Chapter Two

Impacts of Well Stimulation on Water Resources

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2.1. Abstract

We have analyzed the hazards and potential impacts of well stimulation on California's water resources. Our analysis addresses: (1) the characteristics of water use for well stimulation; (2) the volumes, chemical compositions, and potential hazards of stimulation fluids; (3) the characteristics of wastewater production and management; (4) the potential release mechanisms and transport pathways by which well stimulation chemicals enter the water environment; and (5) practices to mitigate or avoid impacts to water.

Available records indicate that well stimulation in California uses an estimated 850,000 to 1.2 million m^3 (690 to 980 acre-feet) of water per year, the majority of which (91%) is freshwater. Hydraulic fracturing has allowed oil and gas production from some new pools where it was not otherwise feasible or economical. We estimate that freshwater use for enhanced oil recovery in fields where production is *enabled* by stimulation was 2 million to 14 million m^3 (1,600 to 13,000 acre-feet) in 2013. (Well stimulation includes hydraulic fracturing, matrix acidizing, and acid fracturing; enhanced oil recovery includes water flooding, steam flooding, and cyclic steaming, described briefly in Section 2.3 below.) Local impacts of water usage appear thus far to be minimal, with well stimulation accounting for less than 0.2% percent of total annual freshwater use within each of the state's Water Resources Planning Areas, which range in size from 830 to 19,400 km^2 (320 to 7,500 mi^2). However, well stimulation is concentrated in water-scarce areas of the state, and an increase in water use or drawdown of local aquifers could cause competition with agricultural, municipal, or domestic water users.

Over 300 unique chemicals were identified as being used in hydraulic fracturing fluids in California. Of the chemicals voluntarily reported as used for hydraulic fracturing in California, over 200 were identified by their unique Chemical Abstracts Service Registry Number (CASRN). Chemical additives reported without a CASRN cannot be fully evaluated for hazard, risk, and environmental impacts due to lack of specific identification. Many of the chemicals reported for use in hydraulic fracturing are also used for other purposes during oil and gas development, including matrix acidizing. In an analysis of acid treatments, including both routine cleaning and matrix acidizing applications, over 70 chemicals were identified as being used in conjunction with acid, of which over 20 were not reported as used in hydraulic fracturing treatments.

Many of the chemicals used in California do not have the basic suite of physical, chemical, and biological analysis required to establish the chemicals' environmental and health profiles. For example, approximately one-half of chemicals used do not have publicly available results from standard aquatic toxicity tests. More than one-half are missing biodegradability, water-octanol partitioning analysis, or other characteristic measurements that are needed for understanding hazards and risks associated with chemicals.

Wastewater generated from stimulated wells in California includes "recovered fluids" (flowback fluids collected into tanks following stimulation, but before the start of production) and "produced water" (water extracted with oil and gas during production). Some information is known about the volumes of recovered fluids and produced water in California. Data from the Division of Oil, Gas, and Geothermal Resources (DOGGR) indicate that there is no substantive difference between the volume of produced water generated from stimulated wells and non-stimulated wells. Recent data submitted to DOGGR by operators show that the volume of recovered fluids collected after stimulation are a small fraction of the injected fluid volumes (<5%) for hydraulic fracturing treatments, but are higher (~50–60%) for matrix acidizing treatments. The data also show that the recovered fluids are a very small fraction of the produced water generated in the first month of operation. These results indicate that some fraction of returning stimulation fluids is present in the produced water from wells that have been hydraulically fractured.

Little is known about the chemical composition of wastewater from stimulated wells and unconventional oil and gas development. Under new regulations, chemical measurements are being made on recovered fluids, and results show that recovered fluids can contain high levels of some contaminants, including total carbohydrates (indicating the presence of guar) and total dissolved solids (TDS). Some data are available on produced water chemistry from conventional wells in California, but there were no data on the composition of produced waters from stimulated wells available during this study. Lack of understanding of the chemistry of produced water from stimulated wells is identified as a significant data gap.

The recovered fluids are typically stored in tanks at the well site prior to injection into Class II disposal wells. In California, produced water is typically managed via pipelines and disposed or reused in a variety of ways. From January 2011 to June 2014, reports

indicate nearly 60% of produced water from stimulated wells was disposed of by infiltration and evaporation using unlined pits. About one-quarter of the produced water from stimulated wells, or about 326,000 m³ (264 acre-feet), was injected into Class II wells for disposal or enhanced recovery. The disposition method for 17% of the produced water from stimulated wells is either not known or not reported. We note that operators have suggested that the data submitted to DOGGR may not reflect current operating practice due to mistakes in reporting to that agency. Although limited data are available on current treatment and reuse practices in California, it is probable that standard practice for oil-water separation and treatment prior to reuse are unlikely to remove most well stimulation chemicals or their byproducts that may be found in produced water.

Several plausible mechanisms and pathways associated with well stimulation can lead to release of contaminants into surface and groundwater. The release mechanisms of highest priority result from operations that are part of historically accepted practices in the California oil and gas industry, such as disposal of produced water in unlined pits, injection of produced water into potentially protected groundwater, reuse of produced water for irrigation, and disposal of produced water into sewer systems. The concerns related to produced water are relevant to well stimulation because (1) produced water from stimulated wells can contain returned stimulation fluids, and (2) the quality of formation water from stimulated reservoirs could differ from that of conventional reservoirs, and the extent to which they differ is currently unknown. Other concerns of medium priority are accidental releases, some of which need to be better studied. These include the possibility of fractures to serve as leakage pathways (since fracturing depths are much shallower in California than in other parts of the country), leakage through degraded inactive or active wells, and accidents leading to spills or leaks. Finally, there are other releases of low priority, such as operator error and illegal discharges that can be controlled with proper training, oversight, and monitoring.

A few sampling studies have been conducted to assess the impact of hydraulic fracturing on water quality. Only one sampling study has been conducted near a hydraulic fracturing site in California (in Inglewood), but incidents of potential contamination from other regions, such as Pennsylvania (Marcellus formation) and Texas (Barnett, Eagle Ford), can be used to determine potential release mechanisms and hazards, and provide considerations for future monitoring programs in California. While some of the sampling studies indicate that there has been water contamination associated with, and allegedly caused by, well stimulation, other studies did not find detectable impacts due to stimulation. Notably, most groundwater sampling studies do not even measure stimulation chemicals, partly because their full chemical composition and reaction products were unknown prior to this study. In general, groundwater contamination events are more difficult to detect than surface releases, because the effects and release pathways are not visible in the short-term, baseline water quality data are frequently absent, and sufficient monitoring has not been done to confirm the presence or absence of well-stimulation-induced contamination.

2.2. Introduction

Oil and gas development uses water resources and generates wastewater that must be managed by reuse or disposal. There is public concern that well stimulation technologies, especially hydraulic fracturing, may significantly increase water use by the oil and gas industry in California. There is further concern that handling, treatment, or disposal of stimulation fluids may contaminate water resources.

The water cycle of well stimulation consists of five stages (Figure 2.2-1):

1. acquisition of water needed for the stimulation fluids;

2. onsite mixing of chemicals to prepare the stimulation fluids;

3. injection of fluids into a target oil or gas formation during stimulation;

4. recovery of wastewater (flowback and produced water) following stimulation; and

5. treatment and reuse or disposal of wastewaters (after U.S. EPA, 2012a).
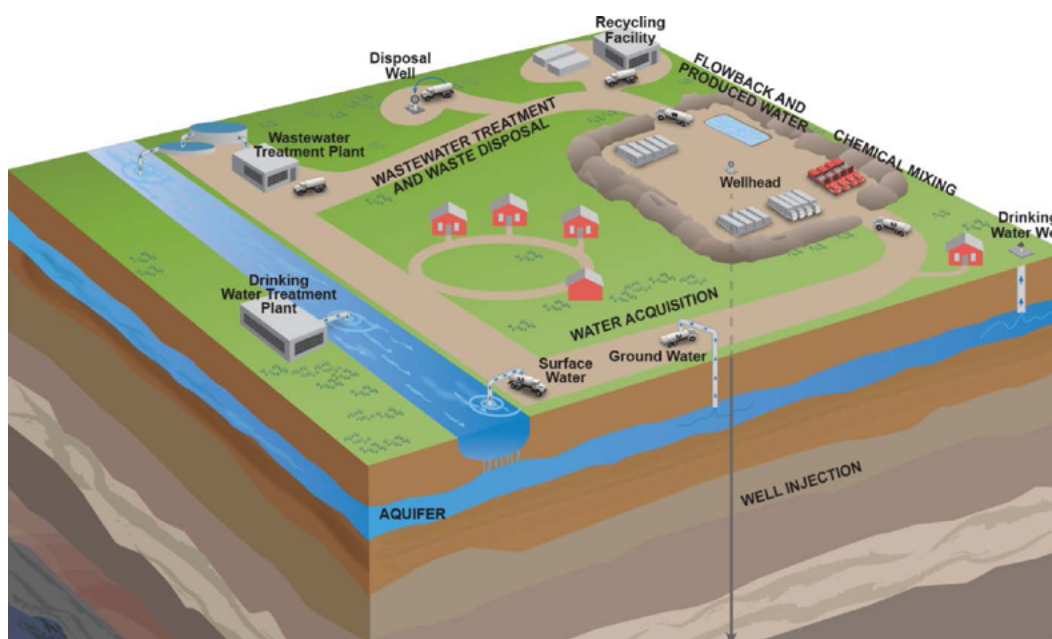

Figure 2.2-1. Five stages of the hydraulic fracturing water cycle (U.S. EPA, 2012a).

In this chapter, we describe and evaluate the hazards posed by well stimulation on California's water resources. Our analysis addresses the following questions:

- What are the volumes of freshwater used for well stimulation in California, and what are the sources of these supplies (e.g., domestic water supplies, private groundwater wells, irrigation sources)? How does water use for well stimulation compare with other uses in California and in the regions where well stimulation is occurring?

- What chemicals are being used for well stimulation in California? How often and in what amounts are these chemicals used? What are the physical, chemical, and toxicological properties of the stimulation chemicals used? To what extent does this chemical use create a hazard for and potential impacts on water resources in California?

- What volumes of recovered fluids and produced water are generated from stimulated wells, and what are the chemical compositions of those waters? Are volumes and chemical compositions of produced water generated from stimulated wells and non-stimulated wells different? How are recovered fluids and produced water managed (e.g., disposal by deep well injection or unlined pits)? Would existing treatment technologies for produced water remove well stimulation chemicals that are being used in California?

- What are the release mechanisms and transport pathways related to well stimulation activities that can potentially contaminate surface and groundwater resources in California? Is there evidence of how these releases can impact both surface and groundwater sources? What is the current state of knowledge about groundwater resources in California, particularly in areas where potential releases can occur?

- What are the best practices and measures that would avoid or mitigate impacts to water?

Our sources of information for addressing these questions consist of publicly accessible data, government reports, industry literature, patents, and peer-reviewed scientific literature. To the extent possible, we use data and information specific to California, which originate from several sources. Data sources for chemical and water use information include the FracFocus Chemical Disclosure Registry (www.FracFocus.org) that was available for early 2011 through mid-year 2014, and documentation required from operators under Senate Bill 4 (SB 4), available as of January 1, 2014, which includes *Well Stimulation Notices* (reporting on planned well stimulation activities) and *Well Stimulation Treatment Disclosure Reports* (reporting after stimulation is complete) (DOGGR, 2014a). We obtained information from the South Coast Air Quality Management District (SCAQMD) on water and chemical use during acid treatments that occurred within their

jurisdiction between June 2013 and June 2014 (SCAQMD 2013; SCAQMD 2014). Data on the location of oil and gas wells in California, both stimulated and non-stimulated, is compiled and distributed by DOGGR as a "shapefile," or geographic data file (DOGGR, 2014b). Additionally, the Central Valley Regional Water Quality Control Board (CVRWQCB) provided data on the disposal practices associated with unconventional oil and gas development (CVRWQCB, 2014; CVRWQCB, 2015). Data on produced water quantity—from both stimulated and non-stimulated wells—were obtained from the Monthly Production and Injection Database maintained by the California Division of Oil, Gas, and Geothermal Resources (DOGGR, 2014c).

In Section 2.3, we summarize the quantities and sources of water currently being used in California for well stimulation. The information on water use data is presented within the context of regional water use and within the context of other oil and gas production activities. Next, in Section 2.4, we describe the type and amount of chemicals being used in stimulation fluids in California. We discuss what is known about hazards associated with well stimulation chemicals, including the physical, chemical, and toxicological properties of the well stimulation chemicals that are used to evaluate risks associated with chemical use. In Section 2.5, we present analyses on the characteristics of wastewater from unconventional oil and gas development in California, including wastewater volumes and composition, as well as their disposal and beneficial reuse practices. In Section 2.6, we describe the release mechanisms and transport pathways relevant to well stimulation activities in California that can potentially lead to contamination of surface and groundwater resources—occurring through spills, surface and subsurface leaks, and current disposal and reuse practices. In Section 2.7, we discuss the potential impacts that the releases can have on surface and groundwater quality by (1) examining incidents (or the lack thereof) of contamination that have been reported in California and other states, and (2) assessing the current state of knowledge about groundwater in California, particularly in areas that may be impacted by well stimulation activities. We then discuss alternative practices that could potentially mitigate hazards induced by well stimulation in Section 2.8. In Section 2.9, we describe several data gaps that were identified through our analyses. We highlight our major findings in Section 2.10 and present conclusions in Section 2.11.

2.3. Water Use for Well Stimulation in California

2.3.1. Current Water Use for Well Stimulation

In this section, we estimate the volume of water currently used for well stimulation in California. Our estimate is based on (1) the average water-use intensity of well stimulation, i.e., the volume of water used per stimulation operation, and (2) the average number of well stimulations occurring in the state each month. We estimated the water-use intensity for each of the three stimulation methods under consideration (hydraulic fracturing, acid fracturing, and matrix acidization) by analyzing records of stimulation fluid volume reported by operators to state regulators and to the website

FracFocus from January 2011 to June 2014.[1] We estimated the number of well stimulation operations occurring each month from a search of oil and gas well records maintained by the California Department of Conservation's Division of Oil, Gas, and Geothermal Resources (DOGGR 2014). In terms of the number of wells that have been hydraulically fractured, we found that over the last decade, operators fractured about 40%–60% of the approximately 300 wells installed per month in California, leading us to estimate that 125 to 175 wells per month are hydraulically fractured in the state. Additional detail on how these quantities were estimated and the associated data sources is provided in Volume I, Chapter 3, *Historical and Current Application of Well Stimulation Technology in California*. Note that limited data were available for certain types of stimulation operations, such as for offshore operations and acid fracturing.

Figure 2.3-1 shows the range of reported water intensity of well stimulation (or the water volume used per stimulation operation) in California by stimulation method and well type. -1 reports our estimated number of well stimulations occurring each month in California and the *average* or *mean* water use intensity of these operations. Based on these data, we estimate that well stimulation in California uses 850,000 to 1,200,000 m³ (690–980 acre-feet) of water per year. We report a range of estimated water use to represent the uncertainty in the number of operations that are currently taking place. Operators use some water *directly* for well stimulation; chemicals are added to this "base fluid" and injected during stimulation operations. In addition, the availability of hydraulic fracturing has opened up some new areas to oil production, contributing to ongoing water uses for enhanced oil recovery. An analysis of production *enabled* by stimulation is presented below in Section 2.3.3.

1. No single source contained complete information on well stimulations in California prior to 2014, when reporting became mandatory under new regulations required by SB 4. Data sources included the FracFocus website, DOGGR All Wells shapefile, DOGGR Well Stimulation Notices, DOGGR Completion Reports, Central Valley Regional Water Quality Control Board, and the South Coast Air Quality Management District.
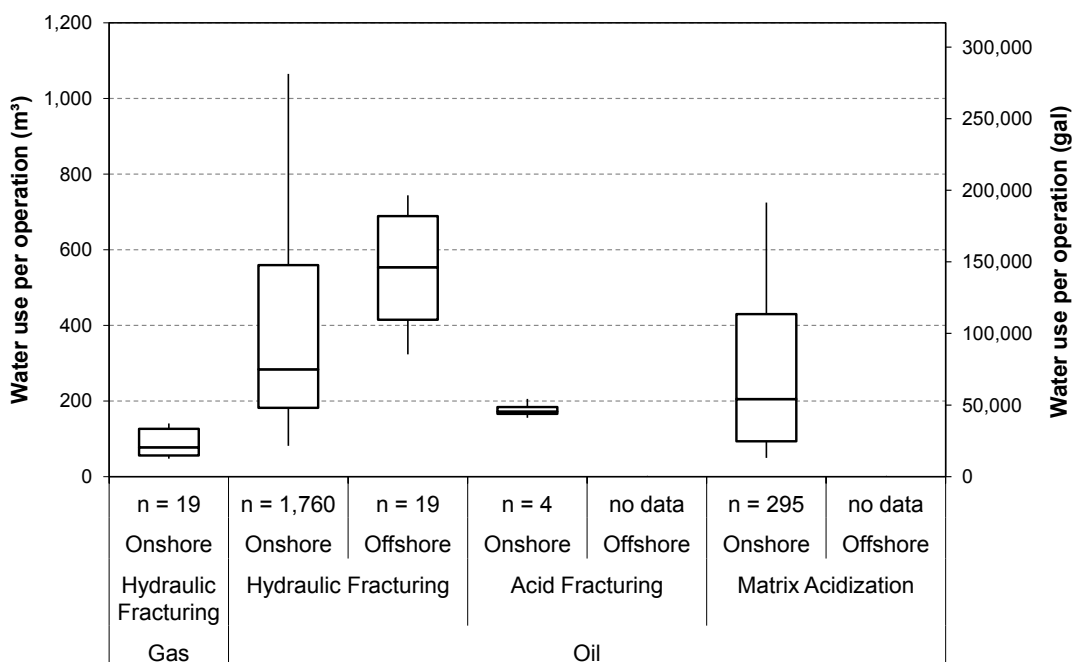
Figure 2.3-1. Boxplots showing range of reported water use per well for well stimulation in California (Jan 2011–Jun 2014) by well type and stimulation type. Box shows the 25th to 75th percentiles of the data. Central line shows the median. Whiskers extend to the 10th and 90th percentiles. Outliers are not shown (Data sources: FracFocus, 2014; DOGGR, 2014a; SCAQMD, 2014; CVRWQCB, 2014).

Table 2.3-1. Estimated volume of water use for oil and gas well stimulation operations in California under current conditions. Number of operations per month estimated for 2004–2014, and average water intensity estimated for Jan 2011 – June 2014.

	Number of operations per month	Average Water Intensity per well (m³ operation⁻¹)	Estimated Annual Water Use (m³)	Annual Water Use (acre-feet year⁻¹)
Hydraulic fracturing	125–175	530	800,000–1,100,000	640–900
Matrix acidizing	15–25	300	54,000–90,000	44–73
Acid fracturing	0–1	170	0–2,000	0–2
Total			**850,000–1,200,000**	**690–980**

Note: We report a range for estimated annual water use to reflect the uncertainty in the number of operations that are currently occurring. As described in Volume I (pages 104-105), we do not know the exact number of stimulation operations that occurred before 2014 because reporting was not mandatory. Our estimate of annual water use was found by multiplying the estimated number of stimulation operations occurring per year in California by the average water-use intensity per operation.

It is worth noting that water use reported to the state by operators for the first 11 months of 2014 (DOGGR, 2014a) was 171,000 m³ (140 acre-feet), significantly lower than our estimate of the typical annual water use for well stimulation of 850,000 to 1,200,000 m³ (690 to 980 acre-feet) per year, which was based on data from January 2011 to June 2014 obtained from multiple sources. This discrepancy appears to be due to a slowdown in the number of stimulation operations in 2014 compared to the three previous years. During 2014, there was an average of 44 stimulation operations each month, down from an estimated 140 to 200 operations per month during the years from 2011 through 2013. There could be several causes for this slowdown, including uncertainty among operators related to new regulations, public pressure, or dropping oil prices in the second half of 2014. The average water use per stimulation operation reported by operators in 2014 also appears to be somewhat lower than the historical rates of water use. Operators used an average of 390 m³ (0.32 acre-feet) for hydraulic fracturing operations in 2014, lower than the average water use of 530 m³ (0.43 acre-feet) during the previous three years.

2.3.2. Water Sources

We investigated where operators are acquiring water for well stimulation by analyzing data from well stimulation completion reports. Under new SB 4 regulations effective January 1, 2014, operators are required to send DOGGR a *Well Stimulation Treatment Disclosure Report*, referred to here as a "completion report," within 60 days after completing stimulation. On this form, operators identify the source of the water they used as a base fluid for stimulation. They also identify the *type* of water that makes up the base fluid, i.e., "water suitable for irrigation or domestic purposes," "water **not** suitable for irrigation or domestic purposes," or "fluid other than water."

There were 495 completion reports filed by operators and published by DOGGR between January 1 and December 10, 2014 (DOGGR, 2014a). Among these reports, there were 15 where the operator reported the volume of water use as zero, which we believe to be an error. We removed these records, and analyzed the remaining 480 reported stimulations. A summary of reported water use by source is shown in Table 2.3-2.

Operators obtained the water needed for well stimulation from nearby irrigation districts (68%), produced water (13%), operators' own wells (13%), a nearby municipal water supplier (4%), or a private landowner (1%). About a tenth of the total water volume was identified as water **not** suitable for irrigation or domestic use. Why the water was deemed unsuitable was not specified, but it is presumed that the water had high salt content. In California, freshwater is defined as having a TDS content less than 3,000 mg L⁻¹ (see Section 2.7).

Table 2.3-2. Water sources for well stimulation according to 480 well stimulation completion reports filed from January 1, 2014 to December 10, 2014.

Water Source	Number of Operations	Total Water Volume		Percent of Total Water Volume
		m³	acre-feet	
Irrigation district	399	117,000	95	68%
Produced water	43	23,000	18	13%
Own well	28	22,000	18	13%
Municipal water supplier	9	7,000	6	4%
Private landowner	1	2,000	2	1%
Total	**480**	**171,000**	**140**	**100%**

Of the 495 completion reports filed, all but two were for operations in Kern County. Many of the Kern County operations (397, or 83%) used water from the Belridge Water Storage District, which was formed to serve farmers in central Kern County with water provided by the State Water Project. The two submitted completion reports from outside of Kern County were in Ventura County and conducted by Aera Energy. These operations both used water from the Casitas Municipal Water Supply District, which provides water to about 70,000 people and several hundred farms in western Ventura County.

2.3.3. Water Use for Enhanced Oil Recovery

In this section, we analyze water use related to enhanced oil recovery. This analysis serves two purposes: first, to understand how the freshwater demand for well stimulation compares to freshwater demand for enhanced oil recovery; and second, to estimate the additional freshwater demand that occurs when stimulation technology allows production from new zones to be developed. The application of well stimulation technology has enabled production in some new pools where it would not have been likely to occur otherwise. The development of these pools creates additional demands for water, particularly for enhanced oil recovery. This water demand can be considered additional to the water that is used directly as the base fluid for well stimulation operations such as hydraulic fracturing. Below, we examine the water use for what we refer to as production *enabled* by well stimulation.

Water is used for a number of different purposes throughout the oil and gas production process, including drilling, well completion (during which well stimulation occurs), well cleanout, and for some types of enhanced oil recovery (EOR). Initially, oil production consists of simply producing oil and gas from the reservoir (primary production). In California, production in most reservoirs has been occurring for a span of time ranging from several decades to more than a century, so primary production has ended. Continued production requires additional processes including water flooding (secondary recovery) or, in California, steam flooding or cyclic steaming (two of many types of tertiary recovery). Water flooding and steam flooding involve continuous injection to push oil

toward production wells, and, in the case of steam, to also reduce the oil's viscosity along with other effects. Cyclic steam injection involves periodic injection of steam followed by a well shut-in period to allow the heat to reduce the oil viscosity, followed by a period of production, after which the cycle repeats.

We obtained information about the location and volume of water used for enhanced oil recovery from DOGGR's Production/Injection Database (DOGGR, 2014c). According to this data, there were 29,061 wells that injected water or steam into oil and gas reservoirs in 2013. DOGGR's database also contained information on the *type* and *source* of water injected.

We performed a series of analysis to determine the volume, type, and source of water used for EOR in California. These results are reported in Table 2.3-3. We found that in 2013, the total volume of water (or water converted to steam) injected by operators totaled 443 million m³ (360,000 acre-feet).

In terms of water *source*, operators reported that two-thirds of the water injected (288 million m³ or 233,000 acre-feet) was produced water, or water that is pumped to the surface along with oil and gas, and subsequently re-injected back into the formation, largely forming a closed loop system. Operators using solely produced water for injection are not generally competing with other water users. Approximately one-third of injected water was not produced water, which means operators obtained this water from another source. We refer to this water here as *externally sourced* water. Another 23% of injected water was externally sourced salt water; this includes saline groundwater (94 million m³, or 76,000 acre-feet) and ocean water (7 million m³, or 5,000 acre-feet).

In addition to produced water, however, operators are also injecting externally sourced freshwater for enhanced oil recovery. In 2013, operators reported 3% of injected water as "freshwater" (15 million m³ or 12,000 acre-feet). However, we estimated freshwater use may be as high as 14%, based on ambiguity in the reporting categories in DOGGR's database. DOGGR's database allows operators to report water type in one of five categories; one of these is labeled "freshwater," but some of the other categories may be composed partly or entirely of freshwater. These ambiguous categories include "water combined with chemicals such as polymers," "another kind of water," and "not reported." By combining these categories with the freshwater category, we estimate injected freshwater in 2013 may have been as high as 60 million m³ (49,000 acre-feet).

In order to understand *where* operators are obtaining freshwater for EOR, we performed another set of queries and analyses using DOGGR's Production/Injection database. In 2013, operators reported that they obtained freshwater for injection from several sources: domestic water systems (72%), water source wells (25%), wastewater from an industrial facility (1.6%), and not reported (1.4%) or reported as "another source or combination of the above sources" (0.1%).

Table 2.3-3. Breakdown of injected water for enhanced oil recovery by source and type of water, in million m³ per year, in 2013. This does not include water for well stimulation.

All sources:	million m³	% total
Produced from an oil or gas well	288	65%
Ocean	<0.001	<0.1%
Other Sources	155	35%
Total	**443**	

Breakdown of water type in "Other sources" above:	million m³	% total
Salt water	94	61%
Water combined with chemicals such as polymers	22	14%
Not Reported	17	11%
Another kind of water	6	3.9%
Freshwater	15	9.8%
Total other sources	**155**	

Source of freshwater listed above:	million m³	% total
Domestic water systems	11	72%
Produced from a water source well	4	25%
Wastewater from an industrial facility	0.2	1.6%
Not reported	0.2	1.4%
Another source or combination of the above sources	0.015	0.1%
Total all externally sourced freshwater	**15**	

Note: Table figures may not add due to rounding.

We analyzed how much freshwater is used for EOR in fields where production is *enabled* by well stimulation technology. To do this, we summarized freshwater use for EOR in pools that we had previously categorized as having production enabled by well stimulation. These are typically formations with low transmissivity where oil or gas production is not economically feasible without fracturing. We identified these pools by analyzing well records maintained by DOGGR, and identified 68 pools where the majority of new production wells from 2002 to 2013 were hydraulically fractured (see Volume I for detailed analysis. We estimate that water use for EOR in these pools ranged from 2 million to 14 million m³ (1,600 to 13,000 acre-feet) in 2013, while freshwater use for EOR in all other oil and gas fields was 13 million to 44 million m³ (11,000 to 36,000 acre-feet) in 2013, as shown in Figure 2.3-2. Thus, we may conclude that between 15% and 30% of freshwater use for EOR in California in 2013 can be attributed indirectly to the application of well stimulation.

We also compared the total volume of freshwater that oil and gas operators use for well stimulation to the volume used for enhanced oil recovery. Based on our estimates above, operators used from 2 to 15 times more freshwater for EOR than they used for well stimulation in 2013. Figure 2.3-2 compares the estimated volume of water used for well stimulation with the volume of water injected for EOR in 2013.
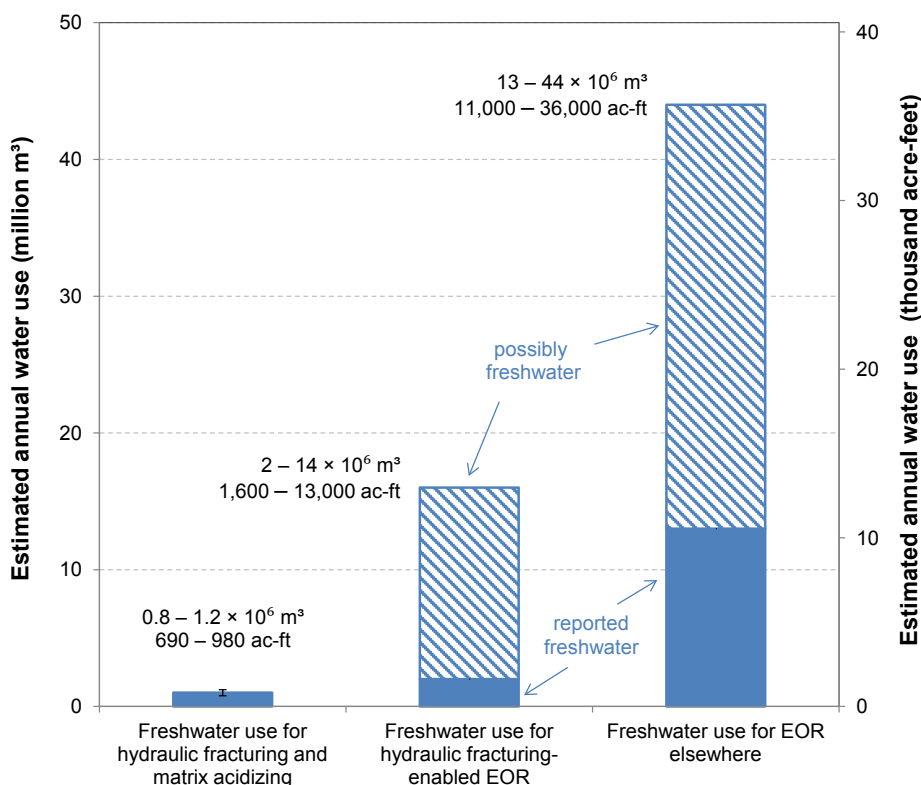

Figure 2.3-2. Estimated annual freshwater use for well stimulation (left), enhanced oil recovery (EOR) in 2013 in reservoir where most wells are hydraulically fractured (middle), and EOR in 2013 in other reservoirs (right). Well stimulation including hydraulic fracturing occurs before the well goes into production. EOR occurs throughout production.

Note: The solid bar in this figure represents water volume explicitly classified as freshwater in the DOGGR Production Database. The hatched area represents water used for EOR that is reported as a type that may be all or part freshwater. When we include "water combined with chemicals such as polymers," "another kind of water," and blank records (unknown water type), freshwater use for enhanced oil recovery may be as high as 60 million m³ (49,000 acre-feet).

2.3.4. Water Use for Well Stimulation in a Local Context

Water use for well stimulation and stimulation-enabled EOR in California is small in the context of the state's total water use; our estimate of this water use for well stimulation is less than 2 million m^3 (<2,000 acre-feet) per year (Table 2.3-1 and Figure 2.3-2), while human water use statewide averages about 56 billion m^3 (45 million acre-feet) per year (DWR, 2014a). Water concerns, however, are local, and the impacts of that water use should be evaluated within a local context. Where oil and gas extraction occurs alongside other uses, it can mean competition over a limited resource, especially where the oil and gas industry is usually willing and able to pay more for water than irrigators or other water users (Freyman, 2014; Healy, 2012).

To get a better sense of water use in regions where well stimulation has been reported, we examined water use within Planning Areas, also referred to as "PAs". PAs are geographic units created by the California Department of Water Resources (DWR) for the planning and management of the state's water resources. DWR divides the state into 56 PAs, ranging in size from 830 to 19,400 km^2 (320 to 7,500 mi^2), with an average size of 6,700 km^2 (2,600 mi^2). PA boundaries typically follow watershed boundaries, but are sometimes coincident with county boundaries or hydrologic features, such as rivers and streams.

From January 2011 to the end of May 2014, well stimulation was documented in 19 of the state's 56 PAs (Table 2.3-4). We estimated the amount of water used for well stimulation and hydraulic-fracturing-enabled EOR by PA and compared that water use to total water use for the area (Table 2.3-4).

Table 2.3-4. Estimated annual water use for well stimulation and hydraulic fracturing-enabled EOR by water resources Planning Area.

Planning Area	For well stimulation operations (m³)	For enabled EOR (m³)	Total water use (stimulation + EOR, m³)	% of water use in Planning Area
Santa Ana	1,300		1,300	0.000082%
Metro Los Angeles	25,000		25,000	0.0013%
Santa Clara	11,000		11,000	0.0018%
Central Coast Southern	270		270	0.000043%
Semitropic	930,000	2,000,000*	2,900,000	0.19%
Kern Delta	2,100		2,100	0.00011%
Kern Valley Floor	18,000		18,000	0.0016%
Uplands	9,300		9300	0.015%
Central Coast Northern	900		900	0.00011%
Western Uplands	2,900		2,900	0.10%
San Luis West Side	260		260	0.000017%
Lower Kings-Tulare	750		750	0.000031%
North Bay	930		930	0.00035%
San Joaquin Delta	440		440	0.000038%
Sacramento River Delta	1,300		1,300	0.00018%
Central Basin, West	480		480	0.000044%
Colusa Basin	2,900		2,900	0.00011%
Butte-Sutter-Yuba	3,100		3,100	0.000098%
Offshore	6,600		6,600	n/a
Total	**1,000,000**	**2,000,000**	**3,000,000**	**0.0057%**

*In this table, we report the low estimate for water use for EOR in fields where production is enabled by well stimulation. In Section 2.3.3, we found that this water use may range from 2 million to 14 million m³ (1,600 to 13,000 acre-feet).

Note: Water use estimates for Planning Areas are for the year 2010 (from DWR, 2014b). Numbers may not sum to the total values due to rounding.
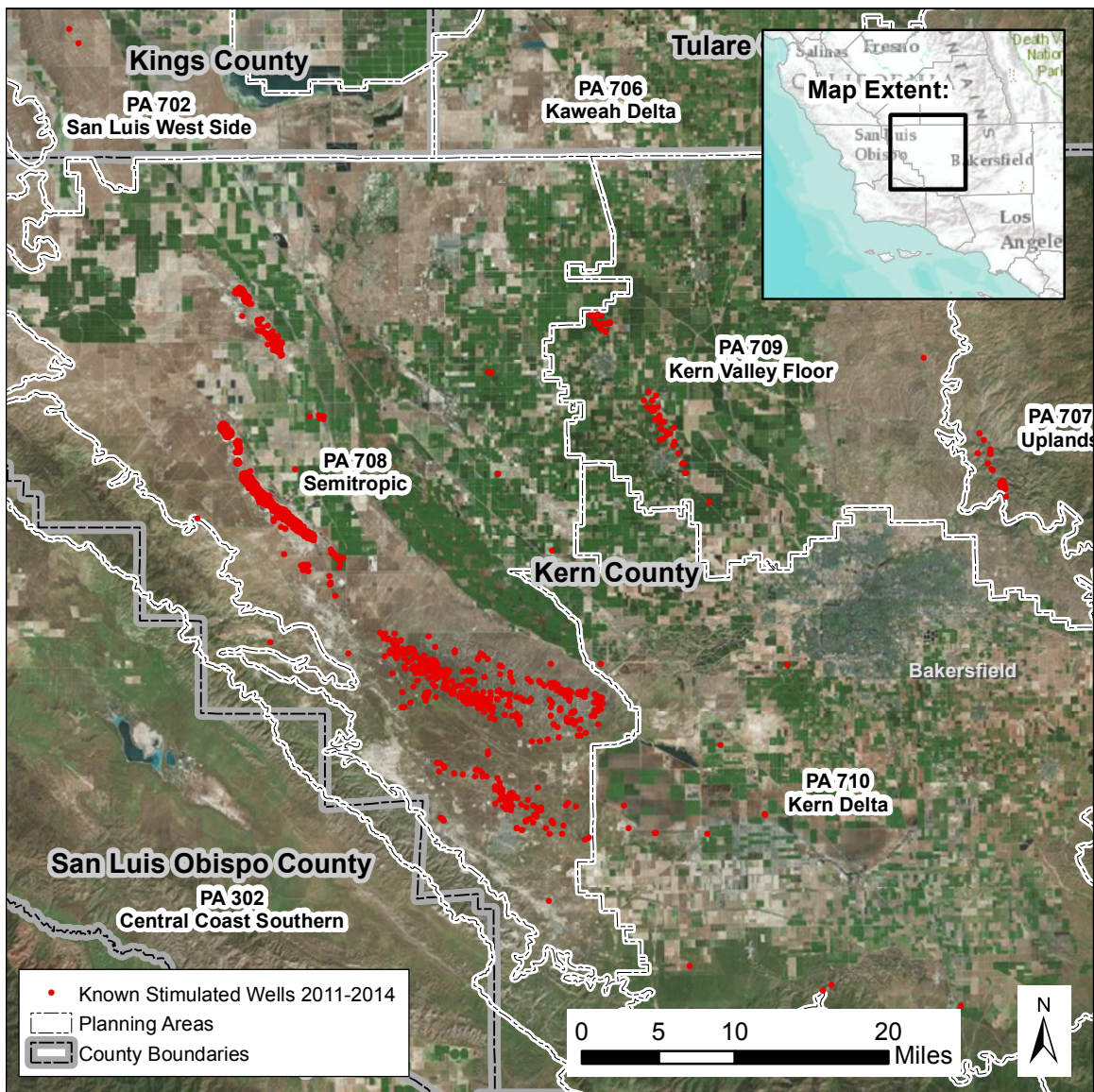
Figure 2.3-3. Map showing oil and gas wells stimulated from January 2011 through June 2014 and Water Resources Planning Areas in the Tulare Lake basin.

The majority of well stimulation operations occurred in western Kern County in the Semitropic PA (Figure 2.3-3). All of the reported matrix-acidizing operations are in this PA as well, as is all the freshwater use for EOR enabled by hydraulic fracturing. Water use for well stimulation and hydraulic-fracturing-enabled EOR comprises less than 0.1% of human water use in almost all PAs where stimulation occurs. Water use by PA attributable to well stimulation ranged from a low of 270 m³ (0.22 acre-feet) in the Central Coast Southern and San Luis West Side PA, to a high of 2,900,000 m³ (2,400 acre-feet) in the Semitropic PA (Table 2.3-4). Even within the Semitropic PA, where the vast majority of well-stimulation-related freshwater use occurs, water use for well stimulation accounts

for only 0.19% of water use (Table 2.3-5). Within this PA, the largest water use is for irrigated agriculture, which used 1,500 million m³ (1.2 million acre-feet) in 2010. This is followed by energy production and urban use.

Table 2.3-5. Estimated annual water use for well stimulation and hydraulic fracturing-enabled EOR in the Semitropic Planning Area compared to applied water volumes estimated by DWR for 2010. Note water use for hydraulic fracturing-enabled EOR was subtracted from energy production water volume estimated by the DWR.

	million m³ year⁻¹	acre-feet year⁻¹
Well stimulation and hydraulic fracturing-enabled EOR	2.9	2,400
Estimated Applied Water in 2010*		
Energy Production	19	15,000
Urban (commercial, industrial, residential)	10	8,000
Agricultural	1,500	1,200,000
Total	**1,530**	**1,220,000**

Numbers may not sum to total due to rounding

Despite its relatively low freshwater use, concerns have been raised by some water analysts and environmental organizations that freshwater use for hydraulic fracturing could have a negative impact because it is concentrated in relatively water-scarce regions, and the additional demand could strain available supplies (e.g., Summer, 2014; Center for Biological Diversity, 2015). Competition for water could become more critical in the face of extended drought.

Most of the hydraulic fracturing in California takes place in the San Joaquin Valley, where groundwater has been over-drafted by agriculture for over 80 years, causing a host of problems, including subsidence of the land surface. The 8-meter drop in the land surface near Mendota, California, is among the largest ever that has been attributed to groundwater pumping (Galloway et al., 1999). New water demands on top of already high competition for water could further deplete the region's aquifers, as has been observed in other water-scarce regions of the U.S. where hydraulic fracturing is occurring (Reig et al., 2014). This could cause concern for smaller communities and domestic users that rely on local groundwater. In the San Joaquin Valley, farmers and communities also depend on imported water delivered by canals, deliveries of which have become increasingly unreliable in recent years (DWR, 2014a). On the other hand, in some areas, produced water from oil fields that have low salt concentrations can be a source of water, and is being reused for a variety of beneficial purposes, including for irrigation and groundwater recharge, as discussed in Section 2.6.

2.4. Characterization of Well Stimulation Fluids

2.4.1. Understanding Well Stimulation Fluids

Understanding the composition, or formulations, of well stimulation fluids is an important step in defining the upper limits of potential direct environmental impacts from hydraulic fracturing and other well stimulation technologies. The amounts of chemicals added to well stimulation fluid define the maximum possible mass and concentrations of chemical additives that can be released into the environment. The chemicals added to well stimulation fluid might also influence the release of metals, salts and other materials found naturally in oil and gas bearing geological formations. Due to the economic value of individual well-stimulation-fluid formulations and competition between oil field service companies, operators and service companies have been generally reticent about releasing detailed information concerning the types and amounts of chemicals used in specific formulations. Often when information is released, the information may be incomplete (e.g., Konschnik et al., 2013). This lack of transparency has heightened uncertainty and concerns about the chemicals used in well stimulation fluid.

We investigated the composition of well stimulation fluids that are used in California with the objectives of (1) developing an authoritative list of chemicals used for well stimulation in California, (2) determining the concentrations at which the chemicals are used, and (3) estimating the amount (mass) of each chemical that is used per well stimulation. Characteristics of stimulation chemicals, including aquatic and mammalian toxicity were also evaluated (see below and Chapter 6). Chemical disclosures include information on the volume of water used as a "base fluid" and the concentrations of chemicals present in individual well-stimulation-fluid formulations, from which the mass of chemicals used per stimulation can be estimated.

We compiled the reported uses of chemical additives in hydraulic fracturing and acid treatments, and evaluated the information using numerous approaches. A list containing hundreds of chemicals can be initially bewildering, even to experts, and it is helpful to understand the significance of individual chemicals or chemicals in mixtures in the context of their frequency of use, the amounts used, and their hazardous properties, such as toxicity. Other information to help understand and evaluate chemicals includes the purpose of their use, the class of chemical to which they belong, and other distinguishing characteristics, such as vapor pressure and water solubility. Previous studies have evaluated and characterized chemical additives to well stimulation fluids that are in common use nationally (Stringfellow et al., 2014; U.S. House of Representatives Committee on Energy and Commerce, 2011; U.S. EPA, 2012a). In this study, we examine chemicals specifically used in California and develop a comprehensive list of well-stimulation-fluid additives for California.

In this section, chemicals known to have been constituents of well stimulation fluids in California are ranked and characterized for their hazardous properties in relation to aquatic environments. Chapter 6 addresses hazards in the context of human health.

Understanding hazard is important; however, the risk associated with any individual chemical is a function of the release of the material to the environment, how much material is released, the persistence of the compound in the environment, and many other properties and variables that allow a pathway to human or environmental receptors. A full risk assessment is beyond the scope of this study. However, information on hazard, toxicology, and other physical, chemical, and biological properties developed in this section are fundamental to the understanding of environmental and health risk associated with well stimulation treatments in general, and well stimulation fluid specifically.

2.4.2. Methods and Sources of Information

Prior to the enactment of SB 4 authorized regulation in California in January 2014, all information from industry on the composition of well stimulation fluid was released on a voluntary basis. A primary source of data for the analysis in this section was voluntary disclosures reported to the FracFocus Chemical Disclosure Registry (http://fracfocus.org/). The data used in this analysis include disclosures entered into the Chemical Disclosure Registry for hydraulic fracturing in California prior to June 12, 2014. This analysis includes listing all the chemicals used in 1,623 hydraulic fracturing treatments conducted in California between January 30, 2011 and May 19, 2014 (Appendix A, Table 2.A-1). The mass used per treatment and the frequency of use were only calculated using well stimulation treatments that had complete records (Appendix A, Table 2.A-1). A complete treatment record was a record that included the volume of base fluid used, the concentration of the base fluid and the concentration of each chemical used as percent of total treatment fluid mass, and where the sum of the reported masses was between 95% and 105%. Of the 1,623 reported applications, 1,406 (87%) met the criteria for complete records.

The Chemical Disclosure Registry only includes disclosures for hydraulic fracturing treatments and does not include other well stimulation treatments, such as matrix acidizing treatments. Sources of information for acid treatments include Notices of Intent and Completion Reports submitted to DOGGR since December 2013 under new SB 4 regulations and chemical use reported to SCAQMD under reporting regulations in effect since 2013 (SCAQMD, 2013).

There were an estimated 5,000 to 7,000 hydraulic fracturing treatments in California between 2011 and 2014, suggesting that the voluntary disclosure record represents only one-third to one-fifth of the estimated total hydraulic fracturing treatments. However, the disclosures include the major producers and service companies operating in California, including Baker Hughes, Schlumberger, and Halliburton. The chemical additives listed in the voluntary disclosures were consistent with additives described in information available from industry literature, patents, scientific publications, and other sources, such as government reports (e.g., Gadberry et al., 1999; U.S. EPA, 2004; Baker Hughes Inc., 2011; 2013; Stringfellow et al., 2014). Therefore, it is concluded that this list is representative of chemical use for well stimulation in California.

The hazard that a material may present if released to the environment is assessed using a number of criteria, including the toxicity of the chemical to aquatic species selected to represent major trophic levels of aquatic ecosystems. Common standard test species include the fathead minnow (*Pimephales promelas*); various species of trout; daphnia, such as *Daphnia magna*; and various species of green algae (U.S. EPA, 1994; OECD, 2013). The test species represent a basic aquatic food chain of primary producers (algae), grazers (daphnia), and predators (minnows). The species tested are typically selected on the basis of availability, regulatory requirements, and past successful use. Other test species (e.g., trout) may be selected for testing based on commercial, recreational, and ecological importance. Standardized test data for lethality are typically reported as median lethal dose (LD_{50}) for mammals and median lethal concentration (LC_{50}) for fish. In the case of aquatic crustaceans and algae, the effective concentration at which 50% of the test population is adversely affected is determined and reported as the median effective concentration (EC_{50}). Since aquatic toxicity tests are highly standardized, the results can be used to compare and contrast industrial chemicals (Stringfellow et al., 2014). Experimental tests against aquatic species are an important component of an ecotoxicological assessment.

For this study, we examine the acute toxicity of individual chemicals to fathead minnows, daphnia, and algae. Acute toxicity data were collected only for the chemicals used in well stimulation in California that were identified by CASRN. Toxicity data were gathered from publicly available sources as shown in Table 2.4-1. Computational methods (EPI Suite) were applied in an attempt to fill data gaps when chemicals have not been thoroughly tested using experimental methods (Mayo-Bean et al., 2012; U.S. EPA, 2013c). The U.S. EPA cautions that EPI Suite is a screening-level tool and should not be used if acceptable measured values are available (U.S. EPA, 2013c). In this study, we only included EPI Suite results if experimental results were not available. In the case of green algae, insufficient experimental results were found, and only EPI Suite results were used in the analysis. The EPI Suite values for freshwater fish were also used to fill data gaps for both fathead minnow and trout toxicity (Appendix B, Figure 2.B-1).

Ecotoxicity results were interpreted in the context of the Globally Harmonized System (GHS) criteria for the ranking and classification of the acute ecotoxicity data. A similar approach was taken to evaluate mammalian toxicity and is described in Chapter 6. The United Nations Globally Harmonized System (GHS) of Classification and Labeling of Chemicals was used to categorize chemicals based upon their LD_{50}, LC_{50}, or EC_{50} values (Appendix A, Tables 2.A-2 and 2.A-3) (United Nations, 2013). In the GHS system, lower numbers indicate greater toxicity, with a designation of "1" indicating the most toxic compounds (Appendix A, Tables 2.A-2 and 2.A-3). Chemicals for which the LD_{50}, LC_{50}, or EC_{50} exceeded the highest GHS category were classified as non-toxic.

Physical and chemical data for fracturing fluid additives was obtained from online chemical information databases, government reports, chemical reference books, materials safety data sheets, and other sources as previously described (Stringfellow et al., 2014).

Physical and chemical data are mostly based on laboratory tests using pure compounds. Physical, chemical, and toxicological properties were selected for inclusion in this study based on their use in environmental fate and transport studies, treatability evaluations, remediation efforts, and risk assessments (Stringfellow et al., 2014). Chemicals used in well stimulation were categorized as *non-biodegradable* or *biodegradable* using OECD guidelines (OECD, 2013). Biodegradability is useful for determining the effectiveness of biological treatment for wastewaters and the fate of chemicals released into the environment. In the absence of measured biodegradation data, computational methods developed for the U.S. EPA (e.g., BIOWIN) were used to estimate biodegradability (U.S. EPA, 2012b).

Table 2.4-1. Sources for physical, chemical, and toxicological information
for chemicals used in well stimulation treatments in California.

U.S. EPA (Environmental Protection Agency), ACToR (Aggregated Computational Toxicology Resource) Database, 2013, http://actor.epa.gov/actor/faces/ACToRHome.jsp
National Library of Medicine, ChemIDplus Advanced. http://chem.sis.nlm.nih.gov/chemidplus/
U.S. EPA (Environmental Protection Agency) and Office of Pesticide Programs, ECOTOX Database Version 4.0, 2013, http://cfpub.epa.gov/ecotox/
European Chemicals Agency (ECHA), International Uniform Chemical Information Database (IUCLID), CD-ROM Year 2000 Edition, 2000.
National Institute of Technology and Evaluation, Chemical Risk Information Platform (CHRIP). http://www.safe.nite.go.jp/english/db.html
R.J. Lewis, N.I. Sax, Sax's dangerous properties of industrial materials, 9th ed., Van Nostrand Reinhold, New York, NY, 1996
Syracuse Research Corporation PhysProp Database
National Library of Medicine, Toxicology Data Network (TOXNET) Hazardous Substance Data Bank (HSDB), 2013, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
SciFinder, Chemical Abstract Service, Colombus, OH, https://scifinder.cas.org
Materials Safety Data Sheets from Sigma-Aldrich, BASF, Spectrum, ExxonMobil, Alfa Aesar, Clariant, and other chemical suppliers
Organization for Economic Cooperation and Development (OECD) - Screening Information Data Set
California Prop 65, Chemicals Known to the State to Cause Cancer or Reproductive Toxicity. http://www.oehha.ca.gov/prop65/prop65_list/files/P65single050214.pdf
International Agency for Research on Cancer (IARC), IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, World Health Organization. http://monographs.iarc.fr/ENG/Classification/ClassificationsCASOrder.pdf
U.S. EPA (Environmental Protection Agency), EPI Suite, Experimental Values
Toxic Substance Control Act Test Submissions 2.0, 2014, http://yosemite.epa.gov/oppts/epatscat8.nsf/ReportSearch?OpenForm

2.4.3. Composition of Well Stimulation Fluids

2.4.3.1. Chemicals Found in Hydraulic Fracturing Fluids

A list of chemical additives reported to have been used in California for hydraulic fracturing treatments is shown in Appendix A, Table 2.A-1. The list includes frequency of use, concentration, and mass of chemicals used for hydraulic fracturing in California, as reported to the FracFocus Chemical Disclosure Registry prior to June 12, 2014. The list contained in Table 2.A-1 includes only the subset of hydraulic fracturing treatment data for which the sum of the reported additives was 100% ± 5%.

As can be seen in Table 2.A-1, not all additives were identified by CASRN, which is a standardized system for the clear and singular identification of chemicals, otherwise known by various common names, trade names, or product names, which may or may not be specific. Of the disclosed chemical additives, there were approximately 230 chemicals or chemical mixtures identified by CASRN; others were identified by name only. Over 100 chemicals could not be positively identified because a CASRN was not provided. After analysis and standardization of chemical names, over 300 chemicals or chemicals mixtures were identified by unique name or CASRN. Since in many cases generic names were used for chemical additives on the disclosures (e.g., surfactant mixture, salt, etc.), any enumeration of the number of chemicals used in hydraulic fracturing should be considered approximate (Table 2.A-1). Many of the additives used in hydraulic fracturing are also used in other routine oil and gas operations, such as well drilling. Other chemicals are specific to well stimulation, such as guar and borate cross linkers.

Disclosures that do not provide CASRN for each entry do not allow definitive identification of the well-stimulation-fluid additive. However, chemical names are generally informative, and each identified substance was investigated and, where possible, referenced to specific products sold by the major suppliers of well stimulation services and chemicals in California. There was a median of 23 individual components—including base fluids, proppants, and chemical additives—used per treatment (Figure 2.4-1). The number of unique components used as reported here differs from a recent study by the U.S. EPA, which reported a median of 19 chemical additives used per treatment in an analysis of 585 disclosures (U.S. EPA, 2015a). The difference between these two studies results in part because of differences in the number of disclosures examined (585 vs. 1,406 for this study), but also because the number here includes base fluids and proppants, while the U.S. EPA study did not include these in developing the median value of 19 (U.S. EPA, 2015a). The disclosures include descriptions for chemicals added for the purpose of stimulation (e.g., water, gelling agents, biocides, etc.) and entries for so-called impurities found in the chemicals used for formulating well-stimulation fluid. In many cases, impurities are reported without concentration data or mass concentrations of <0.001% of the mass of the injected fluid.

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. Table 2.A-1 gives the reported median chemical concentration in well stimulation fluid. Chemicals can be added at hundreds and sometimes thousands of mg kg^{-1} of fluid. Even the impurities, which are not specifically added for a purpose directly related to well stimulation, can occur at high concentrations in well stimulation fluid. For example, magnesium chloride and magnesium nitrate are inactive ingredients (e.g., impurities) found in biocides containing 2-methyl-3(2H)-isothiazolone and 5-chloro-2-methyl-3(2H)-isothiazolone (Miller and Weiler, 1978). Even though impurities are not added specifically for well stimulation, they must be considered during an evaluation of the hazards associated with hydraulic fracturing.
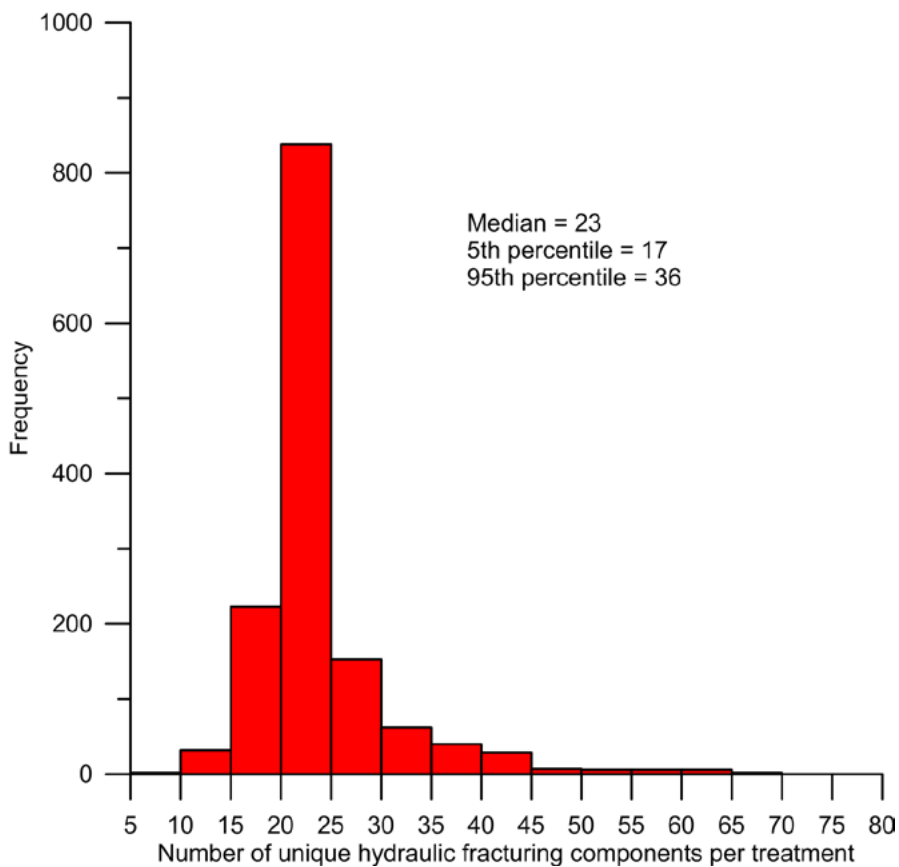

Figure 2.4-1. Frequency distribution of the number of components used per hydraulic fracturing operation in California. Only complete records were included in the analysis where the sum of the treatment components was 100 ± 5% (N=1,406).

2.4.3.2. Chemicals Found in Matrix Acidizing Fluids

There are well stimulation treatments used in California that involve the use of strong acids, including hydrochloric and hydrofluoric acid (see Volume I, Chapter 2 and 3 and California Council on Science and Technology (CCST) et al., 2014). Due to the absence of state-wide mandatory reporting on chemical use in the oil and gas industry, it is not known how much acid is used for oil and gas development throughout California. However, available information suggests that there are approximately twenty matrix acidizing treatments in California per month, but detailed chemical information on specific treatments are not available. Parts of southern California have mandatory reporting on the use of all chemicals used for well drilling, reworks, and well completion activities (http://www.aqmd.gov/). Analysis of these data suggests acid use is widespread and common for many applications in the industry.

As of December 2013, under interim regulations, DOGGR has required operators to submit a "Notice of Intent" for well stimulation treatments, including matrix acidizing. These notices include a list of chemicals that may be used in a planned well stimulation treatment. Analysis of these mandatory Notices of Intent that were publicly available between December 2013 and June 2014 found 70 chemicals identified by CASRN. Seven compounds reported in Notice of Intent documents for matrix acidizing were not found in voluntary notices reported to the Chemical Disclosure Registry for hydraulic fracturing treatments (Table 2.4-2).

Table 2.4-2. Seven compounds submitted to DOGGR in a Notice of Intent to perform matrix acidizing that were publicly available between December 2013 and June 2014 that were not found in voluntary notices reported for hydraulic fracturing to the FracFocus Chemical Disclosure Registry (Table 2.A-1). Notices of Intent are required for all well stimulation treatments as of December 2013 under interim regulations.

Chemical Name	CASRN	Also reported as used in hydraulic fracturing (Table 2.A-1)
Hydroxylamine hydrochloride	5470-11-1	No
Benzaldehyde	100-52-7	No
Cinnamaldehyde	104-55-2	No
Amine oxides, cocoalkyldimethyl	61788-90-7	No
Copper dichloride	7447-39-4	No
Ethylene oxide	75-21-8	No
Sodium iodide	7681-82-5	No

As of January 2014, under SB 4, DOGGR has also required operators to submit a "Well Stimulation Treatment Disclosure Report" within 60 days of completion of well stimulation treatments, including matrix acidizing. These reports include a list of chemicals that were actually used in a well stimulation treatment. Analysis of the

disclosure reports available as of May 2015 identified 25 chemical compounds by CASRN used in matrix acidizing that were not found in the voluntary notices reported to the Chemical Disclosure Registry between 2011 and June 2014 (Table 2.4-3). However, of the 25 compounds identified as being used in matrix acidizing, 11 are also reported in the DOGGR disclosure reports as being used for hydraulic fracturing in 2015. Of the seven compounds submitted to DOGGR in the Notices of Intent for matrix acidizing (Table 2.4-2) that were not reported to the Chemical Disclosure Registry, only three were reported in the Well Stimulation Treatment Disclosure Reports. These results indicate that there is overlap in chemical use between matrix acidizing and hydraulic fracturing, and that mandatory reporting will include some chemicals not listed on voluntary disclosures prior to 2014.

Table 2.4-3. Chemicals used for matrix acidizing in California, as reported in DOGGR's Well Stimulation Treatment Disclosure Reports prior to May 5, 2015 that were not reported for hydraulic fracturing in the FracFocus Chemical Disclosure Registry (Appendix A, Table 2.A-1). Well Stimulation Treatment Disclosure Reports are required within 60 days of cessation of well stimulation treatment under SB 4.

Chemical Name	CASRN	Also reported as used in hydraulic fracturing in DOGGR's Disclosure Reports
1-Eicosene	3452-07-1	Yes
Hydroxylamine hydrochloride	5470-11-1	No
Acetaldol	107-89-1	No
1-Tetradecene	1120-36-1	Yes
1-Octadecene	112-88-9	Yes
Ammonium fluoride	12125-01-8	Yes
Benzyldimethylammonium chloride	122-18-9	Yes
Lauryl hydroxysultaine	13197-76-7	Yes
Benzododecinium chloride	139-07-1	Yes
Miristalkonium chloride	139-08-2	Yes
Nitrilotriacetic acid	139-13-9	No
Fatty acids, C18-unsatd., dimers	61788-89-4	No
Amines, hydrogenated tallow alkyl, acetates	61790-59-8	Yes
1-Hexadecene	629-73-2	Yes
Benzoic acid	65-85-0	No
Poly(oxy-1,2-ethanediyl), alpha-(nonylphenyl)-omega-hydroxy-, branched, phosphates	68412-53-3	No
Benzenesulfonic acid, C10-16-alkyl derivs., compds. with 2-propanamine	68584-24-7	Yes
Benzenesulfonic acid, C10-16-alkyl derivs., compds. with triethanolamine	68584-25-8	Yes
Copper dichloride	7447-39-4	No
Ethylene oxide	75-21-8	Yes

Chemical Name	CASRN	Also reported as used in hydraulic fracturing in DOGGR's Disclosure Reports
Potassium iodide	7681-11-0	No
Nitrogen	7727-37-9	No
Calcium phosphate, tribasic	7758-87-4	Yes
Aluminum chloride	7784-13-6	No
1,3-Propanediaminium, 2-hydroxy-N,N,N,N′,N′-pentamethyl-N′-(3-((2-methyl-1-oxo-2-propenyl) amino)propyl)-, dichloride, homopolymer	86706-87-8	No

As of June 2013, SCAQMD, which regulates air quality in the Los Angeles Basin, has required operators to report information on chemical use for well drilling, completion, and rework operations. Reports from June 2013 through May 2014 were examined for treatments and operations that used hydrochloric acid; it was found that over 70 other chemical compounds identified by CASRN were used in conjunction with hydrochloric acid, according to these mandated reports. Over 20 compounds were identified from this list that were not found in the voluntary notices reported to the Chemical Disclosure Registry (Table 2.A-4).

A full analysis of the environmental risks associated with the use of acid and associated chemicals, such as corrosion inhibitors, requires a more complete disclosure of chemical use. Many of the same chemicals that are used for hydraulic fracturing are also used for matrix acidizing and other acid applications. Concerns specific to matrix acidizing, that may or may not apply to other well maintenance activities or hydraulic fracturing, include the dissolution and mobilization of naturally occurring heavy metals and other pollutants from the oil-bearing formation. The significance of this risk, if any, cannot be evaluated without a more complete understanding of the chemicals being injected and of the fate and effect of well stimulation fluids in the subsurface. The composition of the fluids returning to the surface as return flows and produced water needs to be better understood (Section 2.5).

2.4.4. Characterization of Chemical Additives in Well Stimulation Fluids

2.4.4.1. Characterization by Additive Function

Chemicals added to well stimulation fluids have a variety of purposes, including thickening agents to keep sand and other proppants in suspension (e.g., gels and crosslinkers) and chemicals (breakers) added at the end of treatments to remove thickening agents, leaving the proppant to hold open the newly created fractures (King, 2012; Stringfellow et al., 2014). Table 2.4-4 lists chemical use by function, where the function could be positively identified. It is apparent that treatments using gels and cross-linking agents are more common in California than treatments using friction reducers (Table 2.4-4). In other regions of the country where stimulation is used for

gas production, friction reducers (slicking agents) are commonly used (King, 2012; Stringfellow et al., 2014; U.S. EPA, 2015a). Over 80% of the treatments use an identified biocide and many formulations also include chemicals such as clay control additives. More information on the purposes of various chemicals used in hydraulic fracturing can be found elsewhere (King, 2012; Stringfellow et al., 2014; U.S. EPA, 2015a).

Disclosures frequently include descriptions of the purpose of the chemical added to well stimulation fluid. In the voluntary disclosures examined as part of this study, it was determined that the information entered for the purpose was very frequently inaccurate or misleading. In many cases, the purpose of the chemical additive is obscured because the disclosure reports list multiple purposes for each chemical disclosed. In other cases, the disclosed purposes are obviously incorrect. Impurities are typically not identified as such, and are instead given the same purpose description as the active ingredient in the chemical product. A more transparent explanation of the purpose of each chemical additive would contribute to a better understanding of the risks associated with well stimulation fluids.

Table 2.4-4. Hydraulic fracturing chemical use in California by function, where function was positively identified. This analysis was based on all records (N=45,058), consisting of 1,623 hydraulic fracturing treatments.

Function	Chemicals used for each function	Treatments using chemicals with this function
Breaker	11	1,599
Proppant	20	1,598
Gelling Agent	2	1,593
Carrier	23	1,515
Crosslinker	13	1,405
Biocide	10	1,392
Clay Control	7	1,184
Scale Inhibitor	10	865
Corrosion Inhibitor	8	182
Iron Control	2	60
Friction Reducer	1	13
Diverting Agent	3	10
Antifoam	1	6

2.4.4.2. Characterization by Frequency of Use

Although there are a large number of chemical additives used in well stimulation fluid (Appendix A, Table 2.A-1), the reported frequency of use of these compounds varies. As part of an environmental and hazard evaluation involving such an extensive list of chemicals, it is necessary to set priorities for which chemicals to evaluate first. Although any individual chemical use is potentially important, it is not practical to evaluate

all chemicals simultaneously. In this study, we use frequency of use as one of several parameters (including toxicity and amount used) for recommending specific chemicals for priority evaluation. The more frequently a chemical is used, the more likely any associated hazard, if any, could become an environmental or health risk.

Table 2.4-5 lists the 20 reported additives used most frequently in California. This list excludes proppants (e.g., quartz), bulk fluids (e.g., water), and diatomaceous earth, which is added as a stabilizer or carrier to biocides and other active ingredients (Greene and Lu, 2010). Frequently used chemicals on the list include gels and cross-linkers (e.g., guar gum, boron sodium oxide), biocides (e.g., 5-chloro-2-methyl-3(2H)-isothiazolone), breakers (e.g., ammonium persulfate, enzymes), and other treatment additives. Additives in Table 2.4-5 include solvents and a clay stabilizer. As discussed previously, reporting of chemical use is not mandatory, but the most frequently reported chemicals (Table 2.4-5) are in alignment with what is expected from other lines of inquiry and reported literature (e.g., Stringfellow et al., 2014; U.S. EPA, 2004).

Table 2.4-5. Twenty most commonly reported hydraulic fracturing components in California, excluding base fluids (e.g., water and brines) and inert mineral proppants and carriers. This analysis was based on all records (N=45,058), consisting of 1,623 hydraulic fracturing treatments.

Chemical	CASRN	Treatments using this chemical
Guar gum	9000-30-0	1,572
Ammonium persulfate	7727-54-0	1,373
Sodium hydroxide	1310-73-2	1,338
Ethylene glycol	107-21-1	1,227
2-Methyl-3(2H)-isothiazolone	2682-20-4	1,187
Magnesium chloride	7786-30-3	1,187
Magnesium nitrate	10377-60-3	1,187
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4	1,184
Isotridecanol, ethoxylated	9043-30-5	1,171
Hydrotreated light petroleum distillate	64742-47-8	1,167
Distillates, petroleum, hydrotreated light paraffinic	64742-55-8	1,129
2-Butoxypropan-1-ol	15821-83-7	1,119
Hemicellulase enzyme	9025-56-3	1,098
1,2-Ethanediaminium, N1,N2-bis[2-[bis(2-hydroxyethyl)methylammonio]ethyl]-N1,N2-bis(2-hydroxyethyl)-N1,N2-dimethyl-, chloride (1:4)	138879-94-4	1,076
1-Butoxypropan-2-ol	5131-66-8	973
Phosphonic acid	13598-36-2	790
Amino alkyl phosphonic acid	Proprietary	668
Boron sodium oxide	1330-43-4	666
Sodium tetraborate decahydrate	1303-96-4	520
Enzyme G	Proprietary	480

In Appendix A, Table 2.A-5 contains a list of the approximately 150 chemical additives that were reported less than ten times in 1,623 applications. From a search of product literature, patents, and scientific literature, it can be determined with some certainty that many of the compounds in Table 2.A-5 are impurities (e.g., sodium sulfite), but many are clearly specific products applied for the purpose of well stimulation (e.g., FRW-16A, which is a stimulation fluid additive sold by Baker Hughes). Although the voluntary reporting indicates that these compounds are not widely used in California, the lack of mandatory reporting means that the frequency of use of these chemicals cannot be determined with certainty. Based on our analysis that the voluntary disclosure regime appears to produce representative data, we conclude that the additives that are reported less frequently (Table 2.A-5) deserve a lower priority for a complete risk analysis than compounds that are used more frequently (e.g., Table 2.4-5).

2.4.4.3. Characterization by Amount of Materials Used

Another criterion for selecting priority chemicals for a more thorough evaluation is the amount of material that is used. The concentrations for chemical additives that are used in median quantities greater than 200 kg (440 lbs) per hydraulic fracturing treatment are compiled in Appendix A, Table 2.A-6. This table does not include base fluids (water, saline solutions, or brine), which can account for over 85% of the mass of the well stimulation fluid. As would be expected, at least nine of the compounds in Table 2.A-6 (Appendix A) are proppants and many are solvents, crosslinkers, gels, and surfactants. Since the compounds listed in Table 2.A-6 (Appendix A) are used in significant amounts, they are considered to be priority compounds that warrant further investigation.

2.4.4.4. Characterization by Environmental Toxicity

For assessing environmental toxicity, aquatic species are typically exposed to varying concentrations of chemicals under controlled conditions and, after a specified time, the test species are examined for acute or chronic effects (U.S. EPA, 1994; OECD, 2013). Toxicity to the environment is inferred from tests against a variety of aquatic species that fall into the categories of fish, crustaceans, and aquatic plants, usually represented by algae. In these studies, the test animal is exposed to high concentrations of the test chemical, and the survival or health of the animals as a function of the exposure is determined, with the most common acute metric being the concentration at which 50% of the test population is expected to be adversely effected or dies, if the endpoint is lethality (see methods section). Since aquatic toxicity tests are highly standardized, the results can be used to compare and contrast industrial chemicals (Stringfellow et al., 2014).
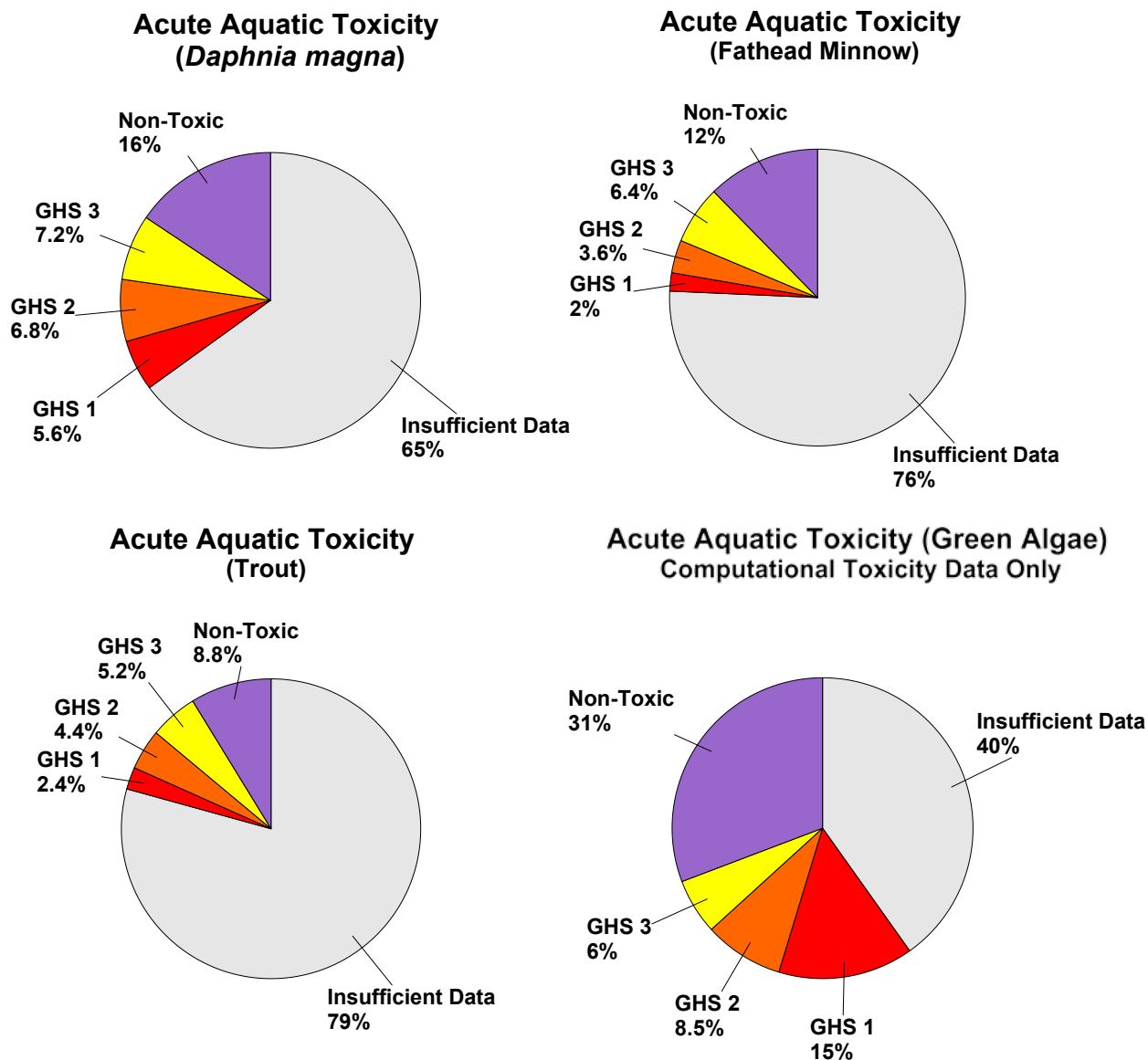
Figure 2.4-2. Aquatic toxicity data for all hydraulic fracturing and acid treatment chemicals. Chemical toxicity was categorized according to United Nations standards in the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), which classifies acute toxicity for aquatic species on a scale of 1 to 3, with 3 being the least toxic.

An overview analysis of the experimental results for acute aquatic toxicity tests are presented in Figure 2.4-2. Thirty-three chemicals have a GHS ranking of 1 or 2 for at least one aquatic species (Table 2.A-7), indicating they are hazardous to aquatic species and could present a risk to the environment if released. Species for which toxicity data were collected are *Daphnia magna*, fathead minnows, and trout. The most toxic chemical additives for these aquatic organisms are shown in Table 2.4-6. Significant data gaps

exist for aquatic species testing. *Daphnia magna* toxicity data are missing for 65% of the chemical additives identified by CASRN, fathead minnow toxicity data are missing for 76%, and trout data are missing for 79% of chemicals (Figure 2.4-2). EPI Suite estimations for green algae toxicity are missing for 40% of the chemicals (Figure 2.4-2).

Table 2.4-6. The most toxic hydraulic fracturing chemical additives used in California with respect to acute aquatic toxicity, based on the United Nations Globally Harmonized System (GHS) of Classification and Labeling of Chemicals system. Lower numbers indicate higher toxicity, with a designation of "1" indicating the most toxic compounds. Results are only shown for chemicals with GHS rating of 1 for any of the aquatic organisms in the analysis (Daphnia magna, fathead minnows, and trout).

Chemical Name	CASRN	GHS rating
2-Propenoic acid, ammonium salt (1:1), polymer with 2-propenamide	26100-47-0	1
2,2-dibromo-3-nitrilopropionamide	10222-01-2	1
2-Methyl-3(2H)-isothiazolone	2682-20-4	1
5-Chloro-2-methyl-3(2H)-isothiazolone	26172-55-4	1
Alcohols, C10-16, ethoxylated	68002-97-1	1
Alcohols, C12-13, ethoxylated	66455-14-9	1
Alkyl dimethylbenzyl ammonium chloride	68424-85-1	1
Chlorous acid, sodium salt (1:1)	7758-19-2	1
Ethoxylated C14-15 alcohols	68951-67-7	1
Glutaraldehyde	111-30-8	1
Hydrochloric acid	7647-01-0	1
Naphthalene	91-20-3	1
Quaternary ammonium chloride, benzylcoco alkyldimethyl, chlorides	61789-71-7	1
Solvent naphtha, petroleum, heavy arom.	64742-94-5	1

It is important to note that acute toxicity levels of many compounds from EPA standard tests of *Pimephales promelus* (fathead minnow) should be interpreted with caution, since they may differ from the sensitivity of California species. We examined relative toxicity (mortality) of a common well stimulation additive in a comparison between California freshwater fish and *Daphnia* and minnow species (Table 2.4-7). Several observations were made, including that (1) toxicity can vary by more than an order of magnitude among fish species, and (2) in almost all cases, fathead minnow was more resistant to the QAC than other California resident species. These data underscore the need to perform standardized toxicity tests with individual well stimulation chemicals and mixtures of well stimulation chemicals against California species, as well as standard test organisms. Additionally, toxicity will differ by life history stage, and many embryos or larvae may show much higher sensitivity to chemicals than adults, further illustrating that standard acute toxicity tests are just a first step in a more complete evaluation of chemicals (U.S. EPA, 2011).

The aquatic toxicity tests reviewed in this report describe the effects that varying concentrations of pure chemicals have on aquatic species, and are most applicable to effluents and other discharges released directly to surface waters. In the context of normal operations during well stimulation treatments, chemicals are injected in the subsurface, where they can interact with subsurface minerals and otherwise undergo chemical reactions before potentially contacting groundwater or surface water. For example, acids injected into formation rock react rapidly, and the acidity of the injected fluid diminishes quickly. Therefore, any comparison made between the concentrations assessed in toxicity tests and the concentrations reported in well stimulation fluids need to account for the fact that well stimulation fluids will typically be diluted and altered prior to any potential contact with either groundwater or surface water. Further study is required to understand how well stimulation fluids are altered as they interact with surrounding formation rock, and gaining knowledge of these chemical transformations needs to be an essential component of future risk assessment studies for unconventional oil and gas development.

Table 2.4-7. Comparison of results between standard test organisms and California native and resident species. Shown is a comparison of the lethal concentration to 50% of test organisms (LC_{50}) values across different aquatic species towards a common quaternary ammonium compound (QAC) used in hydraulic fracturing fluids. If different LC_{50} values for the same experimental conditions were present in the EPA's Pesticide Ecotoxicity Database, a range of test concentrations was noted. In addition, some experiments had different exposure duration when the effect was observed, leading to lower LC_{50} values with increasing exposure duration e.g., for the striped bass. (U.S. EPA and Office of Pesticide Programs, 2013; Bills et al., 1993; Krzeminski et al., 1977).

Species	Alkyl dimethylbenzyl ammonium chloride CASRN 68424-85-1 LC_{50} or EC_{50} ($\mu g\ L^{-1}$)
Water Flea (*Daphnia magna*)[1]	37–158
Fathead Minnow (*Pimephales promelas*)	280–1,400
Bluegill (*Lepomis macrochirus*)	68–5,300
Rainbow Trout (*Oncorhynchus mykiss*)[2]	64–7,690
Brown Bullhead (*Ameiurus nebulosus*)	1,590
Green Sunfish (*Lepomis cyanellus*)	2,250
Redear Sunfish (*Lepomis microlophus*)	740
Smallmouth Bass (*Micropterus dolomieu*)	1,370
Largemouth Bass (*Micropterus salmoides*)	1,130
Striped Bass (*Morone saxatilis*)	2,820–14,200
Channel Catfish (*Ictalurus punctatus*)	980
Brown Trout (*Salmo trutta*)	1,950
Lake Trout (*Salvelinus namaycush*)	420
Goldfish (*Carassius auratus*)	1,490

[1]*In the case of Daphnia magna, results are reported as effective concentration where 50% of the test population is immobilized at the indicated concentration (EC_{50}). For all other species, the results are measured as mortality (LC_{50}).*
[2]*Native California species, all other fish are non-native resident species.*

2.4.5. Selection of Priority Chemicals for Evaluation Based on Use and Environmental Toxicity

Identification of priority chemical additives for further investigation is an important step toward a complete understanding of the potential direct impacts of hydraulic fracturing and other well stimulation treatments. Using the information and analysis discussed above, we can develop a proposed list of priority chemical additives, based on toxicity and mass used (Appendix A, Table 2.A-8). Chemicals on this list were ranked and given a "Tox Code," representing the highest toxicity ranking the compound received under the GHS system for any environmental toxicity test using aquatic species. The Tox Code was combined with the analysis of the mass of chemical used per well stimulation treatment to allow better synthesis of information (Appendix A, Table 2.A-8). In Chapter 6, a similar approach is taken for the ranking of chemicals in the context of public health and expanded to create a human-health-hazard screening index and includes other impact factors in addition to toxicity and mass of chemical used.

The chemicals list in Table 2.A-8 represent the "known knowns," namely chemicals for which we have a CASRN and some level of toxicity information. In addition to the evaluation of these chemicals, we need to consider the "known unknowns," that for the majority of chemicals identified by CASRN we do not have sufficient toxicological information for characterization (Figures 2.4-2, Appendix B, 2.B-1, and 2.B-2). In addition, there are the "unknown unknowns," represented by the large number of chemicals (discussed below) that are not identified by CASRN (Appendix A, Table 2.A-9) and the large number of well stimulation treatments for which no information was reported under the voluntary disclosure system.

2.4.6. Chemical Additives with Insufficient Information to be Fully Characterized

Over 100 of the materials listed in Table 2.A-1 (see Appendix A) are identified by non-specific names and are reported as trade secrets, confidential business information, or proprietary information (Appendix A, Table 2.A-9). These materials cannot be evaluated for hazard, risk, and environmental impact without more specific identification. Chemical additives that are not identified by CASRN cannot be conclusively identified and cannot be fully evaluated. As can be seen from Tables 2.A-1 and 2.A-6, many of these unidentified or poorly identified compounds are used frequently or in significant amounts for well stimulation. Without complete identifying information, it is not possible to know if more than one chemical (a chemical mixture) is being reported using the same common name. Therefore, 100 chemicals could be the minimum number of completely unknown materials. Additives that were not identified by CASRN were not included in the hazard analysis discussed below.

Undefined chemicals should not be ignored, and some hazard information can be inferred from the reported common names. For example, the common names "oxyalkylated amine quat," "oxyalkylated amine," "quaternary amine," and "quaternary ammonium compound"

all indicate that these additives fall into the category of quaternary ammonium compounds (QACs). Similarly, many of the general names suggest that the proprietary additives are surfactants (e.g., "ethoxylated alcohol," "surfactant mixture," etc.) that are widely used in the industry. Surfactants and QACs have broad application in both industry and household use, and QACs can be used as biocides (Kreuzinger et al., 2007; Sarkar et al., 2010). The environmental hazard associated with an individual surfactant or QAC is highly variable, and some QACs can be persistent in the environment (e.g., Garcia et al., 2001; U.S. EPA, 2006a; 2006b; Davis et al., 1992; Arugonda, 1999). In other disclosures, surfactants and QACs used for well stimulation are identified by CASRN, and evaluation of those chemicals can be used to give insight into the hazard associated with proprietary chemicals used for the same purpose.

2.4.7. Other Environmental Hazards of Well Stimulation Fluid Additives

In this report, we performed a hazard assessment of chemicals for which adequate information was available. A hazard is any biological, chemical, mechanical, environmental, or physical agent that is reasonably likely to cause harm or damage to humans, other organisms, or the environment in the absence of its control (Sperber, 2001). A chemical can be considered a hazard if it can potentially cause harm or danger to humans, property, or the environment because of its intrinsic properties (Jones, 1992).

The identification of hazards (or the lack thereof) is the first step in performing risk assessments. Once the hazards are established or defined, then the more involved process of risk assessment can begin. In contrast to hazard, risk includes the probability of a given hazard to cause a particular loss or damage (Alexander, 2000). It is important to note that it was beyond the scope of this study to perform a risk assessment, and that there are extensive data gaps on the chemical mixtures and environmental exposures that need to be addressed to enable future risk assessments. In addition, many of the materials listed in Appendix A, Table 2.A-1 are reactive and are expected to react with one another and/or other materials within the well and mineral formation. These byproducts could be more or less hazardous than the parent compounds examined here. Byproducts are not measured or reported, and thus could not be evaluated here.

2.4.7.1. Chronic and Sublethal Effects of Chemicals

In this chapter, the analysis of potential impacts from chemicals used in well stimulation fluids has focused on acute lethality to aquatic organisms. However, sublethal impacts from acute or chronic exposures are often related to individual survival potential and population viability (U.S. EPA, 1998). Impacts on reproduction and development are directly linked to population viability. Physiological status, disease or debilitation, avoidance behavior, and migratory behavior are identified as important to population viability in the U.S. Environmental Protection Agency's Generic Ecological Assessment Endpoints (U.S. EPA, 2003).

Lack of data on chronic and sublethal impacts of chemicals used in well stimulation treatments represents a critical data gap in the analysis of potential ecological impacts of unconventional oil and gas development in California. However, the limited data available indicate that sublethal impacts may occur. Exposure to the biocide 2,2-dibromo-3-nitrilopropionamide (DBNPA) negatively impacts aquatic organisms at concentrations well below lethal levels. Growth of juvenile trout was impaired after 14 days exposure to 0.04 mg L^{-1} DBNPA (Chen, 2012). The same study showed impaired reproduction in aquatic invertebrates at 0.05 mg L^{-1} (Daphnia magna). *Xenopus laevis* tadpoles exposed to sublethal concentrations of the biocide methylisothiazolinone (MIT) during development showed several neurological deficits affecting behavior and susceptibility to seizures (Spawn and Aizenman, 2012). Chronic sublethal exposure to the surfactants linear alkylbenzene sulfonates (e.g., dodecylbenzene sulfonic acid) can impact the gills and olfactory system of fish (Zeni and Stagni, 2002; Asok et al., 2012) and decrease reproduction in invertebrates (da Silva Coelho and Rocha, 2010). More information is needed to assess the potential chronic and/or sublethal impacts of well stimulation fluids on aquatic species.

2.4.7.2. Environmental Persistence

The risk associated with a given chemical depends on how long the chemical persists in the environment. A toxic compound released into the environment that decays rapidly presents less chance for exposure to occur, damage to be inflicted, and risk to be accumulated. The list of chemicals used in hydraulic fracturing (Table 2.A-1) includes some compounds that could be environmentally persistent. For example, many of the chemical additives are surfactants and related compounds such as QACs. Persistence of surfactants and QACs is directly related to hydrocarbon chain length and other structural properties, with high molecular weight constituents likely to be the least volatile and most slowly degraded by microbes (Garcia et al., 2001; Kreuzinger et al., 2007; HERA, 2009; Li and Brownawell, 2010; Sarkar et al., 2010; Jing et al., 2012). Other compounds that may persist in the environment include the halogenated biocides DNBPA and MBNPA (2-bromo-3-nitrilopropionamide) and copper-EDTA (ethylenediaminetetraacetic acid).

A complete investigation of persistent pollutants found in well stimulation fluid is beyond the scope of this study, but this preliminary analysis suggests that potentially persistent pollutants and the reaction products of well stimulation fluid should be evaluated. Baseline measurements for current environmental levels of these compounds, including concentrations in biota as appropriate, are needed in order to determine whether or not these levels are altered by future exposure to well stimulation fluid.

A major mechanism for environmental attenuation of chemicals is biodegradation. Biodegradation in nature or in engineered treatment facilities removes chemicals from environmental systems. Biodegradable materials do not typically persist in the environment, regardless of whether they are released by accident or on purpose.

Standardized methods to measure the biodegradation potential allow the comparison and ranking of chemicals (OECD, 2013; U.S. EPA, 2011). Biodegradation tests only apply to organic compounds. The percentages of chemicals, which have been tested under standardized OECD test conditions and found to be biodegradable, not biodegradable, or for which biodegradation information is unknown, are shown in Figure 2.4-3. The "biodegradable" category includes all chemicals that are ranked as inherently or readily biodegradable by OECD protocols (OECD, 2013). The majority of chemicals that have been tested are biodegradable and therefore are not expected to persist in the environment (Figure 2.4-3). However, approximately one-half of the organic compounds identified by CASRN have not been tested for biodegradation by standardized methods, and many more compounds not identified by CASRN cannot be evaluated. Additionally, standardized biodegradation tests do not take into account chemical interactions that may occur, such as how the presence of biocides may affect the degradation of otherwise biodegradable compounds. Overall, it can be concluded that there is insufficient information to predict how these chemical mixtures will persist in the environment.

Biodegradability of Organic Chemicals

Not Biodegradable
7%

Unknown
52%

Biodegradable
41%

Ready Biodegradability of Organic Chemicals (EPI Suite)

Not Readily Biodegradable
27%

Unknown
24%
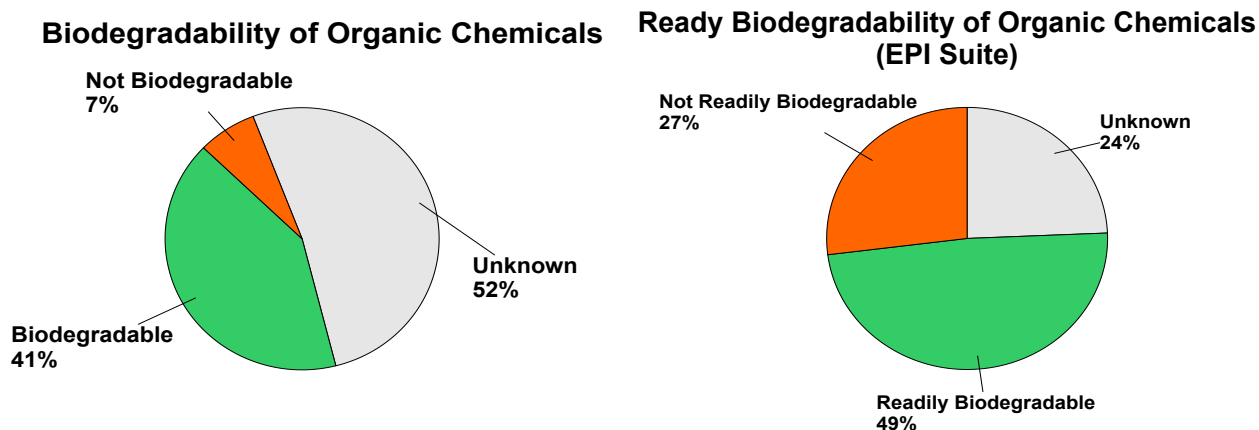
Readily Biodegradable
49%

Figure 2.4-3. Biodegradability of chemicals. For pie charts containing both experimental and computational biodegradability data, the experimental data was used as the value for that chemical in the creation of the pie chart. If only computational data was available, the computational value was used. Computational results are generated for the U.S. EPA BIOWIN program which are not considered as reliable or accurate as experimental results (U.S. EPA, 2012b).

2.4.7.3. Bioaccumulation

Given the large numbers of compounds used in well-stimulation treatments, it is possible that some compounds or reaction products of those chemicals will persist in the environment. Compounds that persist in the environment present a greater risk, if released, than readily degradable compounds. Some persistent compounds may have the potential to "bioaccumulate" or become more concentrated in organisms than in the environment. This is particularly important for organisms higher up on the trophic food chain, such as humans. Trophic transfer of chemicals that bioaccumulate in exposed

organisms to higher concentrations of a chemical, or its transformation products, than are found in the environment are an important exposure mechanism in ecological systems (Currie et al., 1997; Clements and Newman, 2006; Maul et al., 2006; Wallberg et al., 2001; Zhang et al., 2011).

Bioaccumulation is driven by contaminant uptake, distribution, metabolism, storage, and excretion (Connell, 1988; Mackay and Fraser, 2000). The potential for a chemical to bioaccumulate can be indicated by its physiochemical characteristics, such as the octanol-to-water partition coefficient (K_{ow}), which indicates the degree of lipophilicity. However, some chemicals may bioaccumulate despite physiochemical characteristics that indicate otherwise. Active transport of chemicals (Buesen et al., 2003) or the inhibition of efflux transporters (Smital and Kurelec, 1998) can also result in bioaccumulation. An analysis of all chemicals identified in this study indicated that characterization of octanol-to-water partition coefficients for these compounds has not been completed (Figure 2.4-4). Measurement of octanol-to-water partition coefficients and other basic physical and chemical characteristics, such as Henry's constants and sorption coefficients, are needed for development of a complete environmental profile of a chemical (Stringfellow et al. 2014; U.S. EPA 2011).

Availability of Log K_{ow} (Experimental Data Only)

Known 55%

Unknown 45%

Availability of Log K_{ow} (Experimental and EPI Suite Data)
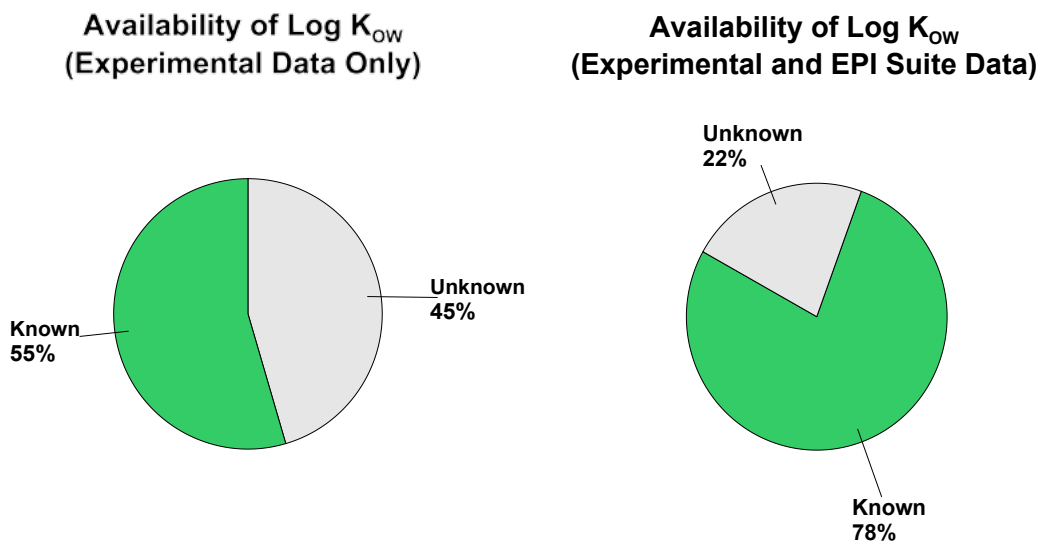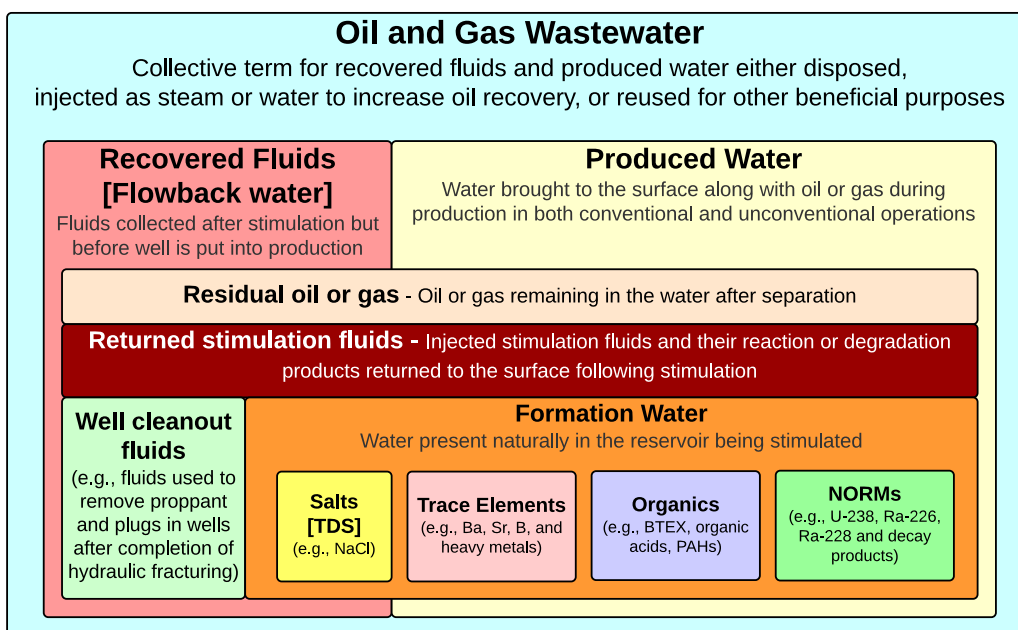
Unknown 22%

Known 78%

Figure 2.4-4. Availability of octanol-water partitioning measurements for hydraulic fracturing and acid treatment chemicals. The potential for a chemical to bioaccumulate can be indicated by its physiochemical characteristics, such as the octanol-to-water partition coefficient (K_{ow}) which indicates the degree of lipophilicity. Physical data such as octanol-to-water partition coefficients are needed to create a complete environmental profile on a chemical. Computational results are not considered as reliable or accurate as experimental results.

2.5. Wastewater Characterization and Management

2.5.1. Overview of Oil and Gas Wastewaters

Both stimulated and non-stimulated wells generate water as part of oil and gas production over the lifetime of the wells. This water byproduct is referred to as "produced water," which consists of formation water mixed with oil and gas that is brought to the surface during production. For stimulated wells, the additional term "flowback" is commonly used to describe the fluids recovered after the well pressure is reduced following stimulation, but *before* the well is put into production (Pavley, 2013; U.S. EPA, 2012a; Vidic et al., 2013). New California regulations introduce another term, "recovered fluids," which is defined as the water returned "following the well stimulation treatment that is not otherwise reported as produced water" (DOGGR, 2014e). The U.S. EPA (U.S. EPA, 2012a) and others use the term "wastewater" to refer to all fluids that return to the surface along with the oil and gas, including recovered fluids, flowback, and produced water. Figure 2.5-1 illustrates the complex nature of wastewater from unconventional oil and gas development.

Oil and Gas Wastewater
Collective term for recovered fluids and produced water either disposed, injected as steam or water to increase oil recovery, or reused for other beneficial purposes

Recovered Fluids [Flowback water]
Fluids collected after stimulation but before well is put into production

Produced Water
Water brought to the surface along with oil or gas during production in both conventional and unconventional operations

Residual oil or gas - Oil or gas remaining in the water after separation

Returned stimulation fluids - Injected stimulation fluids and their reaction or degradation products returned to the surface following stimulation

Well cleanout fluids
(e.g., fluids used to remove proppant and plugs in wells after completion of hydraulic fracturing)

Formation Water
Water present naturally in the reservoir being stimulated

Salts [TDS]
(e.g., NaCl)

Trace Elements
(e.g., Ba, Sr, B, and heavy metals)

Organics
(e.g., BTEX, organic acids, PAHs)

NORMs
(e.g., U-238, Ra-226, Ra-228 and decay products)

* Boxes are not drawn to scale and are separated for visual clarity.

Figure 2.5-1. The water returned from stimulated wells in California consists of recovered fluids (i.e., flowback water) and produced water, which can be disposed of as wastewater or beneficially reused. The recovered fluids in California are typically generated in small quantities and can contain returned stimulation fluids, well cleanout fluids and formation water. The produced water consists primarily of formation water (also referred to as formation brines due to its high salt content), as well as some residual oil or gas, and an unknown amount of returned stimulation fluids. The concentrations and composition of the returned stimulation fluids in both the recovered fluids and produced water is currently unknown. Note that the boxes are not drawn to scale and are separated for visual clarity.

Wastewater from well stimulation operations can contain a variety of constituents, including (1) the additives pumped into the well during well stimulation; (2) compounds that formed due to transformation or degradation of the additives, or to chemical reactions between the additives; (3) dissolved substances from waters naturally present in the target geological formation; (4) substances mobilized from the target geological formation; and (5) some residual oil and gas (NYSDEC, 2011; Stepan et al., 2010). It is expected that the amount of stimulation fluids returned is highest immediately following well stimulation, with a decrease in concentration over time (Barbot et al., 2013; Clark et al., 2013; Haluszczak et al., 2013; King, 2012). The period during which returned stimulation fluids come to the surface following stimulation varies between and within a region, but can range from a few hours to several weeks in shale producing natural gas (Barbot et al., 2013; Hayes, 2009; Stepan et al., 2010; Warner et al., 2013b). Studies have not been conducted to determine the return period for simulation fluids used for oil production in diatomite, as found in California. It is likely that, in California, stimulation fluids, chemical additives, and their reaction byproducts will be present in the water returned to the surface after the well is put into production, and thus will be present in produced water.

New California monitoring and reporting requirements focus on testing and management of recovered fluids and do not require extensive measurement or monitoring of produced water, which is likely to contain some of the stimulation fluids and their degradation byproducts. A recent white paper from DOGGR notes "When well stimulation occurs, most of the fluid used in the stimulation is pumped to the surface along with the produced water, making separation of the stimulation fluids from the produced water impossible. The stimulation fluid is then co-disposed with the produced water" (DOGGR, 2013). The combined handling of wastewaters generated during unconventional oil and gas production makes collection of better data and full characterization of wastewaters over time an important component of understanding the environmental impacts of hydraulic fracturing. The lack of studies on these wastewaters is identified as a major day gap.

In this section, we summarize data available on the quantities and characteristics of wastewater generated from stimulated wells in California. In our analysis, we evaluate the following questions:

- What are the quantities of recovered and produced water generated from stimulated wells within the first few months following stimulation, and are these volumes different from the quantities of produced water generated by non-stimulated wells in California?

- What are the chemical compositions of recovered fluids and produced water from stimulated wells? Is produced water from stimulated wells compositionally different than produced water from non-stimulated wells?

- How are recovered and produced waters from stimulated wells managed, i.e., how are they handled onsite, treated, reused and/or disposed?

2.5.2. Recovered Fluids Generated from Stimulated Wells in California

Recovered fluids are the fluids that are returned to the surface *before* production commences. According to one California operator, the recovered fluids can be a mixture of water from the formation, returned stimulation fluids, and well clean-out fluids (pers. comm., Nick Besich, Aera Energy). Operators are required to disclose "the source, volume, and specific composition and disposition" of the recovered fluids in well completion reports submitted to DOGGR within 60 days following stimulation.

2.5.2.1. Quantities of Recovered Fluids

We determined the quantities of recovered fluids from 506 completion reports filed and posted as of December 15, 2014, for 499 hydraulic fracturing and seven matrix acidizing treatments (DOGGR, 2014a). We first compared the volume of recovered fluid from each well to the corresponding volume of injected stimulation fluids to estimate the maximum recovery of stimulation fluids during the initial phase of wastewater production. One well where the injected volume was reported as zero was excluded from this analysis. Actual recoveries are likely to be lower, but could not be calculated, since the concentrations or masses of stimulation fluid constituents in the recovered fluids are not measured. We also compared the volumes of recovered fluids to the produced water generated during the first month of production, for records where matching production data were available in the DOGGR Production database, to put the recovered fluid volumes in the context of total wastewater generated immediately after stimulation. Wells for which the production volume for the first month or the volume of recovered fluid were reported as zero have been excluded from this analysis.

The volumes of recovered fluids collected from both hydraulic fracturing and acid matrix treatments range from 0 to 1,600 m^3 (9,900 barrels) (Table 2.5-1). The recovered fluid volumes are small (mostly less than 5%) compared to the injected fluid volumes for hydraulic fracturing treatments (Figure 2.5-2). There were eighteen hydraulic fracturing treatments for which the recovered fluid volumes were reported as zero, which could either be errors or indicate that fluids were directly diverted into the production pipeline without capturing any recovered fluid. Hence, the recovered fluid is conclusively a small portion of the fluids injected as part of a hydraulic fracturing treatment. In contrast, the recovered fluids from matrix acidizing potentially represent a much larger fraction (50–70%) of the stimulated fluids for the matrix acidizing operations (Table 2.5-1). The actual recovery of returned stimulation fluids has not been investigated and would require chemical analysis to differentiate between returning well stimulation fluids and connate water. However, the actual recovery of returned well stimulation fluids is likely to be lesser than the reported volumes of recovered fluid, since the recovered fluids can also contain well cleanout fluids and formation water (Section 2.5.2.2).

Table 2.5-1. A comparison of total recovered fluid and injected fluid volumes for stimulated wells located throughout California, as reported in DOGGR completion reports as of Dec 15, 2014 (N=505). All numbers are rounded to two significant figures. St. dev. = standard deviation; min. = minimum, max. = maximum.

	Matrix Acidizing (N=7)			Hydraulic fracturing (N=498)	
	Recovered Volume m³ (barrels)	Injected Volume m³ (barrels)		Recovered Volume m³ (barrels)	Injected Volume m³ (barrels)
Median	150 (970)	240 (1,500)		11 (72)	300 (1,900)
Average	170 (1,100)	270 (1,700)		77 (480)	410 (2,600)
St. Dev.	71 (450)	100 (650)		240 (1,500)	420 (2,600)
Min.	84 (530)	150 (960)		0 (0)	37 (230)
Max.	290 (1,800)	430 (2,700)		1,600 (9,900)	2,600 (16,000)
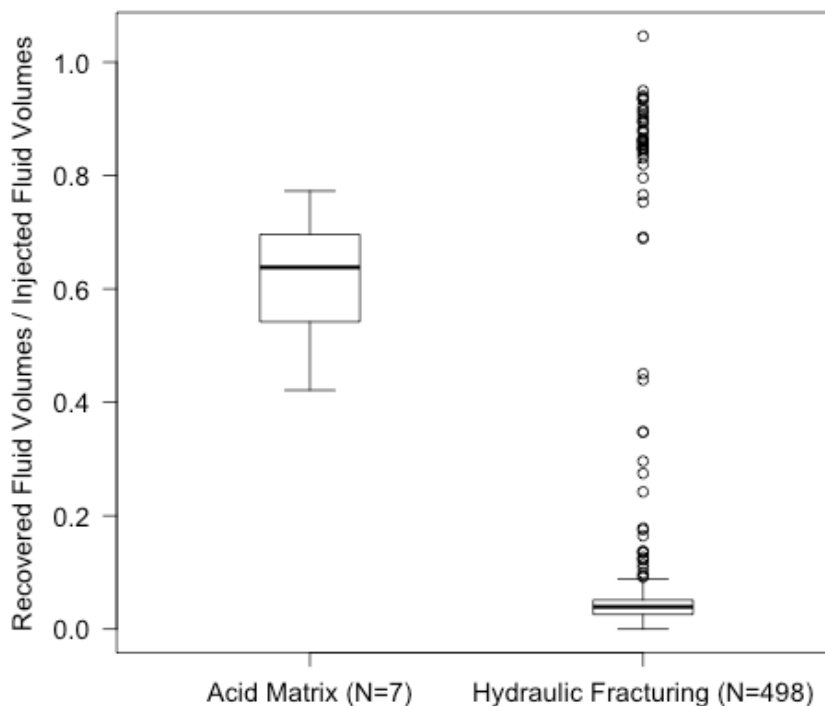
Figure 2.5-2. The fraction of recovered fluid volumes compared to the injected stimulation fluid volumes was significantly higher for acid matrix treatments (50-70%), when compared to hydraulic fracturing treatments. Typically, hydraulic fracturing treatments had very small recoveries (<5%), though there were many cases in which the recovered fluid volumes were much higher. Boxes show the 25th to 75th percentiles of the data, and the central lines show the median. Whiskers extend to 1.5 times the interquartile range from the box. The circles represent the outliers in the data. Data Source: DOGGR Completion reports as of Dec 15, 2015.

The recovered fluids were an extremely small fraction of wastewater generated within just the first month of production (Figure 2.5-3). The volume of produced water in the first month of operations was also substantially larger than the volumes of injected stimulation fluids for both hydraulic fracture and acid matrix treatments.

These analyses show that for hydraulic fracturing operations, the recovered fluids are a fraction of the amount of fluid injected, suggesting that produced water will likely contain some amount of fracturing fluids. Operators are currently required to only report chemical analysis results for the recovered fluids (Section 2.5.2.2), but there is no data available or reported about the masses of stimulation fluids (or their degradation byproducts) present in produced waters. The amount and fate of the injected fracturing fluids that is left behind in the subsurface is unknown.
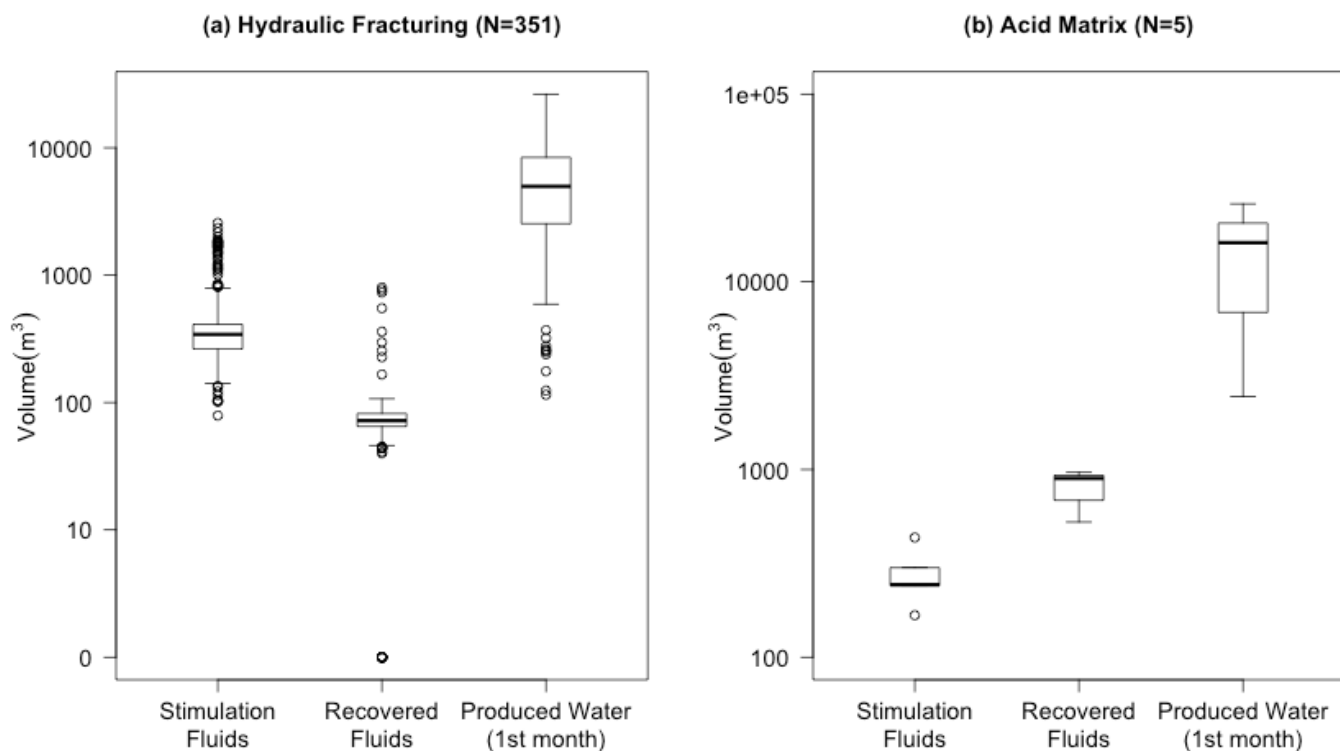
Figure 2.5-3. Volumes (log-scale) of injected fluids, recovered fluids, and produced water in the first month of production for (a) hydraulically fractured and (b) matrix acidizing treatments for wells that were reported in the DOGGR completion reports as of Dec 15, 2014 that had matching records in the DOGGR Production database. Wells that did not have any production within the first month were not considered in this analysis. Boxes show the 25th to 75th percentiles of the data, and the central lines show the median. Whiskers extend to 1.5 times the interquartile range from the box. The circles represent the outliers in the data.

Under new regulations, recovered fluids are now being characterized before disposal, and the results are included in well completion reports submitted to DOGGR. We investigated 45 laboratory chemical analyses that were submitted for onshore stimulated wells as of July, 2014. These data were made available as PDF files and represent waters recovered from operations in two fields (North and South Belridge) by one operator (Aera Energy). Operators are not required to report when the samples were collected after stimulation. According to the operator, the sample "is collected somewhere in the middle of recovery, but operationally that does not always happen." (Aera Energy, Appendix 2.F). Analyses include total carbohydrate, because the carbohydrate guar is a commonly used gelling agent in well stimulation, but this is the only stimulation additive for which a specific measurement was made. Other constituents that were measured include TDS, trace metals, organics, and naturally occurring radioactive materials (NORM) (Table 2.5-2).

Carbohydrates were detected in some of the recovered fluids, suggesting that there may be other stimulation chemicals present as well (Table 2.5-2). Some of the recovered fluids contained high concentrations of TDS, some trace elements (arsenic, selenium and barium), NORM, and hydrocarbons (Table 2.5-2). TDS levels were as high as 260,000 mg L^{-1}. Observed concentrations of the measured parameters were highly variable across wells, even though samples were limited to one operator and two fields. These results confirm that the recovered fluids represent multiple wastewater sources, including formation water and returned stimulation fluids, as was described by the operator (Aera Energy, Appendix 2.F).

The new regulations that go into effect July 2015, are more specific about when the samples for recovered fluids should be collected, and will also require an additional sample for produced water. The new regulations state that the operators must report the "composition of water recovered from the well following the well stimulation treatment, sampled after a calculated wellbore volume has been produced back but before three calculated wellbore volumes have been produced back, and then sampled a second time after 30 days of production after the first sample is taken, with both samples taken prior to being placed in a storage tank or being aggregated with fluid from other wells" (DOGGR, 2014d).

Table 2.5-2. Chemical analyses reported for recovered fluids collected from stimulated wells in North and South Belridge. Measured constituents include salts (TDS), trace metals, organics, NORM and guar (total carbohydrate). Constituents below the detection limit are marked as "ND." A limited amount of data is also available for concentrations of chemical constituents in produced water samples collected (before 1980) from conventional wells across California. All numbers are rounded to two significant digits.

Parameter	Recovered Fluids [a]	Conventional Oil and Gas [b]
General		
Total Dissolved Solids @180 C (mg L^{-1})	430 - 260,000	1,000 – 85,000
Conductivity (µmhos cm^{-1})	240 - 77,000	
pH	6.4 - 9.4	2.6 - 12
Temperature (degrees F)	64 - 130	
Bicarbonate Alkalinity as CaCO$_3$ (mg L^{-1})	ND - 2,900	
Bicarbonate (mg L^{-1})		0 – 13,000
Carbonate Alkalinity as CaCO$_3$ (mg L^{-1})	ND - 470	
Hydroxide Alkalinity as CaCO$_3$ (mg L^{-1})	ND - 0	
Total Alkalinity as CaCO$_3$ (mg L^{-1})	69 - 2,900	0 - 2,100
Major Cations		
Calcium (mg L^{-1})	10 - 13,000	0 – 14,000
Magnesium (mg L^{-1})	7.5 - 700	0 - 2,300
Sodium (mg L^{-1})	93 - 130,000	0 – 100,000
Potassium (mg L^{-1})	2.1 - 66,000	0 – 8,000
Aluminium (mg L^{-1})		0 - 250
Major Anions		
Bromide (mg L^{-1})	ND - 150	1 - 200
Chloride (mg L^{-1})	130 - 190,000	0 - 160,000
Fluoride (mg L^{-1})	ND - 3	
Nitrate as NO3 (mg L^{-1})	ND - 26	0 - 18
Sulfate (mg L^{-1})	28 - 1,900	0 - 15,000
Trace Elements		
Hexavlent Chromium (µg L^{-1})	ND - 9.5	
Antimony (µg L^{-1})	ND - 240	
Arsenic (µg L^{-1})	ND - 1,300	
Barium (µg L^{-1})	ND - 13,000	0 - 170
Beryllium (µg L^{-1})	ND - 50	
Boron (mg L^{-1})	0.26 - 110	0 - 600
Cadmium (µg L^{-1})	ND - 83	
Chromium (µg L^{-1})	ND - 160	0 - 200
Cobalt (µg L^{-1})	ND - 130	
Copper (µg L^{-1})	ND - 1,300	0 - 100
Iron (mg L^{-1})		0 - 540

Parameter	Recovered Fluids [a]	Conventional Oil and Gas [b]
Lead (µg L⁻¹)	ND - 88	
Lithum (mg L⁻¹)	ND - 41	
Manganese (mg L⁻¹)		0 - 50
Mercury (µg L⁻¹)	ND - 0.3	
Molybdenum (µg L⁻¹)	ND - 500	
Nickel (µg L⁻¹)	ND - 260	0 - 30
Selenium (µg L⁻¹)	ND - 510	
Silver (µg L⁻¹)	ND - 42	
Strontium (mg L⁻¹)	0.25 - 230	0 - 600
Thallium (µg L⁻¹)	ND - 0	
Vanadium (µg L⁻¹)	ND - 220	
Zinc (µg L⁻¹)	ND - 1,600	
Radioactivity/NORM		
Recoverable Uranium (pCi L⁻¹)	ND - 95	
Gross Alpha (pCi L⁻¹)	ND - 220	
Radium 226 (pCi L⁻¹)	0.230 - 86	
Radium 228 (pCi L⁻¹)	0-52	
Organics (VOCs)		
Benzene (µg L⁻¹)	ND - 1,300	
Ethylbenzene (µg L⁻¹)	ND - 470	
Toluene (µg L⁻¹)	ND - 3,400	
Total Xylenes (µg L⁻¹)	ND - 3,600	
p&m Xylenes (µg L⁻¹)	ND - 2,500	
o-Xylene (µg L⁻¹)	ND - 1,100	
Organics (PAHs)		
Acenaphthene (µg L⁻¹)	ND - 86	
Acenaphthylene (µg L⁻¹)	ND - 9.8	
Anthracene (µg L⁻¹)	ND - 6.5	
Benzo[a]anthracene (µg L⁻¹)	ND - 9.8	
Benzo[b]fluoranthene (µg L⁻¹)	ND - 3.3	
Benzo[k]fluoranthene (µg L⁻¹)	ND - 4.9	
Benzo[a]pyrene (µg L⁻¹)	ND - 15	
Benzo[g,h,i]perylene (µg L⁻¹)	ND - 0.56	
Chrysene (µg L⁻¹)	ND - 20	
Dibenzo[a,h]anthracene (µg L⁻¹)	ND - 0	
Fluoranthene (µg L⁻¹)	ND - 4.1	
Fluorene (µg L⁻¹)	ND - 140	
Indeno[1,2,3-cd]pyrene (µg L⁻¹)	ND - 0.85	
Naphthalene (µg L⁻¹)	ND - 730	
Phenanthrene (µg L⁻¹)	ND - 180	
Pyrene (µg L⁻¹)	ND - 6.1	

Parameter	Recovered Fluids [a]	Conventional Oil and Gas [b]
Oil and Gas		
Total Petroleum Hydrocarbons -Crude Oil ($\mu g\ L^{-1}$)	ND - 6,700,000	
Methane ($mg\ L^{-1}$)	ND - 5.4	
Stimulation Fluid Constituents		
Total Carbohydrates ($\mu g\ L^{-1}$) - Guar Indicator	0 - 3,700,000	

[a] *From DOGGR Completion Reports. (N=45, submitted from January 2014 to July 2014).*

[b] *Compiled for this report from the USGS Produced Water Database 2.0 (USGS, 2014b). (N=800).*

3.5.2.3. Management of Recovered Fluids

Recovered fluids are typically stored in tanks at the well site prior to disposal or reuse. According to well completion reports, more than 99% of these fluids are injected into Class II disposal wells. A small amount (0.2%) of recovered fluids are recycled, for example, in future well cleanout operations (Aera Energy, Appendix 2.F).

2.5.3. Produced Water Generated from Stimulated Wells in California

The majority of wastewater from stimulation operations is generated after the well is put into production. Data on produced water volumes and disposition are maintained in DOGGR's production database (DOGGR, 2014c). In California on average, approximately ten barrels of produced water are generated for every barrel of oil extracted (Clark and Veil, 2009). In California, well stimulation typically occurs in oil and gas fields that had long-term conventional production (CCST et al., 2014; Volume I). The produced water streams from stimulated wells are combined with those from conventional wells and treated as one waste stream. Operators are required to submit monthly reports to DOGGR on the volume of oil, gas, and water produced from their wells and the disposition method. These data include produced water disposal, as well as reuse in subsequent oil and gas operations or other beneficial uses.

2.5.3.1. Quantities of Produced Water

We compared the volumes of produced water from stimulated and non-stimulated wells to determine if they were different. Monthly produced water volumes for the first six months of oil production from DOGGR's production database were used for this analysis. The records used from the database were for wells in stimulated and non-stimulated pools in Kern County, which had oil production between January 1, 2011 and September 30, 2013. Only wells with at least 10 months of production data were included. Limiting the data to wells in Kern County focused the analysis on wells located where most well stimulation is occurring. Data on non-stimulated wells in other counties were not included, because

of possible regional differences in wastewater production. Multiple stimulation events at individual wells were excluded from the analysis, in order to prevent bias in the results. In this analysis, volumes of produced waters were evaluated for 1,414 stimulated and 3,247 non-stimulated wells.
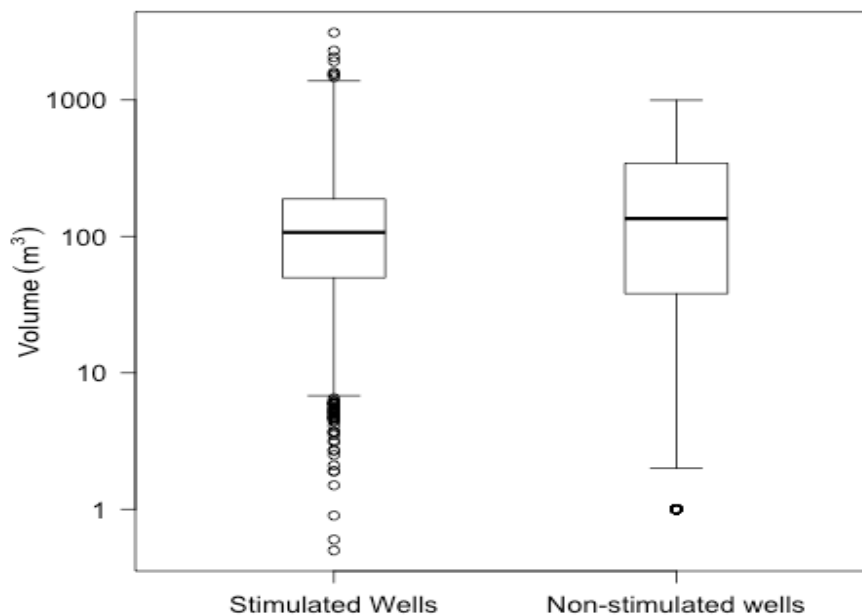

Figure 2.5-4. A comparison of quantities of produced water generated in the first 6 months of oil production from stimulated (N=1,414) and non-stimulated wells (N=3,247) in Kern County. Only wells that had oil production between January 1, 2011 and September 30, 2013 for which there were 10 months of continuous production data were included in the analysis. Note the log-scale in the Y-axis. Boxes show the 25th to 75th percentiles of the data, and the central lines show the median. Whiskers extend to 1.5 times the interquartile range from the box. The circles represent the outliers in the data.

The data do not show substantive differences between the volumes of produced water generated in the first six months from stimulated wells and non-stimulated wells (Figure 2.5-4), even though their distributions were different (Figure 2.5-5).
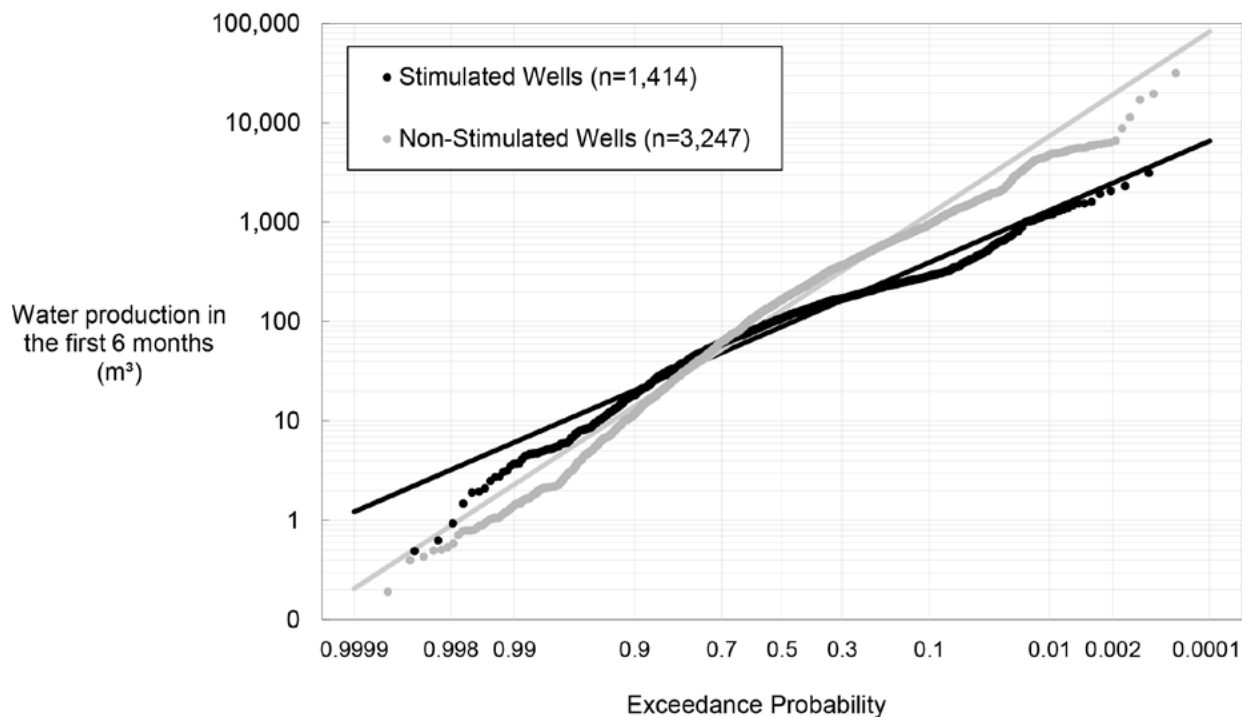
Figure 2.5-5. Probability plot comparing the distributions of produced water volumes for stimulated and non-stimulated wells. The X-axis represents an exceedance probability - i.e., the probability that the produced water generated will exceed a certain value. The Y-axis is on a log scale and has observations of the volumes of produced water in the first 6 months of production, in m³, for oil and gas wells in Kern County, California with at least 10 months of production data from January 1, 2011 to September 30, 2013. For example, there is a 90% probability that the volume of produced water will exceed 10 m³ (~60 barrels) for stimulated wells vs. 15 m³ (~95 barrels) for non-stimulated wells, and a 10% probability that the volume of produced water will exceed ~ 300 m³ (~1,900 barrels) for stimulated wells vs. ~900 m³ (5,700 barrels) for non-stimulated wells. These data show that both of the distributions are different, and that there may be a few cases where the non-stimulated wells produce more water than stimulated wells and vice-versa.

2.5.3.2. Chemical Constituents of Produced Water

There are no published studies that have characterized the chemical constituents of produced water from stimulated wells in California. Operators are not required to report the composition of produced water from stimulated wells. New regulations that take effect July, 2015, will require collection of one produced water sample initially and then another "after 30 days of production after the first sample is taken." This is an inadequate sampling regime to characterize how, or if, well-stimulation-fluid additives or their reaction products are returning with produced water.

Since data on produced water specifically from stimulated wells were not available at the time of writing this report, we identified potential constituents that could be present in produced water from stimulated wells based on (1) studies that have analyzed the compositions of produced water from conventional oil and gas wells in California (e.g., Benko and Drewes, 2008), and (2) a few published studies that have characterized produced water from stimulated wells in other regions (CCST et al., 2014 and references therein). Some historical data on produced water composition in California are available in the USGS produced water database (USGS, 2014b), but data for several constituents are not available (Table 2.5-2). Additionally, the produced water can contain returned stimulation fluids, as discussed above.

Produced water from conventional wells primarily consists of water from the targeted formation. Formation water can contain naturally occurring dissolved constituents, such as salts (measured as total dissolved solids or TDS), trace elements, organic compounds, and naturally occurring radioactive materials (NORM). The most concentrated constituents measured in produced water from both conventional and unconventional wells are typically salts, i.e., sodium and chloride (Barbot et al., 2013; Blauch et al., 2009; CCST et al., 2014; Haluszczak et al., 2013; Warner et al., 2012a; 2012b). Magnesium and calcium can also be present at high levels and can contribute to increased water hardness. The TDS concentrations of produced water from conventional wells in California are typically around 10,000–30,000 mg L^{-1} (CCST et al., 2014), although concentrations can be as high as 85,000 mg L^{-1} (Table 2.5-2).

Formation brines can contain high concentrations of trace elements, such as boron, barium, strontium, and heavy metals, which may be brought up to the surface in the produced water (Table 2.5-2). For example, several studies report measuring high levels of trace elements such as barium, strontium, iron, arsenic, and selenium in the waters recovered from fracturing operations in the Marcellus Shale (e.g., Balaba and Smart, 2012; Barbot et al., 2013; Haluszczak et al., 2013; Hayes et al., 2009). Produced waters from oil and gas operations, including those in California, also contain many organic substances, e.g., organic acids, polycyclic aromatic hydrocarbons (PAHs), phenols, benzene, toluene, ethylbenzene, xylenes, and naphthalene (e.g., Fisher and Boles, 1990; Higashi and Jones, 1997; Veil et al., 2004).

Wastewaters from some shale formations have been found to contain high levels of NORM that were several hundred times U.S. drinking water standards (Barbot et al., 2013; Haluszczak et al., 2013; NYSDEC, 2009; Rowan et al., 2011). In 1996, a study of NORM in produced waters in California conducted by DOGGR (DOGGR, 1996) measured bulk radioactivity and some NORM elements (K-40, U-238, U-235, Ra-226, Ra-228 and Cs-137) in both solid and liquid samples. The study found several produced water samples containing elevated levels of radium greater than 25 pCi g^{-1}, but DOGGR did not consider radium to constitute a public health hazard at the time because "produced waters are not used as a source of drinking water." However, there are several mechanisms by which

produced water can be released into surface and groundwater resources (Section 2.6), and hence elevated levels of potentially contaminating constituents, including NORM, that occur in produced water should be included in future assessments.

More study is needed on produced water in California, particularly characterization of produced water from stimulated wells. Historical (pre-1980) data available on the composition of produced water from conventional wells in California may not be relevant to stimulated wells. The fraction of injected chemicals that return to the surface, and the time period over which they return, are unknown. In addition, the fundamental biogeochemical processes affecting stimulation fluids under reservoir temperature and pressure conditions in the presence of formation minerals have not been investigated. However, it is known that chemical additives are degraded, transformed, sorbed, and otherwise modified in the subsurface, since both specific and non-specific reactions, including strong acid and oxidation reactions, are part of the stimulation process (King, 2012). Other processes, such as biological degradation or transformation of stimulation chemicals, as well as mobilization of formation constituents, can also occur and influence the composition of produced water (Piceno et al., 2014). More data on produced water composition from stimulated and conventional wells in California are needed to assess whether stimulation could affect the produced water chemistry.

2.5.3.3. Management of Produced Water

2.5.3.3.1. Produced Water from Onshore Oil and Gas Operations

As described above, produced water from stimulated wells may contain well-stimulation-chemical additives. Monthly data (1977 to the present) on disposal of produced water are available in DOGGR's Monthly Production database. An analysis was conducted on 2,018 documented well stimulation events which took place between 2011 and 2014 (Volume I, Appendix O) and it was found that data on produced water disposition were available from DOGGR's Monthly Production database for 1,657 wells. For each well for which data was available, we examined disposition during (1) the first full month after stimulation occurred, and (2) from the date of initial well stimulation through June 2014. These results are presented in Table 2.5-3 and Figure 2.5-6.

Table 2.5-3. Produced water disposition during the first full month after stimulation and post stimulation to the present, January 1, 2011-June 30, 2014. Data from the DOGGR Monthly Production database.

	Number of Wells		Total Volume (First Full Month After Stimulation)			Total Volume (Stimulation to June 2014)		
			(m³)	(acre-feet)	%	(m³)	(acre-feet)	%
Evaporation–percolation	890	54%	720,000	580	57%	11,000,000	9,200	58%
Subsurface injection	470	28%	330,000	260	26%	4,100,000	3,300	21%
Other	130	8%	180,000	140	14%	3,400,000	2,700	17%
Not reported	150	9%	31,000	25	3%	510,000	410	3%
Surface body of water	2	0.1%	2,100	1.7	0.2%	95,000	77	0%
Unknown	14	1%	-	-	-	-	-	-
Sewer system	-	-	-	-	-	-	-	-
Evaporation - lined pits	-	-	-	-	-	-	-	-
Total	**1,700**	**100%**	**1,300,000**	**1,000**	**100%**	**19,000,000**	**15,769**	**100%**

Note: All numbers rounded to two significant figures. Numbers may not add up due to rounding. Subsurface injection includes injection into Class II disposal wells as well as injection for enhanced oil recovery, i.e., water flooding and steam flooding.
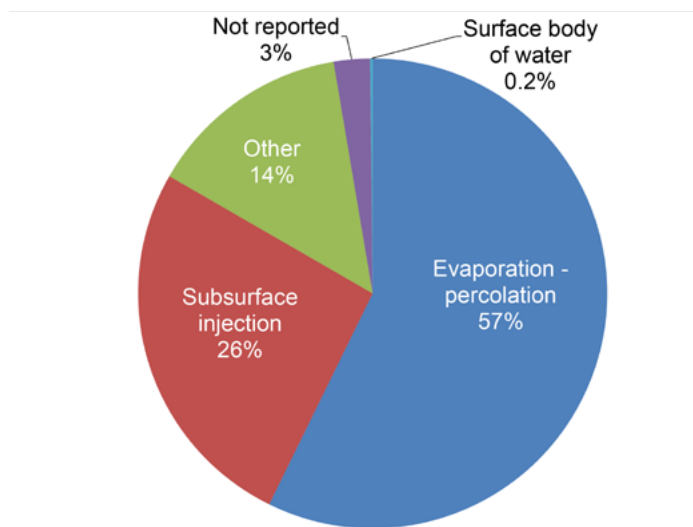*Data Source: DOGGR Monthly Production database*

Figure 2.5-6. Produced water disposition during the first full month after stimulation. Data for stimulated wells throughout California were evaluated for the time period 2011-2014. Data from the DOGGR Monthly Production database.
Note: Subsurface injection includes injection into Class II disposal wells as well as injection for enhanced oil recovery, i.e., water flooding and steam flooding.

Between January 2011 and June 2014, these 1,657 stimulated wells generated a total of 1.3 million m^3 (1,000 acre-feet) of produced water during the first full month following stimulation. Evaporation-percolation in unlined surface impoundments (also referred to as percolation pits, ponds, or sumps) was reported to be the most common disposition method for these stimulated wells. According to California records, nearly 60% of the produced water from stimulated wells, or 720,000 m^3 (580 acre-feet), was disposed to unlined pits for evaporation and percolation during the first full month after stimulation. While produced water disposal in percolation pits has been reported in several California counties (e.g., Fresno, Monterey, and Tulare counties), disposal of produced water from stimulated wells in percolation pits was limited to Kern County and was associated with wells in Elk Hills (65%), South Belridge (27%), North Belridge (5.5%), Lost Hills (2.5%), and Buena Vista (<1%) (Table 2.5-4). Overall, use of percolation pits is common in production areas where well stimulation is applied and an estimated 40% of all produced water from stimulated oil pools is discharged to percolation pits for disposal. There were no reports of discharge to lined surface impoundments for evaporation only as a disposal method.

It is of note that operators have suggested that the information supplied to DOGGR specifying disposal practices for produced water may not be accurate. Chevron, for example, says that it ceased disposing produced water from its Lost Hills operation in unlined pits in 2008 (Appendix 2.E), although DOGGR records indicate this practice was continuing in 2014. Likewise, Occidental Petroleum (now California Energy Resources) says it has used subsurface injection for all produced water in Elk Hills (Nelson, 2014, personal communication). Our analysis is reliant on official data reported to DOGGR, which shows that these and other operators sent the majority of their produced water to unlined pits for evaporation and percolation, but the reports from industry suggest that more produced water may be disposed of in injection wells and less to percolation pits now, than in the past. Further investigation is needed to substantiate current wastewater management practices—particularly in relation to produced water from stimulated wells that may contain hydraulic fracturing fluids—and determine legacy effects from past disposal practices.

Table 2.5-4. Produced water disposition by evaporation-percolation during the first full month after stimulation by field, January 1, 2011 – June 20, 2104. Data from the DOGGR Monthly Production database.

Field	Water volume (m³)	Water volume (acre-feet)	Percent
Elk Hills	460,000	380	65%
South Belridge	190,000	160	27%
North Belridge	39,000	32	5.5%
Lost Hills	18,000	14	2.5%
Buena Vista	2,000	2	0.27%
Total	**720,000**	**580**	**100%**

Note: All figures rounded to two significant figures. Numbers may not add up due to rounding.

Subsurface injection into Class II wells is the second most commonly reported disposition method for stimulated wells in California. Class II wells include saltwater disposal wells, enhanced recovery wells, and hydrocarbon storage wells (U.S. EPA, 2014). With enhanced oil recovery, reinjection of produced water serves multiple purposes, including enhancing product recovery, preventing subsidence, and disposing of produced water generated during production. About one-quarter of the produced water from stimulated wells, or about 330,000 m^3 (260 acre-feet), was injected into Class II wells for disposal or enhanced recovery (Table 2.5-3, Figure 2.5-6). While much of this occurred in Kern County, subsurface injection was the only disposition method reported in several counties, including Colusa, Fresno, Glenn, Ventura, and Orange County (Table 2.5-5).

Table 2.5-5. Produced water disposition by subsurface injection during the first full month after stimulation, by county, January 1, 2011 – June 30, 2014. Data from the DOGGR Monthly Production database.

County	Water volume (m^3)	Water volume (acre-feet)	Percent
Colusa	47	0.04	0.014%
Fresno	1,900	2	0.59%
Glenn	7.6	0.01	0.0023%
Kern	270,000	216	82%
Los Angeles Offshore	52,000	42	16%
Orange	1,700	1	0.52%
Sutter	430	0	0.13%
Ventura	3,500	3	1.1%
Total	**330,000**	**260**	**100%**

Note: All figures rounded to two significant figures. Numbers may not add up due to rounding.

As shown in Table 2.5-3, very few operators discharge produced water from stimulated wells into creeks or streams, with only two wells reported to be discharging a total of 2,100 m^3 (1.7 acre-feet) of produced water into surface water bodies during the first full month following stimulation. There were no reports of produced water from stimulated wells being disposed of in sewer systems.

The disposition method for 17% of the produced water from stimulated wells is either not known or not reported. "Other" was the third most common disposition method reported by operators—accounting for 14% of the produced water from stimulated wells. Similarly, the disposition method for 3% of the produced water was not reported. DOGGR staff confirmed that some operators are using the "other" category to describe disposition that is, in fact, included in some of the other categories, e.g., subsurface injection, surface body of water, sewer disposal, etc. (Fields, 2014). Some disposition methods, however, are not explicitly covered in these categories, such as reuse for irrigation, well stimulation,

or other beneficial purposes, although there is anecdotal evidence that reuse for these purposes is occurring in California (for more information, see Section 2.6). These results suggest a need to improve data collection and better understand wastewater management practices in California.

2.5.3.3.2. Produced water from Offshore Oil and Gas Operations

California has four offshore oil platforms (Esther, Eva, Emmy, and Holly) and several man-made islands (Long Beach Unit, Rincon Island) operating in state waters. Well stimulation operations have been reported on Platforms Esther, Eva, and on the Long Beach Unit (THUMS Islands). There are also 23 oil platforms operating in federal waters off the coast of California, of which well stimulation operations have been reported on Platforms Gail, Gilda, and Hidalgo. Well stimulation accounts for a small fraction of offshore oil and gas production. It is estimated that approximately 12 hydraulic fracturing operations occur per year in state waters, and less than 10% of wells are hydraulically fractured in federal waters (Volume I, Chapter 3).

Options for the management and treatment of produced water on offshore oil platforms and islands are limited by treatment technology footprint, transportation costs, storage capacity, effluent limitations, and disposal options. Operations in state waters typically treat produced water to meet requirements for re-injection for enhanced oil recovery, and operations in federal waters treat produced water for discharge. Permitted disposal options vary as platforms located in federal waters are regulated under a general NPDES permit issued by U.S. Environmental Protection Agency (U.S. EPA), Region 9 (U.S. EPA, 2013a), while operations in California state waters are regulated under individual NPDES permits issued by regional water quality control boards.

On Platforms Esther and Eva, oil, gas, and produced water are separated using three-phase separators. The produced water then goes through a series of treatment processes to remove residual oil and suspended solids (California State Lands Commission, 2010a; 2010b).[2] Once treated, produced water is typically re-injected into the producing formation for enhanced oil recovery. On the Long Beach Unit, a portion of the produced water is reused as base fluid for well stimulation (Garner, 2014, personal communication).

Platforms operating in federal waters off the coast of California are permitted to discharge produced water that has been treated, as stipulated under a general NPDES permit.[3] When well stimulation fluids co-mingle with produced water, the mixture is managed, treated, and discharged according to produced water stipulations. Each of the 23 platforms has a maximum annual allowable produced water discharge volume, which ranges from

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2. There is no evidence of a separate treatment system for managing wastewaters from well stimulation operations on Platform Esther. It is expected that wastewaters from well stimulation operations on Platforms Esther and Eva are subject to the same treatment processes and fate as produced water.

3. NPDES permit No. CAG280000

0.25 million to 8.9 million m³ (206 to 7,192 acre-feet) per platform (U.S. EPA, 2013a). Platforms Gail and Hidalgo are allowed to discharge 0.7 million m³ (560 acre-feet) and 2.9 million m³ (2,350 acre-feet), respectively. Platform Gilda's discharge allowance is combined with that for Platform Gina at 4 million m³ (3,300 acre-feet).

For a permitted discharge, oil and grease levels are measured weekly and must be lower than 29 mg L^{-1} monthly average and 42 mg L^{-1} daily maximum in discharged wastewater, according to effluent limitations in Subpart A of 40 CFR Part 435 in the Clean Water Act. The permit does not allow discharge of free oil, where free oil is defined as oil which will cause a film, sheen, or discoloration to the water surface upon discharge (U.S. EPA, 2014). Fourteen platforms, including Platforms Gail, Gilda, and Hidalgo, have specific monitoring and effluent requirements for produced water discharge, with measurements typically occurring on an annual or monthly basis. Platforms Gail, Gilda, and Hidalgo must also monitor for various aromatic hydrocarbons, but only have effluent limits for undissociated sulfide. All other platforms must monitor 26 constituents of concern.[4] These data are submitted to the EPA. The number of constituents sampled is based on previous studies where constituents present at concentrations above or near the water quality standards were identified and listed in the permits (U.S. EPA, 2013b). Sampling frequency depends on the frequency of discharge; however, constituents must be sampled "at least once during the last two years" of the permit (U.S. EPA, 2013a). Discharges are not monitored for constituents specific to or indicative of hydraulic fracturing, and the timing of sampling is unlikely to coincide with or measure any potential impacts from well stimulation treatments.

2.6. Contaminant Release Mechanisms, Transport Pathways, and Driving Forces

2.6.1. Overview of Contaminant Release Pathways

Well stimulation and associated activities can result in the release of contaminants into the environment, including into surface water and groundwater resources. Releases can occur during chemical transport, storage, mixing, well stimulation, well operation and production, and wastewater storage, treatment, and disposal. The term "release mechanism" refers to the way in which a contaminant migrates from its intended containment (natural or manmade) into the surrounding environment. Once released, contaminants can be transported through various mechanisms (e.g., percolation into soil, transport into groundwater, runoff to local streams) or transformed through physical, chemical, and biological processes. A *physical connection*, either natural or induced, between the release location and the impacted surface or groundwater body is referred to as a "transport pathway." A *driving force* (e.g., differences in hydraulic head or pressure) is required for contaminant migration into the connected surface or groundwater body.

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4. Where the California Ocean Plan also contains criteria for a select constituent, then the more stringent of the two is used, as the California Ocean Plan can regulate "discharge outside the territorial waters of the State [that] could affect the quality of the waters of the State" (SWRCB, 2012).

The extent to which water resources are affected by releases of well stimulation chemicals or wastewaters depends on the amount and type of contaminant(s) released, existence of transport pathways and corresponding driving forces, and the transformations occurring during transport. Other factors that impact the probability of contaminant migration include reservoir depth, physical and hydrological properties of the formation, production strategies, drilling and casing practices, and the unique geologies of each oil and gas-producing region.

Release mechanisms and transport pathways can occur at the surface or in the subsurface, and are associated with a variety of activities during the production process (e.g., well stimulation, wastewater management and disposal, and well operation). Surface releases are typically easier to identify and associate with a particular activity. Subsurface releases are generally more difficult to detect, associate with a particular release mechanism, and mitigate. Reservoir and stimulation fluids can migrate through the subsurface if (1) surface releases eventually percolate into groundwater; (2) produced water is directly injected into protected groundwater; or (3) if transport pathways out of the reservoir being fractured (out-of-zone) have been created through stimulation operations, either through direct fracturing into overlying aquifers or via out-of-zone connection to a preexisting pathway (e.g., a preexisting fracture network, a fault, or some other permeable feature). While transport through preexisting or induced subsurface pathways has been documented in conventional oil and gas operations, it is not known whether stimulation increases the frequency of occurrence of such pathways. Regardless of the uncertainty whether stimulation increases the frequency of leakage pathways, stimulation introduces a new set of water quality concerns for leakage, through pathways documented from conventional oil and gas operations, due to the use of stimulation chemicals and the commingling of produced water and returned stimulation fluids.

2.6.2. Potential Release Mechanisms to Water in California

In this section, we identify potential release mechanisms specific to well stimulation activities that can (1) form transport pathways (natural, induced, or a combination) to water resources and (2) allow stimulation or reservoir fluids to migrate into water resources if the appropriate driving forces are present. We examined several plausible release mechanisms for surface and groundwater contamination associated with onshore well stimulation, based on an exhaustive literature review of release events and hazards that have been reported in the U.S. (Table 2.6-1). While release mechanisms and transport pathways that occur during post-stimulation and wastewater management apply to all oil and gas development in California, they are relevant to stimulated wells because produced water from stimulated wells may contain hazardous chemicals from well stimulation fluids.

Table 2.6-1. Activities and associated release mechanisms
for the different stages of well stimulation

Activities	Release Mechanisms and Transport Pathways	Releases
Preparation: Site development, well drilling, construction and completion	• Erosion and surface runoff* • Well blowout resulting from failure to control well pressure and improper well installation* • Release of drilling fluids and waste during handling, storage and disposal* • Migration through existing or induced pathways or other subsurface features (such as faults, fractures, or permeable adjacent formations)*	• Soil/particulate matter in stormwater runoff • Drilling fluids and wastes • Oil and gas • Formation water
Well stimulation	• Transportation accident • Equipment failure • Leakage from onsite chemical storage • Spills during chemical mixing • Pipe failure (both above and below ground) • Well failure due to stimulation • Problems related to drilling, completion, or well design errors (e.g., poor cementing, wrong perforation depth) • Migration via other pathways intercepted by fractures (including plugged, deteriorated, or abandoned wells) • Fractures or other permeable pathways directly intercepting groundwater resources	• Additives • Stimulation fluids • Oil and gas • Formation water
Post-stimulation: Well cleanout and production	• Pipe failure (both above and below ground) • Well failure due to drilling, completion or well design errors (e.g., leakage through compromised casing and cement) • Migration via other pathways intercepted by fractures (including plugged, deteriorated, or abandoned wells, faults, fractures, permeable adjacent formations)	• Well cleanout fluids • Wastewaters • Oil and gas • Formation water
Wastewater management: Handling, storage, reuse, and disposal	• Spills and leaks during storage and handling • Transportation accident • Pipe failure (both above and below ground) • Overflow from storage reservoir • Percolation (from storage or disposal pits) • Reuse of produced water for beneficial purposes (e.g., irrigation) • Disposal of produced water into sewer system (and subsequent disposal of treatment residuals) • Improper siting of disposal wells (into aquifer or protected groundwater) • Failure of disposal well (e.g., leakage through casing or cement) • Migration through existing pathways during subsurface disposal (e.g., faults, fractures, permeable overburden) • Illegal discharge	• Wastewaters • Oil and gas • Treatment residuals (including disinfection byproducts)

Note: * Release mechanisms that are not within the scope of this assessment since they are part of routine oil and gas development and there are no unique impacts associated with well stimulation. While release mechanisms and transport pathways that occur during post-stimulation and wastewater management apply to all oil and gas development in California, they are of particular relevance for stimulated wells (and are included in this study) because (1) produced water from stimulated wells may contain returned stimulation fluids, and (2) the quality of formation water from stimulated reservoirs may differ from that of conventional reservoirs.

We narrowed the broad set of possible release mechanisms to a subset that is most relevant for California (Figures 2.6-1 and 2.6-2, Table 2.6-2). In the following sections, we list several incidents of contamination that have occurred in California or other oil and gas producing regions, to show that these release mechanisms are viable, and relevant for California.

The California-specific release mechanisms are classified as normal, accidental, and intentional (Table 2.6-2). "Normal" release mechanisms result from practices that are part of routine operations in the California oil and gas industry, and include disposal of produced water in unlined pits, injection of produced water into potentially protected groundwater, reuse of produced water for irrigation, and disposal of produced water in sewer systems. "Accidental" release mechanisms can be of several types, including errors in design and execution of the stimulation operation—such as out-of-zone fracturing, leakage through degraded or impaired wells, leakage through natural subsurface features, surface spills and leaks, or consequences of natural disasters such as earthquakes and floods. It should be noted that in California, where fracturing depths are much shallower than in other parts of the country, fractures induced by hydraulic fracturing could potentially form direct transport pathways to groundwater. Nationally, several incidents have been caused by leakage through degraded abandoned wells and leakage of stray gas from production or other wells into groundwater. Surface releases caused by spills or leaks have been conclusively linked to stimulation operations. "Intentional" release mechanisms are unauthorized or unpermitted releases such as illegal discharges.

Finally, we assigned a priority for each release mechanism based on the release type (e.g., all releases that are part of normal operations are considered high priority), and direct or indirect evidence indicating their likelihood of occurrence in California (Table 2.6-2). We focus on release mechanisms and transport pathways from hydraulic fracturing operations, and assume that this covers concerns associated with matrix acidizing operations, given that the latter follow a similar process as hydraulic fracturing operations, albeit using less equipment, lower injection pressures, and no proppant (Volume I, Chapter 2).

Table 2.6-2. Assessment of release mechanisms associated with stimulation operations for their potential to impact surface and groundwater quality in California. Considerations for the priority ranking include whether the releases occur due to activities that are part of normal operations, and the likelihood of the occurrence in California. References for this table are provided in the text.

Release Mechanism	Release type*	Has occurred in California?	Has occurred in other places?	Evidence associating release to hydraulic fracturing?	Priority
Percolation of produced water from unlined pits	Normal	Yes	Yes	Yes	High
Injection of recovered fluids and produced water into potentially protected groundwater via Class II wells	Normal	Yes	No	Unknown	High
Reuse of produced water for irrigation	Normal	Yes	No	Unknown but likely	High
Disposal of produced water in sewer systems	Normal	Yes	Yes	Unknown in California, yes in other states	High
Leakage through hydraulically induced fractures	Accidental	Unknown	Unknown	Unknown	Medium
Leakage through failed inactive wells (abandoned, buried, idle or orphaned)	Accidental	Unknown	Yes	Unknown	Medium
Leakage through active wells (production, disposal or other wells)	Accidental	Unknown	Yes	Yes	Medium
Leakage through other subsurface pathways (preexisting natural fractures, faults, or other permeable features)	Accidental	Yes	Unknown	Unknown	Medium
Surface and near-surface spills and leaks	Accidental	Yes	Yes	Unknown	Medium
Operator error	Accidental	Unknown	Yes	None in California, yes elsewhere	Low
Illegal discharges of wastewater from oil and gas operations	Intentional	Yes	Yes	Yes	Low

*The type of activity leading to the release. Categories are

Normal: Activity is part of normal operations, and release occurs by design.

Accidental: Release was caused due to an accident, but can be prevented by following proper design and protocols

Intentional: Release was intentional despite being unauthorized, and can be prevented by proper oversight and monitoring.
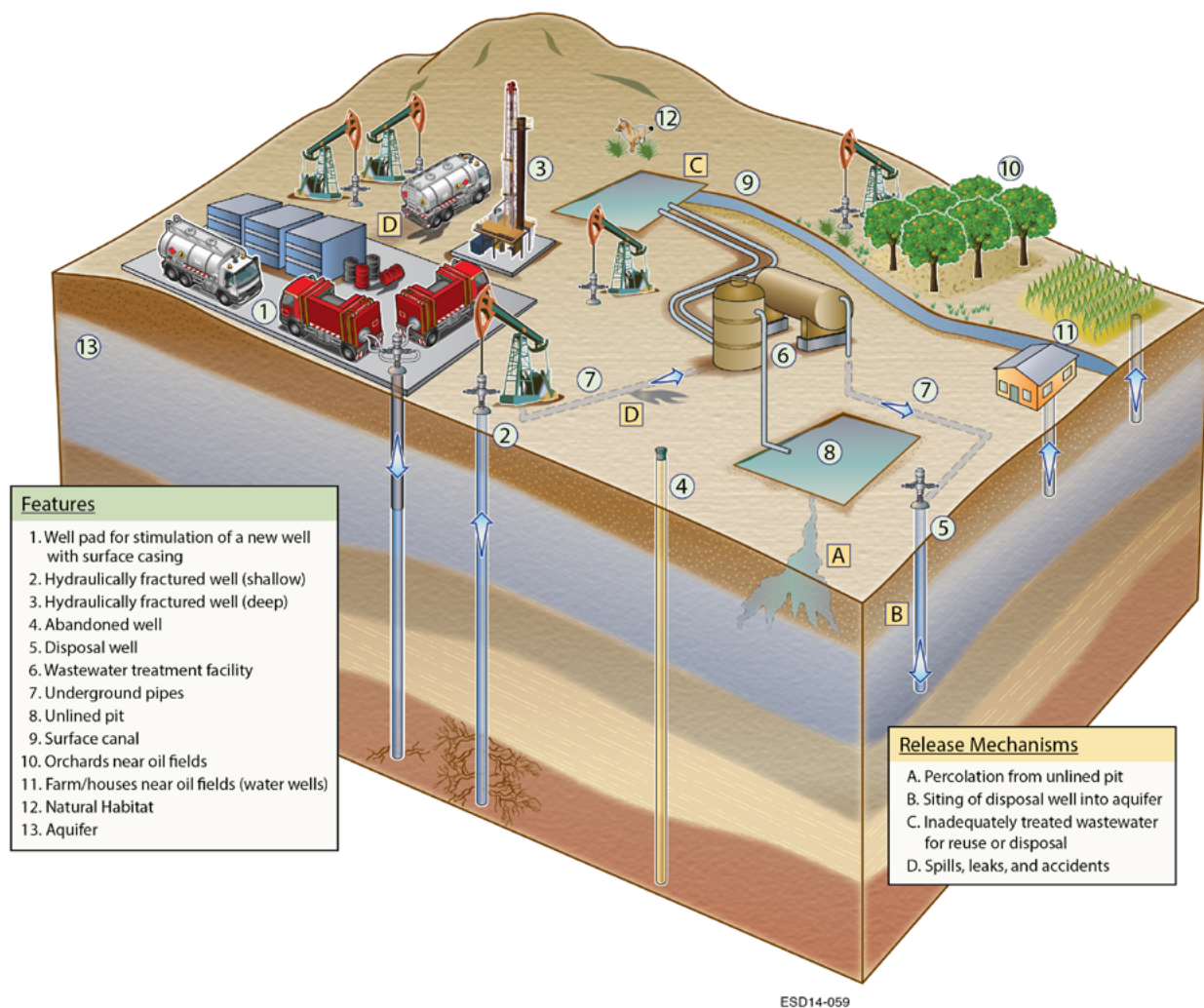
Features

1. Well pad for stimulation of a new well with surface casing
2. Hydraulically fractured well (shallow)
3. Hydraulically fractured well (deep)
4. Abandoned well
5. Disposal well
6. Wastewater treatment facility
7. Underground pipes
8. Unlined pit
9. Surface canal
10. Orchards near oil fields
11. Farm/houses near oil fields (water wells)
12. Natural Habitat
13. Aquifer

Release Mechanisms

A. Percolation from unlined pit
B. Siting of disposal well into aquifer
C. Inadequately treated wastewater for reuse or disposal
D. Spills, leaks, and accidents

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Figure 2.6-1. Potential contaminant release mechanisms that originate at the surface related to stimulation, production, and wastewater management and disposal activities in California. The diagram is not drawn to scale.
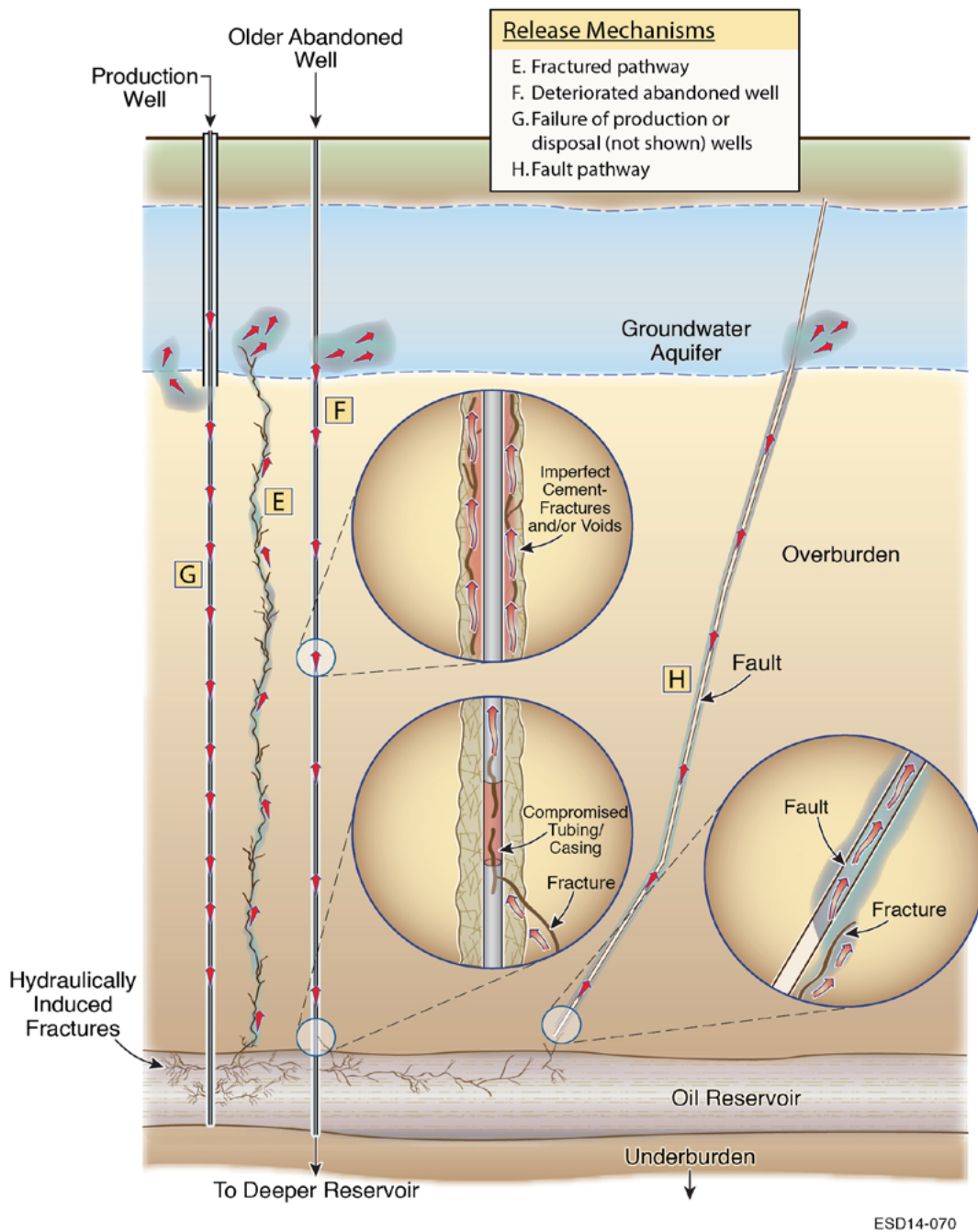
Figure 2.6-2. Potential release mechanisms and transport pathways in California that could originate in the subsurface. These include leakage through failed (production, abandoned or disposal) wells, migration through intercepted fractures and fault activation. The diagram is not drawn to scale.

2.6.2.1. Use of Unlined Pits for Produced Water Disposal

As described above, evaporation-percolation in unlined surface impoundments (percolation pits) is a common disposition method for produced water from stimulated wells in California (Section 2.5). Because the primary intent of unlined pits is to percolate water into the ground, this practice provides a direct pathway for the transport of produced water constituents, including returned stimulation fluids, into groundwater. Some states, including Kentucky, Texas, and Ohio, have phased out the use of unlined pits for disposal (Kell, 2011; 401 KAR 5:090 Section 9(5)(b)(1)).

The state's nine Regional Water Quality Control Boards have primary authority to regulate disposal pits in California.[5] Most of the instances of discharge into percolation pits occurred in the region under the authority of the Central Valley Regional Water Quality Control Board. Within that region, disposal of produced water in percolation pits overlying groundwater with existing and future beneficial uses has been allowed if the wastewater meets certain salinity, chloride, and boron thresholds.[6] Produced water that exceeds the salinity thresholds may also be discharged in "unlined sumps, stream channels, or surface water if the discharger successfully demonstrates to the Regional Water Board in a public hearing that the proposed discharge will not substantially affect water quality nor cause a violation of water quality objectives" (CVRWQCB, 2004). There was previously no testing required, nor thresholds specified, for other contaminants, including chemicals used for well stimulation or other routine oilfield activities. The Central Valley Regional Water Quality Control Board implemented an order on April 1, 2015 requiring operators to conduct a chemical analysis of wastewater disposed in active produced water disposal ponds in the Central Valley; however, the list of constituents to be analyzed does not include any indicators for stimulation fluid constituents (CVWQCB, 2015).

Figure 2.6-3 shows active and inactive unlined pits and ponds in the Central Valley and along the Central Coast. Presumably, the pits are largely used to deliberately percolate wastewater for the purpose of disposal. Active pits are primarily found on the east and west side of the southern San Joaquin Valley, although a small number of active pits can also be found in Monterey and Santa Barbara Counties. The Central Valley Regional Board is currently conducting an inventory of unlined pits in the Central Valley. As of April 2015, a total of 933 pits have been identified, of which 62% are active and 38% are inactive. An estimated 36% of the active unlined pits are operating without the necessary permits from the Central Valley Regional Board (Holcomb, 2015). Central Valley Regional Board

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5. Local Air Districts also regulate some aspects of oilfield pits, e.g., volatile organic carbon (VOC) emissions.

6. According to the Water Quality Control for the Tulare Basin, which was developed by the Central Valley Regional Water Quality Control Board, tdisposal of oil field wastewater in pits overlying groundwater with existing and future beneficial uses is permitted if the salinity of the wastewater is less than or equal to 1,000 micromhos per centimeter (μmhos cm^{-1}) electrical conductivity (EC), 200 milligrams per liter (mg L^{-1}) chlorides, and 1 mg L^{-1} boron (CVRWQCB 2004).

staff expects to issue 180 enforcement orders for facilities that are not permitted or are operating with outdated permits by the end of 2015. Cease and desist orders have been issued for some facilities operating with outdated permits (Holcomb, 2015). An analysis of groundwater quality near these pits can be found in Section 2.7.

There is not one centralized location for reporting and tracking locations of unlined or disposal pits in California, so any list of disposal pits must be considered approximate. The Central Valley Regional Board, which recently launched an investigation into unlined pits, found that more than one-third of the pits located in their jurisdiction were functioning without the proper permits, indicating that there may be additional pits of which the state is unaware (Holcomb, 2015). The DOGGR production database indicates that produced water is sent to evaporation-percolation disposal ponds in counties where there are no reported pit locations, suggesting that there may be unreported pits in those counties. For example, according to the production database, 47,000 m^3 (38 acre-feet) were sent to evaporation-percolation ponds in Ventura County in 2013 (DOGGR, 2014c), despite there being no reported pit locations within or near the borders of that county (Holcomb, 2015).
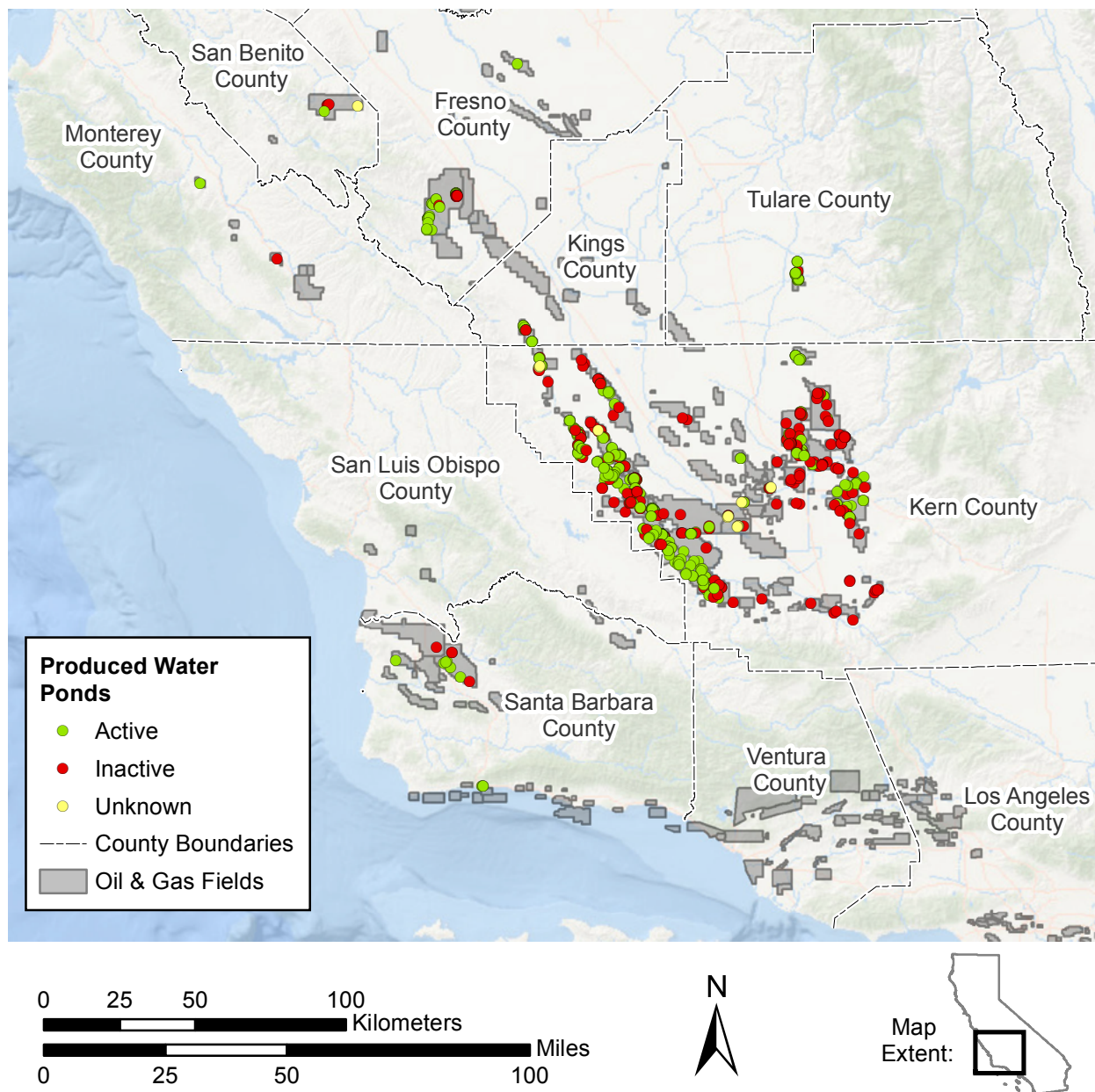
Figure 2.6-3. Unlined pits used for produced water disposal in the Central Valley and the Central Coast, 2015. Data from CVRWQCB 2015; Borkovich 2015a; 2015b (Appendix 2.G).

There is ample evidence of groundwater contamination from percolation pits in California and other states (e.g. CVRWQCB, 2015; Holcomb, 2015; Kell 2011). For example, in California, the Central Valley Regional Water Quality Control Board determined that several percolation pits in Lost Hills and North and South Belridge had impacted groundwater, and ordered their closure (CVRWQCB, 2015). In these cases, monitored natural attenuation rather than active remediation was selected as the method for

corrective action for improving the groundwater quality. Groundwater contamination has also been associated with unlined pits in other states. Kell (2011) reviewed incidents of groundwater contamination caused by oil field activities in Texas between 1993 and 2008 and in Ohio between 1983 and 2007. Of the 211 incidents in Texas over the 16-year study period, 27% were associated with unlined infiltration pits, which have been phased out in Texas starting in 1969 (Kell, 2011). Of the 185 groundwater-contamination incidents in Ohio over a 25-year period, 5% (or 10 incidents) were associated with the failure of unlined pits. Like Texas, unlined disposal pits are no longer used in Ohio, and no incidents have been reported since the mid-1980s (Kell, 2011). While these studies and others linking wastewater percolation and unlined pits to groundwater contamination are not specific to well stimulation fluids, they are illustrative of the implications of this disposal method. Moreover, the presence of stimulation fluids in the produced water is likely to increase the risk of groundwater contamination.

A case in Pavillion, WY, raises additional concerns about the use of unlined pits for produced water disposal. According to the U.S. EPA draft report, released in 2011, high concentrations of hydraulic fracturing chemicals found in shallow monitoring wells near surface pits "indicate that pits represent a source of shallow ground water contamination in the area" (Digiulio et al., 2011). At least 33 unlined pits were used to store or dispose of drilling muds, flowback, and produced water in the area. Neither the company responsible for the natural gas wells, nor the other stakeholders contested these findings (Folger et al., 2012).

2.6.2.2. Injection of Produced Water into Protected Groundwater via Class II Wells

Subsurface injection was the second most common disposal method for produced water from stimulated wells (Section 2.5). Studies show that with proper siting, construction, and maintenance, subsurface injection is less likely to result in groundwater contamination than disposal in unlined surface impoundments (Kell, 2011). However, there are significant concerns about whether California's Class II underground injection control (UIC) program is adequately protective of underground sources of drinking water (USDWs) – defined as groundwater aquifers that are used for water supply or could one day supply water for human consumption.[7]

In 2011, at the request of EPA Region 9, an independent consultant reviewed California's UIC Program and found inconsistencies in how USDWs are defined (Walker, 2011). Specifically, the DOGGR program description refers to the protection of freshwater containing 3,000 mg L^{-1} or less TDS. Current federal regulation, however, defines USDWs as containing less than 10,000 mg L^{-1} TDS. This suggests that USDWs in California containing between 3,000 and 10,000 mg L^{-1} TDS are not adequately protected. More recently, DOGGR acknowledged that it has approved UIC projects in zones with aquifers

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7. The UIC program was developed as a result of the 1974 Safe Drinking Water Act and was intended to protect USDWs.

lacking exemptions, even though those zones would likely qualify for an exemption under current regulations.[8] Additionally, new information has indicated that, for several decades, injection activities have been allowed in 11 other aquifers that were thought to be exempt; however, the geologic basis for those exemptions is "now in question" (Bohlen and Bishop, 2015).

In response to these issues, DOGGR is reviewing more than 30,000 of the state's 50,000 Class II wells, and is expected to complete that review in early 2016. Given their mutual role in protecting water resources, DOGGR and the State Water Board are working together on this review. In 2014, DOGGR ordered the immediate closure of 11 disposal wells in Kern County that potentially present health or environmental risks, and State Water Board staff identified 108 water supply wells located within a one-mile radius of these wells.[9] Subsequent sampling found no sign of contamination from oil and gas operations (SWRCB, 2014b). Currently, 140 active wells are under immediate review by the State Water Board, because they are operating in aquifers that lack hydrocarbons and contain water with less than 3,000 mg L^{-1} TDS. These wells are being reviewed for "proximity to water supply wells or any other indication of risk of impact to drinking water and other beneficial uses" (Bohlen and Bishop, 2015). The State Water Board is reviewing 150 injection wells per month and expects to be done with its review in May 2015. Going forward, DOGGR has proposed a schedule and process to the U.S. EPA to bring California's UIC program into compliance with federal regulations. Further analysis on this subject can be found in Volume III, Chapter 5.

2.6.2.3. Reuse of Produced Water for Irrigated Agriculture

Produced water is commonly reused for beneficial purposes, including steam flooding, irrigation, and industrial cooling. In some cases, the produced water is treated prior to reuse, but in others it is simply blended with freshwater to bring the levels of salts and other constituents down to an acceptable range. In California, in in particular the San Joaquin Valley, there is growing interest in expanding the beneficial reuse of produced water for agriculture, particularly for irrigation, due to the co-location of oil, gas, and agricultural operations and ongoing water scarcity concerns in these areas. The use of produced water from unconventional production raises specific or unique concerns, because of the variety of chemicals used during well stimulation that may end up mingled with produced water and the unknowns concerning the toxicity and environmental profile of those chemicals (discussed in the characterization of chemicals section, above).

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8. An "exempt aquifer" is an aquifer that meets the criteria for protection but that protection has been waived because it is not currently being used — and will not be used in the future — as a drinking water source, or it is not reasonably expected to supply a public water system due to a high total dissolved solids content.

9. Since review, two of the 11 wastewater disposal wells have been authorized to resume operations.

It is not known if produced water from stimulated wells is or has been used for irrigation in California. According to data from the Central Valley Regional Board, there are currently five fields (Deer Creek, Jasmin, Kern River, Kern Front and Mount Poso) where produced water is reused to irrigate crops. Of these fields, well stimulations have only been reported in Kern River and Mount Poso. In Mount Poso, the last reported hydraulic fracture was in 2003. In Kern River, there are five records of fracturing operations in the public data sets reviewed, four in wells operated by Chevron, including some since use of produced water from Chevron's wells for irrigation commenced. Chevron is the only operator in Kern River with a permit to provide produced water for irrigation.

Produced water from the Kern River oil field irrigates the Cawelo Water District, a service area covering 182 km^2 (45,000 acres), of which roughly 82% of crops are permanent crops, including citrus, nuts, and grapes (Cawelo Water District, 2014). The water is treated at the Kern River Area Station 36 Treatment Plant before it is delivered to the water district (CVRWQCB, 2012). The Cawelo Water District sets water quality goals that comply with requirements established by the CVRWQCB in the Tulare Lake Basin Plan. However, these requirements do not include monitoring for constituents specific to, or indicative of, hydraulic fracturing (CVRWQCB, 2012).

2.6.2.4. Treatment and Reuse of Oil and Gas Industry Wastewater

Comprehensive data on current practices applied in California for the treatment of produced water before beneficial reuse are not available. However, in general, the treatment of produced water has been the subject of intensive investigation and standard treatment practices have evolved for the reuse of produced water (e.g., Federal Remediation Technologies Roundtable, 2007). Treatment of constituents commonly found in produced water (e.g., oil and grease, dissolved solids, suspended particles, bacteria, etc.) is generally well documented (Arthur et al., 2005; Drewes, 2009; Fakhru'l-Razi et al., 2009; Igunnu and Chen, 2012; M-I SWACO, 2012). We are unaware of any studies that examine whether commonly used produced water treatment systems would effectively remove hydraulic fracturing chemicals (particularly organic chemicals) that might be found in produced water from stimulated wells.

We evaluated the potential effectiveness of various chemical, physical, and biological treatment technologies commonly used for produced water treatment in California for removing well stimulation chemicals (Appendix 2-C). Results of the analysis indicate that there is no one treatment technology that can independently treat all categories of well-stimulation-fluid additives, but that treatment trains (systems of combined processes in series) could probably be developed to treat most stimulation chemicals known to be used in California. For example, the San Ardo Oil Field Water Management Facility, located in the upper Salinas Valley in Monterey County, treats produced water through several pretreatment processes, followed by a two-pass reverse osmosis (RO) system before use for environmental purposes and groundwater recharge (Figure 2.C-1)—whereas the Kern Front No. 2 Treatment Plant in northern Kern County treats produced water by gravity

separation, followed by air flotation with coagulants and mechanical agitation for use in irrigation (Figure 2.C-2). Based on the analysis in Appendix C, the treatment train at San Ardo would be expected to effectively remove all well stimulation chemicals from influent streams, while the Kern Front No. 2 Treatment Plant would not be expected to remove most chemicals associated with well stimulation operations. In summary, the most common simple treatment trains, for example oil separation followed by filtration, are not expected to be effective at removing most well stimulation chemicals, but more complex treatment trains, potentially including RO, may be effective.

Reuse of produced water for irrigated agriculture, groundwater recharge, or environmental flows is an attractive idea, especially in the face of drought. For a successful reuse program, it will be necessary to identify beneficial uses for reclaimed wastewater from oil and gas production, identify the water quality objectives to support that use, and identify what parameters of the produced waters exceed these water quality objectives. Treatment and reuse of produced water from fields with stimulated wells should consider the presence of well-stimulation-fluid chemicals and their breakdown products as part of this evaluation.

2.6.2.5. Disposal of Produced Water in Sanitary Sewer Systems

There is no evidence that produced water from stimulated wells in California is currently being disposed of in sanitary sewer systems. Statewide, however, an estimated 7 million m^3 and 4 million m^3 (5,700 and 3,200 acre-feet) of produced water was disposed of in sanitary sewer systems in 2012 and 2013, respectively, and some of this has occurred in fields where wells have been stimulated (e.g., Wilmington Oil Field in Los Angeles County and a small amount from the Lost Hills Oil Field and Midway-Sunset Oil Field in Kern County). Oil and gas well operators that discharge produced water into sanitary sewers are required by the sanitation districts to obtain pretreatment permits. Pretreatment of produced water is typically minimal—consisting primarily of oil and water separators, followed by clarification and sometimes air stripping or flotation—and does not remove most chemicals associated with well-stimulation operations.

Additionally, sewage treatment plants are not typically equipped to handle produced water, potentially disrupting the treatment process and discharging salt and other contaminants into the environment. In Pennsylvania, for example, the high salt content of oil and gas wastewater resulted in increased salt loading to Pennsylvania rivers (Brantley et al., 2014; Kargbo et al., 2010; Vidic et al., 2013; Wilson and VanBriesen, 2012). Ferrar et al. (2013) identified concentrations of some chemicals, including barium, strontium, bromides, chlorides, total dissolved solids, and benzene, in treated effluent that exceeded drinking water quality criteria. Similarly, Warner et al. (2013a) studied the effluent from a brine treatment facility in Pennsylvania and found that TDS from the effluent led to an increase in salts downstream, despite significant reduction in concentrations due to the treatment process and dilution from the river. Moreover, radium activities in the stream sediments near the point of discharge were 200 times higher than in upstream and background sediments, and were above radioactive waste disposal thresholds. State

regulators in Pennsylvania subsequently discouraged the practice of discharging waters recovered from fracturing operations to sanitary sewer systems due to water quality concerns, although some discharge into these facilities has continued. Much of the research on disposal to these systems has focused on the produced water constituents and has not specifically addressed the fate of stimulation chemicals commingled with produced water.

2.6.2.6. Leakage through Hydraulic Fractures

One concern related to subsurface leakage through hydraulic fractures is the degree to which induced fractures may extend beyond the target formation to connect to overlying protected groundwater, or to other natural or man-made pathways such as faults, natural fractures, or abandoned wells. Many studies, which are discussed in detail below, reference stimulation activities conducted at significant depth, and thus it has been generally assumed that fractures cannot directly intercept groundwater resources. The situation in California is notably different, due to the shallow depths of fracturing (Volume I, Chapter 3). Additional data about fracture geometry and depths are starting to emerge from the well completion reports that are now being submitted to DOGGR by operators.

The completion reports have data for the horizontal and vertical extent of stimulation, which are reported as "Stimulation Length" and "Stimulation Height." For this assessment, we analyzed the reported stimulation length and height, and calculated the depth (from the surface) to the top of the stimulation using data reported for 499 hydraulic fracturing treatments from a total of 506 well completion reports that were available as of December 15, 2014. The depth from the surface to the top of the stimulation was calculated as:

$$\frac{\text{TVD Wellbore Start} + \text{TVD Wellbore End}}{2} - \frac{\text{Stimulation Height}}{2}$$

where "TVD Wellbore Start" and "TVD Wellbore End" refer to the true vertical depths at the top and bottom of the treatment interval in the well, respectively.

This calculation is based on the assumption that the reported stimulation geometries are accurate. It is also assumed that stimulation propagates equally in both vertical directions from the midpoint of the treatment interval, and so does not account for asymmetrical vertical growth relative to the well interval treated. We also assume that the midpoint of the stimulation height occurs at the midpoint of the true vertical depth of the treated wellbore interval. The original dataset had to be modified to create consistent data formats. Only hydraulic fracturing treatments were considered; data for the seven acid matrix treatments were excluded. The distribution of these depths is shown in Figure 2.6-4.

Summary Statistics (m)
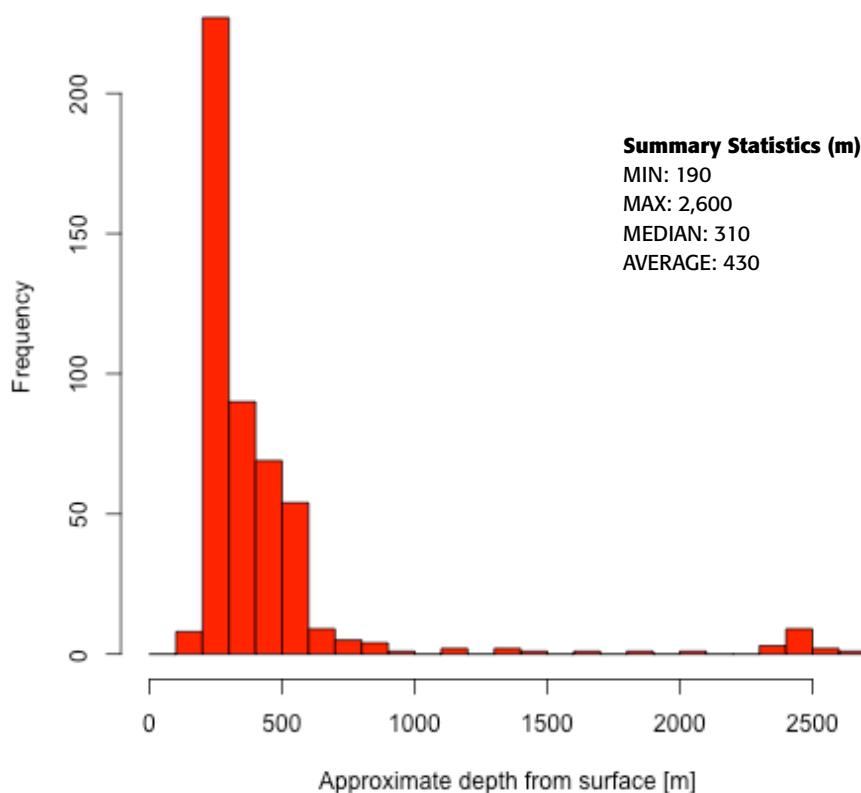MIN: 190
MAX: 2,600
MEDIAN: 310
AVERAGE: 430

Figure 2.6-4. The approximate depth (from the surface) of the top of the hydraulic fracturing stimulations, (calculated by subtracting half the stimulation height from the midpoint of the wellbore treatment interval). Data source: Completion reports submitted to DOGGR as of Dec 15, 2014.

The data show that the true vertical depths to the top of the producing horizon in which the fracturing is induced are mostly shallow, ranging from 200 to 300 m (650 to 1,000 ft), and that in approximately half the operations, fracturing can extend to depths less than 300 m (1,000 ft) from the surface. This result is consistent with an earlier analysis that found the top of the fracturing interval in about half the operations to be less than 300 m (1,000 ft) deep (Volume I, Chapter 3). The shallow depths of fracturing raise concern about the possibility that out-of-zone fractures may directly intercept protected groundwater resources. Additional research is needed to determine how often this occurs, if at all, and the consequences if it does occur.

Most of the reported stimulation heights are between 50 m and 300 m (165 ft and 1,000 ft), while stimulation lengths in lateral directions are typically less than 50 m (165 ft) (Figure 2.6-5); however, the data for stimulation dimensions are inferred from unsubstantiated industry calculations. Based on the data submitted to DOGGR, it appears as though stimulations due to fracturing are oriented more vertically than horizontally (Figure 2.6-6).

(a) Stimulation heights from completion reports

Summary statistics (m)
MIN: 16
MAX: 336
MEDIAN: 211

(b) Stimulation lengths from completion reports

Summary statistics (m)
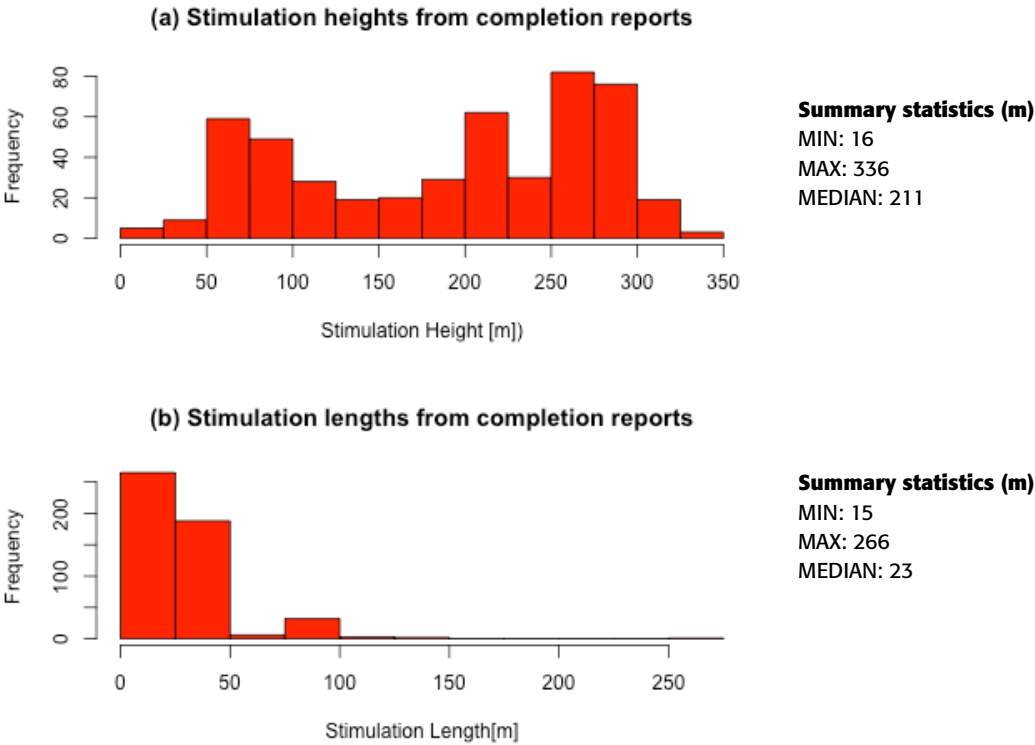MIN: 15
MAX: 266
MEDIAN: 23

Figure 2.6-5. Distribution of (a) stimulation heights and (b) stimulation lengths in California. Data source: Completion reports submitted to DOGGR as of December 15, 2014.
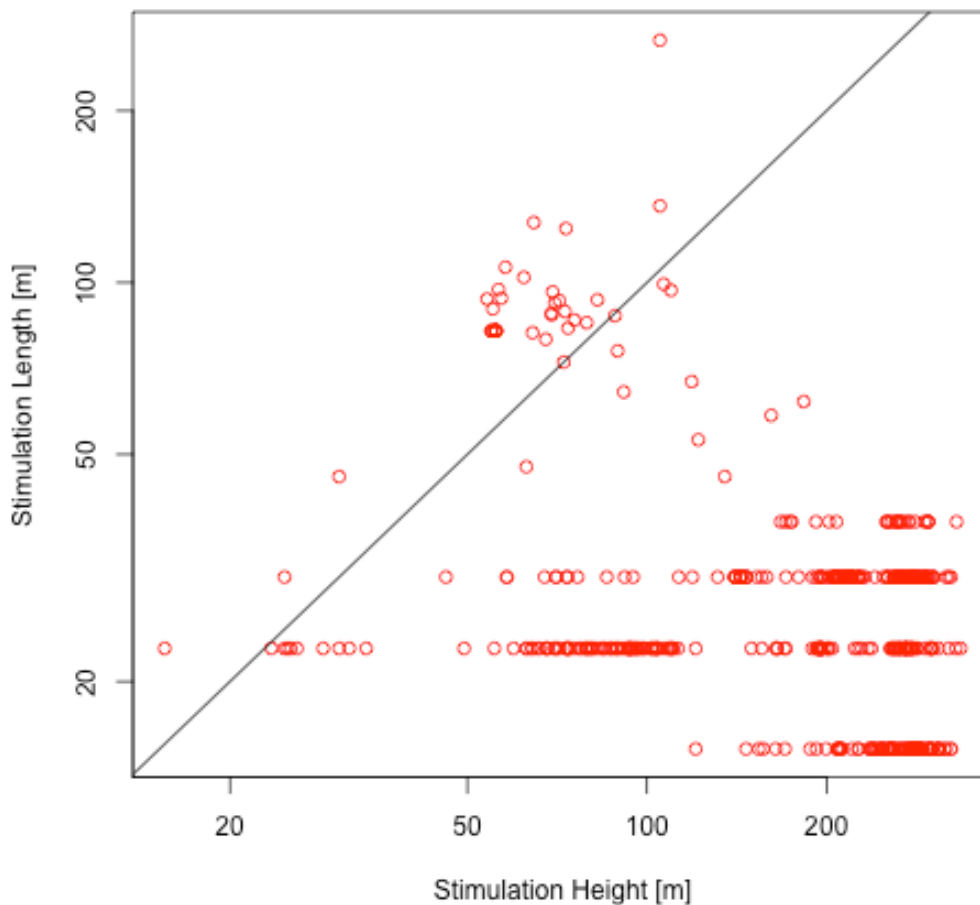
Figure 2.6-6. Comparison of stimulation heights with stimulation lengths for fracturing operations show that stimulations extend more vertically than horizontally. The solid line represents the 1:1 relationship; axes are in log scales. Data source: Completion reports submitted to DOGGR as of December 15, 2014.

The accuracy of the reported data on fracture geometries is unknown, given that operators do not report the methods for calculating the stimulation height and length. Furthermore, examination of hundreds of the well records that record hydraulic fracturing operations indicates operations consisting of only one stage are less than one quarter of all operations. However, all the completion reports indicate only one stage per well. It is unlikely such a substantial change in practice occurred at the same time that mandatory reporting commenced. It is more likely operators are reporting all fracturing stages within a well as one stimulation, and misreporting the number of stages in the well. Consequently, it is not possible to draw definite conclusions from these data regarding the length versus height, and consequently orientation, of fractures from individual stages. However, four-fifths of the reports list a stimulation height that is the same or less than the vertical height of the treatment interval in the well, suggesting almost all fracturing in California is horizontal. This is at odds with the other data submitted by operators (Figure

2.6-6), and with the predominance of vertical fracturing reported in literature regarding the reservoirs in the San Joaquin Basin, where most hydraulic fracturing occurs (Volume III, Chapter 5).

Basic work on understanding induced fractures spans decades (Hubbert and Willis, 1972; Nordgren, 1972; Perkins and Kern, 1961), but literature on studies conducted in California is limited. Emanuele et al. (1998) measured the orientation of fractures resulting from tens of stages in three horizontal wells in the Lost Hills field at a depth of approximately 600 m (2,000 ft) using surface tiltmeter measurements, along with some subsurface tiltmeter measurements. The orientation of all the fractures was within 10 degrees of vertical. Allan et al. (2010) reported on testing of longitudinal versus transverse fracturing in horizontal wells at a depth of approximately 300 m (1,000 ft) in the South Belridge field, reporting that the fractures were likely vertical as indicated by surface and downhole tiltmeter measurements.

However, both fracture *orientation* and fracture *extent* must be evaluated. In work performed outside of California, where fracturing occurs generally much deeper and with less injection volumes, fracture orientations have been different. Flewelling and Sharma (2014) observed that shallow formations are more likely to fracture horizontally rather than vertically, regardless of fracture extent, and capped potential fracture vertical extent at 600 m (2,000 ft) or less. Fisher and Warpinski (2012) compared microseismic data on fracture extent and found that fractures in shallower formations (<1,200 m, or 3,900 ft) have a greater horizontal component, and that deep hydraulic fractures should not be vertically extensive such as to contact shallow aquifers. This paper, however, also stated that earlier work found orientations dependent on the unique stress profiles and rock fabric of a given location (Walker et al., 2002). Coupled flow-geomechanical modeling (Kim and Moridis, 2012) found inherent physical limitations to the extent of fracture propagation—for example, the presence of overlying confining formations may slow or stop fracture growth in the vertical direction, thus containing fractures within the reservoir (Kim et al., 2014). Likewise, Davies et al. (2012) find that the majority of induced fractures (with data focused on high-volume fracturing operations in the Barnett Shale in Texas) range from less than 100 m (330 ft) to about 600 m (2,000 ft) in vertical extent, with approximately a 1% probability of a fracture extending 350 m (1,100 ft) vertically. This leads to a suggested minimum separation of 600 m (2,000 ft) between shale reservoirs and overlying groundwater resources for high-volume fracturing operations conducted in deeper formations elsewhere in the country (King, 2012). For comparison, completion reports show that the fractures in California can be as shallow as 200 m (650 ft) from the surface, which is much less than this suggested minimum, and thus a predominantly vertical fracture orientation increases the likelihood of encountering protected groundwater. More studies are needed to evaluate the fracturing behavior, fracture propagation, and the orientation of fractures relative to reservoir depth in typical hydraulic fracturing operations in California.

2.6.2.7. Leakage through Failed Inactive (Abandoned, Buried, Idle or Orphaned) Wells

Oilfield gas and formation water may reach the surface through degraded and leaking wellbores. Regions with a history of oil and gas production such as California have a large number of inactive (abandoned, buried, idle or orphaned) wells, many of which may be undocumented, unknown, and either degraded, improperly abandoned, or substandard in construction. Fractures created during hydraulic fracturing can create connectivity to inactive wells, particular in high-density fields such as found in the Kern County in California. However, the inactive wells have to fail (for example, due to degradation of cement or casings), and sufficient driving forces must be present for leakage of gas or formation water to occur through inactive wells.

In California, there are more inactive than active wells. Of a total of about 221,000 wells listed in the DOGGR GIS wells file, nearly 116,000 wells have been plugged and abandoned according to state standards. Nearly 1,800 wells are "buried," i.e., older wells which have not been abandoned to standards and whose location is approximate. Finally, the status of 388 wells is unknown, i.e., these are pre-1976 wells whose status is only on a hard copy file. Approximately 53% of the abandoned wells are located in Kern County. DOGGR also has an idle and orphan well program.[10] An idle well is defined as "a well that has not produced oil and/or gas or has not been used for fluid injection for six consecutive months during the last five years". An orphaned well is an abandoned well that has no owner. The DOGGR idle wells inventory lists, as of December 2014, a total of 21,347 idle wells, although this number differs from the number of idle wells reported in the GIS wells file (13,450 wells). DOGGR also lists 110 currently orphaned wells in California and an additional 1,307 hazardous orphaned wells were plugged by DOGGR between 1977 and 2010.

The accuracy of the locations of inactive wells listed in the DOGGR GIS wells file has not been independently verified, and the actual counts of buried wells may be underestimated, since there could be historical wells whose location is unknown. The conditions of the abandoned, plugged, and buried wells are unknown. Under SB 4, operators are required to identify plugged and abandoned wells that may be impacted by the stimulation operation while applying for a permit, but are not required to test their condition. Idle wells are required to be tested periodically to ensure that they are not impacting surface and groundwater by the DOGGR Idle and Orphan well program. The type of testing required is not specified, and can be as simple as a fluid-level survey or may be a more complicated well-casing mechanical integrity test.

Old and inactive wells are a problem in many other states. For example, in Pennsylvania, there are thousands of wells from previous oil and gas booms, with 200,000 dating from before formal record-keeping began and 100,000 that are essentially unknown (Vidic

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10. See http://www.conservation.ca.gov/dog/idle_well/Pages/idle_well.aspx

et al., 2013), and increasing attention has been given to assessing these as transport pathways. Abandoned wells have also been attributed as causes for contamination of groundwater in Ohio and Texas and programs to locate, assess, and cap previously abandoned wells have been subsequently initiated in those states (Kell, 2011). Chilingar and Endres (2005) documents a California incident in 1985, where well corrosion at shallow depths led to casing failure of a producing well and the subsequent migration of gas via a combination of abandoned wells and fault pathways to a Los Angeles department store basement, resulting in an explosion. The paper also documents multiple cases of gas leakage from active oil fields and natural gas storage fields in the Los Angeles Basin and elsewhere, with the most common pathway being gas migration through faulted and fractured rocks penetrated by abandoned and leaking wellbores, many of which predate modern well-casing practice and are undocumented or hidden by more recent urban development. While stimulation technologies are not implicated in these events, they illustrate the real possibility of degraded abandoned wells as pathways.

The hazards of degraded abandoned wells are not just limited to their proximity to stimulated wells, but are also relevant to the issue of disposal of wastewater from stimulated wells by injection into Class II wells. A 1989 U.S. Government Accountability Office (GAO) study of Class II wells across the United States (U.S. GAO, 1989) found that one-third of contamination incidents were caused by communication with an improperly plugged abandoned oil and gas well. Current UIC program permitting requirements require a search for abandoned wells within a quarter mile of a new injection wellbore, and plugging and remediation of any suspect wellbores (40 CFR 144.31, 146.24). However, Class II wells operating prior to 1976 are exempt from this requirement. Thus, 70% of the disposal wells reviewed were pre-existing, grandfathered into the program, and allowed to operate without investigating nearby abandoned wells (U.S. GAO, 1989).

2.6.2.8. Failure of Active Production, Class II, and Other Wells

Operating wells (whether used for production or injection) can serve as leakage pathways for subsurface migration. Pathways can be formed due to inadequate design, imposed stresses unique to stimulation operations, or other forms of human error. Class II deep injection wells with casing or cement inadequacies would also have similar potential for contamination as a failed production well or a well that fails due to stimulation pressures. Examples of potential subsurface releases through wells are illustrated in Figure 2.6-2.

Stimulated wells may be subject to greater stresses than non-stimulated wells, due to the high-pressure stimulation process and the drilling practices used to create deviated (often horizontal) wells (Ingraffea et al., 2014). During hydraulic fracturing operations, multiple stages of high-pressure injection may result in the expansion and contraction of the steel casing (Carey et al., 2013). This could lead to radial fracturing and/or shear failure at the steel-concrete or concrete-rock interfaces, or even separation between the casing and the cement. These gaps or channels could serve as pathways, or (as a worst-case) create connectivity between the reservoir and overlying aquifers. Current practice

does not typically use the innermost casing as the direct carrier of stimulation fluids (or produced fluids and gases). Additional tubing (injection tubing or production tubing) is run down the innermost well casing without being cemented into place, and thus carries the stresses associated with injection. However, less complex stimulation treatments, such as some California operations, may not require such additional steps, and some fracturing operations may use the innermost casing to carry the fracturing fluids and the pressures associated with the fracturing operation.

In addition, several mechanisms—such as surface subsidence, reservoir compaction or heaving, or even earthquakes—can lead to well impairment due to casing shear (Dussealt et al., 2001). The diatomite formations in Kern County are highly porous and compressible, and hence are particularly susceptible to depletion-induced compaction. For example, several wells failed in the 1980s in Belridge (at a peak rate of 160 wells per year) following years of active production enabled by stimulation, which led to reservoir depletion and subsidence (Fredrich et al., 1996; Dussealt et al., 2001). Waterflood programs were then initiated to counter the subsidence, which led to much lower rates of well failure in the late 1990s of around 2–5% of active wells per year or approximately 20 wells per year (De Rouffignac et al., 1995; Fredrich et al., 1996; Dussealt et al., 2001). The current situation with groundwater overdraft in the southern San Joaquin Valley may pose an added risk to wells in the region due to subsidence. Earthquakes can also lead to casing shear; for example, hundreds of oil well casings were sheared in the Wilmington oil field in Los Angeles during five or six earthquakes of relatively low magnitude (M2 to M4) during a period of maximum subsidence in the 1950s (Dussealt et al., 2001).

Failures in well design and construction may allow migration of gas and fluids from the reservoir, or from shallower gas and fluid-bearing formations intersected by the wellbore. Wells can thus serve as pathways for gas migration to overlying aquifers or even to the surface (Brufatto et al., 2003; Watson and Bachu, 2009). Multiple factors over the operating life of a well may lead to failure (Bonett and Pafitis, 1996; Brufatto et al., 2003; Carey et al., 2013; Chilingar and Endres, 2005; Dusseault et al., 2000; Watson and Bachu, 2009); however, the most important mechanism leading to gas and fluid migration is poor well construction or exposed (or uncemented) casing (Watson and Bachu, 2009). A surface casing may not protect shallow aquifers, particularly if the surface casing does not extend to a sufficient depth below the aquifer (Harrison, 1983; 1985).

Watson and Bachu (2008) also noted that deviated wellbores, defined as "any well with total depth greater than true vertical depth," show a higher occurrence of gas migration than vertical wells, likely due to the challenges of deviated well construction increasing the likelihood of gaps, bonding problems, or thin regions in the cement that could create connectivity to other formations. In a review of the regulatory record, Vidic et al. (2013) noted a 3.4% rate of cement and casing problems in Pennsylvania shale-gas wells (that all had some degree of deviation) based on filed notices of violation. Pennsylvania inspection records, however, show a large number of wells with indications of cement/casing impairments for which violations were never noted, suggesting that the actual rate of occurrence could be higher than reported (Ingraffea et al., 2014; Vidic et al., 2013).

The bulk of the peer-reviewed work on contaminant migration associated with stimulation focuses on the Marcellus Shale gas plays of Pennsylvania, West Virginia, Ohio, and New York. This literature features a number of competing studies that focus on fracturing-derived pathways, but also provides a robust debate on the role of deteriorated or poorly constructed wells. A sampling study by Osborn et al. (2011a) and Jackson et al. (2013a) noted that methane concentrations in wells increased with increasing proximity to gas wells, and that the sampled gas was similar in composition to gas from nearby production wells in some cases. Follow-up work by Davies (2011) and Schon (2011) found that leakage through well casings was a better explanation than other fracturing-related processes (also see Vidic et al., 2013). Most recently, other sampling studies (Darrah et al., 2014; Molofsky et al., 2013) found gas compositions in wells with higher methane, ethane, and propane concentrations sometimes match Marcellus gas, likely through leaks in well casings; in other instances, they do not match the gas compositions in the Marcellus Shale, suggesting that intermediate formations are providing the source for the additional methane, probably due to insufficient cementing in poorly constructed wells. The Darrah et al. (2014) study in particular identifies eight locations in the Marcellus (and also for one additional case in the Barnett Shale in Texas) where annular migration through/around poorly constructed wells is considered the most plausible mechanism for measured methane contamination of groundwater.

In California, a 2011 report that studied the over 24,000 active and 6,900 inactive injection wells in the state found that, while procedures were in place to protect freshwater resources, other water resources (with higher levels of dissolved components, but not considered saline) may be at risk due to deficiencies in required well-construction practices (Walker, 2011). In California, there has been little to no investigation to quantify the incidence and cumulative hazard or indicators of wellbore impairment. However, studies from other oil- and gas-producing regions indicate that wellbores have the potential to serve as leakage pathways in California, and need to be investigated.

2.6.2.9. Leakage through Other Subsurface Pathways (Natural Fractures, Faults or Permeable Formations)

Several modeling studies have attempted to elucidate mechanisms of subsurface transport in fractured formations through numerical simulation, although in all cases some simplification of subsurface properties was necessary, since subsurface heterogeneity is both difficult to quantify and to represent in a model. A well-publicized study by Myers (2012) found potential transport between fractured reservoirs and an overlying aquifer, but did so using a highly simplified flow model regarded as unrepresentative (Vidic et al., 2013). Two recent studies modeled higher-permeability pathways intersecting reservoir boundaries. Modeling work by Kissinger et al. (2013) suggests that transport of liquids, fracturing fluids, or gas is not an inevitable outcome of fracturing into connecting pathways. Modeling work by Gassiat et al. (2013) found that migration of fluids from a fractured formation is possible for high-permeability fractures and faults, and for permeable bounding formations, but on 1,000-year timeframes. Flewelling and Sharma

(2014) conclude that upward migration through permeable bounding formations, if possible at all, is likely an even slower process operating at much longer timescales (in their estimate, ~1,000,000 years). Additional modeling studies on gas transport through fractures in shale formations, suggest gas escape is likely to be limited in duration and scope for hydrostatic reservoirs (Reagan et al., 2015; U.S. EPA 2015b). Such studies require corroborating field and monitoring studies to provide a complete view of the possible mechanisms and outcomes.

Sampling and field studies have also sought evidence of migration via fractures, but the bulk of the peer-reviewed work focuses on the Marcellus Shale, and no such studies have been conducted in California. A key conclusion is that pathways and mechanisms are difficult to characterize, and the role of fracturing or transport through fractures has not been clearly established. Methane concentrations in wells increase with proximity to gas wells, and the gas is similar in composition to gas produced nearby (Jackson et al., 2013a; Osborn et al., 2011a), but evidence of contamination from brines or stimulation fluids was not found (Jackson et al., 2011; 2013a; Osborn et al., 2011b), suggesting that gas and liquid migration may not be driven by the same processes. The most recent sampling studies (Darrah et al., 2014; Molofsky et al., 2013) conclude that migration through poorly constructed wells is a more likely scenario than fracture-related pathways. Work on the properties of gas shales (Engelder et al., 2014) proposed that a "capillary seal" would restrict the ability of fluids to migrate out of the shale, but many reservoirs in California contain more mobile water, reducing this possibility.

Fault activation resulting in the formation of fluid pathways is an additional concern when stimulation operations occur in faulted geologies, such as in California (Volume II, Chapter 4). Fault activation is a remote possibility for faults that can admit stimulation fluids during injection (Rutqvist et al., 2013), possibly increasing the permeability of previously sealed faults or creating new subsurface pathways analogous to induced fractures (possibly on a larger scale). Fault activation could also give rise to (small) micro-seismic events, but fault movement is limited to centimeter scales across fault lengths of 10 to 100 m (33 to 330 ft) (Rutqvist et al., 2013). Chilingar and Endres (2005) document a California incident in which the migration of gas via permeable faults (among other pathways) created a gas pocket below a populated area in Los Angeles and resulted in an explosion. While the incident was not related to stimulation operations, it shows how naturally faulted geologies can provide pathways for migration of gas and fluids.

2.6.2.10. Spills and Leaks

Oil and gas production involves some risk of surface or groundwater contamination from spills and leaks. Well stimulation, however, raises additional concerns, owing to the use of chemicals during the stimulation process, the generation of wastewaters that contain these chemical additives (as well as formation brines with potentially different compositions from conventional produced waters), and the increased transportation requirements to haul these materials to the well and disposal sites.

Surface spills and leaks can occur at any time in the stimulation or production process. Spills and leaks can occur during chemical or fluid transport, pre-stimulation mixing, during stimulation, and after stimulation during wastewater disposal. In addition, storage containers used for chemicals and well stimulation fluids can leak (Figure 2.6-1). Releases can result from tank ruptures, piping failures, blowouts, other equipment failures and defects, overfills, fires, vandalism, accidents, or improper operations (NYSDEC, 2011). Additionally, natural disasters (e.g., floods or earthquakes) may damage storage and disposal sites or cause them to overflow. For example, major flooding in 2013 damaged oil and gas operations in northeast Colorado, spilling an estimated 180 m^3 (48,000 gal) of oil and 160 m^3 (43,000 gal) of produced water (COGCC, 2013). Once released, these materials can run off into surface water bodies and/or seep into groundwater aquifers.

In California, any significant or threatened release of hazardous substances must be reported to California Office of Emergency Services (OES) (19 CCR 2703(a)). According to California state law, the reporting threshold for chemical spills varies by chemical. There is no specific reporting threshold for produced water, although any release must still be reported to the appropriate DOGGR district office (Cal. Code Regs. tit. 14, § 1722(i)). All spills into or on state waters must also be reported to OES. OES maintains a database with information on the location, size, and composition of the spill; whether the spill impacted a waterway; and the cause of the spill. OES then conveys information on spills originating from or associated with an oil or gas operation to DOGGR, and DOGGR staff enters these data into the California Well Information Management System (CalWIMS) database. In some cases, DOGGR works with companies after a spill has occurred to obtain additional information and, as a result, some of the data within DOGGR and OES spills databases are inconsistent. For this analysis, we relied on the OES database; however, we discuss the need to standardize these databases in Section 2.9. It is of note that operators are not required to report whether a spill was associated with well stimulation, nor do the reports contain an American Petroleum Institute (API) number, which could be used to link the spill to stimulation records.

Between January 2009 and December 2014, a total of 575 produced water spills were reported to OES, or an average of about 99 spills annually. The majority (55%) of these spills occurred in Kern County, followed by Los Angeles (16%), Santa Barbara (13%), Ventura (6%), Orange (3%), Monterey (2%), and San Luis Obispo (1%), and Sutter (1%) counties. Nearly 18% of these spills impacted waterways.

Chemical spills were also reported in California oil fields, including spills of chemicals typically used in well stimulation fluids, e.g., hydrochloric, hydrofluoric, and sulfuric acids. Between January 2009 and December 2014, a total of 31 chemical spills were reported to OES. Forty-two percent of these spills were in Kern County, followed by Los Angeles (16%), Sonoma (16%), and Lake (3%) counties. Chemical spills represent about 2% of all reported spills attributed to oil and gas development during that period. None of the reported spills contained chemicals used for hydraulic fracturing in California.

Nine of the chemical spills were of acid. This suggests that acid spills are relatively infrequent, representing less than 1% of all reported spills attributed to oil and gas development during that period. Among these was a storage tank at a soft water treatment plant containing 20 m^3 (5,500 gal) of hydrochloric acid in the Midway-Sunset Oil Field in Kern County that ruptured violently, releasing the acid beyond a secondary containment wall. No injuries or deaths were associated with this or any other acid spill. While 10% of the chemical spills were reported to enter a waterway, none of the acid spills was reported to enter a waterway.

2.6.2.11. Operator Error During Stimulation

Human error during the well completion, stimulation, or production processes could also lead to contamination of groundwater. Operator error could create connectivity to other formations that could serve as transport pathways. For example, poor monitoring or control of the fracturing operation could lead to creation of fractures beyond the confines of the reservoir, or increase the extent of fractures beyond desired limits. Such errors, if not found and corrected, could lead to unexpected migration of fluids, or in the case of the high-density well siting often found in California, connectivity between wells that impacts production activities themselves. Fracturing beyond the reservoir bounds due to operator error may also be of particular concern in the case of the shallower fracturing operations that may occur in California.

An example of operator error during stimulation is a 2011 incident in Alberta, Canada (ERCB, 2012), where an overlying formation was inadvertently fractured due to misreading of well fluid pressures, and stimulated fluids were injected into a water-bearing strata below an aquifer. Immediate flowback of fracturing fluids recovered most of the injected volume, and monitoring wells were installed into the aquifer and an overlying sandstone layer. A hydraulic connection between the fractured interval and the overlying aquifer was not observed, but groundwater samples contained elevated levels of chloride, benzene, toluene, ethylbenzene, and xylenes (BTEX), petroleum hydrocarbons and other chemicals. The Energy Resources Conservation Board (ERCB) finding states that the incident presented "insignificant" risk to drinking water resources, but criticized the onsite crew's risk management, noting there were multiple opportunities to recognize abnormal well behavior before the misplaced perforation.

2.6.2.12. Illegal Discharges

Illegal discharges of wastewater from oil and gas production have been noted in California for disposal in both unlined pits and via subsurface injection. For example, in July 2013, the CVRWQB issued a $60,000 fine to Vintage Production California, LLC, for periodically discharging saline water, formation fluids, and hydraulic fracturing fluid to an unlined pit in an area with good-quality groundwater (CVRWQCB, 2013). In a follow-up survey on disposal practices of drilling fluids and well completion fluids, the CVRWQCB identified several other illegal discharge incidents between January 2012 and December 2013

and fined the responsible operators (CVRWQCB, 2014). In a recent GAO review of the UIC programs in eight states, California agencies reported 9 and 12 instances of alleged contamination in 2009 and 2010, respectively, resulting from one operator injecting fluids illegally into multiple wells (U.S. GAO, 2014).

2.7. Impacts of Well Stimulation to Surface and Ground Water Quality

In this section, we review the potential impacts of well stimulation on water quality by examining results from the few sampling studies that have been conducted near hydraulic fracturing operations in the United States. Only one sampling study has been conducted near a hydraulic fracturing site in California (in Inglewood). Thus, we considered studies conducted in other regions of the United States where stimulation operations have occurred, including Pennsylvania, Texas, Ohio, Montana and North Dakota, to (1) examine incidents where water has been potentially contaminated due to oil and gas activities, to determine viable contaminant release mechanisms, and assess whether they apply to well stimulation activities in California; and (2) identify considerations for future sampling studies and monitoring programs in California, based on lessons learned from other states.

While some of the sampling studies have shown no evidence of water contamination associated with well stimulation, other studies found detectable impacts that were associated with, and allegedly caused by, well stimulation operations. A recently released draft report by the U.S. EPA did not find evidence of widespread, systemic impacts on drinking water resources in the United States, but found specific instances of impacts on drinking water resources, including contamination of drinking water wells. (U.S. EPA 2015b).

Notably, most groundwater sampling studies do not even measure stimulation chemicals, partly because their full chemical composition and reaction products were unknown. It should be noted that detecting groundwater contamination is more difficult than detecting surface water contamination because (1) the effects of contamination, the release mechanisms, and the transport pathways are less visible than at the surface; (2) there are many possible pathways and sources for contaminants to be present in groundwater, and definitively attributing contamination to well stimulation is difficult; and (3) impacts on groundwater may not be detected on relatively short time scales because of slow transport processes. These difficulties are compounded by the lack of baseline water quality data and monitoring to detect problems, as well as the lack of knowledge about the full composition of stimulation fluids and standard analytical methods to detect the chemical additives and their degradation products.

2.7.1. Studies that Found Evidence of Potential Water Contamination near Stimulation Operations

Several studies have found evidence of contamination due to stimulation, which were primarily attributed to surface spills or leaks of fluids used in hydraulic fracturing, or improper wastewater disposal (Table 2.7-1). For example, in 2007, flowback fluids

overflowed retention pits in Knox County, KY, killing or displacing all fish (including Blackside Dace, a federally threatened species), invertebrates, and other biota for months over a 2.7 km (1.7 mi) section of a local waterway (Papoulias and Velasco, 2013). In a study examining the effect of spills, the presence of known or suspected endocrine-disrupting chemicals used for hydraulic fracturing were measured at higher levels in surface and groundwater samples in drilling-dense areas of Garfield County, Colorado compared to nearby background sites with limited or no drilling activity (Kassotis et al., 2013). Surface water samples were collected from five distinct sites that contained from 43 to 136 natural gas wells within 1.6 km (1 mi) and had a spill or incident related to unconventional natural gas extraction within the previous six years.

There have been far fewer reports of groundwater contamination caused by subsurface release mechanisms, such as leakage through wells or leakage through hydraulic fractures or other natural permeable pathways. Most of the problems reported were due to the presence of methane gas or other formation water constituents in drinking water wells, and only three reports involve the possibility of contamination by hydraulic fracturing fluids. A recent study in Pennsylvania investigates an incident of contamination by natural gas in potable groundwater, where well waters were also observed to foam (Llewellyn et al., 2015). The authors used 2-D gas chromatography coupled to time-of-flight mass spectrometry (GCxGC-TOFMS) to identify an unresolved complex mixture of organic compounds in the aquifer that had similar signatures to flowback water from Marcellus shale-gas wells. The organic compounds were not present in nearby wells that were outside of the affected area. One compound in particular, 2nbutoxyethanol, which is not a natural constituent of water in the region, was identified in both the foaming waters and flowback water, although the study mentions that it could have also been used in drilling fluids. The authors conclude that, although they were not able to unambiguously prove a direct connection between shale gas operations and the detected organic chemicals in household waters, the timing and presence of similar compounds in "flowback/produced" waters suggest that the hydraulic fracture operations were a likely source (Llewellyn et al., 2015). The contaminant release mechanisms suggested by the authors include surface spills or subsurface leakage and transport through shallow fractures. The study also suggests that the most likely release mechanism for the natural gas was leakage through wells due to excessive annular pressures and lack of proper annular cement (Llewellyn et al., 2015).

There are two other unconfirmed potential groundwater contamination incidents attributed to subsurface leakage of hydraulic fracturing fluid within the United States (DiGiulio et al., 2011; U.S. EPA, 1987), but neither of them has been documented in a peer-reviewed publication (Brantley et al., 2014; Vidic et al., 2013). The first study is a U.S. EPA investigation in Pavilion, Wyoming, where surface storage and disposal of wastewaters was implicated in contamination of shallow surface water as discussed in Section 2.6. Initial results published in a draft report (DiGiulio et al., 2011) suggested that groundwater wells had been contaminated with various fracturing-fluid chemicals (glycols and alcohols) as well as methane, via flow from the stimulated reservoir to

groundwater. However, a follow-up study by the USGS involving resampling of the wells could not confirm some of these findings (Wright et al., 2012). The U.S. EPA is no longer working on this study, which is now being led by the State of Wyoming. The second reported incident of groundwater contamination is based on a U.S. EPA study focusing on operations in Ripley, West Virginia. In this case, a gel used as a constituent in fracturing fluids was reported to have contaminated a local water well located less than 330 m (1,000 ft) from a vertical gas well (U.S. EPA, 1987). Contaminant transport could have either occurred through four abandoned wells located near the vertical gas well during the fracturing process, or by contamination from the flush fluid used to remove loose rock cuttings prior to cementing (Brantley et al., 2014).

Several other studies note the presence of elevated levels of other contaminants in groundwater near stimulation operations. Some studies were unable to attribute the cause to stimulation, while others had to conduct several follow-on investigations to identify the contaminant release mechanisms. For example, some sampling studies found high concentrations of methane and other hydrocarbons in drinking-water wells in Pennsylvania, particularly those near hydraulic fracturing operations. Methane concentrations in the wells increased with increasing proximity to gas wells, but evidence of contamination from brines or fracturing fluids was not found (Dyck and Dunn, 1986; Jackson et al., 2011; 2013a; Osborn et al., 2011a; 2011b). There was significant debate about whether the high methane concentrations were naturally present, or a result of hydraulic fracturing operations. Additional sampling work (Jackson et al., 2013a) found ethane and propane, as well as methane, in water wells near Marcellus production locations. The studies determined that the methane was formed by thermogenic processes at depth (as would be expected for shale gas), and that the isotopic ratios of methane were found to be more consistent with non-Marcellus gas (Molofsky et al., 2013). The most recent sampling study (Darrah et al., 2014) again found isotopic and noble gas compositions inconsistent with a Marcellus (and thus a stimulation-derived) source, and identified eight locations where wells are considered the most plausible mechanism for measured methane contamination of groundwater—including incidents of migration through annulus cement (four cases), through production casings (three cases), and due to underground well failure primarily. In another study in the Marcellus, radon concentrations obtained from previously measured public data were found to increase in proximity to unconventional wells (Casey et al., 2015). Radon is a radioactive decay product of radium, and can dissolve and be transported through groundwater. The researchers also noted that concentrations increased in 2004 from previously fluctuating measurements, just preceding the Marcellus boom in 2005. However, the study had several shortcomings, including the lack of any detailed statistical measures for spatial association of radon with hydraulic fracturing operations, the lack of evidence showing any pathway that could cause an increase in radon concentrations, the reliance on unverified public data that were not necessarily submitted by accredited professionals, and other limitations that led to an acknowledgement by the authors stating that the study was exploratory.

Another study conducted in the Barnett Shale also illustrates the difficulty in tracing the source of the contaminants detected in groundwater near well stimulation operations shale (Fontenot et al., 2013), despite having historical and background water quality data. This study sampled 100 groundwater wells located in aquifers overlying the Barnett, and found that TDS concentrations exceeded the U.S. EPA Secondary Maximum Contaminant Level (MCL) of 500 mg L^{-1} in 50 out of 91 samples located within 3 km (1.9 mi) of gas wells, and that the maximum values of TDS near the wells were over three times higher than those from background wells located in areas that were unimpacted by fracturing enabled oil and gas development. Similarly, trace elements such as arsenic, barium, selenium, and strontium were found to be present at much higher levels compared to background or historical concentrations, and organics (methanol and ethanol) were detected in 29% of samples in private drinking-water wells. However, it was not possible to determine if hydraulic fracturing was the cause of the high TDS, trace element or organic concentrations, since historical, regional, and background values of these constituents were also high.

An extensive review of groundwater-contamination claims and existing data can be found in a report for the Ground Water Protection Council, focusing on Ohio and Texas groundwater-investigation findings during a 16-year study period from 1983 through 2008 (Kell, 2011). The study area and time period included the development of 16,000 horizontal shale gas wells with multistage fracturing operations in Texas and one horizontal shale gas well in Ohio. The report notes that, for the study period, no contamination incidents were found involving any stimulation activities including "site preparation, drilling, well construction, completion, hydraulic fracturing stimulation, or production operations at any of these horizontal shale gas wells." However, there were a total of 211 reported groundwater contamination incidents in Texas caused by other oil and gas activities. Seventy-five of these were caused by wastewater management and disposal activities, including 57 incidents due to improper storage of wastewater in surface containment pits. This practice has mostly been replaced by disposal via Class II injection wells that have a significantly better record of protecting groundwater resources than unlined pits (as discussed in Section 2.6). Other contamination incidents were related to orphaned wells (30 incidents, most of which were caused by inadequately sealed boreholes) and production activities (56 incidents that include 35 releases from storage tanks, 12 releases from flow lines or wellheads, 7 releases from historic clay-lined storage pits, and 2 releases related to well construction including an incident caused by a short surface casing that did not adequately isolate all groundwater). In Ohio, a total of 185 groundwater-contamination incidents were reported from other oil and gas activities, most of which occurred prior to 1993. Of these, 41 incidents were related to orphaned wells in abandoned sites, 39 incidents were caused by production-related activities (including 17 incidents of leaks from storage tanks or lines; 10 incidents caused by onsite produced water storage pits; 12 incidents caused due to well construction issues), and 26 incidents caused due to waste management and disposal activities. The report concludes that, although no documented links have been found implicating the fracturing process itself to contamination incidents, a regulatory focus on activities that could be linked to contamination is critical, along with documentation of hydraulic fracturing operations such that regulators can determine which processes put groundwater at risk.

Table 2.7-1. Examples of release mechanisms and contamination incidents associated with oil and gas activities in the United States.

Year	Location	Media Impacted	Contaminant	Attributed to Well Stimulation?	Evidence of Water Contamination	Release Mechanism	Operator	Source
1982	Jackson County, WV	Groundwater	Gelatinous material (fracturing fluid) and white fibers	Disputed	Fluid and fibers were found in the water sample from a well located <1,000 ft from a vertical gas well.	Unknown; 4 abandoned gas wells drilled in the 1940s are present within 1,700 ft of the new gas well and may have served as conduits for contamination.	Kaiser Gas Co.	Brantley, 2014; U.S. EPA, 1987
2007	Knox County, KY	Surface water	Flowback fluids	Yes	Flowback fluids were released directly into Acorn Fork. The incident killed or displaced all fish, invertebrates, and other biota for months over a 2.7 km section of the creek.	Retention pits overflowed.	Not known	Papoulias and Velasco, 2013
2007	Bainbridge Township, Geauga County, OH	Groundwater	Natural Gas	Yes	Natural gas seeped into an aquifer	Defective cement job in the well casing, compounded by operator error.	Ohio Valley Energy Systems Corp.	Ohio DNR, 2008
2009	Hopewell Township, Washington County, PA	Surface water	Wastewater	Yes	Fluid overflowed the impoundment's banks and ran over the ground and into a tributary of Dunkle Run.	Wastewater pit failure.	Atlas Resources LLC	PA DEP, 2010
2009	Dimock Township, Susquehanna County, PA	Surface water	8,000 gallons of water/liquid gel mixture used in hydraulic fracturing	Yes	Pollution in Stevens Creek and a nearby wetland resulted in a fish die-off.	Unknown	Cabot Oil & Gas	PA DEP, 2009
2011	Alberta, Canada	Groundwater	Fracturing fluids	Yes	Groundwater samples from monitoring wells found elevated levels of chloride, BTEX, petroleum hydrocarbons, and other chemicals.	Inadvertent fracturing of an overlying formation and injection of fluids into water-bearing strata below an aquifer.	Crew Energy Inc.	ERCB, 2012
2013	Colorado	Surface water	48,000 gallons of oil and 43,000 gallons of produced water	Yes		Spill during major flooding in 2013 damaged oil and gas operations.	Multiple	COGCC, 2013

Year	Location	Media Impacted	Contaminant	Attributed to Well Stimulation?	Evidence of Water Contamination	Release Mechanism	Operator	Source
2013	Kern County, CA		Saline water, formation fluids, and hydraulic fracturing fluid	Yes	None	Illegal discharge to an unlined pit.	Vintage	CVRWQCB, 2013
1983-2007	Ohio	Groundwater	Drilling contaminants- e.g., drill cuttings, crude oil, flowback, and produced water	Not known	The Ohio Division of Mines and Reclamation documented 185 groundwater contamination incidents caused by historic or regulated oilfield activities over a 25 year period	41 of the 185 incidents were caused by orphaned wells. 144 were caused by violations at permitted or regulated activities, including drilling & completion; production, on-lease transport, & storage; waste management & disposal; and plugging & site reclamation.	Not known	Kell, 2011
1993-2008	Texas	Groundwater	Multiple - e.g., drill cuttings, crude oil, flowback, and produced water	Not known	The Texas Railroad Commission documented 211 incidents of groundwater contamination caused by historic or regulated oilfield activities over the 16 year period.	75 incidents resulted from waste management and disposal activities, including 57 legacy incidents caused by produced water disposal pits that were phased out starting in 1969 and closed by 1984. 56 incidents related to releases that occurred during production phase activities including storage tank or flow line leaks. 30 incidents were caused by orphaned wells or sites.	Not known	Kell, 2011
2010-2011	Weld County, CO	Groundwater	BTEX	Not known	77 reported surface spills impacting the groundwater	Spills due to 1. Equipment failure (47 spills); 2. corrosion/equipment failure (10 spills); 3. historical impact (i.e., discovery of a spill during inspection) (15 spills); 4. human error (3 spills); 5. Multiple leaks in dump line system (1 spill); and 6. unknown (1 spill).	Not known	Gross et al., 2013
2015	Pennsylvania	Groundwater	Methane, unresolved mixture of organic compounds (including 2-butoxyethanol)	Likely (but not unambiguously) caused by stimulation	Wells that had been previously contaminated with natural gas were observed to be foaming	Suggested release mechanisms are surface spills or release/transport through shallow fractures for the organic compounds. Methane was probably released through a different mechanism (through well casing)	Not known	Llewelyn et al., 2015

Year	Location	Media Impacted	Contaminant	Attributed to Well Stimulation?	Evidence of Water Contamination	Release Mechanism	Operator	Source
Not known	Kansas, Kentucky, Michigan, Mississippi, New Mexico, Oklahoma, and Texas.	Groundwater	Brine	Not known	A majority of the 23 cases were identified by users of the groundwater. The rest were identified by operators or EPA staff during monitoring operations or while reviewing injection records.	Improperly plugged oil and gas wells in the vicinity of Class II injection wells; leaks in Class II injection well casing; and Class II injection into a USDW.	Multiple	U.S. GAO, 1989
Not known	Pavillion, WY	Groundwater	Benzene, xylenes, gasoline-range organics, and diesel-range organics	Yes	High concentrations of hydraulic fracturing chemicals were found in shallow monitoring wells near surface pits.	Infiltration from storage/disposal pits.	Encana Oil and Gas	DiGiulio et al., 2011; Folger et al, 2012
Not known	Pavillion, WY	Groundwater	Elevated concentrations of well stimulation and drilling chemicals	Disputed	Contaminants were detected in deep monitoring wells.	Thought to be related to gas production; however, the gas company disputes this claim.	Encana Oil and Gas	Folger et al., 2012
Not known	Saskatchewan, Canada	Groundwater	Methane	Not known	Elevated levels of methane found in groundwater associated with oil and gas fields.	Unknown; article suggests leakage along the exploration holes or migration through natural fractures.	Not known	Van Stempvoort et al., 2005
Not known	Texas	Surface water	Sediment	Not known	Study shows a strong correlation between shale-well density and stream turbidity.	Sediment runoff from wellpads.	Not known	Williams et al., 2008
Not known	Garfield County, CO	Surface and Groundwater	Endocrine-disrupting chemicals	Not known	Data suggest elevated endocrine-disrupting chemical activity in surface water and groundwater close to unconventional natural gas drilling operations.	Unknown	Not known	Kassotis et al., 2013
Not known	Northeastern PA and upstate NY	Groundwater	Methane	Not known	Study shows that, in active gas-extraction areas, average and maximum methane concentrations in drinking-water wells increased with proximity to the nearest gas well.	Unknown	Not known	Osborn et al., 2011a

2.7.2. Studies that Found No Evidence of Water Contamination Near Stimulation Operations

There are a few sampling surveys that have been conducted near stimulation operations in the United States. Many of these studies found no evidence of water contamination near stimulation operations, including the only sampling study conducted in California (Cardno ENTRIX, 2012).

The California study reviewed ten years of oil and gas production, including two years of well stimulation operations, at the Inglewood field in Los Angeles County. During this period, conventional hydraulic fracturing was conducted on 21 wells and high-volume hydraulic fracturing was conducted on two wells.[11] The Inglewood field is located in a populated area and underlies a freshwater formation that is regulated and monitored for water quality (Cardno ENTRIX, 2012). The study sampled the groundwater for pH, total petroleum hydrocarbons (TPH), benzene, methyl tertiary butyl ether (MTBE), total recoverable petroleum hydrocarbons (TRPH), total dissolved solids (TDS), nitrate, nitrite, metals, and biological oxygen demand (BOD), none of which is a specific analysis for chemicals used in hydraulic fracturing. The study concluded that there were no detectable impacts to groundwater quality due to the production or stimulation activities (Cardno ENTRIX, 2012). There was no evidence of migration of stimulation fluids, formation fluids, or methane gas during the study's timeframe, even though the formation contained faults and fractures connecting shallow formations to deeper formations (Cardno ENTRIX, 2012). Monitoring found no significant differences in pre-drilling and post-stimulation TDS levels. Trace metals were also sampled; arsenic was the only trace element that exceeded drinking water standards. However, the study mentions that arsenic is naturally present at high levels in Southern California, and concentrations were high in the monitoring wells before drilling (Cardno ENTRIX, 2012). Microseismic monitoring in the study indicated that fractures were contained within the hydrocarbon reservoir zone, extending to within no more than 2,350 m (7,700 ft) of the base of the freshwater zone (Cardno ENTRIX, 2012).

Outside of California, a few other studies have sampled water quality near hydraulically fractured wells in several regions, including the Marcellus Shale, Pennsylvania (e.g., Boyer et al., 2011; Brantley et al., 2014 and references therein; Siegel et al., 2015), the Fayetteville Shale, Arkansas (Warner et al., 2013b), the Barnett Shale, Texas (Fontenot et al., 2013), and the Bakken Shale, Montana/North Dakota (McMahon et al., 2015). Many of these studies, which largely examined groundwater quality, did not find statistically significant changes to the water quality of nearby groundwater wells after fracturing,

11. Conventional hydraulic fracturing uses water, sand, and additives to stimulate up to several hundred feet from the well and is typically applied in sandstone, limestone, or dolomite formations. High-volume hydraulic fracturing, by contrast, uses more fluids and is generally applied to shales rather than sandstones.

when compared to baseline trends. The baseline trends were determined from samples collected before drilling (if available) or alternatively from background sites with comparable geology and geochemistry that were considered to be relatively un-impacted by hydraulic fracturing operations.

In an extensive review, Brantley et al. (2014) found that stimulation in Pennsylvania has never been conclusively tied to an incident of water contamination, and that this could indicate that incidents are rare, and that contaminant release was diluted quickly. However, the review notes that it was not possible to draw firm conclusions due to several challenges, including (1) variable background concentrations of constituents in the groundwater and little knowledge of pre-existing contaminant concentrations; (2) lack of information about the timing and locations of drilling and production incidents; (3) withholding of water quality data from specific incidents due to liability concerns; (4) limited sample and sensor data for the constituents of concern; (5) possibility of sensor malfunction or drift. An extensive field study in the Marcellus Shale in southwest Pennsylvania was recently completed, but has not been peer-reviewed (NETL, 2014). The study combined microseismic monitoring of fracture propagation with sampling of produced gas and water from overlying conventional reservoirs. They found no evidence of gas, brine, or tracer migration into the monitored wells. A more recent study by Siegel et al. (2015) that examined an extensive industry dataset in the Marcellus Shale concluded that there was no correlation between the methane concentrations in domestic groundwater wells and hydraulic fracturing operations. However, the findings are questionable, due to the sampling strategy and techniques used (the samples were provided by the operator, Chesapeake Energy) and the lack of true baseline measurements.

In another study, 127 drinking water wells in the Fayettesville Shale were sampled and analyzed for major ions, trace metals, CH_4 gas content and its C isotopes ($\delta13C_{CH4}$), and select isotope tracers ($\delta11B$, $Sr87/Sr86$, δD, $\delta18O$, $\delta13C_{DIC}$). The data were compared to the composition of flowback samples directly from Fayetteville Shale gas wells. Methane was detected in 63% of the drinking-water wells, but only six wells had concentrations greater than 0.5 mg CH_4 L^{-1}. No spatial relationship was found between CH_4 and salinity occurrences in shallow drinking water wells with proximity to shale-gas drilling sites. They concluded, based on the analyses of geochemical and isotope data, that there was no direct evidence of contamination in shallow drinking-water aquifers associated with nearby stimulation operations (Warner et al., 2013b).

Another recent study conducted in the Bakken Shale sampled 30 domestic wells for major ions, nutrients, trace elements, 23 volatile organic compounds (VOCs); methane and ethane; and hydrocarbon-gas chemical (C1–C6) and isotopic ($\delta2H$ and $\delta13C$ in methane) compositions in 2013 (McMahon et al., 2015). This study also concluded that there had been no discernible effects of energy-development activities on groundwater quality, but also mentioned that the results had to be considered in the context of groundwater age and velocity. The groundwater age of the domestic wells ranged from <1,000 years to >30,000 years, based on ^{14}C measurements, and thus it was suggested that domestic wells

may not be as well suited for detecting contamination from recent surface spills compared to shallower wells screened near the water table. The horizontal groundwater velocities, also calculated from ^{14}C measurements, implied that the contaminants would only have travelled ~0.5 km (0.3 mi) from the source, and thus a more long-term monitoring plan was suggested to truly assess the effects of energy development in the area.

In general, it is difficult to detect groundwater contamination, especially in situations where there has not been adequate baseline water quality data or monitoring. In cases where some monitoring has been conducted, potential contaminant release may not have been detected for a number of reasons, such as inappropriate locations for testing, slow transport of contaminants, and high analyte detection limits.

2.7.3. Quality of Groundwater Near Stimulated Oil Fields in California

In order to know if poor groundwater quality is due to oil and gas development activities, the natural quality (background quality) of the groundwater needs to be understood. Contaminants associated with oil and gas development wastewaters, including TDS, trace elements, and NORM, occur naturally in California groundwater, and regional surveys are needed to establish background concentrations in areas of oil and gas development in order to determine how this activity is impacting groundwater. Elevated levels of trace elements, such as arsenic, boron, molybdenum, chromium, and selenium, have been measured in shallow groundwater in several regions in California (e.g., Schmitt et al., 2006; 2009). High levels of uranium, frequently exceeding U.S. EPA MCLs, have also been noted in the Central Valley, and are correlated with high bicarbonate concentrations in the groundwater (Jurgens et al., 2010). Similarly, several counties in California, including Santa Barbara, Ventura, and Kern counties, are considered to be in the U.S. EPA's radon zones 1 and 2, which indicates that they have a high to moderate potential of having radon in soils and groundwater (http://www.epa.gov/radon/zonemap.html).

In studies mostly conducted outside of California, methane concentrations in groundwater have been used as an indicator of unconventional oil and gas development impacts on household sources of drinking water, and as evidence of leakage around active and abandoned wells (Osborn et al., 2011a; Jackson et al., 2013a; Lleweyln et al., 2015). A survey of methane concentrations in Southern California identified eight high-risk areas where methane could pose a safety problem (Geoscience Analytical, 1986). These include the Salt Lake Oil field in Los Angeles; the Newport Oil field; the Santa Fe Springs Oil field; the Rideout Heights area of the Whittier Oil Field; the Los Angeles City Oil field; the Brea-Olinda Oil field; the Summerland Oil field; and the Huntington Beach Oil field. Similar surveys for methane have not been conducted in other parts of California.

Salt content, measured as TDS, is a critical limiting factor for the quality of groundwater. Uses of groundwater typically have a threshold over which higher TDS is aesthetically undesirable or will result in impairment. For instance, the taste of water may become unpleasant and plant growth reduced if TDS levels are above certain thresholds. For these reasons, there are various regulatory limits regarding water quality based on the total

dissolved solids content, some of which are listed in Table 2.7-2.

Table 2.7-2. Some regulatory limits regarding total dissolved solids in water.

Maximum TDS (mg L^{-1})	Applicability	Enforceability	Overseeing Agency
500	Water supplied by a community water system	Not enforceable, but recommended	Federal EPA and CDPH
1,000		Upper limit[1]	CDPH
1,500		Short term limit[2]	
3,000	All surface and groundwater	Limit of suitability[3]	SWRCB
10,000	Groundwater	Protected, unless exempted[4]	Federal EPA, DOGGR, and SWRCB
TDS – Total Dissolved Solids			
EPA – Environmental Protection Agency			
CDPH – California Department of Public Health			
SWRCB – State Water Resources Control Board			
DOGGR – California Division of Oil, Gas and Geothermal Resources			

[1]*Acceptable if it is neither reasonable nor feasible to provide more suitable water (Cal. Cod. Reg. § 64449)*

[2]*Acceptable only for existing systems on a temporary basis pending construction of new treatment facilities that will reduce the TDS to at least the upper limit or development of acceptable new water sources water (Cal. Cod. Reg. § 64449)*

[3]*All groundwater meeting this threshold, along with various other criteria, should be designated by the Regional Boards as considered suitable, or potentially suitable, for municipal or domestic water , with the exception that groundwater designated previously designated as unsuitable may retain that designation under certain conditions (SWRCB Res.No. 88-63 as modified by Res No. 2006-0008)*

[4]*An underground source of drinking water (USDW) is defined as groundwater with TDS less than 10,000 mg L^{-1} in an aquifer with sufficient permeability and of sufficient volume to supply a public water system. Such water must be protected unless otherwise exempted (40 CFR § 144)*

The California State Water Resources Control Board (SWRCB) operates a groundwater quality and water level portal named the GeoTracker GAMA Information System ("GAMA," which stands for Groundwater Ambient Monitoring & Assessment; data portal available at http://www.waterboards.ca.gov/gama/geotracker_gama.shtml) (SWRCB, 2014a). This portal provides access to data extending back several decades.

We conducted an analysis of water quality near oil and gas operations in California, based on the minimum concentrations of TDS reported in the GAMA database. All the TDS data available from GAMA on October 10, 2014, were downloaded. The minimum value was determined in each 5 km by 5 km (3 mi by 3 mi) square area with groundwater wells in sedimentary basins with wells associated with oil and gas production starting operation

from 2002 through late 2013. Figure 2.7-1 shows the results for southern California binned by the TDS thresholds shown in Table 2.7-1. None of the areas with a TDS value has a minimum greater than 10,000 mg L^{-1}, and few have a minimum greater than 3,000 mg L^{-1}. This is likely because groundwater of this quality is of limited use, and so groundwater wells would not tend to exist in these areas.

In general, the minimum TDS is below 500 mg L^{-1} in any area where a result is available (Figure 2.7-1). This is true even in many areas along the west side of the San Joaquin Valley, where Bertoldi et al. (1991) mapped the TDS as greater than 1,500 mg L^{-1}. Groundwater with less than 500 mg L^{-1} TDS occurred in many of the oil fields in this portion of the basin (Figure 2.7-1).
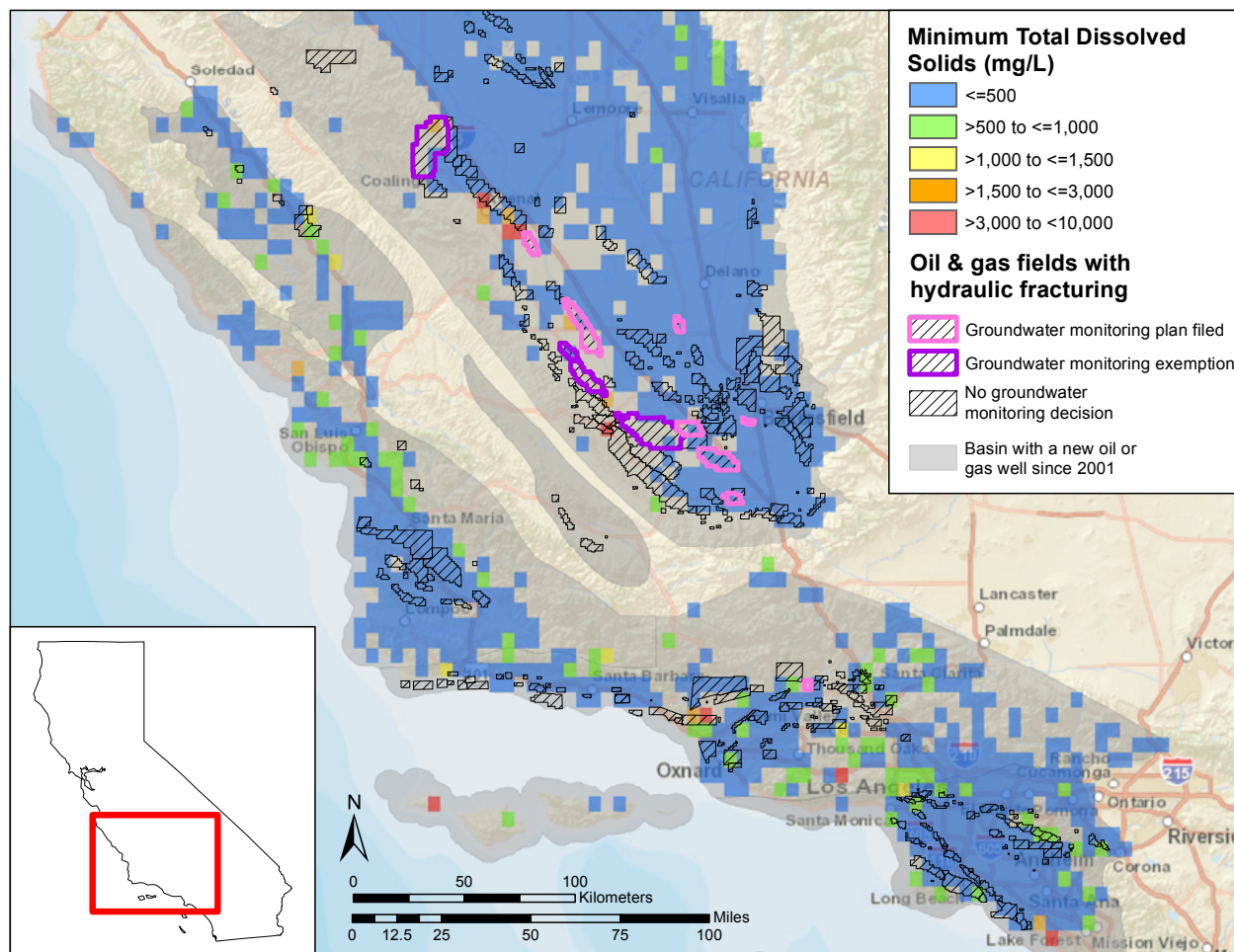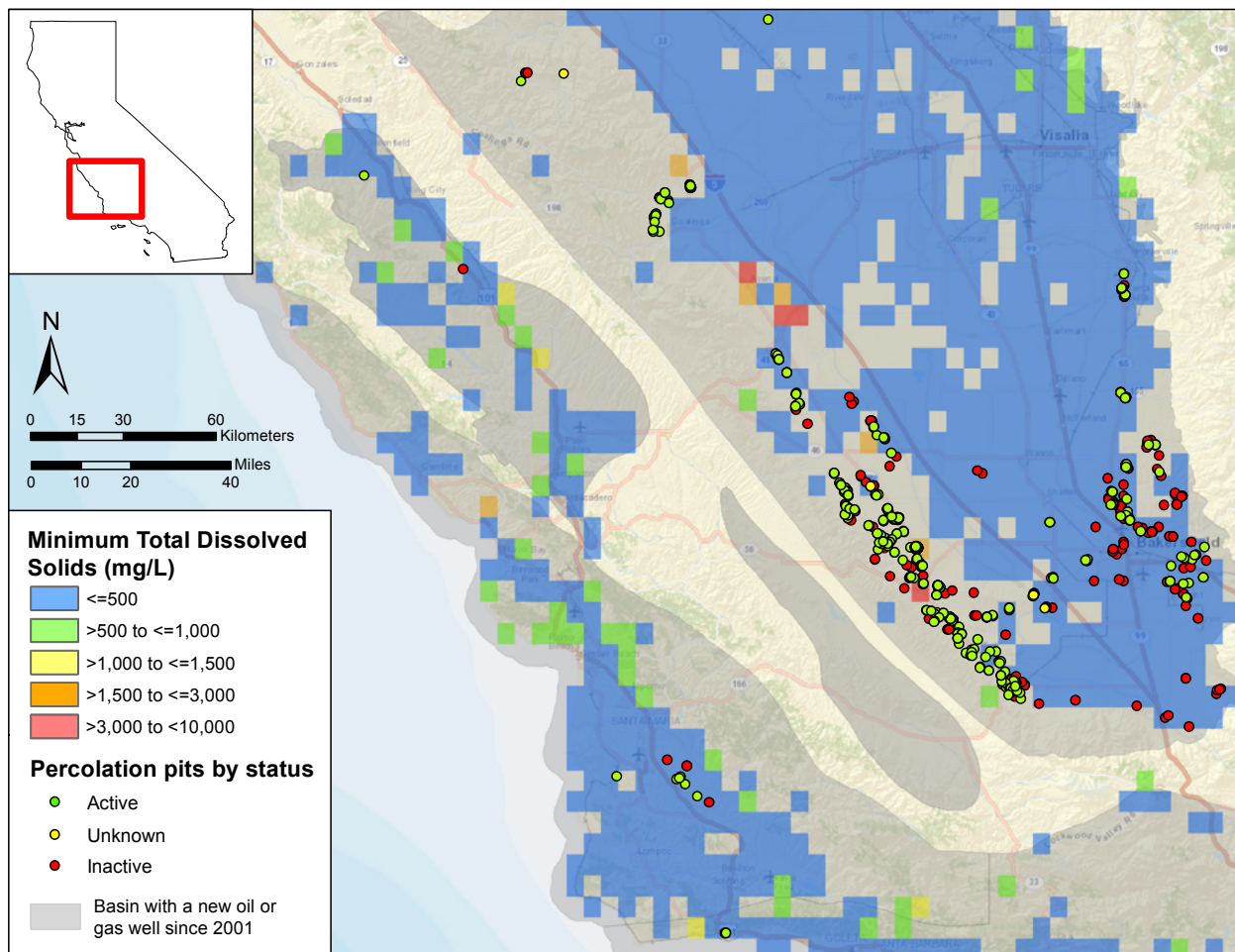

Figure 2.7-1. Minimum total dissolved solids concentration from GAMA in 5 by 5 kilometer (3 by 3 mile) square areas in central and southern California geologic basins with oil production. The status of groundwater monitoring for well stimulation projects is indicated for each field in which they have been filed.

SB 4 exempts groundwater with greater than 10,000 mg L^{-1} TDS from the monitoring requirement, as well as groundwater exempted pursuant to Section 146.4 of Title 40 of the Code of Federal Regulations. The alternative criteria described there include groundwater that occurs with hydrocarbon resources that can be economically produced, as well as groundwater that can be demonstrated to be uneconomical for use. As of October 10, 2014, operators had in some cases applied for and been granted groundwater monitoring exemptions under the TDS and hydrocarbon resource exemption provisions.

The fields for which the SWRCB has approved a groundwater monitoring plan or a groundwater monitoring exemption, according to files posted by DOGGR as of October 10, 2014, are shown in Figure 2.7-1. For the projects that were granted exclusions for groundwater monitoring from the SWRCB, the TDS data available from GAMA were either limited or indicated that the minimum TDS was greater than 1,500 mg L^{-1} (Figure 2.7-1). A possible exception is the North Belridge field.

Figure 2.7-2 shows the locations of unlined percolation pits in the Central Valley and along the Central Coast. According to this figure, percolation pits are active in areas overlying protected groundwater aquifers, especially along the eastern side of the San Joaquin Valley. In some cases, TDS levels are less than 500 mg L^{-1}. It is important to note that groundwater quality beneath the majority of active disposal pits, especially along the West San Joaquin Valley, is not known.
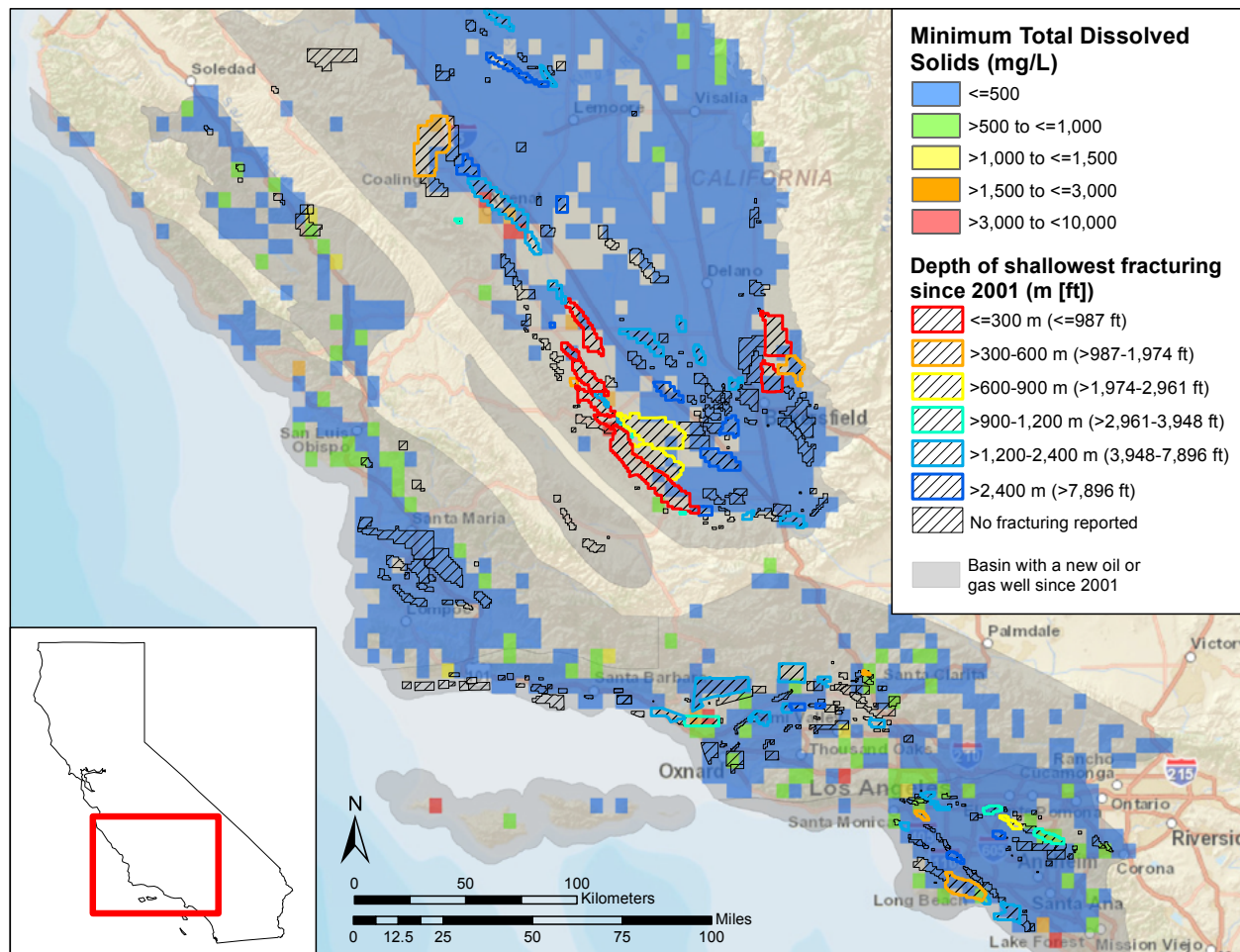
Figure 2.7-2. Minimum total dissolved solids concentration from GAMA in 5 by 5 kilometer (3 by 3 mile) square areas in central and southern California geologic basins with oil production. The location and status of unlined percolation pits in the Central Valley and Central Coast used for produced water disposal is shown. Many unlined pits are located in regions that have potentially protected groundwater.

Figure 2.7-3 provides information about the depth of hydraulic fracturing in each field. Comparison of Figures 2.7-1 and 2.7-2 indicates at least one field, Lost Hills, with hydraulic fracturing of shallow wells (<300 m [1,000 ft] deep) and groundwater of sufficient quality to require monitoring. The minimum depth of fracturing from completion reports discussed in Section 2.6 further supports this. The distribution of minimum fracturing depths indicates most are shallow, and the dataset includes reports of shallow fracturing from fields where groundwater monitoring has been required, indicating protected groundwater is present. The existence of shallow fracturing operations in areas with protected groundwater elevates concern for the hazard of subsurface migration of fluids into groundwater as a result of hydraulic fracturing.

Figure 2.7-3. Minimum total dissolved solids concentration from GAMA in 5 by 5 kilometer (3 by 3 mile) square areas in central and southern California geologic basins with oil production. The available minimum depth of hydraulic fracturing in each field available in Appendix M to Volume I is shown. For most fields, this is the depth of a well in which hydraulic fracturing occurred, so the upper limit of the hydraulic fracture may be in a shallower category. Figure 3-15 of Volume I indicates the type of depth information plotted for each field.

2.8. Alternative Practices and Best Practices

In previous sections, we have examined (1) water use and sources for well stimulation; (2) the known and unknown environmental properties of various chemicals and substances used for well stimulation; (3) the quantities and characteristics of wastewater generated from stimulated wells; (4) the potential surface and subsurface release mechanisms and transport pathways associated with well stimulation; and (5) evidence of possible surface and groundwater contamination from sampling studies conducted near stimulation operations in California and elsewhere. In this section, we describe alternative and best practices that could minimize use of freshwater resources and reduce the risk of water contamination.

2.8.1. Best Practices for Well Drilling, Construction, Stimulation, and Monitoring Methods

Application of good practices while conducting well stimulation can reduce impacts from injected or mobilized fluids. Environmental impacts can be related to surface activities as well as the subsurface aspects of well stimulation. One important concern is the potential loss of containment of subsurface fluids that could result in the contamination of groundwater. Loss of containment is a significant concern for hydraulic fracturing since it is performed at high pressures. Lower-pressure injections (below fracture pressure) of acid for matrix acidizing are less likely to result in loss of containment.

Fracturing in shallower reservoirs has greater potential to result in fractures that have sufficient length to cause loss of containment and possibly impact usable groundwater. The principal way to avoid loss of containment is careful, site-specific characterization of the geologic environment, including determination of the hydrological and geomechanical properties of all stratigraphic layers. This information is then used to develop fracturing models to predict the extent of hydraulic fracturing. The model can then be used to design the injection fluid types, volumes, and rate of injection that should result in fracturing that remains contained within the target reservoir. It should be noted that current industry-standard fracture modeling typically assumes simple bi-wing fracture geometry that is most realistic for gelled fracture treatments (Cipolla et al., 2010; Weng et al., 2011). Tools to model complex fracture geometries (typical of slickwater hydraulic fracturing treatments in very low permeability systems) are relatively less mature (Weng et al., 2011). Traditional bi-wing fracture geometry models tend to overestimate the fracture penetration distance into the reservoir if complex fracture patterns are generated (Smart et al., 2014).

Analysis discussed above has shown that induced fractures that connect with high-permeability structures, such as adjacent wells, are a potential pathway for the contamination of groundwater or the ground surface. Clearly, to avoid problems with leakage along these types of structures, careful characterization of the system is necessary to identify any wells or geologic features within the area expected to be affected by the well stimulation treatment (Shultz et al., 2014). Bachu and Valencia (2014) recommend conducting hydraulic fracturing from offset wells at a safe distance, which is not specified, but would need to be evaluated using fracture modeling and field experience.

Leakage along the well receiving the well stimulation treatment could cause a loss of containment. This is an issue of proper well construction and testing, discussed in detail in Appendix 2.D and reviewed here. The key issue is the isolation of fluid movement up (or down) the well inside the casing, or tubing internal to the casing. Fluid movement along the outside of the casing or fluid exchange between inside and outside the casing, except in zones where such exchange is intended, should be prevented by the casing and cement that bonds the casing to the formation. This aspect of well construction is termed zonal isolation. Factors to be considered as part of well drilling and well construction that are important for achieving zonal isolation are discussed in Appendix 2.D and are available in

technical documents describing accepted industry practices (e.g., API, 2010; ISO 10426 standards) and other technical literature (e.g., Aldred et al., 1999; Cook et al., 2012; Khodja et al., 2010; Lal, 1999; McLellan, 1996). Both internal and external well integrity tests can be performed to check on the integrity of the well and the quality of the zonal isolation.

Hydraulic fracturing treatments are routinely monitored through the pressure and flow rates of injected fluids. These monitoring tools can be used to help prevent loss of containment or identify if treatments remain within the targeted formation. Monitoring the pressure and flow rates into the well are fundamental response parameters that can be used to determine if the hydraulic fracturing treatment is proceeding properly. Both the pressure of the injection fluids and the casing pressure between the production casing and intermediate casing should be monitored. The fluid-injection pressure profile should be compared with the expected pressure profile basing on modeling. If significant deviations from the expected pressure profile are found, the hydraulic fracturing operation should be halted, to gather more information about the system and revisit the fracturing model. For instance, an unexpected drop in pressure could indicate a leak of the fracturing fluids through the casing outside the target formation. Similarly, if pressure builds in the casing annulus, treatment should be halted. This indicates flow behind the production casing, either from the targeted formation, from casing leaks above this zone, or directly from overlying formations into the annulus.

Monitoring can also be performed using geophysical measurements of microseismic (acoustic) signals from the fracturing process and from volumetric responses (dilation or compaction) that occur in response to the fracturing treatment. Such monitoring activities are typically used when new techniques or production areas are being evaluated for development, or if models of hydraulic fracturing require more detailed input (API, 2009), but they are not routine measurements. This type of monitoring provides the most detailed map of the locations where fractures generated of any monitoring method. It is performed using microseismic receiver arrays to detect the very small microseisms (or earthquakes) generated by the fracturing process (Warpinski et al., 2009). Such arrays can be placed in a monitoring hole nearby, in the well being fractured, on the ground surface, or buried in the shallow surface (Gilleland, 2011). The measurement is improved when conducted downhole, closer to where fracturing is taking place. This can be used as an after-the-fact assessment of where fractures were generated, but can also be used interactively, where real-time fracture mapping provides information to adjust the hydraulic fracturing treatment as it proceeds (Burch et al., 2009).

Another geophysical measurement device that can assess the extent of fracture growth is called a tiltmeter. This measurement detects the deformation of the earth associated with fracturing, which can then be interpreted in terms of the fracture orientation and geometry (Cipolla and Wright, 2000). Tiltmeters can be deployed in shallow boreholes or in deeper boreholes and, as for microseismic monitoring, better measurements can be obtained when the device is closer to where fracturing is taking place. Tiltmeters

and microseismic monitoring have some different sensitivities in terms of the types of geometry that can be deduced from the measurements (Cipolla and Wright, 2000). Tiltmeters have also been used in a real-time mode to help guide fracture treatments as they proceed (Lecampion et al., 2004).

Monitoring of wells continues in the post-treatment period to ensure that well integrity is not compromised during production. A principal method is the monitoring of casing pressure (API, 2009). A common indication of a problem is excess pressure in casing annular spaces, which can be accompanied by a buildup of gas. The gas composition can be analyzed to help identify the source of the leak. Casing pressure limits should be established. Guidelines are provided in API RP 90, *Recommended Practice 90, Annular Casing Pressure Management for Offshore Wells*, which can also be used for onshore wells. Other methods to monitor well integrity include conducting a casing inspection log and inspection of tubulars for corrosion.

2.8.2. Best and Alternative Practices for Well Stimulation Fluids

2.8.2.1. Reuse Produced Water for Well Stimulation

Produced water from oil fields is often pumped back into the oil-bearing formation to enhance oil recovery, maintain reservoir pressure, and mitigate subsidence. In California, produced water that is not reused for enhanced oil recovery is sometimes used for other purposes, such as for cooling or agricultural purposes, typically after treatment. However, reuse of produced water for well stimulation treatments is not routine. Well completion reports filed through mid-December, 2014, indicate that there were only 43 documented instances of oil and gas operators using produced water for well stimulation in California, accounting for about 13% of the water used for well stimulation in 2014. Produced water reuse for well stimulation has been shown to be feasible (e. g. Huang et al., 2005) and is becoming more common across the United States. For example, recycling of wastewater for well stimulation has increased in the Marcellus Shale region: prior to 2011, 13% of wastewater was recycled, and by 2011, 56% of wastewater was recycled (Lutz et al., 2013). Reuse for well stimulation is occurring in Texas, New Mexico, and elsewhere. Given constraints on water supplies and concerns about the adequacy of produced water disposal methods, reuse of oil and gas wastewater for subsequent well stimulation may be an attractive option for operators in California.

Reusing oil and gas wastewater for well stimulation has benefits but also some limitations. Reuse as stimulation base fluid reduces reliance on freshwater supplies and provides a disposal option. Additionally, reuse of wastewater for well stimulation can reduce transportation costs, which can be high if freshwater and/or wastewater must be trucked to and from the site, respectively. An advantage of reusing wastewater for well stimulation is that it does not need to be treated as stringently as if it were to be released into the environment (King, 2012). One of the main challenges with reusing produced water is that there are high concentrations of salts, measured as TDS. Base fluids with elevated

levels of TDS can be problematic, because the salts may precipitate in the formation, blocking fractures and reducing formation permeability (Guerra et al., 2011). Removal of TDS typically requires desalination, which often entails extensive pre-treatment to remove organic chemicals that interfere with desalination (e.g., causing biofouling of membrane surfaces). A bench-scale test in New Mexico, however, demonstrated that high-TDS water can be used as a base fluid for cross-linked gel-based hydraulic fracturing fluids (Lebas et al., 2013), eliminating the costly use of RO.

2.8.2.2. Use Alternative Water Supplies for Stimulation Fluids

While most oil and gas operators use freshwater as a base fluid for well stimulation, operators can employ other water sources, such as brackish water or treated municipal wastewater. These alternative water supplies can reduce the use of limited freshwater resources for oil and gas production. For example, Nicot et al. (2012) reports that brackish water accounts for about 20% of water use in the Eagle Ford Shale and 30% of water use in the Anadarko Basin.[12] There are a few documented cases where recycled water from other municipal or industrial users was used as the base fluid for hydraulic fracturing. Operators in the Haynesville Shale gas play in Louisiana, for example, have used treated wastewater from a nearby paper mill (Nicot et al., 2011). A 2012 analysis found that about 30 municipal and industrial facilities provide water to the oil and gas industry in Texas (Nicot et al., 2012).

Use of alternative water supplies can pose a unique set of risks. First, in water-scarce regions with limited freshwater supplies, use of brackish water may compete with more conventional users who may tap this resource and treat it or blend it for municipal or industrial use (Nicot et al., 2012). Second, in areas where the brackish groundwater aquifer is connected to freshwater aquifers, withdrawing brackish groundwater could compromise the quality and availability of water in the freshwater aquifer (Freyman, 2014). An additional risk associated with the use of brackish water is during its transportation and storage, where a spill of this water could have an adverse impact on the local environment. Challenges with using non-oilfield wastewater include guaranteeing a consistent quality of water and the cost of transporting these waters to the well site. Additional research and analysis is needed to determine whether alternative supplies are available for use in stimulation fluids, and whether the use of these supplies poses any concerns for nearby users, including municipalities, industry, and farmers.

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12. Brackish water is generally defined as having a salinity greater than freshwater (TDS <1,000 mg L^{-1}) but less than saline or seawater (~35,000 mg L^{-1}) (USGS, 2014a; NGWA, 2010).

2.8.2.3. Apply Principals of Green Chemistry to Chemical Additives used in Stimulation Fluids

Currently, a large number of chemicals are used in well stimulation that have poor or unknown environmental profiles (Section 2.4). There are few controls on what chemicals are being used in hydraulic fracturing, and some chemicals currently being used are toxic, potentially persistent in the environment, or may degrade to toxic or otherwise environmentally harmful products. Properties such as endocrine effects and carcinogenesis, which complete an environmental profile, are unknown for many chemicals listed in Table 2.A-1.

There are many opportunities to apply green chemistry principles to well stimulation formulations and thereby mitigate many of the potential direct impacts of hydraulic fracturing. The principals of green chemistry include developing industrial processes that use chemicals with the best environmental and health profiles, in other words, industrial processes that use chemicals that are non-toxic, do not have other negative or harmful hazardous properties, do not persist in the environment, and do not degrade to undesirable products (U.S. EPA 2011). Some toxic chemical additives that are used in well stimulation could potentially be replaced by non-toxic alternatives. Ideally, the most toxic and/or persistent chemicals could be replaced first. Determination of alternatives for toxic stimulation chemicals would be beneficial, but there currently is very little incentive for oil and gas producers to employ less toxic additive or to invest in research and development of alternatives.

The sheer number of chemicals used makes a full hazard and risk analysis difficult, if not impossible, due in part to the complexity of understanding interactions between chemicals in combination. Reducing the number of chemicals applied would make it easier to evaluate hydraulic fracturing mixtures, insure public safety, and resolve public concerns. Limiting the number of chemicals that can be used in hydraulic fracturing and acid treatments will also assist and simplify regulation. For example, we identified over 60 different surfactants listed in Table 2.A-1, and it may be possible to limit the number of different surfactants being used without compromising effectiveness. Currently, there is no regulatory incentive for oil and gas producers to minimize the number of chemicals used in well stimulation. However, the American Chemical Society (ACS), in partnership with industry and government representatives, has implemented a Green Chemistry Institute, which aims to address issues of pollution prevention and sustainability in chemical use. More sustainable stimulation chemicals could be pursued within this framework.

Characterization of chemicals—including information on toxicity and environmental persistence—is not required prior to use of these chemicals for well stimulation in California. In some cases, data are missing that are needed in the event of an emergency. Recent events associated with the energy industry have underscored some of the risks of a lack of readily (and publicly available) information on chemicals. For example, emergency response to the release of 4-methylcyclohexanemethanol into the Elk River in

West Virginia was hampered by the absence of basic physical, chemical, and toxicological information on that chemical. In the absence of a complete environmental and health profile on a chemical, implementation of a timely and appropriate response by regulatory agencies following releases of these chemicals into the environment is impeded.

The North Sea compact/OSPAR Convention is a good model for how oil and gas production can be done with an eye towards environmental sustainability. In the compact, it is agreed that chemicals will be tested before they are used in the North Sea. The chemicals must pass certain criteria before they are used, and standards for environmental persistence and acute toxicity must be met (OSPAR Commission, 2013). Similar criteria concerning testing for toxicity and environmental persistence are suggested, but not required, in the United States (U.S. EPA, 2011). In another example, Proctor & Gamble established the Environmental Water Quality Laboratory (EWQL), with the mission to measure the toxicity, environmental fate, and physical-chemical properties of chemical ingredients before they were used in their products (http://www.scienceinthebox.com / leadership-in-sustainability-at-pg). These approaches may represent a good model for insuring the safety of unconventional oil and gas development in California.

2.8.2.4. Investigate Application of Waterless Technologies

Companies are developing technologies to reduce or eliminate the amount of water used for well stimulation. Some low-water or waterless stimulation methods have been in use for decades. Alternatives include the use of foams; pressurized gas, such as carbon dioxide or nitrogen; or fluids other than water, such as liquid propane (see e.g., Friehauf and Sharma, 2009; Gupta, 2010; van Hoorebeke et al., 2010). A recent magazine article cites the case of the Marathon Oil Company, which has begun using propane for fracturing in the Eagle Ford Basin in Texas. The company's president stated during testimony to a Congressional committee that the move to waterless fracturing has reduced water consumption by 40 percent in the first 90 days of operations, and as an additional benefit, "The companies are able to resell the propane when it comes up back from the hole" (Wythe, 2013). One industry analyst cautioned, however, that waterless technologies are not poised to have a large effect on water use in the oil and gas industry, barring a major technological breakthrough (Freyman, 2014).

2.8.3. Best and Alternative Practices for Wastewater Characterization and Management

2.8.3.1. Treat and Reuse Oil and Gas Wastewater for Other Beneficial Uses

With proper treatment and monitoring, wastewater generated from oil and gas production—including wastewater generated from stimulated wells—could be used for various beneficial uses. Guerra et al. (2011) identified several beneficial uses currently being practiced in the western United States, including industrial cooling, dust control, irrigation, and water supply to constructed wetlands and wildlife habitats. The advantages of reusing oil and gas wastewater are that the demand for freshwater

resources is reduced, and since water is typically treated to remove contaminants prior to reuse, the risk of water contamination from improper disposal is reduced, and the total volume of wastewater produced is reduced. However, the reuse of produced water that is commingled with returned stimulation fluids raises new concerns, since it is not known how stimulation fluid additives may impact the safety of beneficial reuse. The types and amounts of well stimulation additives found in these waters is unknown, so it is not certain what treatment methods are adequate to allow reuse. Additionally, potentially hazardous chemicals resulting from degradation of the added chemicals and the interaction of the stimulation fluid with the formation need to be carefully evaluated.

Proper treatment is required to ensure that well stimulation chemicals are removed from wastewater prior to reuse. In Section 2.5, we evaluated whether various chemical, physical, and biological treatment technologies commonly used on produced water in California and elsewhere will be effective in removing well stimulation chemicals. Results of this analysis indicate that there is no single treatment technology that can independently treat all categories of well stimulation fluid additives (also see Appendix 2.C). Adequate treatment would require the use of multiple technologies in treatment trains to satisfy effluent requirements. Treatment trains that provide only the most basic treatment, e.g., air stripping/gas flotation followed by filtration, will be ineffective at removing most well stimulation chemicals. Treatment trains utilizing RO are expected to provide the highest level of treatment, due to the effectiveness of RO at removing small (0.001-0.0001 μm) constituents and the need for multiple pretreatment steps to prevent membrane fouling. However, the high cost and energy requirements of RO systems may reduce the economic viability of treating well stimulation chemicals.

2.8.3.2. Characterize and Monitor Produced Water and Other Wastewaters

More extensive characterization of the compositions of wastewater generated by stimulated wells in California is needed. Additional testing needs to be done for wastewater that is not being disposed into injection wells, especially to see if wastewater that is being reused for irrigation, disposed into sewers or unlined pits have been effectively treated. Wastewater compositions should be analyzed at several time points to be able to identify the patterns for how they evolve over time, and to identify when returned stimulation fluids are present in the wastewater. Analytes should include surfactants, solvents, biocides, and other compounds used in hydraulic fracturing fluids. Other analytes to be measured should include general water quality parameters (such as pH, temperature, chemical oxygen demand, organic carbon etc.), major and minor cations and anions, metals and trace elements, BTEX, gases (methane and H_2S) and NORM. The list of analytes needs to be periodically updated to reflect current scientific research, as well as understanding of the wastewater composition patterns in California oil and gas fields where stimulation is occurring.

2.8.3.3. Improve Management Practices for Oil and Gas Wastewater

Disposal of wastewater from oil and gas production occurs by Class II disposal wells, discharge into sanitary sewers, percolation in unlined pits, and treatment for reuse. Evaporation-percolation in unlined surface impoundments (percolation pits) is a practice that intentionally introduces wastewater and its constituents into near-surface groundwater aquifers. The U.S. Department of Energy recommends that "all evaporation pits should be lined … to prevent downward migration of fluids" (U.S. DOE et al., 2009). Texas and Ohio have restricted or stopped the use of unlined pits and percolation basins as a disposal practice for produced water, due to documented groundwater contamination incidents (Kell, 2011). Given the concerns regarding disposal in percolation pits, injection into properly located, constructed, and permitted Class II wells for EOR or disposal would be a better practice (Kell, 2011; U.S. DOE et al., 2009). The reuse of wastewater should be encouraged, but reuse of water from stimulated wells will require adequate safeguards, including monitoring for appropriate chemical contaminants and applying multi-stage treatment systems before reuse (e.g., Liske and Leong, 2006; Appendix C).

When oil and gas wastewater is discharged into sanitary sewers, the wastewater is conveyed to domestic wastewater treatment plants that were not necessarily designed to remove all of the constituents found in oil and gas wastewater from stimulated wells. Although the discharges into the sanitary sewer must be compliant with local pre-treatment ordinances, it is not clear that these requirements are sufficient to address well stimulation chemicals.

The environmental impacts of discharging oil and gas wastewater into Class II wells in California are not entirely understood. There are federal and state requirements for construction and placement of Class II injection wells (Veil et al., 2004), but there are concerns that Class II wells in California may be contaminating protected groundwater. Site characterization requirements include a confining zone free of known open faults or fractures that separates the injection zone from underground sources of drinking water, and construction requirements to ensure mechanical integrity of the well (40 CFR 146.22). There are also operating requirements that limit injection pressure and monitoring and reporting requirements (40 CFR 146.23). A recent detailed review of California requirements for Class II injection wells suggested that current rules may not be adequate for protection of all beneficial uses of groundwater (Walker, 2011). In addition, EPA is expected to release (in 2015) recommendations for best practices for limiting induced seismicity associated with wastewater injection by the oil and gas industry (Folger and Tiemann, 2014). An alternative practice would be to determine the location of protected groundwater in the state, to investigate and review current practices to resolve outstanding issues concerning the use of Class II wells for disposal in California, and to conduct site-specific studies to ensure the safety of proposed disposal methods.

2.8.4. Best and Alternative Practices for Monitoring for Groundwater Contamination

Groundwater contamination can be difficult to detect. Comprehensive baseline and monitoring measurements collected before and after drilling, including regional characterization of background concentrations of groundwater constituents, are necessary to determine impacts on groundwater quality from well stimulation or any other oil and gas development activity.

Baseline data on groundwater quality have not been collected at appropriate locations and in a systematic manner to allow the impacts of oil and gas development on groundwater resources in California to be determined. Improved collection and organization of groundwater data would be a better practice. Some information on background levels of many inorganic and organic constituents, including TDS, trace metals, and VOCs in California, is available from the USGS Groundwater Ambient Monitoring and Assessment (GAMA) program (USGS, 2013). These data should be fully analyzed in future investigations of the impact of well stimulation on groundwater quality in California. However, the GAMA program has objectives related to monitoring drinking water and does not currently collect data in many regions of the state with active oil and gas development (Figure 2.7-1). Investigations of regional and site-specific groundwater impacts from unconventional oil and gas development should be directed at determining the importance of specific contamination pathways, and the extent of groundwater contamination. Developing specific programs examining groundwater impacts of oil and gas development would be a better practice.

In other parts of the country, studies have shown that measurements of methane in groundwater and elsewhere can be an important indicator of leakage from well bores and other sources, such as fractures. Methane levels over 45 mg L^{-1} (ppm) have been observed in New York, West Virginia, and Pennsylvania groundwater (Vidic et al., 2013). Best practice for the development of a comprehensive groundwater monitoring program includes coordinated examination of the concentrations and isotope characteristics of methane.

The State Water Resources Control Board (SWRCB) is issuing groundwater monitoring regulations, due to take effect on July, 2015. The groundwater monitoring regulations being developed by the SWRCB will include both a monitoring plan for areas where oil and gas well stimulation are being conducted, as well as a regional monitoring plan. The SWRCB released its draft model criteria for area-specific groundwater monitoring on April 29, 2015 (SWRCB, 2015), which outlines the design for groundwater monitoring, including collection of baseline data, as well as sampling and testing requirements. These monitoring requirements are expected to develop baseline water quality information and improve the current understanding of water quality impacts of both conventional and unconventional oil and gas development.

2.9. Data Gaps

Numerous data gaps were identified during the course of this investigation that can and should be addressed in order to provide a better understanding of unconventional oil and gas development in California, and associated impacts on water and the environment. Overall uncertainty in our analysis was increased by reliance on voluntary reporting, poor data quality, and missing or inaccurate information in state agency datasets. New regulations, put in place under SB 4, are mandating reporting of more information, but an evaluation of the completeness and accuracy of reporting, as well as the relevance and appropriateness of information being reported, needs to occur in the future as part of the ongoing efforts to fully understand the actual and potential environmental impacts of unconventional oil and gas development. Data that are complete and accurate also need to be submitted and published in a timely manner. Scientists and regulators need to be engaged in an ongoing effort of data analysis and interpretation of information, to arrive at a better understanding of the environmental impacts of well stimulation in California. Below, we identify some of the most critical data gaps identified in our investigation of water impacts of well stimulation.

2.9.1. Reports and Data Submissions Have Errors, Missing Entries, and Inconsistencies

Mandatory and voluntary reporting requires data entry by operators and other responsible parties. It was apparent during our investigations that information submitted to the state was not subject to systematic quality checks or verified, and, as a result, datasets resulting from these submissions contained errors and inconsistencies. Due to data entry errors and inconsistencies, data sets required extensive editing and organization before they could be analyzed. Analysis of uncorrected data can and will result in significant errors in interpretation (e.g., chemical function is routinely reported incorrectly, counts on the number of chemicals may be exaggerated, etc.). Maintaining standardized and verified data, ideally in electronic format, would allow rapid and accurate analysis of oil field activities on a near real-time basis.

In many cases, the data collected by DOGGR and other government agencies contained simple typos and other obvious mistakes. In other cases, information is missing or meaningless. For example, DOGGR's Production and Injection database contained records for active production wells where the number of production days was zero and the information on the type of produced water generated was missing or identified as "other" or "unknown."

Reporting units and other formats differ between important databases (e.g., FracFocus, SCAQMD, DOGGR), complicating comparative analysis and making data integration more difficult and prone to error. In the SCQAMD reports, units for reporting mass compositions of fluids were non-standard and resulted in predictable data entry errors. The SCQAMD data entry requirements are different from both FracFocus and DOGGR records, and basic

information such as CASRN and API well number are entered in different formats or not at all. FracFocus is not linked or standardized to other information, such as well production information, collected by DOGGR and other agencies.

Implementation of a quality assurance program and standardization would improve the quality of the data and allow ongoing analysis by agencies compiling the data. For example, in the completion reports submitted to DOGGR, it could be required that the percentage of various chemicals reported as added to each operation must always add up to 100% (± 5%). In other cases, simple controls, such as checking that entries match an appropriate range of possible values, would results in marked improvements in data quality. The use of entries such as "other" or "unknown" should not be acceptable for critical parameters or values.

The DOGGR GIS wells file has missing data for many data entry fields, which are needed for assessment of impacts. For example, as of November 2014, only 20% of records have values filled in for well depth. There are also incorrect data for some values; for example, there are some wells that have a latitude or longitude value of zero.

There are also some files where the data is poorly organized, making analysis cumbersome. For example, in the new completion reports, the "Location of Treatment" sheet does not have the actual location of where the stimulation was conducted (such as fields for latitude, longitude, field, area, or county). Instead, this information is located in a different sheet in the file that is intended to list all the chemicals used in each treatment. DOGGR and other agencies should consider normalizing data spreadsheets, and preferably storing the data in an accessible database.

2.9.2. Information is Not Easily Accessible to the Public

Agencies responsible for collecting information do not always make the information easily accessible to the public, limiting the use of these records to inform citizens and policymakers. The use of the industry website FracFocus is a reasonable model for inputting chemical data, but extracting data is difficult, and accessibility to electronic datasets or databases is limited and not freely available to the public. Information on water quality and the location of groundwater extraction wells in GAMA is not reported with appropriate or accurate location information (latitude and longitude or Universal Transverse Mercator [UTM] coordinates) to allow open and public risk analysis. Additionally, lack of publication of well locations hinders the development and public evaluation of monitoring plans that must be submitted under new regulations.

2.9.4. Information is Submitted in Inadequate Data Formats

In many cases, data needed for analysis are only available as PDF documents or displayed on web pages, rather than available in well-organized electronic data structures. The nontransferable nature of the datasets makes data entry and analysis burdensome and

time-consuming, as records need to be retyped or extracted from PDF documents. The use of non-standard data formats and the lack of a well-designed database system may have also resulted in a decreased ability to detect errors in data submission, resulting in incorrect entries, typos, and duplicate records. The use of PDF formats for data reporting is an important problem for reporting all types of data.

2.9.4. Poor Collaboration Between State and Federal Data Collection Efforts

In collecting information for this project, we found that datasets collected by different agencies were frequently contradictory, lacked standardization between datasets (e.g., reporting units differed, etc.) and difficult to harmonize. There are currently separate initiatives by the Central Valley Regional Water Quality Control Board, the South Coast Air Quality Management District, DOGGR, and other agencies to collect information, with each agency having its own purposes. The lack of collaboration and standardization between agencies resulted in duplicated efforts.

In many cases, stimulation events were described differently in different databases. For example, we found data for the same well stimulation operation that was reported in FracFocus, in DOGGR completion reports, and in data submitted to the SCAQMD, but these sources sometimes reported different dates, water volumes, and other information that made comparison or integration of information from different sources difficult. Coordinated integration of data collection, standardization of reporting units, and consistent unique identifiers for authorized treatments would require a new level of interdepartmental coordination and cooperation, but would allow improved regulatory oversight. The unique API well numbers should be included with all reports, data, and other documents concerning activities associated with wells or groups of wells (e.g., wastewater management activities).

2.9.5. Chemical Information Submitted by Operators is Incomplete or Erroneous

Chemical data submitted by operators includes errors and omissions. The product CASRN and chemical name are not always included for each chemical reported. Frequently, the chemical purpose is incorrect or missing. Chemicals that are classified as trade secrets, confidential business information, or used in proprietary blends are listed without CASRNs. Products listed without CASRNs cannot be definitively identified by chemical name alone, and thus cannot be adequately evaluated for hazards, fate, and treatment. Even when CASRNs are provided, they are not always correct. For example, chemical CASRNs are sometimes reversed or missing digits altogether (see comments about quality control above). Frequently, the reported chemical purpose includes all possible uses for the chemicals, to the point that the information provided is meaningless. Furthermore, impurities are typically not identified as such, and are instead given the same purpose description as the active ingredient in the chemical product. Hazard and environmental analysis of chemicals used in stimulation fluids is hindered by the lack of quality control and standardization in reported data.

2.9.6. Chemicals Lack Data on Characteristic Properties Needed for Environmental Risk Analysis

Most of the chemicals being used for well stimulation lack publicly available physical, chemical, or toxicological measurements needed for the development of an environmental profile. An environmental profile is needed to provide a complete hazard and risk assessment on a chemical (OECD, 2013; OSPAR, 2013; Stringfellow et al., 2014; U.S. EPA, 2011). At a minimum, the physical, chemical, and biological information needed to develop an environmental profile includes log octanol-water partition coefficients (log K_{ow}), Henry's constants (K_H), soil organic carbon-water partition coefficients (K_{OC}), biodegradability, and acute toxicology. Other information on chronic effects, potential for bioaccumulation, and other properties are also needed. The technical information in an environmental profile is needed for developing environmental fate and transport models, reviewing waste management plans, preparing for spills and accidents, selecting treatment technologies, evaluating reuse projects, and conducting hazard assessments.

Chemical data generated by industrial groups are sometimes contained in material safety data sheets (MSDS); however, these data are not always publicly available and cannot always be confirmed or reviewed. Material safety data sheets cannot be considered reliable sources for chemical, physical, and toxicological data without a public review and validation of the published information.

Publicly available experimental data on the toxicity of many stimulation chemicals to aquatic species, including algae and aquatic animals, and mammalian species are sparse. In particular, aquatic toxicity data are missing testing of native or resident species that are important to California. Measurement or publication of aquatic and mammalian toxicity data is currently not required prior to using chemicals in well stimulation. This lack of available data increases risk to human and environmental health, since the lack of information prevents the ability to make informed decisions and apply an appropriate response during failures and accidents.

In addition to a basic analysis of acute toxicity, data is needed on the potential impacts of chronic exposure to well stimulation fluids in ecological receptors. Measurements of sublethal impacts on plants and animals, such as survival potential and population viability, are not available for most chemicals used in well stimulation. More data is needed on potential sublethal impacts on ecological receptors due to exposures to fluid additives.

The fate and transport of chemical mixtures in the environment is not well understood. Hydraulic fracturing fluids contain complex mixtures, and the interactions of these chemicals in the environment is unknown. For example, easily degradable but toxic components such as methanol are in admixture with biocides, added to prevent biodegradation from occurring. How biocides would influence the persistence of methanol in the environment is unknown, but the methanol might transport further in groundwater in the presence of the biocide, presenting greater risk than methanol alone. Scientific investigation of the environmental fate of chemical mixtures is needed.

2.9.7. Data on Chemical Use from Conventional Oil and Gas Operations are Not Available

Chemical use information for all oil and gas development operations is not available and would be useful for providing context to chemical use during well stimulation. SCAQMD is now collecting data on chemical use during well drilling, installation, and rework in parts of southern California, but similar data are not available for the San Joaquin Valley where the majority of oil and gas extraction takes place. To our knowledge, no data is being collected on chemical use during other oil and gas development activities, such as EOR. Data collected by SCAQMD do not carefully differentiate between well stimulation treatments and other activities, such as well maintenance, making it difficult to interpret and evaluate well stimulation chemical use in the context of overall chemical use. Many of the same chemicals (e.g., biocides, corrosion inhibitors, surfactants, etc.) are used for other oil and gas development activities as are used in production aided by well stimulation. More complete and consistent reporting and tracking of chemical use for all oil and gas development activities will allow a better understanding of the impacts of well stimulation in the context of overall oil and gas development.

2.9.8. Lack of Data Regarding the Chemical Composition of Produced Water from Stimulated Wells

There is a lack of information regarding the characteristics of produced water and other wastewater generated from well stimulation in California. Produced water from stimulated wells will contain chemicals used in hydraulic fracturing, but the amounts of chemicals returning during production and the time period over which they return has not been measured. Data are needed regarding how wastewater constituent concentrations and composition change over time.

Produced waters will contain reaction products from the complex mixtures of chemicals used in hydraulic fracturing. Lack of knowledge concerning the fate of the injected stimulation fluids in the subsurface, and the potential for them to be transformed, or to mobilize formation constituents over the lifetime of production from the well, needs to be determined. The nature of the reaction byproducts, the amounts and types of materials returning to the surface during the lifetime of the well, and hazards associated with these reaction byproducts are entirely unknown and need to be investigated.

Poor understanding of wastewater composition is a major impediment to the safe and beneficial reuse of produced water from stimulated wells. It is unknown how (or if) well stimulation chemicals or their byproducts have been introduced into the environment via disposal or reuse practices, such as percolation or water flooding. California specific investigations of water reuse and disposal practices are needed to fill this data gap.

There are limited data concerning the composition of produced waters from conventional wells, which prevents a comparison between the conventional and unconventional oil

and gas development. Current practice in California mingles the produced waters from stimulated and non-stimulated wells before treatment. If there are differences between wastewater from conventional and stimulated oil and gas operations, the differences would have implications for how each wastewater should be handled, treated, and disposed. Previous studies on the chemical quality of produced waste in California were conducted decades ago, and new studies need to be conducted characterizing produced water and other oil and gas industry wastewaters in California.

Water quality analyses required under new regulation and submitted to DOGGR with well completion reports do not typically measure specific stimulation chemicals, with the exception of a total carbohydrate test for guar. Analysis is not conducted for major well-stimulation-fluid components of concern, such as biocides or surfactants, or potentially harmful reaction products that may form within the formation following introduction of the stimulation fluids. The operators also do not report the exact time at which the recovered fluid sample was collected relative to the stimulation event, so it is difficult to interpret what the samples truly represent.

2.9.9. Incomplete Information Regarding Wastewater Management, Disposal, and Treatment Practices

Data on wastewater disposal and management are incomplete. There is conflicting or inadequate information on current disposal and reuse practices, especially concerning percolation pits and Class II wells. Cradle-to-grave documentation on wastewater management would allow individual sources of wastewater, such as individual wells, to be related to a specific disposal or reuse site, such as a percolation pit.

Systems for documentation of wastewater management practice need modernization, and ambiguous or uninformative entries should not be allowed. For example, the third most common disposal method reported by operators was "other." DOGGR staff confirmed that some operators are using the "other" category to describe disposal that is, in fact, included in some of the other categories—for example, subsurface injection, discharge to a surface water body, disposal to a sanitary sewer system, etc. (Fields, 2014). Some disposal methods—such as reuse for irrigation or groundwater recharge—are not included as separate categories in the DOGGR production/injection database. During meetings held as part of this study, some operators have suggested that their current practices are not consistent with the data they have reported to DOGGR. Insufficient quality control for operator-submitted data, and inadequate categories for wastewater disposal methods, result in an incomplete picture of current wastewater disposal practices.

There is no central resource for data concerning wastewater treatment practices. In collecting information for this project, data sources for confirmation of common treatment practices varied from NPDES permits and government agency reports, to personal communications, brochures, and factsheets. Due to the lack of a centralized data resource, the frequency of specific wastewater treatment practices and overall trends are unknown.

2.9.10. Incomplete Information on the Impacts of Contamination from Subsurface Pathways

Subsurface pathways and mechanisms are difficult to characterize, and information concerning potential groundwater contamination from hydraulic fracturing is very limited. Peer-reviewed studies investigating the possibility of contaminant transport due to fracturing operations have not been conducted in California. Studies conducted in other areas have suggested contamination is possible or has occurred, but the applicability of those results to California cannot be determined without more investigation, due to the unique conditions existing in California.

2.9.11. Lack of Accurate Information Regarding Old and Abandoned Wells

The extent to which abandoned and deteriorating wells may present a hazard in California needs to be assessed. Documentation of the location, construction, and the method of abandonment for currently unused wells are required before assessment of hazards (or methods for remediation) can be performed. DOGGR has a program that requires operators to conduct regular testing of idle wells to ensure that they are not impacting surface and groundwater, but similar testing is not required for abandoned or buried wells. The datasets regarding idle wells are inconsistent. For example, the DOGGR GIS wells file lists 13,450 wells as idle, but another "Idle Wells" file on the DOGGR website lists a total of 21,347 wells as idle.

2.9.12. Lack of Knowledge about Fracture Properties in California

The process of fracture creation and propagation is currently an area of active research, with the bulk of the work focusing on the properties of gas shales in states other than California. This research applies to deep formations and thus evaluates pathway formation scenarios over large vertical distances. Fracturing has been practiced in California for decades (Walker et al., 2002), but fundamental studies of fracturing behavior, fracture propagation, and the orientation of fractures relative to reservoir depth for California geology are lacking. Fully understanding this behavior is particularly important in California due to the possibility of relatively shallow fracturing depths (200–300 m [650–1,000 ft] from surface) compared to other regions using hydraulic fracturing technology.

Although the reporting of the extent of stimulation geometry has been required for operations occurring after January 1, 2014, the resulting data assessed for this report indicates it generally does not regard the extent of fracturing from single stages, limiting what can be discerned about fracture geometry from these data. Some of the reported data are obviously inaccurate (for example, some of the wellbore end depths are shallower than the corresponding wellbore start depths) or inconsistent with reporting requirements (for example, wellbore start depths are sometimes reported as zero instead of the start of the stimulated interval within the wellbore). Further, if data regarding fracture geometry

were reported, the accuracy of this data would be unknown unless the data supporting the estimates of fracture geometry, and the methods used to analyze the supporting data, were reported by operators.

2.9.13. Incomplete Baseline Data and Monitoring Studies for Surface and Groundwater

Long-term monitoring and studies of surface and groundwater in oil and gas producing regions of California are needed to determine if groundwater resources have been impacted. There is a lack of information on the quality of surface or groundwater near stimulated oil fields, and baseline (or up-gradient) data collection is needed. Significant data gaps exist regarding current knowledge of groundwater quality in California, including the location and extent of protected groundwater that contains less than 10,000 mg L^{-1} TDS. Concentrations of methane, trace metals, NORM, and organic chemicals in groundwater in oil and gas producing regions are unknown, and are needed to assess impacts of unconventional oil and gas development. New regulations implemented under SB 4 and other programs are beginning to address this data gap. The effectiveness of these regulations needs to be evaluated in the future.

2.9.14. Lack of Information on Spills

As discussed above for other types of data, there are numerous inconsistencies between agencies concerning the information collected on spills and accidental releases in California. Databases maintained by OES and DOGGR on surface spills and leaks associated with oil and gas production often do not agree, increasing uncertainty in our understanding of environmental impacts from accidents. Inconsistencies exist concerning the number of spills that have occurred and details regarding those spills. This discrepancy is likely due in part to the fact that OES sends spill reports electronically to DOGGR, and then a subset of the information is entered into DOGGR's database. Although OES is responsible for collecting spill information and submitting it to the appropriate agencies, there are spills in DOGGR's database that are not in OES's. Similarly, there are oil and produced water spills in the OES database that are not in the DOGGR database. DOGGR often coordinates with operators after spills—especially for large spills or when spills impact waterways—but there is no mechanism for conveying this information back to OES. Operators often submit corrections to OES after a spill takes place, and these corrections are not always entered into either DOGGR's database or the OES database that is available online. Another major concern is that DOGGR only captures information on oil and produced water spills, and therefore does not have record of spills associated with chemicals used for oil and gas production.

2.10. Main Findings

2.10.1. Water Use for Well Stimulation in California

1. We estimate that well stimulation in California uses 850,000 to 1,200,000 m³ per year (690–980 acre-feet) of water. Our estimate is based on a combination of data sources to provide a best estimate that reflects the uncertainty in both (a) the number of operations that are occurring, and (b) how much water each operation uses on average.

2. Operators obtained the majority of water needed for well stimulation from nearby irrigation districts (68%), produced water (13%), operators' own wells (13%), a nearby municipal water supplier (4%), or a private landowner (1%).

3. Hydraulic fracturing has allowed oil and gas production from some new pools where it was not previously feasible or economical. We estimate that freshwater use for enhanced oil recovery in fields where production is *enabled* by stimulation was 2 million to 14 million m³ (1,600 to 13,000 acre-feet) in 2013. By comparison, freshwater use for enhanced oil recovery in *all* oil and gas fields was 13 million to 44 million m³ (11,000 to 36,000 acre-feet) in 2013.

4. Local impacts on water usage appear thus far to be minimal, with well stimulation and hydraulic-fracturing-enabled enhanced oil recovery accounting for less than 0.2% percent of total annual freshwater use within each of the state's planning areas, which range in size from 830 to 19,400 km² (320 to 7,500 mi²). However, well stimulation is concentrated in water-scarce areas of the state, and an increase in water use or drawdown of local aquifers could cause competition with agricultural, municipal, or domestic water users.

2.10.2. Characterization of Well Stimulation Fluids

1. Records describing the chemical composition of hydraulic fracturing fluids between 2011 and 2014 were voluntary, and represent one-third to one-fifth of the total hydraulic fracture treatments thought to have occurred in California during that period.

2. Over 300 different chemicals or chemical mixtures were identified as having been used for hydraulic fracturing in California. Of the disclosed chemicals, approximately one third of the chemical additives lacked a CASRN, and therefore any enumeration of the number of chemicals used in hydraulic fracturing should be considered approximate.

3. Information on chemical use during acid stimulation treatments is very limited. Analysis of regional data and data collected as part of new mandatory reporting requirements in effect since January 2014, identified over 70 individual chemicals or chemical mixtures used during acid treatments, approximately one-third of which were different from chemicals used in hydraulic fracturing.

4. Over 60 chemical additives with a median usage of 200 kg (440 lbs) or more per treatment were found. At least nine of these compounds are proppants, and many are solvents, crosslinkers, gels, and surfactants. Since these compounds were used in significant amounts, they are considered priority compounds for characterization of their hazards and risks.

5. Almost two-thirds of the chemicals reported to be used in hydraulic fracturing or acid treatments did not have publicly available information allowing an assessment of environmental toxicity. Environmental profiles need to be developed for these chemicals.

6. Thirty-three chemicals have a GHS ranking of 1 or 2 for at least one aquatic species, suggesting they could present an environmental hazard if released to surface waters.

7. Significant data gaps exist concerning the hazard, toxicity, and environmental persistence of chemicals used in well stimulation. Additionally, over 100 of the reported materials used for well stimulation are identified by non-specific name and reported as trade secrets, confidential business information, or proprietary information. These materials cannot be evaluated for hazard, risk, and environmental impact without more specific identification.

8. A full understanding of the environmental risk associated with unconventional oil and gas development will require a full disclosure of the chemicals used and better understanding of the environmental profile of each chemical. Environmental profiles include an understanding of a chemical's toxicity, transport properties, and persistence in the environment. A formal environmental review process for all chemicals and chemical mixtures, such as the EPA Design for the Environment program, is recommended.

9. Methods for the detection of chemical additives, their byproducts, and degradation products in environmental samples need to be developed. Many of the chemicals being used do not have standard methods of analysis.

2.10.3. Wastewater Quantification, Characterization, and Management

1. Produced water, recovered fluids, and other wastewaters from stimulated wells will contain chemicals from hydraulic fracturing fluids and their reaction byproducts, but the concentrations of these chemicals in wastewaters will change over time and have not been fully characterized.

2. Produced water, recovered fluids, and other wastewaters from stimulated wells will also contain various other contaminants in dissolved substances from waters naturally present in the target geological formation, substances extracted or mobilized from the target geological formation, and residual oil and gas.

3. During hydraulic fracturing, recovered fluids that are captured before production represent a small fraction of the injected fracturing fluids ($\sim$ 5%). In contrast, recovered fluid volumes for acid treatments tend to be a higher percentage of the injected fluid (50–70%), but data on acid fluid recovery is limited and may not be representative.

4. Recovered fluid volumes are a small fraction of wastewater generated within the first month of production. These results indicate that studies from other regions of the country showing significant recovery of "flow-back" fluids have limited application to California.

5. Recovered fluid samples from stimulated wells have been shown to contained high concentrations of salts, trace elements (arsenic, selenium, and barium), naturally occurring radioactive materials, and hydrocarbons. Carbohydrates (gels) were detected in some recovered fluid samples, and this suggests that other stimulation chemicals may also be present. In contrast, produced waters from stimulated wells have not been characterized.

6. Recovered fluids are typically stored in tanks at the well site prior to disposal. According to well completion reports filed and posted through December 2014, more than 99% of recovered fluids are injected into Class II disposal wells. A small amount (less than 0.3%) of the recovered fluids are recycled.

7. The net produced water volumes generated in the first five months of production from stimulated and non-stimulated wells were not substantially different, although their distributions were different. There results suggest there are few differences in the volume of water produced from conventional and unconventional wells, but that some further investigation of these issues could be warranted.

8. There is a lack of information regarding the mass of stimulation fluids recovered after treatment. The concentration of returned stimulation fluids and their reaction byproducts in produced water over time needs to be investigated. The fate of the injected stimulation fluids in the subsurface, and the potential for them to be transformed, or to mobilize formation constituents over the lifetime of the production of the well, needs to be determined.

9. From January 2011 through June 2014, it has been reported that nearly 60% of the produced water from stimulated wells was disposed of by evaporation-percolation in unlined pits. An estimated 36% of the active unlined pits in California are operating without the necessary permits from the Central Valley Regional Board.

10. Subsurface injection in Class II wells, for disposal or enhanced oil recovery, was the second most commonly reported disposition method for stimulated wells in California, accounting for approximately 25% of the produced water from stimulated wells.

11. The impacts on the environment of common disposal practices for produced water that may contain stimulation fluids, including percolation pits and well injection, are poorly understood.

12. Information on current treatment and reuse practices for all wastewater from oil and gas operations in California is limited. Available data suggest that simple treatment technologies (e.g., oil-water separation, water softening, gravity separation, and filtration) are predominantly being used for produced water in California. More complex treatment trains—capable of removing an extensive array of chemicals—are used sporadically.

2.10.4. Contaminant Release Mechanisms, Transport Pathways, and Impacts to Surface and Groundwater Quality

1. Several plausible release mechanisms and transport pathways exist for surface and groundwater contamination associated with onshore well stimulation in California. They are depicted in Figures 2.6-1 and 2.6-2, and summarized in Table 2.6-2.

2. Release mechanisms and transport pathways of high priority for the state are percolation of wastewater from disposal pits; injection of produced water if conducted into protected aquifers; reuse of produced water for irrigation; disposal of produced water into sewer systems; potential leakage through abandoned wells; and potential leakage through fractures.

3. Some of the release mechanisms that were identified are primarily relevant to California, and are uncommon elsewhere, including use of percolation as a disposal method and reuse of produced water for irrigation.

4. Percolation pits provide a direct pathway for the transport of produced water constituents, including returned stimulation fluids, into groundwater.

5. With proper siting, construction, and maintenance, subsurface injection using properly sited Class II wells is less likely to result in groundwater contamination than disposal in unlined surface impoundments.

6. There is growing interest in expanding the beneficial reuse of produced water for agriculture, particularly for irrigation. The use of produced water from unconventional production raises specific or unique concerns. Treatment and reuse of produced water from fields with stimulated wells should include appropriate monitoring and treatment before reuse for irrigated agriculture.

7. According to completion reports, fracturing occurs at shallower depths in California than is typical for other regions of the country. In approximately one-half of the operations, fracturing may extend to depths less than 300 m (1,000 ft) from the surface. The shallow depths of fracturing, combined with the deep groundwater aquifer in the Central Valley, raise concern that fractures may intercept protected groundwater resources. Additional research is needed to determine how often this occurs, if at all, and the consequences if it does occur.

8. Determining where fractures occur is an important component of determining exposure pathways. The reliability of models used by industry to estimate a fracture zone (axial dimensional stimulation area) should be determined.

9. In studies conducted elsewhere, water contamination associated with well stimulation has been documented in some places, but several studies have not found any contamination due to stimulation. No incidents of groundwater contamination due to stimulation have been noted in California to date, although there has been very limited monitoring conducted to detect any water quality impacts.

10. There is a lack of information on the quality of surface or groundwater near stimulated oil fields. Baseline data collection prior to stimulation has not been required in the past. No cases of contamination have yet been reported, but this may be primarily because there has been little to no systematic monitoring of aquifers in the vicinity of oil production sites.

11. Significant data gaps exist regarding current knowledge of groundwater quality in California, including the location and extent of protected groundwater that contains less than 10,000 mg L^{-1} TDS. Concentrations of methane, trace metals, NORM, and organic chemicals in groundwater in oil and gas producing regions are unknown. New regulations implemented under SB 4 and other programs are beginning to address this data gap. The effectiveness of these regulations needs to be evaluated in the future.

2.11. Conclusions

This chapter represents a review and analysis of what is currently known about well stimulation technologies in relation to water resources and the water environment. The quantity of water being used for well stimulation is relatively small and local impacts of water usage appear thus far to be minimal. Well stimulation accounts for less than 0.2% percent of total annual freshwater use within each of the state's planning areas. Water use for well stimulation, however, is occurring in water-scarce regions and, given the critical availability of water in these areas, could reduce the water available for other uses.

A significant analysis included in this chapter is the identification of the chemicals being used in well stimulation in California. An investigation of the properties of these chemicals shows that many of them are poorly characterized for properties important to determining their hazard and potential impact to the environment. A list of priority stimulation chemicals, requiring further review, was developed based on prevalence of use and toxicity. Additionally, it is apparent that many chemicals are being used that cannot be evaluated for their hazards or potential environmental impact.

The chemical characteristics of produced water generated from stimulated wells in California are largely unknown, however it is apparent that produced water from stimulated wells will contain well stimulation chemicals or their reaction by-products. Under SB 4, chemical data are being collected for "recovered fluids," but recovered fluids are not representative of returned injection fluids and other wastewater produced over the life of a well. Time-dependent chemical characterization of produced water from stimulated wells are needed to improve management, treatment, and disposal practices. Additionally, mass balance analyses at individual well sites are warranted to clarify the fate of stimulation chemicals remaining in the formation and the quantities of stimulation chemicals in produced water. Geochemical modeling would complement these efforts to characterize chemical fate and transport for stimulated wells.

In California priority potential environmental release mechanisms include disposal of produced water in unlined pits, injection of produced water into potentially protected groundwater, reuse of produced water for irrigation, and disposal of produced water in sewer systems. Unlike in other parts of the country, contamination of water resources due to spills of well stimulation chemicals have not been documented in California, however spills of produced water have occurred. The transport of contaminants through induced

fractures to groundwater has not been established, but should be evaluated in California, where fracturing depths are much shallower than in other parts of the country. Other potential subsurface release mechanisms include leakage through compromised wells and leakage through natural subsurface fractures, however the importance of these pathways is also unknown.

In California, no incidents of groundwater contamination due to well stimulation have been documented. Historically, baseline data were not collected on groundwater quality prior to initiating well stimulation activities, making it difficult, and in some cases impossible, to attribute possible contamination to nearby stimulation operations. There has not been a coordinated monitoring program for water resources located in the vicinity of oil and gas fields where stimulation is occurring that could detect or identify sources of contamination.

Application of good practices while conducting well stimulation can reduce impacts from injected or mobilized fluids. Practices such as collection of baseline measurements before drilling, proper well construction, and application of green chemistry principles are advisable. Many significant data gaps were identified. Data collection in many cases is not systematic, of high quality, or well organized. Many of the chemicals used in well stimulation have not been properly identified. Wastewater constituents and concentrations are not well understood. Data on the treatment technologies being used at individual well sites are not available. Although it is possible to identify potential chemical release mechanisms and the associated potential contamination pathways, insufficient data exist to confirm or refute concerns that surface and groundwater resources have been or may be contaminated by unconventional oil and gas development.

It is expected that many of data gaps will be addressed under new regulations being promulgated as part of implementation of SB 4 legislation, but there is a clear need for directed scientific studies related to the water environment. These studies are needed to answer important questions concerning the safety and sustainability of unconventional oil and gas development. How green chemistry principals might be applied to hydraulic fracturing requires scientific study. A better understanding of overall wastewater management practices in the industry are needed, including understanding the fate of injected chemicals, the chemical composition of wastewaters over varying time and spatial scales, and a complete understanding of methods and practices of water reuse and disposal. Mass-balance analyses at individual well sites are warranted to clarify the fate of stimulation chemicals remaining in the formation and the quantities of stimulation chemicals in the wastewater. The effects of legacy and current practices on local and regional groundwater quality need priority investigation, and should be complemented with geochemical modeling to characterize the fate and transport of well stimulation chemicals. Coordinated investigations need to be conducted to determine which, if any, of the identified potential pathways pose a significant risk for releasing well stimulation chemicals or other contaminants into the environment.

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