One of these less frequently discussed techniques is acidizing. Acidizing is a term used for all types of acid use that increase or keep up well productivity or injectivity. The use of these unconventional stimulation techniques has greatly increased over the past decade. The expansion of tight oil and shale gas extraction using unconventional oil stimulation has raised concerns about its potential environmental and health impacts. These concerns include potential direct impacts to groundwater and surface water quality, water supplies, and air quality. Much attention has been on the impacts of hydraulic fracturing with little to no attention on acidizing. This research looks at the acidizing process and for the first time defines what the chemicals of acidization are, in what amount they are used, and what their toxicity is.

The analysis of the present data shows 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, which are known carcinogens, mutagens, reproductive toxins, developmental toxins, endocrine disruptors, or high acute toxicity chemicals. Some are used frequently in the range of 100 - 1000 kg per treatment, such as hydrofluoric acid, xylene, diethylene glycol and ethyl benzene. Unlike hydraulic fracturing the chemical concentrations in acidizing are high, ranging from 6-18%, and the waste returns can be highly acidic, in the range of pH 0-3.

In addition to analyzing the chemicals and their potential impacts this research looks at the legal framework for regulating acidizing activities. Provisions of several federal environmental laws can apply to acidizing activities. The federal role in regulating O&G extraction activities has been the subject of considerable debate and legislative proposals for several years. The Administration has pursued a number of regulatory initiatives related to unconventional O&G development, primarily hydraulic fracturing, under existing statutory authorities. Acidizing, however, has been almost entirely been left out of new proposals. This research sheds light on this topic and suggests areas where acidizing can be better regulated.

In addition to looking at the federal laws and state bills in place for regulating acidization, this research specifically looks at a better regulating scheme for stormwater runoff from oil and gas facilities. Contaminated stormwater runoff from oil and gas operations can pose a significant threat to surface waters. The research examines the extent of this threat and recommends more specific permitting requirements and best management practices to protect surface waters.

With increasing use of unconventional oil stimulation techniques like acidizing, it is important to understand the technology, the threats caused by them, and how to best protect the public and environment from any potential harm. This dissertation research attempts to shed light on these issues related to acidizing.

The dissertation of Khadeeja Saba Abdullah is approved.

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This dissertation is dedicated to

my parents Amtul Aziz and Aslam Abdullah
for their lifelong love, sacrifices, and commitment to my education

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for their love, support, and encouragement

my husband Adeel Syed
for his support, without which I could not have reached my goals, and work ethic,
which inspires my own

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and

my teachers
for their commitment to knowledge and giving me the tools to excel

Table of Contents

List of Tables

List of Figures

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American Chemical Society (March 22-25, 2015) Denver, Colorado
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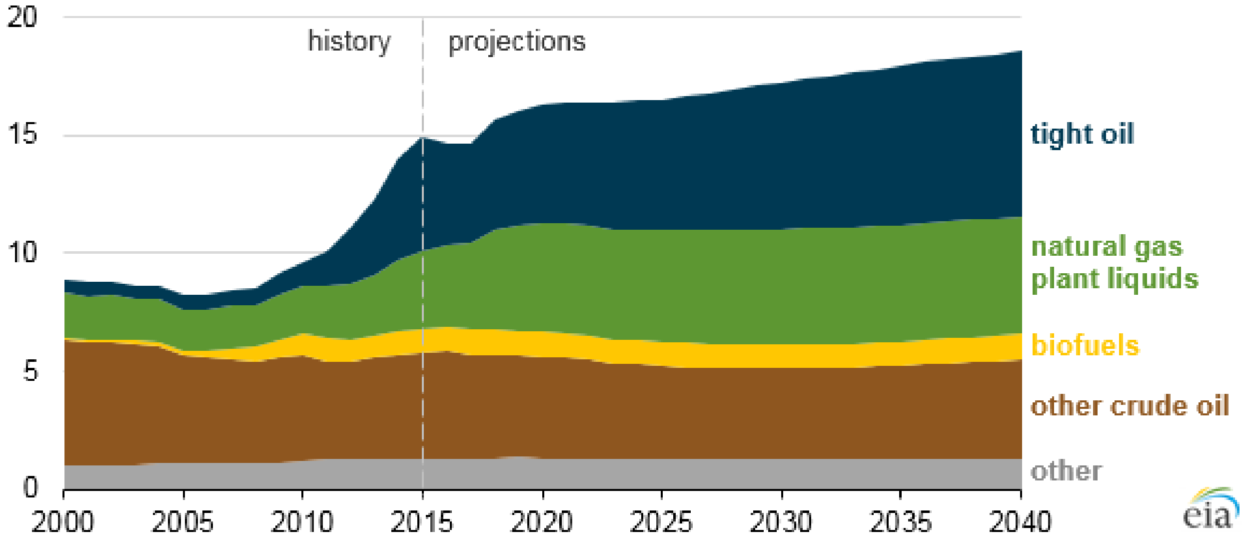
"Transport of Hazardous Waste through Local Communities"

I. Introduction

The United States has seen resurgence in petroleum production, mainly driven by technology improvements in unconventional oil and gas (UOG) stimulation from shale formations. Application of these technologies has enabled oil and natural gas to be economically produced from shale and other unconventional formations. This has contributed to the United States becoming the world's largest natural gas producer in 2009. Use of these technologies has also contributed to the rise in US oil production over the last few years. In 2009, for the first time since 1999, oil production increased annually. Between January 2008 and May 2014, U.S. monthly crude oil production rose by 3.2 million barrels per day, with about 85% of the increase coming from shale and related tight oil formations in Texas and North Dakota (Ratner and Tiemann, 2015). There had been a general increasing trend in production up until late 2014 when a drastic dip in oil prices pushed many companies to scale back their operations. However, since that time oil prices are recovering and the U.S. Energy Information Administration (EIA) recently projected that U.S. petroleum and other liquid fuels production will grow from 14.8 million barrels/day (b/d) in 2015 to 18.6 million b/d in 2040 in its *Annual Energy Outlook 2016* (AEO2016) Reference case.

Figure 1: U.S. Production of Petroleum and Other Liquids (2000-2040) in million barrels/day (Annual Energy Outlook, 2016)



The expansion of tight oil and shale gas extraction using UOG stimulation has raised concerns about its potential environmental and health impacts. These concerns include potential direct impacts to groundwater and surface water quality, water supplies, and air quality. Much of the research on the environmental and health impacts have been centered on only one type of UOG stimulation technique, hydraulic fracturing (HF). Stimulation techniques like acidizing have been grossly left out of the picture. This research is the first of its kind in that it discusses the different types of acidizing techniques and identifies the chemicals and amounts used in California and their toxicological impact.

Furthermore, this research looks at the legal framework available for regulating acidizing and identifies areas of improvement, both on the federal and California state level. States are the primary regulators of oil and gas (O&G) production on non-federal lands. With recent changes in production practices in tight oil, shale gas, and other unconventional hydrocarbon formations, many O&G producing states have revised laws and regulations governing O&G production. However, state rules vary considerably, leading to calls for more federal oversight of UOG extraction activities. The federal role in regulating O&G extraction activities—specifically HF—has been the subject of considerable debate and legislative proposals for several years, but legislation has not been enacted. While congressional debate has continued, the Administration has pursued a number of regulatory initiatives related to unconventional O&G development under existing statutory authorities. Acidizing, however, has been almost entirely been left out of new proposals. This research sheds light on this topic and suggests areas where acidizing can be better regulated.

The last portion of this research looks specifically at surface water protection from contaminated stormwater resulting from O&G activates as a whole. Contaminated stormwater runoff from O&G operations, acidizing included, can pose a significant threat to surface waters. This research examines the extent of this threat and recommends more specific permitting requirements and best management practices to protect surface waters from O&G stimulation activities.

While much of the research around UOG stimulation techniques has been focused on HF the focus of this dissertation is on the less discussed process of acidizing. With this research it is hoped that acidization becomes part of the larger discussion on concerns with O&G exploration and production as a whole and is evaluated by appropriate authorities.

References:

Annual Energy Outlook 2016. US Energy Information Administration.

Ratner, M., Tiemann, M., 2015. An Overview of Unconventional Oil and Natural Gas: Resources and Federal Actions. Congressional Research Service.

II. Background

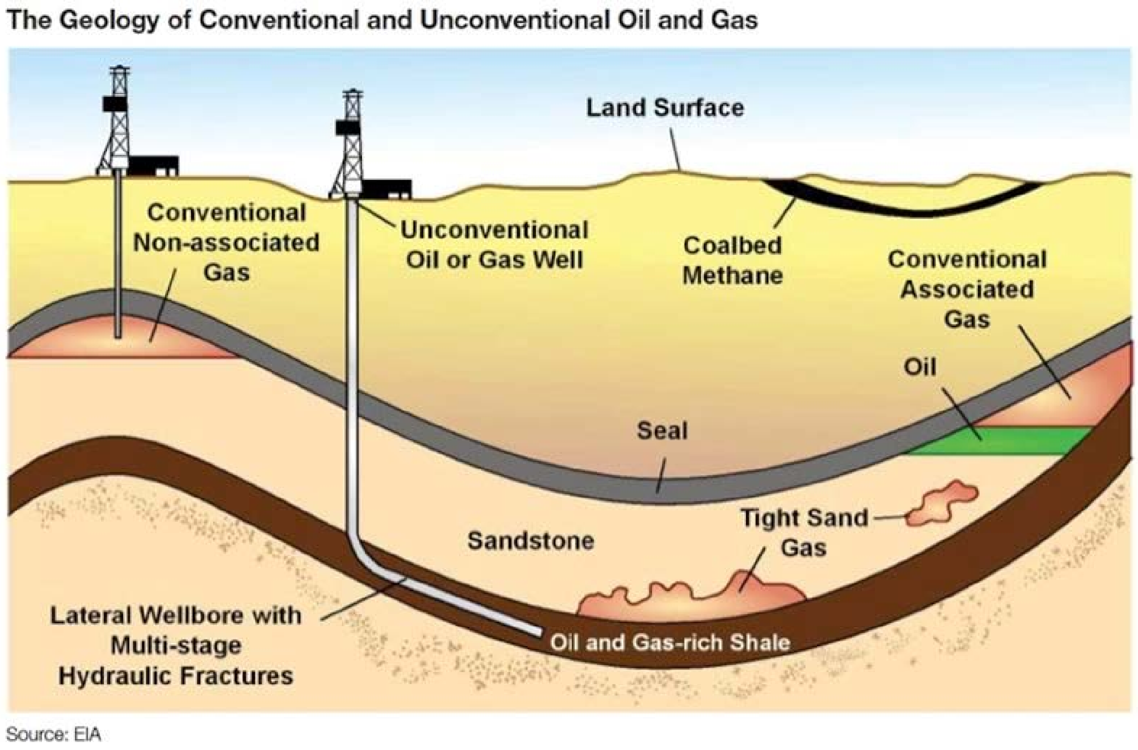
A. What is Unconventional Oil and Gas Stimulation?

All of the O&G we use today began as microscopic plants and animals living in the ocean millions of years ago. As these microscopic plants and animals lived, they absorbed energy from the sun, which was stored as carbon molecules in their bodies. When they died, they sank to the bottom of the sea. Over millions of years, layer after layer of sediment and other plants and bacteria were formed.

As they became buried ever deeper, heat and pressure began to rise. The amount of pressure and the degree of heat, along with the type of biomass, determined if the material became oil or natural gas. More heat produced lighter oil. Even higher heat or biomass made predominantly of plant material produced natural gas.

After O&G were formed, they tended to migrate through tiny pores in the surrounding rock. Some O&G migrated all the way to the surface and escaped. Other O&G deposits migrated until they were caught under impermeable layers of rock or clay where they were trapped (Department of Energy). These trapped deposits are where we find conventional O&G today and are extracted by the known conventional techniques of oil drilling (See figure 2). Conventional O&G stimulation techniques are drilling operations that use the natural pressure of the wells as well as pumping or compression operations to extract crude oil and natural gas. Conventional O&G can be produced commercially without altering the rock permeability or fluid viscosity.

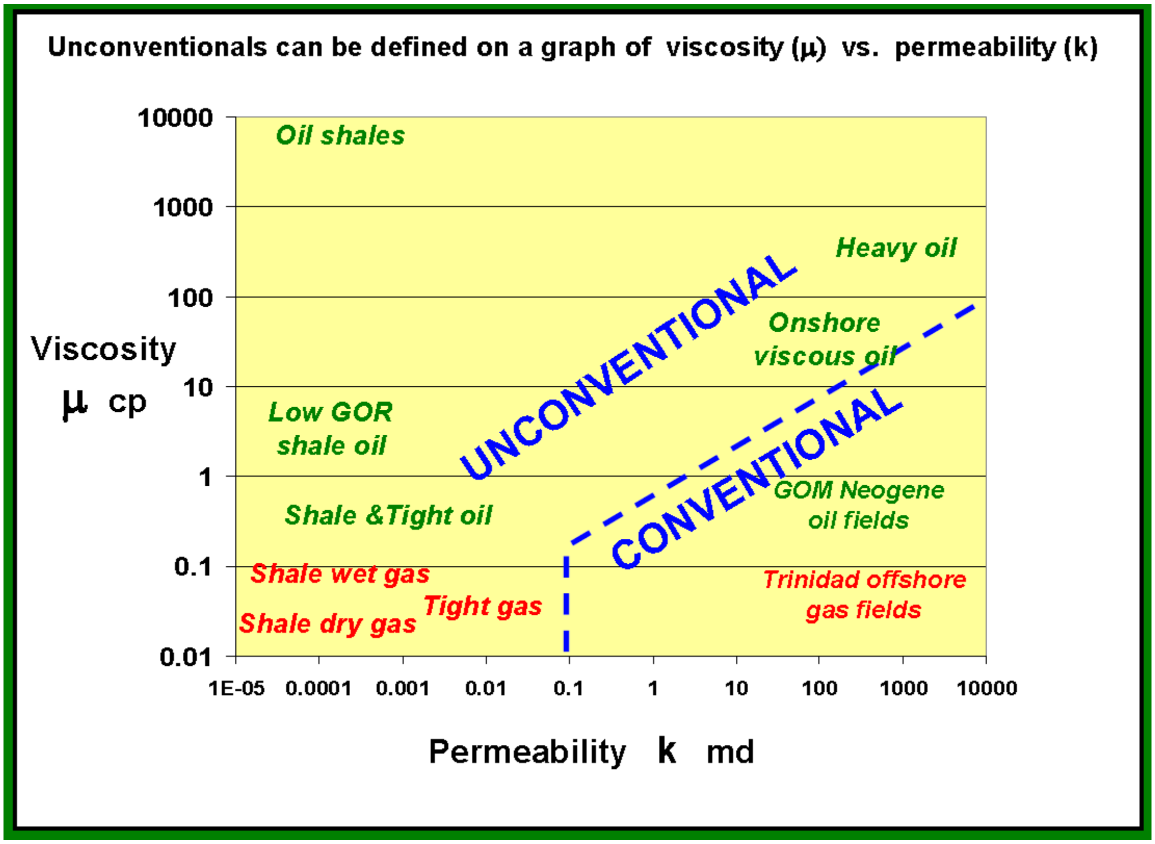
Figure 2: O&G Generation (EIA, 2011)



Source: EIA

In addition to conventional O&G there is O&G that during the migration upwards got trapped in low-permeability rock, including sandstone, siltstone, shale, and carbonates, or gas trapped in fine-grained, organic-rich rock or coal. This O&G is referred to as unconventional resources, and require the use of technology to alter either the rock permeability or the fluid viscosity in order to produce the oil or gas (Cander, 2012). These techniques include but are not limited to horizontal drilling, hydraulic fracturing, matrix acidization, acid fracturing, stem injection, and carbon dioxide flooding (Zou, 2013). The figure below shows the difference in viscosity and permeability of different O&G resources.

Figure 3: Difference in Viscosity and Permeability of Conventional and Unconventional O&G (Cander, 2012)



More viscous oil and impermeable formations require UOG stimulation techniques to either make the oil more fluid or make the rock formation more permeable. Thermal methods are used to allow production of exceedingly viscous oil (Prats, 1982). Such hydrocarbons are called “viscous oil” or “heavy oil.” Thermal methods lower oil viscosity by heating the reservoir, most commonly through steam or hot water injection (Farouq, 2003).

Fracturing methods or worm holing methods increase permeability. There are three main stimulation techniques that increase permeability, hydraulic fracturing, acid fracturing, and matrix acidization (Economides and Nolte, 2000). Because these methods do not reduce oil viscosity, they are primarily targeted at tight (low permeability) rock formations containing gas or lower-viscosity oil, although they may be used in combination with thermal stimulation for heavy oil. Hydraulic fracturing is the injection of a pressured fluid, containing water and chemicals, which fractures the formation. A proppant, like sand is used in the stimulation fluid to lodge itself in the fractures and keep it open to allow oil and gas to flow back through. Acidizing, which includes acid fracturing and matrix acidization, is the focus of this dissertation and will be discussed in the sections to follow.

B. What is Acidization?

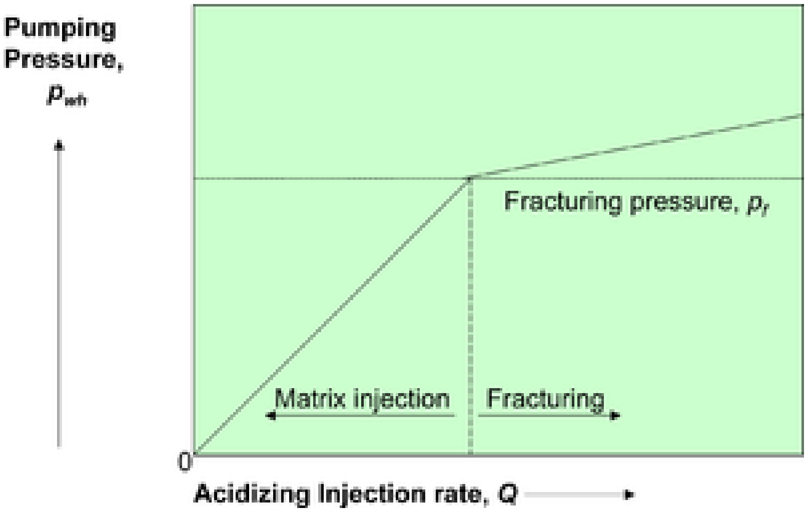
Acids are used in a variety of ways for oil well stimulation. Acidizing, a term used for all types of acid use, is used to increase or keep up well productivity or injectivity. Chemicals are used to clean fractures and pores or to create new flow channels, thus increasing rock permeability. The acidizing techniques include acid maintenance, matrix acidization, and acid fracturing.

Acid maintenance is done very often and is used to remove scales in the wellbore. In acid maintenance, operators inject the acid solutions at a specific location in the wellbore or circulate it back and forth across the casing perforation or formation face to react with the scale. The scale is cleaned off of the surfaces of the wellbore and equipment without penetrating into the formation (Robertson et al., 1989).

Matrix acidization is used to remove formation damage around the wellbore and/or increase reservoir permeability. Permeability is a characteristic that allows O&G to flow through the rock rather than be stuck in pores. Operators inject acid solutions into the well at pressures below the pressure required to fracture the rock, also known as fracture pressure (Robertson et al., 1986). Matrix acidization does not fracture the formation. Instead, acids etch away at the reservoir rock creating channels for O&G to flow through. The mechanisms involved include etching the mineral surfaces by dissolving the minerals and mobilizing particles by decomposing the rock structure (Mcleod, 1986). In California, matrix acidizing is done at depths ranging from 2000-11,000 feet. Matrix acidizing in carbonate formations can create small channels or tubes called wormholes that can propagate as much as 6.10 meters (20 feet) into the formation. This is similar to a small hydraulic fracturing treatment. However in sandstone, acid dissolution is limited to a much smaller distance of less than 0.3 to 0.6 m (one to two feet) into the formation. Matrix acidizing in sandstone primarily removes damaging solids that have reduced the near-well permeability of the reservoir. However, there are some instances of matrix acidizing using HF/HCl reported in the Monterey Formation in California that may have greater penetration because of the presence of natural fractures (CCST, 2014). Matrix acidization is primarily used to remove formation damage but can also increase reservoir permeability.

The last acidizing technique is acid fracturing. Acid fracturing is similar to HF in that a solution is injected into the wellbore above hydraulic pressure to fracture the formation. In acid fracturing an acid is used to “etch” channels in the fracture walls. The rock has to be partially soluble in acid, thus it is mainly used in carbonate formations. In these formations the acid reaction is quick; the acid excessively leaks into the formation, not being able to create long etched fractures (Williams et al., 1976). Both acid fracturing and matrix acidization used acids to etch the reservoir. The main difference is the injection rate. Injection rates resulting in pressures below the pressure needed to fracture are termed matrix acidizing, while those above fracture pressure are termed acid fracturing (McLeod, 1986). Figure 1 shows the difference between matrix acidization and acid fracturing. It shows that until the fracturing pressure is reached, pressure increases linerarly with injection rate. When fracturing pressure is reached the time rate can continue to increase with little change in pressure above fracturing pressure.

Figure 4: Pressure Changes with Increasing Acidizing Injection Rates (Acid Fracturing, 2013)



Acidizing is used in all oil exploration. Recently more attention has been given to UOG stimulation. These are techniques that alter the permeability of the reservoir or the viscosity of the stimulation fluid to extract once trapped oil/gas. HF is an UOG stimulation that alters the permeability of the reservoir, as are matrix acidization and acid fracturing (Zou, 2013). However, the composition of the stimulation fluids is different. In HF a solution consisting of 99.5% water and sand and 0.5% chemicals is used (US DofE, 2009). In both matrix acidization and acid fracturing a much higher concentration solution is used, as will be discussed later.

Table 1 highlights the differences between these three unconventional oil stimulation techniques used to alter permeability.

Table 1: Unconventional Oil Stimulation Techniques and their Differences

	Hydraulic Fracturing	Acid Fracturing	Matrix Acidization

Uses Pressurized Fluid	✔	✔	
Uses Propping Agent	✔	✔(some cases)	
Uses Acid		✔	✔
Increases Reservoir Permeability via Fracturing	✔	✔	
Increases Reservoir Permeability via Acid Etching		✔	✔(some cases)
Removes Formation Damage		✔	✔
Amount of Water Used	3-5 million gallons/well; 130,000-210,000 gallons/well (in California) (CCST 2014)	500,000 gallons/well (in California)	40,000 gallons/well (in California) (CCST 2014)

C. The History of Acidization

Acidizing is an old technique used in oil development. The details have changed but the principles remain the same. A Standard Oil patent for acidizing limestone with hydrochloric acid dates from 1896 (Frasch, 1896). The technique was first used a year earlier by the Ohio Oil Company. Reportedly, oil wells increased in production three times, and gas wells four times. At that time the acid severely corroded the well casing, and thus declined in popularity and wasn't used for about 30 years (Putman, 1933).

In 1928 acid use was brought back to remove scale in the oil wells with an added inhibitor to protect the iron casing from corrosion, but the decline in oil prices and the high cost of the acid made this treatment unused and unexplored (Champman, 1933).

The "modern era" of acidizing links back to events in the 1930s when arsenic was discovered to inhibit the action of hydrochloric acid on metal. Arsenic was used with hydrochloric acid on a limestone reservoir, and a previously dead well started producing

16 barrels of oil per day (Newcombe, 1933). This sparked the interest of industry and acidizing came back into the market.

In 1933 hydrofluoric acid was used to treat a sandstone formation because hydrochloric acid doesn't react with silicate minerals in sandstone. Around the same time a mixture of hydrochloric and hydrofluoric acid was used to treat a well but commercial use didn't begin until the 1950s (Williams et al., 1979).

The principle of acidizing is still the same but additives used have changed quite a bit since the 1950s. Although the main drivers of this mechanism are the acids, there are hundreds of other chemicals used to enable this technique. In addition to the acids these other chemicals could potentially be the most harmful. The chemical makeup of the fluids used is dependent on the geology of the reservoir and the chemistry of the reactions. Although the science of how to extract oil has improved and continues to improve, the science of how it impacts our environment is unknown and is not being explored as rapidly. This research is an attempt to begin that discussion around the impacts to humans and the environment. In the next section we lay out the types of chemical that are used in acidization.

D. Fluid Makeup

Matrix acidizing fluid includes water, acids, and additives. Water is the main solvent and conduit of the chemicals to the wellbore damage and/or the reservoir. Acids are used for mineral dissolution and mobilization of mineral grains by decomposition of the rock structure. Additives are used for various purposes later outlined.

1. Acid Selection

Each type of acid has its own peculiar chemical and physical properties. The type of acid selected for stimulation of a particular oil well depends on various characteristics outlined below.

a) Rock-Dissolving Capacity

The rock-dissolving capacity of the acid refers to the volume of rock that can be dissolved by the acid. This is important when evaluating how much rock needs to be dissolved (Robertson et al., 1989).

b) Acid Spending Time

Operators also consider the spending time of the acid. The spending time of the acid is the time required for the acid to expend 85-90% of its dissolving capacity. After that, the acid reaction is very slow due to acid dilution. Acids with a high spending time are chosen so that they can be pushed away as far as possible from the wellbore into the formation before they are spent (Robertson et al., 1989).

c) Reaction Product Solubility

The acid selected is also dependent on the solubility of reaction products. Insoluble salts can precipitate and plug the formation channels and/or fractures. Thus, a prerequisite for any acid to be used is that the reaction salts must be soluble. Solubility of salts varies with temperature and quantity of similar salts already dissolved in the brine. An additional problem arises when the acid-reaction salts react with other ions present in the formation water to form insoluble salts (Robertson et al., 1989).

d) Acid Corrosion

Acid selection is also dependent on acid reaction with metals, also known as acid corrosion. For most acids, a chemical inhibitor is added to the solution to retard the corrosion process. In the case of many of these inhibitors, a protective thin film forms on the metal surface. This chemical film, which serves as a barrier between the reactive acid and the metal, tends to break down at high formation temperatures. Inhibitors don't produce 100% protection from corrosion for long periods of time (Robertson et al., 1989).

e) Emulsions

Another consideration is emulsion formation when the acids mix with water and oil. If formed in flow channels, the emulsions will increase the pressure gradient required to move fluids in those channels, as well as increase fluid viscosity, plug formation pore channels, and cause a well-fluid cleanup problem. Reaction between acid and oil, especially in the case of concentrated hydrochloric acid (28% and higher) may result in the formation of sludge, which can also plug the channels. Surfactants are used to prevent emulsification and the formation of sludge (Robertson et al., 1989).

f) Density and Viscosity of Spent Acid

Operators also think about the density and viscosity of spent acid water. The density and viscosity increases with increasing concentration of the initial acid. The increase in density makes it difficult to recover treating fluids (Robertson et al., 1989).

g) Etching Pattern

Another important consideration is the etching pattern of the acid. Generally stronger acids and acids of higher concentration produce better-etched flow channels with higher conductivities. These acids tend to etch more erratically and are more effective at containing very small amounts of dispersed insoluble fine particles (Robertson et al., 1989).

h) Reservoir Geology

The choice of acid is also dependent on the geology of the oil reservoir. Matrix acidizing is used on different types of reservoirs including sandstone, carbonates, granites, and basalts and andesites. Each reservoir type has a distinct mineralogy and permeability which determines which acid(s) will be used. See table 2.

Table 2: Acid Selection for Different Minerals (Schieber, 2013)

Nearly all acids dissolve	HF, HCl/HF, HBF4, dissolve
Carbonates:	**Silicates:**
Calcite $CaCO_3$	Quartz SiO_2
Dolomite $CaMg(CO_3)2$	Feldspars (Plahioclase, Orthoclase, …)
	Micas (Biotite, Muscovite)
	Clay minerals (Kaolinite, Smectite, Illite, Chlorite)
	and
	Oxides and Hydroxides:
	Hematite Fe_2O_3
	Goethite FeOOH
	Mahnetite Fe_3O_4
Note: Sulfates (Gypsum [CaSO4 x 2H20], Anhydrite [CaSO4], and Barite [BaSO4]) have low solubility in acids.	

2. Types of Acids Used

The acids used in matrix acidizing can be inorganic, organic, or mixtures of the two.

Table 3: Types of Acids Used in Acidization (Schieber, 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	

3. Additives

Below are classes of common additives:

a) Corrosion Inhibitors

Corrosion inhibitors are used to reduce the reaction of acid with the metallic iron in the pipes. The inhibitor will form and maintain a film on the iron surface. Its effectiveness decreases at very high temperature (Robertson et al., 1989; Williams et al., 1979).

b) Surfactants

Surfactants are "surface-active" chemicals that contain at least two functional groups: one hydrophilic and the other hydrophobic. Surfactants are used in oil well acid treatments to 1) reduce interfacial tension, 2) demulsify acid-oil emulsions, 3) alter formations wettability, 4) prevent sludge formation in the case of concentrated acids (28% HCl or higher), 5) remove heavy hydrocarbon deposits, and/or 6) speed cleanup. Reduced surface tension is supposed to increase the acid's spreading ability on the surfaces of oil or water-wet rocks. It can also facilitate the mixing of live or spent acid with formation waters, which makes removal of fluids easier. Cationic surfactants (organic amines and salts of quarternary amines) and nonionic surfactants (polyoxyethylated alklphenols) are added as a demulsifying agent to stop the formation of acid-spent acid-crude oil emulsions. Ethylene glycol monobutyl ether is frequently used in sandstone acidizing as a mutual solvent to remove heavy hydrocarbons. It helps reduce interfacial tension between oil and water and acts as a solvent to solubilize oil in water (Kalfayan 2008)

c) Mutual Solvents

Solvents are used to improve solubility of additives and to remove hydrocarbons and different additives [Robertson et al., 1989; Kalfayan, 2008].

d) Friction Reducers

Friction reducers are typically high molecular weight polymers (5 to 30 million Dalton) that will uncoil when added in the aqueous solution to decrease pumping pressure losses. The drop in pressure reduces the horsepower required to pump the acid mixture. The most common friction reducers used in oil production are based on anionic polyacrylamide or other copolymers of polyacrylamide combined with different monomers.

e) Acid fluid-loss additives

Fluid-loss additives reduce the rate of fluid loss from an acid mixture. Without these additives water migrates into the permeable formation leaving the other fluid components behind. This happens more when pumping is stopped and the fluid is static, but not yet set. In addition water can be squeezed from the fluid as it passes through constrictions. Fluid loss additives keep the fluid intact and retain the mixture's key characteristics, including viscosity, thickening time, density and compressive strength development (Halliburton, 2014).

f) Diverting (Gelling) Agents

Diverting agents are a viscous gel or suspension of graded solids used to temporarily block off the most permeable sections of reservoir and force the acid into less permeable sections. Diverting agents used for acidizing include solid organic acids, finely divided inert organic resins, deformable solids, acid-sellable polymers, mixtures of waxes and oil-soluble polymers, mixtures of water-soluble polymers (gum guar, gum karaya, cellulose, polyacrlamide, etc.) and inert solids (silica flour, calcium carbonate, rock salt, and oil-soluble resins) (Williams et al., 1979).

g) Iron Control Agents

Complexing agents are used to tie-up ions such as Fe3+ before they can precipitate out. Sources of ion include 1) corrosion products found on the walls of casing and other tubular goods, 2) pipe scale, and 3) iron in a mineralized form found in the formation (Williams et al., 1979).

h) Clay Stablizer

Reservoir rock often contains clays with many different structures. The clays may swell, break off and migrate, or do both in the presence of water or acid-based fluid systems. The clay control additives adhere to the borehole wall, effectively sealing the surface and inhibiting their reaction with the fluid (Weatherford, 2014).

i) Calcium Sulfate Inhibitors

These are used in formations with high sulfate-ion content in the formation water (usually greater than 1,000 ppm) or rock containing anhydrite to prevent the formation of calcium sulfate.

j) Scale Inhibitor

Phosphonates, sulfonates, and polyacrylates are used to prevent formation of calcium scale (Kalfayan, 2008).

k) pH Adjusting Agent

Acids and bases are added to adjust the pH to the desired level.

l) Cleanup additives

Cleanup additives are used to remove spent acid in low-pressure reservoirs. Gaseous nitrogen, alcohols, or surfactants are used.

m) Biocides

Biocides are added to control bacterial growth during and after well stimulation.

E. References

Acid fracturing, 2015. Retrieved May 29, 2014, from http://petrowiki.org/Acid_fracturing

American Association of Petroleum Geologists, 2002. "The Quest for Energy." Annual AAPG Annual Meeting, March 2002. Houston, TX. http://www.apg.org/slide_bankarmentrout_john/index.shtml

Cander, H., 2012. What Are Unconventional Resources? A Simple Definition Using Viscosity and Permeability. Search and Discovery Article #80217.

CCST (California Council on Science and Technology), Lawrence Berekley National Laboratory, Pacific Institute., 2014. Advanced well Stimulation Technologies in California. Sacramento, CA.

Champman, M.E., 1933. Some of the theoretical and practical aspects of the acid treatment of limestone wells. Oil Gas J., Oct 12:10.

Department of Energy. Fossil Energy: How Fossil Fuels Were Formed. http://www.fe.doe.gov/education/energylessons/coal/gen_howformed.html

EIA, 2011. The Geology of Natural Gas Resources. http://www.eia.gov/todayinenergy/detail.cfm?id=110

Harp, L.J. and Bobbs, J.B., 1967. *The Family of Acids Used in Reservoir Stimulation.* The Western Company, Fort Worth, Tex. 16.

Economides, M. and Nolte, K., 2000. Reservoir stimulation. Wiley and Sons LTD, London. http://www.inf-aspirantura.ipter.ru/Biblio/44.pdf

Farouq, SM A. ,2003. Heavy Oil Recovery Journal of Petroleum Science and Engineering Volume 37, Issues 1–2, Pages 5–9

Frasch, H., 1896. Increasing the flow of oil wells. U.S. Patent No. 556,669 (Mar 17)

Halliburton Company., 2014. Fluid loss additives. Available: http://www.halliburton.com/en-US/ps/cementing/materials-chemicals-additives/fluid-loss-additives/default.page?node-id=hfqelaf2 [Accessed 15 September 2014].

Kalfayan, L., 2008. "*Production Enhancement With Acid Stimulation*" 2nd ed. PennWell Corporation

McLeod, H.O., 1986. Matrix Acidizing to Improve Well Performance. *Short Course Manual*. Richardson, Texas: SPE.

Newcombe, R.B., 1933. Acid treatment for increasing oil production. Oil Weekly, May 19: 19.

Putman, S.W., 1933. Development of acid treatment of oil wells involves careful study of problems of each. Oil Gas J., Feb 23: 8.

Prats M., 1982. Thermal recovery. New York, NY

Robertson, J., & Chilingarian, G., 1989. Acidizing Oilwells. *Surface Operations in Petroleum Production*. Elsevier.

Scheiber, J., 2013. *Matrix Acidizing*, EOST Workshop, Kutzenhausen, France, November 13, 2013; EOST: Strasbourg, France.

US DofE (United States Department of Energy), 2009. Modern shale gas development in the United States: a primer. Oklahoma City.

Weatherford, 2014. Clay control additives. Available: http://www.weatherford.com/Products/EngineeredChemistry/FracturingChemicals/ClayControlAdditives/ [Accessed 15 September 2014].

Williams, B.B., Gidley J.L., and Schechter, R.S., 1979. Acidizing Fundamentals. Monograph Series, Society of Petroleum Engineers, Vol 8. New York.

Zou, C., 2013. *Unconventional petroleum geology*. Burlington, Mass.: Elsevier.

Zou C et al., 2013. Types characteristics, genesis and prospects of conventional and unconventional hydrocarbon accumulations: taking tight oil and tight gas in China as an instance. Acta Petrolei Sinica 33(2): 173-187.

III. Toxicity of Acidization Fluids used in California Oil Exploration

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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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

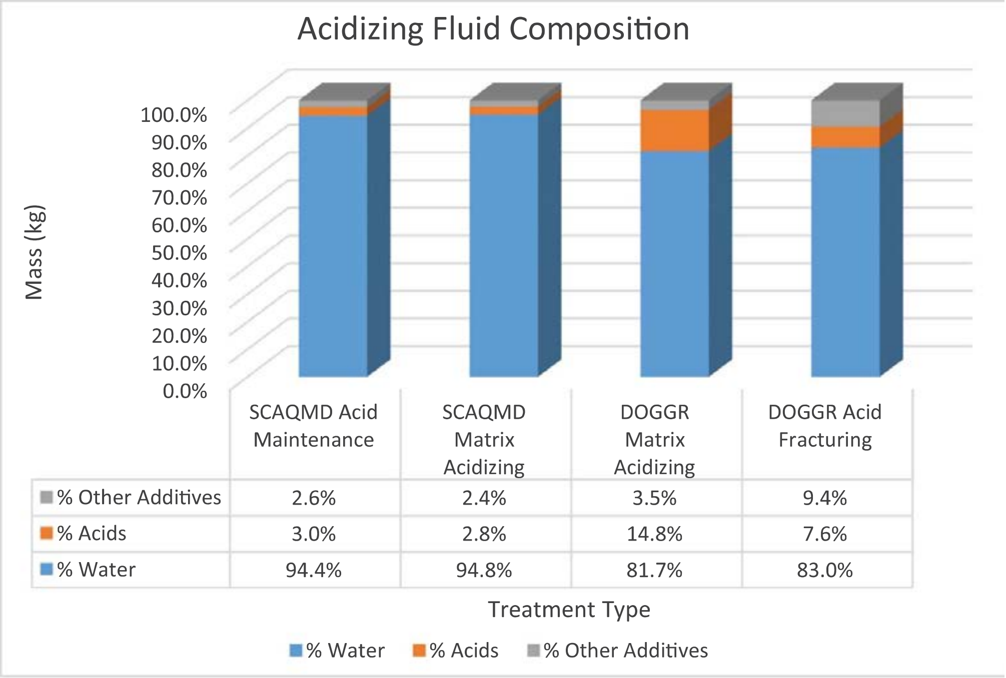
3.2. Acidizing chemicals

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.

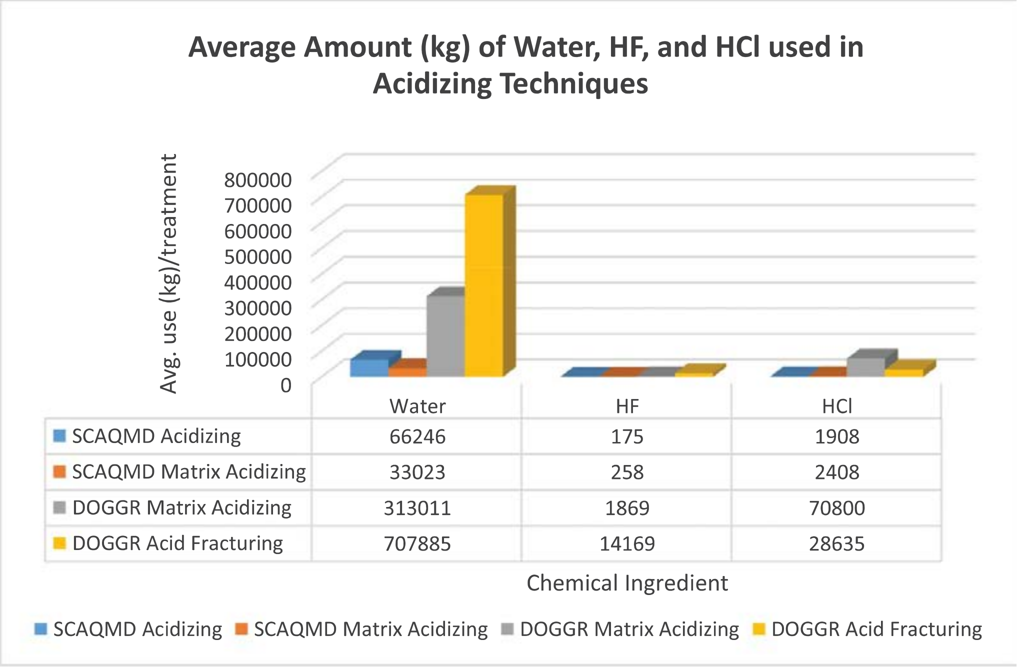


	SCAQMD Acid Maintenance	SCAQMD Matrix Acidizing	DOGGR Matrix Acidizing	DOGGR Acid Fracturing
■ % Other Additives	2.6%	2.4%	3.5%	9.4%
■ % Acids	3.0%	2.8%	14.8%	7.6%
■ % Water	94.4%	94.8%	81.7%	83.0%

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



	Water	HF	HCl
SCAQMD Acidizing	66246	175	1908
SCAQMD Matrix Acidizing	33023	258	2408
DOGGR Matrix Acidizing	313011	1869	70800
DOGGR Acid Fracturing	707885	14169	28635

chniques.

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

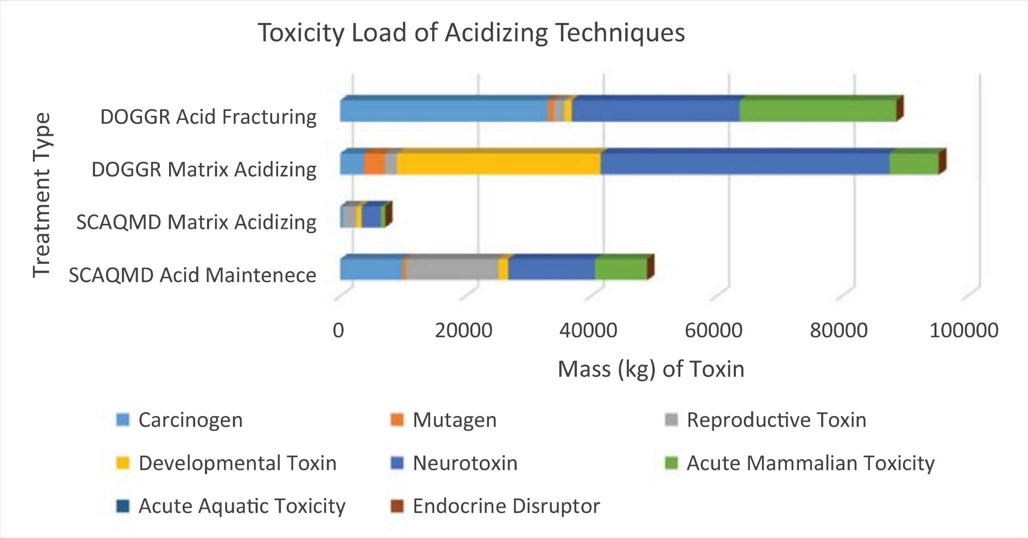


Table 6. Range of pH of matrix acidizing flowback water.

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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References

Bishop, J. 2014. *RE: Underground Injection Control Drinking Water Source Evaluation*. Oakland, CA: State Water Resources Control Boards, California Water Boards. Accessed 16 October 2014. https://www3.epa.gov/region9/mediacenter/uic-review/pdf/ca-class-ii-uic-letter-2014-12-22.pdf.

CCST (California Council on Science and Technology). 2014. *Advanced Well Stimulation Technologies in California*. Sacramento, CA: California Council on Science and Technology, Lawrence Berkeley National Laboratory, Pacific Institute.

CCST (California Council on Science and Technology). 2015. *An Independent Scientific Assessment of Well Stimulation in California*. Vol. 2. Sacramento, CA: California Council on Science and Technology, Lawrence Berkeley National Laboratory, Pacific Institute.

Dissanayake, C.B. 1991. “The Fluoride Problem in the Ground Water of Sri Lanka – Environmental Management and Health.” *International Journal of Environmental Studies* 38 (2–3): 137–155.

DOGGR (Division of Oil, Gas and Geothermal Resources). 2014. *Senate Bill 4 Interim Well Stimulation Treatment Regulations*. Sacramento, CA: California Department of Conservation, Division of Oil Gas and Geothermal Resources. Accessed 9 October 2014. http://www.conservation.ca.gov/index/Documents/FInal%20Text%20of%20Readopted%20SB%204%20Interim%20WST%20Regulations%20with%20Revised%20IWSTN%20Form.pdf

DOGGR (Division of Oil, Gas and Geothermal Resources). 2015. *Interim Well Stimulation Treatment Notices Index*. Sacramento, CA: California Department of Conservation. Division of Oil, Gas, and Geothermal Resources. Accessed 8 August 2015. http://www.conservation.ca.gov/dog/Pages/IWST_disclaimer.aspx

Flewelling, S., and M. Sharma. 2014. "Constraints on Upward Migration of Hydraulic Fracturing Fluid and Brine." *Ground Water* 52 (1): 9–19.

Gassiat, C., T. Gleeson, R. Lefebvre, and J. McKenzie. 2013. "Hydraulic Fracturing in Faulted Sedimentary Basins: Numerical Simulation of Potential Contamination of Shallow Aquifers Over Long Time Scales." *Water Resources Research* 49 (12): 8310–8327.

Gdanski, R.D., and M.A. Peavy. 1986. "Well Return Analysis Causes Re-Evaluation of HCI Theories." In *Seventh SPE Symposium on Formation Damage Presentation*. Lafayette, LA: Society of Petroleum Engineers. doi:10.2118/14825-MS. (SPE 14825).

Kahrilas, G., J. Blotevogel, P. Stewart, and T. Borch. 2015. "Biocides in Hydraulic Fracturing Fluids: A Critical Review of Their Usage, Mobility, Degradation, and Toxicity." *Environmental Science and Technology* 49 (1): 16–32.

Kekacs, D., B. Drollette, M. Brooker, D. Plata, and P. Mouser. 2015. "Aerobic Biodegradation of Organic Compounds in Hydraulic Fracturing Fluids." *Biodegradation* 24 (4): 271–287. doi:10.1007/s10532-015-9733-6.

Kissinger, A., R. Helmig, A. Ebigbo, H. Class, T. Lange, M. Sauter, M Hietfeld, J. Klunker, and W. Jahnke. 2013. "Hydraulic Fracturing in Unconventional Gas Reservoirs: Risks in the Geological System, Part 2." *Environmental Earth Science* 70 (8): 3855–3873. doi:10.1007/s12665-013-2578-6.

Markey, F., T. Betz, J. Gauteplass, K. Taylor, D. Ackwith, and R. Barati. 2014. "Examining Innovative Techniques for Matrix Acidizing in Tight Carbonate Formations to Minimize Damage to Equipment and Environment." In *Unconventional Resources Technology Conference*. Denver, CO: Society of Petroleum Engineers. doi:10.15530/urtec-2014-1935101

McLeod, H.O. 1986. "Matrix Acidizing to Improve Well Performance." In *Short Course Manual*. Richardson, TX: Society of Petroleum Engineers.

National Center for Biotechnology Information. 2015. PubChem Compound Database (accessed Aug. 18, 2015). (CID = 14917). https://pubchem.ncbi.nlm.nih.gov/compound/14917

Putman, S.W. 1933. "Development of Acid Treatment of Oil Wells Involves Careful Study of Problems of Each." *Oil & Gas Journal* 31: 6–13.

Robertson Jr, J., G. Chilingarian, and S. Kumar. 1989. *Surface Operations in Petroleum Production, II*. Vol. 171. New York: Elsevier Science Publishing Company.

SCAQMD (South Coast Air Quality Monitoring District). 2015. *1148.2 Notifications and Reporting Requirements for Oil and Gas Wells and Chemical Suppliers*. Diamond Bar, CA: South Coast Air Quality Monitoring District. Accessed 8 August 2015. http://xappprod.aqmd.gov/r1148pubaccessportal/Home/Index

Scheiber, J. 2013. "Matrix acidizing." *EOST Workshop*. Kutzenhausen: EOST.

Schuchart, C.E. 1995. "HF Acidizing Returns Analyses Provide Understanding of HF Reactions." Society of Petroleum Engineers, SPE European Formation Damage Conference, The Hague, March 16–17.

Stringfellow, W., J. Doman, M.K. Camarillo, W. Sandelin, and S. Borglin. 2014. "Physical, Chemical, and Biological Characteristics of Compounds Used in Hydraulic Fracturing." *Journal of Hazardous Materials* 275: 37–54. doi:10.1016/j.jhazmat.2014.04.040.

Taylor, K.C., H.A. Nasr-El-Din, and R.B. Dajani. 1999. "Analysis of Acid Returns Improves Efficiency of Acid Stimulation: A Case History." *Journal of Petroleum Science and Engineering* 28 (1–2): 33–53.

US DOE (United States Department of Energy). 2009. *Modern Shale Gas Development in the United States: A Primer*. Oklahoma City: United States Department of Energy.

US EPA (United States of Environmental Protection Agency). 1999. *Integrated Risk Information System (IRIS) on Hydrogen Chloride*. Washington, DC: National Center for Environmental Assessment, Office of Research and Development, United States Environmental Protection Agency.

US EPA (United States Environmental Protection Agency). 2015. *Analysis of Hydraulic Fracturing Fluid Data from the FracFocus Chemical Disclosure Registry 1.0*. (EPA/601/R-14/003). Washington DC: Office of Research and Development, United States Environmental Protection Agency.

Vikram, A., J. Bomberger, and K. Bibby. 2015. "Efflux as a Glutaraldehyde Resistance Mechanism in Pseudomonas Fluorescens and Pseudomonas Aeruginosa Biofilms." *Antimicrobial Agents and Chemotherapy* 59 (6): 3433−3440. doi:10.1128/AAC.05152-14.

Washington State Department of Ecology. 2015. Chemical Hazard Assessment. *Green Chemistry*. Accessed 15 January 2015. http://www.ecy.wa.gov/GreenChemistry/chazassess.html

Williams, B.B., J.L. Gidley, and R.S. Schechter. 1979. *Acidizing Fundamentals*.Vol. 8. (Monograph Series). New York: Society of Petroleum Engineers.

Supplemental Section

Table S1: Acid Selection for Different Minerals (Scheiber 2013)

Nearly all acids dissolve

t permeable sections of reservoir and force the acid into less permeable sections (Williams, Gidley and Schechter 1979).

Figure S2: Potential Release Mechanisms and Transport Pathways in California that Could Originate in the Subsurface (CCST 2015).

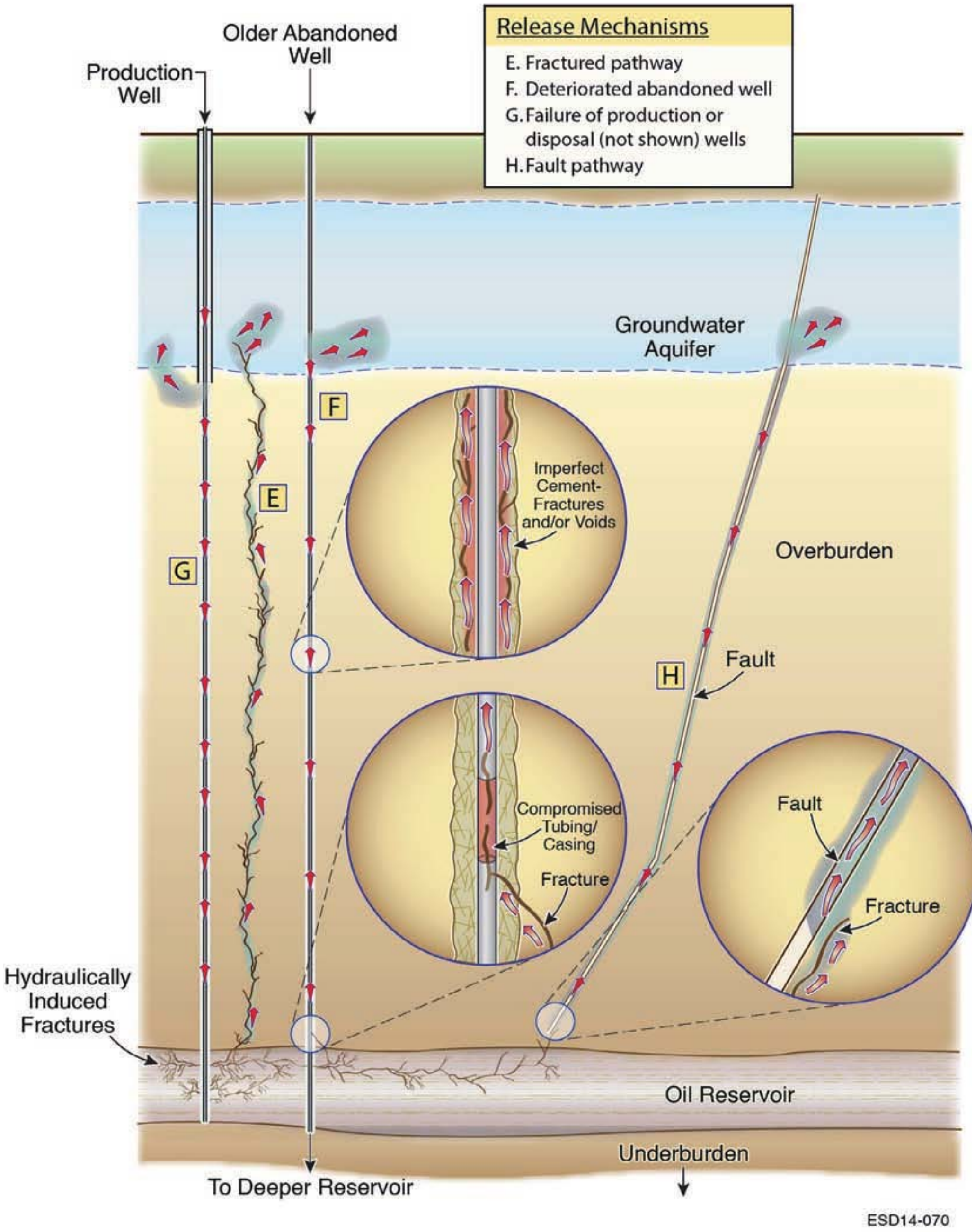

Table S3: QCAT Process for Assigning an Initial Grade

eria are met, the process continues until a grade is determined.

The following tables list chemicals and their amounts that are reported to be in use for the various acidizing techniques in California. Some of the chemicals listed under <1 kg/treatment are impurities that are not added alone but are often found with other chemicals. Impurities are common in industrial-grade chemicals, which are rarely 100% pure. Impurities are frequently residual feedstock materials from the manufacturing process or solvents and other materials added to control product consistency or handling properties.

The tables list the chemical name, purpose (as identified by the operatory), CAS #, Maximum and Average mass used per treatment, frequency (number of times used), and for the SCAQMD lists whether it is an air toxic or not. The chemicals are ordered from most frequently used to least frequently used. The chemicals in red are the QCAT F-graded chemicals. CAS#'s that have an asterisk represent the most

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b$") - *D32 , *(D3/+#) %&" 3	>" 3A, &*@c " &L` 2 - 3$%8%#'	8G: L88LF'	8855G'	F55S'	8R'	c '
N%$" 4#' 4D3&+4(*(+3 &, '	c " &L` 2 - 3$%8%#'	d: RJ GLRFL9'	F55G'	859G'	8J '	c '
i %8(*'T #' 2 +*%'c +4(*(+'	c " &L` 2 - 3$%8%#'	RJ <J FL9SLR'	85F<'	G59G'	8J '	c '
` *(+&" 3	I , 3) " #, '! 3 +&, #@3+D' ! " &*#' 3@b#' &'! " &*#' 3	RJ L8<LS'	F95dG'	<5<G'	8d'	c '
FL` *(D3P , C+&" 3	N, 2 - 3$%8%#'	8GJ L<RL<'	S<58G'	8955G'	8F'	c '
6" 3 , &, '	>" 3A, &*@T $4(+3*, &, ' N%$4, #$+&*'	8G: L: : Ld'	RRG888'	8R: 5J G'	88'	e'
V, &W&, @8GL8RLT 3D3 N, #%A$5	>" 3A, &*@T $4(+3*, &, ' N%$4, #$+&*@c " &L ` 2 - 3$%8%#'	R: RJ : L: <Ld'	G5F G'	G5GR'	88'	c '
` *(D3 &, 'Q3D/" 3	! 3 +&, #'	8G<LF8L8'	J 5RG'	858G'	8G'	e'
` *(D3 &, 'h C%, '	c +'	<SLF8L: '	G55G'	G5GS'	8G'	e'

M(" $4(" #%/'T / % @+3/% 2 '>+3*" HFadK'	**c +'**	**<<S: L: <LJ '**	**F959J '**	**d5<G'**	**9'**	**c '**
T 3/" (" 3$@ 8J L8S @ ` \*( " CD3+\*, . 'H<` h l '	c T '	R: 9S 8LR<L<'	F 95dG'	J 59G'	9'	c '
h CD+3BD3+*, . 'T 3BD34(, &" 3%/' j , $%&'	**>" 3A, &*@c " &L` 2 - 3$%@%#'**	**RdJ F: L9FLF'**	**8d5 G'**	**d5<G'**	**: '**	**c '**
! D/3' (, C+&+2 %&, @>- 3D+*, ' H8a8K'	c " &L` 2 - 3$%@%#'	89: dJ LGFL<'	G59G'	G5FG'	: '	c '
` *%#" &&%/'T / %'	**T / % %%&?'**	**F: G9LF8LJ '**	**8@#SG5BG'**	**J <<59G'**	**<'**	**c '**
M(" $4(" &%/'T / %'	T / % %%&?'	8dS9: LdRLF'	J GS 5GS'	8J d5 G'	<'	c '
M(" $4(" #%/'T / % @+3/% 2 '>+3*" HFadK'	**>/+3 'j , 2 " A, #'**	**<RRJ Ld: LF'**	**G5 : '**	**G5 9'**	**<'**	**c '**
O' #2 %/'T / %'	! " ##" $% &'b&(% %" #@ >/+3 'j , 2 " A+3	RJ L8: LR'	R: S 5 G'	89S 55G'	S'	c '
b$" 4#" 4+&" 3	**! " ##" $% &'b&(% %" #@ c " &L` 2 - 3$%@%#'**	**R<LRdLG'**	**89S 59S'**	**J <5 G'**	**S'**	**e'**
T 3/" (" 3$@ 8GL8J @ ` *(" CD3+*, . '	T &*%>3 . ?%&?'T ?, &*$'	RRJ SSL8SLG'	RJ 5FG'	J S 5 G'	S'	c '
\ " #4(" 3%&, '	**T &*%>3 . ?%&?'T ?, &*$'**	**88GL98L: '**	**S 5dS'**	**d5 G'**	**S'**	**c '**
T 2 %&, $@P D. #" ?, &+*, . ' 6+3B' 1 'T 3BD3@T /, *+*, $'	c +'	R8<9GLS 9L: '	d5FG'	G5RG'	S'	c '
! #D$*+3B%&, '>%B%+'	**>+&. '! " &*#" 3**	**8J : G: LRGL<'**	**R@R95 R'**	**S @G95<G'**	**d'**	**c '**
T 3- 2 %&+'h C%, '	>+&. '! " &*#" 3	8dJ J LF: L8'	8@9F 5<G'	9S R5RG'	d'	c '
b#" &'h C%, 'HQ F" dK'	**>+&. '! " &*#" 3**	**8dG9Ld<L8'**	**8dR5G: '**	**8GG5<G'**	**d'**	**c '**
M' *+$$% 2 'h C%, 'HEF" K'	>+&. '! " &*#" 3	8F 8dRLJ SL<'	8dR5G: '	8GG5<G'	d'	c '
! +3/% 2 'h C%, 'H +" K'	**>+&. '! " &*#" 3**	**8dGSL<: L: '**	**<J 5 G'**	**SS5 G'**	**d'**	**c '**
>" . %2 '>- 3D+*, '	O#%/*%&'j , . - /, #'	<<S<L: FLR'	F R5d8'	8G5 G'	d'	c '
M) *#" 3 - 2 'c +4(*(+'	**>- #O+/*+&***	**R: 99GLdSLF'**	**Fd59S'**	**Fd5FG'**	**d'**	**c '**
\ , $%D3 &, '	N` \ _ i >bOb j '	8G: LR<L: '	d5G<'	F 5 G'	d'	c '
FL\ , #/+4" , *(+&" 3	**! " ##" $% &'b&(% %" #'**	**RGLFJ LF'**	**F55G'**	**F5BG'**	**d'**	**c '**
8@@L6#%2 , *(D3) , &W &, '	N, 2 - 3$%@%#'	S F RL<dL: '	85 G'	85BG'	d'	c '
>- 3D #%/'T / %'	**T $4(+3*, &, 'N%$4, #$+&***	**<RRJ L9dL9'**	**G5B: '**	**G5B<'**	**d'**	**c '**
O' #2 +3 , (D. , @M' 3D2 , #I %(' J LH8 @8LN%2 , *(D3 *(D3KM(, &" 3@ FL\ , *(D3' C%#+&, 'T &. ' h C%#+&, '	N, 2 - 3$%@%#'	dG<GJ LRJ LJ '	G5GS'	G5GJ '	d'	c '
! D/3' 4, &*+$%" C+&, @ F @@@@@@@@G@GL N, /+2 , *(D3L'	**O#%/*%&'j , . - /, #'**	**SJ 8LGFLR'**	**G5GF'**	**G5GF'**	**d'**	**c '**
>- 3D #%/'T / %'T 2 2 " &% 2 '>+3*" H8aFK'	O#%/*%&'j , . - /, #'	<<: dLFGLF'	<5FG'	<5FG'	F'	e'
N% *(D3 &, 'Q3D/" 3	**! " ##" $% &'b&(% %" #'**	**888LJ RLR'**	**G55G'**	**G5 G'**	**F'**	**e'**
>%B%+@T 2 " #4(" - $'L'O- 2 , . '	O#%/*%&'j , . - /, #'	<Rd8L: RL9'	G5FG'	G5FG'	F'	c '
>%" C+&, $'T &. '>%B%" &, $@N% \ , @ , +/*%&'M#" . - /*$'I %(' >%B%+'	**O#%/*%&'j , . - /, #'**	**R<<RFL9GL<'**	**G5FG'**	**G5FG'**	**F'**	**c '**
>%B%" &, 'h %3	O#%/*%&'j , . - /, #'	Rd8J L: RLF 9'	G5FG'	G5FG'	F'	c '

! D/3' *, *#+$%' C+&, @ F@@@@@@@@Lh /*+2 , *(D3L'	O#%*% &'j , . - /, #	SSRLR<LF'	G5GF'	G5GF'	F'	c '
6, *#+$" . %2 ' ` *(D3 &, . %2 %&, *, *#++/, *+*, '	O#%*% &'j , . - /, #	RJ LGFL: '	G5GF'	G5GF'	F'	c '
! D/3' (, C+$%' C+&, @ F@@@@@@@@@G@G@F @FL N" . , /+2 , *(D3L'	O#%*% &'j , . - /, #	SJ GL9<LR'	G5GF'	G5GF'	F'	c '
>" . %2 'P D. #" C%, '	O#%*% &'j , . - /, #	8d8GL<dLF'	G5GF'	G5GF'	F'	e'
! +3/%2 '! (3' #%, 'H +/3FK'	>+3*'	8GGJ dLSFLJ '	8@985<G'	8@985<G'	8'	c '
P D. " /(3' #%'T /%'	I , 3>*%2 - 3+*%&'	R<J <LG8LG'	<: <59G'	<: <59G'	8'	c '
T2 %, $@6+3' 1 @ L7dL HN%2 , *(D3+2 %&" KM#" 4 D3+@ L h C%, $'	N%A, #*%&?'T ?, &*$'	R: RJ <L<<L: '	F9F5FG'	F9F5FG'	8'	c '
M#" 4 D3 &, 'Q3D/" 3	N%A, #*%&?'T ?, &*$'	S<LSSLR'	8<95 G'	8<95 G'	8'	c '
h /*+&, '>- 3D' &%'T /%'	h *(, #'L&?#, . % &*'	SdFJ L: J LS'	8S<5J G'	8S<5J G'	8'	c '
6(% ? 3D/" 3%'T /%'	! " ##" $% &'L&(% %' #	R: L88L8'	9: 5GG'	9: 5GG'	8'	c '
N" . , /D3) , &W/&, '>- 3D' &%' T /%'	>- #O+/*+&*'	F<8<RL: <LG'	9J 5J G'	9J 5J G'	8'	c '
M#" 4 D3 &, 'Q3D/" 3 \ " &" 2 , *(D3` *(, # HMP2 , K'	>- #O+/*+&*'	8G<L9: LF'	9J 5J G'	9J 5J G'	8'	e'
FLh C%+&, 2 , *(+&+2 %&%2 @ c @ @L6#%2 , *(D3L@ (3' #%, ' H8aBK@P " 2 " 4 " 3D2 , #'	! 3+D'>*+) %&/#'	S8: d: Ld8LJ '	RG5BG'	RG5BG'	8'	c '
` *(+&+2 %&%2 @c @ @L 6#%2 , *(D3LFL7HFL\ , *(D3L8L h C" LF LM#" 4, &L8Le3h CD=L@ \ , *(D3>- 3D+*, 'H8aBK@M' 3D2 , #' I %('FLM#" 4, &+2 %, '	Q, 3%&?'T ?, &*'	FRGGRLFFLJ '	J 95 G'	J 95 G'	8'	c '
T#" 2 +*%'T2 %&, @6" O+'>+3*'	! " ##" $% &'L&(% %' #		FJ 5dG'	FJ 5dG'	8'	c '
! +3/%2 'V#" 2 %, '	>+3*'	<<: 9LJ 8LS'	8<59G'	8<59G'	8'	c '
! +#) " &%'T /%'>" . %2 '>+3*' H8aFK'	c +'	J 9<L89L: '	8d5RG'	8d5RG'	8'	c '
Q3D/" 3%'T /%'	>/+3 'j , 2 " A, #'	<9L8J L8'	95 G'	95 G'	8'	c '
>- 3D' &%'T /% $@ 8J L8RL T 3B+&, 'P D. #" CD'T &. '! 8J L8RL T 3B, &, @>" . %2 '>+3*$'	c +'	R: J d9LS<LR'	S5J G'	S5J G'	8'	c '
N" . , /D3) , &W/&, 'Hb2 4- #%DK'	c T '	8FdLG8Ld'	S5J G'	S5J G'	8'	c '
T/, *" &, '	c +'	R<LRJ L8'	d5RG'	d5RG'	8'	c '
Q3D/, #%&, '	>- #O+/*+&*'	SRL: 8LS'	G5FG'	G5FG'	8'	c '
T/, *" 4(, &" &, '	! " ##" $% &'L&(% %' #@ ! 3 +&, #'	9: L: RLF'	G5G8'	G5G8'	8'	e'

f '! (, 2 %+3$'2 " $*O#, X- , &*3D- $, . '%&'+/%%W*% &'+&. '&" *O#, X- , &*3D- $, . '%&'(D. #+- 3%'O#+/*- #%&?'

'

! "#$%&[ )&7%F ,+"$5&D1&4 ".2,G&+,- ,A'.,/0&"5&%=/2% &/&C* R4 3;&,5.% &<& %+2%'5,0B&2%U@%0+<&1 V5%&

C7%F ,+"$& DB2% ,%0.&	?@=/5%&	C*'&&	4 "GF @ & 6YB;Z.2%'.F %0.&	*>%2"B%& 6YB;Z.2%'.F %0.;&	J2%U@%0+<& 1&/5%&	*,2&/G+&&
I +*, #	! +##%#	<<dFL8: LSf '	<R@FG59G'	dd@Fd5J G'	R'	c '
P D. #"/(3'#%'T/%'	I , 3>*%a - 3+*%&'	<RJ <LG8LG'	S@985 G'	F@G: 5J G'	R'	e'
T2 2 "&%2 '! (3'#%, ' Hc (J K! 3K'	N%$43+/, 2 , &*O3 %'	8F8FSLGFL9f '	8@S95Fd'	R8J 5J G'	R'	c '
\ , *(+&"3	! "##"$%&'b&(%%"#	R<LSRL8'	<9G5G'	F9d5GG'	R'	e'
P D. #"O3 "#%'T/%'	I , 3! 3 +&"- *'	<RRJ Ld9Ldf '	R: 95d'	FS<5RG'	R'	e'
`*( D3 &, 'Q3D/"3 \ "&") - *D3` *(, #	>"3A, &*	888L<RLFf '	FJ F5GJ '	: 85FG'	R'	e'
! %#%'T/%'	b#"&! "&*#"3	<<L9FL9'	FG85BG'	: d5dG'	R'	c '
P, +AD'T#"2 +*%'c +4(*(+'	>"3A, &*N%$4, #$+&*@ `2 - 3$%%#	RJ <J FL9J LS'	8J F5R8'	d95RG'	R'	c '
M#"4+#?D3T3/"("3	! "##"$%&'b&(%%"#	8G<L89L<'	8F5BJ '	S5<G'	R'	c '
`*(D3h /*D&"3	! "##"$%&'b&(%%"#	S: <<LJ FL9'	8F5BG'	S5d: '	R'	c '
b$"X- %&"3&, '	! "##"$%&'b&(%%"#	889LRSLd'	8F5BG'	S5J G'	R'	c '
NLi %a "&, &, '	>"3A, &*@N%$"3A, $ M+##+O&'T& 'T$4(+3*, &, '	8d: L: RLd'	8S<59J '	: 95 G'	S'	c '
] - %&+3 %&, '	! "##"$%&'b&(%%"#	98LRdLJ '	8F5BG'	S5J G'	S'	c '
M&, 'h %a	! "##"$%&'b&(%%"#	: GGFGL9GLd'	8F5BG'	S5J G'	S'	c '
g D3 &, '	>"3A, &*	8ddGLFGL<'	8@8d5R8'	8@8d5R8'	F'	c '
`*(D3) , &W&, '	>"3A, &*	8GGLJ 8LJ '	J : J 5G. '	J : J 5G. '	F'	c '
6"3 , &, '	>"3A, &*	8G: L: : Ld'	8R5BJ '	8R5BJ '	F'	c '

f '! (, 2 %+3$'2 "$*O#, X- , &*3D'- $, . '%&'+/%%#*%&'+& '&" *O#, X- , &*3D'- $, . '%&'(D. #+- 3%'O#+/*- #%&?'

! "#$%&\)&7%F ,+"$5&(1&4 ".2,G&+,- ,A'.,/0&"5&%=/2% &/& OI I N;&,5.% &<& %+2%'5,0B&2%U@%0+<&1& V5%&

?@=/5%&	C7%F ,+"$&W"F %&	C*'&&&	4 "GF @ & 6YB;Z.2%'.F %0.&	*>%2"B%& 6YB;Z.2%'.F %0.;&	J2%U@%0+<& 1&/5%&
>"3A, &*@ ! 3 +&, #	`*( D3 &, 'Q3D/"3\ "&") - *D3` *(, #	888L<RLFf '	8J @: S5GG'	<@: S59G'	FG9'
V+$, 'O3 %'	I +*, #	<<dFL8: LSf '	F@S<@R: 5J G'	d8d@8G59G'	89: '
'	`*(D3 &, 'Q3D/"3	8G<LF8L8'	SR5dS'	8G5J G'	89G'

! 3 +&, #'	b$" 4#" 4+&" 3	R<LRdLG'	F@8d5d8'	S<J 5G'	8: S'
'	c "&D3M(, &" 3` *(" CD3+*, '	9G8RLJ SL9f '	8J <5dF'	J 85dG'	8<R'
! " ##" $%&' b&(%%" #'	\ , *(+&" 3	R<LSRL8'	dF@RF5I F'	RGd5<F'	8<J '
>" 3A, &*'	P D. #" /(3' #%'T /%'	<RJ <LG8LG'	FSG@F: 5 J '	<G@GG5GG'	8RF'
T&*% >3 . ?%&?' T?, &*'	N" . , /D3) , &W&, '>- 3D' &%'T /%'	F<8<RL: <LG'	<@SR5 F'	F@SR5GG'	8S9'
b&*, &$%@%#'	O' #2 %'T /%'	RJ L8: LR'	8R@GR5I <'	d@R: 5GG'	8J S'
b#" &' j , . - /%&?' T?, &*'	! %#%'T /%'	<<L9FL9'	8d@Sd5G8'	F@Fd5G'	8J J '
'	` *(" CD3+*, . 'P , C+&" 3	R: J d9LJ SLF'	F@SS5FS'	<9d5RG'	8J d'
'	! %&&+2 +3 , (D. , '	8GJ LSSLF'	S@GR59d'	8@S: 5GG'	8J F'
'	N% *(D3 &, 'Q3D/" 3	888LJ RLR'	S@8d59R'	8@985 G'	8d9'
'	M' 3D-h CDL8@L` *(+&, . %D3K@T 3-(+LP , CD3L h 2 , ?+L'	d8<FRLdJ L: '	S@<J 5Fd'	8@995G'	8d8'
'	FL` *(D3P , C+&" 3	8GJ L<RL<'	8@J d5R'	d9R5dG'	8d8'
'	T3/" (" 3$@ 8FL8R@ *(" CD3+*, . '	R: SS8L8FLF'	d@dd5Gd'	9: S5 G'	88S'
'	` *(D3 &, 'h C%, '	<SLF8L: '	G5GG'	G5GG'	9S'
'	T2 %&, 'h C%, $@ " /" +3D3 %2 , *(D3	R8<: : L9GL<'	8@8F5GR'	S8d5RG'	: 9'
'	>" . %2 'b' . %, '	<R: 8L: FLS'	<G<5BG'	RG5 G'	: 9'
'	V, &W3 , (D. , '	8GGLSFL<'	F: <55S'	8Gd5BG'	: 9'
'	! "44, #N%(3' #%, '	<J J <Ld9LJ '	85 <'	G5<8'	: 9'
>" 3A, &*'	T/, *%'T /%'	RJ L89L<'	8R@GR5I <'	J @FG5FG'	<9'
'	>%%+@T 2 " #4(" - $'L'O- 2 , . '	<Rd8L: RL9'	: 5GJ '	85 G'	<: '
'	T2 2 " &%2 'V%B " #%, '	8dJ 8LJ 9L<'	<F@J d59J '	8<@9J 5G'	<<'
'	P D. #" CD3+2 %&, 'P D. #" /(3' #%, '	SJ <GL88L8'	RS8599'	FF85 G'	RF'
'	P D. #" CB " #%'T /%'	<RRJ Ld9Ldf '	<@RG5RR'	8@R: 5RG'	J 8'
'	T2 2 " &%2 '! (3' #%, '	8F8FSLGFL9f '	RJ @FJ 5 S'	89@<: 5 G'	d<'
'	M' 3D, *(D3 &, 'h C%, '	FSdFFLR: Ld'	dFG5RF'	FS59G'	Fd'
'	M' *+$$%2 'T /, *+*, '	8F<LG: LF'	S5Rd'	G5<G'	F8'
'	6(%- #, +@M' 3D2 , #' I %('O' #2 +3 , (D. , ' +&. '8LM(, &D3 *(+&" &, '	R: S'F<LJ 9L8'	R@: d5BR'	: J S5GG'	FG'
'	O+ **D'T /% $@5+3Lh %3	R8<9GL8FLd'	R@: d5BR'	: J S5GG'	FG'
'	T3/" (" 3$@ 8J L8S@ *(" CD3+*, . 'H<` h I'	R: 9S8LR<L<'	d@GR5FJ '	F995RG'	FG'
'	M#" 4+#?D3T 3/" (" 3	8G<L89L<'	d@GR5FJ '	F9J 5dG'	FG'
'	T3/" (" 3@ 88'i %&, +#@ *(" CD3+*, . '	dJ d9: LG8L8'	RJ : 5dF'	8885 9G'	FG'
'	P , +AD'T #' 2 +*%'c +4(*(+'	RJ <J FL9J LS'	RJ 5 d'	8S5BG'	FG'
'	M#" 4D3 &, 'Q3D/" 3	S<LSSLR'	<5 R'	85RG'	FG'
'	c +4(*+3 &, 'nb2 4- #%DI'	98LFGLd'	85<8'	S5 d'	FG'
'	T3B, &, $@ n8G'TL'	RJ <J dLGFL: '	RJ : 5dF'	J S5G'	89'
'	>" . %2 'Q3D/" 3+*, 'Hb2 4- #%DK	F: dRLdFLG'	RJ : 5dF'	: : 5BG'	89'
'	6#%$" . %2 '` *(D3 &, . %2 %&, *, *#++/, *+*, '	8SGLd: L9'	SRd5G'	S<5I G'	89'

	I$%2 4- #%&D!'				
'	>". %2 'P D. #' C%, '	8d8GL<dLF'	S Rd5G'	S<5 G'	89'
'	T3/" (" 3@ 88L8J @ *(" %D3-*, . '	<: ddGLF8L9'	dFG5RF'	dG5<G'	89'
'	T3/" (" 3@ 9L88L$" @ 8G@ *(" CD3-*, . '	<: ddGLFGL: '	dFG5RF'	dG5<G'	89'
'	T3/" (" 3@ <L9L$" @ : @ *(" CD3-*, . '	<: ddGL'89LS'	dFG5RF'	dG5<G'	89'
'	] - +*, #&+#D'T 2 2 " &%2 '! " 2 4" - & $' ! (3' #%, $'N, #%+*%, $'	R: 9: 9LGGLJ '	dFG5RF'	dG5<G'	89'
'	6#%$" . %2 'c %#%'*#%/, *+*, 'H2 4- #%DK'	SGRJ Ld8Ld'	dFG5RF'	dG5<G'	89'
'	` *(" CD3-*, . 'M#" 4" CD3-*, . 'J L c " &D3-4(, &" 3O' #2 +3 , (D. , 'j , $%&'	dG: J RLdS LR'	dFG5RF'	dG5<G'	89'
'	N%$" . %2 '` *(D3 &, 'N3-2 %&, '6, *#+' T/, *+*, 'n2 4- #%D!'	8d9LddLd'	dFG5RF'	S<5 G'	89'
'	>- 3D #%'T /%'	<RRJ L9dL9'	J 5GF'	85FS'	89'
'	>". %2 '` D*(" #) +*, '	Rd: 8L<<L<'	d@GR5FJ '	F9F5 G'	8: '
'	T3/" (" 3@ 9L! 88@ *(" CD3-*, . '	R: J d9LJ RLd'	RJ : 5dF'	R85<G'	8: '
'	\ , *(D3h C%+&, 'M 3D2 , #I %('h C%+&, '	FS9J LRFL: '	J G<59'	FR5 G'	8: '
'	M *+$$%2 'h 3 +*, '	8J dL8: LG'	S 5Rd'	G5<'	8: '
'	i %&, +#ZV#+&/(, . 'T3/" (" 3` *(" CD3-*, ' H88, " K'	8F<GdRLFJ LF'	: @J G5 R'	: <5 G'	8R'
'	6, *#+$" . %2 ' ` *(D3 &, . %2 %&, *, *#++/, *+*, '	RJ LGFL: '	8<G59S'	: : 5G'	8R'
'	! " /" LT 2 %" LM" 4D3-2 3&, 'h C%, '	R: 8SSLG9L9'	8<5BG'	: 5 S'	8R'
'	T3/" (" 3$@ 8GL8J @ *(" CD3-*, . '	RRJ SSL8SLG'	8<5BG'	: 5 S'	8R'
'	Q3D/, #" 3	SRL: 8LS'	8<5BG'	8J 85G'	8R'
'	N%*" 2 +/, " - $'` +#*(@ +3/%&, . '	98GSdLd9Ld'	8G5FR'	: 5 S'	8R'
'	N%" /" 'N% , *(D3] - +*, #&+#D' T 2 2 " &%2 '! (3' #%, '	R8<: 9L<<Ld'	85<8'	G5 : '	8R'
'	N%/*D3>- 3D' $- //%&+*, '>". %2 '>+3*'	S<<L88L<'	85<8'	G5 : '	8R'
'	\ +?&, $%2 '! (3' #%, '	<<: RLdGLd'	85Gd'	G5 : '	8R'
'	! #D$*+3%&, '>%%+d] - +#*VH>%F K'	8J : G: LRGL<'	G59J '	G5BJ '	8R'
'	N". , /D3) , &W/&, 'H2 4- #%DK'	8FdLG8Ld'	G5B<'	G5 : '	8R'
'	h 3 %'T /%'	88FL: GL8'	G5B<'	G5G9'	8R'
'	! #" $$3%&3*, . 'Mh Z` h LV3' /B'M 3D2 , #'	R: 8FdL8: LF'	8<5BG'	: 5 S'	8S'
'	SL! (3' #' LFL\ , *(D3LF(Li $" *(%W3' 3dL h &, '	FR8<FLSSLJ '	85<8'	G5 : '	8S'
'	\ +?&, $%2 'c %#+*, '	8Gd<<LRGLd'	85<8'	G5 : '	8S'
'	FL\ , *(D3LF(L$" *(%W3dLh &, '	FR: FLFGLJ '	G5B<'	G5G9'	8S'
'	! #%$*") +3%, '	8J J RJ LJ RL8'	G5BG'	G5G9'	8S'
'	P D. #' CD3-2 %&, 'P D. #' /(3' #%, '	8dGJ LFFLF'	R<J 59R'	FJ 95dG'	8J '
'	` *%#" &%'T /%'	F: G9LF8LJ '	R@Rd5F<'	d@FJ 5G'	R'
'	M 3D+2 %&, $'	R: : 8SLRSL8'	FdS 5RS'	88G5 G'	R'
'	` *(" CD3-*, . 'T3/" (" 3! 8FL8S'	R: 8d8Ld9LS'	SRd5G'	88: 5BG'	S'
'	Q- +#Q- 2 '	9GGGLdGLG'	dFG5RF'	: F5 G'	S'
'	! %#- $'6, #4, &, $'	9J FRRLJ <LJ f '	d95F<'	FF5 R'	S'

'	6, *#+$". %2 ' ` *(D3 &, . %2 %&, *, *#++/, *+*, '	RJ LGFL: '	R@: d5BR'	88@J S5FG'	J '
'	M("$4("&%'T/%'	8dS9: LdRLF'	8@: J 5G'	8@<G5GG'	J '
'	\ , *(D3h C%#+&, 'M 3D2 , #'I %('h C%#+&, '	9GGdL88LR'	SRd5G'	8SF5 G'	J '
'	8@L` *(+&, . %2 %&%2 @ 8@FLV%$7FL 7V%$HFL P D. #" CD, *(DK\ , *(D3+2 2 " &%= *(D3L c 8@FLV%$HFLP D. #" CD, *(D3Kc 8@FL N%2 , *(D3L@(3' #%, 'H8a K	8d: : <9L9J LJ '	J <959G'	dF85G'	J '
'	` #D*(" #) %'T/%'	: 9LRSLRf '	J <: 5 F'	F8G5<G'	J '
'	8Lh /*+. , /, &, 'H 8: K	88FL: : L9'	dFG5RF'	8: : 5G'	J '
'	` *(+&" 3	RJ L8<LS'	8d: 5FG'	8Gd5G'	J '
'	6j b` 6P ei ` c ` 'Qj e! h i '	88FLF<LR'	8GF5BF'	S: 5G'	J '
'	>%3+&, *#%;'HdL T2 %&" 4#' 4D3@" 2 " 4" 3D2 , #K	R: J GGLG<L<'	8G85BS'	: 85<G'	J '
'	c " &%&%'T3" CD3+*, '	<GSS9LFSLG'	<: 5S'	J S5GG'	J '
'	dLT2 %&" 4#' 4D3H>%3 +&, *#%3K	S: 8RGL99L9'	8<5R: '	8d5RG'	J '
'	` *(" CD3+*, . '! +$*" #h %3	R8<98L8FLR'	<5 R'	J 5G'	J '
'	N%*(+&" 3+2 %&, '	888LJ FLF'	J 5GF'	d5GG'	J '
'	\ , *(D3b$") - *D3E, *" &, '	8G: L8GL8'	J 5GF'	d5GG'	J '
'	g D3 &, '	8ddGLFGL<'	8@: J 598'	R: F5BG'	d'
'	P D. #" /+#) " &'j , $%&'	8FGGFLJ dLR'	RdR5dG'	J d<59G'	d'
'	h CD+3BD3+*, . 'O+**D'T/%'	R8<98LGGLF'	8: d5dS'	8FG5FG'	d'
'	FLP D. #" CD*#%2 , *(D3 &, @ V%$H6#%2 , *(D3+2 2 " &%2 K N%(3' #%, '	SSRdRLG9LJ '	: <5Fd'	RG5G'	d'
'	6#%*(+&" 3+2 %&, '	8GFL<8LR'	SF5FJ '	J 85dG'	d'
'	` *(" CD3+*, . 'T3" (" 3	R: RGdLFSL: '	J G5B: '	d85 G'	d'
'	O' #2 +3 , (D. , '	SGLGGLGf '	dF5GR'	8F5<G'	d'
'	] - +*, #&+#D'T2 2 " &%2 '! " 2 4" - &. '	8GG<RSLS<L9'	FF59F'	8S5GG'	d'
'	h CD+3BD3+*, . 'T3BD34(, &" 3	8F<G: <L: <LG'	8F5Fd'	8G5FG'	d'
'	M+#+O%&%'M *#" 3 - 2 'N%$*%3+*, '	RJ <J FLSSL: '	885dG'	: 5GF'	d'
'	M *+$$%2 'b' . %, '	<R: 8L88LG'	95B<'	R5GG'	d'
'	8@@'6#%2 , *(D3) , &W&, 'Hb2 4- #%DK	9SLRdLR'	S5Rd'	J 5R9'	d'
'	M 3D+3BD3 &, '	<<SRL9J L<'	J 5S: '	d5GG'	d'
'	b$" *#%, /+&" 3@ *(" CD3+*, . '	9GJ dLdGLS'	G59J '	G5<9'	d'
'	P , 2 %, 3B 3+$, '` &WD2 , '! " &/, &*#+*, '	9GFSLSRLd'	G5dd'	G5F<'	d'
'	FLV- *" CDL8LM#" 4+&" 3	8S: F8L: dL<'	G5GF'	G5GF'	d'
'	V, &W%'T/%'	RSL: SLG'	R@: d5BR'	89@<F5 G'	F'
'	c %#%" *#%/, *%'T/%'	8d9L8dL9'	d@GR5FJ '	8@F<5dG'	F'
'	M 6j h i ` _ \ 'c TMP 6P T'	RJ <J FLJ <L: '	SRd5G'	d8<5 G'	F'
'	P , C+. , /L8L` &, '	RF9L<'dLF'	SRd5G'	J J F5BG'	F'
'	` *(D3) , &W&, '	8GGLJ 8LJ '	dSS5 <'	dGR59G'	F'
'	V, &WD3+- #D3 %2 , *(D3+2 2 " &%2 ' ! (3' #%, '	8d9LG<L8'	dFG5RF'	8: : 5G'	F'

'	V" #%'T /%'HP dVGdK'	8GGJ dLdSLd'	FGS5F8'	8: 95J G'	F'
'	6+#'V+$, $@J - %&" 3%&, 'N, #%A$5@V, &WD3 ! (3' #%, '] - +*, #&%V. '	<FJ : GL<GL<'	8d<558'	88: 5<G'	F'
'	T2 2 " &%2 @N%3D3 %1 , *(D3L@ (3' #%, @ M' 3D2 , #$'	FRGRFL<9Ld'	SR5dS'	J J 5FG'	F'
'	N%1 , *(D3) , &WD32 D#%$*D3+2 2 " &%2 ' ! (3' #%, '	8d9LG: LF'	dF5GR'	8: 5 G'	F'
'	>- 3D, #%V. 'M' 3D' 3, 0%&'	R: Gd<L8dL: '	FF59F'	895 G'	F'
'	h CD+3D3+*, . 'T 3D3+(, &" 3	FRGF<Ld: Ld'	8F5Fd'	8G5FG'	F'
'	V, &WD3 %1 , *(D3+2 2 " &%2 '! (3' #%, '	8FFL8: L9'	S5Rd'	J 5J G'	F'
'	! (" 3%&, '! (3' #%, '	R<LJ : L8'	dF@RF5J F'	dF@RF5J F'	8'
'	>" . %2 '! (3' #%, '	<RJ <L8J LS'	F@8<5RG'	F@8<5RG'	8'
'	M(*(+3%'T /%'	: : L99Ld'	RdR5dG'	RdR5dG'	8'
'	M(*(+3%'T &(D. #%, '	: SLJ J L9'	RdR5dG'	RdR5dG'	8'
'	` *(+&+2 %&%2 @@@L6#%1 , *(D3L\ , *(D3L h C" @(3' #%, @M' 3D2 , #' I %(' M#" 4, &+2 %, '	dSJ F9L89L<'	SRd55G'	SRd55G'	8'
'	o%&D3! " 4" 3D2 , #'	d: 89dLRGL8'	<: 598'	<: 598'	8'
'	6, *#+2 , *(D3+2 2 " &%2 '! (3' #%, '	<SLS<LG'	RJ 5 d'	RJ 5 d'	8'
'	! 8J 'T 3+(+'h 3, %&'` *(" CD3+*, '	: J 8ddLSGLR'	SR5dS'	SR5dS'	8'
'	h CD+3D3+*, . 'T 3D3+(, &" 3%'j , $%&'	RdJ F: L9FLF'	S85J J '	S85J J '	8'
'	>" . %2 'V#" 2 +*, '	<<: 9Ld: LG'	dF5GR'	dF5GR'	8'
'	i %(*T #" 2 +*%'c +4(*(+'	RJ <J FL9SLR'	: 5GJ '	: 5GJ '	8'
'	N%2 2 " &%2 'M, #" C% %- 3+(+*, '	<<F<LSJ LG'	R5J : '	R5J : '	8'
'	h CD+3D3+*, . 'T 3/" (" 3	R: GGFL9<L8'	S5BS'	S5BS'	8'
'	M' 3D' 3` $*, #'	8dd: LJ dL: '	d5GG'	d5GG'	8'
'	M' 3D?3D/" 3` $*, #'	9GGSLR<L: '	F5J d'	F5J d'	8'
'	\ , $%D3, &, '	8G: LR<L: '	85Rd'	85Rd'	8'
'	8@@L6#%1 , *(D3) , &W&, '	SFRL<dL: '	G5 F'	G5 F'	8'
'	8LV- *" CDLFLM#" 4+&" 3	S8d8LRRL: '	G5<R'	G5<R'	8'
'	T 3D3+#D3>- 3D' &+*, '	R: S: J LF<LG'	G5dd'	G5dd'	8'
'	! - 2 , &, '	9: L: FL: '	G58: '	G58: '	8'
'	M' *+$$%2 'P D. #" C%, '	8d8GLS: Ld'	G588'	G588'	8'
'	T/#D3+2 %, '	<9LGRL8'	G5GR'	G5GR'	8'

f '! (, 2 %+3$'2 " $*'0#, X- , &*3D- $, . '%&'+/%%W*% &'+&. '&" *0#, X- , &*3D- $, . '%&'(D. #+- 3%'0#+/*- #%&2'

.

! "#$%&])&C7%F ,+"$5&(1& +,- &2"+.@2,0B&"5&%=/2% &/& OI I N;&,5.%- &<& %+2%"5,0B&2%U@%0+<&(1&/5%&

C7%F ,+"$W'F %&	C*' &&	4 "G,F @# & 6YB;Z.2%'.F %0.&	* >%2" B%& 6YB;Z.2%'.F %0.;&	J 2%U@%0+<&(1&/5%&
I +*, #'	<<dFL8: LSf'	8@8<@9R'	<G<@: J 5 G'	8G'
P D. #' /(3' #%'T/%'	<RJ <LG8LG'	S<@d95GJ'	F: @dS5 G'	8G'
` *%#' &%'T/%'	F: G9LF8LJ'	FJ @<J 5<8'	: @RS5FG'	8G'
` *( D3 &, 'Q3D/" 3\ "&") - *D3` *(, #'	888L<RLFf'	8G@F85RR'	J @8S5 G'	8G'
! %#- $'6, #4, &, $'	9J FRRLJ <LJ f'	R@RF55F'	F@<G5RG'	8G'
b$" 4#' 4+&" 3	R<LRdLG'	8@<F5J R'	: d: 5G'	8G'
M' 3D' CD+3D3 &, $'	R: J d9L' J SLF'	: dF5<: '	8d95FS'	8G'
M' 3D+2 %&, $'	R: : 8SLRSL8'	SdR5S'	FS85GG'	8G'
P D. #' 0B "#%'T/%'	<RRJ Ld9Ldf'	FJ @<J 5<8'	8J @R: 5G'	9'
M("$4(" &%'T/%'	8dS9: LdRLF'	<@R: 5F8'	J @d95 G'	9'
! %#%'T/%'	<<L9FL9'	S@8955G'	d@8S5RR'	9'
h CD+3D3+*, . 'T2 %&, '] - +*'	8d: : <9L' 9J LJ'	8@G<5FJ'	9GR55G'	9'
` #D*("#) %'T/%'	: 9LRSLRf'	8@<S5<'	S9R5 G'	9'
` *(+&" 3	RJ L8<LS'	: S<5 8'	8: S5G'	9'
>%+&, *#%;'HdLT2 %&" 4#' 4D3@P "2 "4" 3D2 , #K'	R: J GGLG<L<'	<<J 599'	J Gd5GG'	9'
g D3 &, '	8ddGLFGL<'	RRJ 5G<'	FGJ 5G'	9'
! "/+2 %" 4#' 4D3V, *+%&, '	R8<: 9LJ GLG'	J FJ 5 8'	dRG5GG'	9'
6j b 6P ei ` c ` 'Qi e! h i'	88FLF<LR'	Fdd5: '	8F: 5<G'	9'
c "&%&%'T 3" CD3+*, '	<GSS9LFSLG'	8<95dR'	995GG'	9'
dLT2 %&" 4#' 4D3H%3 +&, *#%3K'	S: 8RGL99L9'	8F95<'	R<5: '	9'
Q- +#Q- 2 '	9GGGLdGLG'	R95Gd'	dF5RG'	9'
M+#+0D&%'M) *#' 3 - 2 'N%$*%3+*, '	RJ <J FLSSL: '	dJ 558'	8R5dG'	9'
M 6j h i ` _\ 'c TMP 6P T'	RJ <J FLJ <L: '	dJ 558'	8R5dG'	9'
! #D$*+3%&, '>%&/+@ - +#*W	8J : G: LRGL<'	S5<S'	F5<G'	9'
b$" *#%, /+&" 3@ *("CD3+*, . '	9GJ dLdGLS'	S5<S'	F5<G'	9'
8LV- *" CDLFLM#' 4+&" 3	S8d8LRRL: '	J 5: '	F5<F'	9'
P , 2 %, 3 3+$, '` &VD2 , '! " &/, &*#+*, '	9GFSLSRLd'	85G9'	G59'	9'
FLV- *" CDL8LM#' 4+&" 3	8S: F8L: dL<'	G5d'	G5GR'	9'
O' #2 %'T/%'	RJ L8: LR'	R@995d'	d@8859G'	: '
P D. #' /+#) " &'j , $%&'	8FGGFLJ dLR'	F@FJ 5R9'	8@S<5GG'	: '
h CD+3D3+*, . 'O+**D'T/%'	R8<98LGGLF'	8@J G5Rd'	RdG5GG'	: '
6+#'V+$, $@ - %&" 3&, 'N, #A$5@V, &VD3! (3' #%, '] - +*, #&%V. '	<FJ : GL<GL<'	: SS55F'	J <F55F'	: '

! %&&+2 +3 , (D. , '	8GJ LSSLF'	: SS5SF'	J <F5SG'	: '
>- 3D, #%W. 'M' 3D" 3, 0%&'	R: Gd<L8dL: '	8J F5S9'	<: 5: G'	: '
] - +*, #&+#D'T2 2 "&%2 '! "2 4" - &. '	8GG<RSLS<L9'	8J F5S9'	<: 5: G'	: '
M' *+$$%2 'B' . %, '	<R: 8L88LG'	S<5Gd'	d85SG'	: '
M' 3D+3BD3, &, '	<<SRL9J L<'	F: 5S8'	8S5<G'	: '
M' *+$$%2 'T /, *+*, '	8F<LG: LF'	8J 5FR'	<59G'	: '
T /, *%'T /%'	RJ L89L<'	d@G95J 8'	F@: J 5dG'	<'
>" . %2 '! (3' #%, '	<RJ <L8J LS'	RSJ 5: G'	SdS5BG'	<'
6#% *(+&" 3+2 %&, '	8GFL<8LR'	d@<G5J J '	<d: 59G'	R'
h CD+3BD3+*, . 'T 3BD34(, &" 3%'j , $%&'	RdJ F: L' 9FLF'	d9: 5B<'	FR: 5RG'	R'
i %(*'T #' 2 +*%'c +4(*(+'	RJ <J FL9SLR'	RF5Fd'	J F5GG'	R'
8 @@L6#%2 , *(D3) , &W&, '	9SLRdLR'	J G5J J '	F<5d8'	R'
\ , $%D3, &, '	8G: LR<L: '	8F5Rd'	S85G8'	R'
8 @@L6#%2 , *(D3) , &W&, '	SFRL<dL: '	R5dF'	J 5FR'	R'
T 3BD3+#D3>- 3D' &+*, '	R: S: J LF<LG'	F5SF'	85<8'	R'
! - 2 , &, '	9: L: FL: '	85d9'	G59J '	R'
T2 2 "&%2 '! (3' #%, '	8F8FSLGFL9f '	FG@dF5dS'	8<@RG5Gd'	S'
N" . , /D3) , &W&, '>- 3D' &%'T /%'	F<8<RL: <LG'	: FG5: d'	F8d5<G'	S'
\ , *(+&" 3	R<LSRL8'	<8S5S8'	8S959G'	S'
` *("CD3+*, . 'T 3/" ("3	R: RGdL' FSL: '	F<d5J R'	<85FG'	S'
\ , *(D3h C%+&, 'M' 3D2 , #I %('h C%+&, '	9GGdL88LR'	8dR5<d'	dS5RG'	S'
! +4#D3+2 %" 4#' 4D3V, *+%&, '	<d<<FLJ RLG'	J F5J : '	dR5Rd'	S'
Q3D/, #' 3	SRL: 8LS'	J F5J : '	dR5RG'	S'
N% *(+&" 3+2 %&, '	888LJ FLF'	F<5J d'	<5BJ '	S'
\ , *(D3b$") - *D3E, *" &, '	8G: L8GL8'	F<5J d'	<5BJ '	S'
>- 3D- #%'T /%'	<RRJ L9dL9'	F<5J d'	<5FG'	S'
M' 3D, *(D3, &, 'h C%, '	FSdFFLR: Ld'	F<5J d'	<5FG'	S'
` *("CD3+*, . 'T 3/" ("3! 8FL8S'	R: 8d8Ld9LS'	95RR'	J 5J 9'	S'
M' *+$$%2 'P D. #' C%, '	8d8GLS: Ld'	G5: d'	G5SG'	S'
c +4(*(+3, &, '	98LFGLd'	G5Gd'	G5GF'	S'
M(*(+3%'T /%'	: : L99Ld'	F@FJ 5R9'	F@S85J G'	J '
M(*(+3%'T &(D. #%, '	: SLJ J L9'	F@FJ 5R9'	F@S85J G'	J '
` *(D3) , &W&, '	8GGLJ 8LJ '	8995FF'	8dR59G'	J '
FL'P D. #' CD*#%2 , *(D3, &, @%$H6#%2 , *(D3+2 2 ' h &%2 K'N%(3' #%, '	SSRdRLG9LJ '	8FG5G: '	SJ 5: G'	J '
` *("CD3+*, . '! +$*' #'h %3	R8<98L8FLR'	R5J J '	F59J '	J '
M#' 4D3, &, 'Q3D/" 3	S<LSSLR'	R5J J '	F59G'	J '
6, #4, &, 'P D. #' /+#) "&'	R: 9SRLSRL9f '	J @<d5Fd'	J @9G5: G'	d'
c "&D3M(, &" 3` *("CD3+*, '	9G8RLJ SL9f '	R5FG'	J 5<G'	d'
h CD+3BD3+*, . 'T 3BD34(, &" 3	FRGF<Ld: Ld'	R5FG'	J 5<G'	d'

h CD+3BD3+*, . 'T 3BD34(, &" 3	8F<G: <L: <LG'	R5FG'	J 5<G'	d'
V" #%'T /% 'HP dVh dK'	8GGJ dLdSLd'	J : <5Rd'	J G: 5<d'	F'
\ %*- #, 'h 0N%2 , #T & '6#%2 , #O+**D'T /% $'h 0' L&. , 0&%, '! " 2 4" $*% &'N, #%A, . 'O#" 2 '6+3h %	R8<9GL8FLd'	F: 95d9'	8J S5RS'	F'
M#" 4+#? D3T 3/" (" 3	8G<L89L<'	9R5J R'	J : 5J G'	F'
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! #D$*+3%&, '>%%+@ #%$*") +3%, '	8J J RJ LJ RL8'	d8@9S5dS'	d8@9S5dS'	8'
V, &W'%'T /%'	RSL: SLG'	F@G: 5SG'	F@G: 5SG'	8'
` *(D3 &, 'Q3D/" 3	8G<LF8L8'	J GJ 5d8'	J GJ 5d8'	8'
M' 3D" CD+3BD3 &, $'	R: 9S8L' R<L<'	F: 95d9'	F: 95d9'	8'
6(%- #, +'M' 3D2 , #'	R: SF<L' J 9L8'	F: 95d9'	F: 95d9'	8'
T /#D3+2 %, 'T /#D3+*, '! " 4" 3D2 , #'	k9GGdLGRL9'	8SJ 5Sd'	8SJ 5Sd'	8'
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>" . %2 '>- 3D%, '	<<S<L: dL<'	G5B8'	G5B8'	8'
>" . %2 '>- 3D+*, '	<<S<L: FLR'	G5B8'	G5B8'	8'
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8Lh /*+. , /, &, '	88FL: : L9'	G5GR'	G5GR'	8'
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8L6, *#+. , /, &, '	88FGLdRL8'	G5GG89'	G5GG89'	8'
T /#D3' &%#%) '	8G<L8dL8'	G5GGGJ '	G5GGGJ '	8'

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)*Chemical purposes listed are what the oil operator identifies. Those listed in parenthesis are the authors suggestion.

References:

Foshee, W.C., and R.E. Hurst. 1965. "Improvement of well stimulation fluids by including a gas phase." *Journal of Petroleum Technology* 17 (7): 768-772.

Halliburton Company. 2014. Fluid loss additives. Available: http://www.halliburton.com/en-US/ps/cementing/materials-chemicals-additives/fluid-loss-additives/default.page?node-id=hfqelaf2 [Accessed 15 September 2014].

Kalfayan, L. 2008. "*Production Enhancement With Acid Stimulation*" 2nd ed. PennWell Corporation

Robertson Jr, J., G. Chilingarian, and S. Kumar. 1989. "*Surface Operations in Petroleum Production, II.*" New York: Elsevier Science Publishing Company, 171.

US EPA. 2015. Analysis of hydraulic fracturing fluid data from the FracFocus Chemical Disclosure Registry 1.0. Office of Research and Development. EPA/601/R-14/003. United States Environmental Protection Agency.

Weatherford. 2014. Clay control additives. Available: http://www.weatherford.com/Products/EngineeredChemistry/FracturingChemicals/ClayControlAdditives/ [Accessed 15 September 2014].

Williams, B.B., J.L. Gidley, and R.S. Schechter. 1979. Acidizing Fundamentals. Monograph Series, Society of Petroleum Engineers, Vol 8. New York.

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IV. Federal Framework For Regulating Acidization

A. Abstract

Whereas hydraulic fracturing has received increased regulatory attention after rising concerns about health and environmental impacts, other “sister” techniques such as, acidizing have gone unnoticed. Acidizing, a general term for acid use in oil and gas exploration, is used as frequently as hydraulic fracturing but with hazardous chemical concentrations higher than hydraulic fracturing. It is important that acidizing be addressed when discussing how best to protect the public and environment from potential impacts of oil and gas exploration. This paper discusses the legal framework that is currently in place to regulate acidizing at the federal level. In some cases where hydraulic fracturing is exempt from regulation – acidizing is not – as in the Safe Drinking Water Act. The Safe Drinking Water Act will prove to be an important regulation in controlling acidization activities but probably not without a legal battle. In other cases, like the Clean Air Act or Toxic Substances Control Act, there is proposed rulemaking for hydraulic fracturing but none for other unconventional oil and gas stimulation techniques like acidizing. The proposed rules must include acidizing. Under the Clean Water Act, the chemicals used in acidizing warrant classification as hazardous waste and should be disposed of appropriately and require stormwater permits. All unconventional oil and gas exploration techniques, not just hydraulic fracturing, should be considered when thinking about regulating these practices to best protect the public and environment from harm.

B. Introduction

Hydraulic fracturing (HF) is an unconventional oil and gas (UOG) well stimulation technique that pumps pressurized fluid with a propping agent into the ground to fracture a rock formation, allowing oil or gas to flow. A propping agent is a substance like sand that can lodge itself into a fracture and keep it open. Whereas HF has received increased regulatory attention after rising concerns about health and environmental impacts, other "sister" techniques to HF such as acidizing have gone unnoticed. Acidizing, a general term for acid use in oil and gas (O&G) exploration and production, is used as frequently as HF but with hazardous chemical concentrations higher than HF. It is important that acidizing be dealt with in any regulatory program focused upon UOG production methods. This paper outlines the legal framework currently in place at the federal level to regulate acidizing and examines potential revisions.

Acidizing, a term used for all types of acid use, can refer to acid maintenance, matrix acidizing, and acid fracturing processes. These processes are used to increase or keep up well productivity or increase rock permeability (Robertson, Chilingarian, and Kumar, 1989).

In acid maintenance, acid solutions are used to remove scales. Operators either inject the acid solution at a specific location into the wellbore, or it is circulated back and forth across the casing perforation or formation face to react with the scale. The scale is cleaned off of the surfaces of the wellbore and equipment without acid penetrating into the formation (Robertson, Chilingarian, and Kumar, 1989). Acid maintenance is not considered a well stimulation technique.

Matrix acidizing and acid fracturing are different than acid maintenance in that the acid solution is not restricted to the wellbore. Rather, it is intended to reach the formation. In matrix acidizing the acid solution is injected into the formation below fracturing pressure. The acid etches its way through the formation, creating new pathways several centimeters to a meter around the borehole. The increase in the cross-sectional area of channels leads to an increase in permeability and porosity of the reservoir rock (Robertson, Chilingarian, and Kumar, 1989).

In acid fracturing, acid solutions are injected into the wellbore above hydraulic fracturing pressure to fracture the formation and create new flow channels or widen existing fractures (McLoed, 1986). As fluid continues to be injected, the fracture length and width increase, eventually allowing the fluid to enter the fracture, dissolving the minerals and widening the fracture further (Williams et al., 1979).

The main difference between acid fracturing and matrix acidization is the injection pressure. Injection rates resulting in pressures below fracture pressure are termed matrix acidizing, while those above fracture pressure are termed acid fracturing (Williams et al., 1979). Often one cannot determine which technique occurred until after well completion. If the pressure chosen caused the formation to fracture it is considered acid fracturing and if it did not, it is considered matrix acidization.

Although acidizing has been used for decades, and was first introduced over a hundred years ago (Williams et al., 1979), we have only recently started examining its potential impacts. In California acidizing chemicals include at least 22 toxic chemicals, and some of these are used in the 100,000's kg/treatment. The health and environmental impacts linked to HF apply to acidizing as well because many of the chemicals used are the same, and in some cases the process is very similar (Abdullah et al., 2016). Some occupational stressors of UOG stimulation include mortality, exposure to hazardous materials and increased risk of industrial accidents. For communities near E&P sites the major stressors are air pollutants, ground and surface water contamination, truck traffic and noise pollution, accidents and malfunctions, and psychosocial stress associated with community change (Adgate, 2014). There is a growing amount of literature on the impacts from UOG stimulation techniques, such as the EPA report on impacts of HF on drinking water sources (*Assessment of the potential impacts of hydraulic fracturing for oil and gas on drinking water resources: Executive Summary,* 2015). However, long-term environmental and health impacts are not considered.

There has been considerable focus on the impacts of HF and how best to regulate it. Acid fracturing is very similar to HF, the main difference being how the fracture conductivity is created. Yet while a few papers have been published discussing the legal framework for regulating HF (Rahm, 2011; Brady and Crannell, 2013; Kiparsky and Foley Hein, 2013; Konschnik and Dayalu, 2016), none discuss the legal framework for regulating acidizing. A recently published paper showing the types and amounts of hazardous chemicals used in acidizing revealed higher concentrations in acidizing than what is used in HF (Abdullah et al., 2016). It is therefore increasingly important to understand the legal framework for regulating acidization.

The overall objective of this paper is to outline the legal framework currently in place at the federal level to regulate acidizing and examines potential revisions. Thus, this paper defines areas of public concern where better policy is needed. The paper outlines existing relevant laws that regulate acidizing operations at the federal level, highlights the differences in treatment of acidizing operations as compared to HF, and identifies those areas in which new policies or laws are needed.

C. Existing Federal Regulations

The federal government interacts with the O&G industry in two ways: as a landowner and as a regulator.

As a landowner, the Bureau of Land Management (BLM), a federal agency in the Department of the Interior, is charged with administering O&G operations in a manner that protects Federal and Indian lands while allowing for appropriate development of the resource. The BLM oversees approximately 700 million subsurface acres of Federal mineral estate. Currently, nearly 36 million acres of

Federal land are under lease for potential O&G development in 33 states. As of June 30, 2014, there were approximately 47,000 active O&G leases on public lands, and approximately 95,000 O&G wells (Oil and Gas; Hydraulic Fracturing on Federal and Indian Lands, 2015).

As a regulator, the Environmental Protection Agency (EPA) is tasked with protecting human health and the environment by writing and enforcing regulations based on laws passed by Congress. There are multiple federal laws that could regulate acidization. Some exempt acidizing altogether and others have conditions for regulating it. This section outlines the federal laws that BLM and EPA are tasked with upholding to regulate acidizing operations.

1. Federal Acts Upheld by the Bureau of Land Management

a) The Federal Land Policy and Management Act (1976) (FLPMA)

Regulating how public lands are managed and where certain activities like acidizing are allowed is important for protecting the public and environment. The Federal Land Policy and Management Act (FLPMA) governs the way in which the public lands administered by the BLM are managed.

Section 202 of the FLPMA requires the BLM to develop and maintain land use plans or Resource Management Plans (RMPs). These plans are the basis for all land use decisions the BLM makes, including decisions to allow O&G leasing, allow O&G

leasing under certain conditions, or prohibit O&G leasing altogether. The RMP applies to public lands, including the Federal mineral estate; however, it does not apply to Indian land or to surface estates managed by other Federal agencies such as the USDA Forest Service.

The BLM seeks public feedback to identify the issues to consider and address in the RMP. The public must be able to participate in the development, maintenance, and revision of land use plans. If, for example, the public identifies areas as recreational or environmentally important, the BLM may prohibit or restrict O&G development.

Given the nature of acidization activities and the large quantities of toxic chemicals brought on site, leasing of public lands in close proximity to residential developments or sensitive environmental receptors should not be allowed for acidizing under the FLPMA. The BLM is charged with responsibly developing and maintaining land use to protect the public and environment; allowing acidizing activities to occur within feet of sensitive receptors goes against this goal.

b) The National Environmental Policy Act (1969) (NEPA)

Prior to finalizing any RMP, the BLM must conduct a full-scale environmental analysis. This is a requirement of the National Environmental Policy Act (NEPA). NEPA requires federal agencies to review environmental impacts of a proposed action and possible alternatives for actions that involves federal funding, work performed by the federal government, or permits issued by a federal agency. An action can be either exempt, categorically exempt, or require an Environmental Assessment (EA). As a final step, if there are significant anticipated effects, an Environmental Impact Statement (EIS) is prepared, and if there are no significant impacts then a Findings of No Significant Impact (FONSI) is prepared.

Although an environmental analysis is done prior to the RMP being finalized, the BLM generally analyzes the environmental impacts of the alternatives through an Environmental Impact Statement (EIS) once lands are considered appropriate for leasing. Traditionally the BLM has not done a full-scale NEPA review for a specific parcel prior to leasing it. That is usually done once a lessee requests to drill a well or conduct other surface activities. However, in some cases BLM is required to do a full-scale NEPA EIS prior to issuing a lease (*Background for Nepa Reviewers: Crude Oil and Natural Gas Exploration, Development, and Production,* 1992).

The BLM is required to post notices of Applications for a Permit to Drill (APD) for O&G development on public lands for public inspection for 30 days. During this time the public may express any concerns as the agency conducts a site-specific environmental analysis. These concerns and analysis may result in conditions of approval on the operator's drilling permit that require, forbid, or control specified activities or disturbances (*Oil and Gas; Hydraulic Fracturing on Federal and Indian Lands*, 2015).

There are some O&G development activities that are categorically excluded from conducting a full-scale NEPA review. These exclusions were enacted in the 2005 Energy Policy Act. The excluded activities are presumed to have no significant environmental impact, unless the public can prove "extraordinary circumstances in which a normally excluded action may have a significant environmental effect."

Section 390 categorical exclusions (CX) as stated in the legislature are as follows:

1. Individual surface disturbances of less than five acres so long as the total surface disturbance on the lease is not greater than 150 acres and site-specific analysis in a document prepared pursuant to the NEPA has been previously completed.
2. Drilling an O&G well at a location or well pad site at which drilling has occurred within five years prior to the date of spudding the well.
3. Drilling an oil or gas well within a developed field for which an approved land use plan or any environmental document prepared pursuant to NEPA analyzed drilling as a reasonably foreseeable activity, so long as such plan or document was approved within five years prior to the date of spudding the well.
4. Placement of a pipeline in an approved right-of-way corridor, so long as the corridor was approved within five years prior to the date of placement of the pipeline.
5. Maintenance of a minor activity, other than any construction or major renovation of a building or facility.

These exclusions indicate that some environmental assessment was done during the land acquisition process and/or within a certain time frame of activity, and unless there is an extraordinary circumstance, there should be no significant environmental impact. This may be true for some types of activities considered in the CX's, but the nature of oil drilling has changed in recent years and an environmental assessment at an early stage might not include unstudied O&G exploration technology impacts.

Numerous questions were raised about how and when BLM should use these CXs. In 2009 the United State Government Accountability Office (GAO) was asked to report on these issues. GAO found several types of violations of the law, including "approving more than one oil or gas well under a single decision document, approving projects inconsistent with the law's criteria, and drilling a new well after time frames had lapsed (Nazzaro, 2009)." GAO also found in 85% of the field offices sampled that officers did not adequately justify the use of a categorical exclusion. The GAO recommended that BLM improve the implementation of the CXs by "clarifying agency guidance, standardizing decision documents, and ensuring compliance through more oversight."

In addition to ensuring compliance and clarity, it's important to revisit the CXs and see if UOG stimulation techniques of HF and acidizing result in significant environmental impacts.

c) Bureau of Land Management Proposed Rule to Address Hydraulic Fracturing (HF)

The BLM has made an attempt to address HF. Pursuant to the Federal Land Policy and Management Act (FLPMA), Indian mineral leasing laws, and other statutes, and in response to significant public interest in HF, BLM proposed a rule titled Oil and Gas; Well Stimulation, Including Hydraulic Fracturing, on Federal and Indian Lands. This proposed rule was published May 2012 under the Mineral Leasing Act. In May 2013, the BLM published a supplemental notice of proposed rulemaking and request for comments. After the comment period the final rule was published in March of 2015 and effective June 24th, of 2015.

Like other BLM regulations, this final rule applies to O&G operations on public lands, as well as operations on Indian lands. The rule establishes new requirements to ensure wellbore integrity, protect water quality, and enhance public disclosure of chemicals and other details of HF operations. (Oil and Gas; Hydraulic Fracturing on Federal and Indian Lands, 2015).

The rule however has not gone unchallenged. In June 21, 2016 a federal district court judge in Wyoming ruled that BLM lacked statutory authority to promulgate the rule (State of North Dakota, State of Utah, and UTE Indian Tribe vs. United States Department of the Interior, 2016). They cited that hydraulic fracturing is exempt under the Underground Injection Control Program in the Safe Drinking Water Act

(SDWA), and since EPA does not have authority to regulate HF neither does the BLM. This ruling will most likely be appealed.

Whether this rule is promulgated or not, it still grossly overlooks other UOG stimulation practices. These practices should be covered, for they involve much of the same best practice protocol as HF. Ensuring wellbore integrity, protecting water quality, and enhancing public disclosure of chemicals and other details of acidizing operations must be required. The basis on which the BLM's new rule has been struck down may not apply to acidizing. Later in this chapter there is a discussion on the SDWA and what is intended by the hydraulic fracturing exemption. Acidizing could be considered a different technique than hydraulic fracturing and thus not exempt. So if a similar rule were to be passed for acidizing the same argument might not hold true. Nevertheless BLM is attempting to keep up with the changing O&G development technologies but a limited coverage of what is regulated will not accomplish what BLM is tasked to do.

2. Federal Acts Upheld by the Environmental Protection Agency

a) The Clean Air Act (1970) (CAA)

Acidizing operations use many volatile compounds that can be a source of air pollution. A local governing body in Southern California, the South Coast Air Quality Monitoring District, requires reporting of acidizing techniques. Some of the air toxics listed in use for acid maintenance and matrix acidizing include:

- 1,2,4 Trimethylbenzene
- 1-Methoxy-2-Propanol

- 2-Butoxy Ethanol
- Acetophenone
- Aminotriacetic Acid
- Cumene
- Diethylene Glycol
- Ethyl Benzene
- Ethylbenzene
- Ethylene Glycol
- Ethylene Glycol Monobutyl Ether
- Ethylene Oxide
- Formaldehyde
- Hydrochloric Acid
- Hydrofluoric Acid
- Isopropanol
- Methanol
- Naphthalene
- Sodium Hydroxide
- Sulfuric Acid Ammonium Salt (1:2)
- Thiourea, Polymer with Formaldehyde and 1-Phenylethanone
- Toluene
- Xylene

The Clean Air Act (CAA) regulates air emissions of such chemicals from stationary and mobile sources. The CAA defines enforceable emission limitations for hazardous air pollutants (HAPs), National Emissions Standards for Hazardous Airborne Pollutants (NESHAPs), from "major source" and "area source" categories under section 112. Major sources are defined as a "stationary source or group of stationary sources located within a contiguous area and under common control that emits or has the potential to emit considering controls, in the aggregate, 10 tons per year or more of any hazardous air pollutant or 25 tons per year or more of any combination of hazardous air pollutants." An area source is "any stationary source of hazardous air pollution that is not a major source." For major sources, the statute requires the EPA to establish standards that reflect the maximum degree of reduction in HAP emissions through application of maximum achievable control technology (MACT).

There has been some confusion in determining what is considered a "stationary source" and "major source." As of June 2016 the EPA is finalizing a revision to regulations applicable to permitting of stationary sources of air pollution under the

New Source Review (NSR) and title V programs in the Clean Air Act (CAA or Act). The rule clarifies the meaning of the term “adjacent” that is used to determine the scope of a “stationary source” (for purposes of the Prevention of Significant Deterioration (PSD) and Nonattainment NSR (NNSR) preconstruction permitting programs) and the scope of a “major source” (in the title V operating permit program in the onshore oil and natural gas sector). The revised definitions now consider proximity of emitting activities and whether the activities share equipment (Source Determination for Certain Emission Units in the Oil and Natural Gas Sector, 2016).

It should be noted though that section 112(n)(4) of the Act prohibits aggregating emissions from O&G exploration or production wells (and their associated equipment) and emissions from pipeline compressor or pump stations with emissions from other similar units. Since most O&G wells, on their own, do not emit the threshold limit of HAPs under the statutory definition, many O&G exploration and production facilities aren’t considered major sources.

For those facilities considered major sources and area sources the EPA promulgated NESHAP limit emissions from O&G facilities that process, upgrade or store hydrocarbon liquids in 1999 and 2007. Both of these rules do not include sources of air pollution from UOG operations. Both of these standards also exclude facilities that exclusively handle black oil. Black oil is defined in the final rule as a hydrocarbon liquid with an initial gas-to-oil ratio (GOR) less than 0.31 cubic meters per liter (m3/liter) and an American Petroleum Institute (API) gravity less than 40 degrees. Most of the onshore oil extraction in California is black oil (Sheridan, 2006), and thus wouldn't be covered.

The CAA also sets forth allowable emissions for new major sources and major modifications to existing sources through New Source Performance Standards (NSPS). NSPS can extend to pollutants not included in the NAAQS and the NESHAPs.

The EPA in 2012 and 2016 issued NSPSs (Oil and Natural Gas Sector: New Source Performance Standards and National Emission Standards for Hazardous Air Pollutants Reviews, 2012; Oil and Natural Gas Sector: Emission Standards for New, Reconstructed, and Modified Sources, 2016) to regulate methane emission from natural gas wells and natural gas processing plants. These rules also regulate emissions of GHG and VOCs from new, reconstructed and modified O&G sources. These emission sources include HF oil well completions and potentially acid fracturing well completions. According to these rules HF is defined as "the process of directing pressurized fluids containing any combination of water, proppant, and any added chemicals to penetrate tight formations, such as shale or coal formations, that subsequently require high rate, extended flowback to expel fracture fluids and solids during completions." This could potentially include acid fracturing but not matrix acidizing.

With these newer rules in place, natural gas extraction, HF, and potentially acid fracturing are better regulated, but matrix acidizing and acid maintenance are not included. The NESHAPs established in 1999 and 2007 do not cover UOG operations. The 2012 NSPS rule mainly includes natural gas wells that are hydraulically fractured, whereas in California most of the UOG operations are for crude oil, not natural gas (CCST, 2015). In the 2016 NSPS rule, HF and potentially acid fracturing, are included for both oil and gas wells. However, as noted above there are many air toxins used in matrix acidizing and acid maintenance, and these practices are not regulated. The chemicals of acidizing must be reviewed to see what constituents could be problematic. All acidizing should also be included in the new rules set forth.

b) The Safe Drinking Water Act (1974) (SDWA)

In addition to protecting our air, protecting our water sources from acidizing chemical contamination is crucial. Water contamination has been one of the biggest issues raised over UOG exploration. The Safe Drinking Water Act (SDWA) protects public drinking water supplies by setting standards for drinking water quality and implementing various technical and financial programs to ensure drinking water safety. SDWA controls the injection of wastes into groundwater through the Underground Injection Control (UIC) program. For the O&G industry this includes underground injection used for enhanced oil recovery, but not production wells that are used only to bring O&G to the surface, without injection. The UIC program sets requirements for proper well siting, construction, and operation to minimize risks to underground sources of drinking water.

Originally, the SDWA defined “underground injection” as “the subsurface emplacement of fluids by well injection,” without any exceptions (Safe Drinking Water Act, 1974). Surprisingly, at that time EPA considered HF as exempt under the SDWA. In 1997, however, the U.S. Court of Appeals for the 11th Circuit ruled that HF activities constitute ‘underground injection’ under Part C of the SDWA (LEAF. v. U.S. EPA, 1997*).* Thus, the EPA and State UIC Programs were required to regulate HF under the SDWA. In response, the EPA initiated a study of the potential for contamination of public water supplies from the HF of coal seams for methane production and concluded in 2004 that HF poses little or no threat to underground sources of drinking water (Evaluation of Impacts to Underground Sources Of Drinking Water By Hydraulic Fracturing Of Coalbed Methane Reservoirs, 2004).

Despite questions over the report’s accuracy, Congress amended the SDWA in 2005 with the passage of the Energy Policy Act. The Act added two exclusions to the definition of underground injection:

1. The underground injection of natural gas for purposes of storage
2. The underground injection of fluids or propping agents (other than diesel fuels) pursuant to HF operations related to oil, gas, or geothermal production activities.

An important question arises—what is intended by HF in the Energy Policy Act? Matrix acidization and acid fracturing involve injecting fluids for enhanced oil recovery and operationally are not considered HF by those in the O&G industry. This becomes a very important question to answer to know if matrix acidization and acid fracturing must be regulated. To determine what was meant by the HF exemption we looked at:

- The bill language and definitions in the Energy Policy Act of 2005
- The legislative history of the Act including the committee reports, conference report, legislative debates, hearings, committee prints, house and senate documents
- EPA guidance
- Law review articles

The more authoritative sources in determining what is intended by HF in the Act are the bill language itself and committee reports. The committee debates are not as defining because they are exactly that—debates. EPA provides guidance but it isn't binding by law. These are all discussed below.

The bill language itself does not define HF. Looking through the committee reports on the Energy Policy Act of 2005, HF is defined as "a technique used to enhance the recovery of methane gas from coalbeds (H. Rept. 109-215, 2005; H. Rept. 108-65, 2003)." The EPA defines HF as a "temporary and intermittent process in which fluids are injected underground at high pressures to create fractures in the coals seam that enhance the recovery of methane gas by creating pathways for the gas to flow to the surface (H. Rept. 109-215, 2005; H. Rept. 108-65, 2003)." This EPA definition likely goes back to the 2004 EPA report, *Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs*. There is no concise definition provided in the report. Rather, there is a general description of pressurized fluid used to create an initial fracture, followed by fracture propagation, proppant placement, and the subsequent fracturing fluid recovery/groundwater extraction stage of the coalbed methane (CBM) production process. HF concerns today extend to far more than CBM production. The Energy Policy Act of 2005 includes HF operations related to oil, gas, and geothermal production activities, not just CBM.

From the Committee Report and 2004 EPA report that provided the proof to enact the exemption, it seems as though the HF exemption does not include matrix acidization and acid fracturing in the definitions.

If we look at the congressional records/debates, there are a few different definitions of HF mentioned:

- "HF is a drilling technique that injects chemicals into the ground during O&G development." (149 Cong. Rec 167, 2003)
- "HF is a process by which water, sand, and toxic chemicals are injected into rock so the oil and natural gas that they contain can be extracted." (149 Cong. Rec 168, 2003)
- "Involves injecting diesel fuel or potentially hazardous substances such as benzene, toluene, and MTBE underground to fracture rock and release O&G."

(151 Cong. Rec 106, 2005)

- "Involves injecting a fluid under pressure into the ground in order to create fractures in rock and capture methane." (151 Cong. Rec 106, 2005)
- "Involves injecting diesel fuel into groundwater supplied/aquifers/water supply" (151 Cong. Rec 106, 2005)
- "An invasive O&G extracting technique" (151 Cong. Rec 52, 2005)

Some of these definitions are very general. For example "an invasive O&G extracting technique." This definition can include any O&G extracting technique. Other definitions are more specific and in line with how industry defines HF as the use of pressurized fluid, containing a proppant like sand to keep created fractures open and extract the trapped oil or gas.

There are a few EPA guidance documents that describe HF. The first one is EPA's permitting guidance on HF using diesel fuels (Permitting Guidance for Oil and Gas Hydraulic Fracturing Activities Using Diesel Fuels: Underground Injection Control Program Guidance #84, 2014). Page 3 of the guidance contains the following description of HF:

"HF is a technique used to produce economically viable quantities of oil and natural gas, especially from unconventional reservoirs, such as shale, tight sands, coalbeds and other formations. HF involves the injection of fluids (commonly a mixture of water, chemical additives and proppants) under pressures great enough to open and enlarge fractures within the oil-and gas-producing formations. The resulting fractures are held open using propping agents, such as fine grains of sand or ceramic beads, to allow O&G to flow to the production well. The types and concentrations of chemical additives and proppants used in the HF fluids vary depending on site-specific conditions and are usually tailored to the properties of the formation and the needs of the project."

The second document is EPA's Draft Assessment on the impacts of HF on drinking water resources (*Assessment of the potential impacts of hydraulic fracturing for O&G on drinking water resources: Executive summary*, 2015). Chapter 2 of the document includes a description of HF: "HF is a stimulation technique used to increase production of O&G. HF involves the injection of fluids under pressures great enough to fracture the O&G production formations. HF fluid transfers the pressure generated by equipment at the surface into the subsurface to create fractures, and it carries and places the proppant into the fractures so that they remain 'propped' open after the injection pumping pressure is terminated (Gupta and Valko, 2007)."

In the same report acid fracturing is mentioned under Alternative Fracturing Fluids. It is described as follows: "Acid fracturing removes the need for a proppant and is generally used in carbonate formations. Fractures are initiated with a viscous fracturing fluid, and the acid (gelled, foamed, or emulsified) is added to irregularly etch the wall of the fracture and prop open the formation for a higher conductivity fracture (Spellman, 2012; Gupta and Valko, 2007)."

In these EPA guidance documents acid fracturing may be considered to be a type of HF. Matrix acidization though is not considered a type of fracturing stimulation. Acid fluid is injected below fracturing pressure, and acid etches its way through the formation.

Going beyond just the literal definition in the law and regulations, it is also important to see if there were any underlying reasons for exempting HF that can be extended out to other UOG stimulations. The legislative history and discussions around HF show that there was a narrow scope intended. And it seems that the exclusion was a political response to interest groups lobbying to congress. For these reasons acidizing should be seen as a different operation since there were no policy underlying reasons for excluding HF.

This is a debatable topic in which legislators must determine what is intended by the HF exemption. The current regulatory language hints toward both acid fracturing and matrix acidization not being exempt and thus regulated under the SDWA. SDWA may prove to be a powerful legislation in regulating the two acidizing techniques, matrix acidizing and acid fracturing. Under the UIC program this would mean requirements for proper well siting, construction, and operation to minimize risks to underground sources of drinking water from acidizing activities.

c) The Clean Water Act (1977)

In addition to protecting ground water sources, protecting our surface waters from acidizing chemical pollution is also important. The Clean Water Act regulates the treatment and discharge of wastewater into surface waters of the United States. It sets national standards for industrial wastewater discharges to surface waters and municipal sewage treatment plants (also known as publicly owned treatment works or POTWs) based on the performance of treatment and control technologies. There are two types of regulated discharges: direct and indirect. Direct discharge refers to wastewater discharged directly into a stream or other receiving body.

Indirect discharge refers to wastewater that is sent to a POTW. On June 28, 2016, EPA finalized pretreatment standards for O&G extraction. The standard calls for zero discharge of wastewater pollutants associated with onshore UOG extraction facilities to POTWs. This is because industry is already disposing of UOG wastewater via other methods; disposal in UIC wells, wastewater reuse/recycling to fracture another well, or management by centralized waste treatment (CWT) facilities—none of which involve sending wastewater to POTWs. UOG waste is not typical of POTW influent wastewater, some of the wastewater constituents can be discharged, untreated, from the POTW to surface water. The wastewater can also disrupt the operation of the POTW by; inhibiting biological treatment; accumulating in biosolids (also called sewage sludge), limiting their use; and facilitating the formation of harmful disinfection by-products (Natural Gas Extraction - Hydraulic Fracturing, 2016). Treating for these things would be quite costly.

Direct discharges from onshore UOG extraction are subject to NPDES permit regulations, with the exception of CBM. There can be no discharge of water pollutants from any source associated with production, field exploration, drilling, well completion, or well treatment, except for wastewater that is of good enough quality for use in agricultural and wildlife propagation. The program requires permits for the discharge of pollutants from any point source into waters of the United States. However, stormwater from O&G operations is exempted from the NPDES requirement, unless a facility has a discharge of Reportable Quantity (RQ) or contributes to a violation of a water quality standard. Reportable Quantity is a determined limit for specific hazardous chemicals pursuant to section 311 of The Clean Water Act. Certain acidization chemicals are included in this list (Abdullah et. al., 2016):

- Acetic acid
- Ammonium bifluoride
- Ammonium chloride
- Benzoic acid
- Dodecylbenzene sulfonic acid
- Formic acid
- Hydrochloric acid
- Hydrofluoric acid
- Sodium hydroxide
- Xylene (mixed)

Proving a discharge of RQ or even noting a violation of a water quality standard is a very difficult task. Monitoring at the right time and place is necessary to note if stormwater with RQ or violating a water quality standard was released. Such monitoring only happens if a facility is enrolled in the NPDES program.

What can be assumed is that contaminated stormwater does leave acidizing operation sites. Acidizing waste is often stored in unlined impoundments (CCST, 2015). During rain events the waste is undoubtedly released. Furthermore, acidizing operations use chemicals that are listed in the hazardous chemical list well above RQ limits (Abdullah et al., 2016). Stormwater discharge from UOG facilities must require at the least an Industrial Stormwater General Permit under the National Pollutant Discharge Elimination System (NPDES). Specific best management practices for acidizing operations must be identified, and in cases when certain facilities are polluting surface waters from spills, industry-specific or individual permits must be enforced.

d) Toxic Substances Control Act (1976) (TSCA)

The chemicals used in acidizing number over 200 and are used in large quantities, up to 100,000 kg/treatment (Abdullah et al., 2016). Currently we only have self-reported information about the chemicals used in select acidizing techniques in California. There is no requirement to provide information on the chemicals used in acid maintenance in California. In other states there is no requirement to provide information on any of the acidizing techniques.

The Toxic Substances Control Act (TSCA) provides EPA with authority to require reporting, record-keeping and testing requirements, and restrictions relating to chemical substances and/or mixtures. It is likely that many of the chemicals of acidization were in use at the time the TSCA Inventory was created, so they were grandfathered in and not reviewed. On June 7, 2016 Congress passed the Frank R. Lautenberg Chemical Safety for the 21st Century Act, the first time the Toxic Substances Control Act (TSCA) has been substantively amended since its enactment in 1976. The new legislation will significantly change the way EPA approaches chemical management under TSCA. Some of these changes include; an up-to-date inventory of all chemicals in active commerce in the U.S.; a risk screening based on health, hazard, use and exposure information; proof of businesses claiming confidentiality; testing or submission of information through an order rather than a rule. These changes don't directly impact rules regarding UOG but will amend the way chemicals are managed.

On May 9, 2014, however EPA issued an Advance Notice of Proposed Rulemaking (ANPR) under Section 8 of TSCA for HF chemicals and mixtures. EPA is developing an approach to obtain information on chemical substances and mixtures used in HF. This was in response to a citizen petition submitted under section 21 of TSCA. As a first step EPA has sought public input to determine the types of chemical information that could be reported and disclosed under TSCA and the approaches to obtain this information, including non-regulatory approaches. HF activities include the injection of water, chemicals, proppant, and/or tracers to prepare geologic formations for HF, complete an HF stimulation stage, evaluate the extent of resulting fractures, or ensure future ability to continue enhancement of production through stimulation by HF. The notice defines HF as pressurized fluids containing carrier fluids such as water or gas and any combination of proppant and chemicals that are injected into wells to fracture portions of the formation surrounding a selected well section. It is uncertain if acid fracturing is included in the definition of HF.

The EPA has also sought comments on ways to minimize reporting burdens and costs and avoid duplication of state and other federal agency information collections, while at the same time maximizing data available for EPA risk characterization, external transparency, and public understanding. Furthermore, EPA wants incentives and recognition programs that could be used to develop safer chemicals in HF. They have received over 200,000 comments and will finalize a rule by 2017 (Advance Notice of Proposed Rulemaking: Hydraulic Fracturing Chemicals and Mixtures, 2014).

Under TSCA more appropriate steps are being taken to gather chemical information, improve access to information, and promote safer chemical use for HF and potentially acid fracturing. Chemical information, access to information, and promoting safer chemical use for matrix acidizing and acid maintenance is an obvious inclusion that is needed in the ANPR. Improving transparency from industry by focusing on one technology and ignoring an associated sister technology falls short of protecting the public.

e) The Emergency Planning and Community Right-To-Know Act (1986) (EPCRA)

Access to information about acidizing and its chemicals is crucial in having accountability and protecting the public. The Emergency Planning and Community Right-To-Know Act (EPCRA) is focused on community safety and is designed to help communities protect public health, safety, and the environment from chemical hazards. It includes emergency planning, emergency notification of spills above Reportable Quantities defined under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to state and local officials, and "Community Right-to-Know" reporting on hazardous and toxic chemicals. Under Sections 311 and 312 of EPCRA, facilities that manufacture, process, or store designated hazardous chemicals must make Material Safety Data Sheets (MSDS), describing the properties and health effects of these chemicals available to state and local officials and local fire departments. Facilities must also provide state and local officials and local fire departments with inventories of all on-site chemicals for which MSDS exist. Information about chemical inventories at facilities and MSDS must be available to the public. Facilities that store over 10,000 pounds of hazardous chemicals are subject to this requirement. Any hazardous chemicals above the threshold stored at O&G production and processing sites must be reported in this manner.

Section 313 of EPCRA authorizes EPA's Toxics Release Inventory (TRI), which is a publicly available database that contains information on toxic chemical releases and waste management activities reported annually by certain industries as well as federal facilities. A special form must be submitted for each of the over 600 TRI chemicals that are manufactured or otherwise used above the applicable threshold quantities. Some acidizing chemicals are on this list. EPA issues a list of industries that must report releases for the database. To date, EPA has not included O&G extraction as an industry that must report under TRI. This is not an exemption in the law. Rather it is a decision by EPA that this industry is not a high priority for reporting under TRI.

EPA has the authority to designate O&G extraction a high priority industry. Operators acidizing wells should submit information on the TRI chemicals that are manufactured or used above the applicable threshold quantities. The acidizing chemicals reported in California that appear on the list are:

- 1,2,4-trimethylbenzene
- acetophenone
- acrylamide
- acrylonitrile
- benzene
- cumene
- ethylbenzene
- ethylene glycol
- ethylene oxide
- formaldehyde
- formic acid
- hydroflouric acid
- methanol
- naphthalene
- nitrilotriacetic acid
- quinaldine
- sulfuric acid
- toluene
- xylene

Many of these are used far above the applicable threshold quantitates in the 1000's kg/treatment (Abdullah et al., 2016). UOG stimulation activities, including HF and acidizing, undoubtedly should make O&G a high priority industry that must report annually on the TRI chemicals used above threshold quantities.

f) The Resource Conservation and Recovery Act (1976) (RCRA)

The Resource Conservation and Recovery Act (RCRA) creates the framework for properly managing hazardous and non-hazardous solid waste. Subtitle C gives EPA the authority to regulate the generation, transportation, treatment, storage, and disposal of hazardous waste. This is commonly referred to as a “cradle-to-grave” regulatory program. Subtitle D provides a framework for regulating non-hazardous solid waste.

The definition of hazardous waste under RCRA is “a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may cause or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness or pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.” If a waste is classified as a hazardous waste, there are more stringent requirements.

Many O&G wastes are exempt from regulation as hazardous waste. These wastes are generally subject to non-hazardous waste regulation under RCRA Subtitle D and applicable state regulations. Many state governments have specific regulations and guidance for O&G wastes.

As the use of UOG stimulation has increased, it is crucial that wastes from O&G activities be managed properly. O&G waste has changed from 1988, when the EPA determined that O&G field wastes were not hazardous wastes. Chemicals information about HF and acidizing show the use of dozens of hazardous chemicals in large quantities (CCST, 2014; Stringfellow et al., 2014; Abdullah et al., 2016). Besides the chemicals that are injected, the formation water contains many chemicals. Much of the stimulation fluid that returns is saltier than seawater (~35,000 mg/L), and can be >300,000 mg/L; it contains oil and grease, inorganic and organic toxic chemicals, and naturally occurring radioactive material. During 2012, 21.2 billion barrels of produced water were generated in the United States (Veil, 2015). The waste constituents have changed as well as the volumes. States and other federal agencies (BLM) are trying to address the waste management issue, but wastes from acidizing and other UOG stimulations must be considered hazardous waste and regulated under Subtitle C.

g) The Comprehensive Environmental Response, Compensation, and Liability Act (1980) (CERCLA)

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) regulates the clean up of hazardous substance releases. It requires the reporting of hazardous substance releases, as well as the location of hazardous storage, treatment, and disposal sites. The statute also establishes the Superfund, a trust fund to pay for hazardous waste clean up, derived from taxes imposed on oil and chemicals, as well as fines and penalties levied by the EPA. CERCLA is a remedial statute that covers clean up from spills of hazardous substances and thus does not regulate acidization operations directly.

D. Discussion

Table 4 summarizes the federal acts discussed and defines if acidization is regulated.

Table 4: Summary of Regulations

Regulation	Description	Is Acidization Covered?
The Federal Land Policy and Management Act (FLPMA)	Governs the way in which the public lands administered by the Bureau of Land Management are managed.	Yes
The National Environmental Policy Act (NEPA)	Requires federal agencies to review environmental impacts of a proposed action and possible alternatives for actions that involves federal funding, work performed by the federal government, or permits issued by a federal agency.	Yes, but there are certain O&G categorical exemptions.
The Clean Air Act (CAA)	Regulates air emissions from stationary and mobile sources.	Yes, but limited applicability because acidizing operations not considered a "major source," and there are no New Source Performance Standards (NSPS) addressing all acidizing techniques.
The Safe Drinking Water Act (SDWA)	Sets standards for drinking water quality and implements various technical and financial programs to ensure drinking water safety. Controls the injection of wastes into groundwater through the Underground Injection Control (UIC) program.	Possibly covered under UIC program (HF is exempt, but matrix acidizing and acid fracturing may still be covered).
The Clean Water Act (CWA)	Regulates the treatment and discharge of wastewater into surface waters of the United States. Sets national standards for industrial wastewater discharges to surface waters and municipal sewage treatment plants.	Indirect and direct discharges are regulated. However there is no permit required for stormwater run-off from acidizing operation sites.

The Toxic Substances Control Act (TSCA)	Requires reporting, record-keeping and testing requirements, and restrictions relating to chemical substances and/or mixtures.	Yes, but limited applicability (may cover acid fracturing).
The Emergency Planning and Community Right-To-Know Act (EPCRA)	Requires emergency planning, emergency notification of spills above Reportable Quantities defined under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) to state and local officials, and "Community Right-to-Know" reporting on hazardous and toxic chemicals (Toxic Release Inventory (TRI)).	Yes, larger facilities are subject to the requirements but under the TRI O&G is not required to report.
The Resource Conservation and Recovery Act (RCRA)	Creates the framework for properly managing hazardous and non-hazardous solid waste.	Yes, but acidizing waste considered a non-hazardous waste with less stringent management requirements.
The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)	Requires reporting of hazardous substance releases as well as the location of hazardous storage, treatment, and disposal sites. The statute also establishes the Superfund.	N/A, does not regulate acidizing but retroactively addresses damage.

From the outlined research in this paper we see that some federal bills exempt or have limited oversight over O&G operations. There have been recent concerns over the impacts of HF on human health and the environment, and recent discussions have called for increased regulatory oversight. Some acidizing well stimulations operationally are very similar to HF but have not received the same attention. Acidizing techniques use hazardous chemicals in higher concentrations than HF and should be better regulated.

As outlined in the table, we see that the FLPMA gives authority to BLM to determine if acidization can take place on leased land. The public has input in this process. The BLM had proposed new requirements that were challenged by the courts, to ensure wellbore integrity, protect water quality, and enhance public disclosure of chemicals and other details of HF operations under FLMPA but acidizing is not included. NEPA requires an environmental review of proposed acidizing activities if it is not under one of the categorical exclusions (CXs). The CXs can exclude acidizing activities if an environmental assessment occurred at an early stage. The nature of oil drilling, however, has changed in recent years and an environmental assessment at an early stage might not include unstudied O&G exploration technology impacts.

The CAA has limited applicability for acidizing because acidizing operations are not considered a "major source," and there are no New Source Performance Standards for it. The CWA has successfully called for pretreatment standards for indirect UOG wastes going to POWTs but direct discharges from stormwater coming from acidizing sites are still unregulated. Under TSCA EPA issued an Advance Notice of Proposed Rulemaking to obtain information on chemical substances and mixtures used in HF. Acid fracturing may be part of the definition of HF, but matrix acidizing isn't. Under the EPCRA EPA has not included O&G extraction as an industry that must report under Toxic Release Inventory. Thus acidizing is exempt. RCRA governs acidizing waste management, but acidizing waste is considered a non-hazardous waste with less stringent management requirements. Finally CERCLA is a remedial statue that deals with hazardous substance releases and so it doesn't regulate acidizing activity but retroactively addresses damage.

On the federal level there are a few opportunities to better regulate acidization:

- The Bureau of Land Management has proposed a new rule when permitting HF wells. The Clean Air Act has New Source Performance Standards (NSPS) for hydraulically drilled wells. Under section 8 of the Toxic Substance Control Act, EPA issued an Advance Notice of Proposed Rulemaking (ANPR) for HF chemicals and mixtures. In all these cases acidization should be included in new rules.

- The Safe Drinking Water Act may prove to be an effective way to regulate acidization activities. Although the Energy Policy Act of 2005 exempts HF, except where diesel is used, from its underground injection definition, acid fracturing and more likely matrix acidization, are not exempt. This finding will prove to be an area of great debate in the courts.

- A new rule under the Clean Water Act has established pretreatment standards for O&G extraction. This is a positive step. However, currently under the Clean Water Act stormwater discharge from O&G facilities do not require an Industrial Stormwater General Permit, unless a Reportable Quantity of a hazardous chemical is released or there is a violation of a water quality standard. Hazardous acidizing chemicals are used above the RQ limits. This in combination with acidizing waste being stored in surface impoundments creates a threat for surface water contamination. Stormwater discharges from acidizing operations should require permits and specific best management practices for the oil/gas industry should be recommended.

- Section 313 under The Emergency Planning and Community Right-To-Know Act (1986) authorizes EPA’s Toxics Release Inventory (TRI), which is a publicly available database that contains information on toxic chemical releases and waste management activities reported annually by certain industries as well as federal facilities. To date, EPA has not included O&G extraction as an industry that must report under TRI because it is not considered a high priority. There are close to a dozen acidizing chemicals that appear on the TRI inventory list. This should warrant reporting.

With increased oversight for HF, it is important that O&G development and production be reviewed as a whole. Some of the concerns that exist for HF apply to all of O&G exploration. For example, chemical waste returns, chemicals stored on site, and stormwater discharge of chemical laden fluid is a concern for most O&G exploration activities. Chemicals reaching USDWs are concerns for all UOG techniques, including acid fracturing and matrix acidization. These activities should not be ignored, especially when discussions are happening on how to effectively protect the public and the environment from potential harmful impacts of HF. New York State can be taken as an example. They conducted a study on the impacts from hydraulic fracturing and implemented a statewide ban. Although this research is not calling for such a ban, similar studies are being done across the US indicating potential impacts and it is necessary that a national framework be in place to ensure a consistent minimum level of protection for the public and environment.

E. References

149 Cong. Rec 167 (2003)

149 Cong. Rec 168 (2003)

151 Cong. Rec 52 (2005)

151 Cong. Rec 106 (2005)

Abdullah, K., Malloy, T., Stenstrom, M. K., & Suffet, I. H., 2016. Toxicity of acidization fluids used in California oil exploration. *Toxicological & Environmental Chemistry,* 1-17. doi:10.1080/02772248.2016.1160285

Adgate JL, Goldstein BD, McKenzie LM., 2014. Potential public health hazards, exposures and health effects from unconventional natural gas development. Environ Sci Technol 48(15):8307-8320.

Advance Notice of Proposed Rulemaking: Hydraulic Fracturing Chemicals and Mixtures**,** 2014. Toxic Substances Control Act.

Assessment of the potential impacts of hydraulic fracturing for oil and gas on drinking water resources: Executive summary, 2015. Washington, D.C.: EPA, Office of Research and Development.

Brady, W. J., & Crannell, J. P., 2012. Hydraulic Fracturing Regulation in the United States: The Laissez-Faire Approach of the Federal Government and Varying State

Regulations. *Vermont Journal of Environmental Law, 14*(1), 39. doi:10.2307/vermjenvilaw.14.1.39

CCST, 2014. *Advanced Well Stimulation Technologies in California*. California Council on Science and Technology, Lawrence Berkeley National Laboratory, Pacific Institute. Sacramento, CA.

CCST, 2015. *An Independent Scientific Assessment of Well Stimulation in California* Vol 2. California Council on Science and Technology, Lawrence Berkeley National Laboratory, Pacific Institute. Sacramento, CA.

Evaluation Of Impacts To Underground Sources Of Drinking Water By Hydraulic Fracturing Of Coalbed Methane Reservoirs 7-5, 2004. Envtl. Prot. Agency. *available at* http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/wells_coalbedmethanestudy.cfm/

H. Rept. 108-65, 2003. Retrieved from Congrees.gov

H. Rept. 109-215, 2005. Retrieved from Congrees.gov

Kiparsky, M., Foley Hein, J., 2013. Regulation of Hydraulic Fracturing in California: A Wastewater and Water Quality Perspective. Berkeley Law, Wheeler Institute for Water Law & Policy.

Konschnik, K., & Dayalu, A., 2016. Hydraulic fracturing chemicals reporting: Analysis of available data and recommendations for policymakers. *Energy Policy, 88*, 504-514. doi:10.1016/j.enpol.2015.11.002

Legal Environmental Assistance Fund. v. U.S. EPA, 118 F.3d 1467, 1478 (11th Cir. 1997).

McLeod, H.O., 1986. Matrix Acidizing to Improve Well Performance. Short Course Manual, Society of Petroleum Engineers. Richardson, TX .

Natural Gas Extraction - Hydraulic Fracturing, 2016. United States Environmental Protection Agency. Retrieved June 02, 2016, from https://www.epa.gov/hydraulicfracturing

Nazzaro, R. M., 2009. Energy Policy Act of 2005: Greater clarity needed to address concerns with categorical exclusions for oil and gas development under Section 390 of the Act: Report to congressional requesters (United States., Government Accountability Office.). Washington, D.C.: U.S. Govt. Accountability Office.

Oil and Natural Gas Sector: Emission Standards for New, Reconstructed, and Modified Sources, 40 CFR Part 60 (2016)

Oil and Gas; Hydraulic Fracturing on Federal and Indian Lands, 43 CFR Part 3160 (2015).

Oil and Natural Gas Sector: New Source Performance Standards and National Emission Standards for Hazardous Air Pollutants Reviews, 40 CFR Part 60-63 (2012).

Permitting Guidance for Oil and Gas Hydraulic Fracturing Activities Using Diesel Fuels:

Underground Injection Control Program Guidance #84 (2014), Washington, D.C.: EPA, Office of Water.

Rahm, D., 2011. Regulating hydraulic fracturing in shale gas plays: The case of Texas. *Energy Policy, 39*(5), 2974-2981. doi:10.1016/j.enpol.2011.03.009

Robertson Jr, J., G. Chilingarian, and S. Kumar., 1989. "*Surface Operations in Petroleum Production, II.*" New York: Elsevier Science Publishing Company, 171.

Safe Drinking Water Act of 1974, Pub. L. No. 93-523, 88 Stat. 1660, § 1421(d)(1) (1974).

State of Wyoming and State of Colorado vs. United States Department of the Interior, 2015. United States District Court of Wyoming. Case No. 2:15-CV-043-SWS

Stringfellow, W., Doman, J., Camarillo, M.K., Sandelin, W., and Borglin, S., 2014. "Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing." *Journal of Hazardous Materials* 275: 37-54. doi:10.1016/j.jhazmat.2014.04.040.

Williams, B.B., Gidley, J.L., and Schechter, R.S., 1979. Acidizing Fundamentals. Monograph Series, Society of Petroleum Engineers, Vol 8. New York.

Veil, J., 2015. U.S. Produced Water Volumes and Management Practices in 2012. Ground Water Protection Council.

V. California State Regulations for Acidization

A. Introduction

At the state level, California does not regulate all acidizing techniques, just matrix acidizing and acid fracturing. Acid maintenance, although not a “well stimulating” technique uses the same types of chemicals in similar amounts as regulated operations, and deals with more concentrated waste streams at the surface. In the previous chapter, federal regulations that govern acidizing operations were discussed. This section outlines the California state laws that regulate acidization and protect the public and environment from harmful impacts.

B. California State Bills and Regulations

1. The California Environmental Quality Act (CEQA)

The California Environmental Quality Act (CEQA), the state’s implementation of NEPA, requires that the State look at the environmental impacts of a proposed action and possible alternatives. It applies to discretionary projects carried out or approved by a public agency in California. Well stimulation projects are subject to the California Environmental Quality Act. An Environmental Impact Report (EIR) to evaluate the impacts of all existing and potential future O&G well stimulation, including matrix acidizing and acid fracturing in California, was completed in July 2015.

2. Senate Bill 1281

Senate Bill 1281 established the requirement for a quarterly water report, which must be filed online by all O&G well owners. This includes the source and volume of any water reported, along with water used to generate or make up the composition of any injected fluid or gas, as well as the treatment of water. This would include all acidizing techniques. It also requires the Division of Oil Gas and Geothermal Resources (DOGGR) to use a standardized form or format to facilitate reporting, and to use non-custom software, as feasible, to implement online reporting. DOGGR has developed a quarterly water report form in Microsoft Excel. The law provides that a person who fails to comply with specific laws relating to the regulation of oil or gas operations, including failing to furnish a report or record, is guilty of a misdemeanor.

3. Senate Bill 83 Section 45

Section 45 of SB 83 requires that the State Water Resources Control Board (SWRCB) report on the regulation of oil field produced water ponds (surface impoundments) within each region by January 30, 2016, and every six months thereafter. A produced water pond is a surface impoundment used to store and/or dispose of produced water. Acidizing waste can be stored in surface impoundments in California, and are predominantly unlined and used to dispose of produced water through evaporation and/or percolation (CCST, 2015).

4. Senate Bill 4

Senate Bill 4 requires oil companies seeking to “stimulate” wells after January 1, 2014 to file satisfactory certifications of compliance with key safeguards of groundwater testing (before/after), neighbor notification, and public disclosure of chemicals, well history, and locations online. For the public disclosure of chemicals, operators are allowed to withhold certain information if they deem it a trade secret. Acid fracturing and matrix acidizing are considered stimulation techniques covered by this bill. Acid maintenance is not included.

In addition to these requirements for operators, the bill requires that the Secretary of California's Natural Resources Agency complete an independent scientific study on well stimulation treatments, and the State Water Resources Control Board develop model criteria for groundwater monitoring and regional or well specific groundwater monitoring criteria by July 15, 2015.

The model criteria for groundwater monitoring has three main components:

- Area-specific required groundwater monitoring near stimulation wells by operators
- Requirements for designated contractor sampling and testing
- Regional scale groundwater monitoring to be implemented by the State Water Board

For area-specific monitoring the operators are required to submit an approved groundwater monitoring plan or a letter from the State Water Board staff concurring that there is no protected water to monitor for their well stimulation permit.

Table 5: Groundwater Monitoring Model Criteria

Scale	Responsibility	What
Well by well (supply well)	Well operator (permit)	Water supply well within 1 mile of oil and gas (O&G) well
Well by well (protected groundwater)	Well operator (permit)	Protected groundwater in close proximity to an individual or small set of O&G wells
Regional	Water Board	Groundwater basin O&G field

5. New California Industrial Stormwater General Permit Order

Effective July 2015, the new NPDES General Permit requires that O&G exploration facilities that discharge stormwater contaminated by contact with or that has come into contact with any overburden, raw material, intermediate products located on the site of such operations are now covered by the General Permit. At the federal level under the Clean Water Act O&G exploration facilities are not required to file for a permit for stormwater discharges unless there is a water quality violation. In California the O&G industry must obtain a permit or they can apply for a No Exposure Certification if they meet very specific criteria.

C. Conclusion

On the California state level, acid fracturing and matrix acidization operations are being regulated like hydraulic fracturing under Senate Bill 4. Acid maintenance is not regulated. Only recently has DOGGR also begun collecting information on acid maintenance activities but a full chemical disclosure is not required. Acid maintenance uses similar amounts and high concentrations of certain chemicals. The waste that returns is highly concentrated. It should be regulated under SB 4.

Another area that could be improved is how the chemical information is collected under SB4. Currently, operators are allowed to withhold certain information if it is a trade secret. Recent studies have shown that if a “systems approach” is used to collect chemical information operators are much more likely to share chemical information. Companies using the “systems approach” list all chemical ingredients added to the stimulation fluid, rather than linking those ingredients to particular fracturing/etching fluid products. Commentators have recommended this approach believing it enables companies to share more information without fear of reverse engineering by competitors (Konschnik and Dayalu, 2016).

D. References

CCST, 2015. *An Independent Scientific Assessment of Well Stimulation in California* Vol 2. California Council on Science and Technology, Lawrence Berkeley National Laboratory, Pacific Institute. Sacramento, CA.

Konschnik, K., & Dayalu, A., 2016. Hydraulic fracturing chemicals reporting: Analysis of available data and recommendations for policymakers. *Energy Policy, 88*, 504-514. doi:10.1016/j.enpol.2015.11.002

VI. Regulating Oil and Gas Facility Stormwater Discharge

A. Abstract

Contaminated stormwater runoff from oil and gas (O&G) operations can pose a significant threat to surface waters. The purpose of this study is to examine the extent of this threat and recommend more specific permitting requirements and best management practices to protect surface waters. By eliminating the exposure of oil and gas operations to stormwater runoff and controlling pollutants in discharges, surface water is better protected. To determine if a significant threat exists, this paper analyzes spill reports and stormwater permit compliance in two California counties. It also reviews selected spill cases and associated Spill Prevention, Control and Countermeasure Plans and Stormwater Pollution Prevention Plans to identify the adequacy of current industry practices.

The analysis shows that on the federal level stormwater contamination from O&G facilities is not well regulated. The U.S. Environmental Protection Agency does not require O&G

facilities to file for an Industrial Stormwater General Permit even though many O&G industry practices have the potential to contaminate stormwater runoff from the site. When O&G facilities discharge a Reportable Quantity of a hazardous chemical or violate a water quality standard they are required to enroll in the National Pollutant Discharge Elimination System permit program. Spills, although not a direct indication of stormwater runoff, can illustrate the risk of potential polluted runoff discharges that should be regulated. The medium and large spills that reached waterways discussed in this paper potentially violated a water quality standard but did not file for a permit. In California new filing requirements for oil and gas industry require all facilities that discharge stormwater that has come into contact with any overburden, raw material, or intermediate products located on the site, to file for an Industrial Stormwater General Permit. As this study shows, the new requirements in California are capturing a larger pool of facilities within a regulatory framework for the protection of water quality. The federal government should consider such an approach. A further step would be to compel the industry to implement more specific pollution control practices than the current general permit requires.

There is growing evidence that regulatory protocols must be in place to protect surface waters from stormwater runoff pollutants from oil and gas facilities. There are too many spills that are not being contained, and even after spills have occurred, facilities are not complying with regulations that require greater scrutiny over their actions. There is a need to both understand the potential threat from oil and gas activities to surface waters from contaminated stormwater, as well as have the regulations in place to prevent any contamination. The purpose of this paper is to shed light on the threat and the need for appropriate regulations.

B. Introduction

O&G exploration and development is a large global industry, and it is likely to expand in the near future due to technological advances and the increased cost-effectiveness of unconventional oil stimulation techniques. With increased activity, there are a variety of ways in which pollutants can get into our waterways, especially if the activity goes unregulated. Stormwater runoff from these sites has largely been unregulated. Stormwater transports debris, chemicals, sediment and other pollutants, and if those pollutants get into our waterways, they can adversely impact wildlife, cause algae blooms and increase flooding (Stormwater Quality, 2016).

1. Oil and Gas Contamination of Stormwater

There are many O&G field operations that can contribute to contamination of stormwater. They include but are not limited to drilling and production equipment and other machinery, raw materials, waste products and by-products, O&G treatment units, finished products, storage areas, fuels and lubricants, and waste treatment areas (EPA, 2006). The activities, pollutant sources, and pollutants detailed in Table 1 are commonly found at O&G extraction facilities.

Construction activity is a major source of pollutant discharge, both from sediment and also the equipment and materials used. O&G construction sites have the potential to produce as much sediment as other types of construction sites (McBroom et al., 2012; Williams et al., 2008). Well drilling, well stimulations, and well production are all sources of increased total suspended solids (TSS) and total dissolved solids (TDS), and pollutants including oil and grease as well as a large variety of hazardous chemicals listed as chemicals requiring reporting under the Clean Water Act.

In California, surface impoundments are often used to store produced water from unconventional oil stimulation activities. Although no studies have looked at the impact of stormwater runoff from surface impoundments, these impoundments are potentially a source of contaminated stormwater runoff during rain events if not contained.

Vehicles and equipment on site are another source of TSS, TDS, oil and grease, and pH alterations. Oil fields with more wells are greater threats to stormwater pollution. Well density is positively correlated with in-stream turbidity measurements (Entrekin et al., 2011) and increased TSS concentrations (Olmstead et al., 2013).

Table 6: Common Activities, Pollutant Sources, and Associated Pollutants at Oil and Gas Extraction Facilities (EPA, 2006)

Activity	Pollutant Source	Pollutant/Altered Condition
Construction of: access roads drill pads mud/reserve pits personnel quarters surface impoundments storage tanks pipelines	Soil/dirt, leaking equipment, and vehicles	Total suspended solids (TSS), total dissolved solids (TDS), oil and grease
Well drilling	Drilling fluid, lubricants, mud, cuttings, and produced water	TSS, TDS, oil and grease, chemical oxygen demand (COD), chlorides, barium, naphthalene, benzene, lead, arsenic, fluoride

Well completion/ stimulation	Fluids (used to control pressure in well), cement, residual oil, acids, surfactants, solvents, produced water, and sand	TSS, TDS, oil and grease, COD, acid, acetone, toluene, ethanol, xylenes
Production	Produced water, oil, waste sludge, tank bottoms, acids, oily debris, and emulsions	Chlorides, TDS, oil and grease, TSS, pH, benzene, phenanthrene, barium, arsenic, lead, antimony
Vehicle and equipment cleaning and repairing	Cleaning solvents, lubricants, and chemical additives	TSS, TDS, oil and grease, pH
Site closures	Residual muds and oily debris	TSS, TDS, oil and grease, pH
Vehicle fueling	Diesel fuel	TSS, TDS, oil and grease

2. Oil and Gas Exploration and Production Stormwater Regulations

The Clean Water Act regulates the treatment and discharge of wastewater into surface waters of the United States. It sets national standards for industrial wastewater discharges to surface waters – which is known as direct discharge – and municipal sewage treatment plants (also known as publicly owned treatment works or POTWs) – which is known as indirect discharge – based on the performance of treatment and control technologies.

Direct discharges are subject to the National Pollutant Discharge Elimination System (NPDES) permit program. The permit contains limits on what can be discharged, monitoring and reporting requirements, and other provisions to ensure that the discharge does not hurt water quality or people's health. There are two basic types of NPDES permits issued: an individual permit and a general permit. An individual permit is a permit specifically tailored to an individual facility, and a general permit covers a group of dischargers with similar qualities within a given geographical location. In certain cases there are more sector/industry specific permits/requirements, such as the Washington

States boatyard permit (Boatyard General Permit) or California Regional Water Quality Control Board Santa Ana Region's sector-specific general permit for storm water runoff associated with industrial activities from scrap metal recycling facilities (General Permit Exec. Order No. NPDES NO CAS618001).

Stormwater runoff is a direct discharge. Common requirements for the Industrial Stormwater General Permit include development of a written Stormwater Pollution Prevention Plan (SWPPP), implementation of control measures, and submittal of a request for permit coverage, usually referred to as the Notice of Intent or NOI. The SWPPP is a written assessment of potential sources of pollutants in stormwater runoff and measures that will be implemented at the facility to minimize the discharge of these pollutants in runoff from the site. These measures include site-specific best management practices (BMPs), maintenance plans, inspections, employee training, and reporting. The procedures detailed in the SWPPP must be implemented by the facility and updated as necessary, with a copy of the SWPPP kept on-site. The Industrial Stormwater General Permit also requires collection of visual, analytical, and/or compliance monitoring data to determine the effectiveness of implemented BMPs (EPA).

Direct discharges from O&G sites are subject to the NPDES permit program, with the exception of coal bed methane. There can be no discharge of water pollutants from any source associated with production, field exploration, drilling, well completion, or well treatment, except for wastewater that is of good enough quality for use in agricultural and wildlife propagation.

Stormwater, however, has largely gone unregulated at O&G sites. O&G site runoff is exempted from the NPDES program, unless a facility has a discharge of Reportable Quantity (RQ) or contributes to a violation of a water quality standard *(40 CFR 122.26(a)(2))*. This includes discharges that cause a film or sheen, or a discoloration of the water surface or adjoining shorelines, or causes a sludge or emulsion to be deposited beneath the water surface or upon adjoining shorelines. Reportable Quantity is a determined limit for specific hazardous chemicals pursuant to section 311 of The Clean Water Act.

Proving a discharge of RQ or even noting a violation of a water quality standard is a very difficult task. Monitoring at the right time and place is necessary to note if stormwater of such conditions was released. Such monitoring only happens if a facility is enrolled in the NPDES program.

The stormwater discharge exemption proves challenging when trying to prevent waterway contamination from O&G sites. Although this exemption exists there is Residual Designation Authority in the CWA that allows for regulating an activity that may adversely impact surface waters. A delegated state such as California also has this authority. It states that, "the EPA Regional Administrator may designate additional stormwater discharges as requiring NPDES permits where he determines that the discharge, or category of discharges within a geographic area, contributes to a violation of a water quality standard or is a significant contributor of pollutants to waters of the United States (40 CFR 122.26)."

Effective July 2015, California has designated that all O&G facilities that discharge stormwater contaminated by contact with, or that has come into contact with any overburden, raw material, intermediate products located on the site of such operations, must file for an Industrial Stormwater (General Permit Exec. Order No. NPDES NO. CAS000001, 2014). O&G exploration and production facilities that drain to waterways must now submit an application to be covered by the Industrial Stormwater General Permit or file a No Exposure Certification. A No Exposure Certification means that the entity identified does not require permit authorization for its stormwater discharges associated with industrial activity due to the existence of a condition of no exposure. In the new order it also states, "when developing the next reissuance of this General Permit, the State Water Board expects to have a better understanding of the feasibility and benefits of sector-specific and watershed based permitting alternatives, which may include technology – or water quality based numeric effluent limitation (Exec. Order No. NPDES NO. CAS000001, 2014)." This means that the State Water Board recognizes that sector-specific permitting may be a necessary for certain industries, O&G included.

As part of the CWA, EPA also requires certain oil drilling facilities to prepare and implement Spill Prevention, Control and Countermeasure (SPCC) plans to prevent discharge of oil into navigable waters or adjoining shorelines. Facilities that must prepare and implement SPCC plans include: non-transportation related facilities; facilities that have an aggregate above ground storage capacity over 1,320 gallons or a buried storage capacity over 42,000 gallons; and facilities that have a reasonable expectation of discharging into or upon navigable waters or adjoining shorelines (40 CFR 122).

The SPCC plan and the NPDES permit program are intended to capture potential sources of pollutants that may contaminate surface water. However, often the suggested protocol and measures taken are too generic for them to be effective for the specific industry. With no industry specific permits there is no guidance as to where and how representative and effective monitoring should take place, what industry specific constituents should be monitored, or which BMPs serve that industries needs. With no industry specific recommendations, it is left up to operators to implement or not implement measures. If appropriate monitoring is not happening it is not capturing any violations. As this paper will show in the results section there is only a very small fraction of O&G operators that are enrolled in the NPDES permit program.

At the national level, only spills that exceed a Reportable Quantity or contribute to a water quality violation require notification to be covered by the general permit for stormwater discharges. In California, all O&G exploration and production facilities that drain to waterways must submit an application to be covered by the Industrial Stormwater General Permit or file for a No Exposure Certification. At issue is the fact that an important industry is either not being regulated at the federal level or being regulated with very general pollution prevention and control requirements when more specific control measures would be appropriate to reduce the risk of contamination of waterways.

The purpose of this study is to examine if O&G exploration and production operations present a significant threat to surface water and recommend more specific permitting requirements and custom tailored BMPs to eliminate the exposure of O&G operations to stormwater runoff and/or to control pollutants in discharges to protect surface waters. To determine if a significant threat exists—

which if does exist, the EPA Regional Administrator may designate additional stormwater discharges as requiring NPDES permits— this paper analyzes spill reports, Industrial Stormwater General Permit compliance, and current unconventional oil stimulation stormwater permit compliance given the increase in this practice in two California Counties. It also reviews selected spill cases and associated SWPP and SPCC plans to identify adequacy of current industry practices. Finally, the paper looks at waste surface impoundments at O&G facilities in California and the operation and maintenance practices to assess if they too pose a threat. Surface impoundments are used to store a variety of potentially toxic, as well as non-hazardous liquid and solid wastes associated with O&G development. The chemicals may leach into groundwater; contaminate soils and vegetation; or overflow from the sides of the impoundment—either during a rain event, or due to inadequate storage—and pollute soil and surface waters. Drilling fluids and wastes, production chemicals and wastes, and produced water are some of the fluids stored in surface impoundments (*Managing industrial solid wastes from manufacturing, mining, O&G production, and utility coal combustion, 1992)*.

C. Methods

There is no one decisive way to determine if stormwater from O&G exploration and production poses a significant threat. Contaminated stormwater quality and volumes from oil and gas exploration and production sites depends on site-specific consideration including overall housekeeping and spill prevention practices, rainfall, and total runoff area. This study conducted a survey of O&G spills and O&G stormwater permit compliance in Kern County and Ventura County, California for the time period of 2010-2016. Reviewing the types and sizes of spills at oil fields can inform on whether the current industry practices pose a significant threat to the environment. For the larger spills (those above 10,000 gallons), reviewing corresponding facility SPCC and SWPP plans will give a better understanding if written plans are specific enough to prevent such spills. O&G facilities that spill chemicals of Reportable Quantity (RQ) or contribute to a violation of a water quality standard must enroll in the NPDES permit program. Looking at permit compliance would be useful in determining the effectiveness of the current regulatory framework that is being implemented to mitigate stormwater pollution.

The use of unconventional oil and gas (UOG) stimulation techniques has increased dramatically over the last 5 years. Most of the reporting on UOG stimulation in California has really only begun in the last 2 years. Given the new NPDES Industrial Stormwater General Permit requirements for O&G facilities that went into effect July 2015, it would be useful to see how permit compliance has changed in relation to UOG exploration. The analysis will be done for Kern County and Ventura County, California. Kern County is the main hub of UOG stimulation techniques in California; much of the county is oil fields. Ventura County has O&G activity but to a lesser extent than Kern County. Ventura County is more representative of an area that has residential, commercial, and industrial areas spread out over a county. The following sections describe the methods used for the various analyses.

1. Oil and Gas Exploration and Production Spill Analysis

We used data from the California Office of Emergency Services (Cal OES) for hazardous material release information. The data was downloaded in March 2016 from the Cal OES website for the years 2010-2016. The Excel sheets provide spill details including, date, time, location, substance type, amount spilled, and a general description of the cause of the spill. It also provides information on the type of immediate impact, including surface water contamination or fatalities and injuries involved. The responsible party and the agency reported to are also listed.

The data was filtered to include only spills that occurred on oil fields in Kern and Ventura counties. The assumption is that spills entail runoff. The spills were classified by size. There are no standard definitions for small, medium, or large spills. A variation of the United States Coastal Guard (USCG) threshold cutoffs was used. USCG classifies a small spill as less than 24 oil barrels (bbl), a medium spill as less than 240 bbl, and a large spill as greater than or equal to 240 bbl (Anderson, Mayes, LaBelle, 2012). One bbl represents 42 gallons. Ten bbl was used as the lower end of a small spill because according to the Department of Oil, Gas, and Geothermal Resources (DOGGR) it is considered significant for spill management purposes (Department of Conservation, 1998). The study also determined which spills reached waterways.

Table 7: Spill Classification

Spill Size	Spill Amount
Small	10 - < 24 bbl (< 1000 gallons)
Medium	24 - < 240 bbl (1000-10,000 gallons)
Large	≥ 240 bbl (>10,000 gallons)

* 1 bbl (oil barrel) = 42 US gallons

Once the information on oil field spills in Kern County and Ventura County was collected, the State Water Resources Control Board's (SWRCB) Stormwater Multiple Application and Report Tracking System (SMARTS) was used to see which facilities filed for an Industrial Stormwater General Permit. SMARTS was developed as an online database for dischargers to electronically file their stormwater permit documents. The database was searched using the Standard Industrial Code (SIC) 13xx; this applies to the O&G industry. The time frame of the study was from 2010-2016. Some of the information included in the database is the application type (Industrial, No Exposure Certification, etc.), its status (active or terminated), status date, and the operator/owner name and address. As the regulation states, prior to July 2015 in California "when a facility has a discharge of reportable quantity for which notification is required or contributes to a violation of a water quality standard" they are required to be enrolled in the NPDES permit program. Post July 2015, all O&G facilities are required to enroll in the Industrial Stormwater General Permit program if they "discharge stormwater contaminated by contact with or that has come into contact with any overburden, raw material, intermediate products located on the site"(General Permit Exec. Order No. NPDES NO. CAS000001, 2014).

2. Analysis of Selected Spill Cases and Associated SPCC and SWPP Plans

The largest spills in Kern County and Ventura County were identified as case studies to understand the adequacy of current industry practices. SPCC plans for these facilities were sought out. Representatives from DOGGR were contacted to obtain the SPCC plans. The SMARTS site was used to find the associated SWPP Plans.

3. Oil and Gas Facility Industrial Stormwater General Permit Compliance Analysis

This analysis looked at how many O&G facilities filed for an Industrial Stormwater General Permit pre/post the new Industrial Stormwater General Permit requirements for O&G in California. The analysis determined how many facilities had a permit prior to and after July 2015 for Kern and Ventura County. The analysis also focused on UOG stimulation operations to see how many facilities filed for an Industrial Stormwater General Permit pre/post the new Industrial Stormwater General Permit requirements. Reporting on UOG stimulation techniques, including HF, acid fracturing, and matrix acidization, began in 2014 in California through the interim Senate Bill 4 (SB4) and is now required through the SB4 bill as of July 2015. The analysis looked at how many UOG stimulation facilities filed with DOGGR also filed for the Industrial Stormwater General Permit, and how many more were prompted to register after the new requirements. This might give an idea of whether the new permit requirement promoted O&G to file for a permit. Unless a facility is entirely contained it is likely that all operators would need to be covered by the Industrial Stormwater General Permit post July 2015.

Industrial Stormwater General Permit information was obtained from the California State Water Board's SMARTS system using SIC 13xx to narrow down to O&G industry up until April of 2016. To get information on UOG stimulation facilities, a representative at DOGGR gave a list of all the disclosures submitted to them.

4. Surface Impoundments

Section 45 of California Senate Bill 83 requires that the State Water Resources Control Board report on the regulation of oil field produced water ponds within each region by January 30, 2016, and every six months thereafter. This report was reviewed to understand surface impoundment use and makeup in the State of California. The literature was searched to see in what capacity surface impoundments are used and what the operation entails.

D. Results

1. Oil and Gas Exploration and Production Spill Analysis Results

The results for the spill analysis for both counties are below.

Table 8: Oil Field Spill Analysis for Ventura and Kern County, California (January 2010 - March 2016)

	Ventura County	Kern County
# of spills	61	316
# of medium spills (24-240bbl)	7	47
# of large spills (≥240bbl)	0	10
# in contact w/waterways	22	34
# of different facilities/entities reporting spills	14	70
Which facility/entity was covered by NPDES permit	California Resources Production Corp (Industrial)	Inergy (Industrial) Schlumberger (Notice of non-applicability) Chevron (Notice of non-applicability)

There are fewer spills in Ventura County compared to Kern County because it is not as active an oil-producing county. There were a total of 61 reported spills from January 2010 - March 2016. Of those 61 spills, 7 were of medium size (24 – 240 bbl) and the rest were small spills. For the medium sized spill, only 1 of the 4 entities responsible had an active permit. There were 22 spills that came in contact with waterways, of which only 1 entity of the 6 responsible had an active permit. There were 14 different entities that reported the 61 spills, meaning the same entities had repeated spill instances. The only entity that was covered by the Industrial Stormwater General Permit was California Resources Production Corp. If one assumes that the spills met the reporting requirements, few to no facilities filed for a permit.

There were 316 spills in Kern County during the study time frame. Of those 316, 47 were medium sized spills (24 – 240 bbl) with only one of the 14 entities responsible for the spills having a Notice of Non-Applicability. A Notice of Non-Applicability would indicate that the site was either enclosed, there was no stormwater discharge/exposure, they were not required to be permitted by federal regulation, they were regulated by another permit, there was a new facility operator or they never operated the facility. There were 10 large spills (> 240 bbl) and only one of the 5 entities responsible had a Notice of Non-applicability. Of the 34 spills that reached waterways, only one of 20 entities responsible had a Notice of Non-applicability. There were a total of 70 entities responsible for the 316 spills, only 3 filed in the NPDES program; Inergy had an Industrial Stormwater General Permit; Schlumberger and Chevron submitted a Notice of Non-Applicability, Chevron being responsible for one of the large, medium, and contact with waterway spills. In Kern County as well only a very small percentage filed for a permit.

For the medium/large spills and/or those that reached waterways, the responsible entity most likely would have needed to notify the Water board and have been enrolled in the

NPDES program. However, there is very little overlap between who the polluters were and who is covered by the NPDES permit.

2. Analysis of Selected Spill Cases and Associated SPCC and SWPP Plans

After sorting through the Ventura and Kern County oil field spills, the 3 largest spills were chosen in each county as case studies. Information about the spills is taken directly from the Cal OES site and is in the tables below.

Table 9: Ventura County Medium Sized Spills

Entity	Permit Status	Spill Size	Spill Description
California Resources Production Corp.	Active Industrial Stormwater General Permit	100 bbl produced water	A hole in a 4" pipe spilled onto a private road on the leased property (oil production lease); some release entered a nearby metal culvert and then into a soil ravine.
Vintage Productions California	Terminated Permit	65 bbl crude oil	During hydrotesting of a line, built up pressure caused a spray of oil and water onto trees over a dry creek bed.
Vintage Production LLC	Terminated Permit	60 bbl produced water/crude oil	A broken hose caused this release.

The largest spills in Ventura County were of medium size. The 3 case studies involved spills of 60-100bbls of produced water and/or crude oil. Produced water contains many chemicals either from the injected fluid or formation waters (CCST, 2014), and it accounts for 96 to 98 percent of all O&G wastes (*Managing industrial solid wastes from manufacturing, mining, O&G production, and utility coal combustion*, 1992). These medium sized spills were either caused by a faulty pipe/hose, or build up of pressure; in two of the releases, waterways were reached. California Resources Production Corp was the only entity covered by the NPDES general industrial permit.

Ventura County Facility SPPC and SWPP Plans:

There were no SPCC plans obtained for these three sites. California Resources Production Corp. was the only one with a SWPP plan on file (See Supplemental Section). The SWPP plan had specific best management practices listed. Of particular interest were the general BMPs. These included; containing all stored non-solid industrial materials or wastes that can be transported or dispersed by the wind or contact with stormwater during handling; and covering industrial waste disposal containers and industrial material storage containers that contain industrial materials when not in use. The advanced BMP used was berming/containment around tank batteries and well pads. Tank batteries are constructed with secondary means of containment with the volume capacity of the containment designed to exceed the contents of the largest tank within the facility and with sufficient freeboard to contain precipitation. Well pads are constructed of earthen berms and/or well cellars to contain liquids on location. There are open drains within the site, which collect miscellaneous fluids from the containment areas. These drains are piped and transported to a central sump from which they are pumped for proper disposal. Containment structures are inspected regularly for deficiencies and repairs are made as necessary.

Table 10: Kern County Large Sized Spills

Entity	Permit Status	Spill Size	Spill Description
Berry Petroleum	No Permit	700 bbl Water – Produced type used for well kill	A rain event occurred over the area and filled a concrete cellar that a well sits in and floated residual oil to the surface, resulting in the release of crude oil on a dry, unknown creek bed.

Plains All American Pipeline	No Permit	600 bbl Produced Water	Produced water line failure caused the release of approximately 5 gallons of crude oil into a dry waterway; the rest of the release went to land only, impacting no waterway.
Chevron USA Inc.	Notice of Non-Applicability	500 bbl Produced Water	Corrosion on a 3" flow line caused a release to a blue line (stream).

The largest spills in Kern County were 500-700bbl of produced water; the largest of these spills occurring after a rain event. This is just one case that shows that rain events can cause stormwater pollution issues from O&G facilities. Preventing overflows from rain events is possible if the facility is entirely covered or contained. The remaining two spills were caused by faulty pipes lines. Only one operator, Chevron USA Inc. had a Notice of Non-Applicability.

Kern County Facility SPPC and SWPP Plans:

There were two associated SPCC plans obtained; one for the Plains All American Pipeline site and the other for Chevron site. The first SPCC plan had an annual pipeline inspection plan and monthly facility maintenance plan for primarily checking equipment integrity. In addition there was a general spill protocol outlined. There was no discussion of any secondary containment. The SPCC plan was not very specific in its prevention protocol. Chevron's SPCC plan had similar spill and maintenance protocol, but the site was designed with containment berms and had a valve shut-off protocol. Because the facilities was entirely contained Chevron appropriately filed for a Notice of Non-Applicability. In this case the site was contained and the spill did not cause a threat to surface waters. As for SWPP plans there were none found for the spill sites of concern.

From the limited information it seems as though SWPP plans include more specific BMPs to manage stormwater and protect surface water than the SPCC plans. The reason for this may be that an assessment of potential sources of pollutants in stormwater runoff is required in the NPDES program, as are measures to minimize the discharge of these pollutants in runoff from the site. The Industrial Stormwater General Permit also requires collection of visual, analytical, and/or compliance monitoring data to determine the effectiveness of implemented BMPs.

Ideally, there needs to be specific guidance and requirements for O&G facilities to prevent spill and overflow. Currently there are no industry specific requirements. EPA has a list of BMPS for potential pollutant sources at oil and gas extraction facilities that will be discussed later (EPA, 2006), as well as more specific guidance for oil and gas construction sites provided by the Independent Petroleum Association of America (Reasonable and Prudent Practices for Stabilization (RAPPS) of Oil and Gas Construction Sites, 2004).

3. Oil and Gas Exploration and Production Industrial Stormwater General Permit Compliance Analysis

This study also looked at Ventura and Kern County’s active O&G facilities to see how many filed for an Industrial Stormwater General Permit pre/post the new requirements. This covered until March of 2016. In Ventura County there were 36 Active permits, 10 of those filed post July 2015. This is a substantial percentage (28%) that enrolled in a short time frame of 8 months (July 2015 – March 2016) after the new permit requirements. In Kern

County there were 45 Active NPDES permits; 27 of those were post the new requirements. In Kern County 60% enrolled after the new order. The new Industrial Stormwater General Permit requirements had a large proportion of operators enroll in the program in a short time span. Surprisingly, facilities where spills occurred did not file for permits.

Table 11: O&G Facilities Filing for NPDES Permit Pre/Post New NPDES Permit Order

County	# of NPDES Permit Before July 2015	# of NPDES Permits After July 2015
Ventura	36	10
Kern	45	27

There were 9 different UOG stimulation facilities filing for well stimulation permits with DOGGR prior to the new Industrial Stormwater General Permit requirements and only one applied for a Notice of Non-applicability. About 10% of operators filed for a permit. After the new requirements, there were five different entities filing for well stimulation permits with DOGGR; two filed for a Industrial Stormwater General Permit, and one filed a Notice of Non-applicability. Post new requirements, 60% of the UOG facilities filed for a permit.

Table 12: UOG Facilities Filing for NPDES Permit Pre/Post New NPDES Order

	Before July 2015	After July 2015
# DOGGR UOG facilities	9	5
# DOGGR UOG facilities w/NPDES permit	1	3
% UOG facilities obtaining NPDES permit	10%	60%

This analysis shows that the new requirements for O&G facilities to file for a Industrial Stormwater General Permit in California is encouraging more O&G facilities to enroll in the NPDES permit program. This however does not mean better regulatory control or pollution reduction. There needs be specific best management practices for O&G as well as specific requirements for known polluters. However having all O&G at least enroll in the program is a first step that that the federal government can follow California's example in.

4. Surface Impoundments Analysis

Surface impoundments, sometimes referred to as ponds, can be another source of contaminated runoff. They are used for temporarily storing drilling fluids for use in drilling operations, settling/skimming of solids and separation of residual oil, storage of produced waters prior to injection or off-site transport, percolation of liquids via drainage or seepage into surrounding soil, and evaporation of produced waters into the atmosphere (Karami et. al., 2013).

In California, surface impoundments are permitted by the Regional Water Quality Control Boards. In California, surface impoundments are predominantly unlined and used to dispose of produced water through evaporation and/or percolation. Produced waters account for 96 to 98 percent of all O&G wastes (*Managing industrial solid wastes from manufacturing, mining, O&G production, and utility coal combustion*, 1992). An estimated 1.9 billion barrels of water were produced during oil extraction in the Central Valley in 2013. Approximately 12% (12 billion gallons) was disposed into sumps or recycled (Zinky, 2016).

Section 45 of California Senate Bill 83 requires that the State Water Board report on the regulation of oil field produced water ponds within each region by January 30, 2016, and every six months thereafter. The first report contains information from the Central Coast and Central Valley Water Boards, and includes the total number of ponds in each region, the number of permitted and unpermitted ponds, enforcement actions, and the status of permitting the unpermitted ponds. Enforcement Actions include Informational Orders (13267), Notices of Violations and Cleanup and Abatement Orders.

Table 13: SWRCB Oil Field Produced Water Ponds Report as of January 30, 2016

Regional Water Board	Active Ponds		Inactive Ponds		Total Ponds		Enforcement Actions
	Permitted	Un-permitted	Permitted	Un-permitted	Permitted	Un-permitted	
Central Coast	3	41	0	8	3	49	52
Central Valley	530	162	101	269	631	431	1062
Total	533	203	101	277	634	480	1114

In the Central Coast most of the active and inactive ponds were unpermitted and there were enforcement actions against most of them. In the Central Valley about 40% of the ponds were unpermitted, and almost all the ponds had enforcement actions against them. The use of ponds is very pervasive, especially in the Central Valley where most of the O&G exploration and production takes place. Unpermitted ponds and ponds violating code indicate that best protocol to protect surface waters from improper containment practices are not in place.

A survey of the literature concluded that there are no current reports on surface impoundments. The EPA produced a few reports in the 70s and early 80s but none published recently. There were no articles found on surface impoundments and surface water threats.

5. Best Management Practices

Currently the requirements in place for the O&G industry to prevent surface water contamination from stormwater runoff are very general. Ideally, having specific BMPs tailored to the industry would provide better protection. There are a few guidance documents with more specific recommendations for O&G facilities. Two were developed by the US EPA, one looking at BMPs for potential pollutant source (EPA, 2010) and the other providing voluntary practices for oil and gas wastes (EPA, 2014). Another document by the Independent Petroleum Association of America (IPAA) identifies practices for stabilization of O&G construction sites. These documents could be sources to establish requirements for a more industry specific stormwater permit. Currently most of the BMPs recommended in these documents don’t have defined performance standards. The guidance provided by the IPAA provides more details for scoping the BMPs to stabilize O&G construction sites. The table below lists the BMPs the EPA recommends. Although many are general recommendations there is specific guidance that could be used in the permitting process.

Table 14: BMPs for Potential Pollutant Sources at O&G Extraction Facilities (EPA, 2010)

Pollutant Source	BMPs
Construction	• Limit the amount of land disturbed during construction of access roads and facilities and preserve existing vegetation. • Implement erosion and sediment controls such as vegetated swales, diversion berms, or dikes to limit or isolate land disturbance and process areas to retain/detain flows and limit stormwater run-on in these areas. • Divert stormwater away from contaminated areas. Inspect the area regularly to ensure BMPs are implemented and maintained.
Well drilling	• Use diking and other forms of containment and diversion around storage tanks, oil drums, acid, production chemicals and liquids, reserve pits, and impoundments. • Use diking and other forms of containment and diversion around material handling and processing areas. • Use porous pads under drum and tank storage areas.

	• Use covers and/or lining for waste reserve and sludge pits to avoid overflows and leaks. • Use drip pans, catch basins, or liners during handling of materials such as tank bottoms. • Re-use collected stormwater for industrial process or as an irrigation source. • Develop and implement spill plans for pipelines, tanks, drums, etc. • Recycle oily wastes, drilling fluids and other materials on-site, or dispose offsite. • Use oil - water separators. • Inspect the area regularly to ensure BMPs are implemented and maintained.
Well completion	• Utilize diking and other forms of containment and diversion around storage tanks, oil drums, acid, production chemicals and liquids, reserve pits, and impoundments. • Use diking and other forms of containment and diversion around material handling and processing areas. • Use porous pads under drum and tank storage areas. • Use covers and/or lining for waste reserve and sludge pits to avoid overflows and leaks. • Use drip pans, catch basins, or liners during handling of materials such as tank bottoms. • Re-inject or treat produced water instead of discharging it. • Re-use collected stormwater for industrial process or as an irrigation source. • Develop and implement spill plans for pipelines, tanks, drums, etc. • Recycle oily wastes, drilling fluids and other materials on-site, or dispose of offsite. • Use oil water separators. • Inspect the area regularly to ensure BMPs are implemented and maintained.
Vehicle and equipment cleaning and maintenance	Good Housekeeping • Eliminate floor drains that are connected to the storm or sanitary sewer; if necessary, install a sump that is pumped regularly. Collected wastes should be properly treated or disposed of by a licensed waste disposal company. • Prevent and contain spills and drips. • Do all cleaning at a centralized station so the solvents stay in one area. • If parts are dipped in liquid, remove them slowly to avoid spills. • Use drip pans, drain boards, and drying racks to direct drips back into a fluid holding tank for reuse. • Drain all parts of fluids prior to disposal. Oil filters can be crushed and recycled. • Promptly transfer used fluids to the proper container; do not leave full drip pans or other open containers around the shop. Empty and clean drip pans and containers.

	• Clean up leaks, drips, and other spills without using large amounts of water. Use absorbents for dry cleanup whenever possible. • Prohibit the practice of hosing down an area where the practice would result in the discharge of pollutants to a stormwater system. • Do not pour liquid waste into floor drains, sinks, outdoor storm drain inlets, or other storm drains or sewer connections. • Maintain an organized inventory of materials. Eliminate or reduce the number and amount of hazardous materials and waste by substituting nonhazardous or less hazardous materials. • Label and track the recycling of waste material (e.g., used oil, spent solvents, batteries). • Store batteries and other significant materials inside. • Dispose of greasy rags, oil filters, air filters, batteries, spent coolant, and degreasers in compliance with RCRA regulations. Minimizing Exposure • Perform all cleaning operations indoors or under covering when possible. Conduct the cleaning operations in an area with a concrete floor with no floor drainage other than to sanitary sewers or treatment facilities. • If operations are uncovered, perform them on a concrete pad that is impervious and contained. Park vehicles and equipment indoors or under a roof whenever possible and maintain proper control of oil leaks/spills. • Check vehicles closely for leaks and use pans to collect fluid when leaks occur. Management of Runoff • Use berms, curbs, or grassed swales other diversion measures to ensure that stormwater runoff from other parts of the facility does not flow over the maintenance area. • Collect the stormwater runoff from the cleaning area and provide treatment or recycling. • Discharge vehicle wash or rinse water to the sanitary sewer (if allowed by sewer authority), wastewater treatment, a land application site, or recycle on-site. DO NOT discharge washwater to a storm drain or to surface water. Inspections and Training • Inspect the maintenance area regularly to ensure BMPs are implemented. • Train employees on waste control and disposal procedures.
Vehicle fueling	Stationary fueling areas • Conduct fueling operations (including the transfer of fuel from tank trucks) on an impervious or contained pad and under a roof or canopy where possible. Covering should extend beyond spill containment pad to prevent rain from entering. • When fueling in uncovered area, use concrete pad (asphalt is not chemically resistant to the fuels being handled). • Use drip pans where leaks or spills of fuel can occur and where making and breaking hose connections.

	• Use fueling hoses with check valves to prevent hose drainage after filling. • Keep spill cleanup materials readily available. • Clean up spills and leaks immediately. • Use dry cleanup methods for fuel area rather than hosing down the fuel area. Sweep up absorbents as soon as spilled substances have been absorbed. • Do not "top-off" fuel tanks. • Use spill and overflow protection devices. • Minimize/eliminate run-on into fueling areas with diversion dikes, berms, curbing, surface grading or other equivalent measures. • Collect stormwater runoff and provide treatment or recycling. • Provide curbing or posts around fuel pumps to prevent collisions from vehicles. • Regularly inspect and perform preventive maintenance on fuel storage tanks to detect potential leaks before they occur. • Inspect the fueling area for leaks and spills. Train personnel on vehicle fueling BMPs. Mobile fueling areas • Use drip pan under the transfer hose. • Use fueling hoses with check valves to prevent hose drainage after filling. • Ensure the fueling vehicle is equipped with a manual shutoff valve. • Do not allow topping off of the fuel in the receiving equipment. • Train personnel on vehicle fueling BMPs.

E. Discussion

The analysis shows that on the federal level stormwater contamination from O&G facilities is not well regulated. At the federal level O&G facilities do not need to file for an Industrial Stormwater General Permit even though many O&G industry practices contaminate stormwater runoff from the site. When O&G facilities discharge a RQ or violate a water quality standard they are required to enroll in the NPDES program. Spills, although not a direct indication of stormwater runoff, can give some idea of potential polluted runoff that should be regulated. If we assume the medium and large spills in this study that reached waterways violated a water quality standard then those facilities must have an active permit on file. However, what we see is that most of those facilities are not filing for a permit. In California new filing requirements for oil and gas industry require all facilities that discharge stormwater contaminated by contact with, or that has come into contact with any overburden, raw material, intermediate products located on the site of such operations, to file for an Industrial Stormwater General Permit. The new requirements have captured a larger pool of facilities in the program. The federal government should follow suit in requiring similar permitting of all O&G facilities. Nonetheless, the permit is general in nature and may not provide the industry with the more specific requirements that it needs. There is a need for industry tailored stormwater permit requirements.

For the Ventura County and Kern County medium and large sized spill case studies, there were only two associated SPCC plans and one SWPP plan that were obtained. One site's SPCC plans show that measures in place are very general; they may be able to detect faulty equipment but do not address containment issues. The other SPCC plan was for an enclosed facility whose spill did not reach waterways. The SWPP plan provides more specific recommendations for sites that are in contact with waterways. From this limited sample it seems like being enrolled in the NPDES permit program ensures better BMPs to prevent contaminated stormwater releases. Having even more specific BMPs would be more protective.

Surface impoundments at O&G facilities can be a serious threat to waterways. In California there are thousands of these impoundments, currently most are unlined and many are unpermitted. Almost all are in some sort of violation. Proper oversight and development of surface impoundments is needed. Many states have banned the use of surface impoundments for the many problems associated with them, overflows being one of them.

Given the sources of runoff contamination from O&G industry practices, problems with spills, and surface impoundments, all O&G facilities should be covered under the Industrial Stormwater General Permit, which is the current California approach. It should not be left up to facilities to identify when a violation has occurred and then file for a permit. The authors recommend a tiered permitting approach nationally. The tiers should relate to spills as well as toxicity of chemicals used. All O&G facilities should file for the Industrial Stormwater General Permit for potential stormwater discharges as the first tier. The next tier of facilities would be regulated more strictly in cases of spills or use of toxic chemicals. If there is a medium sized spill (24 - 240 bbls) or hazardous chemicals are used that appear on the Reportable Quantity list or have a toxicity grade of an F, as identified in the second chapter, the operator must file for a sector specific permit as the second tier, which calls for more specific protocols for the O&G sector. The BMPs identified in this paper can be incorporated in such a permit. If there is a large sized spill (> 240 bbls) or hazardous chemicals (identified in the second tier of reporting) are used in quantities above identified thresholds the operator must file for a site-specific individual permit under the third tier. This allows for more scrutiny and oversight. A tiered approach gives operators an incentive to prevent spills, use safer chemicals, and employ BMPs.

At the California State level all O&G are required to file for an NPDES permit. To ensure that this happens it can be a requirement for all facilities obtaining a drilling permit from

DOGGR to file for a permit with the Water Board. There can be a permit block from DOGGR stating that no O&G stimulation will be permitted until an NPDES permit has been filed for. Such inter-agency dependency can enhance the effectiveness of rules and better protect the public and environment.

There is growing evidence that regulatory protocols must be in place to protect surface waters from contamination from O&G facilities. In California there are too many spills that are not being contained, and even after spills have occurred, facilities are not complying with regulations that require greater scrutiny over their actions. There is a need to both understand the potential threat from O&G activities to surface waters from contaminated stormwater as well as have the regulations in place to prevent any contamination. It is hoped that this paper sheds light on the threat and the need for appropriate regulations concerning O&G stormwater management.

F. References

Anderson, M., Mayes, M., and LaBelle, R., 2012. Update of Occurrence Rates for Offshore Oil Spills. Department of Interior Bureau of Ocean Energy Management and Bureau of Safety and Environmental Enforcement. BOEM 2012-069 BSEE 2012-069

Boatyard General Permit. Washington State Department of Ecology http://www.ecy.wa.gov/programs/wq/permits/boatyard/index.html

Department of Conservation, 1998. Field Rule, San Joaquin Valley, Oil Spill Reporting Criteria.

Entrekin, S., Evans-White, M., Johnson, B., and Hagenbuch, E., 2011. Rapid expansion of natural gas development poses a threat to surface waters. *Frontiers in Ecology and the Environment, 9*(9), 503-511. doi: 10.1890/110053

EPA. Does Your Facility Need a Stormwater Permit? An Industrial Facility Operator's Guide to EPA's Stormwater Permit Program. Office of Compliance and Enforcement Region 10. EPA 910-K-09-008

EPA, 2006. Industrial Stormwater, Sector 1: Oil and Gas Extraction Facilities. EPA Office of Water. EPA-833-F-06-024

EPA, 2010. Spill Prevention, Control, And Countermeasure (SPCC) Regulation; A Facility Owner/Operator's Guide To Oil Pollution Prevention. Epa 540-K-09-001

EPA, 2014. Compilation of Publicly Available Sources of Voluntary Management Practices for Oil and Gas Exploration & Production (E&P) Wastes As They Address Pits, Tanks, and Land Application. US Environmental Protection Agency Office of Solid Waste and Emergency Response Office of Resource Conservation and Recovery.

Exec. Order No. NPDES NO. CAS000001, 3 C.F.R. 12 (2014).

Exec. Order No. NPDES NO. CAS618001, 3 C.F.R. 12 (2012)

Karami S, Torkashvand P, Mozafari S, Goudarzi A, Ghodsi M., 2013. The basic steps in waste management in the oil and gas exploration and production processes. Annals of Biological Research, 2013, 4 (4):19-22

Managing industrial solid wastes from manufacturing, mining, oil and gas production, and utility coal combustion, 1992. Washington, DC: Congress of the U.S., Office of Technology Assessment.

McBroom, M., Thomas, T., & Zhang, Y., 2012. Soil erosion and surface water quality impacts of natural gas development in East Texas, USA. *Water, 4*(4), 944-958. doi: 10.3390/w4040944

Olmstead, Sheila M., Muehlenbachs, Lucija A., Shih, Jhih-Shyang, Chu, Ziyan, & Krupnick, Alan J., 2013. Shale gas development impacts on surface water quality in Pennsylvania. *Proceedings of the National Academy of Sciences of the United States of America, 110*(13), 6.

Reasonable and Prudent Practices for Stabilization (RAPPS) of Oil and Gas Construction Sites, 2004. Independent Petroleum Association of American.

Stormwater Quality, 2016. https://www.denvergov.org/content/denvergov/en/wastewater-management/stormwater-quality.html

State Water Resources Control Board. http://www.waterboards.ca.gov/losangeles/water_issues/programs/stormwater/sw_industrial.shtml

Williams, H. F. L., Havens, D. L., Banks, K. E., & Wachal, D. J., 2008. Field-based monitoring of sediment runoff from natural gas well sites in Denton County, Texas, USA. *Environmental Geology, 55*(7), 1463-1471. doi: 10.1007/s00254-007-1096-9

Zinky, J., 2016. *Implementation of Senate Bill 4 Requirements*. California State Control Water Resources Board. Lecture presented at American Chemical Society, San Diego. March 2016.

VII. Conclusion

The use of unconventional oil and gas stimulation is projected to rise in the next decades. The research and regulatory communities are starting to address some of the concerns regarding potential impacts to the public and environment. A greater focus has been on hydraulic fracturing (HF), both on its potential impacts and how to best regulate the practice. Acidizing, though a sister-technology, has mostly been ignored. The research shows that it is being used quite frequently, and the concerns that have arisen for HF also hold true for acidizing.

Taking a closer look at its use in California, the analysis 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 chemicals are the most commonly used HF treatment chemicals. Unlike HF, the chemical concentrations in the fluids for acidization are high, ranging from 6-18% chemicals, and the waste that returns is also highly acidic.

The amounts of chemical used per treatment are anywhere between 100's of milligrams to 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.

Furthermore the flow back 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 identify possible impacts we might see in the near to distant future on humans and other living organisms.

Regulating acidizing is also crucial in protecting the public and environment from any unintended consequences. From the outlined research in this dissertation we see that many federal bills exempt O&G operations from regulatory oversight. There have been recent concerns over the impacts of HF on human health and the environment. Recent discussions have called for increased regulatory oversight for HF events. Some acidizing well stimulations operationally are very similar to HF but have not received the same attention. Acidizing techniques use hazardous chemicals in higher concentrations than HF and should be better regulated.

On the federal level there are a few opportunities to better regulate acidization:

- The Bureau of Land Management has proposed a new rule when permitting HF wells. The Clean Air Act has New Source Performance Standards (NSPS) for hydraulically drilled wells. Under section 8 of the Toxic Substance Control Act, EPA issued an Advance Notice of Proposed Rulemaking (ANPR) for HF chemicals and mixtures. In all these cases acidization should be included in new rules.

- The Safe Drinking Water Act may prove to be an effective way to regulate acidization activities. Although the Energy Policy Act of 2005 exempts HF, except where diesel is used, from its underground injection definition acid fracturing and more likely matrix acidization, are not exempt. This finding will prove to be an area of great debate in the courts.

- A new proposed rule under the Clean Water Act is establishing pretreatment standards for O&G extraction. This is a positive step and the acidizing chemicals should be looked at when setting the standards. Currently under the Clean Water Act, stormwater discharge from O&G facilities do not require an Industrial Stormwater General Permit, unless a Reportable Quantity of a hazardous chemical is released or there is a violation of a water quality standard. Hazardous acidizing chemicals are used above the RQ limits. In combination with acidizing waste being stored in surface impoundments creates a threat for surface water contamination. Stormwater discharges from acidizing operations should require permits and specific best management practices for the oil/gas industry should be recommended.

- Section 313 under The Emergency Planning and Community Right-To-Know Act (1986) authorizes EPA's Toxics Release Inventory (TRI), which is a publicly available database that contains information on toxic chemical releases and waste management activities reported annually by certain industries as well as federal facilities. To date, EPA has not included O&G extraction as an industry that must report under TRI because it is not considered a high priority. There are close to a dozen acidizing chemicals that appear on the TRI inventory list. This should warrant reporting.

Taking a more detailed look at protecting surface waters from O&G stormwater, the analysis shows that on the federal level stormwater contamination from O&G facilities is not well regulated. At the federal level, O&G facilities do not need to file for an Industrial Stormwater General Permit even though many O&G industry practices contaminate stormwater runoff from the site. When O&G facilities discharge a RQ or violate a water quality standard they are required to enroll in the NPDES program. The research shows that medium and large spills that reached waterways may have violated a water quality standard but only a few filed for a permit. In California new filing requirements for oil and gas industry require all facilities that discharge stormwater contaminated by contact with or that has come into contact with any overburden, raw material, intermediate products located on the site of such operations to file for an Industrial Stormwater General Permit. The new requirements have captured a larger pool of facilities in the program. The federal government should follow suit in requiring similar permitting of all O&G facilities. Nonetheless, the permit is general in nature and may not provide the industry with the more specific requirements that it needs. There is a need for industry tailored stormwater permit requirements.

There is growing evidence that regulatory protocols must be in place to protect surface waters from contamination from O&G facilities. There are too many spills that are not being contained, and even after spills have occurred, facilities are not following regulations that require greater scrutiny over their actions. There is a need to both understand the potential threat from O&G activities to surface waters from contaminated stormwater as well as have the regulations in place to prevent any contamination.

It's important that O&G development and production be reviewed as a whole. Some of the concerns that exist for HF apply to all of O&G exploration. For example, chemical waste returns, chemicals stored on site, and stormwater discharge of chemical laden fluid is a concern for most O&G exploration activities. Chemicals reaching USDWs are concerns for all UOG techniques, including acid fracturing and matrix acidization. These activities should not be ignored, especially when discussions are happening on how to effectively protect the public and the environment from potential harmful impacts of HF. A national framework is needed to ensure a consistent minimum level of protection for the public and environment.

What is evident from the research of this dissertation on acidization – the chemicals used, their toxicity, the regulatory oversight – is that a narrow scope of looking at just one oil and gas operation like HF is not enough to protect the public and environment. The O&G industry as a whole has evolved and is evolving substantially. Having a comprehensive approach at looking at impacts from all unconventional oil stimulation techniques, like acidizing, is crucial in protecting the public and environment from any future harm. It is hoped that with this research acidization becomes part of the larger discussion on concerns with oil exploration and is evaluated by appropriate authorities.

VIII. Appendix

A. Spill Prevention Control and Countermeasure Plans; Stormwater Pollution Prevention Plan