

California Council on Science and Technology Lawrence Berkeley National Laboratory Pacific Institute

Advanced Well Stimulation Technologies in California

An Independent Review of Scientific and Technical Information

California Council on Science and Technology Lawrence Berkeley National Laboratory Pacific Institute

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of Scientific and Technical Information

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CCST is a non-profit organization established in 1988 at the request of the California State Government and sponsored by the major public and private postsecondary institutions of California and affiliate federal laboratories in conjunction with leading private-sector firms. CCST's mission is to improve science and technology policy and application in California by proposing programs, conducting analyses, and recommending public policies and initiatives that will maintain California's technological leadership and a vigorous economy.

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Acronym List

API Number American Petroleum Institute Number

BWSD Belridge Water Storage District
BLM Bureau of Land Management

BTEX Benzene, toluene, ethylbenzene, and xylenes

CARB California Air Resource Board CAS Chemical Abstract Service

CCST California Council on Science and Technology
CEMA California Emergency Management Agency

cp Centipoise

CSU California State University

CVRWQCB Central Valley Regional Water Quality Control Board

dBA Decibels

DFW Dallas-Fort Worth

DOC (California) Department of Conservation

DOC Dissolved organic carbon

DOE United States Department of Energy

DOGGR California Division of Oil, Gas and Geothermal Resources

EC Electrical conductivity

EDTA Ethylenediaminetetraacetic acid
EGMBE Ethylene glycol monobutyl ether
EGS Enhanced geothermal system
EPS Explosive propellant systems

ERCB Energy Resources Conservation Board

FWS Fish and Wildlife Service

GAMA Groundwater ambient monitoring and assessment

GAO Government Accountability Office

GHG Greenhouse gas

GHS Globally Harmonized System
GIS Geographic information system

GPa Gigapascal

GWP Global warming potential

HCl Hydrochloric acid HF Hydrofluoric acid

ICoTA International Coiled Tubing Association

IUC Underground injection control

KCl Potassium chloride

LBNL Lawrence Berkeley National Laboratory

LPG Liquid propane
Ma Million years ago

MAPDIR Maximum pressure differential and injection rate

MCLs Maximum contaminant levels

MPT Mud pulse telemetry

Acronym List

MWD Measurement while drilling

NEPA National Environmental Policy Act

NORM Naturally occurring radioactive materials

NOx Nitrogen oxides

NPDES National Pollution Discharge Elimination System

NRC National Research Council

NTA Nitrilotriacetic acid

NYSDEC New York State Department of Environmental Conservation

OandG Oil and gas

PAHs Polycyclic aromatic hydrocarbons

PCBs Polychlorinated biphenyls

PI Pacific Institute
PM Particulate matter

SB Senate Bill

SCP Sustained casing pressure

SJVAPCD San Joaquin Valley Air Pollution Control District

SVOCs Semi-volatile organic compounds

TDS Total dissolved solids
TOC Total organic carbon
TSS Total suspended solids
TVD True vertical depth
UC University of California

USGS United States Geological Survey
US DOE United States Department of Energy

US EIA United States Energy Information Administration
US EPA United States Environmental Protection Agency

VOCs Volatile organic compounds
WET Whole effluent toxicity
WSA World shale average

WSPA Western States Petroleum Association

WST Well stimulation technologies WWTPs Wastewater treatment plants

Introduction

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Background and Key Objectives

In the context of rapidly increasing oil production from low-permeability rocks, including hydrocarbon source rocks, elsewhere in the country, the Bureau of Land Management (BLM) as an owner of federal lands with potential for expanded oil exploration

and production in California was interested in an up-to-date independent technical assessment of well stimulation technologies (WST), with a focus on hydraulic fracturing, employed in this state. WST increase the permeability of rocks around a well to allow or increase oil production. The three WST considered in this report include hydraulic fracturing, acid fracturing, and matrix acid stimulation as practiced in California.

The purpose of this report, commissioned in September 2013, is to provide BLM with the required independent technical assessment. (Appendix A provides BLM's charge to the California Council on Science and Technology (CCST).) This information will be used in future planning, leasing, and development decisions regarding oil and gas issues on the Federal mineral estate in California. The report provides a synthesis and assessment of the available scientific and engineering information available up to February 2014 associated with hydraulic fracturing and other WST in onshore oil reservoirs in California.

This report addresses three key questions posed by BLM:

- **Key Question 1:** What are the past, current and potential future practices in well stimulation technologies including hydraulic fracturing, acid fracturing, and matrix acidizing in California?
- **Key Question 2:** Where will well stimulation technologies allow expanded production of oil onshore in California?
- **Key Question 3:** What are the potential environmental hazards of well stimulation technologies in California?

The History of Oil Production in California

The Midway-Sunset field, which is the largest in California in terms of expected total oil production, was discovered in 1894. The twelve largest onshore or partially onshore oil fields were discovered by 1932 and the 43 largest by 1949. All 45 onshore or partially onshore oil fields termed "giant" by DOGGR (more than 16 million m³ (100 million barrels) of expected total oil production) were discovered by 1975 (DOGGR, 2010).

More oil was produced in California in 2013 than in any other state except Texas and North Dakota. California has produced the third most oil of all the states since at least the 1980s. The volume of oil produced in California peaked in 1985 and had declined by approximately half as of 2013 (US EIA, 2014).

Oil production in California has been enhanced by application of a number of technologies through time. Wide deployment of water flooding commenced in the mid-1950s. This technique involves injecting water into the oil reservoir via one set of wells, which causes more oil to flow to the production wells. Wide deployment of cyclic steaming and steam flooding commenced in the mid-1960s (Division of Oil and Gas, 1966). Injection of steam heats highly viscous ("heavy") oil resulting in more flowing to the production well. In cyclic steaming, injection of steam alternates with oil production in the same well. Steam flooding involves continuous steam injection into wells interspersed among the production wells. Intensive deployment of hydraulic fracturing commenced in the 1980s (see Chapter 3).

DOGGR first attributed the portion of oil production due to water flooding and steam injection for production in 1989. It attributed 71% of oil production in that year to these techniques (DOGGR, 1990). A total of 76% of production in 2009, the most recent year with attribution, was due to these techniques (DOGGR, 2010). The portion of production involving hydraulic fracturing was not listed.

In addition to steam injection, fire flooding and downhole heating were tested for heating viscous oil in the subsurface in the early 1960s. Fire flooding involved injecting air into the reservoir to sustain combustion of part of the oil. Downhole heating involved placing pipe loops into wells that circulated hot water or oil. Fire flooding was found to be generally uneconomical. Downhole heating resulted in more modest, and less economic, production increases than steam injection (Rintoul, 1990).

CCST Committee Process

A WST steering committee was assembled and vetted by CCST. Members were appointed based on technical expertise and a balance of technical viewpoints. (Appendix A provides information about CCST's steering committee.) In parallel, BLM contracted with Lawrence Berkeley National Laboratory to support the analysis and develop the findings based on the literature review and analyses. Appendix B provides information about the LBNL review team which authored Sections 2, 3, 4, and 5 of this report.

For each of the three key questions asked by the BLM, investigations conducted by LBNL and their contractors led to a series of findings, and based on these findings, the steering committee reached a series of consensus conclusions. These findings and conclusions are included below. The literature and analyses are described in the bulk of this report in Section 2, 3, 4, and 5.

This report has also undergone extensive peer review. (Peer reviewers are listed in Appendix H, "California Council on Science and Technology Study Process"). Reviewers were chosen for their relevant technical expertise. Following the receipt of peer review comments in May 2014, this report was revised.

Method and Data Sets Available for the Report

This assessment is based on review and analysis of existing data and scientific literature. Preference is given to using the findings in peer-reviewed scientific literature. Peer-reviewed scientific literature is principally found in peer-reviewed scholarly journals. Certain institutions such as the National Academies of Sciences and United States federal regulatory agencies such as the United States Geological Survey also self-publish scientific papers that undergo a rigorous peer review process. Scientific papers that undergo independent peer review by a panel of experts are considered to provide information that is more likely to be accurate than non-peer reviewed literature. Peer review entails experts not involved in the work assessing the thoroughness, accuracy and relevance of the work. If the reviewers find omissions or errors in the work, they provide comments describing these to the authors of the paper and the editor of the publication. In order for the paper to be published, the authors must address these to the satisfaction of the editor. Because of this process, such papers are referred to as "peer-reviewed scientific literature."

During the conduct of this review, it was found that the body of relevant peer-reviewed literature — the source that meets the highest standard of scientific quality control — is very limited. For instance there is little information on water demand in California for hydraulic fracturing. Consequently other material was considered, such as government data and reports including well records collected by the Division of Oil, Gas and Geothermal Resources (DOGGR) and recent notices submitted pursuant to California Senate Bill 4 (SB 4, Pavley, Chapter 313, Statutes of 2013), and so-called "grey literature" if this

literature was topically relevant and met scientific standards for inclusion. We also accessed and analyzed voluntary web-based databases such as FracFocus. In some cases where specific data on California were not available, analogues from other locations were used, while recognizing the limitations of the analogues. Much of the data available to analyze current practice come from voluntary sources plus six weeks of data from well stimulation notices required by SB4. Data from well stimulation notices submitted through January 15th, 2014, were considered. Data through the end of 2013 were considered from the other sources. Relevant scientific literature available as of February, 2014, was reviewed. A reference to a report from US EIA published in June 2014 was added during the peer review process because the updated assessment had a substantial bearing on our findings and conclusions.

Extensive efforts were made to survey all information relevant to this report, including peer-reviewed scientific literature, government-collected data, voluntary reporting by industry, and non-peer reviewed literature. Categories of non-peer reviewed literature considered admissible to the report were government reports, studies issued by universities and non-government organizations, textbooks, and papers from technical conferences. To be considered admissible to the report, literature needed to be based on data that drew traceable conclusions clearly supported by the data. Opinion-based materials were not included in the assessment.

Avenues for finding relevant literature and data included:

- 1. Keyword searches in databases of scientific literature;
- 2. Finding literature and data, regardless of peer-review status, referenced in other literature;
- 3. Soliciting data and literature submissions from the public via two webinars, a website, and a press release;
- 4. Discussions with outside experts in the field, consisting of informal dialogues and organized technical meetings;
- 5. Data mining of voluntary industry reporting to FracFocus.org;
- 6. Data mining of government-collected data; and
- 7. Internet keyword searches.

Further details on the process for reviewing data and literature for the report can be found in Appendix E, "Bibliography of Submitted Literature."

We caution that official government records were not necessarily designed to answer all the questions posed by BLM to CCST. Records filed with DOGGR in the past do not comprehensively record well stimulation events. Voluntarily submitted data, such as those available on FracFocus, although very useful, are not required to be either complete or accurate. We describe the challenges with the quality of the data in order to transparently qualify the limitations in our conclusions.

More information pertinent to this assessment may exist, but was unavailable at the time of writing. This is particularly the case for research and development and exploration results. Oil companies and their service providers spend billions of dollars per year on research and development (IHS, 2013). This compares to hundreds of millions of dollars per year in Federal government funding for all research related to fossil fuels, including coal (US Department of Energy, 2013). The resulting disparity in private versus publicly available information makes it particularly difficult to assess the prospects for further application of well stimulation in California in the future.

Furthermore, due to the timing of this report, the mandatory reporting requirements pursuant to California Senate Bill 4 (SB 4, Pavley, Chapter 313, Statutes of 2013) were only just becoming available for analysis in this study. Effective January 1, 2014, SB4 required that notices have to be submitted at least 30 days prior to each well stimulation operation, and that well stimulation records have to be filed within 60 days after stimulation. These well records will provide information on well stimulation locations, fluid volumes, and constituents, as well as the composition and disposition of flowback fluids. Such information will in the future allow a much improved assessment of potential hazards specific to California associated with well stimulation, including material and equipment supply for stimulation, disposal of stimulation fluids, and land-use changes. For our study, however, no well records had yet been submitted, and only a limited amount of well stimulation notices projecting future activity could be considered, submitted during a 6-week period between November 1, 2013 and January 15, 2014.

In future months, more disclosures required by SB4 will be filed, and the picture we obtained from the limited data available for this report may change. Some important data gaps will likely remain, for example: (1) the depth of the base of groundwater in the vicinity of well stimulations (which varies depending upon the definition of groundwater, the location, and other factors); (2) the means of delivery of stimulation fluids to and removal from well stimulation sites; (3) emissions from venting and flaring of gases from flowback fluids; and (4) the number of oil and gas wells that show indications of structural integrity impairment. Lack of data on structural integrity impairment of oil and gas well casing and cement limits the ability to identify the extent of the sub-surface migratory mechanisms through which fluids and gases can move from the well and the well bore into the environment.

Well Stimulation Technologies

Hydraulic fracturing creates fractures in reservoir rocks in order to enhance the flow of petroleum or natural gases to the well. This is accomplished by pumping fluids into a zone of the well until the fluid pressure is sufficient to break the rock. Then, small particles called "proppant" are pumped into the fracture to keep it from closing back down when the fluid pressure is reduced, e.g., during subsequent fluid production. The hydraulic fracturing fluid that returns up the well bore is called "flowback" fluid. Fluid removed from the well gradually changes from flowback fluid to "produced water" and the time at which a well changes from the hydraulic fracturing process to the production process is not precisely defined

Acid fracturing accomplishes the same goal as hydraulic fracturing by injecting low pH fluids instead of proppants into a created fracture. This process is not intended to create new fractures via high fluid pressures. The acid is intended to non-uniformly etch the walls of the fracture so that some fracture conductivity is maintained after the fracture closes.

Matrix acidizing is the process of injecting strong acids into the formations around a well at pressures below the fracturing pressure of the rock. The most common acid systems used are hydrochloric acid (HCl) in carbonate formations, and hydrofluoric/hydrochloric acid (HF/HCl) mixtures in sandstone formations. Matrix acidizing in carbonates can create small channels or tubes called wormholes that can propagate as much as 20 feet into the formation. This can provide a true stimulation of a well, analogous to that of a small hydraulic fracturing treatment. Because of much smaller reaction rates, the acid dissolution in sandstones is limited to a much smaller distance, of less than one to perhaps two feet into the formation. Because of this limited penetration distance, the benefit of matrix acidizing in sandstones comes primarily from removing damaging solids that have reduced the near-well permeability. However, there are some instances of matrix acidizing using HF/HCl reported in the Monterey Formation in California that may have greater penetration because of the presence of natural fractures.

Report Structure and Content Overview

Section 1 below gives the major findings and conclusions of this study that were developed in a consensus process by members of the steering committee. The detailed technical information in the remainder of this report is presented in four sections. Section 2 covers WST in general, subject to the constraint that the stimulation is used to increase the permeability of the oil reservoir. Section 3 presents information on the past, current and potential future use of WST in California. Section 4 presents information on the petroleum geology of California. Section 5 covers a wide range of items all linked to potential adverse impacts caused by the use of WST in California.

Section 2 presents information on the general types and applications of WST in general, starting with the techniques for drilling and constructing the well. Well drilling methods for vertical and directional drilling are covered and the associated installation of casing and cement are presented. Section 2 also defines and presents well stimulation methods, including the typical types of materials and procedures, and how these methods are applied for different geologic conditions. The stimulation methods described are hydraulic fracturing, acid fracturing, and matrix acidizing.

Section 3 describes the application of the WST for onshore oil production in California. These are discussed in terms of how the horizontal wells and well stimulation technologies have been used in the past along with information about current applications in California. An assessment is provided of the current level of activity for each well stimulation method including the types and quantities of well stimulation fluids currently in use.

Section 4 provides background on the geologic components and processes that affect the development of petroleum systems. The important reservoir rock types currently being produced using well stimulation technologies in California are described and their rock properties are summarized. These rock types and properties are compared with the Bakken shale, an unconventional shale reservoir found in North Dakota, Montana and Canada, that has been extensively developed using WST. The California oil reservoirs are then described in terms of the major sedimentary basins in which they occur, including deeper petroleum source rocks that have not been subject to significant petroleum resource development. Some general observations are provided about the potential application of advanced well stimulation technologies, as currently used elsewhere for petroleum production from unconventional shale reservoirs, to oil-bearing shales in California.

Section 5 brings together all the potential environmental impacts of using well stimulation technologies in California. The section begins with a discussion impacts in terms of the quantities of water being used for well stimulation activities in the state. Water quality are discussed in terms of chemicals used for well stimulation fluids and the composition of fluids recovered at the end of the stimulation during flowback. The potential contamination pathways are then summarized for various types of surface discharge and subsurface pathway formation and fluid migration. Information on known or suspected contamination episodes in California and elsewhere that have occurred as a result of well stimulation activities are presented for both surface and subsurface sources of contamination. The potential effects of well stimulation activities on air quality using information from various US locations are reviewed and put into context for California. In addition, atmospheric emissions of greenhouse gases (CO2 and methane) are also estimated and compared with emission related to overall energy use. The impacts on wildlife and vegetation are discussed in the context of the typical petroleum recovery infrastructure and from which effects of well stimulation activities are inferred. The potential for induced seismic activity as a result of the injection of hydraulic fracturing fluids and injection of flowback for waste disposal are reviewed. Other impacts of increased vehicular traffic and noise as a result of well stimulation activities are also discussed. There is very little definitive

Introduction

information on the direct environmental impacts of WST in California. Most of the available information addresses indirect impacts from oil and gas production, or direct impacts in other states, or provides some partial information on direct impacts in California, but fails to provide complete answers to the question at hand. As a result, the authors surveyed a wide range of literature that offers relevant information but few conclusive answers.

Major Findings And Conclusions

Authored by CCST Steering Committee

Key Question 1: What are the past, current and potential future practices in well stimulation technologies including hydraulic fracturing, acid fracturing, and matrix acidizing in California?

Many of the concerns about WST and hydraulic fracturing in particular arise because practices in other states have come under scrutiny and criticism. Over the last decade, application of horizontal drilling and hydraulic fracturing has allowed a substantial increase in production of oil from low-permeability rocks containing this resource, such as the Bakken Formation in Montana and North Dakota (Pearson et al., 2013; Hughes, 2013). This report critically evaluates the practices in California and the differences between the practice in California and the major hydraulic fracturing practice in other states. In the Bakken and the Eagle Ford, for example, oil is found in thin, but very extensive layers that have very low permeability because they are lacking many natural fractures in the rock. Producers drill long, horizontal wells and create permeability by creating networks of connected fractures. In California, reservoirs that are produced using hydraulic fracturing tend to be thick and not laterally extensive and they typically have higher initial permeability than the shale oil formations mentioned above. Consequently the practice in our state is significantly different than elsewhere.

Conclusion 1: Available data suggests that present day well stimulation practices in California differ significantly from practices used for unconventional shale reservoirs in states such as North Dakota and Texas. For example, California hydraulic fractures tend to use less water, the hydraulic fracturing fluids tend to have higher chemical concentrations, the wells tend to be shallower and more vertical, and the target geologies present different challenges. Therefore the impacts of hydraulic fracturing observed in other states are not necessarily applicable to current hydraulic fracturing practices in California.

Hydraulic fracturing in a variety of forms has been widely applied over many decades in California with records of application in at least 69 onshore oil fields identified through well-record searches in central and southern California out of more than 300 fields in the state. The vast majority (85%) of past and current recorded fracturing activities occur in the North and South Belridge, Lost Hills, and Elk Hills fields, located in the southwestern portion of the San Joaquin Valley, in Kern County. Data from FracFocus, Division of Oil,

Gas and Geothermal Resources' (DOGGR's) well records, well stimulation notices filed from December 1, 2013 to January 15, 2014 pursuant to SB 4 requirements, and well-record searches suggest hydraulic fracturing is conducted in 100 to 150 wells per month. Well-record searches indicate that this rate has increased since the end of the most recent recession, but is the same as before the recession. For comparison, over one million hydraulic fracturing operations are estimated to have occurred throughout the United States, with over 100,000 of these in recent years. (Sections 3.2.1, Historical Use of Hydraulic Fracturing, and 3.2.2, Current Use of Hydraulic Fracturing)

Large-scale application of high-fluid-volume hydraulic fracturing has not found much application in California, apparently because it has not been successful, and for reasons discussed below is unlikely in the future (see Conclusion 3). The majority of the oil produced from fields in California is not in the low-permeability shale source rock (i.e., shale in the Monterey Formation), but rather from other more permeable geologic formations that often contain oil that has migrated from source rocks. These reservoirs do not resemble the low-permeability extensive, and continuous shale layers that are amenable to production with high volume hydraulic fracturing from long-reach horizontal wells. (Section 4, Prospective Application of Well-Stimulation Technologies in California)

According to DOGGR well data and SB 4 stimulation notices, most of the hydraulically fractured wells in California are vertical or near vertical. These shorter wells require less fluid for hydraulic fracturing applications than wells that have long lateral (i.e., horizontal) legs. More than 95% of the hydraulic fracture events in California employ a gel for the stimulation fluid as opposed to applications of "slickwater." Slickwater includes a friction reducer to allow injection of more stimulation fluid volume in a given time period. This is useful where the goal is to create a new network of fractures in rocks that are relatively brittle with low permeability. Gel is used in California because the main rocks targeted for stimulation are less brittle and more permeable than areas where slickwater is used. Additionally, gel is capable of carrying more proppant than slickwater to hold existing fractures open. Because of the predominance of stimulation in vertical and near-vertical wells, and the use of gel, the volumes of water used in hydraulic fracturing in California are much smaller than in oil source rock plays elsewhere.

The average amount of reported water used in the recent past and currently in California for each hydraulic fracturing operation is 490 to 790 m³ (130,000 to 210,000 gallons) per well. These volumes are similar to the annual water use of 580 m³ (153,000 gallons) in an average household in California over the last decade and are significantly less than the average 16,100 m³ of water per well (4.25 million gallons) reported for the Eagle Ford shale tight oil play in Texas. Further, the volume per treatment length in California is 2.3 to 3.0 m³/m (188 to 244 gallons per ft) based on FracFocus and notice data. This is much less than the 9.5 m³/m (770 gallons per foot) used in the Eagle Ford formation. It is slightly below the 3.4 m³/m (277 gallons/ft) for cross-linked gel used in the Bakken formation, in North Dakota, but considerably below the 13.2 m³/m (1,063 gallons/ft) for slickwater used in that location. (Section 3.2.3, Fluid Volume, and 3.2.4, Fluid Type)

Conclusion 2: Acid fracturing is a small fraction of reported WST to date in California. Acid fracturing is usually applied in carbonate reservoirs, and these are rare in California. Matrix acidizing has been used successfully but rarely in California. These technologies are not expected to lead to major increases in oil and gas development in the state.

Acid fracturing is commonly limited to carbonate reservoirs, because the acid-mineral reaction rates in in a sandstone or siliceous shale rock as found in California are too slow to create significant etching of the fracture walls. For the process to work in such rocks as it does in carbonates, the acid-rock reaction rates would have to be increased by many orders of magnitude (4-8 orders). It is not reasonable to expect any innovation that would accomplish this. A few instances of acid fracturing in siliceous rock in California were reported in SB 4 well stimulation notices. However, given that acid fracturing of siliceous rocks is otherwise unknown, these may be cases of misreported matrix acidization.

As mentioned above, acid fracturing is generally applied only to carbonate reservoirs, which include those consisting of dolomite. The only onshore carbonate oil reservoirs identified in California are in the Santa Maria and possibly the Los Angeles basins. The carbonate reservoirs occurring in a few fields in the Santa Maria Basin consist of naturally fractured dolomite. Reports of the use of acid fracturing in these reservoirs in California were not identified in the literature.

Hydrochloric acid mixed with hydrofluoric acid is generally reported as used for matrix acidizing of siliclastic reservoirs, which predominate in California. In these reservoirs, matrix acidizing is typically used to overcome the effects of formation damage (reduction in the rock permeability near the wellbore) that occurs during drilling and completion operations in conventional reservoirs. In the absence of formation damage, matrix acidizing can increase well productivity by only about 20%. In a very-low-permeability reservoir, this limited increase in productivity is far less than the stimulation level necessary to make oil or gas recovery economic.

By comparison, the large-scale fracturing treatments being applied in shale formations like the Eagle Ford or the Bakken increase well productivity by orders of magnitudes above the productivity of an unstimulated well. Thus, matrix acidizing technology is not expected to lead to dramatic increases in oil and gas development as has hydraulic fracturing technology in many shale formations.

Use of matrix acidizing is only reported in three onshore oil fields in California, which contrasts with the tens of fields identified where hydraulic fracturing has been used. Stimulation notices submitted to the State to date indicate matrix acidizing only in the Elk Hills Field. There were 26 matrix acid notices submitted and not withdrawn in the first six weeks of SB 4 permitting, as compared to 208 hydraulic fracture notifications.

All the notices specify use of "mud" acid, either by combining HCl and HF acids directly or by producing an HCl-HF acid mixture by reacting NH_4HF_2 (ammonium bifluoride) with an excess of HCl. The notices indicate an average matrix acidizing water volume per well of 109 m³ (40,000 gallons), which represents a fraction of that needed for hydraulic fracturing. The average volume per treatment length implied by the notices is 1.7 m³/m (137 gallons per ft). (Section 3.3, Acid Fracturing, and 3.4, Matrix Acidizing)

Key Question 2: Where will well stimulation technologies allow expanded production of oil onshore in California?

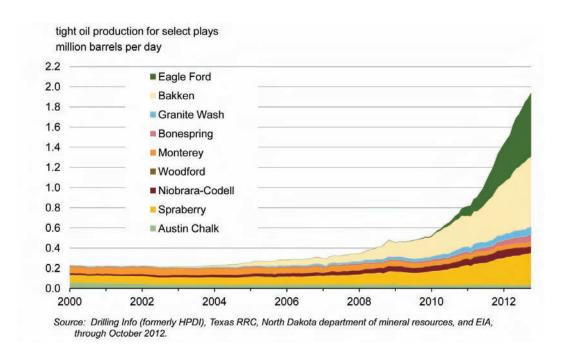


Figure 1-1. Oil production through time from selected low permeability ("tight") oil plays in the United States US EIA (2013).

As shown in Figure 1-1, the current production from low-permeability portions of the Monterey Formation in California is modest compared to production from other low-permeability strata in the United States. Furthermore, the Monterey production level has remained fairly constant between 2000 and 2012, a trend quite different from oil shales such as the Eagle Ford and the Bakken formations. However, in 2011 the United States Energy Information Administration (US EIA) estimated the Monterey Formation contains 2.45 billion cubic meters (m³; 15.4 billion barrels) of recoverable tight oil. The report estimated this to be 64% of the recoverable oil from low-permeability rocks in the United

States (US EIA, 2011). This estimate of recoverable tight oil in the Monterey Formation gained broad attention and raised the question whether California might experience the same type of rapid increase in oil production and development of associated infrastructure as has occurred elsewhere in the country, such as in Montana and North Dakota (e.g. Garthwaite, 2013). Our report examined the assumptions in the original EIA estimate and the likelihood for WST technology to expand production in California. We found the original EIA estimate to be based on a series of highly skewed assumptions that resulted in a very high estimate for the amount of recoverable oil in the Monterey. Notably, since this report was prepared, the EIA has revised their estimate of recoverable oil in the Monterey Formation downward to about one thirtieth of the original estimate (US EIA, 2014).

Conclusion 3. The most likely scenario for expanded onshore oil production using WST in California is production in and near reservoirs that are currently using WST. Thus, existing and likely future production is expected to come from reservoirs containing oil migrated from source rocks, not from the Monterey Formation source rock. Credible estimates of the potential for oil recovery in and near 19 existing giant fields (> 1 billion barrels of oil) in the San Joaquin and Los Angeles basins indicate that almost 10 billion barrels of additional oil might be produced but would require unrestricted application of current best-practice technology, including, but not restricted to WST. In 2011 the EIA estimated about 15 billion barrels of technically recoverable oil from new plays in the Monterey Formation source rock, but these estimates have been revised in 2014 to a value of 0.6 billion barrels. Neither of these estimates of unconventional oil resources in California source rocks are well constrained.

There are significant resources in existing oil fields, and estimates of these resources are relatively consistent. The United States Geological Survey (USGS) estimates that an additional 6.5 billion barrels and 3.2 billion barrels can be recovered from the largest fields in the San Joaquin and Los Angeles basins, respectively, using existing oil production technology (see Figures 1-2(a) and (b)). Figures 1-2(a), (b) and (c) show existing oil and gas fields in California and locations where expanded production might occur in the San Joaquin and Los Angeles basins, respectively. Some but not all of this expanded production requires WST. In California today, WST enables production in the diatomite reservoirs of the San Joaquin Valley and expanded production in similar reservoirs would likely also be enabled by WST. In contrast, WST may not be required to expand production in the Los Angeles Basin where its use is not common today.

New oil and gas production in regions removed from existing fields is more uncertain than increased production in existing oil and gas fields. There is a considerable amount of source rock, including the Monterey Formation and other geologic units within the deeper portions of major basins, which could potentially contain oil that has not migrated ("source" oil), and could perhaps be extracted using WST. However, there is little published information on these deep sedimentary sections, so it is difficult to estimate the potential recoverable reserves associated with these rocks. No reports of significant production of source oil from these rocks were identified.

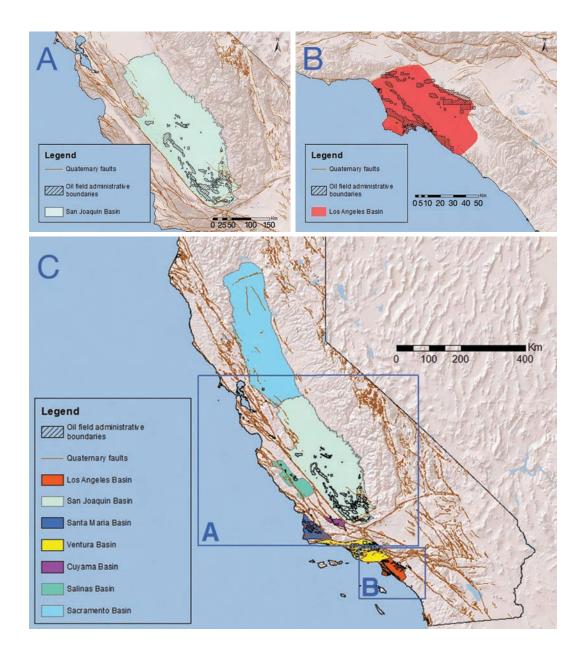


Figure 1-2. Maps of major sedimentary basins and associated oil fields in California.

(a) The San Joaquin Basin with outlines of producing oil fields. USGS estimates an additional 6.5 billion barrels of oil could be recovered from existing fields in the San Joaquin Basin.

(b) The Los Angeles Basin with outlines of producing oil fields. USGS estimates an additional 3.2 billion barrels of oil could be recovered from existing fields in the Los Angeles Basin.

(c) All major sedimentary basins and associated oil fields in California.

Data from DOGGR, Wright (1991), and Gautier (2014).

The US EIA 2011 INTEK report has garnered considerable attention because of its large estimate of 2.45 billion m³ (15.4 billion barrels) of technically recoverable oil in Monterey Formation source rock. Very little empirical data is available to support this analysis and the assumptions used to make this estimate appear to be consistently on the high side. INTEK estimated that the average well in low-permeability source rock in the Monterey Formation would produce 87.5 thousand m³ (550 thousand barrels) of oil. This amount greatly exceeds the production that has occurred to date from low-permeability rocks in known oil accumulations in this formation, with single-well oil production of only 10.7 and 22.4 thousand m³ (67 and 141 thousand barrels) in the San Joaquin and Santa Maria basins, respectively. Consequently the INTEK estimate requires a four- to five-fold increase in productivity per well from an essentially unproven resource.

In addition, the Monterey Formation was formed by complex depositional processes and subsequently deformed in many tectonic events, resulting in highly heterogeneous as well as folded and faulted rocks that are difficult to characterize. INTEK posited production over an area of 4,538 km² (1,752 square miles), but this is almost the entire source rock area estimated in this report. (Note that the updated US EIA (2014b) report has reduced this areal extent significantly to 497 km² (192 square miles). There has not been enough exploration to know how much of the Monterey source rock has retained oil, or if the oil has largely migrated away, but it is unlikely the entire source rock area will be productive, given the extreme heterogeneity in the Monterey Formation. Finally, even if significant amounts of oil do remain in the Monterey Shale, and wells reach this oil, it still remains to be determined if hydraulic fracturing of Monterey source rock will result in economically viable production. For all these reasons, the INTEK estimate of recoverable oil in Monterey Formation source rock warranted skepticism. The EIA has recently issued a revised estimate (0.6 billion barrels) of this unconventional oil resource (US EIA, 2014b); this decrease is mainly due to a nine-fold reduction in the estimated potential resource area. The information and understanding necessary to develop a meaningful forecast, or even a suite of scenarios about possible recoverable unconventional oil in the Monterey shale, are not available.

While major production increases from oil shale source rock are considered highly uncertain, they are not impossible. High-volume proppant fracturing is the enabling technology for significant increases in development of low permeability reservoirs. If large-scale proppant fracturing can be shown to work in source rocks in California as it has in other low permeability plays in the United States, it would change the outlook for oil and gas production in the state. The oil and gas industry is constantly innovating, and research and development could improve the utility of proppant fracturing in the future. Deep test wells in source rock-shale plays have been drilled in California that with research and development may eventually prove successful. (Section 4.5, Oil-Producing Sedimentary Basins in California, and 4.7, Review of the US EIA Estimate of Monterey Source Rock Oil)

Key Question 3: What are the potential environmental hazards of well stimulation technologies in California?

This report focuses on what we refer to as the "direct" environmental impacts caused by application of WST. We define direct impacts as the impacts incurred by the act of using WST themselves, either a single application or the additive impacts of many applications. Direct impacts include, for example, those that might arise from the use of large volumes of water for stimulation, from the addition of chemicals in the WST fluids that may be toxic, or those related to injecting at high pressures into the subsurface to break the rock. Each well stimulation treatment requires the use of water, incurs transportation of materials, can cause emission of pollutants or greenhouse gases, and pumps chemically loaded water underground.

In this report we attempted to carefully assess the direct environmental, climate, and public health impacts of WST within the limits of data availability. The direct impacts in general have not been monitored, but some can be inferred from operations data and California practice. In other cases, it is not possible to make inferences and all that can be done is to review and summarize what has been observed in other states or the published literature. This information should be taken as background material, which can direct further monitoring and observation in California. We do not claim that what has been observed in other states is happening in California or directly applicable to California. The vast majority of California hydraulic fractures are conducted in shallower wells that tend to be vertical rather than horizontal, and use a relatively small amount of water that is more highly concentrated in chemicals in geologic settings that differ significantly from those in other states. Regulations are different in California and some practices in other states are not allowed in California.

WST applications can slow the decline of production in existing fields or increase that production. WST may allow production in new greenfield sites that could not be produced with more conventional technologies. We refer to all of this collectively as "WST-enabled production." Because WST can enable oil production, WST can have indirect environmental impacts in addition to the direct impacts of well stimulation. If well stimulation enables greater oil and gas production¹, which has additional environmental impacts, we refer to these as "indirect" impacts. The report identifies issues and impacts that may arise because of well stimulation-enabled production. Indirect impacts arise because oil and gas production involves building, supplying, and managing oil and gas well operations, including land clearing and construction, general truck traffic to bring and remove materials, energy operations at the wellheads, and wastewater management. The report identifies

¹ Although the focus of the report is on oil production, the fact is that oil contains natural gas in solution which can vaporize from the oil, and therefore we cannot avoid consideration of this "associated gas" along with oil.

indirect issues and impacts that may arise because of well stimulation-enabled production; however, they receive only cursory treatment in the synthesis and assessment conducted here. As noted in the conclusions and the assessments below, there is evidence that the indirect impacts of WST-enabled oil and gas production may be significant, and we recommend that a more detailed analysis should be undertaken. The scientific literature indicates that indirect impacts should not be dismissed and will be the focus of future work. Indirect effects are beyond the scope of this study, but we provide key issues for future study at the end of this summary.

WST-enabled oil and gas production presents environmental, health and safety impacts that can be very different depending on the history of land use where it takes place. For example, environmental impacts of oil and gas production depend on whether it occurs in an existing oil and gas field versus a greenfield location, or if the surrounding area is urban, agricultural, or undeveloped. Local conditions also affect the environmental impacts of expanded production, such as the depth and quality of the local groundwater, availability of surface water, local air quality, distance to human population centers, and the proximity of sensitive species and habitats.

Important conditions that affect impacts associated with expanded production include:

- Quality and depth of groundwater;
- Local air quality;
- Proximity to population centers;
- Proximity to species and habitats;
- · Volume of fluids requiring disposal; and
- Proximity to active faults.

In some cases, the line between direct and indirect effects is not absolutely clear. Wastewater disposal presents an illustrative example of an indirect impact, but some assessment was made in this report. Wastewater includes "flowback water," which is the water used in a hydraulic fracturing operation that returns to the surface, as well as "produced water," which comes up with the produced oil and gas and is subsequently separated and disposed of. Flowback water is directly attributable to WST, whereas produced water is an indirect effect of WST enabled production. After a hydraulic fracturing event, the fluid that comes out of the well changes gradually from flowback water to produced water. There is no formal distinction between the two fluids. In California, the volumes of water used in WST applications are currently a very small fraction of the total

volume of produced water. We refer to this fluid as flowback/produced water, to make it clear we are discussing the combined direct and indirect issues. Produced water disposal in dedicated injection wells (Class II wells according to EPA's regulation for underground injection) presents the possibility of triggering earthquakes. Given concerns about this issue, we briefly address some issues with flowback/produced water disposal.

Although the focus of this report is primarily on the direct impacts of WST, rather than the lifetime processes and environmental hazards of oil and gas production as a whole as enabled by the technologies, it seems likely that the major environmental effects of WST are not from the WST itself, but rather from new or expanded production enabled by WST. Direct impacts represent a very narrowly defined marginal change in risks associated only with actual conduct of the WST itself. The impacts associated with these technologies exist within the overall context of environmental risks associated with oil and gas development in general. For example, dozens of chemical constituents may be present in hydraulic fracturing fluids, but operators typically combine fluids associated with hydraulic fracturing with produced water streams, which, by themselves typically contain high concentrations of salt, trace elements, and hydrocarbons. The volumes of flowback water are extremely small relative to the volume of water produced along with the oil. The emissions associated with WST operations are a small fraction of emissions from the highly energy-intensive oil production industry.

A large number of other impacts associated with WST in California were not covered in this report including local and state economic and employment impacts; local, state, and federal tax and royalty payment impacts; increased industry research and technology investments resulting from expanded WST applications; and of particular importance to Californian, the impact of increased WST-driven production on the level of imported crude to the state from non-U.S. sources. The CCST steering committee recognizes the importance of these impacts which have had material effects in other states, but notes that they were not within the defined scope of the of this report.

Direct impacts on water supply, water quality, air quality, greenhouse gas emissions and induced seismicity are described below.

Water Supply

Conclusion 4: While current water demand for WST operations is a small fraction of statewide water use, it can contribute to local constraints on water availability, especially during droughts.

The upper estimate of current annual water demand for WST in California is 1.4 million m³ (1,200 acre-feet), based on estimates of water use from notices filed with DOGGR; the lower estimate is 560 thousand m³ (450 acre-feet) based on water volumes reported voluntarily to FracFocus. Ninety-five percent of water currently used is fresh water; the remainder is produced water. Most of this demand is in the southwestern San Joaquin

Valley. Stimulation notices indicate the Belridge Water Storage District, supplied by the State Water Project, meets most of the demand in this area. The demand indicated by the notices represents less than 1% of this District's allocation. However, their allocation from the State Water Project can be cut in average and in drier years. The notices indicate use of well water for stimulation fluid as an alternative to supply from the District, but it is unclear under which conditions this would occur. If well water is used, it could draw down the groundwater table. (Section 5.1.1, Quantities and Sources of Water Used for Well Stimulation in California)

Water Quality

Conclusion 5: Of the chemicals reported for WST treatments in California for which toxicity information is available (compiled from the voluntary industry database, FracFocus), most are considered to be of low toxicity or non-toxic. However, a few reported chemicals present concerns for acute toxicity. These include biocides (e.g., tetrakis (hydroxymethyl) phosphonium sulfate; 2,2-dibromo-3-nitrilopropionamide; and glutaraldehyde), corrosion inhibitors (e.g. propargyl alcohol), and mineral acids (e.g. hydrofluoric acid and hydrochloric acid). Potential risks posed by chronic exposure to most chemicals used in WST are unknown at this time.

A list of chemicals used for hydraulic fracturing was developed from disclosures in FracFocus. These data are not required to be either complete or accurate. For matrix acidization, a list of chemicals used was developed from stimulation notices, which did not indicate any undisclosed chemicals. Information on acute oral toxicity was available for some of these chemicals. This toxicological assessment is limited, because it considers only oral toxicity as an indicator of potential impacts to human health, and does not consider other effects such as biological responses to acute and chronic exposure to many of the stimulation chemicals, eco-toxicological effects of fluid constituents, overall toxicological effects of fluids as a mixture of compounds (compared to single-chemical exposure), and potential time-dependent changes in toxicological impacts of fluid constituents, due to their potential degradation or transformations in the environment. Thus, further review of the constituents of injection fluids used in well stimulation jobs in California is needed, which additionally considers information that is now required to be submitted to DOGGR by operators, and some of the above mentioned toxicological effects.

After hydraulic fracturing fluids are injected, they return along with some formation water as flowback water and are subsequently either disposed off or sometimes used for other purposes (see Conclusion 7). At this time, it is not possible to evaluate flowback contaminants in California, because there is very limited information regarding the concentrations of these substances in flowback/produced waters from well stimulation operations in California. Flowback and produced water compositions vary considerably across regions, and their characteristics can change according to the fluids injected during well stimulation, the amount of fluids recovered at the surface, and over the duration of the flowback period. The chemistry of produced waters from unconventional oil production

could potentially differ from that of conventional oil production due to differences in the target formations and interactions of fracturing fluids with formation rocks and water, although this does not generally appear to be the case based on the limited data that is available. More California-specific data will become available starting in 2014 as operators are now required to report the composition of waters recovered from well stimulation operations to DOGGR. (Section 5.1.2, Chemistry of Fluids Related to Well Stimulation Operations)

Conclusion 6: There are no publicly recorded instances of subsurface release of contaminated fluids into potable groundwater in California, but a lack of studies, consistent and transparent data collection, and reporting makes it difficult to evaluate the extent to which this may have occurred. Existing wells are generally considered as the most likely pathway for subsurface transport of WST and subsurface fluids (water, brines, gas). California needs to characterize this potential hazard in order to evaluate risk to groundwater resources. In California, hydraulic fracturing is occurring at relatively shallow depths and presents an inherent risk for fractures to intersect nearby aquifers if they contain usable water. Fracturing has occurred in many fields at a depth less than 600 m (2000 ft). Available research indicates 600 m is likely the maximum distance for vertical propagation of hydraulic fractures, although the maximum vertical length of a fracture may be less than 600 m for fracturing in shallow formations because of the different stress conditions. California needs to develop an accurate understanding about the location, depth, and quality of groundwater in oil and gas producing regions in order to evaluate the risks of WST operations to groundwater. This information on groundwater must be integrated with additional information to map the actual extent of hydraulic fractures to assess whether and where water contamination from WST activities has been or will be a problem.

More complete information about the quality and location of groundwater resources relative to the depth at which hydraulic fracturing is occurring would make it possible to identify inherently hazardous situations that could and should be avoided. Data on the location and quality of groundwater must be obtained in order to assess risks from proposed hydraulic fracturing.

Hydraulic fracturing at shallow depths poses a greater potential risk to water resources because of its proximity to groundwater and the potential for fractures to intersect nearby aquifers. Geomechanical studies conducted for WST in other states have indicated that fracturing directly from the stimulated reservoir into groundwater is unlikely when well stimulation is applied in formations that are sufficiently far below overlying aquifers. However, according to FracFocus and DOGGR's GIS well data files, the depth of roughly half of the wells in California that have been stimulated using hydraulic fracturing lie within 610 m (2,000 feet) of the ground surface, where 600 m (1,969 feet) has been identified as a threshold for vertical disturbance by hydraulic fracturing. Based on well stimulation notices filed to date with DOGGR, much of the current and planned hydraulic

fracturing operations in California occur at depths of less than 305 m (1,000 feet) below the ground surface. Because of the shallow depth of well stimulation and the typically lower injection volumes in California, the stress and damage behavior is very different from high-volume hydraulic fracturing elsewhere, meaning the separation distance of 600 m suggested may not be applicable to the conditions in this state. However, the potential for hydraulic fractures to intercept groundwater in these conditions warrants more careful investigation and monitoring (see Figure 1-3), including geomechanical studies and surveys of fracture extent relative to groundwater location, depth, and quality.

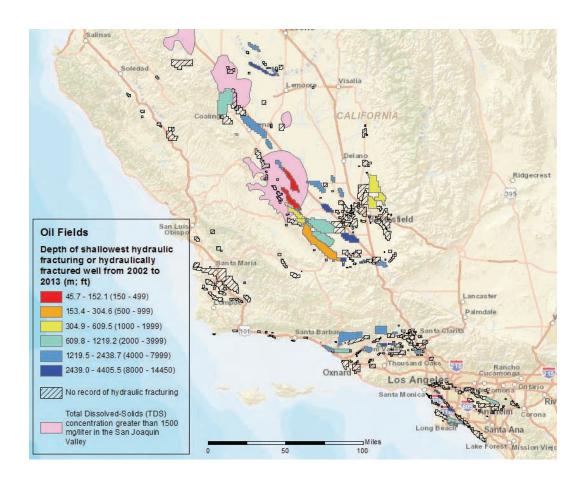


Figure 1-3. A map showing the shallowest hydraulic fracturing depth from the well stimulation notices or hydraulically fractured well total depth (measured depth from DOGGR for wells drilled after 2001 or true vertical depth from FracFocus) in each field. Pink areas show regions in the San Joaquin Valley where the shallow groundwater has total dissolved solids above California's short-term secondary maximum contaminant level for drinking water of 1,500 mg/L. Note the oil fields colored orange and yellow in the San Joaquin Valley, indicating shallow hydraulic fracturing, that are located in areas with better groundwater quality. Data from DOGGR 2014(a), DOGGR 2014(b), FracFocus (2013), and Bertoldi et al. (1991).

Even when well stimulation occurs well below groundwater levels, leakage paths along existing wells or other permeable pathways in the rock—either naturally existing or generated by hydraulic fractures propagating beyond the target reservoir— may cause contamination. Some studies in other regions outside California have found a correlation between the location of hydraulically-fractured production wells and elevated concentrations of methane, arsenic, selenium, strontium, and, to a lesser extent, total dissolved solids (TDS). However, there is no consensus as to whether these are naturally occurring, due to hydraulic fracturing, production well defects, abandoned wells, or a combination of mechanisms. Pathways due to compromised or failed structural integrity of cement in oil and gas wells and well bores are generally considered the most likely potential pathway for groundwater contamination. While well integrity is a concern for all types of wells, including conventional oil and gas exploration wells, the risk of long-term damage or deterioration may be higher for hydraulic fracturing operations because of higher induced pressure and multi-stage fracturing. California-specific studies of the proportion of wells that exhibit indications of compromised wellbore integrity and corresponding groundwater contamination have not been conducted. California needs to determine the locations and conditions of preexisting wells near hydraulic fracturing operations in order to assess potential leakage hazards. Continued monitoring and data collection are warranted to avoid potential risks.

Conclusion 7: Current practice could allow flowback water to be mixed with produced water for use in irrigation. California needs to monitor the quality of flowback/produced water and review regulations on the appropriate use of flowback/produced water, based on its quality and the intended uses.

In California, there are documented cases of intentional and accidental surface releases of flowback fluids or chemicals associated with well stimulation. Detailed assessments are not available as to whether these releases contaminated surface water and/or groundwater, but this is a common pathway for surface and groundwater contamination. In other states, disposal of water in surface facilities causes more groundwater contamination than disposal by injection (Kell, 2011), and surface spills of various constituents have contaminated both groundwater and surface water.

Most flowback water is disposed of by Class II injection in California, but DOGGR does not distinguish between flowback and produced water. Current management practices in California also allow for the disposal of oil and gas wastewater, including the co-mingled well stimulation fluids, into unlined pits if the electrical conductivity (EC) is less than or equal to 1,000 micromhos per centimeter (μ mhos/cm), chloride concentration is less than or equal to 200 milligrams per liter (mg/l), and boron concentration is less than or equal to 1 mg/l, with no testing required for, or limits on, other contaminants. Some produced water is permitted for irrigation, but data do not exist to determine if flowback fluid is included in that water. A more detailed assessment of wastewater disposal practices is needed to determine their levels of risk to surface water, groundwater, or agriculture. A lack of baseline data on groundwater quality is a major impediment to identifying or

clearly assessing the key water-related risks associated with hydraulic fracturing and other well stimulation techniques. (Section 5.1.3, Potential Release Pathways, and 5.1.4, Case Studies of Surface and Groundwater Contamination)

Air Quality and Climate Impacts

Conclusion 8: Estimated marginal emissions of NOx, PM_{2.5}, VOCs directly from activities directly related to WST appear small compared to oil and gas production emissions in total in the San Joaquin Valley, where the vast majority of hydraulic fracturing takes place. However, the San Joaquin Valley is often out of compliance with respect to air quality standards and as a result, possible emission reductions remain relevant.

Three major sources of air pollutants include the use of diesel engines, flaring of gas, and the volatilization of flowback water. The first, diesel engines (used for transport and pumping of estimated fluid volumes required for WST) emit a small portion of total-emissions nitrogen oxides (NOx), particulate matter (PM_{2.5}), and volatile organic compounds (VOC) associated with other oil and gas production operations as a whole.

Emissions from flaring in California are uncertain, because of variability in flare combustion conditions and a lack of information regarding the frequency of flare-use during WST operations. However, current California Air Resource Board inventories of pollutant emissions from all flaring suggest that flares as a whole emit less than 0.1% of the VOCs and are not a major regional air quality hazard.

Emissions from volatilization of flow-back water constituents have not been measured but might be bracketed. The California Air Resource Board has conducted a "bottom-up" VOC emission inventory by adding up all known sources of emissions. It is unknown whether these sources included emissions from WST-related produced or flowback water. However, the sum of the emissions in the inventory matches well with "top-down" measurements taken from the air in the San Joaquin Valley. This agreement between "bottom-up" and "top-down" estimates of VOC emissions from oil and gas production indicates California's inventory probably included all major sources.

The inventory indicates that VOC emissions from oil and gas evaporative sources, such as from flowback water, might occur from stimulation fluids produced back after the application of WST, are small compared to other emission sources in the oil and gas development process. Data suggest that emissions from oil and upstream operations in general contribute to roughly 10% of anthropogenic VOC ozone precursor emissions in the San Joaquin Valley.

Some of the potential air-quality impacts can be addressed by regulation and largely avoided. (Section 5.2.1, Air Quality)

Conclusion 9: Fugitive methane emissions from the direct application of WST to oil wells are likely to be small compared to the total greenhouse gas emissions from oil and gas production in California. This is because current California oil and gas operations are energy intensive. However, all greenhouse gas emissions are relevant under California's climate laws, and many emissions sources can be addressed successfully with best-available control technology and good practice.

While WST will require additional energy use and could result in fugitive methane emissions, it is unlikely that these emissions will be large in comparison to other California oil and gas greenhouse gas emissions. California oil and gas production operations are generally energy intensive, due to steam-based thermal recovery operations and depleted oil fields with high water handling requirements. Therefore, greenhouse gas emissions from California oil and gas operations mostly result from energy consumption that releases ${\rm CO}_2$. The California Air Resources Board (CARB) inventory indicates that methane emissions represent less than 10% of total greenhouse gas emissions, on a ${\rm CO}_{2e}$ basis, from all oil and gas production.

Greenhouse gas emissions due to WST activities would include the same three sources discussed above for air quality. For the same reasons listed above, these sources are likely to be small compared to other oil and gas production sources. Nevertheless, to help achieve California's climate goals, many significant sources of fugitive methane emissions associated with WST could be controlled through the requirement of green completions and by requiring vapor controls for flow-back water.

Emissions estimates from inventories are subject to uncertainty. Evidence across all scales (individual devices to continental atmospheric measurements) suggests that methane emissions from the natural gas and petroleum industries are likely larger than those expected from the US Environmental Protection Agency (EPA) inventories. More specifically to California, atmospheric measurement studies in Southern California indicate that state inventories of methane emissions from oil and gas production activities may be underestimated by a factor of about 5. Adjusting the CARB inventory by this factor would make the global warming potential of oil and gas production-related methane emissions larger, although still less than direct CO₂ emissions from fuel use.

New US EPA regulations requiring reduced emission completions (so called "green completions") for gas wells beginning in 2015 do not apply to the majority of wells in the San Joaquin Valley, as they are principally oil and associated gas wells. Similar control standards could be applied to oil wells in California.

While other regions are currently using WST for the production of oil (e.g., the Bakken formation of North Dakota) or gas (e.g., the Barnett shale of Texas), emissions from these regions may not be representative of emissions from California-specific application of WST. For example, the volume of fluid used for WST operations in California is typically lower than operations in other shale plays, potentially leading to lower evaporative emissions of methane from flowback fluid. (Section 5.2.2, Climate Impacts)

Seismic Risk

Conclusion 10: Hydraulic fracturing rarely involves large enough volumes of fluids injected at sufficient rate to cause induced seismicity of concern. Current hydraulic fracturing for oil and gas production in California is not considered to pose a significant seismic hazard. In contrast, disposal of produced water from oil and gas production in deep injection wells has caused felt seismic events in several states. Expanded oil and gas production due to extensive hydraulic fracturing activity in California would lead to increased injection volumes for disposal. If this produced water is disposed of by injection and not handled through an expansion of water treatment and re-use systems, it could increase seismic hazards.

Induced seismicity is a term used to describe seismic events caused by human activities. These include injection of fluids into the subsurface, when elevated fluid pore pressures can lower the frictional strengths of faults and fractures leading to seismic rupture. Induced seismicity can produce felt or even damaging ground motions when large volumes of water are injected over long time periods into zones in or near potentially active earthquake sources. The relatively small fluid volumes and short time durations involved in most hydraulic fracturing operations themselves are generally not sufficient to create pore pressure perturbations of large enough spatial extent to generate induced seismicity of concern. Current hydraulic fracturing activity is not considered to pose a significant seismic hazard in California. To date, only one felt earthquake attributed to hydraulic fracturing in California has been documented, and that was an isolated, low-energy event.

In contrast to hydraulic fracturing, earthquakes as large as magnitude 5.7 have been linked to injection of large volumes of wastewater into deep disposal wells in the eastern and central United States. To date, compared to some other states, water disposal wells in California have been relatively shallow and volumes disposed per well relatively small. There are no published reports of induced seismicity caused by wastewater disposal related to oil and gas operations in California, and at present the seismic hazard posed by wastewater injection is likely to be low. However, possible correlations between seismicity and wastewater injection in California have not yet been studied in detail. Injection of much larger volumes of produced water from increased WST activity and the subsequent increase in oil and gas production could increase the hazard, particularly in areas of high, naturally-occurring seismicity. Therefore, given the active tectonic setting of California, it will be important to carry out quantitative assessments of induced seismic hazard and risk. The chance of inducing larger, hazardous earthquakes most likely could be reduced by following protocols similar to those that have been developed for other types of injection operations. Even though hydraulic fracturing itself rarely induces felt earthquakes, application of similar protocols could protect against potential worst-case outcomes resulting from these operations as well. (Section 5.3, Potential Seismic Impacts)

Indirect environmental effects of WST-enabled production

Conclusion 11: Based on Conclusions 1 through 10 above, the direct impacts of WST appear to be relatively limited for industry practice of today and will likely be limited in the future if proper management practices are followed. If the future brings significantly increased production enabled by WST, the primary impacts of WST on California's environment will be indirect impacts, i.e. those due to increases and expansion in production, not the WST activity itself. Indirect impacts of WST through WST-enabled production will vary depending on whether this production occurs in existing rural or urban environments or in regions that have not previously been developed for oil and gas — as well as on the nature of the ecosystems, wildlife, geology and groundwater in the vicinity.

The indirect effects of WST were not a focus of this study. However, an understanding of the future of WST in California is incomplete without consideration of the idea that WST and other advanced technologies can enable more and new production. Consequently, we provide here a few comments relevant to future study.

If new plays in formations such as the Monterey Formation source rocks prove to be attractive economic targets, the industry is likely to want to explore them and find WST and production technologies that work in these environments. Existing or as yet unidentified technologies might be developed for these specific circumstances. Then, some years in the future — much like the unconventional gas plays that came into production because of high-volume hydraulic fracturing from horizontal wells — there could be novel technologies appropriate to novel plays in California. Such new technologies could have different environmental impacts over what is experienced today. To the extent that producers develop successful new methods, these technologies will deserve new scrutiny to ensure that they do not damage the environment of California.

Oil and gas production activities in general are known to present environmental, health, and safety risks via an array of industrial activities and technologies — including, but not limited to, drilling, truck traffic, land clearing, gas compressor stations, separator tanks, wastewater processing and disposal, and land subsidence. Our assessment of current WST practices in California suggests that the per-barrel impacts of producing oil with WST are comparable to the impacts of producing oil without WST. As a result, WST will mainly affect California's environment through indirect effects caused by an increase in production.

The intensity and extent of expanded production impacts will vary, depending on where operations occur: in new greenfield sites, existing rural fields, or in existing fields in dense, urban environments. Some locations for expanded production may present few new impacts and some may present unique challenges to public health and safety, because of high population densities, vulnerable demographics, and geographic proximity to oil and gas development activities and their corresponding environmental emissions.

Expanded WST-enable production in California oil and gas fields could have the indirect effect of increasing the risk of contamination to groundwater water systems, by exposing greater areas of groundwater to contaminants and increasing the number of adverse events. The overall risks, however, will depend on groundwater and geological characteristics and operating practices, including (especially) practices to dispose of produced/flowback water and ensure the integrity of well casings and wellbore cement. If the use of WST expands oil and gas production in California, strategies for better understanding and mitigating any increased groundwater risk should be considered during planning and implementation efforts. Similarly, expanded production could lead to an increase in VOC, methane, carbon dioxide and other associated air-pollutant emissions if other measures to reduce these emissions are not undertaken.

There is a large body of work showing that habitats are altered to the detriment of wildlife and vegetation in areas where oil and gas production occurs. While it is obvious that wildlife and vegetation will be impacted if well stimulation converts pristine areas to oil and gas fields, increasing the level of production in existing fields will also have negative impacts on organisms that inhabit the fields. (Section 5, Potential Direct Environmental Effects of Well Stimulation)

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Advanced Well Stimulation Technologies

Authored by James Houseworth (LBNL)

This section provides background information on the currently available well-treatment technologies for increasing the rate of oil flow from the reservoir to the well. This type of treatment is called well stimulation and is used for situations where the natural reservoir flow characteristics are not favorable and need to be improved for effective oil recovery. The review covers the materials and methods used to perform the three commonly used well stimulation methods: (1) hydraulic fracturing, (2) acid fracturing, and (3) matrix acidizing. In addition this section reviews the materials and methods used to perform well drilling, construction, and completion which also play a role in well stimulation. The main points identified here that are used in subsequent sections to help understand the application of well stimulation technologies for oil production in California are:

- (1) The design of a hydraulic fracture is a function of reservoir flow and mechanical characteristics. Reservoirs that have relatively better flow characteristics (within the range of these characteristics where well stimulation is needed) and are relatively weak mechanically tend to require less intensive fracturing, which leads to a relatively smaller volume of fracture fluid used. Reservoirs that have relatively poor flow characteristics and are relatively strong mechanically tend to require more intensive fracturing, which leads to a relatively larger volume of fracture fluid used.
- (2) Acid fracturing is commonly limited in application to carbonate reservoirs, i.e., those rich in limestone and dolomite. This is significant because California's oil resources are primarily found in silica-rich rock rather than carbonate rock.
- (3) Matrix acidizing for silica-rich reservoirs typically has a very limited penetration distance from the well into the reservoir. Therefore matrix acidizing in silica-rich rock has a limited effect on larger-scale reservoir flow characteristics, with the possible exception of reservoirs where natural fracture flow paths are effective in which acidizing may open up natural fractures by dissolving plugging material.

The term stimulation with respect to petroleum production refers to a range of activities used to increase the production of oil from petroleum reservoirs (a body of rock containing oil in pore spaces or natural fractures) by increasing the permeability of the materials through which oil flows to the well. There are two distinct situations that lead to the use of stimulation technologies. The first is damage induced by well drilling and construction and through oil production operations (Economides, Hill, Ehlig-Economides, and Zhu, 2013). Damage may occur in the form of blockage of perforations in the well casing

through which oil flows, e.g., by scale formation (mineral precipitation) or sand production from the reservoir into the well (Ghalambor and Economides, 2002). Damage can also occur to the rock in the immediate vicinity of the well as a result of mechanical disturbances and chemical interaction with the fluids (drilling mud) used during the drilling of the well bore. For example pores may be plugged as a result of drilling mud plugging the rock pores, migration of fine particles in the rock, or swelling of clays in the rock (Ghalambor and Economides, 2002). Mechanical damage in the form of crushing and compaction of the rock may occur as a result of creating the perforations through the casing, a process carried out by literally shooting a projectile through the steel casing to punch holes to connect the well to the reservoir (Ghalambor and Economides, 2002). Techniques to correct these adverse impacts of well construction by clearing blockages in the well, or restoring the permeability of the rock, are termed *well stimulation*.

The term *stimulation* also refers to the use of techniques to enhance the natural permeability of the undisturbed rock containing the reservoir (a rock formation) to the point that it can provide economic rates of oil production (permeability is the ability of the rocks to conduct fluid including oil or water). In this event, stimulation technologies may be applied that increase reservoir permeability sufficiently to allow enhanced rates of oil production. This stimulation is also on occasion termed *well stimulation*, but is perhaps more precisely called *reservoir stimulation* (Economides et al., 2013). However throughout the remainder of this report, the focus will be on stimulation technologies whose purpose is to increase reservoir permeability, and these technologies will be referred to by the term *well stimulation* (WST), or simply *stimulation*. This is in accord with the definition of well stimulation in section 3157 of Division 3 of Chapter 1 of the California Public Resources Code.

This report section presents a review of stimulation technologies for increasing reservoir permeability. This section does not review stimulation technologies used to repair damage induced by well drilling and oil production.

2.1 The Purpose of Stimulation Technologies

As described above the production of oil from a reservoir depends on reservoir permeability, but it is also a function of the thickness of the reservoir, viscosity of the oil produced, well radius, and other factors. As a result, an exact permeability threshold for the use of WST does not exist (Holditch, 2006). However, the likelihood that well stimulation is needed to economically produce oil increases as the reservoir permeability falls below 1 millidarcy (md) $(9.87 \times 10^{-16} \text{ m}^2 \text{ or } 1.06 \times 10^{-14} \text{ ft}^2)(\text{e.g.}$, King, 2012).

An oil reservoir is typically classified as *unconventional* if well stimulation is required for economical production. Guidelines concerning the classification of petroleum resources (World Petroleum Council, 2011) categorize a reservoir as unconventional if it is spatially extensive and yet not significantly affected by natural flow processes. The oil in the Bakken play in North Dakota is an example of such an accumulation. A different and quantitative definition proposed by Cander (2012) is shown in Figure 2-1, in which the

permeability of the reservoir and viscosity of the oil are used to define conventional and unconventional. This definition is a more useful guide to the conditions amenable to well stimulation, in part because it does not include the geographic aspect ("large area") of the first definition.

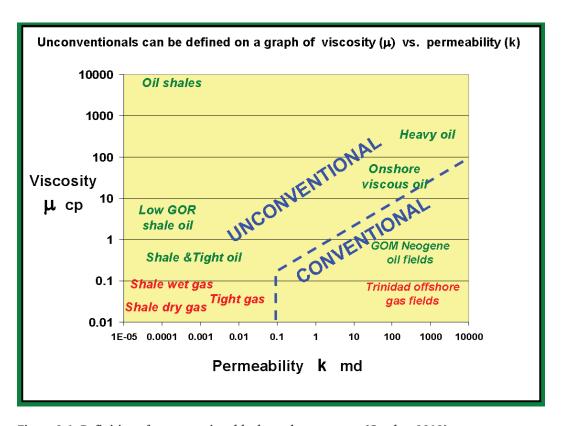


Figure 2-1. Definition of unconventional hydrocarbon resource (Cander, 2012)

The threshold between conventional and unconventional is defined by practical considerations. Unconventional resources require the use of technology to alter either the rock permeability or the fluid viscosity in order to produce the oil at commercially competitive rates. Conversely, conventional resources can be produced commercially without altering permeability or viscosity (Cander, 2012). This report focuses on WST for reservoirs that are unconventional due to low permeability, but this definition of unconventional oil resources also highlights methods for reservoirs that are unconventional due to high oil viscosity. Thermal methods are used to allow production of exceedingly viscous oil (Prats, 1982). Such hydrocarbons are called "viscous oil" or "heavy oil." Thermal methods lower oil viscosity by heating the reservoir, most commonly through steam or hot water injection (Farouq Ali, 2003). According to the California Division of Oil, Gas and Geothermal Resources (DOGGR), a majority of the oil produced onshore in California now involves steam injection (DOGGR, 2010).

There are three main WST: hydraulic fracturing either utilizing proppant (traditional hydraulic fracturing) or acid (also known as acid fracturing) and matrix acidizing. (Economides and Nolte, 2000). Because these methods do not reduce oil viscosity, they are primarily targeted at tight (low permeability) rock formations containing gas or lower-viscosity oil, although they may be used in combination with thermal stimulation for heavy oil.

The main technologies currently used for the production of most unconventional reservoirs are horizontal drilling combined with some form of hydraulic fracturing (McDaniel and Rispler, 2009). Because of this close association, horizontal wells are also discussed in this report. Relatively simple geologic systems have nearly horizontal deposition and layer boundaries and typically have much longer dimensions along the direction of bedding as compared with the dimension perpendicular to bedding. Horizontal drilling allows a well to access the reservoir over a longer distance than could be achieved with a traditional vertical well. An example of horizontal and vertical wells is shown in Figure 2-2 for the Eagle Ford play in Texas, which consists of a calcium-carbonate rich mudstone called a marl. In this case, the horizontal well intercepts about 5,000 m (16,400 ft) of reservoir as compared with about 80 m (262 ft) by the vertical well.

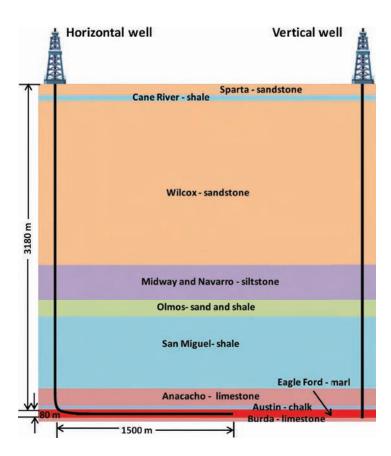


Figure 2-2. Example of horizontal and vertical wells in the Eagle Ford play (stratigraphy from Cardneaux (2012))

Hydraulic fracturing induces fractures by injecting fluid into the well until the pressure exceeds the threshold for fracturing. The induced fractures emanate from the well into the reservoir and provide a high-permeability pathway from the formation to the well, as shown on Figure 2-3. One of the goals of the fracturing operation is to only fracture rock within the target reservoir. After fracturing, a fine granular material (e.g., sand) known as a "proppant,", is introduced into the fractures to prevent the natural overburden stress (compressive) from closing the fractures after the injection pressure is removed. The creation of a highly permeable fracture network connecting the reservoir to the well significantly reduces the average distance that oil must migrate through the low-permeability reservoir rock in order to reach the well. Another variation of hydraulic fracturing is called acid fracturing, where acid is injected instead of proppant. The acid etches channels into the fracture surfaces which then prevents the natural overburden stress from closing the fractures and allows fluid flow pathways to remain along the fractures even after the injection pressure is removed.

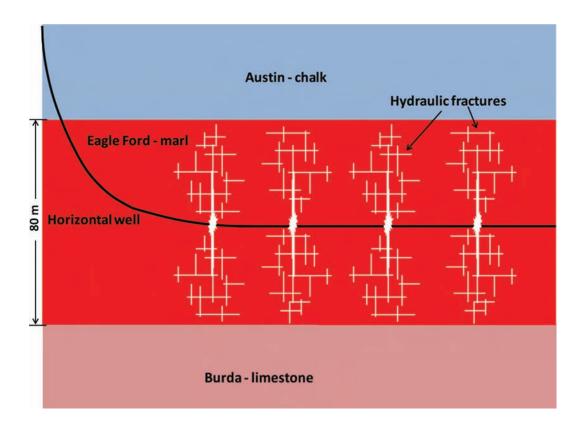


Figure 2-3. Hydraulic fractures initiated from a series of locations along a cased and perforated horizontal well.

Matrix acidizing involves injecting acidic fluids at pressures below the fracture pressure, such that the acid dissolves acid-soluble minerals in the rock matrix. The end result is enhanced flow pathways through the rock matrix. By comparison, however, the penetration into the formation of enhanced permeability caused by matrix acidizing is not typically as extensive as it is after hydraulic fracturing with proppant or acid. The two important exceptions in carbonate reservoirs are the creation of more deeply penetrating channels, known as wormholes, and deeper acid penetration into more permeable fractures of naturally fractured reservoirs (Economides et al., 2013).

Well drilling and construction, hydraulic fracturing, and matrix acidizing are discussed in more detail below.

2.2 Well Drilling and Construction

Well drilling, construction, and completion are necessary steps for conducting production operations from the vast majority of hydrocarbon reservoirs (some shallow hydrocarbon deposits, such as oil sands, can be mined from the surface). Well construction involves the installation of well casing and cement that seals the annular space between the casing and the formation as drilling proceeds. Well casing and cement provide the main barriers against contamination of groundwater by native (e.g., deeper and more saline groundwater), injected, or produced fluids during well operation

Well completion following construction configures and optimizes the well for hydrocarbon production. Completion includes (as needed) sand control, perforation of the production casing, and installation of production tubing. As mentioned above, completion can also include well stimulation to remove formation damage caused by drilling, construction, and other completion activities.

2.2.1 Vertical Wells

Until the 1980s, the vast majority of oil wells were drilled as vertical wells (US Energy Information Administration (EIA), 1993). Although the use of horizontal-well technology has steadily increased since that time, vertical wells are still being drilled for oil production. (Horizontal wells, discussed in Section 2.2.2, are an important technological development for production from unconventional reservoirs.)

Nearly all oil wells (vertical or horizontal) are drilled using the rotary drilling method (Culver, 1998; Macini, 2005). The first major oil discovery using rotary drilling was made at Spindletop near Beaumont, Texas, in 1901 (Geehan and McKee, 1989). There are a number of other methods used to drill wells in general, but most of these alternative methods are used for wells less than 600 m deep (ASTM, 2014) and therefore are not suitable for most oil wells, which average over 1,500 m deep in the US (US EIA, 2014).

2.2.1.1 Rotary Drilling Process and Drilling Muds for Onshore Oil Wells

The rotary drilling process is conducted from a drilling rig at the ground surface. The drill bit and other components, such as weights called drill collars, make up the bottom-hole assembly that is connected to the first section of drill pipe, and then is put in place below the drilling rig floor to begin. The drill pipe is connected to a square or hexagonal pipe called the "kelly." The kelly is turned by a motor via the rotary table in the floor of the drilling rig and a kelly bushing that connects to the kelly. Alternatively, a newer system known as "top drive" can be mounted to the rig derrick that turns the drill pipe (Macini, 2005). In either case, the rotational coupling with the drill string (collectively the drill pipe and bit) permits vertical movements such that the desired downward force can be applied to the drill bit while it is rotating. (More recent technology has led to the development of downhole motors which drive rotation of the drill bit; therefore, rotation of the drill pipe is not required. This technology is particularly important for directional drilling and will be discussed further in Section 2.2.2.) When the hole has been drilled deep enough to hold the bottom-hole assembly and drill pipe, another section of pipe is added and the process is repeated.

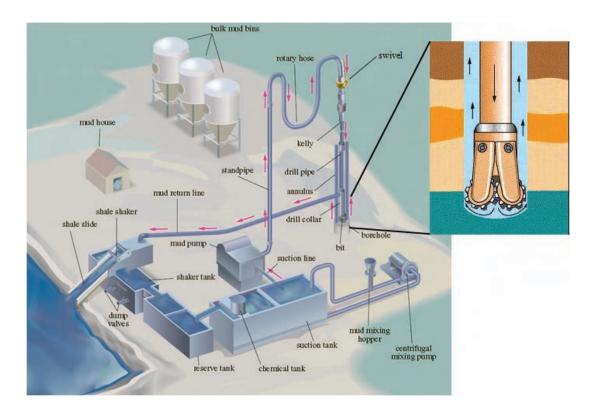


Figure 2-4. Drilling mud circulation system. Arrows indicate mud flow direction (modified from Macini (2005) and Oil Spill Solutions (2014))

As drilling proceeds, the bit is supplied with drilling mud, which is denser and more viscous than water, through a nonrotating hose that connects to the top of the kelly through a connection called a swivel. Drilling mud flows down the drill string and exits through ports on the face of the drill bit. This action flushes drill cuttings away from the drilling face and up the annulus between the drill pipe and the borehole wall or casing pipe. The circulating mud exits the annulus and is recycled back to the well after the cuttings have been separated from the mud (Varhaug, 2011). Figure 2-4 shows the components of the drilling mud circulation system.

Drilling muds have several important functions. As mentioned previously, the mud continuously cleans the cuttings off the bit face and transports them out of the hole. In the same vein, the mud limits the rate at which cuttings settle in the borehole annulus, so that the drill bit is not quickly buried by cuttings whenever the mud flow is temporarily stopped. The mud also serves to lubricate and cool the drill bit. Finally, the mud provides hydraulic pressure to help stabilize the borehole walls and control native fluid pressures in the rock, to prevent an uncontrolled release (blowout) of these fluids through the borehole. The energy of the flowing drilling mud also drives the bit rotation when a downhole motor is used.

There are three basic types of drilling muds: (1) aqueous-based mud; (2) hydrocarbon-based mud; and (3) gas, aerated, or foam muds (Khodja, Khodja-Saber, Canselier, Cohaut, and Bergaya, 2013), in which the classification is based on the predominant fluid in the mud. One of the critical factors that influences the choice of mud used is the clay content of shale encountered by the borehole. Shales make up about 75% of drilled formations, and about 70% of borehole problems can be associated with shale instability (Lal, 1999). Clay hydration caused by water-based muds often lead to reduced rock strength and instability in the borehole. This can result in a variety of problems, including borehole collapse, tight borehole, stuck pipe, poor borehole cleaning, borehole washout, plastic flow, fracturing, and lost circulation and well control (Lal, 1999). Furthermore, borehole wash-out in the shale sections can result in problems for cementing the casing in these sections and impedes the ability to isolate zones and control leakage along the well outside the casing (Brufatto et al., 2003; Chemerinski and Robinson, 1995). Because of these issues surrounding interaction of water with shale, oil-based muds are considered more suitable for drilling through shale. However, because of environmental issues associated with the use and disposal of drilling muds, more suitable water-based muds for drilling through shale continue to be developed (Deville et al., 2011). Another strategy used to minimize the environmental effects of drilling muds is to use water initially to penetrate the freshwater aquifer zone, then progress to more complex, water-based inhibitive muds, and then to oil-based muds at greater depth (Williamson, 2013).

2.2.1.2 Well Casing and Cementing

Wells are secured at discrete intervals as the borehole is being drilled by installing a steel pipe with diameter slightly smaller than the borehole diameter. This pipe, termed casing,

is then fixed in place by filling the annulus between the pipe and the borehole wall with cement. After installing the casing, the pathway for fluid movement along the borehole is restricted to the circular interior of the casing. The casing provides mechanical support to prevent borehole collapse and hydraulically isolates flow inside the casing from the rock formations around the well. Furthermore, the casing, in combination with the cement, impedes fluid movement along the borehole outside the casing between the different formations encountered, as well as to the ground surface. This function is referred to as "zonal isolation" (Nelson, 2012; Bellabarba et al., 2008).

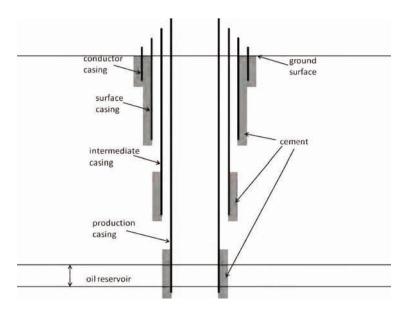


Figure 2-5. Schematic cross section of well casing and cement configuration. Casing extends above ground surface for connection to wellhead. (Redrawn and modified from API, 2009)

Zonal isolation is accomplished by filling the annulus between the casing and the formation with cement, which bonds the casing to the formation. There are different types of cements that are used depending on conditions of depth, temperature, pressure, and chemical environment (Lyons and Plisga, 2005). Cement placement and curing processes have to address numerous factors for the cement to be an effective barrier to fluid movement behind the casing (American Petroleum Institute (API), 2010). After placement and curing of the cement, API guidelines recommend that each section of cemented casing is pressure tested to ensure that the cement is capable of withstanding the pressures to be used during well operations (API, 2009 and 2010). Furthermore, wireline logging tools should be run after the cement job to verify that the well is correctly cemented and there are no hydraulic leakage paths. This is accomplished using acoustic tools (sonic and ultrasonic) that can determine the quality of the cement bond and can detect channels (API, 2009; Griffith et al., 1992).

The first casing to be installed is called the conductor casing (essentially a pipe with diameter larger than any of the other casings in the well), shown in Figure 2-5. This casing prevents the typically weak surficial materials from collapsing into the drill hole. The conductor casing is either driven into the ground by a pile driver or placed in the hole after drilling (API, 2009). The length of the conductor casing is normally 30 to 50 m (98.4 to 164 ft) (Macini, 2005), but generally less than 91 m (299 ft) in length (Burdylo and Birch, 1990). If the conductor pipe is not cemented, it is not strictly considered as part of the well casing (Macini, 2005).

The next casing installed is called the surface casing. The purpose of the surface casing is to protect freshwater aquifers from drilling mud and fluids produced during the life of the well, and to isolate these zones from overlying and underlying strata. The surface casing is necessarily smaller in diameter than the conductor casing and is typically about 91 m (299 ft), but can extend farther up to about 305 m (1,000 ft) in depth (King, 2012). Once the target depth for the surface casing is reached, the surface casing is inserted into the borehole and the annulus between the casing and the borehole wall and conductor casing are cemented. The casing extends from the bottom of the hole to the ground surface.

The surface casing (or conductor casing if it is cemented) is used to anchor the wellhead, which provides the interface between the well and equipment attached to the wellhead above the ground surface. During drilling operations, an operational and safety valve system called a blowout preventer is attached to the wellhead. After drilling is complete, the blowout preventer is replaced by a different valve system called a Christmas tree, which is used for production operations (Macini, 2005).

Drilling then proceeds until the next casing, which could be the production casing or an intermediate casing (needed for deeper wells). In either situation, the next section of casing is assembled and inserted into the borehole, and the annulus is cemented. The production casing is the last section of casing that either enters the reservoir (if the production is to be done through an open hole) or extends throughout the production interval of the borehole. In some instances, a production liner is used that does not extend the full length of the hole. Instead, the liner hangs off the base of and is sealed to the intermediate casing and is not always cemented.

The casing is subject to hydraulic and mechanical stress, including axial tension caused by its own weight as well as dynamic stresses caused by installation and operational activities, external fluid pressures from the formation during cementing operations, and internal fluid pressure during drilling and operations. Thermal stresses are also present. These stresses need to be taken into account when selecting casing type and size (Lyons and Plisga, 2005). For systems that will be used for hydraulic fracturing, the high levels of fluid pressure imposed also need to be taken into account for casing selection (API, 2009).

Cementing the annulus of the casing is essential for control of leakage along the well outside the casing. After a casing segment has been put into the borehole, cement is injected to displace the drilling mud. Oilfield cements are calcium silicate type (Portland) cements containing additives depending on well depth, temperature, and pressure conditions, borehole rock characteristics, and chemical environment (Economides, Watters, and Dunn-Norman, 1998).

Additives are used for a variety of reasons, including altering the curing time, controlling water loss and solids/water separation, and preventing gas migration—among other things. Water loss and curing reactions that result in shrinkage cracking have been identified as significant factors leading to leakage behind the casing (Dusseault et al., 2000). Various polymers are typically used to prevent water loss (Economides et al., 1998), and magnesium oxide is used to cause an expansion of the cement upon curing (Joy, 2011). The ability of the cement to withstand stresses and borehole flexure without fracturing is increased by the addition of elastomeric fibers such as polypropylene (Sounthararajan, Thirumurugan, and Sivakumar, 2013; Shahriar, 2011).

After the desired volume of cement has been introduced to the well, drilling mud is again added to continue driving the cement through the well. When the cement reaches the bottom of the hole, the cement continues to displace the mud ahead of it upward along the outside annulus of the casing. The injection ends when the cement fills the annulus to the top of the casing. Deep intermediate or production casings may not be cemented to the top of the casing. This is because the high fluid pressure associated with the dense cement slurry over these longer intervals can fracture the formation (King, 2012). Once the cement sets, the residual cement and any remaining items from the cement operation that are at the bottom of the hole are drilled out to continuing deepening the borehole. A simple schematic of the casing and cement configuration is shown in Figure 2-5.

A number of problems can occur that lead to incomplete cementing around the casing. These include mixing of the cement and the drilling mud, poor displacement of the drilling mud by the cement, off-center casing that contacts the borehole wall, and gas migration through the cement prior to setting (American Petroleum Institute, 2010; King, 2012). Any of these could lead to incomplete cement behind the casing and the potential for leakage along the casing. To avoid mixing between the cement and the drilling mud, a chemical washer is injected ahead of the cement to help clean out the drilling mud and provide a fluid gap between the cement and the drilling mud. Wiper plugs are placed just in front of and behind the cement slug that is injected, also to prevent cement contamination by the drilling mud (Nelson, 2012). Casing centralizers are used to position the casing in the middle of the borehole to avoid trapping mud between the casing and the borehole wall (leading to mud channels in the cement). Additives are used to reduce cement shrinkage and permeability during setting, and to accelerate setting times, to avoid gas migration problems in the cement (Bonett and Pafitis, 1996).

Leakage along wells is considered the most likely route for injected fracturing fluids or reservoir fluids to migrate into overlying strata (King, 2012). Both casing and cement design need to account for any operational pressures and chemical environments that may occur during well stimulation. If the design is not adequate, leakage can result. Leakage along wells as a potential contamination pathway is described in Section 5.1.3.

2.2.2 Directional Drilling and Horizontal Wells

Directional drilling was initially developed in the late 1920s and 1930s (Gleason, 1934; Kashikar, 2005). Directional drilling refers to well construction with at least one section that has a curved axis. A horizontal well is a special case of a directional well in which the well axis is curved by 90 degrees from the vertical followed by a straight horizontal section, also referred to as a lateral. The technology required several improvements before it started to be utilized the 1970s; its application became widespread by the 1990s (Williams, 2004). By the end of 2012, 63% of wells drilled in the U.S. were horizontal, 11% were directional, and only 26% were vertical (Amer et al., 2013).

2.2.2.1 Drilling Process and Drilling Muds

The operations discussed for vertical wells generally apply to the initial phases of drilling a well that will include intentionally curved deeper sections. Directional drilling begins at a kick-off point after the initial vertical section is drilled. One of the first methods developed for establishing a deviation in direction used a mechanical device known as a whipstock, which is a wedge-shaped tool placed in the bottom of the hole that forces the drill to deviate from the vertical direction (Giacca, 2005). A major improvement in directional drilling was the development of steerable systems that use a downhole motor, in which the energy of the drilling fluid can be used to drive bit rotation. The steerable system eliminates the need for a whipstock for directional or horizontal wells. In this system, the direction of the drill bit is bent slightly relative to the drill string axis. Drilling by rotating the drill string causes the bit to drill in a straight line aligned with the drill string. By setting the drill string at a fixed angle and turning the bit through the energy of the drilling mud flow, the angle between the bit and the drill pipe can be maintained. The bit is rotated using the positive-displacement motor and drills ahead at the angle set by the position of the drill string, which does not rotate, and slides behind the bit. This method creates a somewhat tortuous borehole when drilling curved sections, making drilling more difficult, as well as greater difficulty in formation evaluation and running casing (Williams, 2004).

The latest technology, called rotary steerable drilling, allows for continuous drill-string rotation in curving and straight sections. Changes in direction are imposed by either a point-the-bit system similar to the bent steerable system just discussed, or a push-the-bit system in which pressure is applied by pushing against the borehole wall (Downton et al., 2000). The key difference is that the rotary steerable system mechanics allow continuous rotation of the drill string and produces much smoother and less tortuous curved boreholes. The greatest advantage of a rotary steerable system is that continuous

rotation reduces the friction between the drill string and the formation, allowing better transfer of weight to the bit. Sliding (i.e., no rotation) results in less weight on bit and much slower drilling. Control of the drilling direction is done from the surface by sending signals to steering actuators at the drill bit through a series of pressure pulses in the drilling mud (Giacca, 2005), a process referred to as mud pulse telemetry (MPT) (Downton et al., 2000).

In addition to development of improved directional control (inclination and azimuth) and borehole quality, there has been the development of methods to measure the local temperature and pressure conditions, as well as the orientation and motion of the drill bit. This measurement technique is referred to as "measurement while drilling" (MWD), and the information is transmitted to the surface using MPT (Downton et al., 2000; Amer et al., 2013). Thus, the conditions and path of the drill bit is known in real time to help control the drilling process. More recently, sophisticated technology to perform formation evaluation measurements, such as resistivity, gamma ray, sonic, and magnetic resonance measurements, have been integrated into the drilling process and may also be received in real time through MPT (Amer et al., 2013). For drilling in shales, the inclination, azimuth, and gamma ray activity are the most critical data. The information on borehole trajectory and changes in the formation allow for "geosteering," in which directional drilling is actively controlled using real-time data to properly position the borehole relative to the target formation.

The various drilling muds discussed for drilling of vertical wells are also used for directional drilling. The demands of high-angle and horizontal drilling, and extensive drilling path lengths through shales for unconventional reservoirs, result in greater use of oil-based drilling muds. However, alternative water-based muds for these conditions are being developed because of the greater environmental risks and costs associated with oil-based muds. Success using water-based muds requires development of custom formulations based on the specific reservoir rock and conditions to be encountered (Deville et al., 2011).

Directional wells can be drilled with long, medium, or short radius curves. The longer-radius wells are typically used when the objective is extended horizontal reach (thousands of meters), while medium and short radius wells are used when a shorter horizontal leg (~1,000 m for medium radius and up to 300 m for short radius) is needed, and/or when highly accurate placement is necessary (Giacca, 2005). Directional drilling also allows for the construction of multilateral wells where a single vertical bore is used to kick off one or more lateral legs from a cased hole (Fraija et al., 2002; Bosworth et al., 1998). The lateral leg is initiated using a whipstock and a milling assembly to cut a well lateral from a cased hole (Fraija et al., 2002; Bosworth et al., 1998). The advances in directional drilling technology discussed here have also led to greater capabilities in terms of well depth and lateral drilling distances. Horizontal wells have been drilled to lateral distances in excess of 10 km (32,800 ft) (Sonowal et al., 2009). True vertical well depths up to about 7 km (23,000 ft) have been achieved for horizontal wells with lateral reach up to about 3 km (9,840 ft) (Agbaji, 2009; Bakke, 2012).

2.2.2.2 Well Casing and Cement

The casing and cementing of the vertical section of a directional well are the same as described in Section 2.2.1.2. There is, however, greater variation in the casing and cementing configurations used for horizontal wells. This variation is in part driven by the hydraulic fracturing approach utilized, so the description of horizontal well completions is given in the next section.

2.3 Hydraulic Fracturing

Hydraulic fracturing in general is a relatively old technology for improving gas and oil field production rates. However, there has been a significant evolution of this technology. As discussed in the introduction, the focus of this review effort is on hydraulic fracturing as a means to enhance reservoir permeability.

Hydraulic fracturing was first implemented in 1949; since this time, use of this stimulation method has grown substantially (Montgomery and Smith, 2010). Originally, hydraulic fracturing was used exclusively as a well stimulation method, applied in cases where the natural reservoir permeability was too low for economic petroleum recovery. But in the 1990s, hydraulic fracturing started to be used for higher-permeability reservoirs as a method to remediate formation damage around wells (Ghalambor and Economides, 2002). The general permeability levels used to distinguish high and low permeability reservoirs, which is also influenced by the viscosity of the oil, is shown in Figure 2-1.

Unlike California (Section 3), the main classes of reservoirs where hydraulic fracturing has been used intensively in other areas of the United States are very low permeability, unconventional shale reservoirs and tight-gas sand reservoirs, accounting for over 73% of the hydraulic fracturing activity (Beckwith, 2010). Most of the unconventional shale reservoirs contain natural gas, with the exceptions of the Eagle Ford, which produces oil in the shallower portion of the formation, and the Bakken and Niobrara plays, which mainly contain oil.

The typical hydraulic fracture operation involves four process steps to produce the fractures (Arthur et al., 2008). The long production intervals present in most horizontal wells leads to a staged approach to hydraulic fracturing. For the staged approach, a portion of the well is hydraulically isolated in order to focus the injected fracture fluid pressure on an isolated interval, which is called a "stage." After isolating the stage, the first phase of the fracturing process is the "pad," in which fracture fluid is injected without proppant to initiate and propagate the fracture from the well. The second phase adds proppant to the injection fluid; the proppant is needed to keep the fractures open after the fluid pressure dissipates. This phase is also used to further open the hydraulic fractures. The third phase, termed the "flush," entails injection of fluid without proppant to push the remaining proppant in the well into the fractures. The fourth phase is the "flowback," in which the hydraulic fracture fluids are removed from the formation, and fluid pressure dissipates. Examples of the stages of hydraulic fracturing including the time spent for each phase is given in Section 2.3.7.

An acid preflush is sometimes used prior to injection of the pad. For instance, Halliburton's (2014) fracture-fluid-composition disclosure indicates it is used in about half of their specific formulations (DOE, 2009). The acid preflush may be needed to remove scale, help clean drilling mud and casing cement from perforations, and to weaken the rock to help initiate a fracture (King, 2010; Halliburton, 2014; DOE, 2009). Prior to injecting the acid, corrosion inhibitor, at a level of 0.2 to 0.5% by mass, is added to the fluid to prevent acid corrosion of steel components, such as the casing (DOE, 2009; King, 2010). The pre-flush acid concentrations range from 7.5 to 15% HCl, and volumes range from 0.946 to 26.5 m³ (33.4 to 936 ft³ or 250 to 7,000 gallons) per stage (Halliburton, 2014) injected at a relatively low rate below the fracture pressure.

In the following sections, aspects of hydraulic fracture geomechanics and the attributes of hydraulic fracture fluids and proppants are presented. In addition, the alternative to proppant use for carbonate reservoirs, called "acid fracturing," is discussed further. Following these discussions of the physical mechanisms and materials involved, various engineering alternatives for completion and isolation of the stages and information on the phases of the fracturing process are discussed.

2.3.1 Hydraulic Fracture Geomechanics, Fracture Geometry, and the Role of Natural Fractures and Faults

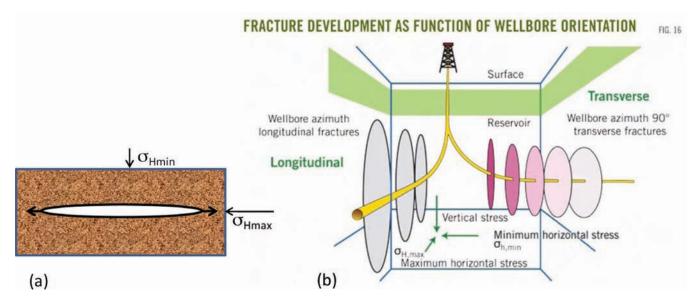


Figure 2-6. Fracture patterns for different orientations of the borehole relative to principal compressive stresses: (a) fractures open in the direction of the minimum principal stress, (b) effects of horizontal well alignment with maximum and minimum horizontal principal stresses (Rahim et al., 2012)

Fluid pumped into deep underground rocks at sufficient pressure will cause the rock to break or "fracture". The technical description of conditions that result in such hydraulic fractures is this: fractures are formed when fluid pressure exceeds the existing minimum rock compressive stress by an amount that exceeds the tensile strength of the rock (Thiercelin and Roegiers, 2000). The operator cannot easily control the orientation of the hydraulic fractures. Rather, it is the stress conditions in the rock that will determine the orientation. Rocks at depth experience different amounts of compression in different directions. Because the compressive stress in rock often varies with direction, the hydraulic fracture will preferentially push open against the least compressive stress for a rock with the same strength in all directions (Economides et al., 2013). Therefore, the fracture plane develops in the direction perpendicular to the minimum compressive stress, as shown on Figure 2-6.

If the compressive stress in the rock were the same in all directions (or nearly so), then the orientation of the fracture would tend to be random. In addition to stress orientation, rock strength varies and fracture geometry also depends on the variation in rock strength in different directions.

Finally, natural fractures are generally present to some degree in natural rock and affect the formation of hydraulic fractures. These features of the rock are often the pathways for hydraulic fractures (Weijermars, 2011). Gale and Holder (2010) found that fractures filled with secondary calcite in siliceous mudrocks are generally weaker than the surrounding rock and may be susceptible to reopening during hydraulic fracturing. However, fractures filled with secondary quartz may be stronger than the surrounding rock and hinder the development of hydraulic fractures. Williams-Stroud, Barker, and Smith (2012) found that shearing of existing fractures played a significant role in hydraulic fracturing, based on discrete fracture network modeling and microseismic measurements from a hydraulic fracturing field test.

Typically, conditions underground favor hydraulic fractures that are vertical. (Vertical fractures result because most rocks at depth experience greater vertical stress than horizontal stress.) Consequently, the question of the vertical fracture height growth is important when considering the potential migration of fracture fluid or other reservoir fluids out of the typically very low-permeability target oil reservoir. Thousands of microseismic measurements have been conducted in the Barnett, Woodford, Marcellus, and Eagle Ford shales to characterize hydraulic fractures. Fracture heights have been investigated over a range of reservoir depths from 1,220 to 4,270 m (4,000 to 14,000 ft) deep, and found that the tallest fractures formed in deeper sections. However, typical fracture heights are in the range of tens to hundreds of feet (Fisher and Warpinski, 2012). The maximum recorded fracture height from these reservoirs and the Niobrara shale was found to be 588 m (1,930 ft) (Davies et al., 2012) (see also Section 5.1.3.2.1). The statistics of fracture height from these measurements show that the probability of exceeding 350 m (1,150 ft) is about 1% (Davies et al., 2012). Fracture height is limited by a number of mechanisms, including variability of in situ stress, material property contrasts, weak

interfaces between layers, and the volume of fracture fluid required to generate extremely large fracture heights (Fisher and Warpinski, 2012). Finally, the minimum stress at shallow depths (305 to 610 m or 1,000 to 2,000 ft) is typically in the vertical direction, which contrasts with the typical minimum stress being horizontal at greater depth. This stress condition favors a horizontal fracture orientation, which tends to prevent vertical fracture growth from deeper into shallower depths (Fisher and Warpinski, 2012). Interaction of hydraulic fracture fluids with faults may also affect fracture height growth. Simulations of hydraulic-fracturing-induced fault reactivation were conducted by Rutqvist et al. (2013), who found fault rupture lengths to be less than 100 m (328 ft). Consequently, in general fault reactivation does not create permeable pathways far beyond the target reservoir (Flewelling et al., 2013). A fracture design that incorporates these factors into the selection of operational variables (pressure, injection rate, fluid type, etc.) for the hydraulic fracture means that fracture height is controllable to a reasonable degree.

Hydraulic fracture development is also affected by neighboring wells, which may undergo hydraulic fracture treatment at the same or at different times. This typically involves multiple parallel horizontal wells that are separated by 457 m (1,500 ft) or less (King, 2010). The fracturing can be carried out simultaneously or in sequence. The idea is to use the change in stress created by neighboring wells and stimulation treatments to alter fracturing directions and increase complexity in the fractures created. Differences in the effects of simultaneous and sequential fracturing are not large (King, 2010).

Fracture geometry also depends on other factors not related to rock mechanics per se, in particular on the magnitude of the stimulation pressure and the fracturing fluid viscosity. These are discussed in Section 2.3.2, where fracture fluids and operations are presented.

2.3.2 Hydraulic Fracture Fluids and their Effects on Fracture Geometry

The design of a hydraulic fracture requires specification of the type of hydraulic fracture fluid. While there are many additives used in hydraulic fracture fluids, most of these are used to mitigate adverse chemical and biological processes. The main property of hydraulic fracturing fluids that influence the mechanics of fracture generation is the viscosity¹. Both laboratory and field data indicate that low-viscosity fracture fluids tend to create complex fractures with large fracture-matrix area and narrow fracture apertures—as compared with higher viscosity fracture fluids, which tend to create simpler fractures with low fracture-matrix area and wide fracture apertures (Cipolla et al., 2010).

The lowest viscosity fracturing fluid is slickwater, which contains a friction-reducing additive (typically polyacrylamide) and has a viscosity on the order of 0.004 Pa-s (4 cp or 8.36×10^{-5} lbf-s/ft²) (about 4 times that of pure water) (Kostenuk and Browne, 2010).

¹ Viscosity is a fluid property that quantifies resistance to fluid flow. It takes little effort to stir a cup of water (viscosity ~ 1 centipoise (cp)), noticeably more effort to stir a cup of olive oil (viscosity ~ 100 cp), and significantly more effort to stir a cup of honey (viscosity $\sim 10,000$ cp).

Gelled fracture fluids generally use guar gum or cellulose polymers to increase viscosity (King, 2012). Further increases in viscosity can be achieved by adding a cross-linking agent to the gel that is typically a metal ion, such as in boric acid or zirconium chelates (Lei and Clark, 2004). The cross-linking binds the gel's polymer molecules into larger molecules and that causes an increase in the solution viscosity. Linear gels have viscosities about 10 times that of slickwater, and cross-linked gels have viscosities that are on the order of 100 to 1000 times larger (Montgomery, 2013). Fracture fluids energized using nitrogen and surfactant with linear gels (to create foams) lead to increased viscosity of the energized fluid over the linear gel, and the viscosity of energized cross-linked gels increase by factors of 3 to 10 over those not using a cross-linking agent (Ribeiro and Sharma, 2012; Harris and Heath, 1996). The type of fracture fluid also affects the ability to emplace proppant (see Section 2.3.3). In particular, cross-linked gels are better for transporting proppant than slickwater (Lebas et al., 2013). The effective viscosity is also influenced by the proppant concentration (Montgomery, 2013).

In general fracture length and fracture-network complexity decrease as the viscosity of the fracturing fluid increases as illustrated on Figure 2-7 (Cipolla, Warpinski, and Mayerhofer, 2010; Rickman, Mullen, Petre, Grieser, and Kundert, 2008). Fracture lengths also increase with the volume of injected fracture fluid. Flewelling et al. (2013) found that fracture length could be represented as approximately proportional to fracture height with a proportionality factor that ranged from 0.5 to 1. Fracture apertures (or widths) are on the order of a few tenths of an inch (Barree et al., 2005; Bazan, Lattibeaudiere, and Palisch, 2012) and tend to increase with viscosity, rate, and volume of the fluid injected (Economides et al., 2013).

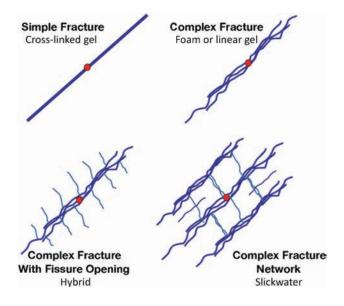


Figure 2-7. Effects of fracture fluid viscosity on fracture complexity (modified from Warpinski, Mayerhofer, Vincent, Cippola, and Lolon (2009)).

The type of fluid used depends on the properties of the reservoir rock, specifically the rock permeability and brittleness (Cipolla et al., 2010; Rickman et al., 2008). Formations with higher intrinsic permeability (but still low enough to warrant hydraulic fracturing) are generally stimulated using a higher-viscosity fracture fluid to create a simpler and wider fracture (Cipolla et al., 2010). The rationale for this selection is that the fracture is needed mainly to help move the fluids as they converge closer to the well, but are able to flow adequately to the fracture farther out in the formation. As reservoir permeability decreases, the resistance to fluid movement through the unfractured portion of the formation increases. Therefore, a denser fracture pattern (narrower spacing between the fractures) is needed to minimize the distance that reservoir fluids must flow in the rock matrix to enter the hydraulically induced fractures (Economides et al., 2013). This leads to the use of lower-viscosity fracturing fluids to create more dense (and complex) fracture networks.

The choice of fracture fluid also depends on rock brittleness (Rickman et al., 2008). Wider fracture apertures are needed as rock brittleness decreases (or as ductility increases) because of the greater difficulty maintaining fracture permeability after pressure is withdrawn (Rickman et al., 2008). Therefore, rock permeability and brittleness both influence the choice of fracturing fluid. Stimulation of natural fractures is also thought to be critical for effective hydraulic fracture treatment in very low permeability shales (Warpinski, Mayerhofer, Vincent, Cippola, and Lolon, 2009; Cramer, 2008; Fisher et al., 2005). Although these characteristics may lead to conflicting requirements for the fracturing fluid, permeability is often found to be lower in brittle rocks and higher in ductile rocks (Economides et al., 2013), and natural fractures are usually more prevalent in brittle rock as compared to ductile rock. Natural fractures in shales can be sealed by secondary minerals. Such fractures do not have much influence on the natural permeability, although in some cases can preferentially reactivate during hydraulic fracturing (Gale and Holder, 2010).

The general trends in fracture fluid types, fluid volumes used, and fracture complexity as a function of rock properties are shown in Figure 2-8. This figure shows that hydraulic fracturing in ductile, relatively higher permeability reservoir rock having low natural fracture density tends to receive a hydraulic fracture treatment using a viscous cross-linked gel with a relatively low volume of fluid injected but a large concentration and total mass of proppant. The fracture response in this case tends to produce a simple single fracture from the well into the rock that has a relatively large aperture filled with proppant. As rock brittleness and degree of natural fracturing increase, and as permeability decreases, hydraulic fracturing treatments tend to use a higher-volume, lower viscosity fracture fluid that carries less proppant. The response of the rock to this fracture treatment is to create more complex fracture networks in which the fractures have relatively narrower apertures and a more asymmetric cross-section in the vertical direction as a result of limited proppant penetration. In short, ductile and more permeable rocks usually receive gel fracture treatments while more brittle, lower permeability rocks with existing fractures are more amenable to slickwater fracturing.

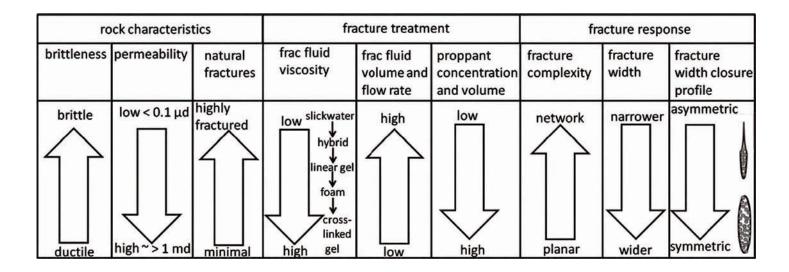


Figure 2-8. General trends in rock characteristics, hydraulic fracture treatment applied, and hydraulic fracture response (modified from Rickman et al. (2008)).

Fracture fluids may contain several other additives in addition to those already identified. These include biocides, corrosion inhibitors, clay stabilizers, and polymer breakers (Kaufman et al., 2008). Example concentrations for slickwater and gelled fracture fluids are given in 2-9.

A summary of the various types of additives is given in Table 2-1. In some cases, acids are injected as a separate pre-flush before injection of the hydraulic fracture pad in order to clean out the casing perforations, help clean out the pores near the well, and dissolve minerals, to aid in initiating fractures in the rock (DOE, 2009). More detailed descriptions of the chemicals used in hydraulic fracturing fluids are given in Section 5.1.2.1.

Recycling of fracture fluid is one way to reduce the amount of water required for hydraulic fracturing. The principal issue involved is that recycled fracturing fluid develops high concentrations of dissolved salts that become highly saline brines. One approach has been the development of more salt-tolerant additives, such as polymers used for slickwater friction reducers (Paktinat et al., 2011). Other processes are also being developed to aid in the reuse of fracturing fluids (Ely et al., 2011).

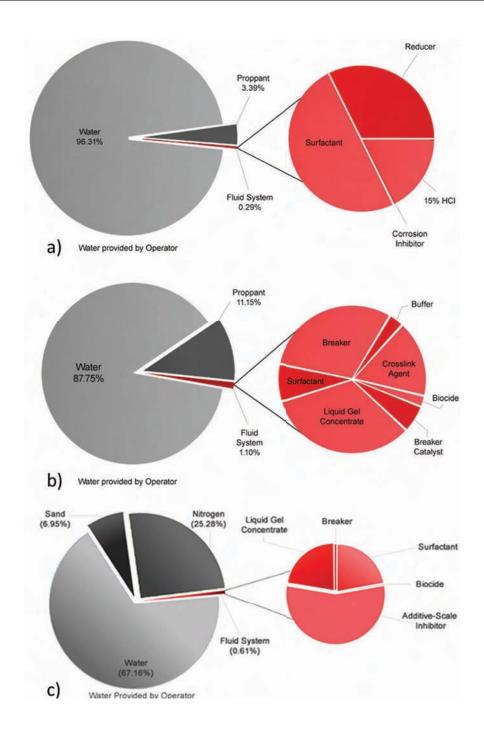


Figure 2-9. Example compositions of fracture fluids a) Colorado DJ Basin WaterFrac Formulation – a slickwater fracturing fluid; b) Utah Vertical Gel Frac Formulation – a cross-linked gel fracturing fluid; c) Pennsylvania FoamFrac Formulation – a gelled nitrogen foam fracturing fluid (source: Halliburton, 2014). Note: although not stated on the website, comparisons of these compositions with information on fracture fluid compositions given on the FracFocus (2014) website indicate these values are percent by mass.

Table 2-1. Additives to Aqueous Fracture Fluids (NYSDEC, 2011)

Additive Type	Description of Purpose	Examples of Chemicals
Proppant	"Props" open fractures and allows gas / f uids to f ow more freely to the well bore.	Sand [Sintered bauxite; zirconium oxide; ceramic beads]
Acid	Removes cement and drilling mud from casing perforations prior to fracturing f uid injection	Hydrochloric acid (HCl, 3% to 28%) or muriatic acid
Breaker	Reduces the viscosity of the f uid in order to release proppant into fractures and enhance the recovery of the fracturing f uid.	Peroxydisulfates
Bactericide / Biocide / Antibacterial Agent	Inhibits growth of organisms that could produce gases (particularly hydrogen sulfide) that could contaminate methane gas. Also prevents the growth of bacteria which can reduce the ability of the f uid to carry proppant into the fractures.	Gluteraldehyde; 2,2-dibromo-3- nitrilopropionamide
Buffer / pH Adjusting Agent	Adjusts and controls the pH of the f uid in order to maximize the effectiveness of other additives such as crosslinkers	Sodium or potassium carbonate; acetic acid
Clay Stabilizer / Control /KCl	Prevents swelling and migration of formation clays which could block pore spaces thereby reducing permeability.	Salts (e.g., tetramethyl ammonium chloride Potassium chloride (KCl)
Corrosion Inhibitor (including Oxygen Scavengers)	Reduces rust formation on steel tubing, well casings, tools, and tanks (used only in fracturing f uids that contain acid).	Methanol; ammonium bisulfate for Oxygen Scavengers
Crosslinker	Increases f uid viscosity using phosphate esters combined with metals. The metals are referred to as crosslinking agents. The increased fracturing f uid viscosity allows the f uid to carry more proppant into the fractures.	Potassium hydroxide; borate Salts
Friction Reducer	Allows fracture f uids to be injected at optimum rates and pressures by minimizing friction.	Sodium acrylate-acrylamide copoly- mer; polyacrylamide (PAM); petro- leum distillates
Gelling Agent	Increases fracturing f uid viscosity, allowing the f uid to carry more proppant into the fractures.	Guar gum; petroleum distillates
Iron Control	Prevents the precipitation of metal oxides which could plug off the formation.	Citric acid
Scale Inhibitor	Prevents the precipitation of carbonates and sulfates (calcium carbonate, calcium sulfate, barium sulfate) which could plug off the formation.	Ammonium chloride; ethylene Glycol
Solvent	Additive which is soluble in oil, water and acid-based treatment f uids which is used to control the wettability of contact surfaces or to prevent or break emulsions	Various aromatic hydrocarbons
Surfactant	Reduces fracturing f uid surface tension thereby aiding f uid recovery.	Methanol; isopropanol; ethoxylated alcohol

Alternative fracture fluids are also under investigation. Some of the purposes of alternative fluids are to reduce water use and to reduce formation-damage effects sometimes caused by aqueous fracture fluids and by additives such as gels. These alternatives include supercritical 2 2 CO $_2$ and supercritical 2 CO $_2$ -nitrogen mixtures, 2 CO $_2$ foam, nitrogen, liquid

propane (LPG), and explosive propellant systems (EPS) (Rogala et al., 2013). These systems generally eliminate or greatly reduce the amount of water involved in fracturing, with attendant benefits according to Rogala et al. (2013) of elimination or reduction of

- Formation-damage effects associated with water sensitivity;
- Formation damage associated with water and chemical (particularly gels) remaining in the reservoir;
- Chemical additives and their environmental effects; and
- Flowback waste water disposal.

Despite the advantages from a water perspective, there are several disadvantages according to Rogala et al. (2013), including,

- Transport and handling of pressurized CO₂ with potential for leakage into the atmosphere;
- Relative difficulty to transport proppant in the fracture, particularly for nitrogen;
- Added problems working with surface pressures/increased injection pressures for CO₂, nitrogen, foams and LPG;
- Risk of explosion with LPG;
- · Greater cost except for EPS; and
- Lower fracture lengths for EPS (10 to 50 m).

2.3.3 Proppants

After injecting the hydraulic fracture pad, the proppant is injected in with the hydraulic fracture fluid. As mentioned, proppants are a solid granular material, such as sand, that act to keep the fractures from closing after hydraulic fracture fluid pressure is released. Proppant size and size distribution are key factors affecting the permeability of proppant-filled fractures. Larger, more uniformly sized proppants result in the greatest permeability. Proppant grain sizes generally lie in the range of 10^{-4} to 2×10^{-3} m (3.28 x 10^{-4} to 6.56×10^{-3} ft) in diameter (Horiba Scientific, 2014).

² Supercritical CO_2 exists when the temperature and pressure are above the critical temperature (31° C, 88° F) and critical pressure (7.4 MPa, 1070 psi). Supercritical CO_2 is a fluid that has properties between those of a gas and a liquid.

In addition to these characteristics, the transportability and strength of the proppant also affect the ultimate fracture permeability. The ability of the proppant to be transported by a given fracture fluid depends in part on the proppant size and density. Greater transportability is desirable because it allows for delivery of proppant deep into the formation fractures. Proppants that are smaller and have a lower density are more easily transported (Economides et al., 2013).

Proppant strength is also important. If the closure stress of the fracture exceeds the compressive strength of the proppant, the proppant grains will be crushed. This reduces the effective proppant size and thus the permeability of the fracture.

The most common proppant is natural sand that has been sieved to a uniform size class (Beckwith, 2011). A number of alternative synthetic proppants have been used as well, including sintered bauxite and ceramics. Ceramic and bauxite proppants can be manufactured to have different mass densities and compressive strengths, and the size and shape can be tightly controlled to produce highly uniform grains (Lyle, 2011). Various types of resin coatings have also been used with all types of proppants, including sand (Beckwith, 2011). Resin coatings can be pre-cured or curable on the fly. Pre-cured resin coatings are used to improve proppant strength and to prevent movement of broken proppant fines. Cureable resin coatings are intended to bond proppant together after placement to help prevent proppant flowback during the flowback phase of the fracturing process and during hydrocarbon production (Beckwith, 2011).

The transport of proppant also impacts the choice of hydraulic fracture fluids. Lower-viscosity fluids are not as capable of delivering proppants and generally are used with lower proppant concentrations during the proppant-injection phase of the operations. Higher proppant settling in lower viscosity fluids will tend to deposit proppant in the lower parts of the fracture as compared with higher viscosity fluids (Cipolla et al., 2010). This is indicated schematically on the right-hand side of Figure 2-8. Furthermore, proppant delivery is more problematic in the more complex fracture networks created by lower-viscosity fracture fluids. Therefore, lower-viscosity fracture fluids are sometimes replaced after injection of the pad with high-viscosity fluids to more effectively deliver proppant. The use of two or more different fracture fluids during the same fracturing event is called a hybrid treatment. Slickwater fracture treatments may only deliver a sparse amount of proppant, resulting in conductivity dominated by the unpropped fracture conductivity (Cipolla et al., 2010). The success of such a treatment may hinge on other factors such as the rock compressive stress varying with direction and the presence of natural fractures being "self-propped" as a result of shearing of the fracture surfaces (Cipolla et al., 2010).

2.3.4 Acid Fracturing

An alternative to the use of proppant to maintain fracture conductivity is to inject hydrochloric acid under fracture pressures. This method is called acid fracturing and is only applicable to strongly reactive carbonate reservoir rock types. The acid etches the faces of the fracture surfaces. The presence of the etched channels allows fractures to remain permeable even after the fracture-fluid pressure is removed and compressive rock stress causes the fractures to close (Economides et al., 2013). Acid fracturing is sometimes preferred in carbonate reservoirs because of the relatively high degree of natural fractures generally present and the difficulties of placing proppant because of fluid leak-off into the natural fracture system. Acid fractures generally result in relatively short fractures as compared with fractures secured with proppant; therefore, it is generally more successful in higher-permeability formations (Economides et al., 2013).

2.3.5 Completions and Multistage Hydraulic Fracturing

As mentioned, multistage hydraulic fracturing refers to the application of the hydraulic fracturing process to multiple, hydraulically isolated intervals along the production interval of the well. Fracturing of a well's entire production interval at once can result in an uneven distribution of fractures. Slight variations in rock strength result in the fracturing fluid flow focused on the weakest rock along the well. The multistage fracturing process allows for greater control over where fractures are generated and produces a more uniform distribution of fractures along the production interval.

The conduct of multistage hydraulic fracturing requires that the completion used in the production interval is capable of stage isolation. The two most common completions used for multistage hydraulic fracturing are cemented liner and uncemented liner (Snyder and Seale, 2011). The cemented liner involves installation of the liner and cementing the annulus following the process discussed in Section 2.2.1.2. For the cemented liner, the cement isolates the annulus between the liner and the rock for multistage hydraulic fracturing. An uncemented liner is called an open-hole completion because of the open annulus outside the liner. However, isolation along the annulus for multi-stage fracturing can still be obtained through the use of a series of hydraulically set mechanical packers that are attached to the outside of the liner (Snyder and Seale, 2011). McDaniel and Rispler (2009) presents a discussion of a wider array of completion configurations for horizontal wells stimulated by hydraulic fracturing.

Multistage stimulation starts at the far end of the production interval first. For blank (unperforated) liners, openings in the liner for communication with the rock are generated using a perforating gun. This device sets off a set of shaped charges. Each shaped charge shoots a fast-moving jet of metal particles that makes a hole (perforation) that penetrates the casing, casing cement, and a short distance (~ 0.4 to 0.9 m or 1.31 to 2.95 ft) into the rock formation (Bell and Cuthill, 2008; Brady and Grace, 2013; Renpu, 2008). The process of multistage hydraulic fracturing using a perforating gun, called "plug and perf," provides the greatest control on placement of fractures. Beginning at the far end of the production interval where a set of perforations are opened, the fracture fluid (pad and fracturing fluid/proppant mixture) is injected and fractures the rock. Then a bridge plug is set that seals off the perforated and fractured segment from the remainder of the

production interval. The next set of perforations is then opened and fractured. This is repeated along the entire production interval (Snyder and Seale, 2011). After all stages have been fractured, the bridge plugs are drilled out to conduct flowback and oil production.

Perforation patterns are typically shot in clusters separated by 10.7 to 22.9 m (35 to 75 ft) or more (King, 2010). Each cluster is 0.305 to 0.71 m (1 to 2 ft) in length with about 20 perforations per meter (6 perforations per foot). The idea of a cluster is to initiate one main fracture from each cluster; the multiple perforations within a cluster help to find the easiest fracture initiation point. With the narrow spacing between perforations in a cluster, only one fracture will grow, because of the effects of the fracture on the local stress field that tend to suppress any other fractures trying to emerge from the cluster (King, 2010). For a typical stage interval of 61 or 91.4 m (200 or 300 ft), this results in about 4 to 7 clusters per stage. The plug and perf and sliding sleeve completions for a horizontal lateral are shown in Figure 2-10.

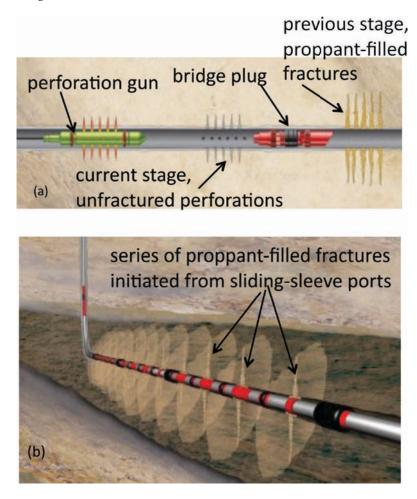


Figure 2-10. Horizontal well completion. a) plug and perf; b) sliding sleeve (source: Allison (2012))

Open-hole completions can also be accomplished using a sliding-sleeve liner which has pre-set ports that can be opened by size-specific actuator balls (Snyder and Seale, 2011). Multistage fracturing is conducted by dropping a series of actuator balls for each fracturing stage that simultaneously opens the pre-set ports in the uncemented liner and also seals off the far end of the production interval. After performing the fracturing operation, the next actuator ball is dropped and the next section is fractured. This is repeated along the entire production interval (Snyder and Seale, 2011). The actuator balls, which act like check valves, are recovered during the flowback phase after all stages have been fractured. Even more complex sliding sleeve liners can be used in which each sliding sleeve can be individually opened or closed from the surface through remote hydraulic actuators.

2.3.6 Fracturing Fluid Flowback

As mentioned, flowback is the fourth phase of a hydraulic fracturing operation. The flowback rates are typically high (0.00795 to 0.0159 $\rm m^3/s$, equivalent to 3 to 6 bbl/min) initially because of the high-pressure charge just delivered to the reservoir. However, these rates typically decrease quickly to less than 0.00265 $\rm m^3/s$ (1 bbl/min) after 24 hours, and to 0.0002 to 0.002 $\rm m^3/s$ (100 to 1,000 bbl/day or 4,600 to 46,000 gallons/day) after 2 or 3 weeks (King, 2012).

Natural formation brines get mixed with the recovered fracturing fluid and affect the composition of the flowback fluid. The natural formation waters of petroleum reservoirs often contain high levels of dissolved solids, organic components from contact with in *situ* hydrocarbons, and frequently higher levels of naturally occurring radioactive materials (NORM). The concentrations of dissolved solids, organics, and radioactive materials can be high because of dissolution of these constituents into the formation water during prolonged contact with rock and hydrocarbon (Guerra, Dahm, and Dundorf, 2011; Zielinski and Otton, 1999). These aspects are discussed in greater detail in Section 5.1.2.5.

Very few well-documented cases of detailed flowback rates and composition have been found. One of the more detailed analyses of flowback rates and composition that has been identified is for the Marcellus shale in Pennsylvania, an unconventional gas resource (Hayes, 2009). The flowback rate and total dissolved solids concentration for a particular case are shown in Figure 2-11. The input fracturing-fluid total-dissolved-solids composition ranges from 221 to 27,800 ppm, where higher levels may be due to recycling of fracturing fluid. The rapid increase in total dissolved solids during flowback indicates that a substantial amount of formation brine is mixing with fracturing fluid in the flowback stream after a few days of flowback (Haluszczak, Rose, and Kump, 2013). Another mechanism that can increase the salinity of the flowback is the dissolution of salt or other minerals from the formation into the fracturing fluid (Blauch, Myers, Moore, Lipinski, and Houston, 2009). See Section 5.1.2.5.1 for further discussion.

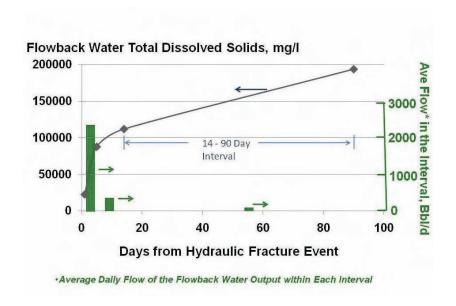


Figure 2-11. Example of flowback rates and totals dissolved solids composition from the Marcellus shale (source: Hayes, 2009).

2.3.7 Hydraulic Fracturing Process: Examples from the Bakken and Eagle Ford Plays

This discussion of the different phases of the hydraulic fracturing process will include examples of fracturing conducted in the Bakken and Eagle Ford plays. These unconventional reservoirs are considered analogous to shale reservoirs in California's Monterey Formation (described in detail in Section 4) because they compare favorably in terms of total organic content, depth, porosity, and permeability. However, there are significant differences in terms of depositional age, extent of natural fracturing, tendency towards great thickness, multiple lithofacies, tectonic activity, and folding (Beckwith, 2013). Section 3 discusses differences between hydraulic fracturing operations as currently implemented in California with hydraulic fracturing for unconventional shale reservoirs such as the Bakken and Eagle Ford.

As mentioned, the Bakken play is located in the Williston Basin in North Dakota, Montana, and Canada (Pearson et al., 2013). The upper and lower members of the Bakken are shales that are source rocks for oil. The middle member is the most frequent production target: It is a silty sandstone to silty dolomite, with permeability in the range of 0.1 md (9.87 x 10^{-17} m² or 1.06 x 10^{-15} ft²), and in North Dakota is found at depths of about 3,050 m (10,000 ft) (Pearson et al., 2013; Wiley, Barree, Eberhard, and Lantz, 2004). Production wells in the Bakken shale are typically horizontal wells with long laterals ranging from 2,290 to 2,900 m (7,500 to 9,500 ft) and use open-hole (uncemented) blank or sliding sleeve liners in the production interval (Pearson et al., 2013). A comparison of fracture

fluid volumes used within the middle Bakken member, shown in Table 2-2, found that slickwater fracture operations used about three times more fluid per length of lateral than wells using a hybrid method, and about four times more than wells employing a cross-linked gel (Pearson et al., 2013). This is in accord with the relationship between fracturing fluid type and volume shown on Figure 2-8.

Table 2-2. Variations in fluid volume and proppant use with treatment type (Pearson et al., 2013)

Treatment type	Average number of stages	Average stage spacing (m (ft))	Average fluid volume per lateral foot (m³/m (bbl/ft))	Average proppant weight per lateral length (kg/m (lbs/ft))
Slickwater	35	84.4 (277)	13.2 (25.3)	613 (412)
Hybrid	26	112.2 (368)	3.91 (7.5)	420 (282)
Cross-linked gel	29	103.3 (339)	3.44 (6.6)	570 (383)

The Eagle Ford play is composed of interbedded calcareous shale and calcisiltite (a rock consisting of fine-grained calcareous detritus), and massive calcareous shale or mudstone (Smith, 1981). The Eagle Ford play ranges in depth from 762 to 4,270 m (2,500 feet to 14,000 ft). Different parts of the play produce either oil and liquid-rich hydrocarbons or mainly gas (Stegent et al., 2010). The permeability of the Eagle Ford ranges from 1 to 800 nanodarcies (nd, which is 10^{-9} darcies) (9.87 x 10^{-12} m² to 7.9 x 10^{-19} m² or 1.06 x 10^{-20} ft² to 7.9 x 10^{-19} ft²). Production wells in the Eagle Ford more commonly used cemented blank liners with plug and perf completions (Greenberg, 2012). In the example discussed below, the horizontal well has a true vertical depth of 4,040 m (13,250 ft) with a lateral length of 1,160 m (3,800 ft), and produces at a high liquid/gas ratio (Stegent et al., 2010).

While acid preflush treatments have not been identified in examples from the Bakken play, Stegent et al. (2010) reported the use of 19.1 m³ (674 ft³ or 5,040 gallons) of 15% HCl for several Eagle Ford play horizontal wells prior to injecting fracture fluids for each stage. Examples from the Bakken and Eagle Ford use pad volumes that are about 20% to 30% of the total fluid injected (Wiley et al., 2004; Stegent et al., 2010). In the case of the Eagle Ford example, a hybrid fracture fluid scheme is used in which a linear gel alternating with a cross-linked gel is used as the pad and a cross-linked gel is used to carry proppant (Stegent et al., 2010). Furthermore, alternating injections of proppant-laden fluid with the pad fluids are used to transition to a final period of extended proppant injection. Pearson et al. (2013) report on the use of slickwater, cross-linked gel, and hybrid fracturing fluids for the Bakken shale. Hlidek and Rieb (2011) indicate an increase in the use of linear gel pad and a cross-linked gel for proppant injection.

The proppant injection stage constitutes the bulk of the remaining fluid injected for hydraulic fracturing. The final stage ends with a 37.9 m³ (10,000 gallons) or less overflush

of fracture fluid without proppant to clear proppant from the well and perforations. The entire injection profiles for the example cases from the Bakken and Eagle Ford plays are shown in Figures 2-12 and 2-13, respectively.

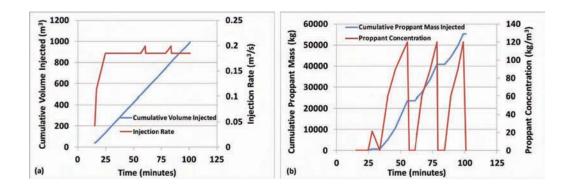


Figure 2-12. Slickwater fluid and ceramic proppant injection profile for the Bakken Shale example (a) Cumulative fluid injection and injection rate; (b) Cumulative proppant injected and proppant concentration (taken from Pearson et al., 2013, Figure 14).

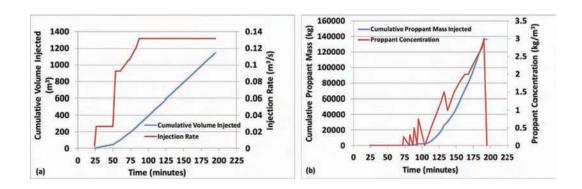


Figure 2-13. Hybrid fluid and sand proppant injection profile for the Eagle Ford Shale example (a) Cumulative fluid injection and injection rate [fluid type initially a linear gel followed by 15% HCl and then by alternating pulses of x-link gel and linear gel, x-link used exclusively from 95 minutes to the end]; (b) Cumulative proppant injected and proppant concentration [proppant mesh size 30/50 initially until 124 minutes and then 20/40 until the end] (Stegent et al., 2010). Note: about 60% of the 20/40 sand was a resin-coated proppant (Stegent et al., 2010).

In the case of the Bakken example, there were up to 30 stages per well for a 2,900-m (9,500-ft) lateral. For the Eagle Ford example, a 1,160-m (3,800-ft) lateral was treated with 11 stages. Therefore, the total fluid usage per well for the Bakken in this example is about 29,900 m 3 (1.06 x 10 6 ft 3 or 7.9 million gallons), as compared to about 12,500 m 3 (441,000 ft 3 or 3.3 million gallons) for the Eagle Ford case.

Based on the number of stages and lateral lengths, the average stage lengths in the two examples were about the same, with a length of 97 m (318 ft) for the Bakken and 105 m (344 ft) for the Eagle Ford. So the volume of fracturing fluid per well length is a bit higher in the Eagle Ford example (10.9 m³/m or 881 gallons/ft [gpf]) than the Bakken example (10.2 m³/m or 824 gpf). The higher fluid volume for the Eagle Ford as compared with the Bakken is consistent with the trend in Figure 2-8 given the lower permeability in the Eagle Ford. However, the much higher permeability in the Bakken than the Eagle Ford suggests there should be a larger difference in fracturing fluid volume. The small difference in fluid volume may result from the choice of fracture fluid not following the trend for permeability in Figure 2-8. The lower permeability of the Eagle Ford suggests that slickwater would be more likely to be used in that play and a gelled fracture fluid in the Bakken instead of the reverse, as was actually done. It may be that the difference in brittleness between the Bakken and Eagle Ford is a more important control on fluid selection than is permeability. These examples suggest the trends in Figure 2-8 may only be true on average, and that individual cases may deviate substantially.

After fracture fluid injection, the well is produced to remove the fracture fluids (but not the proppant). The flowback fluids are initially similar to the injected fracture fluids but gradually are displaced until aqueous-phase fluid compositions are controlled by the aqueous phase present in the reservoir, typically a higher-salinity fluid. The amount of fracture-fluid recovery varies considerably for different reservoirs and generally ranges between 5% and 50% of the injected volume (King, 2012). However, many of the fracture-fluid additives are not recovered because of sorption or are perhaps recovered as products of chemical reactions that occur in the reservoir. Polymers, biocides, and acids react and degrade under *in situ* reservoir conditions, and surfactants are adsorbed on rock surfaces.

2.4 Matrix Acidizing

Matrix acidizing is the oldest well stimulation method, with the first matrix acidizing treatment performed on carbonate formations near Lima, Ohio in 1895 (Kalfayan, 2008). Matrix acidizing may be distinguished from acid fracturing discussed in Section 2.3.4, in that the acid solution is injected below the parting pressure of the formation; therefore, hydraulic fractures are not created by matrix acidizing (Kalfayan, 2008).

The modern application of matrix acidizing is split into two broad categories: carbonate acidizing and sandstone acidizing. Hydrochloric acid (HCl) is very effective at dissolving carbonate minerals. For that reason, carbonate acidizing utilizes concentrated HCl injected into the formation to create wormholes that bypass formation damage around the well. However, because wormholes can penetrate up to 6.1 m (20 ft) from the wellbore, carbonate acidizing may also be used to stimulate carbonate formations that do not have significant formation damage around the well (Economides et al., 2013).

Sandstone acidizing utilizes alternating treatments of concentrated HCl and concentrated mixtures of HCl and hydrofluoric acid (HF), which are effective at dissolving silicate minerals. This type of acidizing treatment dissolves materials (such as drilling mud) that clog the casing perforations and pore networks of the near-wellbore formation. Sandstone acidizing is nearly always limited to treatment of formation damage within one or two feet of the well. The main exception to the limited range of treatment for sandstone acidizing is for naturally fractured siliceous formations, including shales and cherts (Kalfayan, 2008).

Matrix acidizing is not commonly used for stimulation of unconventional reservoirs. This is because these low-permeability reservoirs require the more deeply penetrating and intensive stimulation available from hydraulic fracturing to effectively produce oil or gas. A unique exception that has been identified is the use of sandstone acidizing stimulation to enhance oil production from a producing field in the Monterey Formation in California (Rowe, Hurkmans, and Jones, 2004; Trehan, Jones, and Haney, 2012; El Shaari, Minner, and Lafollette, 2011). Therefore, the remainder of this section will focus on sandstone acidizing.

2.4.1 Sandstone Acidizing

Sandstone acidizing typically consists of three injection phases: (1) an initial injection of HCl preflush; (2) injection of an HCl/HF mixture; and (3) a post-flush of diesel, brine, or HCl. After the injection phases the well is flowed back (Economides et al., 2013). The injection phases are conducted below the fracture pressure. Acid concentrations are dependent on formation mineralogy and permeability. The preflush HCl concentrations typically vary from 5% to 15%, while the HCl/HF mixture may have HCl concentrations from about 13.5% down to 3% and HF from 3% down to 0.5% in various combinations (Kalfayan, 2008). In general, higher permeability formations with lower clay and silt content are treated with higher acid concentrations (Economides et al., 2013).

The purpose of the HCl preflush is to dissolve carbonate minerals and displace formation water. Carbonate minerals react with HF to form insoluble precipitates that can cause formation damage. Organic acids, such as formic-acetic acid blends, are sometimes used alone or in combination with HCl for the preflush (Kalfayan, 2008). The preflush volumes are generally equal to 50 to 100% of the subsequent HCl/HF treatment volume.

The HCl/HF acid treatment is the main acid stage for sandstone acidizing. This acid targets siliceous minerals that are blocking flow paths to the well. These minerals may be siliceous particles from drilling mud, such as bentonite, that have invaded and blocked pores and fractures, or naturally occurring fine-grained sediments in the reservior. The contact time should be limited to 2 to 4 hours per stage to avoid mineral precipitation damage caused by HF reaction products.

Volumes injected generally range from 0.124 to 3.1 m³/m (10 to 250 gpf) of treated interval (Kalfayan, 2008). Injection rates are also important because of the reaction-rate kinetics, both for mineral dissolution and precipitation, the transport times for the acid to penetrate the formation, and because the injection pressure needs to remain below the fracture pressure (Economides et al., 2013). High-volume, high-rate treatments are typically limited to high-permeability, high-quartz content sands and fractured rock, including shales.

Sandstone acidizing is normally used only when formation damage near the well is impeding flow into the well. This is because penetration of a sandstone acidizing treatment into the formation is generally limited to about 0.3 m (1 foot). The maximum benefit of enhancing permeability in this limited region around the well for an undamaged formation is only about 20% (Economides at al., 2013). However, there is much less known about sandstone acidizing in siliceous reservoirs with permeable natural fractures, such as in some parts of the Monterey Formation (Kalfayan, 2008). In these circumstances, sandstone acidizing may be able to penetrate and remove natural or drilling-induced blockage in fractures deeper into the formation (Rowe et al., 2004; Patton, Pits, Goeres, and Hertfelder, 2003; Kalfayan, 2008). Kalfayan (2008) indicates that HCl/HF acidizing in naturally fractured siliceous rock uses high volumes > 1.24 m³/m (> 100 gpf). However, both low volume 0.248 m³/m (20 gal/ft) and higher volume 3.1 m³/m (250 gal/ft) HCl/HF treatments in fractured Monterey reservoirs have been reported (Patton, et al., 2003; Rowe et al., 2004).

The post-treatment flush displaces any live acid from the well and may be done with diesel, ammonium chloride solutions, and HCl (Economides et al., 2013). The volume of the post-flush should at least be sufficient to displace acid from the wellbore. After the injection phases are completed, the well is typically flowed back to recover spent-acid-reaction products to minimize damage caused by precipitation.

2.4.1.1 Sandstone Acidizing Fluid Composition

Similar to hydraulic fracturing fluids, a number of additives are generally included in the acid treatment fluids. In particular, corrosion inhibitors and iron control agents are always used. Corrosion inhibitors are needed to protect steel components in the well, such as the casing and tubing. Iron control agents react with dissolved iron and other dissolved metals to limit solids precipitation. Surfactants and mutual solvents are also often used, but not in all cases. Surfactants are needed to enhance the removal of spent acid during the backflow and to leave the formation in a water-wet condition (meaning water adheres to the rock more strongly than oil). Mutual solvents have been found to be useful in helping remove corrosion inhibitors that tend to adsorb onto rock and leave it in an oil-wet condition (meaning oil adheres to the rock more strongly than oil, which reduces oil production). Table 2-5 gives further information on these and other additives that are used in some cases.

Table 2-3. Sandstone acidizing additives (Kalfayan, 2008)

Additive type	Description of purpose	Examples of chemicals	Injection phase used	Typical concentration range
corrosion inhibitor	prevent corrosion of metal- lic well components	cationic polymers	all injection phases	0.1 – 2%
iron control agent	inhibit precipitation of iron, prevention of sludge formation	ethylenediaminetetraacetic acid (EDTA), erythorbic acid, nitrilotriacetic acid (NTA), citric acid	all acid phases	EDTA: 30-60* erythorbic acid: 10- 100* NTA: 25-350* citric acid: 25-200*
surfactant	aid in recovery of spent acid products	nonionic, such as polyethylene oxide and polypropylene oxide	all acid phases	0.1-0.4%
mutual solvent	help remove corrosion inhibitors	ethylene glycol monobutyl ether (EGMBE)	post-f ush	3-5%
nonemulsifiers	prevent acid-oil emulsions	nonionic or cationic surfactant	all acid phases	0.1-0.5%
antisludging agent	prevents formation of sludge from acid and high asphaltenic oils	surfactant and iron control agents	all acid phases	0.1-1%
clay stabilizer	prevent migration/ swelling of clays	Polyquaternary amines, polyamines	post-f ush	0.1-0.4%
fines-stabilizing agent	prevent migration of non-clay fines	organosilanes	all phases	0.5-1%
calcium carbonate / calcium sulfate scale inhibitor	prevent formation of calcium scale	phosphonates, sulfonates, polyacrylates	all acid phases	NA
friction reducer	reduce pipe friction	polyacrylamide	all injection phases	0.1-0.3%
acetic acid	reduce precipitation of aluminosilicates	acetic acid	HCI/HF phase	3%

^{*} pounds per thousand gallons of acid

2.4.1.2 Diversion

Placement of acid is an important element for effective sandstone acidizing. This is because the acid tends to flow into formation pathways that are most permeable. This is problematic, because acidizing treatments are generally intended to contact and improve the permeability of zones that are plugged and have a low permeability. Therefore, methods to divert acidizing treatments away from permeable zones and into the low-permeability zones are needed (Economides et al., 2013).

The main diversion methods are mechanical, including packer systems, ball sealants, and coiled tubing, and chemical, including particulate diverters, foams, and gels. Direct mechanical diversion is provided by packers which isolate the zones where the acid contacts the formation. Packers are an effective but somewhat resource-intensive diversion method.

Ball sealers are also a mechanical diversion method that injects 0.0159 to 0.0318 m (0.0512 to 0.104 ft) diameter balls made of nylon, hard rubber, or bio-degradable materials such as collagen, into the well (Kalfayan, 2008). The balls seat on and seal perforations, preferentially closing perforations that are taking most of the flow, thereby diverting flow to other perforations (Samuel and Sengul, 2003). The method requires high pumping rates and perforations that are in good condition to be effective. Coiled tubing is another mechanical diversion method. Coiled tubing is any continuously-milled tubular product manufactured in lengths that require spooling onto a take-up reel and have diameters ranging from 0.0191 to 0.102 m (0.0625 to 0.333 ft) (ICoTA, 2014). The tubing is sent down the well to the location where treatment is desired, and the treatment fluids are pumped through the tubing. The method is effective at delivering fluids at locations needed, but can result in pump-rate limitations because of the small tubing diameter, and the tubing can be damaged by acid corrosion causing leaks and tubing failure (Kalfayan, 2008).

Particulate diverters are a chemical diversion technique that uses benzoic acid, which precipitates into flakes or fines when the acid solution mixes with formation waters at reservoir conditions. The particulates then plug off the more actively flowing zones, and the acid treatment is diverted to locations where less of the diverting agent has been deposited. Gels and foams are viscous diversion treatments that reduce flow into higher permeability zones by the establishment of a bank of higher viscosity fluid in the region. Gels are more reliable, but can lead to problems if they cannot be subsequently broken and/or removed after the acidizing treatment (Kalfayan, 2008).

A final method that is applicable for high-rate injection schemes is known as maximum pressure differential and injection rate (MAPDIR) (Paccaloni, 1995). A similar approach is also used for carbonate acidizing (Economides et al., 2013). This method pumps the acid treatments at the highest rate possible without exceeding the formation fracture pressure. One of the advantages of this method is that diverting agents may not be needed. The method is useful for treating long, damaged, naturally fractured intervals.

2.5 Main Findings

The main findings of this section that are used in subsequent sections that evaluate hydraulic fracturing in California are the following:

(1) The design of a hydraulic fracture is a function of the reservoir's flow and mechanical characteristics. Reservoirs that are more permeable (within the permeability range where well stimulation is needed) and ductile tend to require less intensive fracturing. This leads to the use of a more viscous gelled fracturing fluid and a relatively smaller fracture fluid volume. Gelled fluids typically have more types and a higher total mass of chemical additives than slickwater. Reservoirs that have relatively low permeability and are brittle tend to require more intensive fracturing. This leads to the use of a less viscous slickwater fluid and a relatively larger fluid volume injected.

- (2) Acid fracturing is commonly limited in application to carbonate reservoirs. This is significant because California's oil resources are primarily found in siliceous rock rather than carbonate rock as shown in Section 3.
- (3) Matrix acidizing for siliceous reservoirs typically has a very limited penetration distance from the well into the formation. Therefore, this type of matrix acidizing tends to have a small effect on larger-scale reservoir permeability, with the possible exception of reservoirs where permeable natural fractures are present.

2.6 References

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Historic and Current Application of Well Stimulation Technology in California

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This chapter reviews the application of each of the three well stimulation technologies (WST) described in Chapter 2 for onshore oil production in California, and includes a review of the history of each technology's application, estimates of current deployment rates for each technology and the stimulation-fluid volumes and types typically utilized in California.

Hydraulic fracturing has been applied in numerous onshore oil fields in California for decades, starting in 1953. Intensive use of the technique commenced in the late 1970s and early 1980s. This was shortly before oil production in the state peaked (California Division of Oil, Gas, and Geothermal Resources (DOGGR) 2010). Data indicate hydraulic fracturing of 100 to 150 wells per month is a reasonable estimate of current activity. This amount of activity is the same as was occurring in the years prior to the recent recession. Most hydraulic fracturing currently occurs primarily in a few fields in the southwestern portion of the San Joaquin Valley in Kern County. In contrast to hydraulic fracturing predominantly of horizontal wells in the low-permeability Eagle Ford reservoir in Texas and Bakken in North Dakota, hydraulic fracturing of reservoirs in California occurs primarily in vertical wells requiring correspondingly smaller volumes of hydraulic fracturing fluid. This is in part because vertical wells have shorter treatment intervals than horizontal wells. It is also in part because gel, predominantly cross-linked, is used almost exclusively in California as compared to less viscous gels and slickwater in the other locations. The volumes per treatment length of less viscous fluids are typically up to several times the volumes used of cross-linked gel.

Based on available data, matrix acidizing has occurred in just a few fields, and more recently in just one field. A few tens of wells per month may be matrix acidized using combinations of hydrochloric and hydrofluoric acid. Recent data indicate all of this activity occurs in one field in the southwestern portion of the San Joaquin Valley in Kern County. The average acidizing fluid volume per well is a third to a fifth of the average hydraulic fracturing fluid volume in California. However, the average fluid volume per length of well treated is one half to two thirds of that used for hydraulic fracturing.

Acid fracturing generally uses hydrochloric acid in carbonate reservoirs, of which there are few in California. Those that do occur tend to be naturally fractured and no record of the use of acid fracturing in these reservoirs was identified. There is a recent record of acid fracturing of three wells using a hydrochloric and hydrofluoric acid combination. These are located in the same field as all recent matrix acidizing activity. The total fluid volume per well is similar to that for hydraulic fracturing, but the fluid volume per length of well treated implied by the available data is less than half that for matrix acidizing and a third to a fourth of that for hydraulic fracturing.

Section 2 explains that horizontal drilling technology is integral to hydraulic fracturing practice in many locations. Consequently, this section begins by considering the application of horizontal wells in California. The combination of horizontal wells and hydraulic fracturing in unconventional plays like the Eagle Ford and Bakken (primarily in Texas and North Dakota, respectively) has provided for economic development of those resources. However, horizontal wells can be used with or without well stimulation, as discussed in the next section. Discussion of horizontal wells is followed by discussion of well stimulation history and practice in California.

3.1 Horizontal Wells

In California, horizontal wells are used with and without well stimulation. This section discusses the historic application of horizontal wells without well stimulation followed by an assessment of recent horizontal well installation activity. Historic and recent stimulation of horizontal wells is discussed in Section 3.2 regarding hydraulic fracturing.

3.1.1 Historical Horizontal Well Utilization

The first horizontal-well-drilling technology was developed in the 1920s, but the immaturity of the technology led to only periodic use until the mid-1980s. By that time, the technology had been sufficiently developed such that the number of horizontal well installations for onshore oil production increased until the 1990s, when they became common (Ellis et al., 2000). Many thousands of horizontal wells had been installed in the United States by the mid-1990s (Joshi and Ding, 1996). The following is a review of the use of horizontal wells in California. Note that all of the fields mentioned in the discussion are located in the mid- to southern San Joaquin Valley.

Horizontal wells of a sort were drilled in the Kern River field in the early 1980s, but horizontal drilling technology had not yet reached maturity (Dietrich, 1988). Rather than advancing the horizontal lateral by turning a boring from vertical (as described in Section 2.2.2), the horizontal borings were drilled straight out in eight equiangular directions from within a large shaft excavated in the field. Production from these wells was below anticipated, and operation of the installation ended after recovering an additional 2.5% of the oil in place.

Horizontal wells as described in Section 2.2.2 have a number of applications in oil production (Ellis et al., 2000). They can have greater contact area with the petroleum-containing reservoir in near-horizontal layered geologic systems. In thinner reservoirs, vertical wells may not produce a volume of oil sufficient to make the well economic due to the short contact length between the well and the reservoir. Horizontal wells may be economic in these situations because they have a longer contact length with the reservoir, and so may produce a volume of oil that is sufficiently larger to make the horizontal well economic. Horizontal wells can also more readily intersect more natural fractures in the reservoir that may conduct oil, owing not only to their intersecting more of the reservoir than a vertical well, but also because fractures are typically perpendicular to rock strata, and so are nearly vertical in near-horizontal strata.

Horizontal wells can parallel water-oil or oil-gas contacts and so can be positioned along their length to produce more oil, without drawing in water or gas, than is possible from a vertical well. Due to their orientation parallel to geologic strata, horizontal wells can improve sweep efficiency during secondary or tertiary oil recovery, which involves the injection of other fluids, such as steam, to mobilize oil to a production well. A horizontal well also provides for more uniform injection to a particular stratum. On the production side, a horizontal well provides a more thorough interception of the oil mobilized by the injection. Vertical wells are more readily bypassed by mobilized oil due to variation in the permeability of the reservoir rock. Similar to being better positioned to intercept oil mobilized by injection, horizontal wells are also better positioned to intercept oil draining by gravity through a reservoir.

In California, horizontal wells have been used to access thin reservoirs, provide a more uniform distribution of steam injected to mobilize viscous oil, and better intercept oil draining by gravity. An example of a thin reservoir development is the installation of a horizontal well in a Stevens Sand layer of the Yowlumne field— a layer too thin to be developed economically using vertical wells. It was completed in 1991 at a true depth of over 3400 m (11,200 ft) with a 687 m (2,252 ft) lateral. The well tripled the production rate from the previous vertical wells in the reservoir (Marino and Shultz, 1992).

The use of horizontal wells for the second purpose, to improve the efficiency of steam injection for oil recovery began in the early 1990s. Steam injection reduces the viscosity of highly viscous oil, allowing it to flow more readily to production wells. For example three horizontal wells were installed in 45° dipping (tilted) units with a long history of steam injection in the Midway Sunset field. Two of the wells were installed with 121 m (400 ft) sloping laterals. They produced a volume of oil two to three times that of the nearby vertical wells, but these horizontal wells cost two to three times as much as vertical wells and so did not provide an economic benefit. A third horizontal well with a longer horizontal lateral of 213 m (700 ft) produced six times more oil than nearby vertical wells and so was more economically successful (Carpenter and Dazet, 1992).

Horizontal wells were also installed in a shallow, tilted (dipping) geologic bed in the Coalinga field in the early 1990s. Steam injection with oil production via vertical wells started in this zone in the late 1980s. The horizontal wells were installed in the same reservoir but deeper along the tilted bed. The wells were initially operated with steam cycling. This process entails injecting steam for a period, then closing the well to let the steam continue to heat the oil and reservoir, then opening the well and producing oil. However, the increase in production resulting from steam cycling was lower than expected. Vertical wells for continuous steam injection were subsequently installed shallower along the tilted bed from the horizontal wells. This resulted in a large sustained production rate that justified the horizontal wells, which led to considering further opportunities for installing horizontal wells in the Coalinga field (Huff, 1995).

By the late 1990s, horizontal well installation projects for production of shallow oil, using vertical steam injectors, involved tens of wells each. Nearly a hundred horizontal wells were installed in shallow sands containing heavy (viscous) oil in the Cymric and McKittrick fields from the late 1990s to early 2000s. These wells were installed in association with vertical wells that injected steam to reduce the viscosity of the oil by heating, allowing it to flow to the horizontal wells. The wells were installed in phases, allowing optimization with each phase that reduced the cost per well by 45% by the last phase (Cline and Basham, 2002). By the late 2000s and early 2010s, installation programs in reservoirs with steam injection involved as many as hundreds of wells. For instance, over 400 horizontal wells were installed in the Kern River field between 2007 and 2013, targeting zones identified with low oil recovery to date. These wells provided a quarter of the field's daily production (McNaboe and Shotts, 2013).

The third application of horizontal wells in California is for more efficient production of oil by gravity drainage. A prominent example of this is the installation of horizontal wells in a steeply dipping (60° from horizontal) sandstone reservoir in the Elk Hills field. Pressure to produce oil from this zone was maintained by injection of natural gas updip in the reservoir. The position of the gas-oil contact grew deeper as oil production proceeded. Production from vertical wells in the oil zone was reduced to limit the amount of overlying gas they drew in, which then had to be re-injected. The wells were also reconfigured periodically to move the top of the interval from which they produced to greater depths (Mut et al., 1996).

The first horizontal well in this reservoir was installed in Elk Hills in 1988; the second in 1990. The wells' laterals were installed 12 m (40 ft) above the oil-water contact and about 76 m (250 ft) downdip of the gas-oil contact. This allowed production rates multiple times that from the adjacent vertical wells without drawing in the overlying gas or water from below. Production was also more constant over time compared to the necessarily declining rates from the vertical wells (Gangle et al., 1991); production from one of the first two wells remained constant for at least five years (Gangle et al., 1991). Given the successful production from these wells, another 16 had been installed by early 1995 (Mut et al., 1996).

3.1.2 Recent Horizontal Well Installation

The GIS data files made available by DOGGR regarding oil, gas, and geothermal wells in California (DOGGR, 2014a) include the county and field in which the well is located, the date drilling was initiated, and whether the well was vertical (listed as "not directional" in the file), directional, horizontal, or had an unknown path. Review of a sample of recent well records available from DOGGR for directionally drilled wells indicates they are typically near-vertical in the reservoir, with the directional drilling employed primarily to offset (shift) where the well encounters the reservoir relative to the point from which it is drilled.

Of the more than 5247 wells with a drilling initiation date in 2012 or 2013, 85% list the type of well path. A total of 315 of these wells are listed as horizontal, which is 7% of the wells with a known path. Over 91% of the wells identified as horizontal are located in Kern County, and 68% are in the fields discussed in this section or indicated as having horizontal wells in Section 3.2.1 (on the history of hydraulic fracturing). The Kern River field alone contained 47% of the wells identified as horizontal. All but three of the horizontal wells—over 99%—were in pre-existing fields as defined by DOGGR. The three outside pre-existing fields were in Kern County. So in sum, a small percentage of recently installed wells in California are horizontal, the vast majority of these are in Kern County, and almost all are in pre-existing oil fields rather than in new development areas.

3.2 Hydraulic Fracturing

3.2.1 Historical Use of Hydraulic Fracturing

The earliest fracturing reported in California dates back to 1953 in the Cymric field of the San Joaquin basin—according to DOGGR (1998) — and in the Brea-Olinda and Esperanza fields in the Los Angeles basin—according to Ghauri (1960). The technique was applied in other fields, such as the Buena Vista, Sespe, and Holser fields, in the following decades (Erickson and Kumataka, 1977; Norton and Hoffman, 1982). This early fracturing was accomplished with water- and oil-based fluids, both gelled and ungelled (Ghauri, 1960; Erickson and Kumataka, 1977). Ungelled, oil-based fluids provided the best results (Erickson and Kumataka, 1977; Norton and Hoffman, 1982). These applications were typically in low-permeability sandstone to shale (Ghauri, 1960; Erickson and Kumataka, 1977; Norton and Hoffman, 1982).

The first reported hydraulic fracturing of diatomite in California occurred in the late 1960s. Diatomite is a high-porosity, low-permeability rock consisting primarily of siliceous matter from diatoms, a type of marine algae. It is a reservoir rock containing oil in some fields (see more information in Section 4). Multistage fracturing from vertical wells successfully treated a 230 m (750 ft) vertical interval of diatomite in the Lost Hills field. Oil production increased relative to untreated wells, but only for two months. The increase was insufficient for the treatments to be economic (Yarbrough et al., 1969). Further

development of the technique in the diatomite led to its economically viable application by the late 1970s (Emanuele et al., 1998). Hydraulic fracturing of the diatomite in the San Joaquin Valley became relatively standardized within companies in the following decades, but practice varied from company to company (Allan et al., 2010).

The first successful production resulting from hydraulic fracturing in diatomite at the South Belridge field occurred in 1977 (Allan et al., 2010). By the early 1980s, one operator had hydraulically fractured hundreds of wells in the diatomite at South Belridge, as well as at several other fields (Strubhar et al., 1984). Water flooding of the diatomite in the South Belridge field started in the late 1980s, and hydraulic fracturing of both injectors and producers was standard practice (Yang, 2012). Water flooding involves injection of water into an oil reservoir to drive more oil to the producing wells.

The first horizontal wells were installed in the South Belridge field in the early 1990s. They were installed in permeable sands with oil overlying the diatomite and (therefore) were not hydraulically fractured; they did not produce sufficiently. Horizontal wells were subsequently installed in the diatomite and hydraulically fractured in stages. Vertical wells were found to be a better approach in zones with oil thicker than 137 m (450 ft) toward the center of the field. Horizontal wells were installed in the thinner oil zones consisting of diatomite recrystallized to opal CT (see Section 4.2.2) along some margins of the field. Orienting the wells for longitudinal fractures was found to result in greater production (Allan et al., 2010). (As described in Chapter 2, a longitudinal fracture is oriented in the same direction as, rather than perpendicular to, the horizontal well from which it extends, which is generally an advantage in relatively more permeable formations.)

The development history of the diatomite in the Lost Hills field is similar to that in the South Belridge field. Hydraulic fracturing was implemented in the Lost Hills field in 1976 (Fast et al., 1993); fracturing was from vertical wells (Strubhar et al., 1984; Hansen and Purcell, 1989). In the early 1990s, water flooding of the diatomite in the Lost Hills field was implemented to improve production and reduce ground subsidence. The vertical injectors and producers were hydraulically fractured (Wilt et al., 2001). By the mid-1990s, over 2,700 hydraulic fracture stimulations had been completed (since the late 1980s) in diatomite at Lost Hills (Nelson et al., 1996). Subsequently, tens to hundreds of hydraulically fractured vertical wells were installed per year through at least 2005 (Hejl et al., 2007). Horizontal wells in the thinner oil zones along the margins of the field were first installed in the mid-1990s. The first test wells were oriented for transverse fractures (perpendicular to well direction). Based on the results, subsequent horizontal wells were installed oriented for longitudinal fractures (Emanuele et al., 1998).

Hydraulic fracturing of the siliceous shales in the Lost Hills field is reported as early as the 1960s as well (Al-Khatib et al., 1984). These shales are diatomaceous mudstones that recrystallized due to the large depth of burial, as discussed further in Section 4.2.2. Hydraulic fracturing during the 1960s through most of the 1970s, in an area with naturally-occurring fractures, did not significantly improve production. In 1979, oil was

found in nearby areas without natural fractures and was successfully produced after hydraulic fracturing. This was followed in the early 1980s by the installation of hundreds of vertical wells fractured over 30 to 120 m (100 to 400 ft) vertical intervals.

The reported hydraulic fracturing fluid types used since the 1970s are all water-based and predominantly gels. For instance, Hejl et al. (2007) reports the various gels used to fracture the diatomite at Lost Hills starting in the 1980s. Fracturing with gels is noted in the McKittrick field in the mid-1990s (Minner et al., 1997; El Shaari et al., 2005) and in the Belridge field at the same time (Allan et al., 2010). One of the Stevens Sand reservoirs at Elk Hills field was fractured with gels starting in the late 1990s (Agiddi, 2004, 2005).

A similar progression from vertical to horizontal wells occurred in the North Shafter field. Production was established from hydraulically fractured vertical wells starting in 1982, and installation of hydraulically fractured horizontal wells commenced in 1997 (Ganong et al., 2003). Horizontal wells in the similar Rose field nearby were oriented for longitudinal fractures, but fracturing resulted in complex fractures with both transverse and longitudinal components. This was attributed to almost equal stress in all directions (Minner et al., 2003). Production from these fields is from a quartz-phase shale (Ganong et al., 2003). This is a more recrystallized form of diatomite, due to greater burial depth, as explained in Section 4.2.2.

As described above, hydraulic fracturing has been used to produce oil from diatomite, opal CT and siliceous shale, and quartz-phase shale. These represent the various rock types from diatomite at different depths, indicating the broad range of applicability of hydraulic fracturing to this rock sequence. Besides diatomite and rock derived from diatomite, hydraulic fracturing has also been used in low-permeability sandstones. For instance, such rocks have been successfully targeted in the Elk Hills, North Coles Levee, and Mount Poso fields (Underdown et al., 1993; Agiddi, 2004; Evans, 2012).

For decades all the reported fluids have been water-based, but the type of fluid used has changed through time in some locations to better match conditions. For example, ungelled water was successfully used for fracturing in the Edison field. Ungelled water subsequently replaced the gels used for hydraulic fracturing previously in the Tejon field. The ungelled fractures provided economically viable results as opposed to the gelled fractures (Mathis et al., 2000). Research starting in 2002 led to switching from cross-linked gels, described in Section 2.3.2, to low-polymer-concentration gels to minimize plugging of the natural pores in a low-permeability sandstone reservoir in the Elk Hills field (Agiddi, 2005).

To develop a more comprehensive understanding of hydraulic fracturing activity over the last decade, well records were sampled to estimate the percent of all wells hydraulically fractured, the result of which was then used to extrapolate the number of hydraulically fractured wells in California. The well records in the sample were searched to identify wells in which hydraulic fracturing operations have occurred. Well records are publicly available from DOGGR in the form of scans without searchable text (DOGGR, undated).

Through application of optical character recognition software, DOGGR provided versions of the records with searchable text for all wells identified as first producing oil after 2001 outside of Kern County, and for a selected sample of such records inside Kern County (Bill Winkler, DOGGR, personnel communication). Presuming the 20% of the wells were fractured, the size of the well record sample size was selected to provide a 95% probability of the estimated proportion being within 2% of the actual proportion, using a finite population correction factor.

The well-record search provided information on the number of hydraulic fracturing operations over time. An operation consists of all the stimulation stages performed in a well during a single entry, typically over a period of hours to days. Records indicating that a well was hydraulically fractured were identified using the search term "frac". The space after the term avoided occurrences of the term "fracture," which appears in the template information on some forms, and consequently the term is not correlated with wells that have been hydraulically fractured. The term "frac" was found to correctly identify more such records of hydraulic fracturing than other potential terms, such as "fracture," "stimulation," "stage," and "frack." The few records containing the latter term also all included the term "frac". Records containing "frac" were reviewed to determine if hydraulic fracturing indeed occurred. In some cases a record containing "frac" was for a well that was not hydraulically fractured because this term was also used in descriptions of geologic materials and the fracture gradient (the minimum fluid pressure per depth that will fracture the rock in a particular location). For Kern County well records, over 90% of the records containing "frac" indicated hydraulic fracturing had occurred. For all other counties as a group, fewer than 40% of the records containing "frac" indicated hydraulic fracturing had taken place.

Figure 3-1 shows the average annual number of wells with first production (in three different time periods) that have a record of hydraulic fracturing. This figure does not represent an estimate of the total amount of hydraulic fracturing activity, however, because not all hydraulic fracturing jobs were recorded in the well records, and this well-record search pertained only to production wells and did not include injection wells, which are also hydraulically fractured in some locations. Injection well records were not searched.

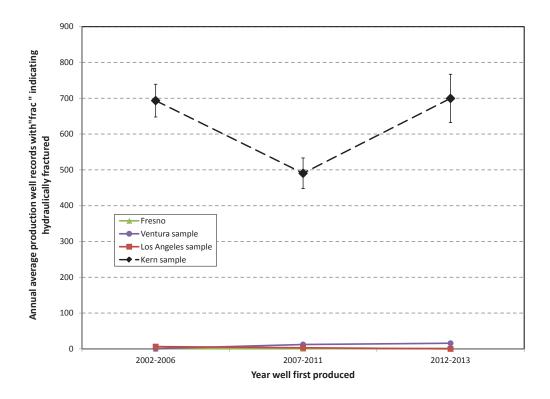


Figure 3-1. Average annual number of wells with first production in different time periods that were hydraulically fractured. There is a 95% chance that if all the well records had been searched rather than a sample, the average annual number of wells indicated as hydraulically fractured would be within the range indicated by the vertical bars.

Hydraulic fracturing occurred in Kings, Monterey, and Santa Barbara counties, in addition to those shown in Figure 3-1. Kings County is not shown on the figure because the average annual number of operations was less than two. For Monterey and Santa Barbara counties, records were available for a portion of all the wells. For the 2007-2011 time period in these counties, the search results from this well record sample and the size of the sample compared to the total number of wells indicate a 95% likelihood that the average annual number of hydraulic fracturing operations is fewer than two. In the other time periods for Monterey and Santa Barbara counties, and in all three time periods for Orange and San Luis Obispo counties, no hydraulic fracturing operations were identified in the available well records. However, because records for many wells in these counties were not available, the well record sample size is too small to provide confidence in a quantitative result.

Figure 3-1 indicates that about 60 production wells per month are fractured, with almost all this activity in Kern County. It also indicates that the number of recent hydraulic fracturing operations is similar to that before the recession in 2008. This contrasts with the fact that hydraulic fracturing activity increased substantially in other parts of the country.

3.2.2 Current Use of Hydraulic Fracturing

There is no comprehensive source of information on hydraulic fracturing activities in California. However, in addition to the results of the well-record search above, there are four useful sources of data regarding recent and pending hydraulic fracturing in California: FracFocus, FracFocus data compiled by SkyTruth, DOGGR GIS data files, and well stimulation notices. These are each described below.

FracFocus is a website used by the oil and gas industry to voluntarily disclose information about drilling and chemical use in hydraulic fracturing. The site was created in 2011 by two industry groups, the Interstate Oil and Gas Compact Commission, and the Groundwater Protection Council. Operators uploaded information on their hydraulic fracturing activities, which were (and still are) posted on the site as PDF documents for each individual fracturing job. The reports include a unique identifier for each well (an American Petroleum Institute (API) number), the well name and location, and information about the type and quantity of chemicals used. Many of the reports also include the volume of water used, although they do not report the source or type of water, i.e., operators do not report whether they used freshwater or produced water, nor whether water was withdrawn from a well, public supply, or another source. FracFocus provides voluntary disclosures that are not required to be either accurate or complete.

FracFocus data for hydraulic fracturing in California through the end of 2013, available as of January 21, 2014, were provided for this review by a DOGGR staff member with administrative access to the site (Vincent Aguseigbe, DOGGR, personal communication). The FracFocus data file provided was missing data for some fields. Upon inspection, it was determined much of the missing data were present in the individual PDF reports posted on the FracFocus website, and also available in the database compiled from the data available in FracFocus as of the end of July 2013 by the organization SkyTruth. This included data on hydraulic fracturing operations through April 2013. The information in the SkyTruth database was used to fill in almost all the missing records, with information from the PDFs on FracFocus entered for a few missing water volumes (Skytruth, 2013).

The third data source is geographic information system (GIS) data files maintained by DOGGR regarding oil, gas, and geothermal wells in California (DOGGR, 2014a). These files include some information on wells that was not available in the FracFocus database, such as whether a well had been directionally or horizontally drilled. These additional columns were added to the FracFocus database by joining records based on the API number for the well, which is a unique identifier for each well in the United States. The GIS well data file also included the dates that drilling and installation of some wells commenced, the measured depth of some wells, and voluntary identification of wells that were hydraulically fractured.

The fourth data source is well stimulation notices filed by operators posted by DOGGR as required by California Senate Bill 4 of 2013 (SB 4), which took effect on January 1, 2014. Under SB 4 operators must obtain permits at least 30 days prior to commencing a well stimulation treatment, and the notices must include basic information about water and chemical use (Pavley, 2013). Operators began filing notices in December 2013 for operations beginning in January 2014. Notices posted by DOGGR as received through January 15, 2014 are considered (DOGGR, undated).

The FracFocus database described above was the main source of information for analysis. However, these data are based on voluntary reports by operators and do not capture the full extent of hydraulic fracturing in California. There is evidence that the reports posted on FracFocus underestimate the extent of hydraulic fracturing occurring in California, especially before May 2012. FracFocus includes reports of 89 fractured wells in 2011, while the Western States Petroleum Association (WSPA) reports that during the same year, "WSPA member oil companies conducted some form of hydraulic fracturing operation on 628 wells" (WSPA, 2013). WSPA is the main oil and gas industry organization in California, and represents 80% of the state's suppliers (Kiparsky & Hein, 2013, note 14, page 48). The number of hydraulically fractured wells reported by WSPA is equivalent to over 50 wells per month on average in 2011, This contrasts with about 15 wells per month hydraulically fractured in 2011 according to FracFocus, indicating FracFocus did not capture all hydraulic fracturing operations during that period.

Data from the first three sources were loaded into a relational database (Microsoft Access), to perform queries and summaries. The data were cleaned to remove obvious errors, including typos, missing information, and duplicates. In total, the database of known hydraulically fractured oil and gas wells in California between January 30, 2011 and December 31, 2013 included 1,478 records of hydraulically fractured wells, of which 1,453 were distinct wells (several wells have been fractured more than once).

Analyses of the FracFocus data along with DOGGR's GIS well layer provide some understanding of recent hydraulic fracturing activity in California. The number of onshore hydraulic fracturing operations for oil per month reported in FracFocus and DOGGR's well database is shown on Figure 3-2. For the DOGGR data, the date shown in Figure 3-2 is when drilling started, because that is the only date available. The fracturing operation presumably occurred sometime later.

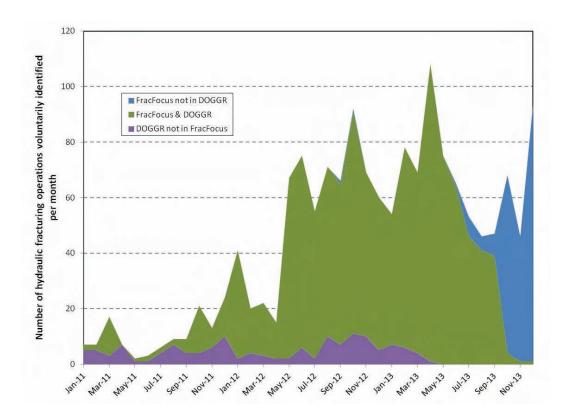


Figure 3-2. The number of fracturing operations per month summed from FracFocus and DOGGR's well table.

Figure 3-2 shows a sharp increase in the number of hydraulically fractured wells reported to the FracFocus in mid-2012. This followed a DOGGR notice to operators in March 0123 requesting they voluntarily report data on their fracturing operations to FracFocus (Kustic, 2012). This provides further evidence that the FracFocus data do not capture all hydraulic fracturing activity, particularly in 2011 and 2012. Considering only the period after April 2012, the average number of reported operations is 69 per month.

Figure 3-3 shows the comparison between the FracFocus data and the results of the well-record search, accounting for the Kern County well-record sample proportion of one quarter for the 2012 to 2013 time period. Figure 3-3 shows the well-record search identified about 80% of the wells in FracFocus. The well-record search identified about 10% more wells compared to the number of hydraulic fracturing operations in FracFocus. Based on the FracFocus average of 69 wells per month, this suggests a total monthly activity of 76 operations.

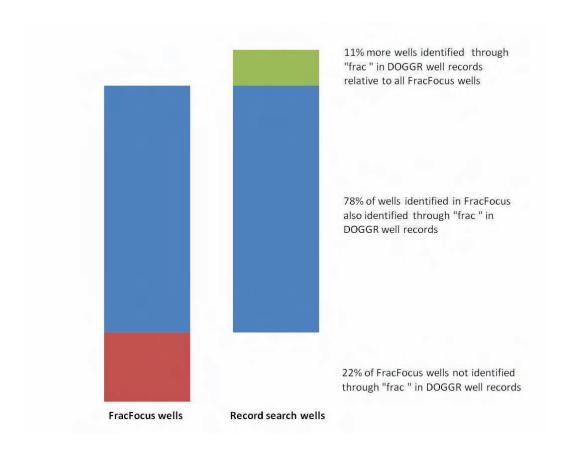


Figure 3-3. Overlap between wells indicated as fractured in FracFocus and in well records during May 2012 through October 2013, which is the period of greatest overlapping coverage between the two sources.

However, because this number is based on voluntary and incomplete reports, the count of hydraulic fracturing notices received by DOGGR provides a check. As of this writing, DOGGR has posted the notices it received in December 2013 and the first half of January 2014. DOGGR received 195 hydraulic fracturing notices in December. Of these 190 were approved and five were subsequently withdrawn. In contrast, 18 notices have been posted for the first half of January, but that number is low because DOGGR stopped approving submittals received without groundwater monitoring plans as of January 1, 2014 (Vincent Agusiegbe, DOGGR, personal communication). The number of notices submitted in December 2013 suggests the monthly average number of hydraulic fracturing events may be greater than 76 based on FracFocus and the well record search. Because of this, for the purposes of this study, the estimated monthly number of hydraulic fracturing events per month in California is taken as 100 to 150. For comparison, over one million hydraulic fracturing operations are estimated to have occurred throughout the United States (King 2012), with over 100,000 of these in recent years (Ellsworth 2013).

The December notice count suggests a number of operations per month two to three times as great as indicated by the voluntary data sources, if it is assumed that all these operations were to be carried out in January. However, while the notices must be submitted in advance of the fracturing operation by at least 30 days, a notice can be submitted some indeterminately greater amount of time in advance. The December notices include large groups of notices identical except for the well details, suggesting that operators submitted project plans for a period longer than a month. Doing so would provide some level of efficiency for the operator. Thus, the December notice count provides a high-side estimate of monthly activity for the post-SB 4 period.

All of the data sources also provide for estimating where hydraulic fracturing occurs. Joining FracFocus to DOGGR's GIS well data file provided information on the oil field where each well is located. This indicated that 93% of the wells in FracFocus are located in North and South Belridge, Lost Hills and Elk Hills fields on the west side of the southern San Joaquin Valley. Considering wells indicated as hydraulically fractured whose drilling started after April 2012 in DOGGR's GIS well files, 94% are in these four fields. From the well-record search, 87% of the wells identified as fractured with first production after 2011 were in these four fields, while 91% identified from the previous decade were in these fields. A total of 94% of the first 208 hydraulic fracturing notices posted (those listed as received through January 15, 2014) list these four fields. Consequently, all the data sources indicate that most of the hydraulic fracturing activity is in these four fields.

The three data sources (well-record search results, FracFocus, and DOGGR's GIS well data files) along with the literature identify 69 fields with a record of hydraulic fracturing out of the 303 onshore oil fields with field boundaries from DOGGR (DOGGR, 2014b). None of the data sources described above provides thorough identification of onshore oil fields that have been hydraulically fractured, and it is unlikely that they provide such thorough identification in combination. More fields have likely been hydraulically fractured than are shown in Figure 3-4. Ventura County was the only other county besides Kern with wells indicated by the hydraulic fracturing notices. Three notices were submitted for wells in Ventura County.

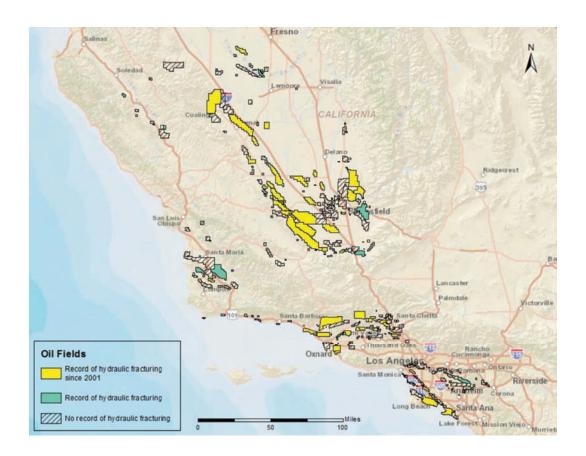


Figure 3-4. Onshore oil fields with a record of hydraulic fracturing.

3.2.3 Fluid Volume

Based on voluntary disclosures by operators in the FracFocus database, average water use for hydraulic fracturing in California was 490 $\,\mathrm{m}^3$ (130,000 gallons) per operation. This is similar to the average annual water use of 580 $\,\mathrm{m}^3$ (153,000 gallons) in each household in California over the last decade. This is based on residential water use of 0.54 $\,\mathrm{m}^3$ (143 gallons) per person per day (Department of Water Resources, 2013) and an average household size of 2.93 people (US Census Bureau, 2014).

There is considerable variation in the water use per operation, as shown on Table 3-1 and Figure 3-5. The minimum water use was 23 m 3 (6,000 gallons) per well, and the maximum was 17,000 m 3 (4.4 million gallons) per well. As a result, the coefficient of variation for these data is high (1.7), meaning that the standard deviation is larger than the mean, or that there is a large spread in the amount of water used. The 90% confidence interval for the mean water use is 470 to 540 m 3 (120,000 to 140,000 gal) per well.

Table 3-1. Base water volume statistics from FracFocus and hydraulic fracturing notices.

	FracFocus Voluntary (2011–2013)	•	Hydraulic Fracturing Notices (Dec. 2013 - Jan 2014) 213		
Number of Records:	1,478				
	Cubic meters	Gallons	Cubic meters	Gallons	
Minimum	23	6,000	240	63,000	
10%-ile	83	22,000	760	200,000	
25%-ile	180	48,000	760	200,000	
50%-ile (Median)	280	74,000	760	200,000	
75%-ile	530	140,000	760	200,000	
90%-ile	1,100	280,000	950	200,000	
Maximum	17,000	4,400,000	1,800	250,000	
Average (arithmetic mean)	490	130,000	790	210,000	
Standard deviation	830	220,000	230	60,000	
Coefficient of Variation	1.7	1.7	2.8	0.28	

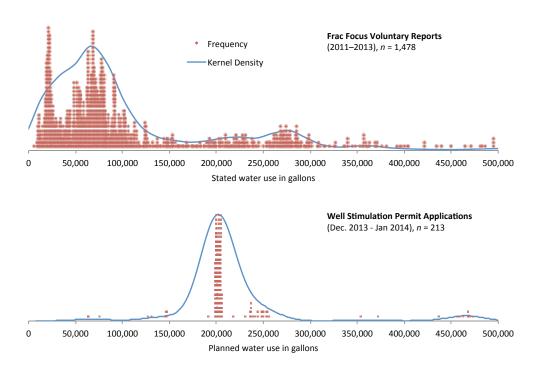


Figure 3-5. Water use per hydraulic fracturing operation in California according to (top) FracFocus voluntary reports and (bottom) hydraulic fracturing notices.

In Figure 3-5, each dot represents a single fracturing operation. The overlay line represents the smoothed data density. Note that the bulk of the reported water use from 2011 to 2013 in the FracFocus database is below 100,000 gallons per well, but that the data set is highly skewed with a "long tail," or many high observations. Of the 1,478 FracFocus reports, there are 47 observations over 500,000 gallons per operation, and 11 observations over 1 million gallons per operation. The distribution is also represented in log space on Figure 3-6, which shows that it is relatively log normal, with some right skew due to the few highest values.

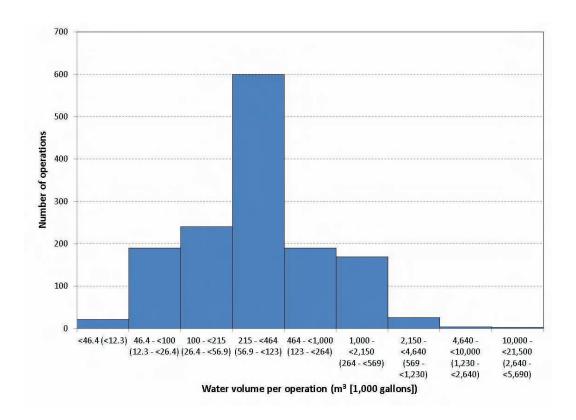


Figure 3-6. Distribution of water volumes in FracFocus per hydraulic fracturing operation.

Table 3-1 and Figure 3-5 summarize the water volume used per hydraulic fracturing operation according to two data sources. The notices contain a water-volume estimate because operators are required to file a water-management plan with the following information (California Public Resource Code Section 3160, subdivision (d) (1) (C)):

- i. An estimate of the amount of water to be used in the treatment. Estimates of water to be recycled following the well stimulation treatment may be included.
- ii. The anticipated source of the water to be used in the treatment.

iii. The disposal method identified for the recovered water in the flowback fluid from the treatment that is not produced water included in the statement pursuant to Section 3227.

As indicated in Table 3-1 and Figure 3-5, planned future water use for hydraulic fracturing reported by operators is somewhat higher than historical water use over the last three years. Among the 213 notices for hydraulic fracturing, planned water use averaged 790 m³ (210,000 gallons) per operation, with a standard deviation of 230 m³ (60,000 gallons). Thus, the planned water use in the notices is higher than the historical average reported in the FracFocus database, but has a smaller variance.

Among the hydraulic fracture notices, many report the same planned water use. It is of note that one company, Aera Energy LLC, which submitted the majority of the hydraulic fracturing notices (174 of 213), included the identical water plan in 171 of those cases. This plan stated that "the maximum [emphasis added] volume of fresh water used in the treatment will be 4,800 barrels (201,600 gallons)." In this case, the planned water use of 763 m³ (201,600 gallons) per operation was entered in the database. Because this represents a maximum planned water use, it may bias the results upwards, causing an estimated higher average water use than will actually take place. Because the majority of hydraulic fracturing notices are exact copies of one another, they may not capture the variability in water use that is likely to occur in the field.

The relationship between water use and a number of independent variables (e.g., time, well depth, perforation length, region, and operator) was examined. It does not appear that there is a significant trend in water use over time as shown in Figures 3-7, nor does there appear to be a strong relationship between the volume of water used and the depth of the well as shown in Figure 3-8. Water use has varied widely from early reports in 2011 until the end of 2013, and there is not a statistically significant trend in water use with time. However, each of the four largest observations of water use (all over 11,400 m³ (3 million gallons)) occurred during the second half of 2013. It is not known whether these high outliers are isolated experiments or indicative of future trends.

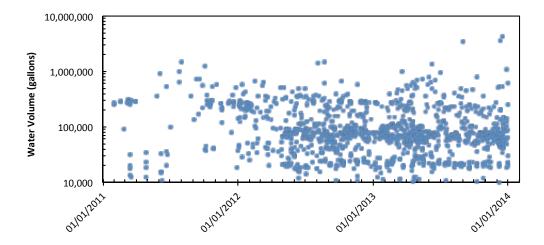


Figure 3-7. Time series of water volume used for each hydraulic fracture operation in California according to information voluntarily reported by operators to FracFocus during 2011-2013.

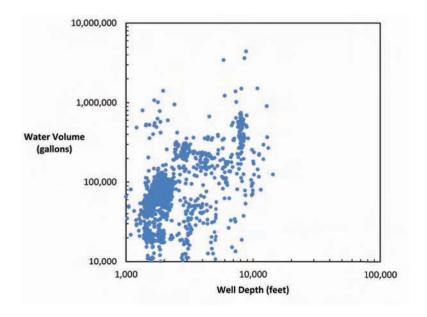


Figure 3-8. Volume of water used for each hydraulic fracture operation in California versus the absolute vertical depth of the well, according to information voluntarily reported by operators to FracFocus during 2011-2013.

The DOGGR well database contained data on well configuration for a total of 1,090 wells that are also listed in FracFocus. It was found that hydraulic fracturing operations in horizontal wells use more water on average in California than in directional and non-directional wells (DOGGR's term for vertical wells). Average water use per operation for each well configuration is shown in Table 3-2. Water use for operations in directional wells was slightly higher on average than for wells that were non directional; however, the difference in the means is not statistically significant (according to a two-tailed t-test for difference in sample means, P = 0.16). Operations in horizontal wells use significantly more water than vertical wells (two-tailed t-test, P < 0.001); average water use in these operations is nearly three times higher than the water use for operations in other wells.

Table 3-2. Average water use per hydraulic fracture operation in wells in California by their directional drilling status

		Not directionally drilled	Directionally drilled	Horizontally drilled
Past Fracturing Activity in the FracFocus database	Number	213	833	44
	Water Use (m3)	370	420	0.17
	Stdev (m3)	350	500	1,000
	Water Use (gallons)	99,000	110,000	300,000
	Stdev (gallons)	92,000	130,000	270,000
Future fracturing activity from Well Stimulation Notices	Number	11	194	8
	Water Use (m3)	760	780	1,800
	Stdev (m3)	0*	130	40
	Water Use (gallons)	200,000	210,000	460
	Stdev (gallons)	0*	35,000	11,000

^{*} Aera Energy submitted each of the 11 notices for non-directionally drilled wells to be hydraulically fractured, and states in each notice that "the maximum volume of fresh water used in the treatment will be 4,800 barrels," or 201,600 gallons, thus there is no variability among these 11 observations.

The average volumes from both FracFocus and the notices for California hydraulic fracturing operations contrast with the average volume per operation of 16,000 m³ (4.25 million gallons) reported by Nicot and Scanlon (2012) for fracturing horizontal wells in the Eagle Ford in Texas. Table 3-2 indicates part of this difference is caused by the predominance of hydraulic fracturing of vertical and directional wells over horizontal wells in California, while horizontal wells are predominant in the Eagle Ford. This is particularly the case as review of a small sample of directionally-drilled-well records indicates they are typically vertical or close to vertical through the producing zone. The well path primarily deviated from vertical above the production zone to offset the location at which the well entered the producing zone from the location where the well was drilled. The well records available from DOGGR for the wells indicated as horizontal

by DOGGR were also examined. Only half of these wells are actually horizontal according to the records. The average hydraulic fracturing water volume per operation in just those wells is 1,700 m³ (450,000 gallons) with a standard deviation of 170 m³ (48,000 gallons). This volume, as well as that listed on Table 3-2 from the hydraulic fracture notices for horizontal wells, are both about one-tenth the average volume per well in the Eagle Ford.

Average water use intensity per unit length of well hydraulically fractured was estimated using information in the hydraulic fracturing notices submitted by operators to DOGGR. Most of the notices for vertical and directionally-drilled wells provide the anticipated measured top and bottom depth of the stimulation interval, as well an estimated water volume. The average intensity is given on Table 3-3. Water use intensity was also calculated for the 21 wells with water usage in FracFocus indicated as horizontal in DOGGR's well file and confirmed as horizontal in each well's record. The hydraulic fracturing treatment length is not available for these wells, so the intensity calculation used the distance between the shallowest and deepest production casing perforations listed in well records. This small data set contained a high outlier where the water use intensity (water volume per well length stimulated) was 13 m³/m (1,000 gallons per foot, or gpf). The average water use intensity for these horizontal wells, excluding this high observation, is also given on Table 3-3. The perforated length explains about 40% of the variability in water use among the remaining 20 operations. The comparison to average water use intensity in the Eagle Ford and Bakken on Table 3-3 indicates intensities in California are similar to gels in the Bakken, but considerably less than the average intensity in the Eagle Ford and slickwater in the Bakken.

Table 3-3. Average water use intensity from hydraulic fracturing notices and FracFocus horizontal well disclosures compared to average intensity in the Eagle Ford (Nicot and Scanlon, 2012) and for different fluid types in the Bakken (described in section 2.3.7)

	Notices	lotices FracFocus- Eagle Ford		Bakken		
	Notices	horizontal	•		Hybrid	Slickwater
		m3/m (gallons per ft)				
Average intensity	3.0 (244)	2.3 (190)	9.5 (770)	3.4 (277)	3.9 (315)	13.2 (1063)
Standard deviation	0.9 (74)	1.6 (130)	3.4 (277)			

The water volume per hydraulic fracture operation was mapped to determine whether there are geographic patterns to water use. There are several apparent clusters of similar water use, as shown in the example in Figure 3-6. This figure shows a cluster of water volumes per operation of 950 $\rm m^3$ to 1100 $\rm m^3$ (250,000 to 300,000 gallons) per well. These wells are operated by XTO Energy/Exxon Mobil. Operations immediately to the north and south have a water use averaging about 190 $\rm m^3$ (50,000 gallons) and were

conducted by Area Energy LLC. Another cluster of high-water-use operations occurs near the border of Belridge North and Belridge South fields and were conducted by BreitBurn Energy Partners L.P.

The FracFocus data indicate that the water used in each fracturing operation varies by company and that the operator of a well is a more important predictor of water use than any other factor, as shown in Table 3-4, which ranks companies from high to low in terms of their average per-operation water use. A statistical test (single factor or one-way ANOVA) among the six companies with more than 10 hydraulically fractured wells indicates water use varies significantly by company (P-value less than 10^{-56}). In fact, the operator is a better predictor of water use per operation than any other factor considered. This is consistent with the statement by Allan et al. (2010) that fracturing of diatomite has become relatively standardized within companies, but varies from company to company.

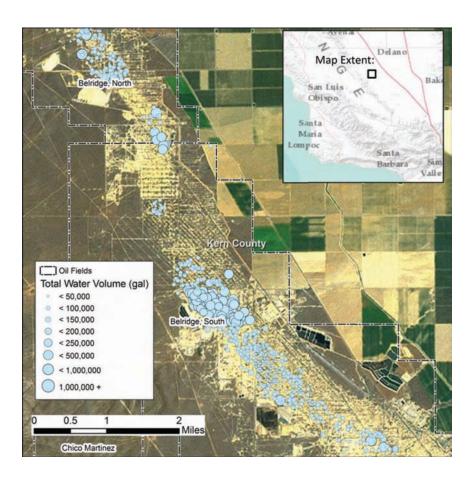


Figure 3-9. Hydraulically fractured oil wells in the Belridge North and Belridge South fields in Kern County, California. The diameter of the point is proportional to the volume of water used in hydraulic fracturing.

Table 3-4. Water volume used per hydraulic fracturing operation per operator according to data voluntarily reported to FracFocus for January 2011 to December 2013.

Operator	Number of	Water use per operation (million gallons)			
	operations reported	Min	Average	Max	
Seneca Resources Corporation	18	0.27	0.60	3.4	
BreitBurn Energy Partners L.P.	8	0.26	0.28	0.36	
XTO Energy/ExxonMobil	106	0.110	0.27	0.3	
Chevron USA Inc.	38	0.03	0.26	1.50	
Occidental Oil and Gas	284	0.010	0.23	4.4	
Plains Exploration & Production Company	2	0.13	0.15	0.17	
Aera Energy LLC	999	0.0060	0.077	1.4	
The Termo Company	3	0.038	0.071	0.11	
Venoco Inc	20	0.011	0.035	0.23	

3.2.4 Fluid Type

In this section, the chemical composition of hydraulic fracturing fluid in use in California is described. Chemical constituents were available in the FracFocus data set for 1,386 onshore oil hydraulic fracturing operations. Guar gum, a gelling agent, was included in over 96% of the operations; borate compounds, which serve as cross linkers, are included in 90% of the operations. In addition, 210 of the 213 hydraulic fracturing notices received by DOGGR before 16 January 2014 indicate the use of a gelled fluid based on the components listed. These data indicate hydraulic fracturing in California is primarily performed with gels, and the gels are predominantly cross-linked. More information on fluid composition in well stimulation fluids is given in Section 5.1.2.1.

Of the 1,386 operations with chemical data, 3.4% included a friction reducer, indicating an operation involving slickwater fracturing. This includes all operations listing acrylimide compounds, as well as those involving compounds with "friction reducer" listed as the purpose. Compounds with this purpose listed included petroleum distillates (which are likely a carrier fluid in an additive with another friction-reducing compound) and undisclosed constituents.

There is a strong correlation between water volume and the type of hydraulic fracturing fluid used. The average water volume for operations involving slickwater is 2,200 m³ (590,000 gallons), which is almost four times the average volume for all operations. Additionally, the three highest volume events (12,900, 13,600 and 16,700 m³ (3.4, 3.6 and 4.4 million gallons)) involved slickwater.

3.3 Acid Fracturing

No reports of the use of acid fracturing in California were found in the literature. As described in Section 2.3.4, acid fracturing is used in carbonate reservoirs (which includes dolomite). The only such reservoirs identified in California were in some of the fields in the Santa Maria basin and possibly the Los Angeles basin (Ehrenberg and Nadeau, 2005; see Section 4.7 for basin locations). The fields in the Santa Maria basin consist of naturally fractured dolomite (Roehl and Weinbrandt, 1985). The dolomite reservoir in one of these fields (West Cat Canyon) was characterized as producing oil from the natural fractures (Roehl and Weinbrandt, 1985).

The highest concentration of hydrochloric acid in hydraulic fracturing fluid disclosed in the FracFocus data set is less than 3.5%, and the highest concentration of hydrofluoric acid is less than 0.5%. These concentrations are too low to indicate an acid fracturing operation (Economides et al., 2013). In addition, nine of the ten operations with greater than 1% hydrochloric acid in the hydraulic fracturing fluid also include guar gum and borate cross-linkers. Four of these, along with the one operation without guar gum or borate cross linkers, also included polyacrylamide or another component identified as a friction reducer.

The three hydraulic fracturing notices received from Occidental Petroleum by DOGGR on 31 December 2013 specify a sandstone matrix acidizing fluid, indicating these planned stimulations are acid fracturing. This is a novel type of stimulation relative to stimulation approaches characterized in the literature. The fluid components, including hydrochloric acid and ammonium biflouride, are the same as those listed on about half of the matrix acidizing notices submitted by Occidental and received by DOGGR on or before 15 January 2014. The planned stimulations are in the Elk Hills field at vertical depths ranging from 2,100 m to 3,224 m (6,888 to 10,575 ft).

The estimated water volume for these three planned stimulations ranges from 493 to 760 m³ (130,000 to 200,000 gallons). This is less than or almost equal to the average volume for hydraulic fracturing from the notices. Based on the top and bottom depth of the treatment interval listed, the water use per well length ranges from 0.60 to 0.74 m³/m (48 to 72 gpf). This volume per treatment length is less than that from the matrix acidizing notices given in Section 3.3.3. This raises the question of whether the notices that indicate acid fracturing are actually matrix acidizing, with the wrong box checked on the notice. If these notices really do represent acid fracturing, the treatment volumes per treatment length suggest limited penetration into the reservoir. Another possibility is that the treatment is applied to only a portion of the well length implied by the top and bottom depth of the treatment interval listed on the notices, such as if multiple short intervals were treated within that depth range.

3.4 Matrix Acidizing

3.4.1 Historic Use of Matrix Acidizing

The use of sandstone matrix acidizing for well stimulation in the Monterey Formation is relatively recent. The first and most detailed report of production enhancement as a result of high-volume sandstone acidizing for onshore production from the Monterey is from Rowe et al. (2004) for the "NA shale" reservoirs at Elk Hills. A series of 21 horizontal wells were drilled and stimulated between 1999 and 2001. The treatment process started from low-volume sandstone acidizing treatments, first using 0.0248 m³/m (2 gpf) of production interval with a 17% HCl acid. Diversion was accomplished by a mechanical method employing coiled tubing. Subsequent wells were treated with an increased volume of 0.35 m³/m (28 gpf). Apparent damage due to the water-based drilling mud led to drilling with an oil-based mud. Despite the use of a nondamaging mud, HCl acid treatments were effective for roughly doubling oil production. Subsequent wells were then treated with 17% HCl followed by a 12% HCl, 3% HF acid, with 0.256 m³/m (20.6 gpf) and 0.373 m³/m (30 gpf), respectively. Treatment volumes were increased to 1.86 m³/m (150 gpf) of the 12% HCl, 3% HF acid, resulting in nine-fold oil production increases. Treatments were eventually tested with 3.1 m³/m (250 gpf) of 17% HCl and 3.1 m³/m (250 gpf) 12% HCl, 3% HF, which was found to be optimum. The reported recovery of spent acid from the formation was 50%, either by natural flowback or using nitrogen gas lift. Although fracture characterization was not presented, Rowe et al. (2004) concluded that the acidizing treatment must have resulted in the mitigation of drilling damage from natural fractures. While this is possible, the use of nondamaging drilling muds in some of the wells and the positive response to acidizing suggests that the treatment may also be opening up natural fractures plugged with some type of natural fracture-filling material.

The use of successful sandstone acidizing at Elk Hills is also reported by Trehan et al. (2012), who employed a high-rate injection (MAPDIR)/foam diversion approach to the acid treatment. The treatment was applied to intervals of 457 to 610 m (1,500 to 2,000 ft) in length. A foamed HCl/HF acid was successfully applied to producing wells in shallow sands with steam injection in the South Belridge field in the early 1990s as an improvement over previous sandstone acidizing with lower concentrations and volumes per treatment length in the same reservoir (Dominquez and Lawson, 1992). The more successful treatment used $1.9~\rm m^3/m$ (150 gallons per ft) of 15% HCl and 5% HF.

The possibility of the high-volume sandstone acidizing treatment in naturally fractured siliceous shales is supported by Kalfayan (2008), who states, "There are few cases requiring greater volumes of HF than 1.86 to 2.48 m³/m (150 to 200 gpf). These are limited to high-permeability, high-quartz sands and fractured formations, such as shales, where high volumes of acid can open fracture networks deeper in the formation". Similar conclusions were reached by Patton et al. (2003), who utilized sandstone acidizing for offshore production from the Monterey. The hypothesis for the improvement in production is that

the HCl/HF treatment is effective at removing clay and chert from natural fractures and improving permeability of the fracture system. However, note that the injection volumes cited by Patton et al. (2003) are not large, only 0.248 $\rm m^3/m$ (20 gpf) for the 12%/3% HCl/HF acid.

A review of stimulation methods in the Monterey Formation by El Shaari et al. (2011) provides an alternative view that sandstone acidizing in the Monterey is effective at removing formation damage in fractures, but that good fracture-network permeability must exist naturally beyond the near-wellbore region if the treatment were to result in high oil production rates. For poorly fractured zones, such as at Elk Hills, El Shaari et al. (2011) postulate that either the treatment provides improved connection between the well and fractured calcareous intervals, or that the treatment in long production intervals characteristic of the Monterey, such as reported by Trehan et al. (2012), can significantly boost the overall magnitude of production, if not provide a large increase in the stimulation ratio.

A different acid system has been applied to the Stevens Sandstone in the North Coles Levee field in the early 1980s and continuing at least through the early 1990s (Hall et al., 1981; McClatchie et al., 2004). Termed "sequential hydrofluoric acid", the system involves alternating injection of HCl and ammonium fluoride. These react on clay surfaces producing HF, thus targeting the fine-grained material in the sandstone for dissolution. The HCl concentration used in these treatments was 5%. Typical treatment volumes were 36 m³ (9,750 gallons). The typical treatment volume per well length was 0.44 m³/m (49 gallons per ft). This treatment resulted in an approximately four times larger increase in production compared to stimulation with an HCl and HF mix (Marino and Underwood, 1990).

3.4.2 Current Use of Matrix Acidizing

The only data on matrix acidizing currently comes from the matrix-acidizing notices submitted to DOGGR by operators. A total of 22 notices were received by DOGGR in December 2013 after the 11th and 14 were received in January 2014 before the 12th of that month. All the notices were for stimulations in the Elk Hills field. Ten of the notices received in January were subsequently withdrawn for unknown reasons, although this may have resulted from DOGGR's not approving submittals without groundwater monitoring plans after January 1, 2014 (Vincent Agusiegbe, DOGGR, personal communication), rather than from the operators deciding that the stimulations were not desired. Given this uncertainty, the suggested activity rate is 30 matrix-acidizing operations per month.

3.4.3 Fluid Volume

Water use for matrix acidizing is listed on the notices. Planned water use ranged from 29 to 550 m^3 (8,000 to 140,000 gallons), with an average of 160 m^3 (42,000 gallons). The 90% confidence interval for the mean water use, based on 36 notices, is 120 to 200 m^3

(31,000 to 51,000 gallons). Based on the notices that list top and bottom depth of the treatment interval, the average water use per well length and standard deviation are $1.7 \, \text{m}^3/\text{m}$ and $1.5 \, \text{m}^3/\text{m}$ (140 and 123 gallons per ft), respectively. These volumes are in the higher treatment range, suggesting treatment of fractured formations based on the discussion in Section 3.3.1.

3.4.4 Fluid Type

All the matrix-acidizing notices indicated use of HCl. About half of the treatments included HF and half included ammonium biflouride. However, ammonium bifluoride produces HF acid when mixed with HCl acid (McClatchie et al. 2004). The chemicals included in the acidizing fluids (according to the notices) are further assessed in Section 5.2.1.

3.5 Conclusions

Available data suggest that present-day well stimulation practices for oil production in California differ significantly from practices in states such as North Dakota and Texas. For example, California hydraulic fractures tend to use less water and the wells tend to be more vertical. Large-scale application of high-fluid-volume hydraulic fracturing has not found much application in California, apparently because it has not been successful. As pointed out in Section 4, the majority of the oil produced from fields in California is not from the shale source rock (i.e., shale in the Monterey Formation), but rather from reservoirs containing oil that has migrated from source rocks. These reservoirs do not resemble the extensive, and continuous shale layers that are amenable to oil production with high water –volume hydraulic fracturing from long-reach horizontal wells, such as found in North Dakota.

Hydraulic fracturing has been the main type of well stimulation applied in California to date, based both on the total number of wells and fields where it has been used based on the literature and available data. Data indicate that hydraulic fracturing is performed in more than 76 wells per month on average, and perhaps up to 190 wells in some months. Given this range, hydraulic fracturing of 100 to 150 wells per month is a reasonable estimate.

Most of this fracturing occurs in the southwestern San Joaquin Valley in Kern County. For instance, 85% or more of recent hydraulic fracturing as well as fracturing over the last decade has occurred in the North and South Belridge, Elk Hills and Lost Hills fields in this area.

Data indicate average water use per well of 490 m³ (130,000 gallons) to 790 m³ (210,000) per hydraulic fracture operation. This is considerably less than in other hydraulically fractured plays in the United States. For instance, average water use per operation in the Eagle Ford in Texas is 16,000 m³ (4.25 million gallons). This results in part from the predominance of fracturing in vertical wells, which have shorter treatment intervals in California, as compared to the predominance of horizontal wells in major unconventional oil plays like the Eagle Ford and Bakken.

Water use per treatment length is also lower in California than elsewhere. The average and standard deviation water use in a set of horizontal wells disclosed as fractured is 2.3 m³/m (190 gpf). The average value from hydraulic fracturing notices is 3.0 m³/m (240 gpf). This compares to an average of 9.5 m³/m (770 gallons/ft) in the Eagle Ford (Nicot and Scanlon, 2012) and 3.4 m³/m (280 gallons/ft) for cross-linked gel, 3.9 m³/m (320 gallons/ft) for hybrid gel and 13 m³/m (1100 gallons/ft) for slickwater used in the Bakken, as described in section 2.3.7.

As indicated by the information from the Bakken, as well as engineering guidance discussed in Section 2.3.2, gels are associated with lower volumes per treatment length than slickwater, and cross-linked gel is associated with the least water volume among the gel types. The predominant fracturing fluid type in California is gel, of which most is cross-linked.

Acid fracturing is a small fraction of reported well stimulations to date in California. Acid fracturing is usually applied in carbonate reservoirs and these are rare in California. Matrix acidizing has been used effectively but rarely in California. These technologies are not expected to lead to major increases in oil development in the state. As explained in Chapter 2, these technologies increase the natural permeability of reservoirs consisting of silicate minerals only a limited amount.

The use of matrix acidizing is reported in far fewer fields in the literature than is hydraulic fracturing and the number of notices submitted for use of this technology is a small fraction of the number submitted for hydraulic fracturing. A total of 36 notices were received in the month from submittal of the first notice. All the notices were for stimulations in the Elk Hills field. Ten of the notices were subsequently withdrawn, but the timing suggests they may have been withdrawn due to action by DOGGR rather than because the operator did not want to perform them. Given this uncertainty and short timeline, the number of matrix-acidizing stimulations per month is estimated at 30.

Proposed water use for matrix acidizing on the notices averaged 160 m³ (42,000 gallons) per operation. The volume per treatment length from the notices averaged 1.7 m³/m (140 gallons per ft). This is somewhat less than for hydraulic fracturing, but in the higher part of the range identified for matrix-acidizing stimulations in general. This suggests that the treatments are targeted more toward treating natural fractures than the rock matrix (pores in the rock itself).

References to acid fracturing in California were not identified in the literature. Section 2.3.4 indicates that it is only applied in carbonate reservoirs. Only a few such reservoirs were identified in California, and these are naturally fractured, suggesting that acid fracturing is not applicable. However, three hydraulic fracturing well stimulation notices for wells in the Elk Hills field specify use of an HCl and HF mix, indicating acid fracturing. The minimum and maximum water volumes per treatment length implied by the three notices are 0.60 and 0.74 m 3 /m (48 and 72 gpf), respectively. This is smaller than indicated by the notices for matrix acidizing, and far less than the water use intensities for hydraulic fracturing. This suggests the treatment extent relative to the well is quite limited.

3.6 Acknowledgments

Staff at DOGGR and the California Department of Conservation (DOC) advised on and provided much of the data analyzed in this section, for which the authors are grateful. In particular, Bill Winkler of DOGGR patiently worked with the authors to develop a well-record sampling plan for assessing hydraulic fracturing activity over a longer period than available from FracFocus. He then arranged for the selected well records to be processed with text recognition software, in order to make them searchable, and then provided the records. Vincent Agusiegbe of DOGGR provided data output from FracFocus that made possible the inclusion of its data for the period after May 2013 in the analyses presented here. Undoubtedly, there were many DOGGR and DOC staff that participated in these efforts that are unknown to the authors, but we extend our appreciation.

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Prospective Application of Well Stimulation Technologies in California

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This section provides a brief introduction to petroleum systems, followed by a review of key hydrocarbon source rocks (typically shales) associated with petroleum systems found within onshore California sedimentary basins. Key aspects of the geology will also be discussed, such as the tectonic and structural features that have affected basin development and diagenetic processes impacting the types of minerals formed and rock properties. Where available, data describing the rock properties will be summarized. This is followed by a brief description of the Bakken Formation in the Williston Basin, from which significant unconventional shale oil production is occurring in North Dakota, along with a comparison with the Monterey Formation in California. This is followed by descriptions of the major sedimentary basins in California, along with a discussion of the results of exploration activities in deep portions of these basins, where hydrocarbon source rocks are within the oil window. The section concludes with some general observations regarding the potential application of unconventional techniques to oil-bearing shales in California.

4.1 Overview of Significant Findings

Oil-bearing sedimentary basins in California are relatively young in geologic time, but are structurally complex due to the presence of a very dynamic transform plate boundary, currently represented by the San Andreas Fault System. The dominant source rock for hydrocarbon generation in many of these basins is the Monterey Formation, a thick Miocene age sequence of marine sediments consisting of siliceous, phosphatic, organic, and clay-rich shales and mudstones, dolomites, and intercalated turbiditic sandstones. Most oil fields in California are located in reservoirs associated with structural traps at depths above where the oil is actively generated (the oil window), indicating that the oil in these petroleum systems has migrated from the source rocks to the reservoirs. While there have been few new onshore oil discoveries in the past two decades (the 30 largest onshore oil fields in California were all discovered prior to 1950; California Division of Oil, Gas and Geothermal Resources (DOGGR), 2010), the United States Geological Survey (USGS) has recently estimated that almost 10 billion barrels of oil can be recovered using existing technologies (including well stimulation methods) from the largest existing oil fields in the San Joaquin and Los Angeles Basins (Tennyson et al., 2012; Gautier et al., 2013). Much of the current well stimulation in California has occurred in diatomite reservoirs in the Monterey Formation (see Sections 2 and 4.5.2 for more details), and it is likely that this type of reservoir rock will continue to be a focus of future well stimulation activity in California.

Technological advances in well completion and stimulation techniques have led to dramatic increases in oil recovery from shale oil deposits elsewhere in the United States. Based in part on large increases in drilling and oil production in the Bakken Formation in North Dakota and the Eagle Ford Formation in Texas, the US Energy Information Administration (EIA) (2011) predicted that even larger oil resources could be tapped from the deeper portions (the active source rock) of the Monterey Formation in California, estimating that there are 15.4 billion barrels of technically recoverable oil. However, the assumptions used to develop this estimate are not supported by historical well production rates in the Monterey (Hughes, 2013), suggesting that this estimate is highly inflated, and a more recent estimate by the US EIA (2014b) has reduced the estimated unproved technically recoverable shale oil from the Monterey/Santos play to a value of 0.6 billion barrels. Recent exploration wells that have targeted deeper portions of the Monterey, where active source rocks may retain unmigrated oil, have not resulted in the identification of new oil reserves to date. The potential of discovering significant oil resources from new plays in the deep source rocks of the Monterey is highly uncertain.

4.2 Introduction to Oil Deposits

Petroleum systems require the following key elements: a source rock that contains sufficient concentrations of organic matter, a reservoir rock that accumulates the generated oil and gas, a seal rock that traps the hydrocarbons in the reservoir, and overburden rock that provides the burial depths needed for oil generation to occur (e.g., Doust, 2010; Magoon and Dow, 1994). The generation of hydrocarbons in the source rock requires the presence of abundant organic matter; the organic matter is transformed into oil and gas over time when subjected to sufficient pressure and temperature, which are related to sediment burial depth. The migration of hydrocarbons into the reservoir requires transport pathways and sufficient time. The reservoir must have a relatively impermeable barrier or "trap" so that oil can accumulate in commercial quantities without escaping, as shown on Figure 4-1. A variety of trapping mechanisms is possible, including stratigraphic traps (where an impermeable formation overlies a porous and permeable reservoir rock), structural traps (faults or folds that form a barrier to the continued upward migration of buoyant hydrocarbons), and diagenetic traps (where the alteration of the reservoir rocks associated with burial and fluid flow causes changes in flow properties of the rock).

Insoluble organic matter in the source rock (kerogen) must undergo sufficient maturation through burial and heating over time for oil and gas to be generated (McCarthy et al., 2011). The "oil window" is defined as the range of depths for which a source rock, having undergone burial and heating, will generate oil – this is a function of the type of organic matter and the integrated time-temperature history of the source rock (Fig. 4-2). This process is characterized by progressive changes in vitrinite reflectance. Vitrinite is a type of woody kerogen (a type of insoluble organic matter) that changes predictably and consistently upon heating, and its increased reflectance indicates increasing source rock maturity. The top of the oil window (where oil first is generated) corresponds to temperatures of around 50°C and a vitrinite reflectance (Ro) of 0.6 (although some

workers suggest that oil generation in some of the California basins is initiated at lower vitrinite maturity levels (Walker et al., 1983; Petersen and Hickey, 1987). Higher levels of heating will result in the transformation of organic matter to natural gas; the base of the oil window (where all hydrocarbons will be transformed into gas) corresponds to a vitrinite reflectance of ~ 1.2 . The depth to the top of the oil window depends on the burial and thermal histories of the basin. Oil can be traced back to its source rock through the use of biomarkers and stable isotopic compositions, which serve as chemical fingerprints that link it to the organic matter (kerogen) from which it was generated (Kruge, 1986; McCarthy et al., 2011; Peters et al., 2007; 2013).

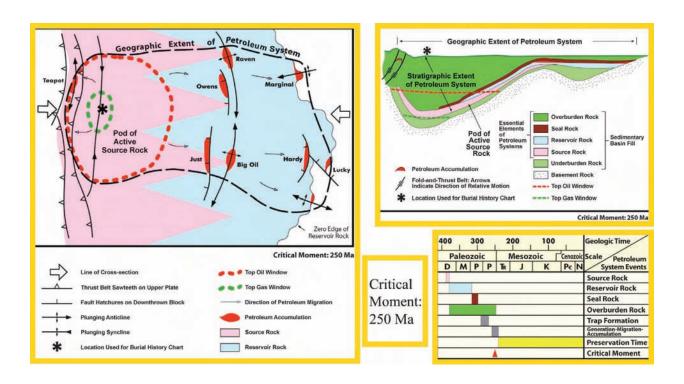


Figure 4-1. Example of a hypothetical petroleum system showing plan view map, cross section, and timeline for system formation. Figure taken from Doust (2010), which was modified from Magoon and Dow (1994).

In the case of an unconventional shale oil system, the source rock also serves as the reservoir rock, because the oil stays trapped within the source rock due to its low permeability. Producing oil from low permeability source rocks requires reservoir stimulation techniques such as those discussed in Section 2.

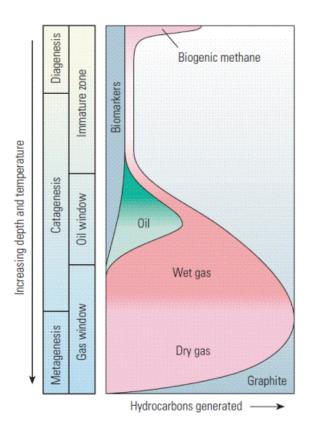


Figure 4-2. Thermal transformation of kerogen to oil and gas, depicting the location of the oil window (McCarthy et al., 2011).

There are three general categories of prospective target areas for oil production in California involving well stimulation. The first target consists of continued or increased oil production from discovered oil fields (or similar undiscovered reservoirs) that produce from formations with low permeability (also known as tight oil formations). The producing oil reservoirs in these fields generally lie above the oil window, indicating that the oil has migrated upwards from deeper source rocks and is now contained by structural, stratigraphic, and/or diagenetic traps, as shown on Figure 4-3. The largest fields in California, situated in the San Joaquin and Los Angeles Basins, have produced billions of barrels of oil, and the USGS estimates that there are over 9 billion barrels of additional oil that could be recovered from these two basins using current technology, which might include well stimulation technologies such as hydraulic fracturing (Gautier et al., 2013; Tennyson et al., 2012). Of these producing fields, many have oil sourced from the Miocene Monterey Formation (or Monterey Formation-equivalent rocks), a formation that contains organic, siliceous, phosphatic, and clay-rich shales, diatomites, and dolomites (Section 4.4.1). A significant fraction of these fields also have oil reservoirs

in the Monterey Formation, often hosted in diatomites, fractured siliceous shales, or in interbedded sandy turbidite deposits; the oil has migrated from the deeper active source rock into shallower reservoirs with overlying seals. To date, most of the hydraulic fracturing well stimulation activity in California has been in the Monterey Formation diatomites in South Belridge, Lost Hills, and Elk Hills fields of the San Joaquin Basin (Agiddi, 2004; Martinez et al., 1994; Rowe et al., 2004; Strubhar et al., 1984; Wright et al., 1995). It is possible that hydraulic fracturing well stimulation methods, or others adapted from unconventional shale oil production in other regions, could be applied more widely in the Monterey Formation to increase oil recovery and production.

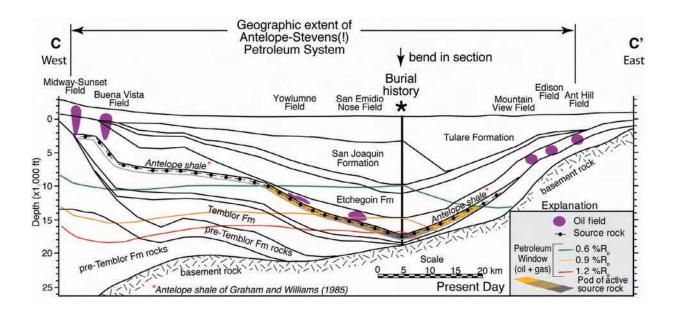


Figure 4-3. Cross section depicting the Antelope-Stevens Petroleum System in the southern San Joaquin Valley (Magoon et al., 2009). The Antelope Shale and Stevens Sand are subunits of the Monterey Formation. Note that the bulk of the oil fields are located on the margins of the basin, and that the oil appears to have migrated updip from the source region (below the top of the petroleum window) in the center of the basin.

A second target area consists of organic-rich shales located deep in the basins within the oil window. (These areas correspond to the active source rock colored according to the different vitrinite reflectance contours (Ro values) in Figure 4-3). These zones have not been a major target for oil exploration in California. However, these shales have been the source rocks for much of the oil that has been discovered and produced in California. Depending on how much oil still remains in these rocks, there may be significant potential associated with these rocks. Exploitation of the source rock would constitute a true shale oil play. This target corresponds to the Monterey shale oil play described by US EIA (2011) – however, estimates of the potential size of recoverable oil associated with this target are highly uncertain (see Sections 4.6 and 4.7).

A third potential target would be oil-bearing shales in basins where little oil production has occurred. Very little published information is available about these basins, except for some data relating to the presence and distribution of potential source rocks.

4.3 Sedimentary Basins in California

Most of the Neogene (the time period spanning between 23 to 2.6 million years before present) sedimentary basins in California (Behl, 1999) consist of marine depositional environments located along the continental margin as shown on Figure 4-4. All of the oil and gas fields in California are located in these basins (DOGGR, 1982; 1992; 1998). The basins are typically formed and bounded by faults, with many of the faults associated with the San Andreas Fault System. More detailed descriptions of many of these basins will be presented in Section 4.5.

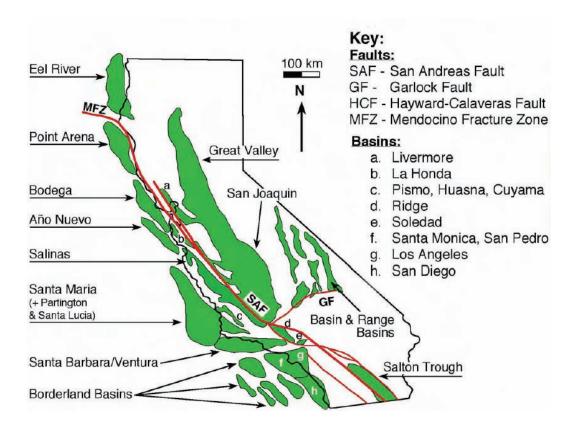


Figure 4-4. Neogene sedimentary basins in and along the coastal margins of California (from Behl, 1999).

The oil-bearing sedimentary basins in California are filled with mostly marine sediments, which consist of both biogenic (produced by marine organisms) and clastic (derived by erosion of existing rocks) materials. In each basin, distinct packages of sedimentary rocks have been identified as formations, which are composed of rock units that represent a similar time-depositional sequence and have distinctive and continuous characteristics that allow them to be mapped. Formations can be divided into subunits, known as members, which in turn have specific lithologic characteristics. The same geologic formations can often be found in adjacent basins; they would represent units that were deposited at the same time, and presumably under similar conditions. A discussion of key source rock formations (dominated by organic-rich shales) in California is presented in Section 4.4; descriptions of the main sedimentary basins where these rocks were deposited are given in Section 4.5.

4.3.1 Structural Controls

Oil reservoirs in California have a complex structural history that resulted in folding and faulting. The most important aspect of these processes is that they took place along the margins of the North American continent over time periods when the tectonic forces caused a radical change of the Pacific and North American plate boundary from a subduction zone to a strike-slip margin in the region that is now California. The result was the formation of a number of structural depressions (basins) where sediments with a wide range of compositions were deposited. These sediments were subjected to burial and then deformation (faulting and folding). The following technical discussion describes these processes.

Regional tectonism plays a large role in the creation of sedimentary basins in California and the distribution of sedimentary facies within these basins (Graham, 1987). In many cases, faulting accompanied basin formation and filling, and played an integral role in the types and rates of sedimentation. The dynamic tectonic environment of the California continental margin has contributed to the structurally complex nature of many of these sedimentary basins, and has led to the creation of structural traps (faults and folds) in many of the oil and gas fields. Wright (1991) finds that over 90 percent of the oil found in oil fields in the Los Angeles Basin is associated with anticlinal or fault traps, associated (in turn) with Miocene and younger tectonism. Ingersoll and Rumelhart (1999) and Ingersoll (2008) have postulated a three-stage tectonic evolution of the Los Angeles Basin (Fig. 4-5) involving transrotation (simultaneous occurrence of strike-slip faulting and rotation) between 18 and 12 million years ago (Ma), transtension (simultaneous occurrence of strike-slip faulting and extension) between 12 and 6 Ma, and transpression (simultaneous occurrence of strike-slip faulting and compression) from 6 Ma to the present.

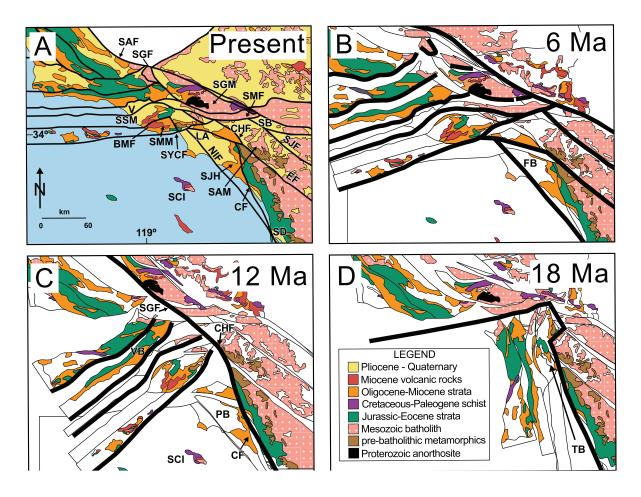


Figure 4-5. Three-stage tectonic evolution of the Los Angeles Basin. A – Present day structural setting, B, C, D – Palinspastic reconstructions of basin at 6, 12, and 18 Ma (details described in Ingersoll and Rumelhart, 1999).

Other California basins have experienced complex tectonic histories related to strike-slip movement along the San Andreas Fault. Graham (1978) described the role of wrench tectonics in the formation of the Salinas Basin, where right-lateral offset along the Rinconada-Reliz fault zone (located parallel to and between the San Andreas and San Gregorio-Hosgri faults) led to the formation of en echelon depressions and uplifts. A shift from transtension to transpression in this region followed the deposition of the Miocene Monterey Formation (Colgan et al., 2012; Titus et al., 2007).

Faults and fractures play a critical role in the migration and accumulation of hydrocarbons (Fig. 4-6) in many California oil fields (Chanchani et al., 2003; Dholakia et al., 1998; Dunham and Blake, 1987; Finkbeiner et al., 1997). Compressive stresses can lead to the development of folds, which can form structural traps with effective cap rocks when the formations deform plastically. Under similar forces, more brittle rocks develop fractures, which can provide flow pathways for upward hydrocarbon migration by providing fracture permeability—this is especially important when matrix permeabilities are low in clay-rich shales and siliceous mudstones (Hickman and Dunham, 1992).

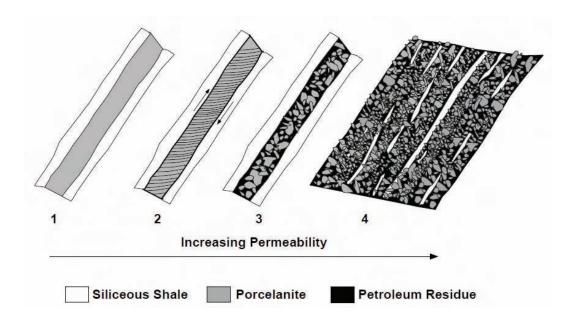


Figure 4-6. Schematic depiction of the development of bed-parallel faulting in the more brittle porcelanite layers in the Monterey Formation, which leads to the formation of petroleum-filled breccia zones (Dholakia et al., 1998).

4.3.2 Diagenetic Controls

As sediments are progressively buried over time, they undergo compaction and heating, and reductions in matrix permeability and porosity (Zieglar and Spotts, 1978) during diagenesis, a process that represents the chemical, physical, and biological changes that transform sediments into sedimentary rocks. In addition to these physical changes, mineralogical and textural changes occur in many sedimentary rocks. For instance, silica-rich diatomaceous sediments, such as those that occur in the Monterey Formation, undergo significant mineralogic changes that affect their physical properties (Behl and Garrison, 1994; Behl, 1998; Chaika and Dvorkin, 2000; Chaika and Williams, 2001; Eichhubl and Behl, 1998; Isaacs et al., 1983; Isaacs, 1980, 1981c, 1982; Keller and Isaacs, 1985; Pisciotto, 1981). Changes in temperature result in the transformation from opal-A to opal-CT to microcrystalline quartz. This transformation is also affected by the amount of detrital minerals mixed with the silica phase (Fig. 4-7). This can lead to a significant change in physical properties from a diatomite, which has very high (>60%) porosity, to porcelanites and cherts, which have much lower porosities; all of these rocks have intrinsically low matrix permeabilities. The porcelanites and cherts are much more brittle than diatomite, and thus often develop natural fractures that can conduct fluid (Behl, 1998; Eichhubl and Behl, 1998; Hickman and Dunham, 1992). Contrasts in rock properties associated with these changes in mineralogy in the Monterey Formation can result in the formation of diagenetic oil traps, such as those observed in the Rose oil field, where the top of the reservoir in the McLure shale member occurs at the transition from opal-CT to quartz (Ganong et al., 2003).

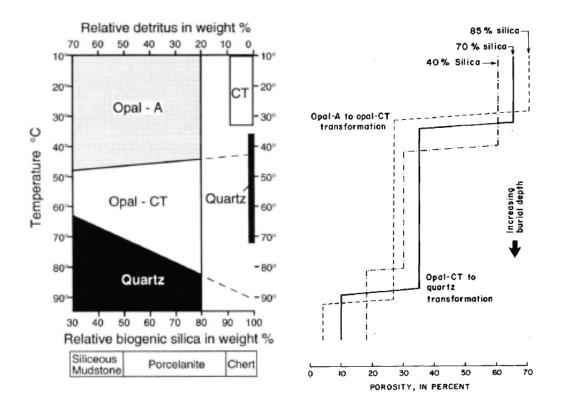


Figure 4-7. (a) Sediment composition and temperature effects on silica phase changes in the Monterey Formation (Behl and Garrison, 1994). (b) Changes in porosity as a function of silica phase transformation and burial (Isaacs, 1981c).

4.4 Primary Oil Source Rocks in California

As described above, each basin with oil has at least one source rock unit. In California basins, the dominant source rocks are in the Monterey Formation. However, the source rocks in some basins may include other geologic units. The various units identified as including source rock in California are discussed below.

4.4.1 Monterey Formation

The Miocene Monterey Formation is dominated by deep water marine sediments, comprising siliceous, phosphatic, and calcareous materials, along with a significant organic component, making it one of the major hydrocarbon source rocks in California (Behl, 1999; Bramlette, 1946; Graham and Williams, 1985; Isaacs, 1989; Tennyson and Isaacs, 2001). It forms extensive deposits within many of the Neogene sedimentary basins in California, including all of the major oil-producing regions (Fig. 4-4).

4.4.1.1 Lithologic variability of the Monterey Formation.

The main lithologies encountered (Figs. 4-8 and 4-9) include thinly laminated beds of chert, siliceous mudstone, porcelanite, phosphatic shale, clay shale, and dolomite (Behl, 1999; Bramlette, 1946; Dunham and Blake, 1987; Isaacs et al., 1983; Isaacs, 1980). While many of these lithologic units have informally been called "shales", they are more appropriately classified as mudstones, given that they are fine-grained but are relatively poor in actual clay mineral content (e.g., Behl, 1999; MacKinnon, 1989). Areas closer to the continental margin (e.g., the San Joaquin and Los Angeles Basins) have higher amounts of terriginous clastic input and contain turbiditic sandstones (Link and Hall, 1990; Redin, 1991). These coarser grained deposits form important subunits within the Monterey, such as the Stevens and Santa Margarita sandstones (e.g., Magoon et al., 2009). The unit is characterized by its wide range in lithologic variability (Fig. 4-10). This variability can be characterized through studies of outcrops and cores, but is most easily achieved in the subsurface through the use of geochemical (e.g., Hertzog et al., 1989) and integrated formation evaluation (e.g., Zalan et al., 1998) logging tools.

A variety of different lithological characterizations have been developed for the Monterey, based upon the varying amounts of silica, carbonate, and detrital minerals present (e.g., Carpenter, 1989; Dunham and Blake, 1987; Isaacs, 1981a, 1981b). In general, the lower portion of the Monterey is carbonate-rich, the middle section has abundant phosphatic, organic-rich shales, and the upper section tends to be dominated by siliceous mudstones, porcelanite, chert, and diatomite (Behl, 1999; Govean and Garrison, 1981; Isaacs et al., 1983; Isaacs, 1981b). A type section of the Monterey in the southwestern San Joaquin basin, at Chico Martinez Creek, is over 6,000 ft (1,830 m) thick, and consists of four major shale subunits: the Gould, Devilwater, McDonald, and Antelope shales (Mosher et al., 2013).

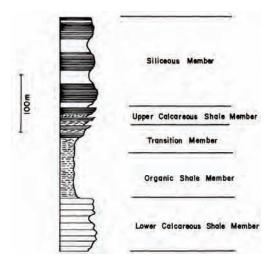


Figure 4-8. Generalized stratigraphic section of the Monterey Formation from the Santa Barbara coastal region (Isaacs, 1980). Open pattern depicts massive units, broken stipple indicates irregularly laminated beds, and thinly lined pattern denotes finely laminated units.

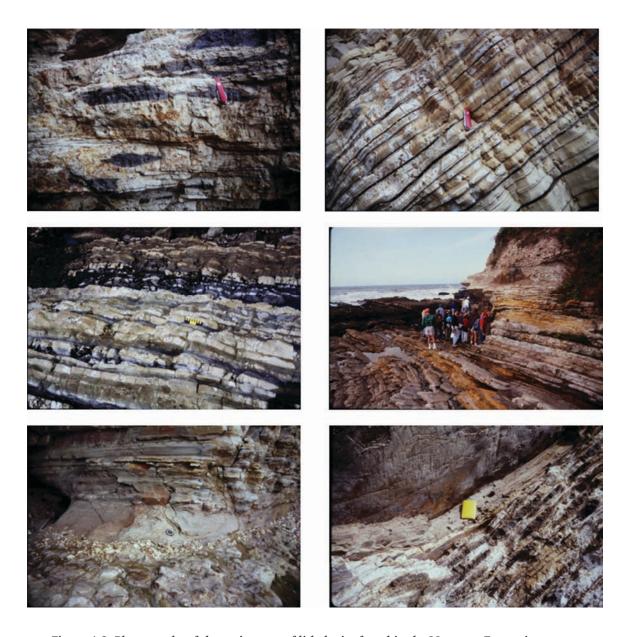


Figure 4-9. Photographs of the main types of lithologies found in the Monterey Formation.

Upper left – dark lenses of chert within porcelanite, Point Buchon; Upper right – Porcelanite with thin organic-rich clay shale interbeds, Point Buchon; Middle left – Interbedded phosphatic mudstones and dolomites, Shell Beach; Middle right – Orange dolomitic layers interbedded with siliceous shales and porcelanite, Montana de Oro State Park; Lower left – Pebbly phosphatic hardground, Montana de Oro State Park; Lower right – Sandy turbidite lens (with yellow field book) between fractured chert and porcelanite layers, Point Buchon. These localities are described in Bohacs and Schwalbach (1992). Photos: P. Dobson.

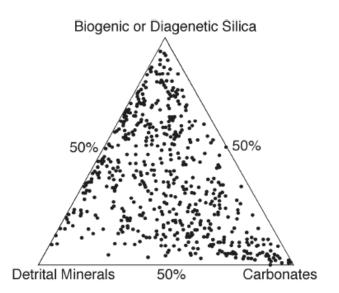


Figure 4-10. Lithologic variability of the Monterey Formation (Behl, 1999).

One of the main constituents of these marine sedimentary rocks comprises silica-rich diatoms. The physical properties of these diatoms are dramatically impacted by diagenetic processes, which result in a progressive change (with increasing temperature and burial depth) from opal-A to opal-CT to microcrystalline quartz (Fig. 4-7). This transformation results in significant changes in porosity, permeability, Young's elastic modulus (the ratio of longitudinal stress to longitudinal strain), and the brittleness of the rocks, with cherts and siliceous mudstones particularly susceptible to fracturing (Hickman and Dunham, 1992; Isaacs, 1984).

In addition to being an important oil reservoir, the Monterey Formation is also a major petroleum source rock (Graham and Williams, 1985; Isaacs, 1989, 1992a; Peters et al., 2013, 2007; Tennyson and Isaacs, 2001). The Monterey contains several organic-rich shale intervals with elevated total organic carbon (TOC), including the Reef Ridge, McLure, Antelope, McDonald, Devilwater, and Gould shales. Graham and Williams (1985) reported TOC values for the Monterey in the San Joaquin Basin ranging from 0.40 to 9.16 wt. %, with a mean value of 3.43 wt. %; higher TOC values with unit averages ranging between 4 and 8% TOC (6 and 13% organic matter) were reported for the Santa Maria Basin and the Santa Barbara coast by Isaacs (1987). TOC abundances are generally highest in the phosphatic shale section in the Middle Monterey (Fig. 4-11), where reduced dilution with biogenic sediments occurs (Bohacs et al., 2005). This TOC-rich portion of the Monterey would be the most likely target for unconventional shale oil. The kerogen in the Monterey has been interpreted to be mostly of marine origin (Tennyson and Isaacs, 2001).

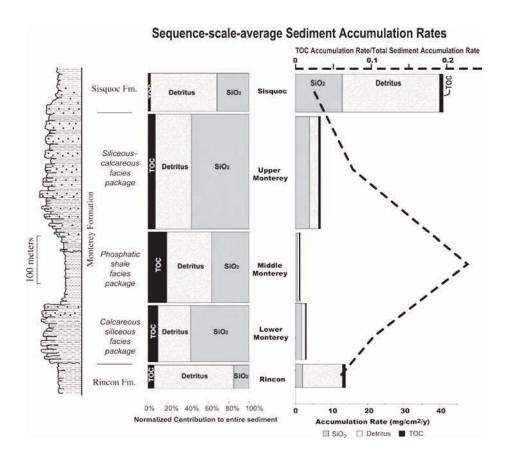


Figure 4-11. Distribution of organic matter, detrital sediments, and biogenic silica accumulations as a function of stratigraphic position in the Monterey Formation (Bohacs et al., 2005).

Key processes affecting the distribution and mineralogy of the Monterey involve original facies variations associated with the deposition of sediments and subsequent diagenetic processes, which had a profound impact on siliceous materials. These facies variations depend on paleoceanographic conditions which control the relative amounts of biogenic production of diatoms, coccoliths, and foraminifera relative to clastic sedimentation (Behl, 1999; Bohacs and Schwalbach, 1992).

4.4.1.2 Physical Properties of the Monterey

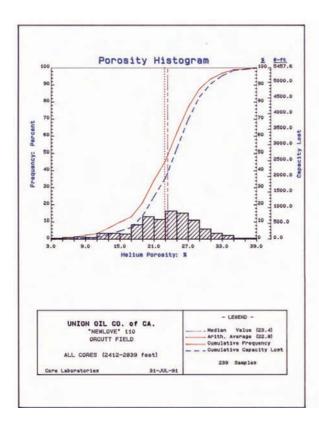
The physical properties of a rock are critical in determining if a rock can serve as a reservoir rock and how it might be stimulated by hydraulic fracturing. The porosity of a rock represents the open pore and fracture volume of a rock. The matrix and fracture porosity not only provide storage volumes for fluids, but they also provide potential pathways for fluid flow in rocks provided the pores and fractures are interconnected. The permeability of a rock measures the ability of a rock to transmit fluids; the goal of well stimulation is to improve well production by enhancing the permeability of the

surrounding reservoir rock. The ability to stimulate a rock through hydraulic methods depends on the ability to shear or dilate existing fractures (causing them to open), or to create new fractures. The strength and elasticity and spatial variations of these properties of the rock will determine how hydraulic fractures will develop. Young's modulus, the ratio of longitudinal stress to longitudinal strain, is used to estimate the rigidity of a rock. The total organic content determines whether a particular lithology could serve as a potential hydrocarbon source rock.

Physical properties (porosity, permeability, total organic content (TOC), Young's elastic modulus) have been determined for a variety of Monterey rock samples. Note that the presence of natural fractures in the more brittle lithologies of the Monterey would result in a fracture permeability that would have a significant impact on oil migration (Behl, 1998; Eichhubl and Behl, 1998; Hickman and Dunham, 1992).

The Newlove 110 well (API 08222212) in the Orcutt field was the subject of a detailed hydrofracture research study conducted jointly by Unocal and the Japan National Oil Company (Shemeta et al., 1994). Prior to the hydrofracture, the well had a thick section of continuous core sampled from the Monterey section (which extends from 2,030 to 2,805 ft (619 to 855 m) in the well). Core Laboratories drilled 239 one-inch-diameter (2.54 cm) core plugs parallel to bedding from this core between the depths of 2,412 and 2,820 ft (735 and 860 m) and measured horizontal air permeability, helium porosity, fluid saturation, and grain density. The porosities ranged from 3.7 to 37%, with an arithmetic average of 22.8% and a median value of 23.4% (Fig. 4-12a). Matrix horizontal air-permeability values ranged from 0.00 md to 5,080 md, with an arithmetic average of 99.6 md, a geometric average of 2.59 md, a median value of 1.67 md, and a harmonic average of 0.12 md (Fig. 4-12b). Grain density values ranged from 2.19 to 2.96 g/cm³, with an arithmetic average of 2.50 g/cm³ and a median value of 2.49 g/cm³.

Isaacs (1984) reports the physical properties of three different siliceous Monterey Formation lithologies that illustrate the effects of diagenesis. Opal-A bearing diatomaceous mudstones have porosities ranging from 50-70%, matrix permeabilities from 1-10 md, and grain densities of 2.2-2.4 g/cm³. Opal-CT porcelanites have porosities ranging from 30-40%, matrix permeabilities from <0.01 to 0.1 md, and grain densities of 2.2-2.35 cm³. Quartz porcelanites have porosities of 10-20%, matrix permeabilities of <0.01 md, and grain densities of 2.1-2.4 g/cm³. Chaika and Williams (2001) observed that permeability reductions associated with silica phase transformation at increasing depth of burial in the Monterey appear to have two different trends: (1) a silica-rich host rock that has an abrupt porosity reduction (from 55 to 45%) associated with the change from opal-A to opal-CT, lending itself to a more brittle, fractured rock below this transition, and (2) a more gradual porosity reduction associated with this transformation for siliceous shales and mudstones with a higher abundance of detrital minerals. This second, more clay-rich rock tends to retain higher matrix porosity, which could lead to higher volumes of hydrocarbon storage.



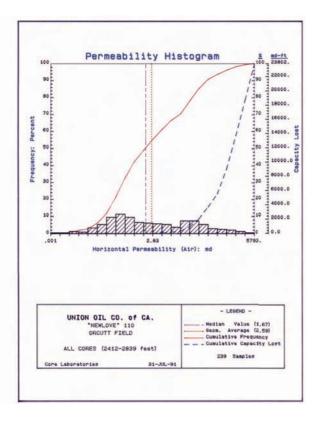


Figure 4-12. Helium porosity (a) and horizontal air permeability (b) measurements of 239 Monterey Formation core samples from the Newlove 110 well, Orcutt oil field, Santa Maria basin. The Core Laboratories report can be found on the DOGGR website at: http://owr.conservation.ca.gov/WellRecord/083/08322212/08322212 Core Analysis.pdf

Measurements of physical properties were conducted on samples of the Antelope Shale member of the Monterey Formation in the Buena Vista Hills field, located between the giant Elk Hills and Midway-Sunset fields in the SW portion of the San Joaquin Basin (Montgomery and Morea, 2001). Four different rock types were studied: opal-CT porcelanite, opal-CT porcelanite/siltstone, clay-poor sandstone, and sandstone/siltstone. The porcelanite samples (399) had an average porosity of 33.8%, a median permeability of 0.1 md, and an average density of 2.31 g/cm³; the porcelanite/siltstone samples (451) had an average porosity of 25.7%, a median permeability of 0.07 md, and an average density of 2.36 g/cm³; the sandstones (19) had an average porosity of 21.1%, a mean permeability of 6.3 md, and an average density of 2.62 g/cm³; and the sandstone/siltstone samples (57) had an average porosity of 20.8%, a mean permeability of 0.16 md, and an average density of 2.57 g/cm³.

Liu et al. (1997) analyzed a number of Monterey core samples from the Santa Maria Basin. They reported lithotype, porosity, density, and TOC values (Table 4-1) for 10 Monterey Formation samples obtained from two wells (with sample depths ranging from 4,560 to 5,553 ft (1390 to 1693 m) in the Santa Maria Basin (Liu, 1994).

Table 4-1. Physical properties of Monterey core samples from the Santa Maria Basin (Liu et al., 1997).

Lithology	Number of core samples	Porosity (%)	Grain density (g/cm³)	Total organic carbon (wt. %)
Porcelanite	2	10-11.4	2.14-2.17	2.28-2.4
Siliceous shale	1	4.3	2.24	6.81
Shale	3	18-21	2.02-2.35	8.19-18.2
Siliceous dolomite	3	11-19	2.38-2.70	0.52-8.12
Dolomite	1	3.0	2.72	0.19

Morea (1998) performed reservoir characterization studies of siliceous shales and mudstones from the Antelope and Brown shale members of the Monterey Formation from the Buena Vista Hills field. As part of this study, seven core samples recovered from depths ranging from 4,191 to 4,799.3 ft (1277.4 to 1462.8 m) were analyzed for Young's modulus. These samples, consisting of porcelanite and clayey porcelanite, have values ranging from 1,172,000 psi up to 2,724,000 psi (8.8 to 18.9 GPa), with an average value of 1,990,000 psi (13.7 GPa).

At the Belridge oil field, diatomites corresponding to the uppermost portion of the Monterey Formation are an important oil reservoir rock. Schwartz (1988) reports that the diatomites have elevated porosities ranging from 54 to 70%, permeabilities ranging from 0.00 to 7 md, and grain densities from 2.2 to 2.5 g/cm³. Similar rock-property values (55-60 % porosity, 0.03 to 0.3 md permeability, and 2.2 to 2.5 g/cm³ grain density) are reported for this unit by De Rouffignac and Bondor (1995). These properties vary as a function of stratigraphic depth and are related to cyclical changes in biogenic and clastic sedimentation (Schwartz, 1988). Bowersox (1990) reports lower effective porosities (36.7 to 55.4%) and higher permeabilities (1.86-103 md) for the producing diatomite intervals. The highly porous diatomites are soft rocks that have very low Young's modulus values as follows: 20,000 -500,000 psi (0.14 - 3.4 GPa) (Allan et al., 2010); 50,000 - 200,000 psi (0.34 - 1.4 GPa) (Wright et al., 1995); 25,000 - 80,000 psi (0.17 - 0.55 GPa) (De Rouffignac and Bondor, 1995); ~100,000 psi (0.69 GPa) (Vasudevan et al., 2001). In spite of the low rigidity of these rocks as indicated by the low Young's modulus values, diatomite units have been successfully subjected to hydraulic stimulation to increase oil production from this highly porous but low-permeability lithology (Allan et al., 2010; Wright et al., 1995).

In conclusion, the different lithologies of the Monterey Formation exhibit a wide range of physical properties. Silica-rich diatomites have the highest porosities of any Monterey lithology (typically > 50%), but with diagenesis, these rocks are converted into porcelanites, which have significantly lower porosities (generally 20-40%). All of the Monterey lithologic units have intrinsically low matrix permeabilities (typically less than a millidarcy). However, the porcelanites, siliceous shales and mudstones, and dolomite units are quite

brittle, and often develop natural fractures, which can lead to higher fracture permeability for these rock types. Most of the shale (clay-rich) lithologies in the Monterey Formation have TOC values greater than 2%, making them prospective hydrocarbon source rocks. The organic-rich phosphatic shales found within the Middle Monterey (Fig. 4-11) are the most prospective source rocks (and most likely unconventional oil shale target) within the Monterey Formation.

4.4.2 Vaqueros Formation

The Vaqueros Formation is an early to mid-Miocene marine sedimentary unit consisting of sandstones and shales, typically found in basins on the western side of the San Andreas Fault (Dibblee, 1973). The lower portion of this unit is the Soda Lake Shale Member, consisting of shale, claystone, and siltstone. This is overlain by the Painted Rock Sandstone Member. Lillis (1994) used biomarkers and stable isotopic compositions to conclude that much of the oil produced from the Cuyama Basin comes from the Soda Lake Shale source rock (see Section 4.5.5 for more details).

4.4.3 Tumey and Kreyenhagen Formations

The Tumey Formation, an Eocene age unit that just overlies the Kreyenhagen Formation, contains a thin calcareous shale and is often combined with the Kreyenhagen in stratigraphic sections (Milam, 1985; Peters et al., 2007). The Kreyenhagen Formation is a shale-rich formation of Eocene age that serves as a source rock for hydrocarbons in the San Joaquin Basin, and has a thickness of over 1,000 ft (305 m) at its type section at Reef Ridge, just south of Coalinga (Von Estorff, 1930). It consists of shales, laminated sandstones and shales, siltstones, and pebbly green sands (Isaacson and Blueford, 1984; Johnson and Graham, 2007; Milam, 1985). In some locations, it contains a turbiditic sandstone that can exceed over 1,600 ft (488 m) in thickness known as the Point of Rocks sandstone; in these areas, the lowermost Kreyenhagen member is known as the Gredal Shale member, and the uppermost Kreyenhagen member is the Welcome Shale member (Dibblee, 1973; Johnson and Graham, 2007). Hydrocarbons derived from the Kreyenhagen and Tumey Formations have been chemically distinguished from the Monterey on the basis of isotope geochemistry and biomarkers (Clauer et al., 2014; Lillis and Magoon, 2007; Peters et al., 1994; 2013).

4.4.4 Moreno Formation

The Moreno Formation is a shale-rich formation of Cretaceous-Paleocene age (McGuire, 1988). It consists of four members that represent different clastic depositional facies. The base of this unit consists of the Dosados Member (and lower portion of the Tierra Loma Member), which consists of silty shales and turbidites with interbedded sandstones. The rest of the Tierra Loma member consists of brown to maroon shales. This is in turn overlain by the Marca Shale Member, consisting of diatomaceous and siliceous shales. The uppermost section of the Moreno is formed by the Dos Palos Shale Member, formed

by clay shales, silty shales, and glauconitic sandstones (the Cima Sandstone) and siltstones. The stratigraphic section of the Moreno Formation, exposed in Escarpado Canyon in the Panoche Hills on the western margin of the central San Joaquin Valley, has a thickness of around 800 m (Fig. 4-13). He et al. (2014) have characterized the geochemical signature of oils sourced from this formation.

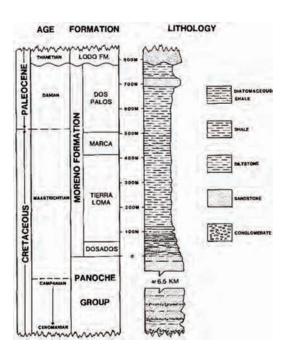


Figure 4-13. Stratigraphic column of the Moreno Formation, Escarbado Canyon, Panoche Hills, western margin of the central San Joaquin Basin (McGuire, 1988).

4.4.5 Comparison of the Monterey Formation with the Bakken Formation

The Monterey Formation in California can be compared with the Bakken Formation in North Dakota, which has seen a dramatic increase in drilling and oil production over the past five years (Fig. 4-14). The Bakken, along with the Eagle Ford Formation of Texas, are two of the largest producing unconventional shale oil units in the United States (US EIA, 2014a). The introduction of horizontal drilling and hydraulic stimulation techniques to these fields has led to near-quantum leap in oil production from these tight oil units. The jump in oil production from the Bakken and Eagle Ford through the use of unconventional well completion and stimulation techniques led to the identification of the Monterey as a potential next big shale oil target (US EIA, 2011). Thus, a comparison between the nature of the Bakken and Monterey Formations can provide insights into assessing the possible increases in oil production in California resulting from implementation of well stimulation methods.

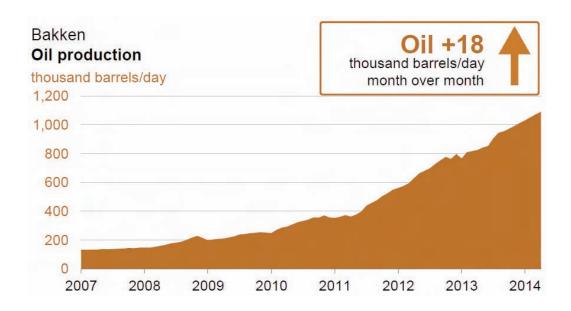


Figure 4-14. Increases in oil production from the Bakken Formation (US EIA, 2014a).

The Upper Devonian-Lower Mississippian Bakken Formation is a shale oil unit located in the Williston Basin, and found in North Dakota, Montana, Saskatchewan, and Manitoba (Gaswirth et al., 2013). It consists of three main zones: an upper unit, consisting of an organic-rich black shale; a middle unit, consisting of a silty dolostone or limestone to sandstone; and a lower unit, consisting of an organic black shale (Pitman et al., 2001). A fourth unit has been proposed for the Bakken, the Pronghorn unit, which underlies the lower shale unit and consists of a sandy unit previously known as the Sanish (LeFever et al., 2011). The Bakken has a maximum thickness of 160 ft (49 m) in the central portion of the basin (Fig. 4-15). The unit generally has a total thickness of less than 100 ft (30 m) (Lefever, 2008). The main target for production has been the middle dolomitic zone, while the upper and lower shales are considered the primary source rocks for hydrocarbons found in the Bakken. The shales are organic rich, with TOC values ranging from less than 1% up to 35%, and averaging around 11 wt. % (Webster, 1984). The Bakken petroleum system is located below the top of the oil generation window (Fig. 4-16), so hydrocarbons sourced from the shale unit are not required to have undergone significant migration (only into the adjacent dolomite unit (Sonnenberg et al., 2011)). This type of petroleum system is called a continuous petroleum accumulation (Nordeng, 2009). Unconventional techniques (horizontal drilling into the middle Bakken combined with multiple zone well stimulation) have been employed to maximize oil production from this formation (Jabbari and Zeng, 2012). Around 450 million barrels of oil have been produced using these techniques from the Bakken and Three Forks Formations in the Williston Basin between 2008 and 2013 (Gaswirth et al., 2013). The successful production of oil from the Bakken has prompted discussions regarding the possible recovery of oil from other shale oil formations such as the Monterey (Price and LeFever, 1992).

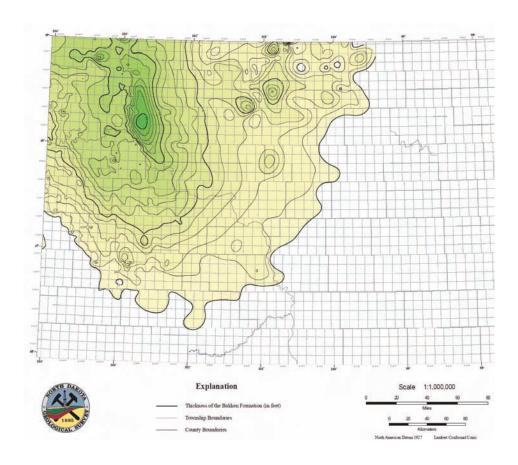


Figure 4-15. Isopach map of the Bakken Formation (Lefever, 2008).

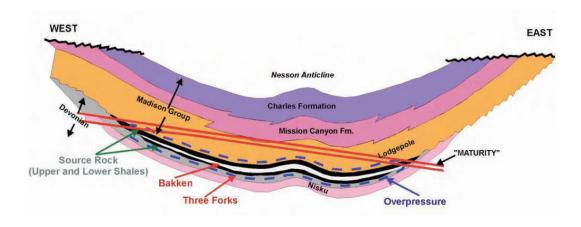


Figure 4-16. Schematic EW cross section of the Bakken petroleum system. Note that the Bakken lies below the top of the oil window (Sonnenberg et al., 2011).

4.4.5.1 Physical Properties

Core samples from the Middle Bakken unit obtained from the Parshall field have porosities ranging from 1-11% and permeabilities that average 0.0042 md (Simenson et al., 2011); a similar range of values of 1.1 to 10.2% (porosity) and <0.001 to 0.215 md (permeability) were reported by Ramakrishna et al. (2010). Production sweet spots involve areas with enhanced porosity and the presence of natural fractures (Pitman et al., 2001; Sonnenberg et al., 2011). Log-derived Young's modulus values for the Middle Bakken are around 7 GPa (Ramakrishna et al., 2010).

4.4.5.2 Similarities and Differences Between the Monterey and the Bakken Formations

The range of permeabilities of the Bakken dolomite reservoir unit (Middle Bakken) is similar to the permeability of porcelanites in the Monterey. The porosities of most of the Monterey lithologies, while varying significantly as a function of burial depth and degree of diagenesis, tend to be higher than those in the Middle Bakken dolomite.

The ages of these deposits are very different. The Monterey is Miocene in age and is still actively producing hydrocarbons, while the Bakken is much older (Upper Devonian-Lower Mississippian) in age.

The thicknesses of these units are dramatically different. The Bakken is typically less than 100 ft (30 m) in thickness, with a maximum thickness of 160 ft (49 m), and the producing middle dolomitic unit is generally less than 50 ft (15 m) thick, with a maximum thickness of around 90 ft (27 m). In contrast, the type section of the Monterey in the San Joaquin Basin is about 6,000 ft (1,830 m) thick (Mosher et al., 2013), and even greater thicknesses can be encountered in some of the basin depocenters. It is important to note that the organic-rich phosphatic shale portion of the Monterey, which would be the primary candidate for an unconventional oil resource in this formation, is considerably thinner (Figure 4-11).

The lithologic variability of the Bakken and Monterey are quite different. The Bakken Formation consists primarily of two distinct lithologies: (1) organic-rich shale, which makes up the upper and lower members of the Bakken (serving as the source rock), and (2) dolomite, which is the primary rock type of the producing middle Bakken member. In contrast, the Monterey consists of organic-rich, silicecous, and carbonate-rich shales and mudstones, porcelanite and diatomite, as well as interfingering sandstone turbidite bodies.

The structural setting of the Williston Basin in which the Bakken Formation resides is much less complex than those corresponding to the main sedimentary basins in California. The Williston Basin is an intracratonic basin that is not structurally controlled (Sloss, 1987), whereas the Neogene sedimentary basins in California are tectonically controlled, with faults and folds strongly influencing the trapping and accumulation of hydrocarbons in many of the major oil fields (Wright, 1991). The presence of wrench fault structures,

combined with a basement of highly deformed Mesozoic subduction complex rocks, has led to the creation of numerous trapping structures in many of the oil regions in California (Graham, 1987).

Because of the extreme variability of the Monterey, where bed lithologies vary on a centimeter scale, and diagenesis has dramatically affected rock physical properties, effective hydraulic stimulation methods vary significantly for different portions of the Monterey (El Shaari et al., 2011).

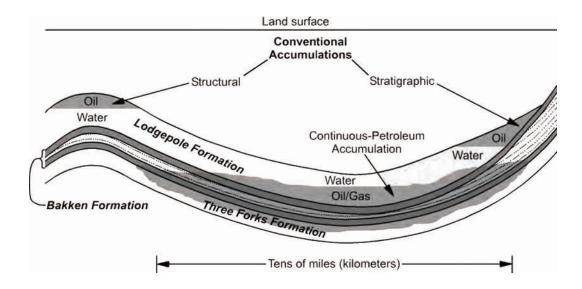


Figure 4-17. Schematic cross section illustrating conventional oil reservoirs (with migrating oil) and a continuous petroleum accumulation, as illustrated by the Bakken petroleum system (Nordeng, 2009).

The style of oil accumulation for the discovered resources associated with the Monterey Formation is different from that in the Bakken Formation. The producing oil fields that are hosted in the Monterey represent a conventional oil system where the oil has migrated from the source rock up into a reservoir zone that is capped by a trapping feature (structural, stratigraphic, or diagenetic trap). In contrast, the Bakken petroleum system represents a continuous petroleum accumulation (Fig. 4-17), where the oil is formed from organic-rich shales and migrates locally into an adjacent formation (the dolomite of the Middle Bakken) that is slightly more permeable and porous than the source shales (Nordeng, 2009). We note that the dolomite still has low enough permeability so that it requires stimulation for commercial production. The absence of faults and extensive fractures precludes hydrocarbon migration away from this region. It is possible that a similar type of oil accumulation could exist within the deeper portions of the Monterey, but significant amounts of oil that have been generated from these depocenters (areas where thickest accumulations of sediment have occurred) have migrated and accumulated

to form the main oil fields in California. The complex tectonic history for sedimentary basins in California, and the presence of natural fractures in the siliceous mudstones in the Monterey, would both indicate that oil generated in the basin depocenters would migrate via higher permeability fracture and fault pathways.

4.5 Oil-producing Sedimentary Basins in California

California is one of the largest oil producing states in the U.S., and hosts several giant (> 1 billion barrels of oil) oil fields. Detailed information on these oil fields can be found in DOGGR (1982; 1992; 1998) and on the DOGGR website http://www.conservation.ca.gov/dog/Pages/Index.aspx. Below is a summary of selected sedimentary basins in California (Fig. 4-18), including the two most prolific oil-producing regions (the San Joaquin and Los Angeles Basins), several regions with abundant oil production (the Ventura and Santa Maria Basins), and two basins with a few significant oil fields (the Salinas and Cuyama Basins). The Sacramento Basin has almost exclusively gas production (the Brentwood field is the exception (Ditzler and Vaughan, 1968)), and thus is not included in this discussion.

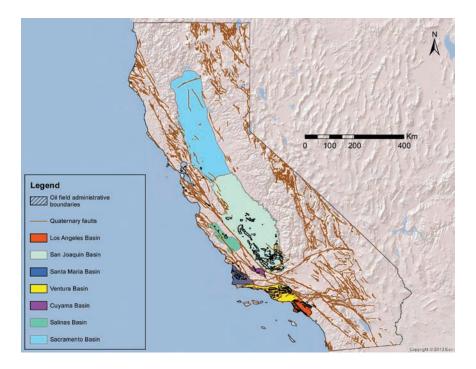


Figure 4-18. Map of major sedimentary basins and associated oil and gas fields in California.

For each of the basins described in this section, figures were generated that depict the basin boundaries, mapped Quaternary faults, the locations of active oil fields, the areal extent of the main source rocks, and where these rocks lie within the oil window (see

Figs. 4-19, 4-23, 4-24, 4-25, 4-26, 4-29, 4-31, 4-32, 4-35, and 4-36). The existing oil fields would correspond to the first type of well stimulation target mentioned in Section 4.2, whereas the deeper source rocks located within the oil window would constitute the second "unconventional shale oil" target.

4.5.1 Los Angeles Basin

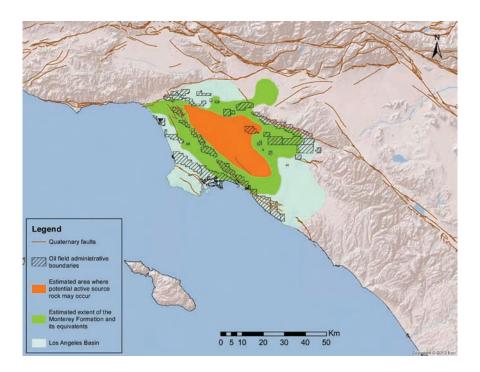


Figure 4-19. Map of the Los Angeles Basin with outlines of producing oil fields. The orange shaded area depicts where deep source rocks within the oil window are located. Data from DOGGR, Wright (1991), and Gautier (2014).

The Los Angeles Basin is an active margin Neogene sedimentary basin (Fig. 4-19) that has undergone transrotation, transtension, and more recently, transpression (Fig. 4-5) in response to active faulting over the past 18 Ma (Beyer, 1988; Ingersoll and Rumelhart, 1999). This complex deformational history has led to folding and faulting, creating structural traps for hydrocarbons (Wright, 1991). For example, the supergiant Wilmington oil field is hosted by a faulted, doubly plunging anticline (Mayuga, 1970; Montgomery, 1998). Sedimentation in this basin has been dominated by submarine fan deposits (Redin, 1991). Thick accumulations of Miocene and Pliocene sandstones of the Puente and Repetto Formations serve as the primary oil reservoir rocks. Organic-rich Miocene shales, also described as nodular organic shales, serve as the source rock for these prolific oil fields (Behl and Morita, 2007; Beyer, 1988; Hoots et al., 1935; Lanners, 2013; Walker et al., 1983); these shales are interpreted to be time correlative with the Monterey

Formation. Cross sections of four oil fields, West Beverly Hills, East Beverly Hills, Inglewood, and Huntington (Fig. 4-20) depict the oil reservoir rocks, the structural traps, and the underlying source rocks (Lanners, 2013).

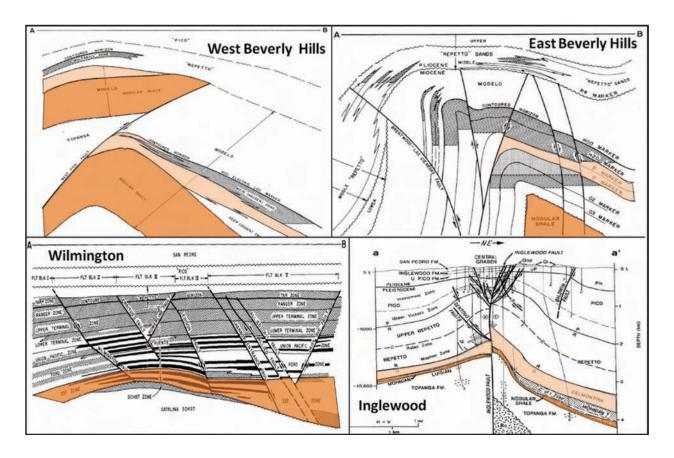


Figure 4-20. Cross-sections of the West Beverly Hills, East Beverly Hills, Wilmington, and Inglewood oil fields (Lanners, 2013). Dark-shaded areas depict location of main oil reservoir sections, orange-shaded areas depict organic-rich source rocks of Miocene age.

The USGS has recently conducted an assessment of the recoverable oil from of the ten giant (each with accumulations greater than 1 billion barrels of oil) oil fields in the Los Angeles Basin (Gautier et al., 2013). Based upon a probabilistic assessment of the original oil in place, the amount of oil produced, and expected recovery factors employing existing oil field technology, the USGS calculated a mean estimate of an additional 3.2 billion barrels of oil that could be recovered from these fields. According to Gautier et al. (2013), the recovery of this quantity of oil in place in these fields would require the "unrestricted application of current best-practice technology, including improved imaging and widespread application of directional drilling, combined with extensive water, steam, and CO₂ floods"; it does not indicate whether hydraulic and acid stimulation methods

would be applied. This estimate does not include potential contributions from the other 58 existing oil fields in the basin, nor does it consider the discovery of new conventional fields, nor resources derived from unconventional sources, such as shale oil.

4.5.2 San Joaquin Basin

The San Joaquin Basin is located in the southern portion of the Great Valley, a large topographic depression between the Sierra Nevada and the Coast Ranges (Fig. 4-21). It first formed as a forearc basin (located between the subduction zone and the volcanic arc (the Sierra Nevada batholith represent the intrusive roots of this system)) during the Mesozoic and was associated with subduction along the continental margin. A change from a convergent to a transform plate boundary during the Cenozoic led to periods of subsidence and uplift (Goodman and Malin, 1992; Hosford Scheirer and Magoon, 2008; Schwochow, 1999). The basin is filled with a thick sequence of Cretaceous to Quaternary sediments, with mixed marine and continental sources (Hosford Scheirer and Magoon, 2008; Johnson and Graham, 2007; Schwochow, 1999)

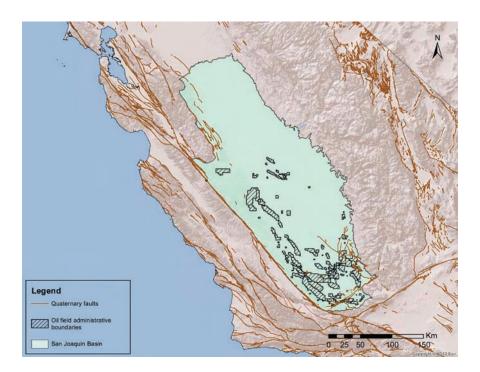


Figure 4-21. The San Joaquin Basin and producing oil fields (Oil field data from DOGGR).

Mega-sequences (2nd order) SYSTEM NORTH CENTRAL SOUTH East West East West East Ma basin axis basin axis basin axis PLEIS Tulare Fm. San Joaquin Fm San Joaquin Fm_ PLIO. Etchegoin Fm Etchegoin Fm 5 Reef Ridge Sh Mbr E. McLure Shale Mbr 10 McDonald Sh Nibr Devilwater Sh Temblor Fm Media Sh Mbi ion and ` ` _ magmatism` 20 ion 25 Subduct ZEMORRIAN 30 Wygal Ss Mi REF. Tumey formation 35 Diablo Range uplift and basin subsidence 40 hagen Formation Kreyenhagen Formation ULATSIAN Kreyenhagen Formation 45 Canoas Sits Mb Domengine Fm V B=Buttonbed Ss Mbr PH=Pyramid Hill Sd Mb KR=Kern River Fm Domengine Fm subduction nd Laramide orogeny -Gatchell sd - Arroyo Hondo Sh Mbr PENUTIAN Potential nonma reservoir rock 55lab 60-Oil-prone source Hiatus or loss by CHENEYIAN Flat undifferentiated Cretaceous 65 70-CAMPANIAN 75 Panoche Fm | -Convergent margin and Sierran magmatism 80 SANT. 85 RVS=Ragged Valley si CON 90 TUR undifferentiated Cretaceous undifferentiated Cretaceous 95 marine and nonmarine strata 100 160 Ma 105 Basement rocks

SAN JOAQUIN BASIN PROVINCE

Figure 4-22. Summary stratigraphic sections for the San Joaquin Basin, highlighting relative locations of source and reservoir rocks (Hosford Scheirer and Magoon, 2008

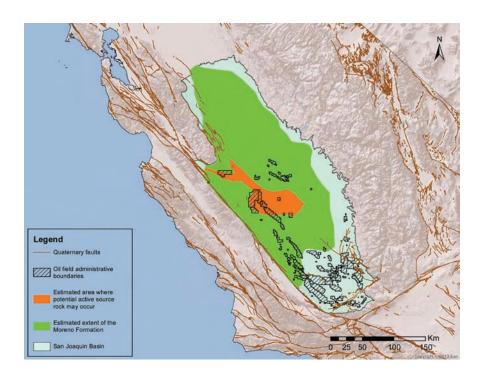


Figure 4-23. Distribution and estimated active source area of the Moreno Formation in the San Joaquin Basin (Magoon et al., 2009).

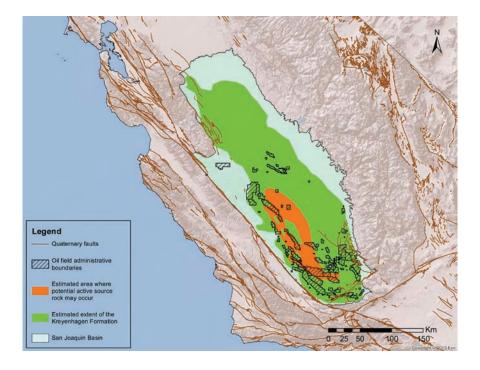


Figure 4-24. Distribution and estimated active source area of the Kreyenhagen in the San Joaquin Basin (Magoon et al., 2009).

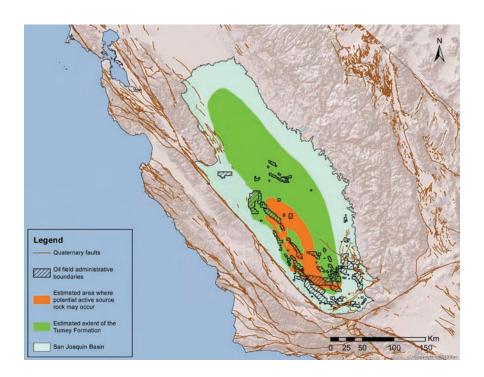


Figure 4-25. Distribution and estimated active source area of the Tumey in the San Joaquin Basin (Magoon et al., 2009).

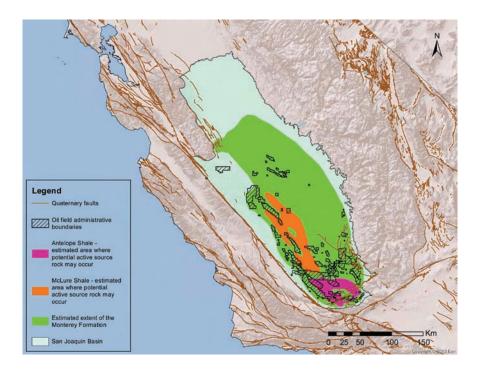


Figure 4-26. Distribution and estimated active source area of the Monterey in the San Joaquin Basin (Magoon et al., 2009).

The Monterey is the dominant source rock for producing oil fields in the San Joaquin Basin and also serves as a reservoir rock for many oil fields. However, many of these reservoirs are located above the oil window (Fig. 4-3), and the kerogen present at reservoir depths is thermally immature, suggesting that the oil migrated updip from deeper in the basin (Graham and Williams, 1985; Kruge, 1986).

In several fields in the San Joaquin, such as South Belridge and Lost Hills, significant oil production occurs from the upper Monterey diatomite unit (Bowersox, 1990; Schwartz, 1988). These reservoir rocks have high matrix porosities, but low permeabilities (see Section 4.4.1.1 for more details). Directional wells targeting specific pay zones coupled with hydraulic fracturing (Fig. 4-27) have been employed to improve hydrocarbon recovery from the South Belridge and Lost Hills fields (Allan et al., 2010; El Shaari et al., 2011; Emanuele et al., 1998; Wright et al., 1995). While some oil production occurs from low-permeability diatomite and fractured siliceous mudstones in the Monterey at the Midway-Sunset field, the most productive intervals are interbedded turbidite sands (Fig. 4-28) (Link and Hall, 1990; Mercer, 1996; Underwood and Kerley, 1998). These sands have much more favorable reservoir properties (porosity ~33%, permeabilities between 800-4,000 md) than the Monterey lithologies that surround them (Link and Hall, 1990).

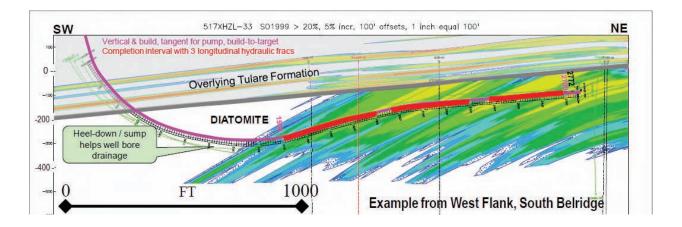


Figure 4-27. Schematic of directional well for the South Belridge field targeting the top of the diatomite unit, oriented longitudinally along the flanks of the anticline, with hydraulic fracturing to improve well performance (Allan and Lalicata, 2012).

Production also occurs from diagenetically transformed diatomite, porcelanite, in the Elk Hills field (Reid and McIntyre, 2001). Oil production out of the Antelope shale member of the Monterey at the Buena Vista Hills field (mostly consisting of porcelanite) has been hampered by low primary recovery values of 4-6%. Attempts to stimulate the reservoir using hydraulic stimulation techniques led to the generation of a complex system of fractures, which seemed to increase flow tortuosity near the well bore. The failure to stimulate longer vertical fractures was thought to be due in part to the wide contrast in

rock strength on a bed-to-bed scale, leading to delamination and poor transmission of proppants into the fracture network (Montgomery and Morea, 2001). Enhanced oil recovery using CO₂ flooding was proposed as a means to improve oil recovery in this field.

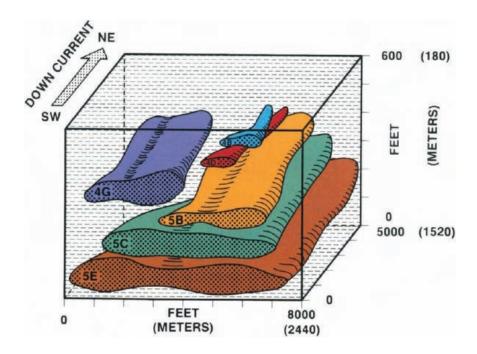


Figure 4-28. Block diagram depicting location of Webster sand turbidite lobes within the Antelope Shale Member of the Monterey Formation in the Midway-Sunset field (Link and Hall, 1990).

The USGS has recently conducted an assessment of the recoverable oil from nine major oil fields in the San Joaquin Basin (Tennyson et al., 2012). Based upon a probabilistic assessment of the original oil in place, the amount of oil produced, and expected recovery factors employing existing oil field technology, the USGS calculated a mean estimate of an additional 6.5 billion barrels of oil that could be recovered from these existing fields. Tennyson et al. (2012) note that "much of the potential reserves could come from improved recovery in diatomite reservoirs of the Monterey Formation". Given that the increased production of oil from Monterey diatomite reservoirs in the San Joaquin (such as at South Belridge) has been associated with most of the well hydrofracturing conducted in California (see Section 3), this increased recovery would certainly require similar well stimulation methods. This estimate does not include potential contributions from the other oil fields in the basin, nor does it consider the discovery of new conventional fields, nor resources derived from unconventional sources, such as shale oil. Results of exploratory drilling in deeper portions of the San Joaquin Basin, which would test the viability of the Monterey Formation source rock oil play, are discussed in Section 4.6.

4.5.3 Santa Maria Basin

The Santa Maria Basin is located along the coast of California between Point Arguello and San Luis Obispo (Fig. 4-29). It is bounded by the San Rafael Mountains and Sur-Nacimiento fault to the northeast and the Santa Ynez Mountains and Santa Ynez fault to the south (Sweetkind et al., 2010; Tennyson and Isaacs, 2001; Tennyson, 1995). Changes in plate interactions have led to a complex tectonic evolution of this basin, with episodes of extension and subsidence, shortening and uplift, and rotation (McCrory et al., 1995). It contains a thick sequence of Neogene sediments, most of which are Miocene and younger. The Monterey Formation is the principal source rock for oil fields in this basin, and most of the production occurs from fractured siliceous mudstone, porcelanite, chert, and dolomite in the Monterey (Isaacs, 1992b; MacKinnon, 1989; Tennyson and Isaacs, 2001). Fractured diagenetic dolomites have been identified as a significant component of some of the producing oil fields from this basin (Roehl and Weinbrandt, 1985). Oil fields in this basin are localized in faulted anticline structures, and deeper synclines are interpreted to represent the source region for the migrated hydrocarbons produced from these fields (Fig. 4-30). A brief description of the results of deep exploration drilling in the Santa Maria Basin is presented in Section 4.6.

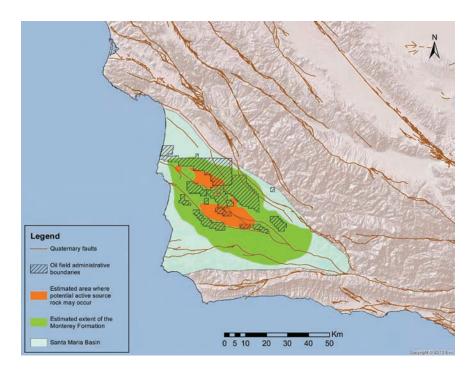


Figure 4-29. Santa Maria Basin and producing oil fields (Oil field data from DOGGR). Distribution of Monterey Formation (green) and portion below top of oil window (~6,700 feet depth - Tennyson and Isaacs, 2001) highlighted in orange) determined using data from Sweetkind et al. (2010).

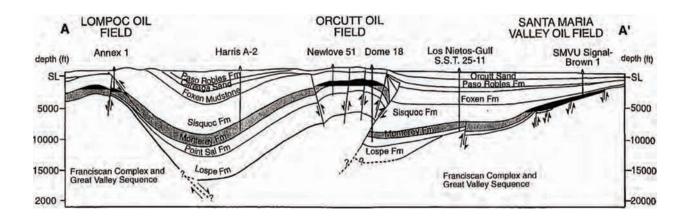


Figure 4-30. NS cross section through the Santa Maria Basin (Tennyson and Isaacs, 2001). Oil fields are located in faulted anticlinal traps – oil presumed to be generated in deeper synclines.

4.5.4 Ventura Basin

The Ventura Basin (and the adjacent offshore Santa Barbara Basin) is a structurally complex faulted and folded synclinal trough between the Santa Ynez Mountains to the north and the Santa Monica Mountains and Channel Islands to the south (Fig. 4-31) (Dibblee, 1988; Keller, 1988; 1995; Nagle and Parker, 1971; Tennyson and Isaacs, 2001). It contains a thick sequence (up to 36,000 ft (11,000 m) of Upper Cretaceous, Tertiary, and Quaternary sediments. In the primary depocenter, the Plio-Pleistocene sedimentary section can reach thicknesses of up to 20,000 ft (6,100 m) (Dibblee, 1988; Nagle and Parker, 1971) (Fig. 4-32). Most of the oil accumulations in the basin are associated with faulted anticlinal traps (Keller, 1988; Nagle and Parker, 1971; Tennyson and Isaacs, 2001). While the main source rock for this basin is thought to be the Monterey, the overlying Sisquoc Formation and the underlying Rincon shale may also be sources of hydrocarbons. The Monterey is age-correlative with the Modelo Formation, which contains a much higher proportion of sandstone (Nagle and Parker, 1971). The most prolific oil fields in this basin produce from sandstones from the Pliocene Pico and Repetto Formations (Keller, 1988; Nagle and Parker, 1971; Tennyson and Isaacs, 2001). Production from the fractured Monterey is limited to a few fields, including the offshore South Elwood and Hondo fields (Tennyson and Isaacs, 2001).

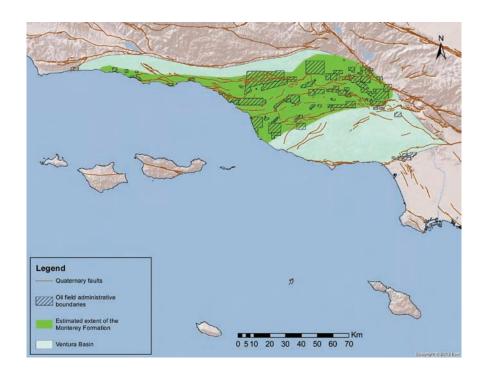


Figure 4-31. The Ventura Basin and producing oil fields (Oil field data from DOGGR). Distribution of the Monterey (green) from Nagle and Parker (1971). No data were available to constrain the distribution of the active source rock for this basin.

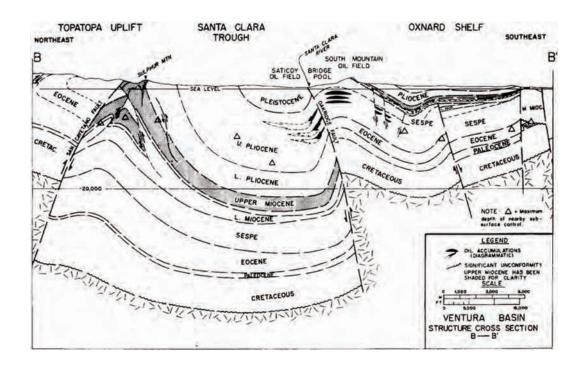


Figure 4-32. NE-SW cross-section through the Ventura Basin (Nagle and Parker, 1971).

4.5.5 Cuyama Basin

The Cuyama Basin is a Neogene basin located in the southern Coast Ranges in central California, just west of the San Andreas Fault (Fig. 4-33). The basin contains nonmarine and marine sediments, and has been affected by strike-slip and thrust faulting (Baldwin, 1971).

In the Cuyama Basin, the Saltos shale forms the lower part of the Monterey Formation, while the Whiterock Bluff shale forms the upper section. The Branch Canyon sandstone is intercalated with both of these shale units, and is more abundant in the SE portion of the basin, which had a larger input of terrigenous sediments (Lagoe, 1982; 1984; 1985). The Saltos shale has a larger terrigenous sedimentary component than the Whiterock Bluff shale and consists of interbedded sandstones, mudstones, and impure carbonates. In contrast, the Whiterock Bluff shale is dominated by biogenic sediments, and consists of siliceous and diatomaceous shales and mudstones with minor dolomitic interbeds (Lagoe, 1985).

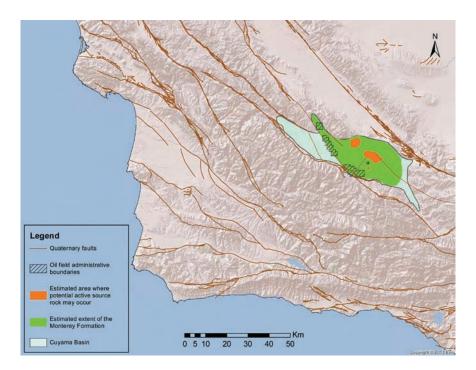


Figure 4-33. Cuyama Basin and associated oil fields (DOGGR), along with distribution of Monterey source rock (Sweetkind et al., 2013) and portion below top of oil window (~2.7 km depth based on data from Lillis (1994)).

Oil production from this basin is predominantly from the Painted Rock Sandstone member of the Miocene Vaqueros Formation, which underlies the Monterey Formation (Fig. 4-34) (Isaacs, 1992a). Based on carbon stable isotope compositions and biomarker data, Lillis (1994) determined that the source rock is the Soda Lake shale member of the Early Miocene Vaqueros Formation. The distribution of the Soda Lake shale member and the portion of this unit that lies within the oil window are depicted in Figure 4-35.

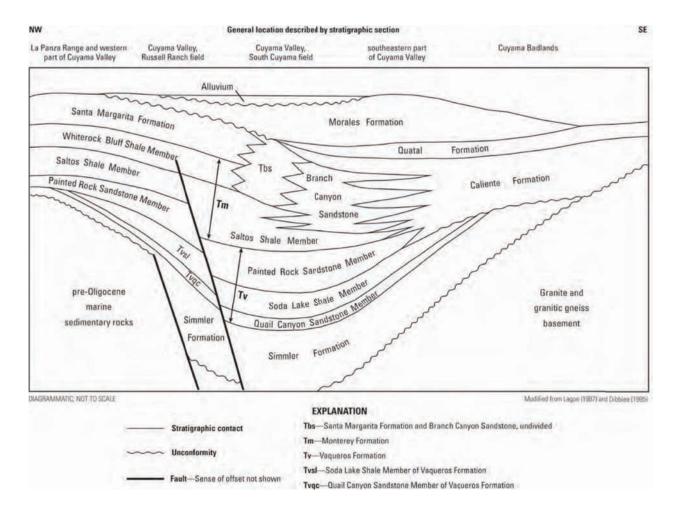


Figure 4-34. Diagrammatic NW–SE stratigraphic section across the Cuyama Basin (Sweetkind et al., 2013).

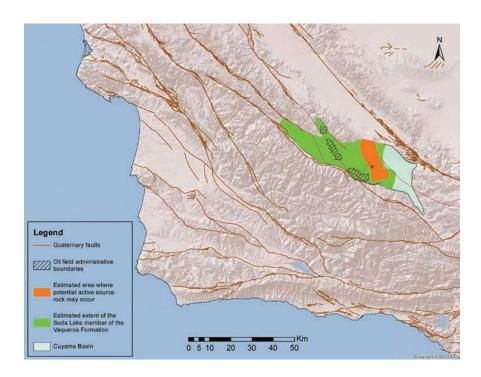


Figure 4-35. Cuyama Basin and associated oil fields (DOGGR), along with distribution of Vaqueros source rock (Sweetkind et al., 2013) and portion below top of oil window (\sim 2.5 km depth based on data from Lillis (1994)).

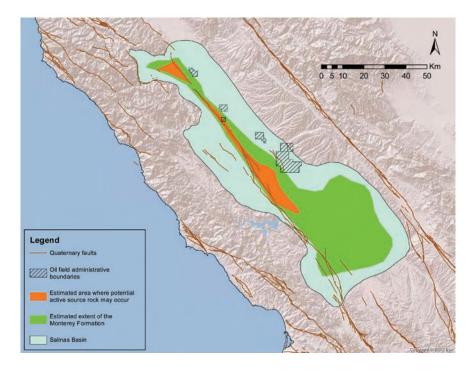


Figure 4-36. Salinas Basin and associated oil fields (DOGGR), along with distribution of source rock (green) and portion below top of oil window (\sim 2,000 m - Menotti and Graham, 2012), with data from Durham (1974) and Menotti and Graham (2012).

4.5.6 Salinas Basin

The Salinas Basin is a Neogene basin dominated by wrench tectonics, with mid-Miocene subsidence associated with transfersion and subsequent uplift, folding, and faulting associated with transpression (Colgan et al., 2012; Durham, 1974; Graham, 1978; Menotti and Graham, 2012) (Figure 4-36). The period of basin subsidence coincided with deposition of a thick sequence (up to 3 km) of Monterey Formation sediments (Menotti et al., 2013). Laminated marine shales from the lower portion of the Monterey have elevated total organic carbon contents (TOC), with moderately laminated shales having average TOC values of 3.12% and well-laminated hemipelagic Monterey sediments having an average TOC value of 4.59%, making them good candidates for oil source rocks (Mertz, 1989). The Salinas Basin contains a single large oil field, the San Ardo field (Baldwin, 1976; Isaacs, 1992a). A cross section through this field (Fig. 4-37) illustrates the important role that structural features play in the migration and trapping of oil (Menotti and Graham, 2012).

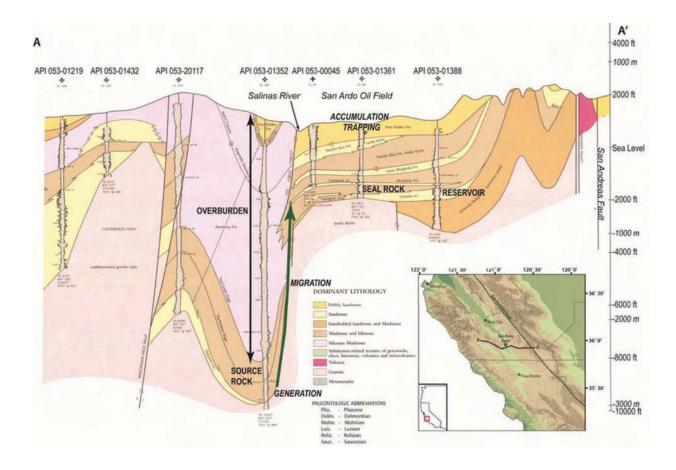


Figure 4-37. E-W cross section through the San Ardo oil field, Salinas Basin, depicting key components of the petroleum system (Menotti and Graham, 2012).

4.5.7 General Observations of Neogene Sedimentary Basins in California

While there are numerous differences between different Neogene sedimentary basins in California, they do share a number of common characteristics. They all have complex tectonic histories that have been shaped by the transform plate boundary characterized by the San Andreas Fault system. Phases of rotation, extension, and compression associated with this faulting led to episodes of basin deepening, uplift, and deformation. During the Miocene, there was extensive deposition of silica-rich fine-grained marine sediments in many of these basins, resulting in the Monterey Formation. The organic-rich phosphatic shale portion of this thick and areally extensive unit is the primary source rock for most of the major oil fields in California. The structural complexity of the basins led to the development of structural traps on the margins of the basins, where most of the producing oil reservoirs are encountered. The zones where oil generation occurs (within the oil window) are in the deeper portions of the basins. Oil has migrated from the active source rock areas into the reservoir rocks, and has been trapped by impermeable seals that overlie the reservoirs. Areas with potentially active source rock have been identified in each basin, but as discussed below in Section 4.6, exploration wells drilled into these active source rocks as a shale oil play have not yet resulted in the discovery of new oil fields in California.

4.6 Results of Exploratory Drilling of Deep Shales in California

Relatively few of the hundreds of thousands of oil wells drilled to date in California have targeted deep exploration zones (Schwochow, 1999), in part due to the higher costs, and also because many of the discovered oil fields are hosted in relatively shallow reservoirs with structural traps that lie above the oil window (Fig. 4-3). As noted in Section 4.5, source rocks within the Neogene sedimentary basins in California are found at depths typically greater than 8,000 to 10,000 feet (2.4 to 3.0 km), which marks the top of the oil window. Deep wells are needed to ascertain if these source rocks retain significant hydrocarbons and could serve as unconventional shale oil reservoir rocks.

Deep drilling beneath the existing oil reservoirs at the Elk Hills oil field (San Joaquin Basin) was conducted by the United States Department of Energy (DOE) to evaluate the prospects for hydrocarbon production from deeper reservoir intervals (Fishburn, 1990). Three deep wells were drilled, ranging in depth from 18,270 to 24,426 ft (7,455 m). While these wells did not encounter commercial quantities of hydrocarbons beneath the main production units of the field, they did have oil and gas shows. Cores of shale recovered from the Eocene Kreyenhagen Formation, the top of which was encountered at a depth of 15,700 ft (4,785 m) in the 987-25R well, exuded oil and gas from fine fractures. This shale overlies a 325 ft (99 m) thick section of oil-stained sands from the Eocene Point of Rocks sandstone, which is just above an 800 ft (244 m) thick section of salt. Measured porosity values for this sandstone range from 14-16% in this well, but are quite a bit lower (around 6%) for the same stratigraphic section in the 934-29R well, which encountered it at depths between 21,640 to 22,890 ft (6596 to 6977 m). Much higher porosities (20-35%) are observed for this unit where it is encountered at

significantly shallower depths (<3000 feet) in other oil fields in the San Joaquin Basin (Schwochow, 1999), suggesting that compaction due to burial and diagenesis has led to significant porosity reduction. Average measured core permeabilities for this sandstone were around 4 md in the 987-25R well and less than 1 md in the deeper occurrence in the 934-29R well. The location of the oil window beneath the Elk Hills field based on vitrinite reflectance measurements is estimated to be between depths of 12,900 to 19,200 ft (3,930 to 5,850 m). The only oil field that has reported significant production of oil from the Point of Rocks Sandstone where it is encountered at depths greater than 9,000 ft (2,740 m) is the McKittrick field; this pool also has substantial gas production (Schwochow, 1999).

Another potential deep target consists of shales that have been displaced deeper due to thrust faulting and folding such as a fault displacement gradient fold at the Lost Hills field (Fig. 4-38) as described by Wickham (1995). Based upon a subthrust play developed for the East Lost Hills, several exploratory deep wells were drilled into the footwall. The first well, spudded in 1998, encountered a high gas pressure surge while drilling in the Temblor at a depth of 17,640 ft (5377 m), and as the crew attempted to circulate out the gas, the venting gas and hydrocarbons ignited, engulfing the rig in flames. It took more than 6 months to bring the well under control (Schwochow, 1999). However, of the 65-70 deep wells that were drilled to a depth greater than 15,000 ft (4,570 m) in the San Joaquin Basin by 1999, none proved to be commercially productive (Schwochow, 1999).

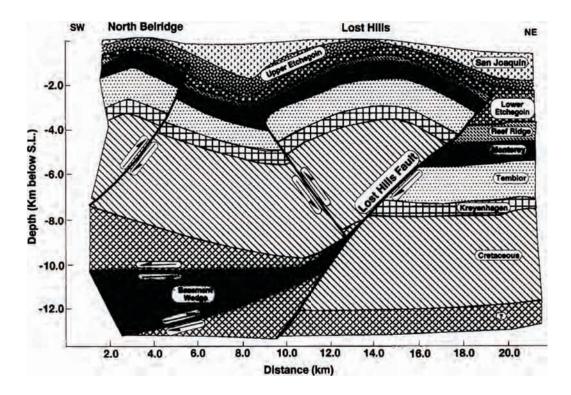


Figure 4-38. Cross section through the Lost Hills oil field constrained by seismic data depicting relative downward offset of Monterey and other units in footwall block of Lost Hills thrust fault.

Within the Santa Maria Basin in the Los Alamos field, innovative drilling techniques were used to drill a deep target (~10,000 ft true vertical depth (TVD)) in the Monterey, where a fractured siliceous shale interval had been identified (Witter et al., 2005). However, even though a highly deviated well course that intersected numerous fractures was drilled, the well did not result in sustained commercial production.

With the success of unconventional drilling and well completion methods in other oil shale areas in the U.S., there has been renewed focus on the Monterey to explore the effectiveness of using these methods (Durham, 2010, 2013; Redden, 2012). Venoco and Oxy have drilled a number of deeper wells targeting zones between 6,000 and 14,000 feet, and have employed well stimulation techniques in an attempt to increase hydrocarbon production. As part of this exploration effort, Venoco has drilled a number of deeper wells in the Semitropic field that target the Monterey, which lies below the Randolph sands of the Pliocene Etchegoin Formation, where most current production from this field occurs. One of these new wells, the Scherr Trust et al 1-22 (API 03041006), was spudded in Dec. 2010 and drilled to a depth of 14,015 ft (4272 m) (13,921 ft (4243 m) TVD) (Fig. 4-39) (http://owr.conservation.ca.gov/Well/WellDetailPage.aspx?domsa pp=1andapinum=03041006). The primary target was the Monterey "N" chert; this zone was perforated (depth interval of 12,495-12,510 ft (3808-3813 m) and then fracture stimulated, but only a very limited amount of oil was produced in subsequent flow tests.

Based on reviews of DOGGR records for new wells from this field and the neighboring Bowerbank field, these deeper Monterey wells have not been very successful to date. A review of drilling results for unconventional oil reservoirs in the Monterey for a number of fields in the San Joaquin Basin from 2009 to 2013 by Burzlaff and Brewster (2014) indicates that average initial production rates are on the order of 75-150 barrels of oil per day. Projected expected ultimate recovery (EUR) from these wells is estimated to be on the order of 20,000-25,000 barrels for wells in fields on the west side of the San Joaquin Basin and about 90,000-100,000 barrels for wells located in fields on the eastern margins of the basin, with much higher gas-to-oil ratios for the west side wells. An industry report of testing of hydraulic fracturing and oil production in the Kreyenhagen indicates the presence of mobile oil (Petzet, 2012). However, no evidence has been found to suggest any further development of oil production from the Kreyenhagen.

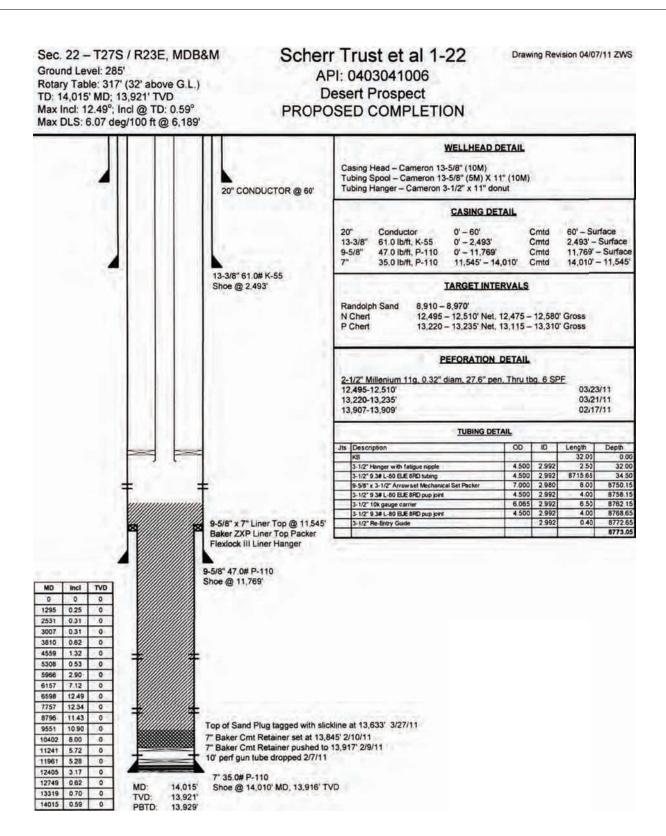


Figure 4-39. Schematic well completion diagram for Scherr Trust et al 1-22 well in Semitropic field, with Monterey "N" chert interval perforated and hydrofractured (DOGGR records).

4.7 Review of the US EIA 2011 Estimate of Monterey Source Rock Oil

US EIA (2011) estimated that there are 15.4 billion barrels of technically recoverable shale oil resources in the Monterey/Santos play in southern California. This estimate was based on the play covering an area of 1,752 square miles (4,538 km²), with 16 wells per square mile, and each well recovering an average of 550,000 barrels of oil. This prospective play area covers parts of the San Joaquin, Los Angeles, Ventura, Santa Maria, Cuyama, and Salinas Basins, and includes offshore regions. For this play, the oil shale is located at depths varying between 8,000 and 14,000 ft (2,440 and 4,270 m) and with thicknesses ranging from 1,000 to 3,000 ft (305 to 914 m). Other estimated shale play properties include an average porosity of 11% and a TOC of 6.5 % (US EIA, 2011).

The calculated total areas of estimated active (below the top (Ro > 0.6) and above the bottom (Ro < 1.2) of the oil window) Monterey (and Monterey equivalent) source rocks for the major onshore oil basins in California (as depicted in Figures 4-18, 4-25, 4-28, 4-30, 4-32, and 4-35) are summarized in Table 4-2. The calculated areal extent of the potential unconventional Monterey resource (4532 km²) is similar to that reported by US EIA (2011), which is 4538 km². Given that the onset of oil generation may begin at lower vitrinite reflectance levels in the Monterey (Walker et al., 1983; Petersen and Hickey, 1987), the extent of active oil generation may be greater, as this could extend the oil window to shallower depths.

Table 4-2. Estimated extent of potential Monterey Formation unconventional oil shale play.

Basin	Areal extent of source rock (km²)	References
Los Angeles	455	Wright, 1991; Gautier, 2014
San Joaquin (Antelope)	1309	Magoon et al., 2009
San Joaquin (McLure)	2309	Magoon et al., 2009
Santa Maria	204	Tennyson and Isaacs, 2001; Sweetkind et al., 2010
Ventura	unconstrained	Nagle and Parker, 1971
Cuyama	33	Lillis, 1994; Sweetkind et al., 2013
Salinas	222	Durham, 1971; Menotti and Graham, 2012
Total	4532	

The assumed average oil production amount per well for the US EIA report (550,000 barrels) significantly exceeds the observed long-term cumulative productivity of wells in this formation in conventional oil fields. Hughes (2013) conducted an extensive review of all oil wells in the San Joaquin and Santa Maria Basins that were drilled since 1980 and that produce from the Monterey Formation. For wells with a production history of at least 10 years, Hughes found that the average cumulative oil production of wells with vertical and directional completions was 127,000 barrels and 97,000 barrels from the San Joaquin

Basin and 67,000 and 141,000 barrels from the Santa Maria Basin (Fig. 4-40). Based on these observed historical production rates, it is unlikely that the average recovery per well from Monterey source rocks will be as high as the average cumulative production of 550,000 barrels assumed in the US EIA report. A 4 to 5-fold increase in average well productivity relative to current production in the conventional reservoirs would need to be achieved to meet the assumed levels for unconventional production in what is essentially an unproven resource.

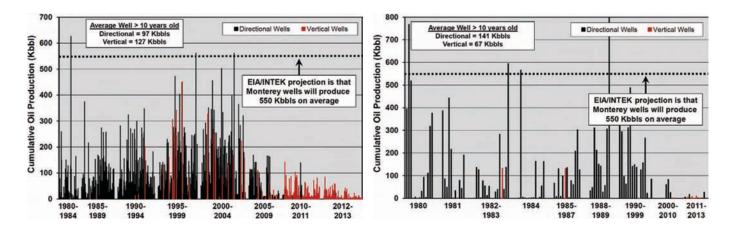


Figure 4-40. Cumulative oil production grouped by year of first production, 1980 through June 2013. Left – Monterey wells from the San Joaquin Basin; Right – Monterey wells from the Santa Maria Basin. Figures from Hughes (2013) based on data obtained from the Drillinginfo production database. Dashed line denotes average cumulative well production assumed in US EIA/INTEK report.

The US EIA (2011) estimate of total recoverable oil from the Monterey source rock appears to be overstated given that the assumed average oil recovery per well is significantly higher than historical production from wells in oil fields that have Monterey reservoir rocks. Due to a lack of operational experience, the potential recovery factor for this shale oil target is poorly constrained, but it is likely to be lower than what is currently obtained for Monterey-hosted oil reservoirs for a number of reasons, including expected lower permeability and porosity of the deeper source rocks. In addition, there is little information regarding the amounts of oil remaining in place in the deep (below oil window) portions of the Monterey. The thickness of the Monterey used in the INTEK model may also be overstated, as only a portion of the Monterey Formation has elevated organic contents which would allow it to serve as a source rock (Fig. 4-11). Well stimulation would likely be required to produce any remaining oil present in these source rocks given their intrinsically low matrix permeabilities.

The EIA Assumptions to the Annual Energy Outlook 2014 report (US EIA, 2014b) has revised the estimated unproved technically recoverable shale oil from the Monterey/Santos to a value of 0.6 billion barrels. This revision is based on new estimates of the potential area, the well density, and the production per well (Table 4-3). The biggest change in the new EIA analysis results from a nine-fold reduction in the prospective area estimate; the projected well production rate is only 20% lower than that used in the INTEK model. The revised model has also assumed the use of wells with horizontal completions, thus resulting in fewer wells per square mile.

Table 4-3. Comparison of model parameters for 2011 INTEK and 2014 EIA estimates of unproved technically recoverable oil from Monterey/Santos play.

	INTEK (2011)	EIA (2014)
Areal extent (mi²)	1752	192
Wells/mi ²	16	6.4
Production/well (Kbbl oil)	550	451
Total recoverable oil (Bbbl oil)	15.4	0.6

4.8 Prognosis

The Monterey Formation (and its Miocene equivalents) is the dominant source rock for much of the oil production in California. It also serves as an important reservoir rock with significant resources of migrated oil produced from several active fields, both from interbedded turbidite sandstones (such as the Stevens sand), as well as from diatomite and fractured siliceous shale, porcelanite, and dolomite. The large areal extent of the Monterey over most of the main sedimentary basins in California, as well as its thickness (up to 6,000 ft (1,830 m)), make it a significant petroleum resource target. The Monterey is a very young unit (Miocene), and it is currently still generating hydrocarbons.

All of the sedimentary basins in California have been impacted by active tectonism, which has resulted in the development of faults and folds, which serve as key structural components for the major oil fields. Understanding the interplay between structures and fluid flow in the subsurface will be critical in discovering new resources, as well as designing well stimulation methods that interact with the natural fracture network and improve recovery rates of hydrocarbons.

Almost all of the existing major oil fields that involve the Monterey occur at depths that are shallower than the oil window. This suggests that these fields contain oil that was sourced from deeper portions of the Monterey and subsequently migrated upwards and was trapped in the shallower intervals by either structural, stratigraphic, or diagenetic traps. This is confirmed by evaluation biomarker maturity indicators, which demonstrate that the oil found in most Monterey Formation oil reservoirs in the San Joaquin was not generated in situ, but instead was sourced from deeper Monterey shales (Kruge, 1986).

For the Monterey Formation source rocks to also be reservoirs for unconventional production of oil, they would need to retain oil that was self-sourced (i.e., was formed in place and has not migrated). There is a considerable amount of the Monterey Formation within the deeper portions of major basins that lies within the oil window, but only a portion of the total thickness of this formation (primarily the organic-rich phosphatic shales in the Middle Monterey (Fig. 4-11)) would serve as a prospective unconventional oil shale target. These intervals could potentially host oil that has not migrated, and could perhaps be extracted using well stimulation methods. However, there is little published information on these deep sedimentary sections, so it is difficult to estimate the potential recoverable reserves associated with these rocks. Few deep wells have been drilled to date, and there are no reports of successful production from such depths. Reservoir quality of these rocks may be reduced through compaction and diagenesis, which would reduce porosity and permeability with depth (Schwochow, 1999).

Because of the higher depths and temperatures encountered within the oil window, compaction and diagenetic effects would result in the conversion of what was originally biogenic opal-A to opal-CT or microcrystalline quartz. This would cause a reduction in matrix porosity, but could also result in siliceous shales that are more brittle and that have developed natural fractures (Chaika and Williams, 2001). The presence of such fractures could lead to increased formation permeability that could permit upward migration of oil.

The Monterey Formation is fundamentally different from the other major low-permeability unconventional oil units, such as the Bakken, in its highly variable mineralogy, lithology, and changes in silica phase (El Shaari et al., 2011) and the structural complexity of the basins within which is it located (e.g., Wright, 1991; Ingersoll and Rumelhart, 1999). This variability makes it more challenging to discover and produce source-rock oil, as evidenced by the available information regarding the results of deep drilling in the San Joaquin Basin. There is a lack of data regarding oil saturations for the Monterey Formation at depths below the oil window. This is due in part to the lack of deep wells. One other factor is that oil-based muds are often used when drilling through shale units, as the presence of swelling clays can be problematic for wellbore stability if water-based drilling fluids are used. This could obscure the presence of naturally occurring oil in these well sections.

Within the San Joaquin Basin, there are several other deeper shale units that serve as source rocks and that could potentially host additional unconventional shale oil resources. Based on the distributions of the Moreno, Kreyenhagen, and Tumey Formations and the depth to the top and the base of oil window reported by Magoon et al. (2009), potential active source regions (with Ro > 0.6 and < 1.2) for each of these units were identified (Figs. 4-23, 4-24, and 4-25). The calculated areal extents of the potential unconventional resource plays for the Moreno, Kreyenhagen, and Tumey are 2529, 3629, and 3527 km², respectively. However, there is very little information available on how much generated oil these deep shale units still retain.

The potential volume of migrated oil in new conventional onshore discoveries in California is relatively small. The USGS assessed the mean of this potential for the San Joaquin Basin as 393 million barrels of additional recoverable oil (Gautier et al., 2003). Fig. 4-40, which shows the history of onshore oil field discoveries in California, provides some perspective on this assessment. Only one new field, Rose (Ganong et al., 2003), has been discovered since 1990. Hydraulic fracturing has been used to develop this field, suggesting well stimulation could play a role in producing future migrated oil discoveries.

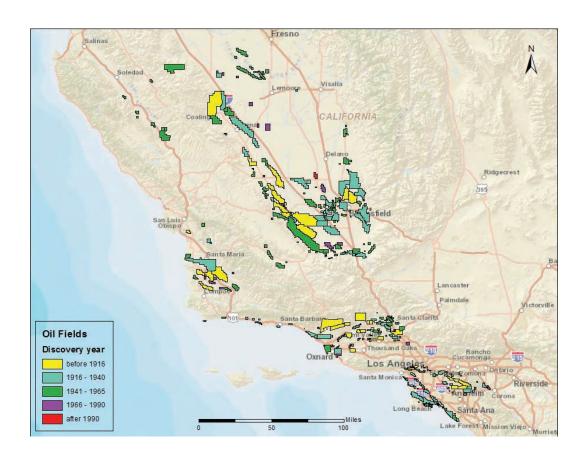


Figure 4-41. Discovery year of onshore oil fields (DOGGR, 1992; 1998; California Division of Oil and Gas, 1987; Minner et al., 2003).

Well stimulation methods could be used to a larger degree to increase the recovery efficiency of oil within the Monterey Formation from existing oil fields, as has been done in the South Belridge and Lost Hills fields, as well as oil within other geologic units. The USGS predicts that nine of the largest oil fields in the San Joaquin Basin could have 6.5 billion barrels of additional oil production using current recovery technology, with 2.8 billion barrels hosted in Monterey diatomite reservoirs (Tennyson et al., 2012). The USGS used probabilistic models to obtain a mean estimate of an additional 3.2 billion barrels of oil that could be recovered from the 10 largest oil fields in the LA basin (Gautier et al., 2013). Part of this recovery effort would likely involve well stimulation methods.

4.9 Summary

Credible estimates of the potential for increased recovery enabled by well stimulation technologies (WST) indicate that about 5 to 16 billion barrels might be produced in and near 19 existing giant fields in the San Joaquin and Los Angeles Basins where the WST and production technologies in use today work well. The 2011 US EIA estimates of about 15 billion barrels of technically recoverable oil from new plays in the Monterey Formation source rock have been revised in 2014 to a value of 0.6 billion barrels (US EIA 2014b); these estimates of unconventional oil resources are not well constrained.

There are significant resources in existing fields and estimates of these resources are relatively consistent. The USGS (Tennyson et al., 2012; Gautier et al., 2013) estimates that an additional 6.5 billion barrels and 3.2 billion barrels can be recovered from the largest fields in the San Joaquin and Los Angeles Basins, respectively, using existing oil production technology (see Figures 4-19 and 4-26).

New oil and gas production in regions removed from existing fields is more uncertain than increased production in existing oil and gas fields in the near term. There is a considerable amount of source rock including the Monterey Formation and other geologic units within the deeper portions of major basins that could potentially contain oil that has not migrated ("source" oil), and could perhaps be extracted using WST. However, there is little published information on these deep sedimentary sections, so it is difficult to estimate the potential recoverable reserves associated with these rocks. No reports of significant production of source oil from these rocks were identified.

The US EIA 2011 INTEK report has garnered considerable attention because of its large estimate of 15.4 billion barrels of technically recoverable oil in Monterey Formation source rock. Very little empirical data is available to support this analysis and the assumptions used to make this estimate appear to be consistently on the high side. INTEK estimates that the average well in low-permeability source rock in the Monterey Formation will produce 550 thousand barrels of oil. This amount greatly exceeds the production that has occurred to date from low-permeability rocks in known oil accumulations in this formation, with single-well oil production of only 67 and 141 thousand barrels in the San Joaquin and Santa Maria Basins, respectively (Hughes 2013). Consequently the INTEK estimate requires a four to five-fold increase in productivity per well from an essentially unproven resource.

In addition the Monterey Formation was formed by complex depositional processes and subsequently deformed in many tectonic events, resulting in highly heterogeneous as well as folded and faulted rocks that are difficult to characterize. INTEK posits production over an area of 4,538 km² (1,752 square miles), but this is almost the entire source rock area estimated in this report (note that the updated US EIA (2014b) report has reduced this areal extent significantly to 497 km² (192 square miles). There has not been enough exploration to know how much of the Monterey source rock has retained oil, or if the oil

has largely migrated away (Hughes 2013), but it is unlikely the entire source rock area will be productive given the extreme heterogeneity in the Monterey Formation. Finally, even if significant amounts of oil do remain in the Monterey Shale, and wells reach this oil, it still remains to be determined if hydraulic fracturing of Monterey source rock will result in economically viable production. For all these reasons, the INTEK estimate of recoverable oil in Monterey Formation source rock warrants some skepticism. The EIA has issued a revised estimate (0.6 billion barrels) of this unconventional oil resource (US EIA, 2014b); this decrease is mainly due to a nine-fold reduction in the estimated potential resource area.

Although there is potential for new production from undiscovered migrated oil accumulations in the Monterey Shale, the potential is small. A major reason for the reduced potential is that the USGS assessment of (migrated) oil in new, undiscovered conventional fields in the San Joaquin Basin is less than 400 million barrels, much smaller than the estimate given above for recoverable oil from known fields.

4.10 Acknowledgments

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Potential Direct Environmental Effects of Well Stimulation

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This section provides an assessment of potential direct environmental effects from the use of well stimulation. Direct environmental effects include potential impacts to water supply, water quality, air quality due to emissions of hazardous air contaminants and climate forcing pollutants, induced seismicity, and other miscellaneous impacts. This assessment considers potential effects from the stimulation process itself, as well as potential effects from transportation of stimulation supplies to the site and disposal of flowback/produced waters following the stimulation. Examples of direct environmental effects of well stimulation reviewed in this assessment are emission of air pollutants from diesel engines operating the pumps injecting the stimulation fluid, and spills of hydraulic fracturing fluid. The approach taken is literature review and data mining to infer potential impacts based on a wide foundation of knowledge and experience for well stimulation operations across the U.S. However, the interpretation of hazards and risks associated with well stimulation techniques, and more broadly oil and gas development is beyond the scope of this document.

Well stimulation technology (WST) can enable new or expanded production of oil. Consequently, indirect effects of well stimulation (such as additional emissions of air pollutants or methane due to expanded production or combustion of oil produced subsequent to stimulation, potential contamination due to leaks or spills that may occur during storage and transportation of oil, and ecological disruption from oil fields under production) can result from oil and gas production that has been enabled by WST. Indirect effects occur with all oil and gas production, whether or not well stimulation techniques have been used, and these will not be comprehensively evaluated in this assessment.

Section 5.1 concerns potential impacts of WST to water resources and reviews the effects on water use and water quality. Section 5.1.1 focuses on issues concerning water supply and demand due to the expected usage of freshwater in well stimulation operations, and compares water demand for stimulation activities in California to elsewhere in the country. Section 5.1.2 describes the typical chemistries of waters used in well stimulation treatments, and identifies potential contaminants that can impact water quality near well stimulation operations. This includes characterization of the injection fluids used in well stimulation in California, and an overview of the constituents typically present in flowback and produced waters from well stimulation operations across the United States

(since California-specific data were not available at the time of this assessment). Section 5.1.3 discusses the possible surface and subsurface pathways through which the potential contaminants identified in Section 5.1.2 might be released into surface and groundwater. Section 5.1.4 presents findings from water quality studies that have been conducted for surface and groundwater near sites where WST have been used in the United States and in California, and reviews episodes of known or possible contamination that may have occurred as a result of well stimulation activities.

Section 5.2 concerns potential impacts to the atmosphere in terms of air quality and climate caused by well stimulation operations. Section 5.2.1 provides an overview of possible air quality hazards related to increased well stimulation operations. Studies of air quality effects and emissions of pollutants from oil and gas production operations across the country are reviewed and discussed in the context of the practices common in California. Estimates of pollutant emissions attributable to a stimulation job (from diesel engines, such as trucks and pumping equipment) for practices typical in California are compared to emission estimates for high-volume fracturing practices typical outside of California. Emissions (including fugitive emissions) of volatile organic compounds (VOCs) and pollutants from flares are assessed in the context of current California inventories, the California regulatory context, and general scientific uncertainty.

Section 5.2.2 describes greenhouse gas (GHG) emissions related to well stimulation operations. Overall, oil and gas production operations in California include energy-intensive operations, such as steam generation for enhanced oil recovery, and this section compares energy use and CO₂ emissions from well stimulation operations to overall energy use and CO₂ emissions within the oil and gas production sector. The section also describes methane emissions. Methane can play an important role in total GHG emissions from oil and gas production because methane has a global warming potential (GWP) more than 30 times that of carbon dioxide (on a per mass basis) over 100 years and more than 80 times that of carbon dioxide over 20 years. Methane emissions from oil and gas operations are uncertain, with atmospheric measurements suggesting higher emission rates than standard bottom-up inventories (both nationally and in California). Current California inventories of methane emissions from well stimulation and oil and gas production are discussed in the context of local atmospheric-measurement campaigns.

Section 5.3 evaluates the hazard of induced seismicity due to well stimulation technologies. The processes considered include both the well stimulation itself, and the disposal of wastewater fluids through underground injection following stimulation. The mechanics of induced seismicity were reviewed to provide context for this assessment.

Section 5.4 concerns other impacts of well stimulation operations. The implications of well stimulation for wildlife and ecology are reviewed in Section 5.4.1. The review found no information on the specific impacts of well stimulation, because existing studies focus on the impacts of oil and gas development in general and because wildlife responds to the entire oil field infrastructure and activities. Consequently, this section reviews literature

regarding the hazards of oil production development on wildlife in general and makes some inferences regarding the potential hazards of well stimulation. Section 5.4.2 reviews impacts of traffic and noise as a result of well stimulation operations. Well stimulation operations generate noise and lead to an increase in heavy truck traffic for transporting water, chemicals used in fracturing fluids, and equipment needed for well stimulation. Estimates for noise levels and increased truck traffic are provided.

Finally, Section 5.5 provides a summary list of findings from the potential environmental impacts of WST in California. Due to lack of data specific to operations in California, a number of findings are supported by, or partially based on, an analysis and interpretation of information from well stimulation activities elsewhere in the United States.

5.1 Potential Impacts to Water

This section discusses issues related to water usage and water quality that may arise due to the use of WST in unconventional oil production. This assessment considers water demand for well stimulation in California, and several aspects of water quality including a review of potential contaminants that can be present in injection and wastewater fluids from well stimulation operations, potential pathways by which the contaminants can be released into surface and groundwater, and specific cases of known or possible contamination that may have been related to well stimulation in the United States.

Section 5.1.1 examines the water demand for stimulation in California, discusses the water sources, and puts this information into context with other areas across the United States. Section 5.1.2 discusses the chemicals used for well stimulation in California according to an analysis of voluntary disclosures of well stimulation practices reported to the FracFocus Chemical Disclosure Registry (FracFocus). This discussion includes statistical analysis of the usage (Section 5.1.2.1) and the toxicity (Section 5.1.2.2), if toxicity data were available, of any chemicals used in more than 2% of the reported stimulations. Section 5.1.2.3 provides an overview of the amount and typical chemical properties of flowback and produced fluids recovered from well stimulation operations across the U.S, since California-specific data were not available at the time of this assessment. Potential contaminants that can be present in the recovered fluids are discussed — namely those constituents that may be present due to the injection fluids (Section 5.1.2.4) or those that naturally are present in the formation waters such as total dissolved solids (TDS)/salts, trace metals, radioactive elements, and organics (Section 5.1.2.5). A more detailed assessment of the hazards associated with flowback/ produced water in California was not conducted due to the lack of data regarding the masses of materials used in well stimulation, recovery factors for flowback waters, and concentrations of potential contaminants in flowback/produced waters.

Section 5.1.3 reviews the documented types of surface and subsurface pathways for potential water contamination associated with well stimulations. Potential surface pathways by which well stimulation could result in water contamination are considered

in Section 5.1.3.1. The section opens with consideration of surface spills and leaks, management and disposal of flowback water, and storm runoff and flooding. The discussion of flowback water considers the difficulty of distinguishing between flowback and produced water based on composition. The review of subsurface release pathways in Section 5.1.3.2 focuses on the two components of subsurface pathways that could result in contamination hazards: (1) the possibility of forming permeable pathways that intercept groundwater or surface water resources during the hydraulic fracturing process; and (2) the potential for transport of gas and formation fluids through these pathways into overlying groundwater resources. The former involves the potential failure of confining geological formations that protect groundwater quality, the potential failure of well casing or well cement during fracturing, during production, or at any point during the active or inactive lifetime of the well, and the potential interception of pre-existing pathways (old wells, permeable faults) via induced fractures. The latter includes discussion of the hydrological processes that govern flow and transport through any such induced or intercepted pathway. While actual data are limited, we attempt to evaluate current debate regarding contamination of groundwater resources through subsurface pathways by focusing on existing knowledge and published works in reservoir engineering and related fields.

Section 5.1.4 reviews further information on known or possible contamination cases that have occurred as a result of well stimulation activities. Section 5.1.4.1 considers contamination events that have occurred as a result of legal, accidental, or illegal surface discharges. Section 5.1.4.2 reviews literature regarding groundwater quality near well stimulation sites and possible contamination of groundwater due to fracturing activities. The discussion focuses on the direct effects of constituents that may be present in well stimulation, flowback, and produced fluids identified in Section 5.1.2. It should be noted that the constituents of fluids associated with well stimulation could also have "indirect effects" that can potentially alter water quality due to additional reactions with the surface or groundwater, or with aquifer sediments. For instance, changes could occur in redox conditions resulting from migration of methane into the formation that can trigger microbial methane oxidation and subsequent consumption of oxygen, or due to the introduction of oxygen from the stimulation fluids. Changes to redox can degrade water quality and trigger a host of subsurface geochemical reactions, such as the dissolution of trace metals and radioactive elements into groundwater aquifers. The potential impacts on water quality due to these effects are beyond the scope of this project and have not been investigated for this report.

5.1.1 Quantities and Sources of Water Used for Well Stimulation in California

This section discusses actual total water use for well stimulation activities in California based on the assessments of water use per well for hydraulic fracturing and matrix acidizing from Sections 3.2.3 and 3.4.3, respectively. The available information on the sources of this water is considered, followed by some comparison to water use in other regions across the United States. This section finds that actual water use per well in California is less than in other areas due to a combination of factors described in

Section 3.2.2, including the use of vertical wells with shorter treatment lengths and use of cross-linked gels used in smaller volumes than slickwater. Total water use for well stimulation depends on the level of activity. Assuming a rate of 100-150 well stimulations per month, current total annual water use could be as much as 1.4 million m³ (1,200 acre-feet). An acre-foot of water is enough to serve two average California households for a year at current water use rates (California Department of Water Resources (DWR) 2012). Farmers in California typically use 3 to 6 acre-feet per year to irrigate one acre of cropland (DWR 2013). While current water demand for WST operations is a small fraction of statewide water use, it can contribute to local constraints on water availability, especially during droughts. The type of impact and its magnitude will depend on local conditions, as well as the where, when, or how much water is used, and thus would require analysis on a site-specific basis.

5.1.1.1 Water Use

It is difficult to accurately estimate the volume of water currently used for hydraulic fracturing and other well stimulation techniques in California due to the lack of comprehensive data. Before 2013, companies engaged in oil and gas production were not required to publish or otherwise disclose information about their water and chemical use. However, some producers voluntarily reported information to state regulators and to the website FracFocus. According to these data, there were 792 reports of hydraulic fracturing in California in 2013 that used a combined total of 300 acre-feet of water. As noted, this estimate is based on voluntary disclosures and may not capture the full extent of hydraulic fracturing activity in California. Further, it does not include water use for matrix acidizing because these data are not included in FracFocus.

An approximate current rate of water use for hydraulic fracturing was determined by estimating the number of hydraulic fracturing operations that take place each month along with an average water use per operation (see Sections 3.2.2 and 3.2.3). A rate of 100 to 150 hydraulically-fractured wells per month was assumed.¹ Voluntary reports in FracFocus for 2011–2013 suggest that the average water use for hydraulic fracturing is 500 m³ (130,000 gallons) per well, with the 90% confidence interval ranging from 470 to 540 m³ (120,000 to 140,000 gallons). Based on these estimates, annual water use for hydraulic fracturing is estimated at 560,000 to 970,000 m³ (150 million to 260 million gallons, or 450 to 780 acre-feet) per year. Assuming a higher average water use of 810 m³ (210,000 gallons) per well, as estimated from well stimulation notices filed with Division of Oil, Gas and Geothermal Resources (DOGGR) in December 2013 and January 2014, total annual water use could be from 950,000 to 1,400,000 m³ (770 to 1,160 acre-feet) per year.

¹ This estimate is based on the 76 operations per month implied by FracFocus, DOGGR's GIS well files, and well-record searches in combination, and the 190 hydraulic fracturing notices approved by DOGGR in December 2013.

Water use for matrix acidizing was estimated from information contained in well stimulation permit applications, or notices, filed by operators. DOGGR posted 36 well stimulation notices planning to use acid stimulation on oil wells through mid-January 2014, although 10 of the notices were subsequently withdrawn. All 36 of these notices were filed by Occidental of Elk Hills, Inc. for wells in the Elk Hills oil field in Kern County. The 90% confidence interval for the mean water use, based on 36 notices, is 120–200 m³ (32,000–53,000 gallons). Assuming a rate of 30 matrix-acidizing stimulations per month over the coming year results in an annual water use of 43,000-72,000 m³/year (11–19 million gallons, or 35–58 acre-feet per year).

5.1.1.2 Water Sources

According to the well stimulation notices filed through the middle of January 2014, of the 249 planned well stimulation operations, operators plan to use *fresh water* for the majority of treatments (238 of 249), *produced water* for 10 operations, and both fresh and produced water for one operation. The average planned water use is 720 m³ (210,000 gallons) per well, and the mean or variance does not appear to change depending on the water source (Table 5-1). Furthermore, the notices indicate that most planned hydraulic fracturing activity will occur in Kern County, and most operators plan to purchase water from nearby irrigation districts (Table 5-1). One district, the Belridge Water Storage District, is specified as the water source for 171 of the 213 permits and provides two-thirds of the estimated water supply. In some cases, operators frequently state a primary water source in their water management plans, while noting that water may also be withdrawn from on-site wells.

Table 5-1. Total planned water use for well stimulation by water source, from hydraulic fracturing notices posted in December 2013 through the middle of January 2014.

	Number of operations	Total Water (m³)	Volume (acrefeet)
"District water"	9	16,000	13
Belridge Water Storage District; own wells	171	130,000	110
Casitas Municipal Water District	3	2,400	2
West Kern Water District*	55	21,000	17
Not specified	11	10,000	8
Total	249	180,000	150

^{*}Note: All 36 permits for matrix acidizing operations filed to date are planned in the Elk Hills field by Occidental corporation, and plan to use water from the West Kern Water District

² Available through http://maps.conservation.ca.gov/DOGGR/iwst_index.html.

The Belridge Water Storage District is an irrigation district formed to serve farmers in central Kern County. The primary source of water is from the State Water Project, although limited groundwater supplies are also available. The total planned water use by oil field operators filed during the first one and a half months of the program totals 110 acre-feet (130,000 m³). This is less than 0.1% of the District's water use in 2012 but about 50% of the District's water used for oil production for that year (Belridge Water Storage District (BWSD) 2013). Deliveries of surface water from the State Water Project can be curtailed or even eliminated during drought years. Indeed, the State Water Project has announced that irrigation districts such as Belridge should plan to expect only 5% of its water allocation this year due to severe drought. The majority of crops within the District's service area are permanent crops that require water every year, increasing competition for limited water resources in the region. As an indication of the constraints on water in the region, Starrh and Starrh Farms, located within the BWSD service area, purchased 1,700 acre-feet of water from a nearby irrigation district at a cost of \$1.97 million, or \$1,130 per acre-foot (Henry, 2014).

As described above, operators noted that on-site groundwater wells may also be used for water for well stimulation treatments. There is a risk that accessing this water may come at the expense of other users, especially agricultural users in regions adjacent to oil and gas production fields. However, none of the operators specifies when, or under what circumstances, they would switch from purchased canal water to pumping from on-site wells. Groundwater pumping has a number of well-known and possibly detrimental impacts. Despite this, the state does not regulate the quantity of groundwater extracted from wells. Possible impacts of groundwater withdrawals, in addition to competition with agricultural uses, include decreases in river flows, land subsidence, permanent reductions in aquifer storage, increased pumping costs for neighbors, or nearby wells that run dry and need to be re-drilled and deepened. The type of impact and its magnitude will depend on local conditions, as well as the where, when, or how much water is used, and thus would require analysis on a site-specific basis. An additional area of interest and concern is the possible use of produced water for agricultural production. This is briefly addressed in Sections 5.1.3 and 5.1.3.1.4.

5.1.1.3 Comparison of Water Use to Other Regions Across the United States

There are few published estimates in the literature of water use for hydraulic fracturing in unconventional oil deposits. As described in Section 3.2.3, water use per well for hydraulic fracturing to produce oil in California is considerably lower than that reported to produce oil from the Eagle Ford unconventional play in Texas (Nicot and Scanlon, 2012). More generally, much of the published information on water use regards hydraulic fracturing to produce shale gas, which provides another basis for comparison. Average shale-gas water-use intensities of 3,800–23,000 m³ (1–6 million gallons) per well have been reported in Texas (Nicot and Scanlon, 2012). A study for the US Department of Energy (DOE) reported median volume of fracturing water per well for select shale gas plays of 1,900–3,100 m³ (2.3–3.8 million gallons; Ground Water Protection Council and ALL Consulting, 2009).

The smaller volume per well in California appears to result from a combination of factors as described in Section 3.2.2, including that vertical wells are predominant as opposed to horizontal wells in the comparison areas (Nicot and Scanlon, 2012; Ground Water Protection Council and ALL Consulting, 2009). Vertical wells presumably have shorter treatment lengths. In addition, gel, mostly cross-linked, is the predominant fracturing fluid. As discussed in Section 2.3.2, gels, particularly cross-linked, are typically used in smaller volumes than slickwater.

5.1.2 Chemistry of Fluids Related to Well Stimulation Operations

This section reviews the chemical compositions of waters related to well stimulation operations – namely the injection fluids (also referred to as well stimulation fluids or fracturing fluids), and the wastewaters recovered from well stimulation operations (i.e. flowback and produced waters). In addition, some contaminants that may be present in the injection and wastewater fluids are identified. This section also provides context for subsequent sections discussing the potential for fluids involved in WST operations to leak into shallow water resources through surface and subsurface pathways.

For the injection fluids (Sections 5.1.2.1 and 5.1.2.2), an evaluation is provided based on an analysis of acute, oral toxicity information for individual constituents that have been used in well stimulation operations in California. The list of chemicals was compiled from disclosures in FracFocus for hydraulic fracturing operations, and from stimulation notices submitted to DOGGR since December 2013 for matrix acidization operations. Both of these sources are dependent on self-reporting and may, therefore, not be comprehensive. The majority of the chemicals applied in California, for which toxicity information is available, are of low toxicity or non-toxic. However, some chemicals of concern were identified, including biocides (e.g. tetrakis(hydroxymethyl)phosphonium sulfate; 2,2-dibromo-3-nitrilopropionamide; and glutaraldehyde), corrosion inhibitors (e.g. propargyl alcohol), and mineral acids (e.g. hydrofluoric acid and hydrochloric acid). Approximately one-third of the chemicals had insufficient available information for evaluation. This toxicological assessment is limited as it considers only one chemical property (i.e. acute mammalian oral toxicity) that may impact human health, and does not consider other effects such as biological responses to acute and chronic exposure, eco-toxicological effects, overall toxicological effects of mixtures of compounds (compared to single-chemical exposure), and potential time-dependent changes in toxicological impacts of fluid constituents, due to their potential degradation or transformations in the environment. Thus further review of the constituents of injection fluids used in well stimulation jobs in California is needed.

For flowback and produced waters, Section 5.1.2.3 first outlines the general characteristics of flowback and produced waters across the U.S., to enable the reader to understand their typical constituents. However, flowback and produced water compositions vary considerably across regions, and their characteristics can change according to the fluids injected during well stimulation, the amount of fluids recovered at the surface,

and over the duration of the flowback period. The chemistry of produced waters from unconventional oil production could potentially differ from that of conventional oil production in the same region due to differences in the target formations and interactions of fracturing fluids with formation rocks and water, although this does not generally appear to be the case based on the limited data that is available.

Sections 5.1.2.4 and 5.1.2.5 focus on identifying potential contaminants that could be present in flowback or produced waters, either due to the presence of injection fluids used in fracturing operations or due to dissolved constituents that may be present in formation waters brought up to the surface. Injection fluid constituents typically measured for their residual concentrations in flowback or produced waters include friction reducers, surfactants, PCBs, biocides, alcohols, glycols and organic acids, of which organic chemicals and biocides appear to be of particular concern. Furthermore, formation waters in oil reservoirs can contain naturally occurring dissolved constituents that can potentially degrade water quality, such as some major cations and anions that contribute to salinity and hardness (sodium, calcium, magnesium, chloride), trace elements including heavy metals, radiological material (NORMs), and organics. The list of potential contaminants identified in Section 5.1.2.5 is based on reports of contamination possibly related to well stimulation activities in the United States, but may not necessarily be applicable to California. It was not possible to provide an assessment of problems that may occur in California as there is no publicly available information about the composition of flowback and produced waters from well stimulation operations in California at the time this assessment was conducted.

Ultimately, the constituent concentrations in injection fluids, flowback and produced waters, as well as the specific exposure pathways, will determine potential hazards to human and ecological health. More data on the composition of injection fluids, and flowback and produced waters will enable a more comprehensive evaluation of the hazards to water quality due to fracturing operations in California.

5.1.2.1 Well Stimulation Injection Fluid Composition

As discussed in Section 2.3.2, fracturing fluids contain a series of reagents which serve various functions during the fracturing process. For example, sand is typically used as a "proppant" that ensures that the newly created fractures remain open. Other compounds such as guar gum are added to facilitate efficient delivery of proppant throughout the fracture zone, biocides are added to prevent the growth of bacteria, and other chemicals are added to minimize the mineral deposits (scaling) in the well. Classes of relevant chemicals include gelling and foaming agents, friction reducers, cross-linkers, breakers, pH adjusters/buffers, biocides, corrosion inhibitors, scale inhibitors, iron control chemicals, clay stabilizers, and surfactants (King, 2012; New York State Department of Environmental Conservation, 2011; Stringfellow et al., 2014, US Environmental Protection Agency (US EPA), 2004; Wilson and Schwank, 2013). Lists of common or widely used chemicals have been compiled based on regional or national usage (Stringfellow et al., 2014, US EPA, 2004; Wilson and Schwank, 2013), but no prior investigations have examined chemical use specific to California.

Extensive lists of chemicals frequently used during hydraulic fracturing nationwide are available in the literature (e.g. Stringfellow, et al., 2014). An example short-list of chemicals frequently used during hydraulic fracturing in Michigan is given in Appendix F (Table AF-1.) For this report, a list of constituents used in hydraulic fracturing in California was compiled using information voluntarily disclosed by industry on the FracFocus Chemical Disclosure Registry (http://fracfocus.org/). The FracFocus registry is not easily accessible and data from FracFocus have been compiled by SkyTruth (http://skytruth.org/) and DOGGR into searchable data sets. The data available from SkyTruth for the period between January 2011 (the earliest available) and May 2013 were combined with data compiled by DOGGR (Vincent Agusiegbe, personal communication, see Section 3 for details) for the remainder of 2013 to develop a list of chemicals used in hydraulic fracturing that is specific to California. This list is also presented in Appendix F (Table AF-2). Most of the data included in this analysis are from after April 2012 (see Figure 3-2 for details), which corresponds to an increase in data submissions shortly after a request DOGGR sent to operators in March 2012 asking for voluntary disclosure (Kustic, 2012).

The disclosed list of chemicals compiled by SkyTruth and DOGGR was ranked in terms of their frequency of use in fracturing for on-shore oil production in California; therefore hydraulic fracturing operations applied to natural gas and offshore oil production were not included in this analysis. All chemical used in more than 2% of the wells in California, where hydraulic fracturing was applied and disclosures to FracFocus were made, were included in this analysis. In total, 114 chemicals or chemical mixtures were reported as being used in more than 2% of the wells that have been hydraulically fractured in California. The majority of these additives were identified by Chemical Abstract Service (CAS) number (Table AF-2), but 17 were just identified by common name, group names, or names suggesting mixtures of compounds (Table AF-3). Chemicals can have multiple names, including common names, so CAS numbers are assigned to individual chemicals by the CAS of the American Chemical Society (https://www.cas.org/) to uniquely and definitively identify chemical compounds. Disclosure of chemical usage without reporting CAS numbers has limited value. The 97 chemicals reported with CAS numbers and used in more than 2% of the fracturing operations were further considered. For Table AF-2, chemical names (based on CAS Numbers) were selected from an US EPA report (US EPA, 2012) in order to provide consistency with previous publications.

In addition to hydraulic fracturing, well stimulation techniques also include matrix acidizing (discussed in Sections 2.4). A list of compounds used in matrix acidizing are given in Table AF-4. This list was developed from stimulation notices submitted to DOGGR between December 2013 and mid-January 2014 by operators and others who intended to perform well stimulation operations in the first part of 2014. Submitting a "Notice of Intent" is a new requirement in California as of December 2013, and although the list of compounds in Table AF-4 cannot be considered comprehensive, it is representative of current practices in California. All 70 listed compounds were used in at least 3% of the reported events, with 69 chemicals being applied to 47% or more events.

Comparison of Tables AF-1 and AF-2 suggests that chemicals used for hydraulic fracturing in California differ from chemicals used in other parts of the country. This conclusion is supported by comparison with lists of chemicals reported in the literature (King, 2012; New York State Department of Environmental Conservation, 2011; Stringfellow et al., 2014, US EPA, 2004; Wilson and Schwank, 2013). For example, the use of isothiozolone biocides appears to be more common in California and the use of glutaraldehyde and quaternary ammonia biocides less common in California than elsewhere. Overall, this voluntarily disclosed information of chemicals listed in Table AF-2 is consistent with earlier observations that the large majority of hydraulic fracturing applications in California use a gel-matrix approach and that the use of slick-water applications is less common in California than in other regions of the country. This conclusion is indicated by the high reporting frequency for guar gum and related compounds (used in gel treatments) and the absence of polyacrylamide compounds (used in slick-water treatments) in Table AF-2. The significance of these differences between chemical use in California and other regions of the country needs to be further investigated and confirmed, since chemical usage in industry is an important component of hazard assessment and risk analysis.

5.1.2.2 Preliminary Assessment of Hazards Associated with Well Stimulation Chemicals

Hazards associated with chemicals include physical, health, and environmental hazards (United Nations 2003). Physical hazards include properties such as flammability and oxidizing potential; health hazards include properties such as acute toxicity and skin irritation; and environmental hazards include both narrow and broad effects to environmental systems, particularly effects on aquatic organisms. A complete assessment of hazards associated with chemicals used in well stimulation in California is beyond the scope of this document, so for this report, only acute mammalian toxicity was investigated (see Appendix G). Mammalian toxicity is relevant for the evaluation of chemicals handled during well stimulation operations, especially in the context of the potential exposure of workers and the contamination of drinking water resources. Acute toxicity tests are commonly used as a reference point in both hazard and risk assessment. Examining acute oral toxicity has value for identifying potential chemicals of concern, but it is only the first step in understanding hazards associated with the chemicals used in well stimulation.

Tables 5-2 and 5-3 summarize the number of identified chemicals found in each Global Harmonized System (GHS) category (see Appendix G) for hydraulic fracturing and matrix-acidizing fluids, and provide the number of constituents for which no oral-toxicity information could be located. For this report we also identified compounds with categories above (>5), which may be interpreted as compounds that are non-toxic (Stringfellow et al., 2014). In Tables AF-2 and AF-4, GHS Categories are color-coded. There are no GHS Category 1 compounds (red color) found in the lists of well stimulation chemicals. However, for almost one third of the chemicals reported with CAS numbers, acute oral toxicity data could not be found (Table 5-2). The majority of the chemicals listed are in GHS Category 5 or above, suggesting they have low hazard potential in terms of oral toxicity. Examples of these lower toxicity or non-toxic compounds include guar gum (CAS 9000-30-0), a gelling agent, and ethanol (CAS 64-17-5), which is a common solvent.

Table 5-2. Grouping of chemicals found in hydraulic fracturing fluids in more than 2% of California hydraulic fracturing jobs based on GHS Categories for oral toxicity data (GHS category 1: most toxic; category 5: least toxic).

GHS Category	Number and Percent of Chemicals							
	Oral Rat LD ₅₀		Oral Mo	use LD ₅₀	Oral Rabbit LD ₅₀			
	[N]	[%]	[N]	[%]	[N]	[%]		
1	0	0%	0	0%	0	0%		
2	1	1%	1	1%	0	0%		
3	7	7%	2	2%	2	2%		
4	15	15%	13	13%	6	6%		
5	17	18%	12	12%	2	2%		
> 5	25	26%	12	12%	9	9%		
No/insufficient data	32	33%	57	59%	78	80%		
TOTAL	97	100%	97	100%	97	100%		

Table 5-3. Grouping of chemicals found in injection fluids in more than 2% of California matrix acidizing operations based on GHS Categories for oral toxicity data (GHS category 1: most toxic; category 5: least toxic).

GHS Category	Number and Percent of Chemicals							
	Oral Rat LD ₅₀		Oral Mo	ouse LD ₅₀	Oral Rabbit LD ₅₀			
	[N]	[%]	[N]	[%]	[N]	[%]		
1	0	0%	0	0%	0	0%		
2	1	1%	3	4%	0	0%		
3	6	9%	3	4%	0	0%		
4	16	23%	9	13%	4	6%		
5	15	21%	8	11%	2	3%		
> 5	12	17%	10	14%	8	11%		
No/insufficient data	20	29%	37	53%	56	80%		
TOTAL	70	100%	70	100%	70	100%		

For both hydraulic fracturing and matrix acidizing chemicals, oral toxicity data for rats were more readily available than data for mice or rabbits, providing information on 65 of 97 (66%) and 50 of 70 (71%) chemicals applied in hydraulic fracturing and matrix acidizing, respectively (Tables 5-2 and 5-3). Chemicals that had mice or rabbit toxicity data almost always also had data for rats, therefore, rat-based toxicity information provided the most complete basis for a qualitative comparison between oral toxicological effects of constituents found in hydraulic fracturing and matrix-acidizing fluids.

Using acute oral toxicity data for rats, most chemicals (59%) used in hydraulic fracturing are Category 4, 5 and above, and only 8% (representing 8 compounds) are Category 2 or 3. As discussed above, no compounds were in Category 1, the most toxic category. For matrix acidizing fluids, 61% of chemicals are in Categories 4, 5 and >5 and 10% are in Categories 2 and 3. Hence, based on this qualitative analysis, compounds added to injection fluids used in hydraulic fracturing and matrix-acidizing jobs for which oral toxicity data are available are characterized by a similar distribution of oral toxicities for rats.

Although acute oral toxicity data are useful for investigating hazards of industrial chemicals, as discussed above, oral toxicity is only one aspect used during the determination of hazards associated with chemicals. For example, constituents in matrix-acidizing fluids, such as hydrofluoric acid (CAS 7664-39-3), are hazardous, even if there is an absence of data on rat acute oral toxicity (Table AF-4). For example, hydrofluoric acid is toxic when inhaled; it is a contact hazard, causing skin corrosion or chemical burns when in contact with skin; and it is a dermal toxin, due to potential dermal absorption of fluoride.

A more complete analysis of hazards associated with well stimulation chemicals is needed. The total amounts of chemicals used and the concentrations at which they are applied needs to be determined. Other properties that need to be assessed include variables such as corrosivity, ignitability, and chemical reactivity. Future assessments need to evaluate whether the well stimulation chemicals are carcinogens (substances that can cause cancer), endocrine-disrupting compounds (chemicals that may interfere with the body's endocrine system and produce adverse developmental, reproductive, neurological, and immune effects), and bioaccumulable materials (chemicals that increase in concentration in a biological organism over time compared to their concentrations in the environment). Previous studies suggest that some of the compounds listed on Table AF-1 may be endocrine disrupting compounds (Colborn et al., 2010, Kassotis et al., 2013). Chemicals that are endocrine disrupting, carcinogenic, or that bioaccumulate potentially can cause long-term or chronic impacts on ecosystems. Long-term and chronic effects are not necessarily indicated by results of LD₅₀ tests as presented in this report.

Potential toxicological hazards may not only involve effects on humans, but also any impacts on aquatic organisms and other receptors. An evaluation of eco-toxicological effects, including the potential impacts of these chemicals on aquatic organisms is needed. Such an analysis will need to consider the large variety of types of toxicity tests applied in this area, which confounds direct comparisons between chemicals. A more complete evaluation of potential eco-toxicological effects of injection fluids applied during well stimulation is needed in the future.

Future analysis should also take into account and evaluate the potential interactive effects between chemicals. The toxic effects of a mixture of two or more compounds can be substantially different from that suggested by simply adding the effects of the single compounds. Overall effects can potentially be smaller or larger, depending on the specific interactions between compounds in the mixture, changes in uptake, etc. To our

knowledge, no studies are currently available in the peer-reviewed literature describing the overall toxicological effects of fracturing fluids as mixtures of many different types of compounds; however, a few examples of studies are available where combined effects of small subgroups of fracturing fluid chemicals have been evaluated. For instance, a combination of two biocides (Di-Me Oxazolidine and glutaraldehyde) has been shown to achieve equivalent performance of either alone in fracturing fluids while improving the overall ecotoxicity profile (Enzien et al., 2011). For endocrine-disrupting chemicals acting through a common biological pathway, additive effects of mixtures have been observed, even when individual chemical concentrations were present at levels below an observed effect threshold (Christiansen et al., 2008; Silva et al., 2002; Christiansen et al., 2009).

The use of effluent toxicity tests may be useful for evaluating the effects of mixtures of well stimulation chemicals and associated wastewaters (Riedl et al., 2013). Whole Effluent Toxicity (WET) tests are specifically designed to evaluate the aggregate toxic effects of an aqueous sample without precise information about the chemicals causing that toxicity (US EPA, 2002). For instance, in California, these US EPA methods have been applied in order to evaluate the water quality of agricultural drains in the San Joaquin River and Sacramento River watersheds (Vlaming et al., 2004). Other researchers have evaluated complex mixtures for endocrine disrupting activity using whole water samples (Soto et al., 2003; Zhao et al., 2011). The application of toxicological and eco-toxicological methods for testing mixtures of fracturing fluids is recommended in future studies.

Finally, degradation and transformation reactions affecting fracturing-fluid constituents in the environment need to be considered for future studies. Degradation and transformation reactions could cause either an increase or decrease in toxicological effects. For example, some biocides, such as glutaraldehyde, degrade relatively quickly in the subsurface, leading to lower toxicities in flowback water compared to the injected fluid (Blotevogel et al., 2013). In contrast, a photochemical degradation of polyacrylamide polymers may result in increased environmental hazard, since acrylamide monomer units are more toxic than the parent polymer and acrylamide is a mammalian neurotoxin and a probable carcinogen (Brown et al., 1980).

In summary, numerous chemicals are used for well stimulation in California. A full assessment of the hazards associated with those chemicals is needed. The extensive list of possible WST chemicals provides only part of the information needed to assess risk; additional information on concentrations, synergistic interactions, exposures, and more are also needed to assess risks and environmental impacts from WST. A preliminary assessment, using mammalian acute oral toxicity as a screening criteria, suggests that only a few of the well stimulation chemicals can be considered highly toxic and most compounds are of equivalent toxicity to many commonly used industrial and household chemicals (such as anti-freeze). We note, of course, that many household and industrial chemicals also have potential toxicity under certain circumstance or in different combinations, and we recommend that all such risks be carefully assessed as part of future investigations of risks associated with WST. Numerous compounds can be classified as non-toxic and

some are allowed as food additives or are found in food naturally. It is emphasized that mammalian oral toxicity is a very limited screening criteria and that a more complete hazard assessment must include physical, health, and environmental hazards. Other factors that must be considered to fully evaluate hazards associated with these chemicals include eco-toxicological effects, endocrine disruption, bioaccumulation, environmental transformation, and the properties of mixtures of compounds.

5.1.2.3 General Characteristics of Flowback and Produced Waters

After completion of the stimulation process, the pressure in the well is released and the direction of flow is reversed, bringing some of the injected stimulation fluid and formation water to the surface (see Section 2.3 for a description of the hydraulic fracturing process). This fluid is generally classified as either flowback or produced water. Flowback is commonly defined as the return of injected fluids and produced water is water from the formation (US EPA, 2012). The distinction between flowback and produced water during operations is not clear-cut, since mixing occurs in the formation. In practice, the term flowback is used to refer to initial, higher flows in the period immediately after well stimulation and produced water refers to long-term, typically lower flows associated with commercial hydrocarbon production. After the pressure in the well is reduced, flowback water is returned to the surface at high rates for up to several weeks, and this flow is, initially, predominantly fluids that were injected, but over time the fraction of the fluid that represents formation water increases (Barbot, et al. 2013; Clark et al., 2013; Haluszczak et al. 2013: King 2012). Produced water flows to the surface, along with the gas or oil, throughout the production life of the well and originates from water naturally trapped in the geologic formation (King 2012).

Flowback fluids consist of (1) fracturing/injection fluids pumped into the well previously, which include water and the additives described in Section 5.1.2.1, (2) new compounds that may have formed due to chemical reactions between additives, (3) dissolved substances from waters naturally present in the target geological formation, (4) substances that have become mobilized from the target geological formation due to the interaction of fracturing fluids with formation rocks and water, and (5) some oil and/or gas (New York State Department of Environmental Conservation, 2011; Stepan et al., 2010). Thus, the chemistry of flowback waters is generally different from that of the injection fluids, as shown by the example in Table 5-4.

The composition of flowback fluids usually changes over the course of the flowback time-period, gradually evolving from being more similar to the injection fluids to approaching the chemical characteristics of the formation waters. For example, fluid-composition changes were observed in studies conducted in the Marcellus shale (Hayes, 2009; Barbot et al., 2013) and the Bakken (Stepan et al., 2010), indicating concentration increases in the flowback water collected over time for constituents such as TDS (such as shown on Figure 5-1), chloride, and some cations/metals (such as shown on Figures 5-2 and 5-3). In the Marcellus study, water hardness and radioactivity levels were found to increase during the flowback period, but sulfate and alkalinity levels decreased with time.

Table 5-4. An example of differences in the composition of injection fluids and 14-day flowback water collected from seven horizontal wells in the Marcellus shale (Table from Haluszczak et al., 2013, based on data from Hayes, 2009)

	Concentrations in mg/L					
	Injected fluid median, day 0	Flowback median, day 14	Flowback range, day 14			
рН	7.0	6.2	5.8-6.6			
Alkalinity as CaCO ₃	126	71	26–95			
Total dissolved solids	735	157000	3010-228,000			
Total organic carbon	205	14	1.2-509			
Chemical oxygen demand	734	8370	228–128,000			
Cl	82	98300	1070-151,000			
Br	<10 (<0.2-19)	872	16–1190			
SO ₄	59	<50*	0.8-89			
NH ₃ -N	16	193	4–359			
P	0.36	0.55*	0.04-2.2			
Al	0.3*	0.5	0.15-0.91			
Ва	0.6	1990	76–13,600			
В	0.5	20	2.7-3880			
Ca	32	11200	204-14,800			
Fe	0.68	47	14–59			
K	<50 (3-57)	281	8-1010			
Li	0.04	95	4–202			
Mg	3.7	875	22-1800			
Mn	0.074	5.6	1.2-8.4			
Na	80	36400	1100-44,100			
Sr	0.82	2330	46–5350			
Zn	0.08	0.09	0.07-0.14			

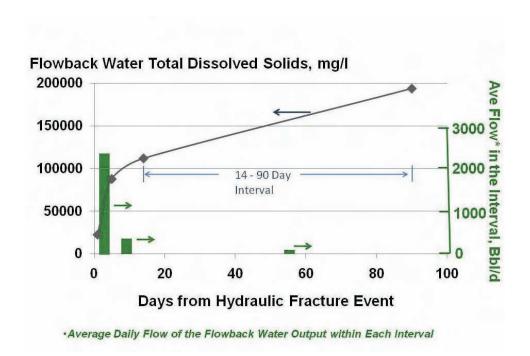


Figure 5-1. TDS content of flowback waters typically increases during the flowback period (Figure from Hayes, 2009 showing data from the Marcellus shale)

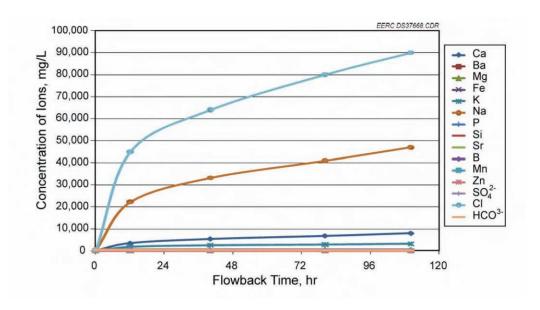


Figure 5-2. Concentrations of some cations (e.g. calcium, potassium, sodium, iron) and anions (e.g. chloride) typically increase during the flowback period in the Bakken shale (Figure from Stepan et al., 2010).

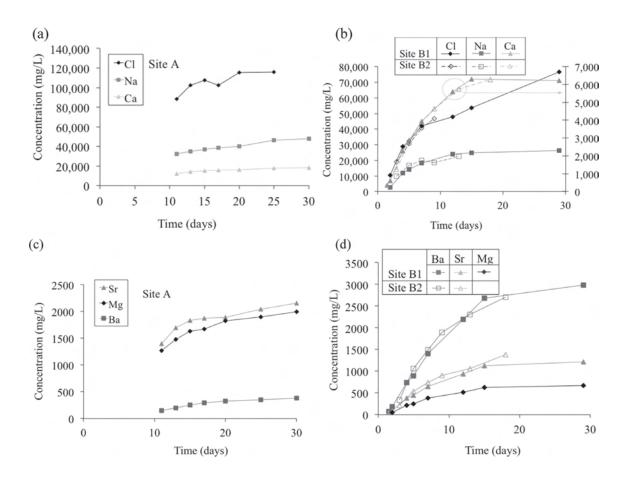


Figure 5-3. Concentrations of some cations (e.g. calcium, sodium, strontium) and anions (e.g. chloride) typically increase during the flowback period in the Marcellus shale (Figure from Barbot et al., 2013). The concentrations of these ions increase over time because the chemistry of the fluid changes from resembling the injection fluids (that are made using waters with low TDS) to formation waters (these typically have high TDS because the waters in most formations are of marine origin).

The duration of the flowback periods can range anywhere from two days to a few weeks, and can vary between producers within a region (e.g., Hayes, 2009; Stepan et al., 2010; Warner et al., 2013; Barbot et al., 2013). Besides variation during the duration of the flowback period, compositions of flowback and produced waters are known to vary geographically, as shown in Table 5-5 (Bibby et al., 2013). The chemical composition of these waters ultimately determines the options available for their treatment, reuse, and disposal, as discussed in Section 5.2.3.1.4.

Once the well is placed into production, the waters recovered from the operations are "operationally defined" as "produced waters." One question that this report addresses is whether produced waters from WST operations in California are different from waters recovered during conventional oil and gas production. It turns out it is difficult to evaluate this question, given the wide variations in the water chemistries of flowback

and produced waters, as well as the scarcity of recent data from unconventional and conventional production. A limited number of studies in other regions suggest that the hydraulic fracturing operation has little effect on the eventual produced water chemistry. For example, an industry-sponsored study by the Gas Coalition Institute focusing on fracturing operations in the Marcellus shale (Hayes, 2009) concluded that the general water chemistries of produced water from conventional and unconventional productions are similar. A subsequent study from Pennsylvania State University (Haluszczak et al., 2013) used four different data sources, including the data from the Gas Coalition Institute, and similarly concluded that the general chemistry of later flowback/produced water resembled brines produced from conventional wells, although they also noted that the concentrations of NORMs in the flowback waters (226Ra and 228Ra) were high. Specifically for California, the samples for which data is reported in the "USGS produced water database 2.0" (United States Geological Survey (USGS), 2014), were collected from conventional hydrocarbon wells before 1980. Thus these samples may not be representative of modern produced waters from conventional extraction or of produced water from well stimulation operations. More data is needed on the composition of flowback/produced waters from well stimulation operations in California to assess whether the fluid chemistries would differ significantly from conventional production.

Table 5-5. Comparison of produced water compositions from unconventional and conventional oil and gas operations.

Parameter	Marcellus ^a	Bakken ^b	Conventional Oil ^c	Conventional Oil and Gas (California) ^d
рН	5.1-8.4	5.5-6.5	5.2-8.9	2.6-11.5
Conductivity (mS/cm)		205–221		
Alkalinity (mg/L as CaCO3)	8–577		300–380	
TSS (mg/L)	4–7600			
TDS (mg/L)	680-345000	150000-219000		1000-84891
Chloride (mg/L)	64-196000	90000-130000	36-238534	0-156000
Sulfate (mg/L)	0-1990	300-1000		0-14879
Bicarbonate (mg/L)	0-763	300-1000	8-13686	0-12809
Bromide (mg/L)		300-1000	1–2	1-207
Nitrate (mg/L)	5-802		0–92	0-18
Oil and Grease- HEM (mg/L)	195–36600			
COD (mg/L)	1–1530			
TOC (mg/L)			15-3501	0-2054
Aluminium (mg/L)		ND	0.0-0.1	0-250
Arsenic (mg/L)			0.2-0.9	

Parameter	Marcellus ^a	Bakken ^b	Conventional Oil ^c	Conventional Oil and Gas (California) ^d
Barium (mg/L)	0 - 13800	0 - 25	0.1 - 7.4	0 - 174
Boron (mg/L)		40-192		0 - 602
Calcium (mg/L)	38 - 41000	7540 - 13500	4 - 52920	0 - 13613
Cadmium (mg/L)			0.0 - 0.2	
Chromium (mg/L)			0.1 - 1.0	0 - 200
Copper (mg/L)		ND	0.3 - 2.7	0 - 100
Iron (mg/L)	3 - 321	ND	0.1 - 0.5	0 - 540
Potassium (mg/L)		0 - 5770	2 - 43	0 - 7987
Magnesium (mg/L)	17 - 2550	630 - 1750	2 - 5096	0 - 2260
Manganese (mg/L)		4 - 10	1 - 8	0 - 50
Sodium (mg/L)	69 - 117000	47100 - 74600	405 - 126755	0 - 99920
Nickel (mg/L)			3 - 10	0 - 30
Strontium (mg/L)	1 - 8460	518 - 1010	0 - 2	0 - 600
Zinc (mg/L)		2 - 11	6 - 17	
Ra 226 (pCi/L)	3 - 9280		0 - 10	
Ra 228 (pCi/L)	0 - 1360			
U235 (pCi/L)	0 - 20			
U238 (pCi/L)	0 - 497			
Gross alpha (pCi/L)	37 - 9551			
Gross beta (pCi/L)	75 - 597600			

^a Barbot et al. (2013)

Another open question that remains is the extent of recovery of stimulation fluids during the flowback period. The volume of flowback water recovered may affect the fate of the injected fluid retained in the formation, and the potential for future mobilization of fracturing-fluid constituents in subsurface environments. Recoveries of flowback water will depend on various factors, including how much free water is present in the formation, as well as the rock and fluid properties in the target. A considerable amount of water can be retained in the formation, given that recoveries of fracturing fluids are relatively low - e.g., ranging between 9% and 53% in the Marcellus shale (New York State Department of Environmental Conservation, 2011; Vidic et al., 2013), and between 5% and 41% in the Bakken (Stepan et al., 2010).

Although it is unlikely that retained fracturing fluids will migrate out of the reservoir as discussed below in Section 5.1.3.2, these fluids can potentially interact with formation rocks over time. Hence, the resulting products of these fluid-mineral interactions, which

^b Stepan et al. (2010)

^c Alley et al. (2011)

^d Compiled for this report from the USGS Produced Water Database 2.0 (USGS, 2014)

can potentially include environmental contaminants, may appear in produced waters at a later stage. While some consider the environmental risks associated with "trapped chemicals" to be low (King, 2012), more studies are needed on the interactions of injection fluids and their additives with formation rocks and the overall fate of injection fluids in the subsurface environment, in order to determine if these have the potential to alter the chemistry of produced waters over the long term (such as causing slow release of trace metals or radioactive elements).

Available California data do not include specifics on the recovery of fracturing fluids during well stimulation. However, somewhat different recoveries may be expected in California, for two reasons. First, targets in California vary from those in other states geologically. For instance, diatomite, which is one of the main targets for hydraulic fracturing (see Section 3.2.1), has high porosity (as described in Section 4.3.2). Regarding matrix acidizing using mud acid, hydrofluoric and hydrochloric acids are expected to become consumed due to acid-mineral interactions over short penetration depths, while the remaining fluid often migrates over further distances. Assuming the rock is not fractured, acid penetration depths in sandstones have typically been reported to be on the order of 0.3 m (12 inches; Economides and Nolte, 2000) or less than 0.3-0.6 m (1-2 feet; Kalfayan, 2008). However, for high-permeability, high-quartz sands and fractured formations, such as the Monterey Formation (in places), higher than typical volumes of mud acid 3.1 to 3.7 m³/m (250 or 300 gallons per ft) have been applied to open fracture networks deeper in the formation (Kalfayan, 2008; Rowe et al., 2005).

Second, as described in Section 3.2.4, the predominant fracturing fluid applied in California is a gel, which may vary from the fluids used in the Marcellus and Bakken flowback fraction studies cited. This in turn may affect the penetration depth of injection fluids, the later recovery of fluids, as well as the recovery of specific, individual constituents. Additional information regarding the total estimated volume of recovered fluids in California should become available in the near future, due to new DOGGR reporting requirements (DOGGR, 2013).

5.1.2.4 Fracturing-Fluid Constituents in Flowback and Produced Waters

With respect to fracturing fluid constituents, degradation reactions and interactions with mineral phases within the reservoir may affect their individual recoveries and/or recovery rates. Fracturing fluid constituents that are typically evaluated for their residual concentrations in flowback or produced waters include friction reducers, surfactants, polychlorinated biphenyls (PCBs), biocides, alcohols, glycols, and acids, such as acetic acid (New York State Department of Environmental Conservation, 2011).

For instance, Orem et al. (2014) reported that the general composition of organic substances in produced and formation waters from coalbed methane and gas shale plays across the U.S. were similar. However, the researchers noted that produced water from hydraulic fracturing operations at the Marcellus shale contained a range of additional

organic chemicals used as fracturing-fluid constituents, such as solvents, biocides, and scale inhibitors, at levels of 1,000s of μ g/L (parts per billion) for individual compounds. Elevated total organic carbon (TOC) concentrations as high as 5,500 mg/L were present in produced waters from hydraulic fracturing operations in the Marcellus shale compared to about 8 mg/L for conventional production. While the concentrations of hydraulic fracturing chemicals and TOC decreased rapidly over the first 20 days of water recovery, some residual organic contaminants remained up to 250 days after hydraulic fracturing. In particular, biocides, which are toxic by necessity, are expected to persist in flowback water, and limit the options for flowback water disposal in the case of high concentrations (Rimassa et al., 2011).

An assessment of fracturing fluids being present in flowback/produced waters in California was not conducted due to the lack of data. Additional information regarding the specific composition of recovered water associated with well stimulation treatments should become available in the near future, due to new California reporting requirements (DOGGR, 2013).

5.1.2.5 Potential Direct Contaminants from Target Formations in Flowback and Produced Waters

The groundwater present in oil and gas reservoirs can contain naturally existing dissolved constituents such as stray gas (e.g., methane), salts, trace metals, NORMs (naturally occurring radioactive materials) and organic compounds that are released into the waters upon their interaction with formation rocks. The amount of dissolved material present in the fluids will depend on several characteristics of the formation, such as its geology, geochemistry, and microbiology. These dissolved constituents can be present in flowback and produced waters recovered at the surface, and can potentially degrade the water quality of shallow groundwater and surface-water resources, if released into those environments.

This section discusses potential contaminants that can be naturally present in the formation, i.e., those substances that have not been added to the injection fluids and include TDS (salts), trace metals, NORMs and organic compounds. Such contaminants could be present at higher levels in flowback and produced waters from unconventional production, as compared to oil and gas conventional production due to differences in the geology of the targets and chemistry of the formation waters. Formation waters are typically high in TDS, and organics, and several studies (particularly in the Marcellus shale) have noted high TDS values present in flowback and produced fluids from stimulation operations. Well stimulation could also lead to the potential release of trace metals due to decrease in pH (that may be relevant in acid stimulation operations) or complexation with organic ligands present in the injection fluids. The source rock (e.g. many shales) may also contain high concentrations of radioactive elements, which may be dissolved in formation waters.

The section outlines some of the problems that have been reported for these potential contaminants in regions where well stimulation has been conducted in the United States (several of these are in the Marcellus shale). Since the composition of flowback and produced waters varies considerably with geography, the relevance of these issues to California is discussed wherever possible. However, it is not currently possible to evaluate whether this list of potential contaminants is complete or even relevant to California since data about the chemistry of flowback and produced waters from stimulation operations in California was not available at the time this assessment was done.

The discussion for this report emphasizes contaminant concerns that are amplified due to the use of well stimulation; the report does not review some of the problems typically associated with conventional oil and gas operations, e.g., contamination by hydrocarbons such as benzene, toluene, ethylbenzene, and xylenes (BTEX), generation of H₂S due to biosouring of wells (Chilingar and Endres, 2005), or contaminants originating from drilling mud, cuttings, and fluids. It should be recognized that contaminants detected in conventional oil and gas operations, although not within the scope of this report, can also be a concern in well stimulation operations.

The interaction of well stimulation fluids with a formation containing unconventional oil can also result in effects such as transformations of the constituents of formation waters and sediments. These include changes to redox conditions, which can occur due to the introduction of oxygen from the stimulation fluids (for instance). Changes to redox can trigger a host of subsurface geochemical reactions such as oxidation of iron, pyrite, or organic matter present in a formation. Introduction of the stimulation fluids to the formation can also lead to changes in microbial communities (Mohan et al., 2013; Struchtemeyer and Elshahed, 2011). The potential changes to flowback fluids due to these effects were not investigated for this report.

5.1.2.5.1 TDS, Salinity and Water Hardness

TDS is defined as the total concentration of solids that will pass through a 0.2 μ m filter in solution. Typical TDS values in fresh water are <1,000 mg/L, between 15,000-30,000 mg/L in saline water, between 30,000-40,000 mg/L in seawater, and >40,000 mg/L in brine (wqa.org). Formation waters can contain high TDS concentrations, with salinities far exceeding seawater values, because many shales have marine origins (King, 2012). Thus, flowback and produced waters from well stimulation operations can contain high concentrations of TDS, although the concentrations change during the flowback and production periods. The source of the TDS and salinity in recovered wastewaters could either be salts present in formation brines or salts dissolved from formation rocks (Blauch et al., 2009). Some studies suggest that the TDS in the recovered wastewaters could result from mixing of injection fluids with formation brines (Haluszczak et al., 2013; Engle and Rowan, 2013). But another study of Marcellus shale produced waters found that, while most major cations were correlated with chloride, the variations in their concentrations could not be explained by dilution of existing formation brine with fracturing fluid

(Barbot et al., 2013). A study using strontium isotopes to characterize the signatures of produced waters suggested a basin-wide source of TDS in the Marcellus shale (Chapman et al., 2012).

The most concentrated ions found in flowback and produced waters are typically sodium and chloride (Barbot et al., 2013; Blauch et al., 2009; Haluszczak et al., 2013; Warner et al., 2012). Table 5-6 indicates this is the case in California as well. Magnesium and calcium can also be present at high levels and can contribute to increased water hardness. Typically, sulfate and alkalinity (measured as carbonate or bicarbonate) concentrations were low.

Table 5-6. Average concentrations of major ions and TDS (mg/L) in produced water samples from conventional oil and gas basins in California. Data from the USGS produced water database (USGS, 2014). All samples were collected before 1980.

BASIN	DATA POINTS	рН	BICAR- BONATE	CAL- CIUM	CHLO- RIDE	MAGNE- SIUM	POTAS- SIUM	SODIUM	SULFATE	TDS
COASTAL BASINS	14	7.9	1469	154	5257	82	71	3777	68	11169
LA BASIN	318	7.4	1060	604	16428	300	151	9399	35	27773
SACRAMENTO	12	6.4	372	191	9890	68	26	5980	18	16633
SAN JOAQUIN	344	7.4	1407	764	11121	133	259	5208	88	19570
SANTA MARIA	41	7.4	1354	435	10703	200	118	6047	849	18922
VENTURA	41	7.4	1670	958	13234	167	134	5972	170	26396

TDS can be a concern if present in high concentrations in flowback/produced waters. For example, the TDS content in the Marcellus shale is high, with ranges in flowback waters between 680 and 345,000 mg/L (ppm; Hayes, 2009). Such high TDS values are consistent with waters in the Marcellus being the second saltiest of all basins in the United States (Vidic et al., 2013). One study (Haluszczak et al., 2013) concluded that flowback waters from hydraulic fracturing of Marcellus wells resembled brines produced from conventional gas wells in the region. A study in the Bakken found large differences in the salinities of flowback water, not only between different producers, but also among different wells of a single producer, with values ranging from 60,000 mg/L to over 200,000 mg/L (Stepan et al., 2010).

The TDS values of flowback/produced waters from well stimulation operations in California may be lower than those reported in other regions. Produced waters in California have historically tended to have lower TDS concentrations as shown in Table 5-6. TDS values ranging from 10,000 to 40,000 mg/L have been reported for the formation waters in the San Joaquin and Sacramento basins at depths ranging from \sim 1,500 to \sim 3,500 m (Kharaka et al., 1985). A study of produced waters collected from the San Joaquin Basin found TDS of waters produced from depths <1,500 m were <4,000 mg/L (typically

<2,000 mg/L), whereas waters produced from depths >1,500 m were more saline (typically >25,000 mg/L) (Fisher and Boles; 1980). This depth-salinity pattern was found to be consistent with the transition in the basin from nonmarine strata at shallow depths to marine strata at greater depths. Since fracturing operations in California are conducted at shallower depths than in other regions - e.g. more than half the wells that have been stimulated using hydraulic fracturing are within 610 m (2000 feet) of the ground surface (Section 5.1.3.2.1), it is expected that TDS values of target formation waters, and hence of flowback/produced waters will be relatively low (as compared to wastewaters from stimulation operations in other regions in the United States) based on the depth-salinity gradient patterns in the formation, It is also possible that the TDS content of waters recovered from stimulation jobs using gels will be different from TDS values reported for slickwater fracturing. Well stimulation using gels is more common in California (Section 3.2.4).

Contamination by TDS/salty brines has been a problem in some areas where wastewaters recovered from WST operations ultimately ended up in freshwaters (Section 5.2.3.1.4). However, contamination of freshwaters is expected to be less problematic when the recovered fluids are disposed into Class II injection wells or reused in well stimulation operations, as is expected to be the case in California. High TDS values in flowback and produced waters can still be a concern if improperly handled at the surface during management, disposal or reuse.

5.1.2.5.2 Trace Metals

Formation brines can contain high concentrations of trace metals, which may be brought up to the surface in flowback and produced waters. Several studies report measuring high levels of barium, strontium, and iron in the waters recovered from fracturing operations in the Marcellus shale (e.g., Hayes et al., 2009; Barbot et al., 2013; Haluszczak et al., 2013). However, concentrations of trace elements in flowback and produced waters can vary widely across shale plays. For example, barium concentrations in the Fayetteville, Barnett, and Bakken shales can be much lower than elsewhere (Jackson 2013; Stepan et al., 2010). There is no current information available on the trace-element composition of flowback or produced waters recovered from stimulation operations in California.

The Monterey formation is high in trace elements compared to the World Shale Average (WSA) abundance (http://energy.cr.usgs.gov/TraceElements/faq.html). In particular, the lower and middle portions of the Monterey formation consist of different types of lithologies that might be relevant to mobilization of trace metals from the formation, i.e., carbonate-rich, organic-rich shales and phosphatic rock units as discussed in Section 4.3.1. The Monterey formation is also known to have selenium-enriched stratigraphic zones (Issacs 1999). Concentrations of some elements such as chromium, copper, nickel, antimony, selenium, uranium, vanadium, and zinc have been found to be highly correlated with organic carbon content. Other trace metals that were somewhat correlated with organic carbon include As, Ba, Cd, and Mo (Isaacs 1999). Borehole cuttings from the Santa Maria and Santa Barbara areas also had similar patterns showing high trace-element concentrations.

However, the release of trace elements present in the source rock into formation waters is dependent on several factors, such as pH, redox conditions, temperature, and the presence of organics (Kharaka et al., 1985). In general, trace elements can be mobilized as a result of decreases in pH, changes to redox, and the presence of organic ligands that can form complexes with metals (Stumm and Morgan, 1986). Some trace elements (particularly those present as cations) can be potentially mobilized due to decreases in pH, which may be relevant in matrix acidizing jobs. However, some contaminants (e.g., anionic species like arsenate) can be favorably attenuated as a consequence of pH decrease. The injection of biodegradable organic chemicals could result in both pH and redox changes in the subsurface that could alter trace metal mobility. These potential effects are not fully understood.

5.1.2.5.3 Naturally Occurring Radioactive Materials (NORMs)

NORMs include elements such as uranium, radium, and radon gas that are present in low concentrations in ambient soil and groundwater. Formation brines in contact with organic-rich shales can naturally contain high concentrations of radiogenic material. Uranium and thorium are present in many shale source rocks, are typically associated with high organic content (Ferti and Chillinger, 1988), and can decay to ²²⁶Ra, ²²⁸Ra and radon (Rowan et al., 2011).

The Monterey Formation is approximately six times more enriched in uranium than the WSA values (http://energy.cr.usgs.gov/TraceElements/monterey.html). Uranium concentrations in the Monterey formation rocks range from <2 ppm to more than 1,850 ppm (USGS, 1987). However, the uranium content of California crude oil is not typically high; for example, uranium concentrations in crude oil samples from Tertiary rocks in California ranged from 0.1 to 37.7 ppb (Bell, 1960).

Problems with elevated levels of radium have been noted in oil field equipment that process produced waters from conventional oil and gas production (USGS, 1999), particularly because radium is easily incorporated into barite (barium sulfate) scales, which precipitate when produced waters are brought to the surface. The hazard to operators and to the general public due to radioactive material trapped in scales within oilfield equipment are expected to be low (ALL Consulting, 2008). Moreover, in a survey of oil field equipment conducted by the American Petroleum Institute in 1989, the measurable radioactivity on external surfaces of equipment in California was at or near background level (USGS 1999).

However, flowback and produced waters from some shale formations can potentially contain high levels of NORMs that can be several hundred times U.S. drinking water standards. Several studies have measured high levels of radioactivity in samples collected from the Marcellus shale, which is known to contain radioactive elements (Hill et al., 2004). For example, the highest level of total radium measured in a study of flowback waters from Pennsylvania was 6540 pCi/L (Haluszczak et al., 2012) and uranium

concentrations in produced waters from N. Pennsylvania ranged from 0-20 pCi/L for U-235 and 0-297 pCi/L for U-238 (Barbot et al., 2013). Production brine samples from New York showed elevated gross alpha and gross beta results, ranging 14,530 - 123,000 pCi/L, with concentrations of ²²⁶Ra ranging from 2,472 to 16,030 pCi/L (NYSDEC, 2009). A study of various samples from the Marcellus shale found radium activities to range from non-detect to 18,000 pCi/L (Rowan et al., 2011). The high concentrations of NORMs found in flowback/produced waters from other shale plays do not imply that a similar situation will occur in California. No information about radioactive element concentrations in flowback or produced waters from stimulation operations in California could be located for this assessment, which is a major data gap in evaluating the hazards associated with WST.

5.1.2.5.4 Organics

Produced waters from oil and gas operations typically contain many organic substances that can originate from sources such as the formation water, formation rocks (e.g. organic-rich shales), oil present in the formation, and (in the case of well stimulation) from chemical additives added to the injection fluids (Orem et al., 2014). Section 5.1.2.1 lists the most commonly disclosed constituents of the stimulation fluids, including organics. The presence of organics in produced waters from conventional oil and gas operations have been extensively described in the literature, including in California (e.g., Fisher and Boles, 1990; Higashi and Jones, 1997). Organic compounds typically found in conventional produced waters include organic acids, polycyclic aromatic hydrocarbons (PAHs), phenols, and volatile organic compounds (VOCs) such as BTEX and naphthalene (Veil et al., 2004).

Very few studies have examined the presence of organics in produced waters from WST operations. Often organics are not measured, since these analyses are expensive and time-consuming. One industry-sponsored study by the Gas Coalition Institute (Hayes, 2009) measured a suite of organics in Marcellus shale flowback waters at the suggestion of the Pennsylvania Department of Environmental Protection, including VOCs, semi-volatile organic compounds (SVOCs), pesticides, and PCBs. The concentrations of most organic constituents were found to be below detection limits, and those VOCs that were measurable were similar to those found in conventional produced waters. The study concluded that it was unnecessary to measure pesticides, PCBs, and a large fraction of VOCs and SVOCs in produced waters from well stimulation. It is worth noting that this study did not measure the non-volatile, polar and water soluble compounds used in well stimulation fluids (Section 5.1.2.1).

As described in Section 5.1.2.4 regarding fracturing fluid in flowback/produced waters, the constituents of injection fluids make up the large fraction of organics additionally present in produced waters from hydraulic fracturing in the Marcellus Shale. These organics are not typically detected in conventional produced waters (Dahm et al., 2012; Orem et al., 2014). No information about organic constituents in flowback or produced waters from stimulation operations in California was identified.

5.1.3 Potential Release Pathways

There are a variety of activities associated with oil and gas development that can potentially release contaminants into surface water and groundwater aquifers. This section provides an overview of surface and subsurface release pathways, emphasizing those pathways and contaminants that are unique to the well stimulation treatments under consideration in this assessment.

In Section 5.1.3.1, surface pathways for water contamination are reviewed. Surface pathways include (1) surface spills and leaks; (2) the management and disposal of flowback/produced water; and (3) stormwater runoff. Produced water and flowback of well stimulation fluids are not managed separately in California, and most flowback/ produced water is injected into Class II wells. However, current management practices in California allow for the disposal of flowback/produced water into unlined pits in some areas and reuse for agriculture without prior treatment. A more detailed assessment is needed of disposal and reuse practices to determine if they pose a risk to water resources. Furthermore, there is one documented case of the intentional release of flowback fluids in California, as well as other documented cases of the accidental release of chemicals associated with well stimulation in other states. Detailed assessments are not available as to whether these releases contaminated surface water and/or groundwater aquifers, but this is a potential pathway for surface and groundwater contamination. Furthermore, data on the water quality impacts of well stimulation are limited. Much of the available literature is focused on unconventional natural gas production; far less is available on shale oil production or about well stimulation technologies that may be used to access these resources, e.g., acid fracturing and matrix acidizing.

Section 5.1.3.2 discusses mechanisms for groundwater contamination via migration through subsurface pathways. Potential subsurface pathways include (1) natural and induced high-permeability pathways, the latter possibly created by hydraulically induced fractures propagating outside the target reservoirs; (2) engineered subsurface penetrations such as old wells that have not been properly abandoned and have been intersected by fracturing operations; and (3) direct introduction of contaminants via failing, degraded, or poorly constructed operating wells. Mechanisms of pathway formation, and leakage and transport through these existing, induced, and propagated failures are discussed and, for each pathway, the manner in which contamination may occur and the documentation of such an occurrence are provided, where available.

It is important to note that pathways must first exist (whether natural, preexisting, or induced by operations) before migration can occur. A summary of the literature on the subject, however, suggests that pathway formation via hydraulic fracturing itself is likely to be limited in vertical extent, and documented instances of contamination across the U.S. have been shown to be correlated with nearby operations, but not conclusively linked except in cases of direct injection of contaminants via operator error or well failure (US EPA, 2012).

Well stimulation notices filed to date with DOGGR indicate that much of the current and planned hydraulic fracturing operations in California occur at depths of less than 2000 feet below the ground surface, which is substantially shallower than in other states. Hydraulic fracturing at shallow depths poses a greater risk to water resources because of its proximity to groundwater and the potential for fractures to intersect nearby aquifers. In addition, migration of fracturing fluids via other permeable pathways is also possible. Some studies in other regions across the United States have found a correlation between the location of hydraulically-fractured production wells and elevated concentrations of methane (Osborn et al., 2011; Warner et al., 2012; Warner et al., 2013), arsenic, selenium, strontium (Fontenot et al., 2013) and, to a lesser extent, TDS (Warner et al., 2013). However, there is no consensus as to whether these are naturally occurring, or due to hydraulic fracturing, production well defects, abandoned wells, or a combination of mechanisms. More complete information about the location and quality of groundwater resources relative to the depth at which hydraulic fracturing is occurring in California would make it possible to identify inherently hazardous situations that could and should be avoided.

5.1.3.1 Surface Release Pathways

5.1.3.1.1 Surface Spills and Leaks of Fracturing Fluids

Oil and gas production involves the possibility of surface or groundwater contamination from spills and leaks. Well stimulation, however, raises additional concerns, due to the use of additional chemicals during the stimulation process, the generation of flowback fluids that contain these chemicals, and the increased transportation requirements to haul these materials to the well and disposal sites. Surface release of these chemicals and fluids can run off into surface water bodies and/or seep into groundwater aquifers. In this section, we describe concerns associated with well stimulation chemical usage at the surface and associated transportation concerns. The management and disposal of flowback and produced water are described in Section 5.1.3.1.2.

Well stimulation necessitates the transport and usage of chemicals (see Section 5.1.2). Chemicals needed for well stimulation are typically transported to the site by truck and are stored in the containers in which they were transported. Liquid chemicals and other additives are transported via hose to a blending unit, where they are mixed with the base fluid. Dry additives are poured by hand into the blending unit. This solution is then mixed with a proppant, if necessary, and pumped directly into the well (NYSDEC, 2011). Some of the fluids can be mixed and stored in preparation for the treatment; however, many are added only as the stimulation process is taking place (Cardno ENTRIX, 2012; King, 2012). This ensures that any chemical reactions occur at the appropriate time and in the proper location, and enables operators to ensure that there are no unused mixed fluids for storage or disposal.

These processes can result in chemical releases to the environment. Surface spills and leaks can occur during chemical or fluid transport, pre-stimulation mixing, or as the stimulation process is taking place. In addition, storage containers used for chemicals and well stimulation fluids can leak. These releases can result from tank ruptures, piping failures, blowouts, equipment failures and defects, overfills, fires, vandalism, accidents, or improper operations (NYSDEC, 2011). For example, in September 2009, two pipe failures and a hose rupture in Pennsylvania released 8,000 gallons of a liquid gel mixture during the hydraulic fracturing process, polluting a local creek and wetland (PA Department of Environmental Protection, 2009a; 2009b).

Data on hazardous materials spills are maintained by the California Emergency Management Agency (CEMA). According to California law, any *significant* release or threatened release of hazardous substances must be reported to CEMA.^{3,4} According to these data, spills of chemicals typically used in well stimulation fluids, e.g., hydrochloric, hydrofluoric, and sulfuric acids, have occurred at oil and gas operations in California. For example, in February 2012, a storage tank containing 5,500 gallons of hydrochloric acid exploded in the Midway-Sunset Oil Field in Kern County, spreading the acid beyond a secondary containment wall. It is not possible, however, to discern whether stimulation was the intended purpose of this chemical, because acids are used to clear out drilling debris before the well is brought into production and are not uniquely associated with well stimulation.

5.1.3.1.2 Management and Disposal of Flowback/Produced Water

Produced water is generated by both conventional and unconventional oil and gas operations. Flowback fluids, by contrast, are unique to the well stimulation techniques under consideration in this report. In California, produced water and flowback water are managed together. As noted in a recent white paper from DOGGR, "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). Given that these fluids are co-mingled, surface release pathways that may be associated with how these fluids are collectively managed are described. Although these fluids are sometimes referred to collectively as "wastewater," this report uses the term "flowback/produced water" in order to avoid confusion. A detailed assessment of the location and method of flowback/produced water disposal for specific wells was beyond the scope of this report. Consequently, we have conducted a review of the hazards associated with wastewater management and disposal in general.

³ Hazardous materials are defined as "any material that, because of its quantity, concentration, or physical or chemical characteristics, poses a significant present or potential hazard to human health and safety or to the environment if released into the workplace or the environment" (HSC 25501).

⁴ Spills on highways must be reported to the California Highway Patrol, who then notifies CEMA.

5.1.3.1.3 Onsite Storage and Transport of Flowback/Produced Water

Once at the surface, flowback/produced water may be temporarily stored at the well site in pits, embankments, or tanks, and then transported to a disposal site. Currently, oil and gas operations in California typically use closed loop systems to re-inject produced water onsite or transport these fluids through a pipeline network to a nearby disposal site. In some areas, however, trucks may be used. The onsite storage and transportation of flowback can result in the accidental releases of flowback fluids from spills and leaks that can reach surface water and groundwater aquifers. Spills or leaks can occur as a result of tank ruptures, piping and equipment failures, surface impoundment failures, overfills, vandalism, accidents (including vehicle collisions), fires, drilling, and production equipment defects, or improper operations (New York State Department of Environmental Conservation (NYSDEC), 2011).

There is evidence that surface spills of flowback/produced water affect surface water and groundwater aquifers. For example, in 2007, flowback fluids overflowed retention pits in Knox County, KY, releasing the fluid directly into Acorn Fork. The incident killed or displaced all fish, invertebrates, and other biota for months over a 2.7 km (1.7 miles) section of the creek. Papoulias and Velasco (2013) found that fish exposed to Acorn Creek waters showed signs of stress and higher incidence of gill lesions, consistent with exposure to low pH and toxic concentrations of heavy metals. Further, they found that the release degraded water quality sufficiently to have adverse impacts on the health and survival of *Chrosomus cumberlandensis* (Blackside Dace), a federally threatened species. Additionally, in an analysis of surface spills between July 2010 and July 2011 in Weld County, CO, Gross et al. (2013a) found that surface spills of produced water from the fracturing process or crude oil from fractured wells released BTEX to groundwater at levels that exceeded National Primary Drinking Water Maximum Contaminant Levels (MCLs) for each compound. In general, remediation efforts were sufficient to address these spills.

Data on flowback/produced water spills associated with oil and gas operations in California are reported to the DOGGR. According to Title 14, Section 1722 of the California Code of Regulations, "significant" water leaks must be promptly reported to the appropriate DOGGR district office (*California Code of Regulations*, n.d.). The reporting requirements are vague. There is no definition of what constitutes a significant leak, and all spills are likely not reported. According to the available data, between January 2009 and February 2014, 423 surface spills at oil and gas fields in California released nearly 2.8 million gallons of flowback/produced water, or an average of 6,500 gallons per incident. Of these, 34 spills released a total of 88,000 gallons of flowback/produced water into California waterways. Corrosion and sensor failures that cause tanks to overflow are the most common causes of these spills. As described previously, surface spills also have the potential to intercept groundwater aquifers, although lack of data on underlying groundwater quality before and after spills, and/or lack of data on the chemical composition of the spills, and varying conditions across the state limit the ability to evaluate general potential impacts in California.

5.1.3.1.4 Flowback/Produced Water Disposal

Problems with disposal of wastewaters recovered from well stimulation operations have been noted in some regions where flowback and produced waters ultimately ended up in fresh surface waters. For example, in the early development of the Marcellus region (2008-2009), flowback and produced waters were legally discharged into public twastewater treatment plants (WWTPs) that were not equipped to handle the high TDS content of these fluids, which resulted in increased loading of salts to Pennsylvania rivers (Brantley et al., 2014; Vidic et al., 2013; Kargbo et al., 2010). Bromide was also found to be a contaminant of concern due to the presence of carcinogenic disinfection byproducts in the WWTPs, formed from the reaction of elevated levels of bromine present in flowback/produced waters with organics (Ferrar et al., 2013). State regulators in Pennsylvania subsequently discouraged the practice of discharging waters recovered from fracturing operations into WWTPs, due to the many concerns about water quality degradation. There is some evidence that produced water is being discharged into municipal WWTPs but an assessment of this practice is beyond the scope of this report.

In California, disposal of flowback/produced water is typically done by one of three other methods: injection in Class II wells; reuse and recycling for oil and gas production or other beneficial uses; and percolation in unlined surface impoundments. Disposing of oil and gas flowback/produced water introduces surface release pathways that are unique to the disposal method under consideration. Each is described in more detail below.

Class II Wells

The majority of flowback/produced water from oil and gas operations in California is injected into Class II wells (Kiparsky and Hein, 2013). Injection wells are classified according to the location and type of fluid injected. According to the US EPA, Class II wells are used to inject brines and other fluids associated with oil and gas production. Class II well types include saltwater disposal wells, enhanced recovery wells (e.g., water flooding), and hydrocarbon storage wells (US EPA, 2014). Of the more than 30,000 Class II wells in California, about 95% are used for enhanced oil production and ~3% are used for disposal. More than 80% of Class II wells are located in District 4, representing Kern, Inyo, and Tulare Counties (Walker, 2011). There are a few documented cases of contamination associated with injection in Class II wells, as discussed in Section 5.2.3.2.2 of this report. However, as described below, groundwater contamination incidents in Ohio declined after injection in Class II wells replaced earthen pit disposal (Kell, 2011).

Reuse

While injection is the primary mechanism for managing flowback/produced water from oil and gas operations in California and in the rest of the United States (Guerra, Dahm, and Dundorf, 2011), flowback/produced water may also be reused for oil and gas operations (e.g., hydraulic fracturing) or other beneficial purposes (e.g., for irrigation, livestock

watering, and some industrial uses). Produced water/flowback may be treated prior to reuse or simply blended with fresh water to bring the levels of TDS and other constituents down to an acceptable range (Veil, 2010).

As described previously, well stimulation notices filed with DOGGR since December 2013 indicate that oil and gas operators are currently using fresh water for well stimulation, and thus flowback/produced water is not being used for subsequent treatments (DOGGR, 2014). Flowback/produced water, however, is used to supplement irrigation water in California in some places. For example, in October 2011, the Central Valley Regional Water Quality Control Board (CVRWQCB) issued a general waiver to allow a discharger to pipe oilfield wastewater to an existing irrigation reservoir, where the water is mixed with groundwater (7% oilfield wastewater/93% groundwater) to irrigate 120 acres of citrus trees in Kern County (CVRWQCB 2011). Also in Kern County, produced water/flowback is treated and delivered by pipeline to a reservoir, where it is blended with surface water and groundwater. The blended water is then used to irrigate farmland throughout the Cawelo Water District service area during the irrigation season and is used to recharge groundwater during the nonirrigation season (CVRWQCB 2012). The Tulare Basin Plan notes that produced water "is used extensively to supplement agricultural irrigation supply in the Kern River sub-basin" (CVRWQCB 2004).

The use of produced water can potentially provide a new source of water supply, e.g., to farmers in San Joaquin Valley, where water resources are extremely constrained. The use of produced water comingled with flowback fluids, however, raises a set of unique concerns that are not yet well understood, especially when the mixture is not treated prior to reuse. In particular, the toxicity, persistence, and mobility of stimulation chemicals and constituents in the flowback/produced water, resulting from degradation of those chemicals and the interaction of the stimulation fluid with the formation, have not yet been evaluated.

Surface Impoundments

In some areas, wastewater from oil and gas operations is also disposed of via percolation in unlined surface impoundments—also sometimes referred to as sumps or pits. Sumps are primarily regulated by the state's nine Regional Water Quality Control Boards. Each regional board is required to formulate and adopt water quality control plans, or basin plans, for all areas within the region. The plans establish water-quality objectives to protect beneficial uses and policies to implement the objectives.

Much of the state's oil production occurs within the jurisdiction of the CVRWQCB and is covered within the Tulare Basin Plan. The Tulare Basin Plan notes that hundreds of sumps are in use in the region to separate oil from wastewater and to dispose of oil

⁵ Local Air Districts also regulate some aspects of oilfield sumps, e.g., VOC emissions.

field wastewater via percolation. Disposal of oil field wastewater in sumps overlying groundwater with existing and future beneficial uses is permitted if the electrical conductivity (EC) (represents salinity) of the wastewater is less than or equal to 1,000 micromhos per centimeter (μ mhos/cm), and a maximum of 200 milligrams per liter (mg/L) chlorides, and 1 mg/L boron, with no other testing required for, or limits on, other contaminants. Oil field wastewater that exceeds these specified salinity limits may 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."

There is evidence of groundwater contamination associated with disposal of flowback/ produced water in unlined surface impoundments in other parts of the United 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, more than 35% (or 75 incidents) were associated with waste management and disposal activities. Fifty-seven of these incidents were associated with produced water disposal pits, which were banned in 1969 and closed no later than 1984. Of the 185 groundwater contamination incidents in Ohio over the 25-year period, 5% (or 10 incidents) were associated with the failure of unlined pits. Like Texas, earthen pits are no longer in use in Ohio, and no incidents have been reported since the mid-1980s. Kell (2011) further notes that while there are cases of groundwater contamination incidents associated with Class II injection operations, "documented groundwater contamination incidents dropped significantly after subsurface injection replaced earthen pit disposal as the primary method of produced water management." While these studies and others linking unlined surface impoundments to groundwater contamination do not specify whether well stimulation fluids were the cause of the contamination, they are illustrative of the hazards of this disposal method.

A case in Pavillion, WY, raises additional concerns about the use of surface impoundments to contain flowback and produced water. The Pavillion gas field is located in central Wyoming in the Wind River Basin, the upper portion of which serves as the primary source of drinking water for the area. Oil and gas exploration began in the area in the 1950s and increased dramatically between 1997 and 2006. In 2008, domestic well owners began complaining about taste and odor problems, and residents believed these issues to be linked to nearby natural gas activities. In response to complaints from local residents, the US EPA initiated an investigation, collecting water samples from residential, stock, shallow monitoring, deep monitoring, and two municipal wells. According to the US 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 surface pits were used to store/dispose of drilling muds, flowback, and produced water in the area. These findings were not contested by Encana Oil and Gas, the company responsible for the natural gas wells, or other the stakeholders (Folger, Tiemann, and Bearden, 2012). There

was, however, considerable controversy about US EPA's other findings, i.e., the presence of hydraulic fracturing chemicals in deep wells and thermogenic methane in monitoring and domestic wells, as discussed in Section 5.1.3.2.3.

Illegal Discharges

Illegal waste discharges may result in the release of contaminants to surface water and groundwater aquifers. Kiparsky and Hein (2013) note that lax enforcement of regulations and insignificant penalties can incentivize illegal dumping when the punishments are less costly than proper disposal or reuse. In July 2013, for example, the Central Valley Regional Water Quality Board (CVRWQB) issued a fine to Vintage Production California LLC in the amount of \$60,000 for periodically discharging saline water, formation fluids, and hydraulic fracturing fluid to an unlined sump for 12 days. The sump was located next to a newly drilled oil well near the City of Shafter in Kern County. Discharge of high-salinity water into an unlined sump is prohibited in areas with good-quality groundwater, and the Board's Executive Officer noted that there is concern "that similar discharges may have occurred elsewhere throughout the Central Valley" (CVRQCB, 2013). In response, the CVRQCB issued an Order in November 2013 seeking information from oil and gas operators about the discharge of drilling fluids and well completion fluids since January 2012. This information will help the Board identify the characteristics and volumes of waste discharged to land and to evaluate the potential impacts or threatened impacts to water quality posed by the discharge of these fluids to land.

5.1.3.1.5 Stormwater Runoff, Including Floods

Stormwater runoff carries substances that can be harmful to water quality and ecosystem health from the land surface into local waterways. While runoff is a natural occurrence, disturbances to the land surface can increase its timing, volume, and composition. For example, a one-acre construction site with no runoff controls can contribute 35-45 tons of sediment each year, compared to less than 1 ton of sediment per year from forest land (US EPA, 2007a).

There is some evidence that oil and gas operations exacerbate stormwater runoff impacts to water resources. However, it is not clear the degree to which impacts are more generally associated with oil and gas activities or specific to the well stimulation treatments under consideration in this report. Olmstead et al. (2013) found that shale gas operations increased total suspended solid (TSS) concentrations in downstream surface water bodies. The particular mechanism by which this occurred, e.g., precipitation events or initial construction activities, could not be determined.

While limited studies that examine runoff associated with well stimulation activities are available, there are likely to be some impacts that are unique to well stimulation treatments. Specifically, runoff from well pads can pick up spilled chemicals used during well stimulation as well as residual process and flowback fluids that may be located

onsite. Additionally, precipitation events and flooding may damage storage and disposal sites or cause them to overflow, washing these materials into waterways. For example, major flooding in 2013 damaged oil and gas operations in northeast Colorado, spilling an estimated 48,000 gallons of oil and 43,000 gallons of produced water (COGCC, 2013). Furthermore, the additional truck traffic associated with transporting materials, equipment, and flowback/produced water can increase wear and erosion on local roads and/or result in the development of new paved and unpaved roads with impacts to surface runoff.

Stormwater discharge is regulated by state and local governments. The National Pollution Discharge Elimination System (NPDES) program regulates stormwater runoff at the federal level. States can receive primacy to administer their own permitting program and can implement stronger requirements, if desired.⁶ At the federal level, oil and gas operations have been afforded special protections and are exempt from some provisions in the Clean Water Act. Consequently, oil and gas operators are not required to obtain a stormwater permit unless, over the course of operation, the facility generates stormwater discharge containing a reportable quantity of oil or hazardous substances or if the facility violates a water-quality standard (40 CFR 122.26(c)(1)(iii)).⁷ In 2005, the definition of oil and gas exploration and production was broadened to include construction and related activities, although regulations still require well pads larger than one acre to apply for an NPDES stormwater permit. A 2005 study on the surface water impacts of natural gas drilling noted the difficulty of monitoring and suggested that few facilities were monitoring in a way that would allow them to determine whether a NPDES permit was required (US EPA, 2007b).

5.1.3.2 Subsurface Release Pathways

The consideration of potential subsurface contamination pathways is organized into three parts. The first part regards the formation of high permeability pathways by hydraulic fracturing, which regards the extent and permeability of induced fractures and the possibility of connection to overlying aquifers. By definition, a hydrocarbon reservoir is likely to be capped or bounded by low-permeability layers. Thus, contaminant migration requires a pathway, whether natural or induced. The second part addresses issues with wells (drilling, completions, and failures) that may create opportunities for hydrocarbons or fracturing fluids to enter groundwater aquifers. The third part discusses transport processes that could occur within permeable pathways, if they exist, and the evidence for such migration.

⁶ California's Regional Water Quality Control Boards have authority to issue stormwater permits, where they are required.

⁷ This requirement will not be met by sediment discharges alone.

In a recent progress report concerning ongoing US EPA studies of the potential impacts of hydraulic fracturing on groundwater resources (US EPA, 2012), the authors state clearly that data concerning hydraulic fracture communication outside of target reservoirs is currently very limited, with few peer-reviewed studies in place to confirm or deny the possibility of contaminant transport due to fracturing operations. In response, the US EPA is performing case studies at multiple locations in the US where contamination of water resources has been alleged in areas with historic oil and gas operation (Texas, Pennsylvania, Colorado, North Dakota). Water sampling from wells and surface water sampling and monitoring is under way to understand the impact of prior drilling, current drilling, and fracturing work, and in the case of North Dakota, the aftermath of a well blowout accident. In conjunction with field studies, modeling studies are being performed to assess the mechanics of fracture propagation and flow processes governing various gas and fluid leakage scenarios (US EPA, 2012). In addition, the US EPA report describes out a number of hypothetical leakage scenarios, but these scenarios have yet to be evaluated. Beyond a literature review, the data and modeling results for the transport studies have not been released to the public or to the general scientific community. Therefore, an independent examination of the literature is required.

5.1.3.2.1 Formation of High Permeability Pathways

One possible concern about hydraulic fracturing operations, in particular those using high-volume injections, is the degree to which induced fractures may extend beyond the target formation to connect to higher permeable aquifers, or to natural or man-made pathways such as faults, natural fractures, or abandoned wells. The current state of understanding about the formation of such permeable pathways due to hydraulic fracturing is surrounded by some controversy, due to concerns about groundwater contamination above hydraulically fractured reservoirs. The bulk of previous published work in the area of hydraulic fracturing has been in the form of data and literature reviews, geomechanical modeling studies, and analysis of existing microseismic data to assess fracture formation and propagation, all with a focus on the creation of permeability for oil and gas production. Basic theoretical and geomechanical work spans decades, with early work on fracture propagation such as that by Hubbert and Willis (1972) and Nordgren (1972), and work on fracture width evolution by Perkins and Kern (1961). The review by Adachi et al. (2007) summarizes much of the early work with a focus on numerical simulation. However, the latest and most relevant published work, directly addressing concerns about possible leakage of gas and fracturing fluids, has occurred since 2011, with multiple papers creating a vigorous debate about the nature and extent of artificial fractures and the processes creating them.

Myers (2012) discusses transport in porous media and in fractures and pathways driven by both natural advection and fracturing-related pressure increases within porous media in the Marcellus shale. Using a simplified flow simulation, the work determined that pressure increases are localized, subside in a year or less, and that the injection-stimulated systems could re-equilibrate in pressure with a year or less. The simulation operates under the assumption of the existence of out-of-formation fracturing or connectivity to permeable faults, which, if present, could drive fluids or gas into overlying formations on decadal scales or more quickly. Supporting this assumption is a published letter by Warner at al. (2012b) stating that microseismic monitoring indicates fracture propagation is more likely in the vertical direction, increasing the possibility of fractures reaching upward toward more permeable formations, or into pathways that are inferred in a previously published geochemical study. However, Myers' (2012) simulation work lacks key coupled hydrological processes, particularly the properties of unsaturated shales (Vidic et al., 2013), and did not include coupled geomechanical modeling.

A later study by Flewelling and coauthors (Flewelling et al., 2013) developed a novel relationship between injected fluid volumes and maximum possible fracture height, calibrated via a dataset of the observed extent of microseismicity during well stimulation operations. The study capped potential vertical fracture propagation at 600 m (2,000 ft) or less. Additional limitations created by injected volumes, combined with the observation that shallow formations are more likely to fracture horizontally rather than vertically, led to the authors' lack of concern about the possibility of fracturing at depths greater than 150 m (500 ft) intercepting shallow groundwater resources, thus disputing Myers' underlying assumptions. In a similar vein, work by Fisher and Warpinski (2012) and a review by Davies and collaborators (Davies et al., 2012) attempted to demonstrate that fracture propagation is inherently limited.

Specifically, Fisher and Warpinski (2012) compare fracture extent as mapped by microseismic data to water well depths for active shale production regions in the Barnett, Woodford, Eagle Ford, and Marcellus formations. They find that vertical fracture extent for deep hydraulic fracturing operations does not bring the fractures in close contact with shallow aquifers, and uses mineback data (artificial fractures excavated and examined *in situ*) and experience to posit fracture growth-limiting mechanisms that would lead to well-contained fractured reservoirs. This work also indicates the likelihood of fractures in shallower formations (<1,200 m or 3,900 ft) having a greater horizontal component (due to decreasing vertical normal stress at shallower depths), with the consequence of reduced likelihood of extended vertical propagation toward shallow aquifers.

Davies et al. (2012) also argues that the height of artificial fractures is limited. The study reviews data on both natural and stimulated fractures, comparing the mechanisms proposed for formation of natural "pipes" and "chimneys" (clusters of large fractures/faults extending hundreds or thousands of meters, typical in sub-seafloor environments) with fractures artificially created for stimulation purposes, or as a result of production accidents or blowouts. Using a variety of datasets, they plotted frequency versus fracture height for natural and artificial fractures, estimating the probabilities that induced fractures could reach specific heights. They find that the majority of artificial fractures (with data focused on the Barnett Shale) range from <100 m (330 ft) to ~600 m (2,000 ft) in height, with approximately a 1% probability of a fracture exceeding 350 m (1,100 ft). They correlate this data with previous studies suggesting that artificial fracture growth

is also limited by fracturing fluid volume, similar to the findings of Flewelling et al. (2013). The limited scale of induced fractures is compared with larger, more extensive natural fractures systems, or "pipes," that are created by processes that involve much larger fluid volumes, overpressures, longer time frames, and other factors such as erosion or collapse of surrounding strata. Thus, a minimum separation of 600 m (2,000 ft) between shale reservoirs and overlying groundwater resources is suggested for thigh-volume fracturing operations, although local geology must always be evaluated.

In California, an industry study (Cardno ENTRIX, 2012) evaluated the effects of ten years of hydraulic fracturing and gas production from a Los Angeles Basin oil and gas field. Microseismic monitoring indicates that fractures were contained within the reservoir zone, extending to within no more than 2,350 m (7,700 ft) of the base of the fresh-water zone. However, microseismic inversion depends on an initial velocity model, and thus the characterization of hydraulic fractures via this method can result in some inaccuracy or ambiguity (Johnston and Shrallow, 2011).

Recent studies include coupled flow-geomechanical modeling to increase the fundamental understanding of how fractures form and propagate during injection and pressurization (Kim and Moridis, 2012). A coupled flow-geomechanical simulator (Kim and Moridis, 2013) has been developed using the established TOUGH+ subsurface flow and transport simulator (Moridis and Freeman, 2013) and validated against analytical solutions for poromechanical effects, static fractures, and fracture propagation. The initial work looked at fracture development versus injection rate, and found that shear failure can limit the extent of fracture propagation. Later work using full 3D domains suggests possible inconsistencies between fracture volume and the volume of injected water, resulting from the difference between the propagation of the water front (a flow process) and the propagation of the fractures themselves (a geomechanical process), with the net result that injected fluid volume may underestimate fracturing extent. However, the work also suggests inherent physical limitations to the extent of fracture propagation, for example, the presence of overlying confining formations may slow or stop fracture growth, thus containing fractures within the shale reservoir (Kim et al., 2014).

Application of this work to California requires an understanding of the depth of hydraulic fracturing operations relative to groundwater aquifers. Data regarding hydraulic fracturing depth are available only from the well stimulation notices. Data regarding the true vertical depth of some wells hydraulically fractured are available from FracFocus, and the measured depths of some wells hydraulically fractured are available in DOGGR's GIS well data files. The proportion of wells at various depth-levels is shown on Figure 5-4. A large fraction of the depths are less than 610 m (2,000 ft). The distribution of depths for the hydraulic fracturing intervals is necessarily shallower than the well depth distributions.

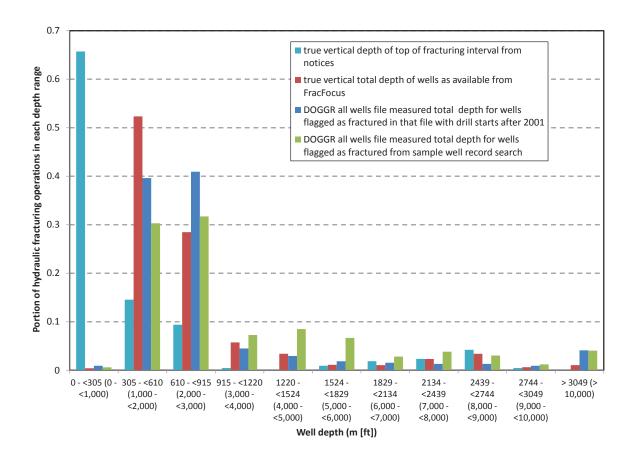


Figure 5-4. Portion of hydraulic fracturing operations vs. depth range (DOGGR data is only for wells drilled after 2001).

Figure 5-5 indicates the depth of the shallowest well hydraulically fractured in each field. The shallowest well depth in a number of fields is less than 610 m (2,000 ft) and in even more fields is less than 1,220 m (4,000 ft). This suggests that the separation between some fracturing intervals and groundwater is less than the suggested 600 m separation based on Flewelling et al. (2013) and Davies et al. (2012), which would imply that the likelihood of propagation of fractures into groundwater aquifers may be higher in California. However, it is important to remember that this depth-separation suggestion was based on high-volume hydraulic fracturing conducted in deep shale reservoirs, meaning the subsurface stress conditions as well as the WST operations are quite different from the situation in California. For example, fractures may primarily propagate horizontally at shallower depth and, due to relatively smaller fracturing fluid volumes, the height distribution of fractures in California may also be smaller than that used as the basis for the depth-separation suggestion (Fisher and Warpinski, 2012).

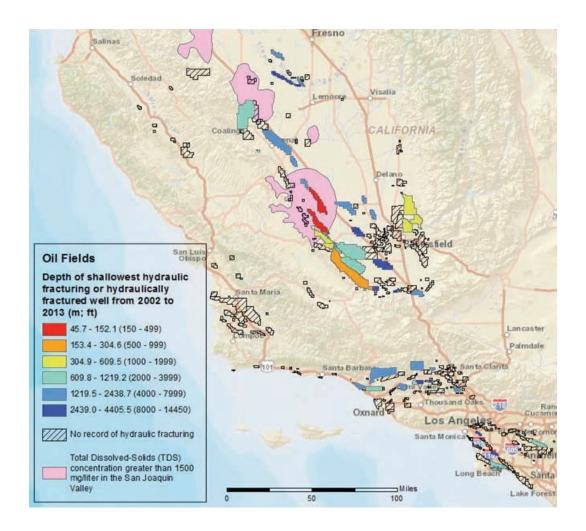


Figure 5-5. A map showing the shallowest hydraulic fracturing depth from the well stimulation notices or hydraulically fractured well depth in each field (measured depth from DOGGR for wells drilled after 2001 or true vertical depth from FracFocus). Pink areas show regions in the San Joaquin Valley where the shallowest groundwater has total dissolved solids above California's short-term secondary maximum contaminant level for drinking water of 1,500 mg/L. Note oil fields colored orange and yellow in the San Joaquin Valley, indicating shallow hydraulic fracturing, located in areas with better groundwater quality. Data from DOGGR 2014(a), DOGGR 2014(b), FracFocus (2013), and Bertoldi et al. (1991).

Also highlighted in Figure 5-5 are regions with relatively poor groundwater resources containing > 1,500 mg/L of total dissolved solids (TDS), from Bertoldi et al. (1991). California has established secondary maximum contaminant levels (SMCLs) for various constituents in drinking water. The SMCLs are based on odor and taste rather than health thresholds. The recommended SMCL for TDS is 500 mg/L and the upper SMCL is 1,000 mg/L. There is also a short-term SMCL of 1,500 mg/L allowed in rare circumstances

(State Water Resources Control Board, 2010). The proportion of fracturing operations vs. depths are re-plotted in Figure 5-6, for operations that occur in regions with groundwater containing < 1,500 mg/L of total dissolved solids (TDS). Comparison of Figure 5-4 with Figure 5-6 suggests that the majority of shallow operations occur in regions where groundwater is of poor quality. However, the well records search results indicate up to 3% of hydraulically fractured wells are shallower than 610 m (2,000 ft) in regions with good to reasonable groundwater quality. This percentage equates to tens of shallow wells being fractured per year given estimates of the number of wells hydraulically fractured. It is unknown if the fracturing intervals in these wells are sufficiently deep to preclude induced fractures propagating into potable groundwater. Because most of the wells are vertical, the fractured interval must be shallower than the total vertical well depth. Page (1973) indicates the base of water with < 2,000 mg/L TDS is up to a thousand meters (thousands of feet) deep in some areas. So the separation between hydraulically fractured well intervals and groundwater may be much less than 600 m (2,000 ft) at tens of wells per year. For instance the shallowest hydraulically fractured well in the Kern River Field, which is shown in yellow just north of Bakersfield in Figure 5-5, is less than 610 m (2,000 ft) deep. Groundwater with less 2,000 mg/L TDS is implied to that depth and deeper by Page (1973). A portion of the produced water from this field is used for irrigation (Coburn and Gillespie, 2002). While the water is treated, it is not known if the treatment would remove all the fracturing fluid constituents that might be of concern.

Further, it is not clear that 1,500 mg/L TDS is the threshold for groundwater to be considered with regard to protection from entry of well stimulation fluids. DOGGR has historically protected groundwater with < 3,000 mg/L and the federal definition of underground sources of drinking water requiring protection is < 10,000 mg/L (Walker 2011). The number of hydraulically fractured intervals within a few hundred meters of groundwater with concentrations less than 20,000 mg/L is necessarily larger than the tens of wells per year mentioned above with regard to groundwater with < 1,500 mg/L TDS. The potential for hydraulic fractures to intercept groundwater resources in cases of shallow well stimulation warrants more careful investigation and monitoring.

For fracturing intervals more than 600 m (2,000 ft) from overlying aquifers, our review of the existing literature suggests that creation of permeable pathways connected to these aquifers solely through hydraulic fracturing operations seems unlikely in most cases, considering the relative separation of the formations and the difficulty of creating very long, extensive fractures or fracture networks. A review by Jackson et al. (2013b) comes to the same conclusion, noting that no "out-of-zone" fracturing has been documented, while at the same time reiterating that studies are limited and data are sparse. However, fracturing that creates connectivity to preexisting pathways, whether naturally formed (pre-existing permeable fractures or faults) or artificial (abandoned, degraded, poorly constructed, or failing wells) cannot be discounted, nor can we ignore the possibility of human error in the drilling, completion, and stimulation processes. Of particular concern is the creation of connections to abandoned or degraded wells, since the existence of such pre-existing pathways is likely in regions targeted for WST operations, and such

wells provide a clear case of a potentially permeable feature that connects to shallow formations. Additional research is required to better quantify this hazard (Jackson et al., 2013b).

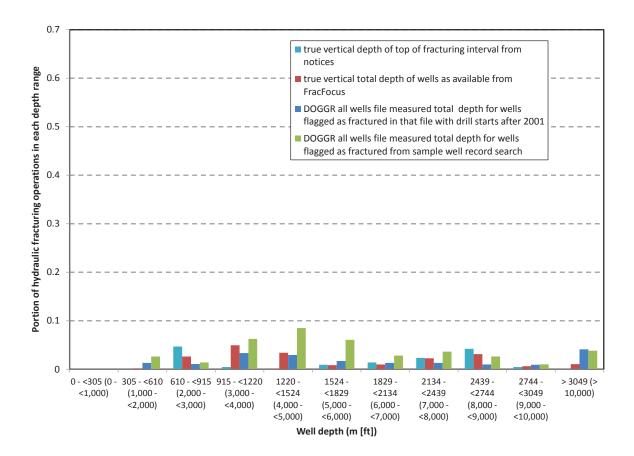


Figure 5-6. Portion of hydraulic fracturing operations vs. depth range, for locations where the overlying groundwater has TDS of less than 1,500 mg/L (DOGGR data is only for wells drilled after 2001).

5.1.3.2.2 Leakage from Wells During Injection, Production, or Stimulation

The possibility of operating wells serving as leakage pathways for subsurface migration has been known for a long time. Papers by Harrison (1983; 1985) indicate that overpressured annuli are a likely mechanism for contamination of groundwater with produced gas or other formation fluids, even for wells using a surface casing to protect shallow aquifers and particularly if the surface casing does not extend to a sufficient depth below the aquifer. Failures in well barriers (cement and casing strings) may allow intrusion of gas and fluids from producing formations below the casing shoe or shallower gas and fluid-bearing formations intersected by the wellbore to lower-pressure annuli, resulting

in annular gas flow or sustained casing pressure (SCP) and a pathway for gas migration to the surface (Brufatto et al., 2003; Watson and Bachu 2009) of two overlying aquifers. Multiple factors over the operating life of a well may lead to barrier failure including improper or inadequate cementing, poor mud displacement, and fractures in the cement due to hydraulic and mechanic stresses during construction or associated with tectonic activity and subsidence events; radial cracking of the cement due to thermal and pressure fluctuations in the casings during stimulation and production; and general degradation of the well structure due to age (Bonnet and Parfitis, 1996; Dusseault et al., 2000; Brufatto et al., 2003; Watson and Bachu 2009; Carey et al., 2012). Corrosive subsurface environments (e.g., H₂S, CO₂) also pose a threat to cement and casings throughout the life of a well and after abandonment/plugging, particularly if cement is already impaired (Brufatto et al., 2003; Chilingar and Endres 2004;). The most important mechanism leading to gas and fluid migration, however, is poor well construction or exposed or uncemented casing (Watson and Bachu, 2009).

Unconventional wells may be subject to greater stresses due to mechanical stresses induced in high pressure stimulation and lateral drilling practices. The casing and cement of the vertical section of the well, from the surface casing down to the production zone, is subject to hydraulic and mechanical stress during drilling and operations (see Section 2.2.1.2). For wells used in hydraulic fracturing operations, the high levels of fluid pressure imposed also need to be taken into account during casing selection and well design. During hydraulic fracturing operations, there has been concern that the expansion and contraction of the steel casing during the multiple stages of high-pressure injection may result in radial fracture and/or shear failure at the steel-concrete or concrete-rock interfaces (Carey et al., 2012). This expansion and contraction of the casing, not typically present in conventional oil and gas operations, could lead to separation between the casing and the cement. These processes could create gaps or channels that would serve as conduits between the various strata through which the well penetrates. Current cementing technology may not be sufficient to control for such defects. However, with current practice, the fracturing fluid is pumped down a tubing string within the innermost casing, such that the casing and surrounding cement are not experiencing the high injection pressure associated with the fracturing operation. Monitoring of the annulus between the tubing string and production can identify problems or failures that lead to high casing pressure.

Watson and Bachu (2009) also noted that deviated wellbores, defined as "any well with total depth greater than true vertical depth", show a higher occurrence of sustained casing pressure and gas migration than vertical wells, likely due to centralization and cementing challenges increasing the likelihood of gaps, bonding problems, or thin regions in the cement. Creation of such annular permeable pathways may create connectivity to higher formations. In a review of the regulatory record, Vidic et al. (2013) noted a 3.4% rate of cement and casing problems in Pennsylvania wells 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 that reported by Vidic et al. (2013).

Human error during the well-completion and hydraulic fracturing process must also be considered. A 2011 incident in Alberta, Canada (Energy Resources Conservation Board (ERCB), 2012) involved inadvertent fracturing of an overlying formation and injection of fluids into water-bearing strata below an aquifer. Misreading of well fluid pressures resulted in the perforation gun being fired at 136 m depth (446 ft) rather than the specified 1,486 m (4,875 ft), with subsequent pressurization creating a fractured interval above the base of groundwater protection. Immediate flowback of fracturing fluids recovered most of the injected volume, and monitoring wells were installed at the perforation depth and at 81 m (266 ft) in an overlying sandstone aquifer at a distance of 50 m (164 ft). A hydraulic connection between the fractured interval and the overlying aquifer was not observed, and a surface gas release nearby was not linked to the injected fluids. The 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.

Well integrity must also be evaluated for Class II deep injection wells, which have become the method of choice for the disposal of flowback and produced fluids. The regulatory review by Kell (2011) reviewed incidents of contamination associated with deep injection in Ohio and Texas. The injection process was implicated in six contamination incidents in Texas (none in Ohio); however, properly permitted Class II injection wells still have a significantly better record of protecting groundwater resources than older methods of earthen pit disposal (see Section 5.2.3.1.3). In California, a 2011 report studied the over-24,000 active and 6,900 inactive injection wells in the state and found that, while procedures were in place to protect fresh-water 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). Zonal isolation of saline formations via cement placement is not mandated, nor is the isolation of hydrocarbon-containing zones, thus leading to potential migration of fluids into overlying groundwater resources. Depending on the target formation, injection pressures must be monitored and maintained at or below levels appropriate for the geology. In addition, operators are required to perform mechanical integrity tests on Class II wells every five years.

An earlier US Government Accountability Office report (US GAO, 1989) regarding Class II wells across the United States found that, although the total extent of drinking water contamination was unknown, several cases of contamination had been documented. In one-third of the cases, the contamination was caused by communication between injection wells and improperly plugged (abandoned) oil and gas wells nearby, causing injected brines to migrate vertically through the abandoned wellbores. Injection wells built and operating prior to 1976 are exempt from Underground Injection Control (IUC) program permitting requirements (40 CFR 144.31, 146.24) which mandate an area search for abandoned wells within a quarter mile of a new proposed injection wellbores. The GAO report notes that 70% of the injection wells studied were grandfathered and as such the presence of nearby degraded wells was discovered only after contamination had occurred.

Although the work was not specific to hydraulic fracturing, the hazards of degraded wells and well failure are highlighted in a review paper by Chilingar and Endres (2004). They document multiple incidents in which oilfield gas reached the surface through degraded, abandoned, and leaking wellbores. The paper highlights a 1985 incident where well corrosion at shallow depths led to casing failure of a producing well and the migration of gas via faults and other pathways, creating a gas pocket in a permeable collecting zone below a populated area in Los Angeles. Methane accumulated underneath a department store until overpressurization drove gas into the building's basement, resulting in an explosion. A vent well was used to reduce the hazard, but failure of the vent well resulted in another release of gas in 1989, although this was detected before another explosion could occur. While these incidents are not related directly to fracturing operations, they show that cement and casing impairments in modern wells and inadequately cemented abandoned wells may provide pathways for vertical migration of formation gas and fluids.

5.1.3.2.3 Mechanisms of Leakage via Transport Through Subsurface Pathways

To reiterate, contaminant migration requires a pathway, whether natural or induced. If such pathways have been created through hydraulic fracturing operations, whether the result is a direct fracturing into overlying aquifers or a connection to a preexisting pathway for fluid flow outside of the reservoir, reservoir and fracturing fluids may migrate through the subsurface. Data concerning such contamination mechanisms are currently very limited, with few peer-reviewed studies in place and ongoing US EPA assessments as yet unpublished (US EPA, 2012; Jackson et al., 2013b). Transport through preexisting pathways has occurred in conventional oil and gas operations (see previous section), but whether hydraulic fracturing is likely to enhance the problem remains to be determined. In a manner similar to the issue of fracturing and fracture propagation, the core literature consists of a few groups of competing and contentious studies, none of which provides direct evidence of fracturing leading to contaminating groundwater.

Although mechanisms for transport through fractures and faults have been proposed, few conclusions can yet be made about the conditions under which liquid or gas release can occur. Overburden thickness, formation permeabilities, production strategies (assuming no drilling or casing incidents), and other site-specific factors may all regulate the probability of contaminant migration. The study by Myers (2012), mentioned previously, attempted to model flow through artificially created pathways, but did so using a highly simplified flow and hydrologic model (Vidic, 2013). A more recent modeling study by Kissinger et al. (2013) performs porous-media modeling of liquid and gas migration through specific, previously characterized fractured systems. The study, although limited to one set of geological models (and thus to one set of subsurface geometries), does highlight factors that may increase or decrease the risk of contamination. Fluid migration resulting from a two-week fracturing-related overpressure is shown to drive fracturing fluids only a limited distance from the fractured reservoir, even when high-permeability pathways are assumed. Long-term tracer transport and transport of methane to overlying aquifers are shown to be a function of pathway porosity, permeability, and irreducible gas saturation,

but only under the assumption of a continuous permeable pathway from the reservoir to the aquifer. Factors such as production strategy or ranges of overburden thickness are not evaluated, but Kissinger et al. (2013) suggest that transport of liquids, fracturing fluids, or gas is not an inevitable outcome of fracturing into connected pathways, and that further evaluation of a range of geological systems is warranted.

Several studies have noted the presence of methane in groundwaters near hydraulic fracturing operations, and have tried to determine the source and pathways for methane migration based on the chemical and isotopic composition of the gas. Methane found in groundwater can either be formed as a result of thermogenic processes at depth or microbial processes in shallower horizons. Biogenic methane typically consists of pure methane and carbon dioxide, whereas thermogenic methane, such as that found in shale gas, will also contain higher-chain hydrocarbons (ethane, propane, butane, and pentane). Biogenic and thermogenic methane are also isotopically different, with the former having a lower ratio of carbon-13 to carbon-12 isotope (more negative δ C13 values (-64‰)) than the latter (-50‰) (Osborn et al., 2011a). Earlier studies (Révész et al., 2010) show the presence of both biogenic and thermogenic methane, as well as some ethane, in well water near Marcellus gas production, but variation over time (i.e., before and after production activities commenced) had not been established. However, correlations have been shown to exist between gas reservoir locations and gas production activity and the presence of methane in groundwater and surface water.

The most recent controversies began with the research of Osborn et al. (2011a) that performed geochemical studies of sampled water from 60 drinking-water wells in a gas producing region of northeastern Pennsylvania. They noted that methane concentrations in wells increased with increasing proximity to gas wells, compared to neighboring wells away from production activity. Isotopic ratios of the sampled gas, as well as the presence of longer-chain hydrocarbons, indicated a thermogenic source for the gas, along with matching the geochemistry of gas from nearby production wells. However, evidence of contamination from brines or fracturing fluids was not found in the sampling. This result highlights an important issue, specifically that liquid and gas transport do not necessarily occur together, and that gas migration and liquid migration within the subsurface may occur at different rates and timescales. The absence of brine migration led to the conclusion that methane transport via liquid migration is unlikely to be the source, but rather that leakage and migration of gas through any number of possible permeable pathways (well casings, artificial fractures, or enlarged fractures due to hydraulic fracturing) could have provided the pathway for the contamination. The paper notes the existence of a preexisting fracture network within the overlying formation, combined with numerous undocumented, uncased abandoned wells that could serve as conduits for gas migration. In response, letters by Davies (2011) and Schon (2011) state that leakage through well casings is a better explanation than any fracturing-related process, referencing PA Department of Environmental Protection reports that document specific casing-failure incidents. The responders also promote the hypothesis that the high methane concentrations may be pre-existing, noting that such processes are already documented and well-understood (Dyck and Dunn, 1986) for oil and gas producing formations, and that a lack of evidence for fracturing fluids in the contaminated water supports ongoing natural processes. Further discussion, in a letter to *PNAS* by R. B. Jackson and colleagues, and a follow-up paper (Osborn et al., 2011b; Jackson et al., 2011; 2013a), counters those conclusions, pointing out that methane contamination has indeed occurred, but that natural migration pathways or abandoned wells are the less likely scenarios as, although abandoned wells are common in Pennsylvania, few abandoned wells are known in the area of this particular study. Jackson, however, agrees that casing leakage from poor well construction is a plausible mechanism, while still maintaining that, since it is neither proven nor disproven, hydraulic fracturing operations could be involved in the subsurface processes. A key conclusion of this series of studies is that there is a strong correlation between gas well location and the appearance of stray gas contamination.

Another sampling study by Jackson et al. (2013a) found ethane and propane, as well as methane, in water wells near Marcellus production locations, and also noted isotopic compositions that suggest a "Marcellus-like" origin for the thermogenic component of the methane. The concentration of methane was again correlated most strongly to distance from production activities, as was the ratio of longer-chain hydrocarbons to methane. The authors propose leakage caused by well casing and cementation problems as the most plausible mechanism, noting the number of violations recorded for well-construction issues in nearby production operations. In contrast, another isotopic study by Molofsky and colleagues (Molofsky et al., 2013) states that the isotopic ratios of methane found in Pennsylvania wells are more consistent with samples of shallower Upper Devonian gas rather than Marcellus formation gas, thus casting doubt on the source of the dissolved gas and the existence of connecting pathways.

Geochemical evidence for natural migration of fluids has been published by Warner et al. (2012b), who revisited northeastern Pennsylvania and collected new water samples for comparison to older data published in the 1980s. The study indicated that elevated salinity levels in the region may predate shale gas production in the area, and that geochemical signatures matching that of the Marcellus fluids led to the conclusion that natural permeable pathways may have already existed between the shale and overlying formations. These natural permeability pathways could create contamination hazards if oil and gas operations occur near the zones of enhanced connectivity. In response, Engelder (2012), disputes this possibility, noting that recent drilling data for hundreds of wells suggests the saturation of water in the pore space is typically in the range of 13% to 33%, which is near or below the irreducible water saturation for the shale. Such low saturations would result in capillary binding of the water, restriction of brine migration, and the possible sequestration of fracturing fluids left in the formation, as the aqueous phase would be drawn into the pore space of the shale and rendered immobile. This capillary seal would be expected to trap both gas and liquids within the Marcellus, and this concept is supported by differences in the isotopic signature of Marcellus gas and gas that exists in the overlying formations (see also Molofsky et al., 2013). The previously referenced work by Flewelling et al. (2013) also addresses this issue of formation

isolation, pointing out that the occurrence of permeable pathways overlying significant hydrocarbon accumulations is inherently contradictory. Therefore, their work finds that some mechanism that activates pre-existing, but impermeable features or creates new pathways is necessary to allow liquid and gas migration, while noting the potential constraints to vertical fracture propagation mentioned in the previous section. A further response by Warner et al. (2012b) maintains that there are insufficient data to support the capillary binding hypothesis, and that recent production data counter the notion that the shale has little mobile brine—in fact, the opposite has been true for some production wells—but also concedes that mechanisms for rapid brine transport are neither indicated nor understood.

For Marcellus production in Pennsylvania, an extensive review by Brantley et al. (2014) assesses both the scientific literature and the regulatory record, in an attempt to establish a relationship between production activities, known production problems and violations, and the existence of subsurface migration pathways. The paper states up front that fracturing fluids or flowback have never been conclusively tied to a water-contamination incident, and that distinguishing common tracers is challenging, because background concentrations are spatially and temporally variable. The true processes are clouded by lack of information about drilling and production incidents, unreleased water quality data, the sparseness of available data, and lack of knowledge of pre-existing contaminants. Attempts to perform mathematical risk assessments of contamination through all mechanisms have primarily highlighted the lack of knowledge (Rozell and Reaven, 2012) with envelopes of uncertainty spanning orders of magnitude, although when risk is formally assessed, the consequences of wastewater disposal (i.e., potentially large spills) generated more concern than that for subsurface leakage and migration. However, over a thousand complaints about water quality issues have been recorded in areas near Marcellus gas production. The review delves into the regulatory record and finds numerous Notices of Violation, particularly for well-construction problems, in the regions of Pennsylvania where contamination is suspected. While postglacial processes and bedrock fracturing may make the gas-producing regions of the state more susceptible to gas and fluid migration even without stimulative fracturing, there is also the presence of thousands of pre-Marcellus wells, with 200,000 dating from before formal record-keeping began and 100,000 that are essentially unknown (noted in a companion study by Vidic et al., 2013). These potential hazards were highlighted by a 2012 incident in which fracturing operations intercepted an old offset well, resulting in a blowout and the release of gas, but not of fracturing or formation fluids, through the compromised abandoned well. This is consistent with the previous conclusion that care must be taken to avoid situations where hydraulic fracturing creates connectivity to abandoned or degraded wells.

The literature, particularly peer-reviewed literature, is heavily weighted toward regions where public concern over new stimulation technologies has been strongest—currently, regions overlying the Marcellus. In California, there is a history of oil and gas production (Chilingar and Endres, 2005), including the use of hydraulic fracturing technologies, but at present, there is no comprehensive source of information on well stimulation

activities (Section 3.2.2). Recently, an industry study (Cardno ENTRIX, 2012) reviewed ten years of hydraulic fracturing and gas production from the Inglewood field, a Los Angeles Basin oil and gas field. The Inglewood field is located in a populated area, and underlies a fresh-water formation that, while not used for drinking water and while likely not connected to nearby drinking water resources, is still regulated and monitored for water quality. Microseismic monitoring indicates 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 fresh-water zone. The 2011-2012 study showed no impacts to groundwater quality, either through migration of fracturing fluids, formation fluids, or methane gas, even though the formation includes faults and fractures connecting shallow formations to deeper formations. No evidence was found of well-casing failure, when wells have been constructed to industry standards, and thus no direct contamination occurred via stimulation or production activities. However, the review of Chilingar and Endres (2005) documents a history of gas-transport incidents associated with other conventional oil and gas production in the L.A. Basin. The paper 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 issue 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. These features led to several documented cases of methane from oil and gas operations traveling and reaching near-surface formations or reaching the surface—between leaking wells and near-surface formations, through near-surface faults, and between pressurized gas-storage reservoirs and abandoned wells. While stimulation technologies are not implicated in these events (with the possible exception of water-flooding procedures creating increased pressures that drive transport), they illustrate the real possibility of flow through permeable pathways if such pathways, natural and/or induced, exist and are allowed to communicate with hydrocarbon reservoirs.

It is clear that methane appears in groundwater near hydraulic fracturing operations for shale gas operations, but studies have essentially established only correlation, not causation of leakage pathways. Thus, additional research is required to better quantify this hazard (Jackson et al., 2013b), with a focus on (1) establishing background values of various contaminants, (2) field experiments and monitoring, and (3) better modeling studies to elucidate possible transport mechanisms. In this regard, additional studies are under way to identify tracer materials that could be useful for the monitoring of the migration of fracturing fluids in the subsurface, as well as fracturing fluid-shale interactions. For instance, nanoparticles are currently tested, which could be added as nonreactive tracers to fracturing fluids in the future (Maguire-Boyle et al., 2014). The analysis of strontium (Sr) isotope ratios has been proposed as a useful approach to evaluate fluid-rock interactions (Chapman et al., 2012). In either case, these tracers could provide relevant tools for elucidating open questions regarding potential contaminant pathways related to well stimulation applications in the future.

5.1.4 Case Studies of Surface and Groundwater Contamination

This section examines evidence of the contamination of surface water and groundwater aquifers from well stimulation treatments, and discusses the findings from groundwater quality studies that have been conducted at sites located near well stimulation operations. No reports of water contamination resulting from well stimulation in California were found, although only one study for a site in California was identified in the Inglewood oil field. While limited information is currently available in peer-reviewed literature, two studies provide evidence of surface water contamination. Reports from state agencies provide additional evidence of contamination. Based on the limited data that are available, it appears that groundwater quality near hydraulic fracturing has not been significantly impacted due to well stimulation treatments, although two reported instances of potential groundwater contamination by hydraulic fracturing fluid were identified. Neither of these studies was documented in peer-reviewed literature, and the findings from one (at Pavillion, Wyoming) have been questioned in subsequent studies conducted at the site. Elevated levels of some contaminants that could have been brought up from the target formation, such as methane, TDS, and some trace metals, have been observed in the groundwater near some hydraulic fracturing sites in the United States. However, the sources of these contaminants are in dispute (as described in Section 5.1.3), and cannot be directly linked to well stimulation treatments.

The potential impacts of well stimulation on surface water and groundwater quality are ultimately dependent on reliable and current baseline data describing water characteristics prior to drilling operations (or if not possible, for representative background sites), and on comprehensive monitoring conducted during and after well stimulation. It should be noted that water quality data near well stimulation sites are sparse, and an absence of studies (or data) neither supports nor refutes evidence of problems. Proper pre-drilling baseline and post-stimulation monitoring data are essential to evaluating the impacts of well stimulation on nearby groundwater. Efforts should be made to collect such data in the future, and the findings from water quality monitoring should be included in reporting requirements for operators.

5.1.4.1 Surface

There are no reports of surface water contamination associated with well stimulation in California, although there are documented cases in other parts of the U.S. For example, in 2007, flowback fluids overflowed retention pits in Knox County, KY, killing or displacing all fish, invertebrates, and other biota for months over a 2.7 km section of the creek. Papoulias and Velasco (2013) found that fish exposed to Acorn Creek waters showed signs of stress and higher incidence of gill lesions, consistent with exposure to low pH and toxic concentrations of heavy metals.

In another study, (Kassotis, Tillit, Davis, Hormann, and Nagel, 2013) examined the presence of known or suspected endocrine-disrupting chemicals used for well stimulation in surface

and ground water samples in drilling-dense areas of Garifeld County, Colorado. Nineteen surface water samples were collected from five distinct sites that contained from 43 to 136 natural gas wells within one mile and had a spill or incident related to natural gas drilling processes within the past six years. Additional samples were collected from the Colorado River, which captures drainage from this region, and from nearby reference sites. The study found that most water samples exhibited greater estrogenic, antiestrogenic, and/or antiandrogenic activities than water samples from nearby references sites with limited or no drilling activity.

Additional surface water contamination incidents have been reported, although these are not captured in peer-reviewed studies. Some of these incidents were reported to the appropriate local and/or state agencies, while others may not have been reported. For example, in 2009, a fish kill event in an unnamed tributary to Brush Run in Hopewell Township was reported to the Pennsylvania Department of Environmental Protection. Responders found an overland pipe transporting flowback fluid had failed, releasing about 250 barrels into the tributary (Pennsylvania Department of Environmental Protection, 2010a). Also in Pennsylvania, a wastewater pit overflowed its embankment, polluting a tributary of Dunkle Run. While the company cleaned up the spill once it was discovered, it failed to report the incident to the Pennsylvania Department of Environmental Protection, 2010b).

5.1.4.2 Subsurface

5.1.4.2.1 General Findings from Groundwater Quality Studies in the United States

Typically, monitoring studies sample the natural groundwater in wells in the vicinity of well stimulation operations and draw conclusions based on a comparison of pre-drilling baseline data (if available) and post-drilling monitoring. If pre-drilling baseline data were not available, some studies collected groundwater samples at nearby background sites that had comparable geology and geochemistry, but were relatively unimpacted by well stimulation operations. The list of parameters measured in the groundwater quality studies varied according to the topic under investigation, and included subsets of the following:

- Acidity (pH), alkalinity
- Dissolved gases: Methane, carbon dioxide, oxygen
- General water quality parameters: Total Dissolved Solids (TDS), Total Suspended Solids (TSS), specific conductance, turbidity, Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC)
- Major cations: Sodium, potassium, magnesium, calcium, ammonium
- Major anions: Chloride, bromide, nitrate, nitrite, phosphate, fluoride, cyanide

- Trace metals: Ag (silver), Al (aluminium), As (arsenic), Ba (barium), Be (beryllium), B (boron), Cd (cadmium), Cr (chromium), Co (cobalt), Cu (copper), Fe (iron), Li (lithium), Mn (manganese), Hg (mercury), Mo (molybdenum), Ni (nickel), Pb (lead), Se (selenium), Sb (antimony), Sn (tin), Sr (strontium), Ti (titanium), Th (thorium), U (uranium), Zn (zinc).
- NORM (Naturally occurring radioactive material): Gross alpha, gross beta, ²²⁶Ra, ²²⁸Ra, Radon, Uranium
- Organics: Oil and grease, Volatile organic compounds (VOCs), Semi-volatile Organic Compounsd (SVOCs), pesticides, Polychlorinated Biphenyls (PCBs)
- Stable isotopes: dC13 (carbon), dO18 (oxygen), dD (hydrogen)
- Selected constituents of injection/fracturing fluids

A limited number of studies have investigated groundwater quality in the vicinity of hydraulic fracturing in several regions, including the Marcellus shale, PA (e.g. Boyer et al., 2011, Brantley et al., 2014 and references therein), the Fayetteville shale, AK (Warner et al., 2013), and one study in California in the Inglewood oil field (Cardno ENTRIX 2012). Most studies comparing baseline trends to post-stimulation measurements did not determine any statistically significant changes in the water quality of nearby groundwater wells resulting from well stimulation operations. Studies reporting elevated levels of some contaminants that were detected in groundwater situated near fracturing operations are discussed below. However, none of the studies could directly link the elevated levels of measured contaminants to the use of well stimulation technologies.

An extensive review of groundwater-contamination claims and existing data can be found in the report of Kell (2011) for the Ground Water Protection Council. The report focuses on Ohio and Texas groundwater-investigation findings from 1983 through 2008, and notes that the literature provides no conclusive documentation of groundwater contamination resulting from the hydraulic fracturing process itself. The study area and time period included development of 16,000 horizontal shale gas wells with multistage fracturing operations in Texas, and one horizontal shale gas well in Ohio. However, the report notes that there is evidence of groundwater contamination due to improper storage of flowback and produced fluids in surface containment pits (as discussed in Section 5.1.3.1.4), a practice that has mostly been replaced by disposal via Class II injection wells that have a significantly better record of protecting groundwater resources than earthen pit disposal. Sections 5.1.3.2.1 and 5.1.3.2.3 discuss the report's findings on abandoned wells being a leakage pathway. The report concludes that, although no documented links have been found implicating fracturing operations in 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.

5.1.4.2.2 Detection of Well Stimulation Fluids in Groundwater

Very limited information is currently available in peer-reviewed literature about the detection of fracturing-fluid additives in groundwater. Two reported instances of potential groundwater contamination due to subsurface leakage of hydraulic fracturing fluid within the United States were identified, neither of which has been documented in a peer-reviewed publication (Brantley et al., 2014, Vidic et al., 2013). The first study is a US EPA investigation in Pavillion, WY, where surface storage and disposal of flowback/produced waters was implicated in contamination of shallow surface water (as discussed in Section 5.1.3.1.4). Initial results published in a draft report (DiGiulio et al., 2011) suggested that groundwater wells had been contaminated with various fracturing-fluid chemicals, 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 these findings (Wright et al., 2012). The US EPA is no longer working on this study, but the State of Wyoming is continuing to investigate these data, with a report due in September 2014.

The second reported incident of contamination is based on a U.S. EPA study focusing on operations in Ripley, WA. In this case, a gel used as a constituent in fracturing fluids was reported to have contaminated a local water well located <330 m (1,000 ft) from a vertical gas well (US 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 (not used in hydraulic fracturing) used to remove loose rock cuttings prior to cementing (Brantley et al., 2014).

Kassotis et al. (2013) evaluated the potential of elevated activities of endocrine disrupting chemicals in surface and groundwater systems close to natural gas extraction sites utilizing hydraulic fracturing. Surface and groundwater samples were collected in a drilling-dense region in Garfield County, CO, and analyzed for estrogen- and androgen-receptor activities using reporter gene assays in human cell lines. Based on a comparison with reference control sites, the authors concluded that these data suggest elevated endocrine-disrupting chemical activity in surface and groundwaters close to unconventional natural gas drilling operations. However, potential contaminant pathways were not discussed in this publication and are currently unknown.

5.1.4.2.3 Detection of Direct Contaminants from Target Formations in Groundwater

A number of studies have monitored the groundwater in the vicinity of hydraulic fracturing operations for contaminants other than those present in fracturing fluids, such as methane, TDS (including chloride and bromide), heavy metals, NORMs, and organics. None of these studies definitively traced the source of or migration pathway for these contaminants to application of hydraulic fracturing, as discussed in Section 5.1.3.2.3. The contaminants could have either been naturally present in the formation or could have migrated along alternate pathways, unrelated to well stimulation, into the groundwater.

Elevated methane in groundwater near hydraulic fracturing operations was a particular focus of many of the studies. Leakage of fugitive methane into groundwater wells situated near hydraulic fracturing sites is a public concern due to fire and explosion hazard. The US Department of the Interior recommends a warning at dissolved methane levels of 10 mg/L (ppm) and requires action at concentrations greater than 28 mg/L (ppm).

Regions where shale gas production is feasible tend to have naturally high methane concentrations, and have been sites for previous natural gas extraction activities. For example, concentrations as high as 45 to 68.5 mg/L (ppm) have been observed in New York, West Virginia, and Pennsylvania groundwaters (Vidic et al., 2013). A survey of methane concentrations in Southern California, which was carried out following the Ross Department Store explosion, 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. Comprehensive baseline measurements collected before drilling can help determine whether high methane levels detected in wells, post-production, are a result of well stimulation.

As extensively discussed in Section 5.1.3.2.3, some studies have found high concentrations of thermogenic methane in drinking-water wells in Pennysylvania, particularly those within a 1 km radius of hydraulic fracturing operations (Osborne et al., 2011; Jackson et al., 2013a), although the source of the methane detected in those studies is under debate. Another study measuring pre-drilling and post-stimulation methane concentrations in 48 water wells in Pennsylvania located within 760 m (2,500 ft) of Marcellus shale gas wells found no differences in methane levels before and after drilling, except in one well where drilling had been completed nearby (Boyer et al., 2011).

Several studies also focused on measurements of TDS in groundwater, particularly due to the high levels of TDS present in flowback and produced fluids recovered from some shale plays. As discussed in Section 5.1.3.2.3, high salinities detected in some shallow Marcellus groundwater wells could have resulted from migration of brines from deeper formations through natural pathways that were unrelated to hydraulic fracturing (Warner, 2012). A study of 100 groundwater wells located in aquifers overlying the Barnett shale found that that TDS concentrations exceeded the US EPA Maximum Contaminant Level (MCL) of 500 mg/L in 50 out of 91 samples located within 3 km of gas wells, and that the maximum values of TDS near the wells were over three times higher than the maximum value from background reference wells unimpacted by fracturing. However, the study was conducted in aquifers that naturally have high levels of TDS. TDS concentrations in 7 out of 9 samples collected from the background wells also exceeded the MCL, and the average TDS values near the hydraulic fracturing sites were similar to historical data for the region (Fontenot et al., 2013). Monitoring for TDS in the Inglewood oil field near Los Angeles (Cardno Entrix, 2012) found no significant differences in pre-drilling and post-stimulation TDS values; TDS values ranged from 510 to 2,500 mg/L in shallow wells and 1,400 to 3,900 mg/L in deep wells.

Fontenot et al. (2013) also reported that the heavy metals arsenic, barium, selenium, and strontium were found to be present at much higher levels in groundwater wells located < 3 km from production wells in the Barnett shale, when compared to background or historical concentrations. Although the trace elements of concern were known to be naturally present in the formation at low levels, the authors suggest further investigation to determine if the high concentrations detected in the groundwater were a result of fracturing operations. The study did not investigate the complex biogeochemistry that can lead to mobilization of trace elements such as arsenic, but suggested some possible mechanisms by which the development of wells for oil and gas (and indirectly) well stimulation could cause release of trace metals into the groundwater. These include lowering of the water table due to excessive water withdrawals, and mechanical disturbances due to drilling that could loosen iron oxides (potentially mobilizing arsenic and selenium) or sulfate/carbonate scales (potentially mobilizing barium and strontium) from the casings of private wells.

The only study that has identified trace-element concentrations in groundwaters near well stimulation operations in California was conducted in the Inglewood oil field (Cardno Entrix, 2012). Arsenic was the only trace element that exceeded drinking water standards in that study. However, arsenic is naturally present at high levels in Southern California, and concentrations were high in the monitoring wells even before drilling. Information on background levels of trace metals in California is available as part of the USGS Groundwater Ambient Monitoring and Assessment (GAMA) program. High levels of some trace elements such as arsenic, boron, molybdenum, chromium, and selenium have been measured in shallow groundwaters in several regions in California (e.g. USGS, 2006; USGS, 2009). These data should be considered in future investigations that attempt to determine the impact of well stimulation on groundwater quality in California.

In general, there have been no reports of high levels of NORMs found in groundwater near well stimulation operations. It should also be noted that uranium concentrations in some California groundwaters have historically been high. For example, high levels of uranium, frequently exceeding US EPA MCLs, have been noted in the Central Valley and are correlated with high bicarbonate concentrations in the groundwater (Jurgens et al., 2005). Radium levels in California groundwaters are typically low (Ruberu et al., 2005).

A couple of studies have reported measuring some organic constituents in groundwaters near well stimulation operations. These include the US EPA investigation in Pavillion, WY, where glycols and alcohols were detected (DiGuilio et al., 2011) and a study in the Barnett shale, where methanol and ethanol were detected in 29% of samples in private drinking-water wells (Fontenot et al., 2013). However, the presence of organics could not be linked to fracturing operations in either case.

Several articles note that there is a clear need for future studies and the monitoring of multiple water-quality parameters, to ensure that groundwater resources near well stimulation operations are not impacted by well stimulation and related activities (Brantley et al., 2014; Jackson, 2013; Bibby et al., 2013; Vidic et al., 2013). Future conclusions regarding potential impacts of well stimulation on groundwater quality are ultimately dependent on reliable and current baseline data describing groundwater characteristics prior to drilling operations, or if not possible, for representative background sites. The USGS is currently conducting a broad, US-wide water-quality study, which includes the following objectives (besides others): (1) determine current baseline concentrations of major ions in surface water and groundwater in areas of unconventional oil and gas production; (2) evaluate potential changes in water quality over time; and (3) identify spatial and temporal data gaps where further information is needed to evaluate existing water quality and water-quality trends (Susong et al., 2012). Specifically for California, the USGS has published a series of reports describing groundwater quality for a number of CA basins, such as the Monterey Bay and Salinas Valley basins, and the Los Angeles, Southern San Joaquin and Central Coast basins, as part of the GAMA Priority Basin Project (e.g., USGS, 2011). However, these studies may not be formulated to provide baseline data specific to the question of groundwater contamination due to well stimulation.

5.1.4.2.4 Groundwater Monitoring for Well Stimulation Operations in California

DOGGR requires the reporting of constituents in injected and recovered fluids including chemical composition and radiological information (DOGGR Interim Well Stimulation Reporting Requirements Instructions, 2013). In addition, all well stimulation notices submitted to DOGGR as of January 1, 2014, must include a monitoring plan, regardless of the specific groundwater quality in close proximity to the wells (Vincent Agusiegbe, DOGGR, personal communication). Most of the notices submitted and received in December and subsequently approved did not have monitoring plans because groundwater in those oil fields was exempt from beneficial use.

A monitoring plan, which was approved as part of a well stimulation permit in the Rose oil field as of January 2014, included pre-stimulation and semi-annual measurements of temperature, pH, electrical conductivity, BTEX, and TDS at locations where the property owner requested it for up to two years after the well stimulation was concluded. While the operators claim that this list of constituents provides an appropriate evaluation of the potential impacts of well stimulation, many published scientific studies suggest the need for more comprehensive monitoring plans (e.g., Jackson, 2013; Bibby et al., 2013; Vidic et al., 2013). This would include measuring a larger set of parameters (such as those mentioned above) that are based upon an evaluation of regional geology and typical groundwater and formation water chemistries at more locations than just those requested by the landowners (both monitoring wells near the oil fields and residential wells can be used to collect the data).

5.2 Potential Impacts to Air Quality and Climate

The following sections address air quality and climate impacts. Although air quality and climate impacts are treated separately below, certain aspects of the analysis and literature

review in each section may inform discussion in the other section. For example, many processes that lead to emissions of local pollutants also lead to emissions of greenhouse gases. Diesel fuel combustion leads to emissions of nitrogen oxides (NO_x) and particulate matter (PM) but also carbon dioxide. Processes in WST that lead to emissions of volatile organic compounds (VOC) also frequently lead to emissions of methane (methane is a potent greenhouse gas). Some methods to control emissions for air quality also control greenhouse gas emissions, for example reduced emission, or "green," completions control both VOC emissions and methane emissions. In both the Air Quality and Climate Impacts sections comparison are made between "bottom-up" inventories, in which all known sources of emissions are summed to generate a total emission estimate, to "top-down" emission estimates, in which ambient measurements of pollutants or greenhouse gases are used to characterize likely emissions.

5.2.1 Air Quality

This section evaluates the pollutant emission and potential air quality impacts related to well stimulation in California. Most well stimulation activity in California occurs in the San Joaquin Valley, an air basin that is designated as a non-attainment area for ozone and particulate matter (PM) standards, thus marginal changes to air quality may be relevant.

Ideally, one would connect emissions of pollutants directly to air quality impacts through the use of an air quality model that could account for dispersion and chemical transformation of the emitted pollutants as they travel through an air basin. Use of an air quality model is out of the scope of this report. Air quality impacts are instead evaluated by comparing estimates of emissions related to WST to estimates of total emissions from oil and gas processes or other sectors. If emissions are much smaller than emissions from other sectors we assume the air quality impacts are small.

Well stimulation activities that lead to emissions include the use of diesel engines, flaring or venting of gas and the volatilization of chemicals in flowback water. This section presents separate emission estimates for each of the above activities and describes how those emissions compare to emissions from other relevant sectors.

It is reported in this section that emissions of $\mathrm{NO_x}$ and $\mathrm{PM_{2.5}}$ in California from diesel equipment used for WST, both for on-road trucks and off-road equipment such as pumps, produces negligible emissions compared to other related sectors. Furthermore, emissions from both diesel off-road equipment and on-road trucks could be controlled if the use of diesel engines with $\mathrm{NO_x}$ and $\mathrm{PM_{2.5}}$ exhaust controls were mandated.

Emissions from flaring in California are uncertain because of variability in flare combustion conditions and to a lack of information regarding the frequency of flare-use during WST operations. However, current California Air Resource Board inventories of pollutant emissions from all flaring suggest that flares as a whole emit less than 0.1% all VOCs and are not a major regional air quality hazard.

Emissions from venting of gases during completion and from volatilization of flowback water constituents have not been measured in California but might be bracketed. The California Air Resources Board (CARB) has conducted a "bottom-up" VOC emission inventory by adding up all known sources of emissions. It is unknown whether these sources included emissions from WST-related produced or flowback water. However, the sum of the emissions in the inventory matches well with "top-down" measurements taken from the air in the San Joaquin Valley (Gentner et al., 2014). This agreement between "bottom-up" and "top-down" estimates of VOC emissions from oil and gas production indicates that California's inventory probably included all major sources. The CARB inventory suggests that venting and VOC emissions from flowback water are small compared to other production related sources of VOC emissions. Emissions from venting during WST could be controlled by requiring reduced emission ("green") completions. Requiring tighter vapor controls on temporary tanks that hold the flowback water could control emissions from fluids produced during WST.

Oil and gas production operations are a major (~10%) source of total anthropogenic ozone precursor emissions in the San Joaquin Valley. Although the marginal emissions from WST alone are small, the potential increase to VOC emissions due to additional oil and gas production activities enabled by WST could potentially impact ozone air quality in the San Joaquin Valley.

5.2.1.1 Air Quality Overview

Most of the WST activity in California takes place in the San Joaquin Valley, a region of California that is designated as a non-attainment area for ozone and particulate matter (PM) standards. Since the region is not currently meeting national standards, any marginal increase to emissions can present a challenge for local regulators in that they will have to find an equal source of emission reductions from a different sector just to maintain the current pollution levels, let alone reduce total emissions so that air quality measurements fall below the standards.

The air quality of a region is characterized by measurements of specific pollutants, including $\mathrm{PM}_{2.5}$ and ozone, from central monitors in that region. Before the pollutants emitted from WST encounter and are measured by the monitors, they are dispersed by wind and may undergo chemical transformation in the atmosphere. The manner in which the same emissions will affect air quality will differ depending on the meteorological conditions and the other pollution already present in the atmosphere (the chemical transformations depend on total pollution levels).

There are several methods one might employ to evaluate how WST emissions impact air quality. One could try to determine the impact of WST emissions through analyzing air quality measurements, comparing air quality on days with high WST activity to days with low WST activity. However, the day-to-day variation in WST emissions is unknown and the variability in meteorology and atmospheric chemistry between days would

likely overwhelm any signal that might exist otherwise. Instead of depending only on measurements, air quality models are often used to describe how pollutants are dispersed through the atmosphere and chemically transformed. The models connect the pollutant emissions to their air quality impacts. It is out of the scope of this report to develop air quality modeling of WST related emissions. Instead, we can compare WST related emissions to emissions from other sectors. If the magnitude of emissions is much smaller than other known sectors we can assume the air quality impacts from those emissions are much smaller as well. In this report, emissions from WST activities are evaluated by comparison to the sum of total emissions from the oil and gas production and processing sector.

To estimate emissions we would, ideally, have direct measurements of emissions from a representative sample of WST activities in California. There are, however, very few measurements of emissions from WST in California, let alone a representative sample, as WST emissions can vary over wells, reservoirs, operator practices, control technologies and other factors. An additional challenge is that independent scientists have limited access to well pads to conduct emission measurements. In fact, emissions from oil and gas production activities are the subject of numerous scientific studies, reviewed below, and continue to be a source of uncertainty regarding total environmental impacts from oil and gas production.

Given these limitations we estimate emissions from WST in California using a "bottom-up" approach, meaning we break WST into a series of processes and estimate emissions for each process separately. The estimates for each process are based on estimates of activity (for example gallons of fuel-used) and emissions per activity (for example pollutant emissions per gallon of fuel). In some cases, information regarding an activity is limited, and we can develop only a qualitative emissions estimate based on available literature. We compare emissions estimates to the CARB emission inventory, which lists emission estimates by air basin for thousands of separate source-types, including more than 200 oil and gas source-types. Although the total emission estimates from the CARB inventory are publically available, CARB releases relatively little detail on the methodology used to create these emission estimates. In the sections below we note when we believe our comparisons to CARB's emission inventory may be uncertain due to a lack of knowledge of particular details of CARB's underlying methodology for inventory development.

The separate WST processes we evaluate include: (1) Bringing supplies to the well pad, including fluids; (2) Pumping the fluid into the well; (3) Venting of gases from the well during WST or completion; (4) Flaring of gases produced during WST or completion; and (5) Evaporation of chemicals from liquids produced during WST and completion.

Each of those practices releases a different set of pollutants. The diesel equipment used to pump the fluid into the well and the diesel trucks used to bring supplies to the well are primarily a concern because of nitrogen oxides (NO_x) and particulate matter (PM) emissions. Increased chronic exposure to particulate matter is associated with increased rates of premature mortality. NO_x is of concern for multiple reasons. NO_x emissions can

lead to ozone formation, ozone, a key constituent of photochemical smog, is an irritant and also associated with negative short and long term health impacts. NO_x can also undergo chemical transformation in the atmosphere and condense to a solid form adding to the total $PM_{2.5}$ burden.

Venting of gases from the well and evaporation of chemicals from flowback or produced liquids are of concern due to emissions of VOCs. There are thousands of potential chemicals that fall under the VOC category. Some VOCs are carcinogens or endocrine disruptors and directly hazardous to humans. Many VOCs can react in the atmosphere to increase ozone formation. Some VOCs are transformed to form PM. If gases are flared, instead of vented, then most, but not all, of the VOCs are burned. The combustion during flaring may cause $PM_{2.5}$ and NO_x emissions.

Below we review studies of air quality near oil and gas production operations across the US. This literature review provides context for the range of concerns related to air quality and oil and gas production, including concerns related to WST. However, it should be stressed that environmental impacts from WST operations vary greatly by region and in response to local regulations. Many of the following sections include explicit description of known differences between WST processes observed in other regions and the WST processes that are observed in California. There are also certain studies performed outside of California, for example studies measuring ambient levels of certain toxic VOCs, that have not been replicated inside California. In those cases we report the concerns found in other regions with the caveat that it is unknown whether these same issues are relevant or not to California. The sections following the literature review present emissions estimates for each of the five WST processes listed above. Available technology or practices that could be used to control emissions is mentioned at the end of each emission estimate section.

5.2.1.2 Air Quality Literature Review

The review here focuses on studies in which an attempt has been made to link air quality measurements directly to oil and gas production activities. The studies reviewed below present air quality measurements taken far away from the actual well pads and present a variety of methods to attribute measured pollution levels to oil and gas production sources. These types of studies fall in the general category of "top-down" measurement studies. In some cases top-down measurement studies can be used as a way to ensure the assumptions about activity and emission rates in a parallel bottom-up inventory are correct. Other studies reviewed below use other methods to link air quality to oil and gas emissions, for example, air quality modeling. Together the studies represent the range of concerns related to air quality from oil and gas production and provide examples of techniques used to measure the air quality effects. The studies also show the difficulty and uncertainty inherent in characterizing total air quality impacts from oil and gas production, and show the limits to which air quality impacts from separate processes within oil and gas production, for example WST, can be measured.

A common technique for calculating the air-quality impacts of oil and gas operations is to measure both total pollution and the relative abundance of chemicals associated only with oil and gas production operations. For example, $C_2 - C_6$ alkanes, like propane (C_3H_8) , are emitted from oil and gas operations but not other activities. Measurements in spring 2002 presented by Katzentstein et al. (2003) indicated that oil and gas operations were responsible for "major quantities" of VOC emissions across regions in Texas, Kansas and Oklahoma. Katzentstein et al. (2003) also found evidence that the oil and gas emissions led to surface ozone formation.

In Colorado, Gilman et al. (2013) found that VOC emissions related to oil and gas operations were important sources of ozone precursors (during winter 2011). They used the ratio of propane (associated with oil and gas operations) to ethyne (not associated with oil and gas operations) to distinguish between "urban emissions" and those related to oil and gas operations. Compared to ambient measurements in U.S. cities, including Pasadena, CA, the propane-to-ethyne ratio in Northeastern Colorado was often one to two orders of magnitude larger, indicating the presence of emissions from oil and gas operations. Also in Colorado, in locations with both gas development and residential areas, Colborn et al. (2014) found the presence, in ambient air samples, of potentially health-damaging VOCs, including methylene chloride, various endocrine disruptors, and harmful levels of polycyclic aromatic hydrocarbons (PAHs) associated with oil and gas production. The VOCs were highest during the drilling phase and did not increase during hydraulic fracturing. However, venting and condensate tank flashing emissions accounted for 95% of all VOC emissions in Weld County in Colorado (Bar-Ilan et al., 2008; Bar-Ilan et al., 2008; Pétron et al., 2012). Pétron et al. (2012; 2014) found higher VOC emissions from oil and gas operations than listed in a standard bottom-up inventory in Colorado. Venting and condensate tank flashing emissions accounted for a lower fraction of VOC emissions in other regions of the United States. For example, Zavala-Araiza et al. (2014) report that condensate tanks account for close to 50% of total VOC emissions in the Barnett Shale.

Olaguer (2012) modeled near-source air-quality effects in the Barnett Shale, finding that emissions of NO_{x} associated with compressor engines and flaring can increase peak 1 hr ozone by 3 ppb 2 km and and farther downwind of the source. Olaguer (2012) states: "Major metropolitan areas in or near shale formations will be hard pressed to demonstrate future attainment of the federal ozone standard, unless significant controls are placed on emissions from increased oil and gas exploration and production." Formaldehyde emissions from flares and compressors were also found to be of concern.

A few papers and public reports examine links between oil and gas production and related air pollution and health effects. For example, McKenzie et al. (2012) found residents living in Wyoming within 0.5 miles of wells were at greater cancer risk due to exposure to benzene and other emissions than residents living farther away from production activity. In contrast, Bunch et al. (2014), in an industry-funded study, examined ambient VOC measurements in regions around the Barnett Shale, and found little evidence of toxic

health effects linked to increased gas production activity. Pinto (2006) described high winter ozone episodes in Wyoming associated with oil and gas production and, separately, a report from the Wyoming Department of Health describes the association between observed high ozone levels and increased respiratory health clinic visits (Pride et al., 2013).

In California, Gentner et al. (2014) found that oil and gas operations in the San Joaquin Valley were responsible for about 8% of the anthropogenic precursors to ozone, consistent with the $\sim 10\%$ of total anthropogenic reactive organic gas that is attributed to oil and gas operations in the CARB inventory (CARB, 2009). In the San Joaquin Valley, ozone sensitivity varies by location and characteristic wind direction, and some urban locations would likely see higher sensitivity to increased VOC emissions than rural areas (Jin et al., 2013).

We can conclude from this literature review that in other regions of the country expanded oil and gas production has caused air-quality hazards. Specifically, high measurements of ozone (NO_x and VOC emissions are precursors to ozone) and emissions of toxic VOCs are of concern in multiple regions around the United States. A major challenge revealed in the literature lies in attributing emissions to specific processes within oil and gas operations. Many of the observations used to evaluate air-quality impacts of oil and gas operations are taken as ambient measurements and can be attributed generally to oil and gas sources based on their chemical characteristics, but cannot be attributed specifically to well stimulation processes versus general production processes. An additional challenge is the lack of peer-reviewed literature analyzing emissions of toxic VOCs from oil and gas operations in California. In fact, Allen (2014) points out, in a review of the air quality impacts of natural gas production and use, that in general, "data are sparse on toxic air pollutant impacts of natural gas production..." While we point to concerns related to emissions of toxic VOCs from oil and gas production in other regions, we are not able to make a definitive statement about how relevant those concerns are for operations in California.

Previous sections of this report describe a number of important differences between well stimulation employed in California compared with other regions. Section 5.1.1 indicates less fluid is used per stimulation operation, and Section 5.1.3.2.1 finds that most hydraulic fracturing in California occurs in relatively shallow wells. Because of these differences, published emission estimates from regions in Colorado or Texas, for example, should not be directly applied to California.

5.2.1.3 Qualitative Discussion of Enhanced Emissions Due to Well Stimulation

As described in the introduction, the processes within WST that can lead to significant emissions include trucking supplies to the well pad, pumping the fluid into the well, venting or flaring of gases from the well during WST or completion, and evaporation of chemicals from liquids produced during WST and completion.

In California, a high emission scenario would occur at a deep oil field remote from pipeline infrastructure. In this situation, infrastructure would not be available to transport fluids,

oil, or natural gas by pipeline. All materials and fluids would need to be trucked to and from the site, and any methane produced during well completion would need to be flared. Additionally, the field would have some properties similar to those of unconventional plays outside of California, such as the Marcellus shale, and require massive amounts of fluid, $\sim 10^5$ bbl per well stimulation, and use $\sim 10^4$ gallons of diesel fuel per well stimulation to power the pumps (Rodriguez and Ouyang, 2013).

The assumption in the scenario is that the diesel pumps would be at least five years old and the trucks used to bring fluids and supplies would be older than 2007 model year (older diesel engines can emit an order of magnitude more $PM_{2.5}$ and NO_x per gallon of fuel burned compared to the newest engines that have post-combustion controls). Produced fluids would be stored in temporary open-air ponds or tanks before disposal or treatment, allowing dissolved VOC to evaporate.

In this scenario, high levels of uncontrolled diesel combustion, uncontrolled flaring combustion, and potential evaporation and venting of VOCs could lead to high emissions of a number of key pollutants that may cause air-pollution problems, such as described in the literature.

In contrast to the above, a lower emission scenario potentially more common in California, and perhaps representative of current well stimulation in California's South Belridge oil field, will lead to smaller amounts of emissions. In this scenario, pipelines deliver the fluid for well stimulation, removing the burden of trucking the fluid to each well (although other supplies, such as sand, must be trucked to the site if needed). Significantly less fluid, $\sim 10^3$ bbl per well, is needed for well stimulation compared with practices in other regions. Infrastructure exists to pipe away associated gas, and gas produced during completion, so that, ideally, flaring or venting is not performed. Although not required in the San Joaquin Valley, produced fluids would not be allowed to equilibrate with the atmosphere before disposal to a different well or removal to a water treatment facility. Finally, and also not required, newer diesel equipment (trucks and pumps) would be employed to significantly reduce the emissions per gallon of fuel burned.

The comparison of the two scenarios above demonstrates how important local conditions and practices are in determining the amount of emissions related to well stimulation. When evaluating the air pollution hazards of well stimulation, these questions should be asked explicitly: How much fluid will be needed? Will the fluid be delivered by truck or pipeline? How much fuel will be used for pumping during well stimulation? How will fluids recovered from the well be stored and disposed? Will flaring occur? Will direct venting occur? These questions are considered quantitatively below.

5.2.1.4 Quantitative Discussion of Enhanced Emissions Due to Well Stimulation

This discussion focuses on emissions from three broad categories: (1) exhaust from diesel engines including diesel-powered pumping associated with well stimulation and diesel

trucks used to bring and remove supplies and waste (fluids, sand, chemicals, equipment); (2) flaring and venting of gases produced during completion, well workovers, or other practices associated with well stimulation; and (3) evaporative emissions from fluids recovered from the well and fugitive emissions throughout the process.

The type of pollution varies by activity type. Diesel engines are associated with NO_x and $PM_{2.5}$ emissions. Flaring is associated with NO_x , PM, and VOC emissions. Evaporative and general fugitive emissions are a concern due to VOC content within the gas or liquids.

5.2.1.4.1 Exhaust from Diesel Pumps

For emissions from diesel trucks and diesel pumps we focus on NO_x and $PM_{2.5}$ emissions. We use a fuel-use-based approach to estimate total emissions per activity as the product of fuel use and an emission factor (mass emitted per mass of fuel used).

We base our estimates of fuel-use for pumping during well stimulation on published estimates of fuel-use in locations outside of California. To adapt the values to California we assume pumping related fuel-use scales linearly with the total fluid volume pumped and then scale fuel-use based on reported fluid volumes in California. One caveat to this approach is that there are other factors that could affect fuel used for pumping than total fluid volume, for example, the pressure to which the fluid was pumped. There is not enough information to characterize these other factors.

In addition to the total fuel used, we need to estimate the emission rate, mass emitted per mass of fuel used, in order to generate emission estimates. We base emission rates on published emission rate estimates and briefly describe here the regulatory framework that controls emissions from diesel engines.

From a regulatory standpoint, diesel equipment is divided into on-road and off-road categories, and the emissions of pollutants per fuel burned vary with the equipment category along with the specific piece of equipment. In California, on-road vehicles (such as the trucks used to deliver fluids, sand, and other supplies) must meet more stringent emission requirements than off-road vehicles. The most dramatic difference is that most on-road heavy-duty trucks must be equipped with some form of post-combustion particle-control device that removes most of the $PM_{2.5}$ emissions compared to an uncontrolled vehicle. Similar regulations regarding $PM_{2.5}$ and NO_x emissions from off-road diesel equipment and NO_x emissions from on-road vehicles will be phased in slowly over the next 10–15 years. Thus, over the next few years, $PM_{2.5}$ emissions from on-road trucks will be significantly lower (on a per mass of fuel basis) compared with $PM_{2.5}$ emissions from diesel pumps (off-road equipment).

Emission standards for on-road equipment and mobile off-road equipment are regulated by CARB. The emission rate from diesel pumping equipment is 28.0 grams of NO_x/kg fuel (0.028 lb emitted/lb fuel) and 1.5 grams $PM_2 s/kg$ fuel (0.0015 lb emitted/lb fuel)

according to Rodriguez and Ouyang (2013). This $\mathrm{NO_x}$ emission factor is similar to other previous measurements and analysis of off-road equipment, specifically Tier 2 rated off-road equipment (Abolhasani et al., 2008; Frey et al., 2008; Millstein and Harley, 2009). The $\mathrm{PM_{2.5}}$ emission factor is roughly half of the US EPA's estimate reported in Millstein and Harley (2009) and based on the US EPA's NONROAD model. The difference for the $\mathrm{PM_{2.5}}$ emission factor between the US EPA and Rodriguez and Ouyang (2013) is related to assumptions regarding the age of the equipment.

Total emissions are calculated as the product of fuel use \times emission rate, where, fuel use is a function of the total volume of fluid pumped, and the pressure at which the fuel is pumped. Equipment other than the pumps only contributes a small portion of total fuel-use during the pumping phase (Rodriguez and Ouyang, 2013).

Rodriguez and Ouyang (2013) reported on stimulations in the Marcellus and Eagle Ford shales. The stimulations studied typically pumped about 135,000 bbl of fluid using about 21,000 gallons of diesel fuel over a two-day period. This fuel-use resulted in ~1900 kg (4200 lb) of NO_x emissions and 100 kg (220 lb) of $PM_{2.5}$ emissions over the period. These estimates are within the range of estimates presented by Litovitz et al. (2013) using similar methodology: 3800-4600 kg (8,400 – 10,100 lb) NO_x and 87-130 kg (192 – 287 lb) $PM_{2.5}$ per total well-site development. This estimate includes emissions from hydraulic fracturing itself, but also other activities.

For California, the emissions estimate is based on pumping 175,000 gallons (5,550 bbl) of fluid based on the average water volumes discussed in Section 3.2.3. This volume is between the average from FracFocus and the average from the well stimulation notices. Lacking any information on actual fuel use, the total amount of fluid pumped is used to estimate total emissions from the pumping phase: 5,550 bbl/135,000 bbl = 1/24 of the emissions compared to the high-emissions case. Note that other aspects of the pumping process, such as the pressure used to pump the fluid, may affect fuel use, but in this example only change due to fluid volume is considered. Total pumping emissions are 1/24th the amount estimated for the prior Marcellus and Eagle Ford example. This is approximately 80 kg (176 lb) of NO_v emissions and 4 kg (9 lb) of $PM_{2.5}$ over a 1-day period.

Assuming a rate of 125 hydraulic fracturing operations per month (the center of the 100–150 operations per month estimate used in Section 5.1.1) allows a daily emission estimate. This rate implies the equivalent of four stimulations per day, which would emit an estimated 320 kg (704 lb) of NO_x and 16 kg (35 lb) of $PM_{2.5}$. For reference, CARB estimates ~16 metric tons (18 short tons) and 0.5 metric tons (0.6 short tons) NO_x and $PM_{2.5}$ emissions per day, respectively, in the San Joaquin Valley in 2008 from off-road diesel engines for use in oil drilling, workovers, and pumping (CARB, 2009).

We conclude, based on the above estimates, that pumping for well stimulation is not currently a major air pollution hazard in California as the estimates for pumping here are only 2-3% of the total emissions from off-road diesel engines associated with oil and gas

production in the San Joaquin Valley as estimated by CARB. However, if well stimulation requires significantly more fluid in the future, such as due to a transition to using slickwater, then emissions from diesel pumps could become more important. Technology exists to control emissions from diesel pumping. The use of US EPA classified "Tier 4" nonroad diesel engines would reduce emissions from diesel equipment by 90% compared to diesel equipment from the 1990s.

5.2.1.4.2 Exhaust from Diesel Trucking Activity

To estimate emissions from diesel trucking activity we use similar methods to those used to estimate pumping related emissions. Again we use a fuel-use-based approach to estimate total emissions per activity as the product of fuel use and an emission factor. To estimate fuel-use we reference published estimates of fuel economy for bulk tankers, include the fluid volume estimates from the above example, and chose an arbitrary delivery distance of 100 miles. Emission rates for on-road heavy-duty diesel trucks are based on previous literature.

Heavy-duty trucks, such as bulk tankers and tractor-trailers, consume 6.5 gallons per 10^3 short ton-miles (14 kg of fuel per 10^3 metric ton-kilometer; Davis et al., 2013). Applying emission factors of ~ 30 g NO_x/kg fuel and ~ 1 g PM_{2.5} / kg fuel (Dallmann and Harley, 2010) results in freight emission factors of about 686 g NO_x and 23 g PM_{2.5} per 10^3 metric ton-miles.

In the Marcellus and Eagle Ford example based on Rodriguez and Ouyang (2013), 135,000 bbl of fluid were delivered, although the delivery method and distance are not specified. The 135,000 bbl delivered would weigh about 16,000 metric tons. If delivered by truck, and over a hypothetical distance of 100 miles that would be 1.6×10^6 metric ton-miles. Multiplying by the above emission factors yields about 1.1 metric tons (1.2 short tons) NO_x and 37 kg (81 lbs) PM_{2.5} per well stimulation operation.

As described in the California example above, the fluid volume commonly used in California is 1/24th the fluid used in the Marcellus and Eagle Ford example from Rodriguez and Ouyang (2013). Consequently, emissions from delivering the fluid in California would equal about 46 kg (101 lb) NO_x and 1.5 kg (3.3 lb) $PM_{2.5}$ per well stimulation. These emissions may be lower as fluid is often delivered by pipeline close to the well, according to many of the hydraulic fracturing notices.

Based on the data in FracFocus, a reasonable estimate of the average mass of proppant used per hydraulic fracture operation is about 100 metric tons (110 short tons). Transporting this proppant for 100 miles by truck emits 7 kg $\rm NO_x$ and 0.2 kg $\rm PM_{2.5}$ per well stimulation.

Summing the emissions from fluid and sand delivery gives emissions of 53 kg NO_x and 1.7 kg $PM_{2.5}$. Based on the 125 hydraulic fracture operations per month used in the pumping emission estimate, the annual trucking emission estimate is about 79 metric tons

(87 short tons) NO_x and 2.6 metric tons (2.9 short tons) $PM_{2.5}$ per year for sand and fluid deliveries. CARB (2009) estimates on-road diesel trucks emit about 75,000 metric tons (82,000 short tons) of NO_x per year and 2,700 metric tons (3,000 short tons) of $PM_{2.5}$ per year in the San Joaquin Valley. Emissions from delivering supplies are small in comparison.

As with pumping emissions, the above estimates indicate that delivery of supplies, particularly fluids and sand for well stimulation, is not a major contributor to $\mathrm{NO_x}$ and $\mathrm{PM_{2.5}}$ emissions in California. The basic point being, given current activity levels, the trucking activity required for WST is negligible compared with the trucking activity for other sectors in the San Joaquin Valley. However, if future well stimulation techniques require significantly more fluid, then emissions from the diesel trucks that might deliver the supplies could become more important. As with diesel pumping equipment, technology to control emissions from trucks is available. In fact, most trucks built since 2010 are required to include exhaust controls for $\mathrm{PM_{2.5}}$ and $\mathrm{NO_x}$ emissions. Simply requiring that the newest trucks be employed could largely reduce emissions from diesel trucking activity associated with WST.

5.2.1.4.3 Emissions from Flares

Information on the number of flares used for well stimulation or completion operations is not available. The combustion conditions and efficiency of the flares are also unavailable. Thus, emissions of CO, $\mathrm{NO_x}$ or $\mathrm{PM_{2.5}}$ from flaring cannot be estimated quantitatively. Instead, in this section we review basic information about flaring in California and report the results of emission estimates developed by the State.

Emissions during flaring consist of unburned VOC, partially combusted VOCs, $PM_{2.5}$, carbon monoxide (CO), and NO_x produced during combustion. The characteristics of emissions from flares vary across uses and conditions. For example Torres et al. (2012) found combustion efficiency of flares varied under various operating conditions, although this study focused on large industrial flares, which would not necessarily represent the types of flares found in use during well completion activities. Note there are very few studies of flaring efficiency relevant to oil production in the United States. Allen et al. (2013) report 99.5% efficiency for a production flare in the Marcellus Shale, but this does not provide enough data to derive general conclusions about flaring efficiency related to WST. In the San Joaquin Valley, permanent facilities are required to obtain permits in order to operate a flare. Well drilling, completion, and stimulation are considered temporary, however, and would not need to file for a specific permit (personal communication, Mike Oldershaw, San Joaquin Valley Air Pollution Control District (SJVAPCD)).

The official CARB inventory shows emissions from flares, as a percent of total oil and gas emissions in the San Joaquin Valley, are equal to 0.3, 3.6, 1.0, 5.7, 1.5, and 1.6% for VOCs, CO, NO, SOx, PM, respectively (CARB, 2009). It is unclear, however, if the

reported emissions account for flaring during completion stages. It is also unclear how the volume of gas flared during completion stages would compare to the volume of gas that was assumed flared in CARB's above emission estimates.

CARB's oil and gas survey (Detwiler, 2013) estimates annual total carbon dioxide emissions from flaring in California of 242,454 metric tons (267,260 short tons). A first-order estimate of unburned VOC emissions can be derived from this estimate. Given the lack of relevant peer-reviewed studies addressing flaring efficiency, we assume a standard efficiency of 98% for flaring during production, and a "generic" composition of 80% methane, 15% ethane, and 5% propane (Shires et al., 2009), to find total annual flaring is estimated to emit 335 metric tons (369 short tons) of non-methane hydrocarbons or only 82 metric tons (90 short tons) of VOCs (reactive organic carbon such as propane; methane and ethane are not considered reactive, or precursors to ozone).

This total would not include VOC produced from combustion itself. It is also unclear if this total includes flaring operations during completion or well stimulation operations, or is limited to more permanent flares. However, CARB estimates a total of 369 short tons of anthropogenic reactive VOC emitted per day, or about 135,000 short tons per year in the San Joaquin Valley. VOC emissions from flaring would need to be more than an order of magnitude larger than the oil and gas survey estimated to be of consequence to VOC atmospheric concentrations at the regional level.

In conclusion, although emissions from flaring are uncertain, the two inventories described above indicate that current flaring associated with WST is likely to have a negligible effect on air quality in the San Joaquin Valley. Control technology is not available to control flaring emissions; however, alternate practices can reduce the use of flares, for example requiring reduced emission completions, or "green completions."

5.2.1.4.4 Fugitive and Evaporative Emissions

A representative set of direct measurements of fugitive and evaporative VOC emissions from oil and gas processes in California is not available. In this section we review published emission inventories. We compare a top-down measurement study of VOC emissions from oil and gas production in the San Joaquin Valley to CARB's bottom-up inventory.

As mentioned in the literature review, Gentner et al. (2014) found that ambient VOC measurements from a field campaign in the San Joaquin Valley indicated that oil and gas operations were responsible for 8% of organic compound ozone precursor emissions, consistent with CARB's estimates. Note that estimates from both CARB and Gentner et al. (2014) take into account, to a certain extent, the reactivity of the organic compounds. For example, Gentner et al. (2014) indicate that while petroleum operations comprised 22% of anthropogenic non-methane organic carbon at Bakersfield, petroleum operations account for 8% of anthropogenic ozone precursor emissions. CARB's inventory attributes 60% of all oil and gas-related VOC emissions in the San Joaquin Valley to the top five oil

and gas source types, all of which are related to production, as opposed to processing and marketing. The top five sources are listed as "(1) tertiary oil production - cyclic wells, (2) tertiary oil production - steam drive wells, (3) i.c. reciprocating engines, (4) fugitive losses – fittings, and (5) fugitive losses – valves." None of the top five source types is related to evaporative sources; they are instead related to combustion sources and to fugitive emissions during production processes.

Based on CARB's estimate, vented and evaporative emissions from liquids related to WST are not a major source of VOC emissions. The agreement between CARB's bottom-up estimate of emissions from oil and gas operations in the San Joaquin Valley and the top-down estimate for the same sector reported by Gentner et al. (2014) indicate that it is unlikely that there is a large unknown source of VOC emissions. However, one potential problem with CARB's estimate is that it is unclear if VOC emissions during fracturing and completion are incorporated into the inventory, as they are not considered stationary sources by the SJVAPCD. It should be noted that while initial measurements and inventories in the San Joaquin Valley are in agreement, Zavala-Araiza et al. (2014) report that emission inventories for production processes in the Barnett Shale region are not in agreement with atmospheric measurements and Allen et al (2013) find that emissions from liquid unloadings may be poorly represented and potentially underestimated.

In conclusion, evaporative VOC emissions directly from WST have not been directly measured but current California inventory indicates they are unlikely to cause significant impacts to ozone air quality. Technology exists that could control evaporative VOC emissions, such as requiring vapor controls on temporary tanks in which WST flowback water is stored. Additionally, requiring green completions could control vented VOC emissions related to WST. It is important to note that, in the San Joaquin Valley, the oil and gas industry contributes ~8% of anthropogenic ozone precursors, thus any marginal increase to total oil and gas production could potentially lead to increased ozone levels.

5.2.1.5 Air Quality Conclusions

Estimated marginal emissions of NO_x , $PM_{2.5}$, and VOCs directly from activities directly related to WST appear small compared to oil and gas production emissions in total in the San Joaquin Valley where the vast majority of hydraulic fracturing takes place. However, the San Joaquin Valley is often out of compliance with respect to air quality standards and as a result, possible emission reductions remain relevant.

Three major sources of air pollutants include the use of diesel engines, flaring of gas and the volatilization of flowback water. The first, diesel engines (used for transport and pumping of estimated fluid volumes required for WST) emit a small portion of total emissions of nitrogen oxides (NO_x), particulate matter ($PM_{2.5}$), and VOCs associated with other oil and gas production operations as a whole.

Emissions from flaring in California are uncertain because of variability in flare combustion conditions and to a lack of information regarding the frequency of flare-use during WST operations. However, current CARB inventories of pollutant emissions from all flaring suggest that flares as a whole emit less than 0.1% of the VOCs and are not a major regional air quality hazard.

Emissions from volatilization of flowback water constituents have not been measured but might be bracketed. CARB has conducted a "bottom-up" VOC emission inventory by adding up all known sources of emissions. It is unknown whether these sources included emissions from WST-related produced or flowback water. However, the sum of the emissions in the inventory matches well with "top-down" measurements taken from the air in the San Joaquin Valley (Gentner et al., 2014). This agreement between "bottom-up" and "top-down" estimates of VOC emissions from oil and gas production indicates California's inventory probably included all major sources.

The inventory indicates that VOC emissions from oil and gas evaporative sources, such from flowback water, might occur from stimulation fluids produced back after the application of WST, are small compared to other emission sources in the oil and gas development process. Data suggest that emissions from oil and gas production and upstream processing in general contribute to $\sim 10\%$ of anthropogenic VOC ozone precursor emissions in the San Joaquin Valley. Although the marginal emissions from WST alone are small, the potential increase to VOC emissions due to other oil and gas production activities enabled by WST may impact ozone air quality in the San Joaquin Valley.

Emissions from diesel equipment and diesel trucks can be controlled through use of the cleanest engines, such as US EPA classified Tier 4 engines for off-road equipment or on-road truck engines that meet 2010 engine standards. Requiring reduced emission completions can control emissions from flaring and venting related to WST. Emissions from evaporative sources related to WST could be limited by requiring vapor controls on the temporary tanks to which flowback water is stored.

As described above, some of the potential air-quality impacts can be addressed by regulation and largely avoided. Most WST takes place in the San Joaquin Valley. WST is subject to a variety of regulatory processes in the San Joaquin Valley. For example, there are requirements on emissions from individual pieces of equipment, and new drilling operations must meet New Source Review and other regulations. Evaluation of opportunities to reduce emissions of pollutants from WST and other production-related operations would benefit from independent, on-the-ground studies of emissions from individual processes within petroleum production in the San Joaquin Valley.

If practices in California changed, for example if more fluid was used in WST or production moved to remote locations, emissions from activities directly related to WST could become important if left uncontrolled.

5.2.2 Climate Impacts

This section presents estimates of GHG emissions associated with WST. GHG emissions in California occur in a context of needing to reduce total emissions to 2005 levels under AB32 and a Governor's executive order that requires 80% emission cuts by 2050. The oil and gas enterprise worldwide is responsible for a large fraction of the total GHGs emitted to the atmosphere. By far the largest factor in these emissions is burning the fuel, not producing it. Nevertheless oil and gas production produces GHGs and in California these are subject to control under the state's climate laws.

GHG emissions from WST come from fuel-use associated with pumping and supply delivery and also from fugitive methane emissions. We find that ${\rm CO_2}$ emissions from fuel-use directly related to WST are negligible.

Fugitive methane emissions in this case include vented and leaked methane during WST and also methane that is emitted from flowback water. Methane emissions from oil and gas operations are uncertain and are currently a major research topic. Because of the uncertainty regarding methane emissions and because methane is a potent greenhouse gas it is a focus of this section.

We review measurement studies and current inventory estimates of methane emissions from oil and gas production in California. A number of measurement studies in California suggest higher methane emissions from oil and gas production activities than is listed in the State inventory. However, even if accepting the higher rate of emissions indicated by the measurement studies, the marginal fugitive methane emissions from the direct application of WST to oil wells are likely to be small compared to the total greenhouse gas emission impacts from current energy–intense oil and gas production in California. Methane emissions related to WST could be controlled by requiring reduced emission, "green," completions and by requiring tighter vapor controls on temporary tanks that hold flowback water.

5.2.2.1 GHG Emissions in California

According to California's official GHG emission inventory, oil and gas extraction processes account for $\sim \! 16$ million tons of ${\rm CO}_2{\rm eq}$ emissions, or 3.5% of California's total GHG emissions (CARB 2013). In California, Assembly Bill 32 requires reductions of total GHG emissions to below a cap in 2020 and a Governor's executive order requires 80% emission cuts by 2050, thus increases to emissions from sectors accounting for only a few percent of total emissions may become important if state total emissions are close to the cap.

The marginal GHG emissions from WST are small, of course, compared to the emissions from burning the fuel that is produced from stimulated wells. However, this section focuses on the marginal emissions from WST and not on emissions from combustion of the produced fuel. Emissions of GHG from well stimulation come from fuel combustion and fugitive methane emissions (methane that is vented or leaked from wells or equipment). Emissions of CO_2 are tied directly to fuel-use or flaring.

Per ton emitted, methane is considered to cause much more warming than ${\rm CO_2}$ (Myhre et al., 2013). Because methane is such a potent greenhouse gas, small leaks of methane can be important sources of greenhouse gas emissions. Much of this section focuses on methane emissions during WST and oil and gas production in general for this reason.

Another reason that methane emissions are a focus of this section is that methane emissions from oil and gas operations are uncertain. Methane emissions from oil and gas operations are currently a major research topic. Methane leak rates are likely not normally distributed, but heavily skewed so that a few locations may have high leak rates compared to an average location (Brandt et al., 2014). Because of the uncertainty regarding the distribution of methane emissions among locations and across geographies, and the lack of easy access to production locations, most field campaigns designed to measure methane leakage and venting from specific processes during production are unable to capture a representative sample. One potential solution that would allow for a field campaign to derive a representative sample would be for a regulatory agency to compel companies to allow independent researchers access to production areas, for example see the City of Fort Worth Natural Gas Air Quality Study (Eastern Research Group; Sage Environmental 2011). "Bottom-up" estimates of methane emissions, based on counting equipment and processes and applying an average emission factor to each type of equipment and process, commonly produce estimates of total methane emissions that are significantly lower than "top-down" regional measurement campaigns (Brandt et al., 2014).

In this section, a short literature review describes top-down and bottom-up estimates of methane emissions. This is followed by assessments of GHG emissions from three processes that occur during WST: (1) diesel fuel-use for pumping and supply delivery; (2) emissions from flaring; and (3) emissions of fugitive methane.

Some of the same processes associated with VOC emissions from venting, flaring and evaporative sources, described earlier in Sections 5.2.1.4.3 and 5.2.1.4.4, will also lead to methane emissions. As published literature does not provide specific enough information to develop fugitive methane emission estimates from WST, our approach to evaluate fugitive methane emissions will be to compare current California bottom-up inventories of methane emissions from oil and gas production to top-down methane measurements and attempt to bracket total emissions. The total methane emission estimates will then be put in context of total GHG emissions estimates from all oil and gas production activities. Carbon dioxide emissions will be related directly to fuel use, and thus be related directly to processes used to calculate NO_x and PM_{2.5} emissions in the air-quality section.

5.2.2.2 Methane Emissions Literature Overview

In the case of California, top-down measurement studies indicate higher oil and gas emissions than bottom-up inventories. For example, Wennberg et al. (2012) and Peischl et al. (2013), using aircraft measurements, find high emissions of methane from the overall oil and gas system in Southern California compared with bottom-up inventories. Peischl

et al. (2013) estimate emissions separately for the oil and gas production and processing sector and the gas transmission and distribution sector, and report higher emissions of methane compared to the bottom-up inventories for both of those sectors. Jeong et al. (2014) compare bottom-up and top-down inventories in California and found that if the emissions rates estimated for the oil and gas industry in southern California by Peischl et al. (2013) were extended across the state, state total methane emissions from oil and associated gas production would be equal to 1% of CA total CO₂eq (100 yr), roughly five times the official state inventory estimate for oil and associated gas production. Gentner et al. (2014) also found qualitative evidence that dairies were responsible for the majority of methane emissions in the San Joaquin Valley, but did not provide quantitative estimates of methane emissions. Jeong et al. (2014) estimated that even accounting for the higher emission inventory for oil and gas production based on ambient measurements, dairies still emit eight times the methane in the San Joaquin Valley compared with oil and gas production, and so the higher California emission estimates are not in conflict with work by Gentner et al. (2014).

Outside of California, Pétron et al. (2012) find that approximately 4% of total methane production is emitted to the atmosphere, approximately two times the methane emissions estimate from a standard bottom-up inventory in Colorado. Karion et al. (2013), using airborne measurements of methane from a large field in Uintah County, Utah, find high emissions: 6.2%-11.7% (1σ) of production. The Petron et al. (2012) emission estimate does not distinguish between emissions by well type (petroleum or natural gas) and should not be directly compared to national inventories that estimate emissions from petroleum production and natural gas production separately (see for example, Brandt et al. 2014.) The Karion et al. study focuses on the gas-bearing portion of the basin, and so should not suffer from this problem. Maps in the Karion et al. paper show clear divergence between oil and gas regions of the Uintah, and a flight path that would isolate the gas wells.

From a national perspective, a report by the US Government Accountability Office (GAO) indicates that up to 5% of total gas production can be vented and flared, and in some cases a majority of the venting and flaring activity occurred during completion (US GAO, 2010). Similarly, Howarth (2011) estimated that up to 3.2% of lifetime gas production is emitted as methane during the flowback period following stimulation in shale gas. However, note that Cathles et al (2012) and O'Sullivan and Paltsev (2012) contest some of the methodology employed by Howarth et al., (2011) and an analysis by the Department of Energy and Climate Change in the United Kingdom (MacKay and Stone 2013) concluded that the result presented in Howarth et al (2011) is an outlier (six times greater than the next highest estimate).

Allen et al. (2013) estimates, based on measurements of a sample of individual completion events and other activities, that only 0.42% of national gross gas production is leaked or vented to the atmosphere. The 0.42% rate includes only production operations and not gathering, processing, and other sectors. However, the work by Allen et al. (2013) depends on measurements of a small sample of facilities, and it is unclear whether the sample is representative of oil and gas operations at large.

The range of emission values reported in the studies above indicates there is a high degree of variability and uncertainty in emissions from oil and gas production. Estimates of methane leakage from oil and gas production across the country are highly variable and depend on specific features of the fields being measured, and are often not directly comparable. The topic of methane emissions from oil and gas production is an active area of research. The limited number of studies in California indicate that current bottom-up inventories have smaller estimates of methane emissions compared to top-down estimates in Southern California.

5.2.2.3 Assessment of Emissions from Diesel Fuel Use Related to Well Stimulation

The approach to estimate CO_2 -related emissions is to base the estimates on the amount of diesel fuel use estimated under the scenarios presented in the air-quality section. In the high-fluid-volume scenario, $\sim 10^4$ gallons of diesel fuel were used for pumping during well stimulation. At about 10 kg CO_2 /gallon diesel, that is about 100 metric tons CO_2 (110 short tons) per well stimulation event. Carbon dioxide emissions from delivery of supplies are similar in magnitude (see Sections 5.2.1.4.1 and 5.2.1.4.2), so the total emissions in the high-volume scenario are about a couple hundred metric or short tons per well stimulation event from both fluid delivery and pumping.

The low-emissions scenario, based on hydraulic fracturing fluid volumes in California and following the methods in the air-quality section, results in an estimate of about 3 metric tons CO_2 (3.3 short tons) per well stimulation event or about 4,500 metric tons (5,000 short tons) per year, based on the estimate of 125 operations per month.

For perspective, the California Air Resources Board estimated 13 million metric tons per year of direct CO_2 (14.3 million short tons) emissions from steam generators, turbines, and combined heat and power production within the oil and gas industry in California (Detwiler, 2013). The same report estimated that only 45 thousand metric tons CO_2 (50 thousand short tons) were emitted from all water and other non-crude oil pumps. Consequently, a drastic change in well stimulation activity or volume would be needed to materially impact the CO_2 emissions from the oil and gas industry. We conclude that GHG emissions from diesel fuel use during WST are negligible.

5.2.2.4 Emissions of CO₂, CH₄, and N₂O from Flaring

There is little available information regarding flaring in California beyond what is reported in official state inventories, thus in this section we review the state's inventories to generate conclusions. CARB's oil and gas survey (Detwiler, 2013) reported 196 flare "units," accounting for 242×10^3 , 812, and 0.4 metric tons of CO_2 , CH_4 , and N_2O , respectively $(267\times10^3, 895, 0.44$ short tons, respectively). Note that it is unclear what portion of those emissions is related directly to well stimulation or well-completion activities, or even if well stimulation and completion activities were incorporated in that total. As described in Section 5.3.1.4.3 regarding air quality and flaring, in the San Joaquin Valley, where

much of California's well stimulation activity takes place, drilling, fracturing, and well completion are considered temporary activities, and thus operators are not required to obtain permits for flaring.

There is uncertainty about the efficiency of flares. Without site-specific information, the standard efficiency assumption for flares, as defined by the American Petroleum Institute (Shires et al., 2009), is that 98% of the gas is combusted, leaving 2% vented. Due to the high GWP of methane, a reduction in average efficiency of a group of flares from 98% to 97% could have a significant impact of total GHG emissions. However, as with fuel use, the relatively low baseline of GHG emissions from flaring from all oil and gas production and processing (as opposed to only well stimulation-related activities) in California suggests that even doubling or tripling the activity of flaring in the State would have only a marginal effect on total GHG emissions from the oil and gas production sector. Current use of flaring in WST causes negligible GHG emissions and could be controlled by requiring green completions.

5.2.2.5 Fugitive Methane Emissions

In this section, we review bottom-up estimates of fugitive methane emissions and compare them to top-down studies. The discrepancy between the bottom-up inventories and top-down measurements of methane emissions (top-down measurements indicate higher methane emissions) from oil and gas operations indicates the high level of uncertainty regarding methane emissions from the sector as a whole. Below we describe what the implications are for GHG emissions if the top-down estimates are correct. Note that additional uncertainty exists when attempting to estimate emissions from a process, such as well stimulation, within the larger group of production activities.

Table 5-7 shows methane and CO_2 emission estimates for oil and gas production from CARB's bottom-up survey. This again shows that CO_2 emissions (primarily due to steam generation for enhanced oil recovery, which is not evaluated in this report) are dominant over methane emissions. Even after increasing the oil and associated gas production methane emissions by a factor of five, as suggested by Jeong et al. (2014), direct CO_2 emissions still dominate total GHG emissions from oil and gas production. Quantifying the portion of fugitive emissions from production processes attributable to well stimulation is not possible without more detailed information on the well stimulation activities. To conclude, the marginal methane emissions from WST are uncertain, but likely much smaller than the direct CO_2 emissions from oil and gas extraction. The marginal fugitive methane emissions from WST could be controlled through the requirement of green completions and by requiring vapor controls for flowback water.

Table 5-7. Estimated greenhouse gas emissions from oil and gas production in 2007 (Detwiler, 2013).

Process	Constituent	Total Statewide, 10 ⁶ metric (short) tons CO _{2e}
Venting (from well workovers)	CH ₄	0.07 (0.08)
Venting (from well completions)	CH ₄	NOT ESTIMATED
Oil and Associated Gas Production Total	CH ₄	1.07 (1.18)
Oil and Associated Gas production and processing total	CH₄	2.1 (2.31)
Oil and Gas CO ₂ + CH ₄ total (mostly generating steam)	CO ₂ + CH ₄	18.6 (20.5)

5.2.2.6 Climate Impact Conclusions

Fugitive methane emissions from the direct application of WST to oil wells are likely to be small compared to the total GHG emissions from oil and gas production in California. This is because current California oil and gas operations are energy intensive. However, all GHG emissions are relevant under California's climate laws and many emissions sources can be addressed successfully with best available control technology and good practice.

Fugitive methane emissions for oil and gas production are uncertain and are currently an active area of scientific research. A number of measurement studies in California suggest higher methane emissions from oil and gas production activities than is listed in the State inventory. However, even if accepting the higher rate of emissions indicated by the measurement studies, methane emissions from oil and gas production are still likely to be small compared to direct CO₂ emissions associated with oil and gas production. Additionally, methane emissions directly related to WST are likely to account for only a small portion of total production related methane emissions.

Methane emissions related to WST can be addressed successfully with best controls, such as requiring reduced emission, or "green," completions and requiring vapor controls on temporary tanks in which flowback water is stored. For example, Allen et al. (2013) reported low leakage rates from well completions after some of the controls listed above were implemented compared to uncontrolled processes and ICF International (ICF 2014) analyzed the costs and viability of methane reduction opportunities in the U.S. oil and natural gas industries. We note that while green completions will be required nationally for gas wells starting in 2015, they will not be required for wells that produce oil or oil and associated gas, such as most of the wells in the San Joaquin Valley. Other emissions such as CO₂ from diesel fuel used for pumping fluid or delivering supplies were found to be negligible.

While other regions are currently using WST for the production of petroleum (e.g., the Bakken formation of North Dakota) or gas (e.g., the Barnett shale of Texas), emissions from these regions may not be representative of emissions from California-specific applications of WST. For example, the volume of fluid used for WST operations in California is typically lower than operations in other shale plays, potentially leading to lower evaporative emissions of methane from flowback fluid.

5.3 Potential Seismic Impacts

Induced seismicity is a term used to describe seismic events caused by human activities. These include injection of fluids into the subsurface, when elevated fluid pore pressures can lower the frictional strengths of faults and fractures leading to seismic rupture. Induced seismicity can produce felt or even damaging ground motions when large volumes of water are injected over long time periods into zones in or near potentially active earthquake sources. The relatively small fluid volumes and short time durations involved in most hydraulic fracturing operations themselves are generally not sufficient to create pore pressure perturbations of large enough spatial extent to generate induced seismicity of concern. Current hydraulic fracturing activity is not considered to pose a significant seismic hazard in California. To date, only one felt earthquake attributed to hydraulic fracturing in a California oil or gas field has been documented, and that was an anomalous slow-slip event that radiated much lower energy at much lower dominant frequencies than normal earthquakes of similar size.

In contrast to hydraulic fracturing, earthquakes as large as magnitude 5.7 have been linked to injection of large volumes of wastewater into deep disposal wells in the eastern and central United States. To date, compared to some other states, water disposal wells in California have been relatively shallow and volumes disposed per well relatively small. There are no published reports of induced seismicity caused by wastewater disposal related to oil and gas operations in California, and at present the seismic hazard posed by wastewater injection is likely to be low. However, possible correlations between seismicity and wastewater injection in California have not yet been studied in detail. Injection of much larger volumes of produced water from increased WST activity and the subsequent increase in oil and gas production could increase the hazard, particularly in areas of high naturally-occurring seismicity. Therefore, given the active tectonic setting of California, it will be important to carry out quantitative assessments of induced seismic hazard and risk. The chance of inducing larger, hazardous earthquakes would most likely be reduced by following protocols similar to those that have been developed for other types of injection operations, such as enhanced geothermal. Even though hydraulic fracturing itself rarely induces felt earthquakes, application of similar protocols could protect against potential worst-case outcomes resulting from these operations as well.

5.3.1 Overview of Seismic Impacts

Earthquakes attributed to human activity are termed induced seismicity, and have been observed for many years. Activities that can induce earthquakes include underground mining, reservoir impoundment, and the injection and withdrawal of fluids as part of

energy production activities (see National Research Council (NRC), 2013). Note that some authors distinguish between "induced" and "triggered" events according to various criteria (e.g. McGarr et al., 2002; Baisch et al., 2009). In this report we do not make this distinction, but refer to all earthquakes that occur as a consequence of human activities as induced seismicity. With respect to seismicity related to well stimulation for oil and gas recovery, we will address the effect of fluid injection during the initial hydraulic fracturing stimulation and flowback periods as well as the impact of waste fluid disposal during the entire period of stimulation and subsequent production.

An earthquake is a seismic event that involves sudden slippage along a fault or fracture in the Earth. This process occurs naturally as a result of stresses that build up owing to deformation within the Earth's crust and interior. The size, or magnitude, of an earthquake depends primarily on the surface area of the fault patch that slips and the amount of stress relieved. Earthquake sizes range over many orders of magnitude. There are many more small than large events; roughly, a decrease of one unit in the magnitude scale corresponds roughly to a ten-fold increase in the number of events. As a result, the vast majority of earthquakes can only be detected by sensitive instruments. If, however, the slip area is sufficient to generate an earthquake larger than magnitude 2 to 3 the amount of energy released during the event can generate seismic waves sufficient to produce ground motions that can be felt by humans and in some cases cause structural damage (usually above magnitude 4). Over 1 million natural earthquakes of magnitude 2 or more occur worldwide every year (NRC, 2013).

The mechanism that explains how well stimulation activities can cause earthquakes - i.e., reduction in the forces holding a fault together due to increased fluid pressure in the fault - is fairly well understood (Hubbert and Rubey, 1959). However, applying this knowledge in a predictive sense is difficult because of uncertainties in in situ rock material properties and stress conditions and complexities in well stimulation procedures and the resulting pressure perturbations. Assessing the seismic hazard in a local area due, for example, to fluid injection requires knowledge of pre-existing faults, the state of stress on those faults, rock properties, and subsurface fluid pressures. As in seismic hazard in general, an important part of the hazard assessment procedure is to properly characterize the uncertainties in these input parameters, which are usually large.

To date, the largest observed event caused by hydraulic fracture stimulation itself is the magnitude 3.6 earthquake that occurred in the Horn River Basin in 2011 (see Table 5-8). The lower magnitudes of events associated with hydraulic fracturing relative to those induced by wastewater disposal are generally attributed to the short durations, smaller volumes and smaller pressure disturbances involved in hydraulic fracturing, compared with the longer time periods and much higher volumes of wastewater injection. None of the events related to hydraulic fracturing reported in the literature has occurred in California and (with the possible exception of one paper that discusses a highly anomalous event) we have found no published study that addressed this topic in California. If hydraulic fracturing operations carried out in California to date have, in fact, not caused

normal seismic events above magnitude 2, one possible explanation is the small injected volumes employed so far (Section 3.2.3). A shift to larger volumes, perhaps also combined with a shift to deeper stimulation, could increase the probability of such events occurring, and hence increase the hazard.

The largest observed earthquake suspected to be related to wastewater disposal in the US to date is the 2011 magnitude 5.7 event near Prague, Oklahoma (Keranen et al., 2013; Sumy et al., 2014), although the cause of this event is still under debate (Keller and Holland, 2013; McGarr, 2014). The typical wastewater volumes injected per well in California are generally less than those related to shale hydraulic fracturing operations in other parts of the country where induced events have occurred. For example, to date typical California volumes are about four times less than in the Barnett shale in Texas. This would suggest that at the present time the potential seismic hazard from wastewater disposal in California is low compared with other regions in the US. Expanded hydraulic fracturing activity would, of course, require disposal of larger volumes of fluid, which could potentially increase the hazard.

5.3.2 Mechanics of Earthquakes Induced by Fluid Injection

This section summarizes the physical mechanisms responsible for earthquakes induced by fluid injection and the geological and tectonic conditions that influence their occurrence. The characteristics of pore pressure perturbations and induced seismicity resulting from both well stimulation and wastewater disposal and their potential impact on seismic hazard are discussed in Section 5.4.4.

During fluid injection there can be two types of rock failure, tensile and shear. Below we describe these two types of failure in the context of injection operations related to hydraulic fracturing stimulation.

5.3.2.1 Tensile Fracturing

The primary objective of stimulation is to inject fluid into the earth to create a new fracture (a hydraulic fracture) that connects the pores and existing fractures in the surrounding rock with the well, thus forming a permeability pathway that enables the oil and/or gas (and water) in the pores and fractures to be recovered. Hydraulic fractures are created by the rock failing in tension when the fluid pressure exceeds the in situ minimum principal stress (see Section 5.4.2.3 below). In this type of failure the walls of the fracture move apart perpendicular to the fracture plane. These large-scale hydraulic fractures form slowly (hours) and can extend hundreds of meters away from the well. Although the physical processes at the crack tip are not yet fully understood, it appears that the amount of seismic energy radiated as it propagates is small and difficult to detect. Therefore, hydraulic fracture growth is responsible for little if any of the seismicity recorded in the field, and it probably makes little or no contribution to seismic hazard.

5.3.2.2 Shear Failure on Pre-Existing Faults and Fractures

Shear failure on existing faults and fractures can occur during both stimulation and wastewater disposal. During stimulation shear events serve to enhance the permeability of small, existing fractures and faults and to link them up to create conductive networks connected to the main hydraulic fracture. Shear slip is the type of failure that occurs in most natural tectonic earthquakes, and it is shear events on larger faults that can produce perceptible or damaging ground motions at the Earth's surface.

During a shear event the two faces of the fault slip in opposite directions to each other parallel to the fault surface. The conditions for the initiation of shear slip are governed by the balance between the shear stress applied parallel to the fault surface, the cohesion across the fault and the frictional resistance to sliding (shear strength). Stress is the force applied per unit area. Assuming that the cohesion is negligible, these conditions are summarized in the Coulomb criterion,

$$\tau = \mu(\sigma - p)$$
,

in which an applied shear stress (τ) is balanced by the shear strength, which is the product of the coefficient of friction (μ) and the difference between normal stress (σ) and pore-fluid pressure (p). Shear stress is directed along the fault plane, while normal stress is directed perpendicular to the plane. Nearly all rocks have μ values between 0.6 and 1.0. The quantity (σ -p) is called the effective stress. Effective stress represents the difference between the normal stress, which pushes the two sides of the fault together and increases the frictional strength, and the fluid pressure within the fault, which has the opposite effect. The Coulomb criterion states that slip will occur when the shear stress (τ) exceeds the strength of the fracture (right hand side of the equation). So failure can be instigated by decreasing the effective stress either by decreasing the normal stress (σ) which holds a fracture closed, or by increasing the fluid pressure in the fracture thus pushing the sides of the fracture apart, or by simply increasing the shear stress itself.

5.3.2.3 State of Stress

To assess when a fault will slip according to the Coulomb criterion, it is necessary to know the local state of effective stress, also called in *situ* stress. The *in situ* effective stress state is fully described by pore pressure and three orthogonally directed principal stresses, which are related to the normal and shear stress on a fault by the fault orientation. Within the Earth, the load of the overburden at a given depth usually leads to a compressional state, with one principal stress oriented vertically (σ_v) and having a magnitude equal to the weight per unit area of the overlying rock. This simplifies the problem of determining the complete stress state to estimation of the minimum (σ_h) and maximum (σ_H) horizontal stresses and the azimuth of one of them. However, determining the in situ stress state is still a challenging problem because often only approximate stress directions and the type of stress regime — normal, strike-slip or thrust faulting — are known (e.g., Heidbach et

al., 2008). Stress parameters are inferred from available, often sparse measurements in the region, such as earthquake focal mechanisms, wellbore breakouts and drilling-induced fractures (Zoback and Zoback, 1980; Heidbach et al., 2008). In principle, the relative magnitudes of the principal stresses and the stress azimuths enable identification of the faults that are most favorably oriented for slip and calculation of the normal and shear stress acting on them. However, the scarcity of stress measurements usually permits estimation of resolved stresses acting on faults only with significant uncertainty (e.g. NRC, 2013).

In contrast, Townend and Zoback (2000) proposed that, in general, the ambient pore fluid pressure is near-hydrostatic throughout the brittle, upper crust of the Earth in the interiors of tectonic plates. In this case, pore pressures can be estimated relatively reliably just from the thickness of the overburden. Townend and Zoback (2000) used deep crustal permeability data over nine orders of magnitude acquired from six different regions to suggest that faults within the brittle crust are constantly in a state of critical stress; i.e., an incremental increase in shear stress or increase in pore pressure can lead to rupture. However, the difficulty in accurately estimating the shear and normal stress components often prevents precise determination of how near a particular fault is to failure. Exceptions to commonly assumed hydrostatic pressures occur in some deep basins, such as the Raton Basin in Colorado, where Nelson et al. (2013) showed using drillstem tests that deep formations are underpressured. If the crust within these basins is also critically stressed, then an increment in pore pressure less than that required to reach hydrostatic could bring favorably-oriented faults to failure.

5.3.3 Earthquake Measurements

5.3.3.1 Earthquake Recording and Analysis

Seismic waves radiated by earthquakes are recorded by networks of seismometers placed on the Earth surface or deployed in boreholes. Seismic recordings are used to analyze earthquake source parameters, including location in space and time, magnitude, source type and the direction and amount of fault slip, as well as to understand the properties of the rock layers along the propagation path between the earthquake and seismometer. Record fidelity is commonly referred to as "signal-to-noise," the ratio of signal amplitude to background noise. Placing seismometers in boreholes greatly enhances signal-to-noise, often enabling recording of very small earthquakes (magnitude less than zero).

Earthquake detectability, the minimum magnitude that can be detected at a given location, depends upon the spacing of seismic recording stations within the region. Detectability is usually stated in terms of a threshold magnitude above which a particular earthquake catalog is considered complete. As shown in Figure 5-7, the present completeness threshold is less than magnitude 1 in large areas of California, and less than magnitude 2 over most of the state. This is significantly better than in most other regions of the US, where the completeness threshold provided by the USGS's Advanced National Seismic System (ANSS) backbone monitoring array and regional networks is generally about magnitude

2.5 or greater (see the Figure on p.131 of NRC, 2013). Temporary arrays of seismometers are often installed at sites of particular interest to increase detectability and improve signal-to-noise in order to enable detailed analyses of the spatial and temporal distributions and mechanisms of microearthquakes (e.g., Frohlich et al., 2011).

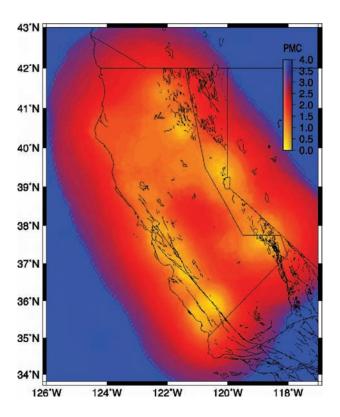


Figure 5-7. Earthquake detectability in California. The map shows the distribution of earthquake magnitudes that can be detected with 99% probability by the USGS ANSS network currently deployed in California (from Bachmann, 2011).

5.3.3.2 Earthquake Magnitude

The size of an earthquake is most commonly expressed as a magnitude, which is a measure of the amount of energy released by slip on the fault. In general terms, the magnitude depends on the size of the area on the fault that undergoes slip. Several magnitude scales are in common use, most of which (e.g. local magnitudes, M_L , and body-wave magnitudes, m_b) are defined based on trace amplitude or signal duration measured on recorded seismograms. However, the moment magnitude (M_w) scale is preferred by most seismologists because M_w is calculated from seismic moment (Hanks and Kanamori, 1979), a more fundamental measure of earthquake size (and energy) that is directly proportional to the product of slip and slipped area. To give an idea of how magnitude relates to slip area, M_w 4.5 and M_w 3.5 earthquakes rupture fault areas of about 2.5 and

0.2 km², respectively. In the remainder of this report we use moment magnitudes when they have been reported and published magnitudes otherwise. In cases when the scale is not specified magnitudes are denoted by "M".

5.3.4 Earthquakes Induced by Subsurface Fluid Injection

In this section, the two fluid injection activities associated with well stimulation that have been observed to induce earthquakes are discussed in terms of their spatial and temporal effects on the distributions of fluid pore pressures.

Fluids are injected into the subsurface for both hydraulic fracturing and wastewater disposal. If elevated pore pressures produced by either hydraulic fracturing or wastewater injection reach nearby faults or fractures, the resulting decrease in effective stress on the fault/ fracture planes can lead to shear slip according to the Coulomb failure mechanism discussed in Section 5.3.2.2. Therefore, in both activities the aim should be to prevent the pressure perturbation from reaching larger faults capable of generating significant seismic events, both to minimize the seismic hazard and, in the case of stimulation, to prevent break out and subsequent leakage from the hydrocarbon reservoir. In general, induced seismicity related to well stimulation is dominated by pore-pressure perturbations, not changes in principal stress (NRC, 2013).

The probability of inducing seismic events is determined by the scale of the injection operation, the spatial extent of the affected subsurface volume, ambient stress conditions, and the presence of faults well-oriented for slip. The primary factors affecting the magnitude and extent of a pore-pressure perturbation include the rate and pressure of fluid injection, the total volume injected, and the hydraulic diffusivity (a measure of how fast a pore-pressure perturbation propagates in a saturated rock). At early stages the size of the pressure perturbation depends on the reservoir's hydraulic diffusivity and the duration of the injection, while the maximum pore pressure depends on the product of injection rate and duration divided by permeability (NRC, 2013). At the later stages of wastewater injection the induced pore-pressure field does not depend on the injection rate or permeability, but becomes proportional to the total volume of fluid injected.

Beginning with the earthquakes induced by fluid injection at the Rocky Mountain Arsenal in the 1960s (Healy et al., 1968), the cases of injection into deep disposal wells discussed below indicate that reactivation of basement faults is the predominant cause of lager magnitude induced earthquakes, including the largest events observed to date. This is because the higher stresses at basement depths and the brittle rheologies of crystalline basement rocks mean that favorably-aligned faults are more likely to reactivate under increased pore pressure. This can occur even when the faults lie below the injection interval as a result of hydraulic communication with the injection zone (Justinic et al., 2013). Although the matrix permeability of basement rock is generally very low, critically stressed faults and fractures in this part of the brittle crust can serve as high permeability channels (Townend and Zoback, 2000). This was shown to be the case during an enhanced geothermal system (EGS) stimulation, in which hydraulic shearing of basement rocks

resulted in migration of microseismicity consistent with a basement hydraulic diffusivity equivalent to sandstone (Fehler et al., 1998; Shapiro et al., 2003).

5.3.4.1 Spatial and Temporal Characteristics

The volume of the subsurface affected by pore-pressure perturbations directly related to hydraulic fracturing treatments are usually largely confined within at most a few hundred meters of the injection interval, as evidenced by observed microseismicity. Davies et al. (2013) suggest possible fluid pathways that may explain how pore pressure reactivates faults in the vicinities of stimulation zones. Induced shear events are mainly caused by fluids "leaking off" into preexisting fractures intersected by the hydraulic fracture. Shear failure may also occur on nearby, favorably oriented fractures isolated from the pressure perturbation due to perturbation of the local stress field near the tip of the propagating hydraulic fracture (e.g. Rutledge and Phillips, 2003).

In contrast, wastewater disposal operations have been shown to generate overpressure fields of much larger extent. For example, at the Rock Mountain Arsenal, CO significant earthquakes caused by fluid injection occurred 10 km away from the well (Healy et al., 1968; Herrmann et al., 1981; Nicholson and Wesson, 1990). Hydrologic modeling of injection into the deep well at the site indicated that the seismicity front tracked a critical pressure surface of 3.2 MPa (Hsieh and Bredehoeft 1981).

The time delay between cessation of injection and the occurrence of larger (M>2) magnitude seismicity can be quite long. For hydraulic fracturing cases, the longest time delay observed so far is almost 24 hours at the Horn River Basin, BC site (BC Oil and Gas Commission, 2012). The 2011 M2.3 earthquake in Blackpool, UK, occurred about 10 hours after injection ceased at the Preese Hall 1 stimulation well (de Pater and Baisch, 2011). In wastewater disposal cases, much longer time delays are sometimes observed. For example, at the Rocky Mountain Arsenal an $M_w4.3$ earthquake occurred 15 years after the injection stopped (Herrmann et al., 1981).

These spatial and temporal observations are critical for understanding the causal relationships between injection activities and induced seismicity. Overall there is a lower potential seismic hazard from short-duration hydraulic fracture operations, because of the relatively small volumes of rock that experience elevated pressures, than from disposal of large volumes of wastewater into a single formation over time periods of months to years (NRC, 2013).

5.3.4.2 Maximum Magnitude

McGarr (2014) proposed estimating upper bounds on induced earthquake magnitudes based on net total injected fluid volume, observing that such a relationship is found to be valid for the largest induced earthquakes that have been attributed to fluid injection. Shapiro et al. (2011) proposed a similar approach to estimating maximum

magnitude, based on the dimensions of the overpressurized zone deduced from observed microseismicity. Brodsky and Lajoie (2014) concluded that induced seismicity rates associated with the Salton Sea geothermal field correlate with net injected volume rate, which lends support to the proposed general dependence of induced seismicity on net injected volume. However, the approaches proposed by both McGarr (2014) and Shapiro et al. (2011) appear to imply that fault rupture induced by the injection occurs only within the volume of pore-pressure increase. While both are based on observations, the alternative, and perhaps more likely, hypothesis is that a rupture that initiates on a fault patch within the overpressured volume can continue to propagate beyond its boundaries, in which case the possible maximum magnitude is determined by the size of the entire fault. Indeed, McGarr (2014) does not regard that his relationship determines an absolute physical limit on event size.

5.3.5 Observations of Induced Seismicity Related to Well Stimulation

The vast majority of earthquakes induced by fluid injection in general do not exceed ~M1 (e.g. Davies et al., 2013; Ellsworth, 2013). However, larger magnitude earthquakes (M>2) have resulted from both wastewater injection and hydraulic fracturing. Table 5-8 summarizes observations of seismicity M>1.5 that have been reported and then investigated due to their correlation in space and time with wastewater injection or hydraulic fracturing activity. The table also includes observations of wastewater injection induced seismicity not related to well stimulation activities because the underlying physical mechanism of induced seismicity from wastewater injection is the same regardless of the source of wastewater; these observations are denoted with a single asterisk in the 'Proximate Activity' column. Where a series of earthquakes occurred, only the largest magnitude is reported.

After first summarizing criteria for classifying an event as induced, we discuss three cases of induced seismicity that resulted from hydraulic fracturing. Then we discuss four cases of seismicity generally accepted as being attributable to wastewater disposal as well as three cases in which the available evidence could not rule out a natural explanation. The seven additional examples of induced seismicity caused by fluid injection not related to well stimulation are listed in Table 5-8 for completeness, but are not discussed further here.

5.3.5.1 Criteria for Classifying an Earthquake as Induced

The following criteria proposed by Davis and Frohlich (1993) have been commonly used to determine whether an earthquake sequence was induced by fluid injection or occurred naturally:

- Are these events the first known earthquakes of this character in the region?
- Is there a clear correlation between injection and seismicity?
- Are epicenters near wells (within 5 km)?

- Do some earthquakes occur at or near injection depths?
- If not, are there known geologic structures that may channel flow to sites of earthquakes?
- Are changes in fluid pressure at well bottoms sufficient to encourage seismicity?
- Are changes in fluid pressure at hypocentral locations sufficient to encourage seismicity?

These criteria provide a basic foundation for establishing whether or not a given sequence has been induced, and have enabled a clear link between seismicity and injection operations to be established in some of the cases listed in Table 5-8. However, used alone, they have proven inadequate to establish conclusively that other sequences were induced. It is often very difficult to prove causality for the following reasons: (1) In some of the cases – including some of those for which the evidence from in-depth scientific study is generally regarded as being conclusive - there is no clear temporal and/or spatial correlation between injection and the occurrence of specific earthquakes, the largest events having occurred several years after the beginning (e.g. Prague OK) or cessation (e.g. Ashtabula OH) of injection, or up to ~ 10 km from the injection well (e.g. Rocky Mountain Arsenal and Paradox Valley in Colorado); (2) Often regional seismic network coverage is too sparse to locate the earthquakes with sufficient accuracy - particularly in depth - to investigate in detail their relationship to the injection well; (3) Even if detailed scientific studies are carried out, they are often hampered by lack of densely-sampled volume and pressure data and adequate site characterization. In particular, subsurface pressure measurements are rarely available; (4) While it is relatively straightforward to apply the first criterion to initially identify suspected cases in regions of low naturally-occurring seismicity such as the central and eastern US, discrimination is much more difficult in active tectonic regions like California, where the rate of naturally-occurring seismicity is much higher.

Table 5-8. Observations of seismicity (M>1.5) correlated with hydraulic fracturing and wastewater injection.

Site/Location	Country	Date	Magnitude	Proximate Activity	Induced?	Reference(s)
Rocky Mountain Arsenal, CO	USA	09 Aug 1967	4.85 M _w	Wastewater injection*	Induced	Healy et al., 1968; Herrmann et al., 1981
Matsushiro	Japan	25 Jan 1970	2.8	Wastewater injection*	Induced	Ohtake, 1974
Rangely, CO	USA	1962 – 1975	3.1 M _L	Wastewater injection*	Induced	Nicholson and Wesson, 1990

Site/Location	Country	Date	Magnitude	Proximate Activity	Induced?	Reference(s)
Love County, OK	USA	1977 – 1979	1.9	Hydraulic Fracturing	Unclear	Nicholson and Wesson, 1990
Perry, OH	USA	1983 – 1987	2.7	Wastewater injection*	Induced	Nicholson and Wesson, 1990
El Dorado, AR	USA	09 Dec 1989	3.0	Wastewater injection*	Induced	Cox, 1991
Paradox Valley, CO	USA	24 Jan	4.0 M _w	Wastewater injection*	Induced	Block et al., 2014
Ashtabula, OH	USA	26 Jan 2001	4.3 m _b	Wastewater injection*	Induced	Seeber et al., 2004
Dallas/Fort Worth, TX	USA	16 May 2009	3.3 m _b	Wastewater injection	Induced	Frohlich et al., 2011
Cleburne, TX	USA	09 Jun 2009	2.8 m _b	Wastewater injection	Unclear	Justinic et al., 2013
Garvin County, OK	USA	18 Jan 2011	2.9 M _L	Hydraulic fracturing	Induced	Holland, 2013
Guy-Greenbrier, AR	USA	27 Feb 2011	4.7	Wastewater injection	Induced	Horton, 2012
Blackpool	UK	01 Apr 2011	2.3 M _L	Hydraulic fracturing	Induced	de Pater and Baisch, 2011; Green et al., 2012
Prague, OK	USA	05 Nov 2011	5.7 M _w	Wastewater injection	Induced	Keranen et al., 2013
Youngstown, OH	USA	31 Dec 2011	3.9 M _w	Wastewater injection	Induced	Kim, 2013
Horn River Basin, BC	CAN	19 May 2011	3.6 M _L	Hydraulic fracturing	Induced	BC Oil and Gas Commission, 2012
Raton Basin, CO	USA	23 Aug 2011	5.3 M _w	Wastewater injection	Induced	(see McGarr, 2014)
Timpson, TX	USA	17 May 2012	4.8 M _w	Wastewater injection	Unclear	Frohlich et al., 2014

 $^{^{*}}$ Disposed fluids did not result from hydraulic fracturing

5.3.5.2 Observations of Induced Seismicity Attributed to Hydraulic Fracturing

Several series of M>2 earthquakes have been linked to hydraulic fracturing treatments through detailed scientific investigation. These include the sequences on April 2011, $M_L 2.3$ in Blackpool, UK (de Pater and Baisch, 2011; Green et al., 2012); January 2011, $M_L 2.9$ in Garvin County, OK (Holland, 2013); and May 2011, $M_L 3.6$ in the Horn River Basin, British Columbia (BC Oil and Gas Commission, 2012).

The $M_L 2.3$ earthquake near Blackpool, UK, was attributed to hydraulic fracturing in the Preese Hall 1 well (de Pater and Baisch, 2011). A second $M_L 1.5$ event occurred near the same well in May 2011. Both events occurred at about 2 km (1.2 mi) depth. These events are believed to have resulted from hydraulic connection out to distances further than anticipated, facilitated by bedding planes. Prior to August 2012, this event was the only documented observation of hydraulic fracturing-induced seismicity of magnitude greater than 1.

In January 2011, a sequence of earthquakes (maximum $M_L 2.8$) occurred in close proximity to a hydraulic fracturing treatment operation in the Eola Field, Oklahoma. Initial reporting of the events (Holland, 2011) could not establish a conclusive link to well stimulation. Only after the operator released detailed production data, including underground pressure and injection rate, were the events clearly identified as having been induced (Holland, 2013). This clarification was made possible in part because the earthquake activity ceased during a two-day break in well stimulation due to bad weather and then began again when stimulation resumed.

The largest magnitude earthquakes observed to result from hydraulic fracturing (maximum M_L 3.6) occurred in the Horn River Basin in British Columbia, Canada between April 2009 and December 2011 (BC Oil and Gas Commission, 2012). Twenty earthquakes in this series were above M_L 3. Although the regional earthquake recording system is unable to detect M<2 earthquakes, all seismic events detected in the Horn River Basin occurred during or between hydraulic fracturing treatments. There are numerous north-south trending sub-parallel faults in the region. Average total fluid volume injected per well was 61,612 m^3 (16,276,000 gal) with an average injection rate of 18,720 m^3 /day (4,945,000 gal/day).

Nicholson and Wesson (1990) reported on two earthquake series in Oklahoma that occurred in June 1978 and May 1979. The largest of these was M1.9. In each case, nearby hydraulic-fracturing operations correlated with the seismic events, but a lack of local seismic recording resulted in large location uncertainties and prevented a clear determination that the events were induced.

5.3.5.3 Observations of Induced Seismicity Attributed to Water Disposal

There are many cases in which disposal of wastewater related to hydraulic fracturing via Class II wells is the most likely explanation of seismicity. These include seismic events in Dallas-Fort Worth, TX, Guy, AR, Youngstown, OH, Prague, OH, and Raton Basin, CO. In other cases (Cleburne, TX; Timpson, TX), wastewater injection represents one possible explanation, but it was impossible to rule out that the earthquakes were of natural origin.

Texas, like many states east of the Rocky Mountains, had a low rate of natural seismicity before well stimulation began in the Barnett Shale. For example, there were no local felt earthquakes in Dallas-Fort Worth (DFW), TX between 1850 and 2008. Beginning in October 2008, seven weeks after Chesapeake Oil and Gas Company began injecting

wastewater in a disposal well in the DFW area, felt earthquakes ($m_b 2.5 - 3.3$) began to be reported by the public. This prompted researchers to deploy a local seismometer array in the area. The local array enabled a reduction in the location uncertainty of the 11 recorded earthquakes from ± 10 km (6 mi) to ± 200 m (0.125 mi) (Frohlich et al., 2010). These events were all located within 1 km of a northeast-trending normal fault, favorably oriented in the N40 – 47°E regional stress field, and 200 m north (on average) of a water disposal well. Brine-injection volumes for this well averaged 950 – 1,310 m³/day (252,000 – 346,500 gal/day) during the period covered by the temporary array, which is a typical rate for disposal wells in this and neighboring counties. The depth of wastewater injection in this well (3.1 – 4.1 km; 10,100 – 14,400 ft) was ~1 km (3,300 ft) above the average depth of recorded seismicity (4.4 – 4.8 km; 14,400 – 15,700 ft). Felt seismicity (M>2) continues to occur in the DFW area more than two years after injection ceased in the disposal well.

The following month, in Cleburne, TX, about 50 km southwest of DFW, another series of earthquakes occurred (maximum magnitude $m_b 2.8$) in another area of prior quiescence that contained nearby active water-disposal wells (Justinic et al., 2013). Continuous injection began two years prior to the onset of seismicity. The lack of fluid-pressure data barred detailed understanding of how seismicity correlated with injection, and ultimately prevented positive identification of this series as natural or induced.

On May 17, 2012, a third case of potentially induced seismicity in Texas occurred near Timpson (Frohlich et al., 2014). Epicenters of the earthquake series (maximum $M_w4.8$) lie along a mapped basement fault about 6 km long. Four active water disposal wells lie within about 3 km of the epicenters and near the largest magnitude event. Total injected volumes for the two largest volume wells were 1,050,000 m³ and 2,900,000 m³ (277 billion gallons and 766 billion gallons), with average injection rates exceeding 16,000 m³/mo (420,000 gallons/mo). The injection interval for all four wells was 1.8 - 1.9 km (5,900 – 6,200 ft), and the top of the basement is at a depth of approximately 5 km (16,000 ft). The five largest earthquakes occurred between depths of 2.75 and 4.5 km (9,000 and 14,800 ft). Although the evidence favors the conclusion that these events were induced, Frohlich et al., (2014) could not rule out the possibility that they occurred naturally.

In central Arkansas, disposal of wastewater from hydraulic fracturing operations in the Fayetteville Shale has been correlated with 224 earthquakes of magnitude M>2.5 that occurred between 2007 and 2011. The largest event, M4.7, occurred on February 27, 2011 (Horton, 2012). In an area of generally diffuse seismicity, 98% of the recent earthquakes occurred within 6 km (3.7 mi.) of three Class II disposal wells. One injection well appears to intersect the Guy-Greenbrier fault within the basement, which is suitably oriented for slip within the regional tectonic stress field (Horton, 2012).

The largest earthquake suspected of being related to injection of wastewater from well stimulation was an M_w 5.7 event that occurred within a region of previously sparse seismicity near Prague, OK on November 6, 2011 (Keranen et al., 2013; Sumy et al., 2014). This

event is the second largest earthquake instrumentally recorded in the eastern US, and it destroyed 14 homes and injured two people. The hypocenter was located on the previously mapped NNE-SSW-striking Wilzetta fault system and was followed two days later by an M_w5.0 about 2 km to the west. Sumy et al. (2014) proposed that the M_w5.7 mainshock was triggered by an M_w5.0 foreshock that occurred the previous day approximately 2 km from two active wastewater injection wells located within the Wilzetta North oilfield. One well injected into the previously depleted Hunton Limestone reservoir, while the other injected into two deeper formations. The zone of well-located aftershocks of this event extends along the strike of the fault to within about 200 m of these wells. Although injection into the first well began in 1993, the cumulative rate of injection was increased by starting injection into the second, deeper well in December 2005, accompanied by a tenfold increase in wellhead pressure; pressures at both wells averaged approximately 3.5 MPa (508 psi) between 2006 and December 2010, falling to 1.8 MPa (261 psi) in 2011. Keranen et al. also note that local earthquake activity began with an M_w4.1 earthquake a few km from the 2011 mainshock in 2010, during the period of near-peak wellhead pressures, but they do not mention microseismicity before or after this event.

Keranen et al. (2013) concluded that the November 5, 2011 M_w 5 event was likely induced by a progressive buildup of overpressure in the effectively sealed reservoir compartment and on its bounding faults (part of the Wilzetta fault system) after the original fluid volume capacity of the depleted reservoir had been exceeded as a result of injection. However, this explanation apparently does not take into account injection into the deeper formations, which are separated from the reservoir by a (presumably relatively low-permeability) shale layer. An alternative explanation might be that the triggering mechanism involved only the more recent injection into the deeper formations, the lowest of which directly overlays basement. McGarr (2014) proposed that the M_w5.7 mainshock was induced directly by injection of much larger volumes into three wells located 10 to 12 km southeast of the epicenter. However, if, as asserted by Keranen et al., the faults of the Wilzetta system form barriers to lateral (SE-NW) flow that compartmentalize the oilfield then it would not be expected that the wells discussed by McGarr would be in hydraulic communication with the westernmost fault of the system on which the earthquake apparently occurred. The occurrence of these events close to several high-volume injection wells strongly suggests that they were likely induced. However, the six-year delay between the significant increase in injection rate and pressure in the Wilzetta North wells and the conflicting hypotheses regarding the source and magnitude of the pressure perturbation mean that natural causes, as proposed by Keller and Holland (2013), cannot at present be ruled out.

During a 14-month period in Youngstown, OH, an area of relatively low historic seismicity, 167 earthquakes (M≤3.9) were recorded in proximity to ongoing wastewater injection (Kim, 2013). Earthquake depths were in the range 3.5–4.0 km and located along basement faults. Given that relatively small fluid volumes (~700 m³; ~180,000 gallons) were injected prior to the onset of seismicity, there is believed to be a near-direct hydraulic

connection to a pre-existing fault. Periods of high and low seismicity tracked maximum and minimum injection rates and pressures. The total injected volume over this period was 78,798 m³ (20,816,000 gallons) with an average injection volume of 350 m³/day (1,150 gallons/day) at a pressure of 17.2 MPa (2,490 psi).

Induced seismicity ($M_W \le 5.3$) near Raton Basin, CO, is believed to have been caused by injection of 7.8 million m³ (2.1 billion gallons) of wastewater near the southwestern extension of the local fault zone (Rubenstein, et al., 2014, submitted; manuscript referenced in McGarr, 2014). Since this study has not yet been published we are unable to report its conclusions.

5.3.6 Factors Affecting the Potential for Induced Seismicity in California

All of the US cases of induced seismicity related to fluid injection listed in Table 5-8 occurred within the stable continental interior, where tectonic deformation rates are low. California, on the other hand, is situated within an active tectonic plate margin, where the relatively rapid shear stressing rate on the numerous active faults result in much higher seismicity rates, as can be seen in Figure 5-9. If, as discussed in Section 5.3.4 and 5.3.2.3, the Earth's upper crust is generally in a critically-stressed state, then the high loading rates would imply that a relatively high proportion of faults in California will be close to failure at any given time, and hence susceptible to earthquakes triggered by small effective or shear stress perturbations. The abundance of faults large enough to generate M5 and greater earthquakes would suggest that there exists the potential for inducing earthquakes in California at least as large as those observed to date in the mid-continent, and also raises the question of whether earthquakes induced by stress perturbations at typical oil reservoir depths (<5 km) could trigger large (magnitude >6) tectonic earthquakes. However, whereas earthquakes in intraplate regions are often observed to nucleate within the upper few km, suggesting that the seismogenic crust in these regions extends to shallow depths (e.g. Adams et al., 1991; McGarr et al., 2002), evidence suggests that within active plate boundaries like California large earthquakes tend to nucleate at the base of the seismogenic crust at depths on the order of 10 km or greater (e.g. Mori and Abercrombie, 1997; Sibson, 1982). (One notable exception to this was the 1992 M_w7.3 Landers earthquake under the Mojave desert, which nucleated at a depth of 3-6 km.) Mori and Abercrombie (1997) (see also Scholz, 2002) proposed that the upper crust in active regions is more heterogeneous and the prevailing stresses are lower, so that earthquake ruptures that nucleate there are more likely to be arrested before they can grow into large events. Therefore, according to this argument, induced earthquakes in intraplate regions nucleate at or near the top of the seismogenic crust and are more likely to grow into larger events given a sufficiently large fault, but the magnitudes of earthquakes induced at reservoir depths in California are likely to be limited, perhaps below $M_{w} \sim 5.5$.

Assessment of the potential for induced seismicity, and hence the possible increase in seismic hazard, in California requires data on present and possible future WST activities, and the locations and characteristics of faults and in situ stresses in relation to those activities. Details of WST activities are described in Chapter 2. In the following sections,

available fault and stress data are first summarized, followed by a discussion of recorded seismicity and its relation to current and likely future locations of injection activity.

5.3.6.1 California Faults and Tectonic Stress Field

Unlike the central and eastern US, a large number of active faults have been mapped and characterized in California. Figures 5-8 through 5-10 show the surface traces of active faults in California south of latitude 37° contained in the Uniform California Earthquake Rupture Forecast, Version 3 (UCERF3) Fault Model 3.1, prepared by the Working Group on California Earthquake Probabilities (Field et al., 2014). This database contains characterizations, including geometry and average slip rates, of faults known of believed to be active during the Quaternary (the last 2.6 million years). While particular attention should paid to these faults in assessing the potential for induced seismicity (and in siting WST activities), inactive local faults that are suitably oriented for slip in the prevailing in *situ* stress field need to be taken into account (see Section 5.3.6 and 5.34.2.3). The possible presence of unmapped faults, such as the basement faults activated in some of the recent cases of induced seismicity discussed above, also need to be considered. These may be detectable in seismic data acquired during exploration and reservoir characterization, or may be illuminated by microseismicity recorded during early stages of injection.

The most recent published stress data for California are contained in the World Stress Map catalog compiled by Heidbach et al. (2008). Figure 5-8 shows only the highest quality (quality A in the catalog) stress measurements for the southern part of California. These point measurements of the orientation of the tectonic stress field, and in some cases the magnitudes of principal stress components, are derived from observations of wellbore breakouts, earthquake focal mechanisms, tiltmeter monitoring of hydraulic fractures, and geological strain indicators

Although there are a large number of stress measurements in California compared with other regions of the US, the catalog provides only a sparse sampling of the stress field. While overall trends appear relatively uniform, for example a NW-SE maximum horizontal stress direction in the southern San Joaquin and Santa Maria Basins, significant variations are evident. This is to be expected because stress states at the local scale are complicated by heterogeneous distributions of fractures and fracture orientations and are influenced by changes in lithology and rock material properties (e.g. Finkbeiner et al., 1997). Ideally, stress measurements at a given injection site are needed to assess the potential for induced seismicity. To achieve this, it may be possible to employ other measurement techniques in addition to using borehole data. For example, in a hydraulic fracturing experiment in the Monterey formation, Shemeta et al., 1994 studied the geometry of the vertical fracture using continuously recorded microseismic data, regional stress information, and well logs. They found that the microseismic and well data were consistent with both the regional tectonic stress field and fracture orientations observed in core samples and microscanner and televiewer logs. The results of this study suggest that observations of the natural fracture system can be used as indicators for the orientations of induced fractures and hence of the in situ stress.

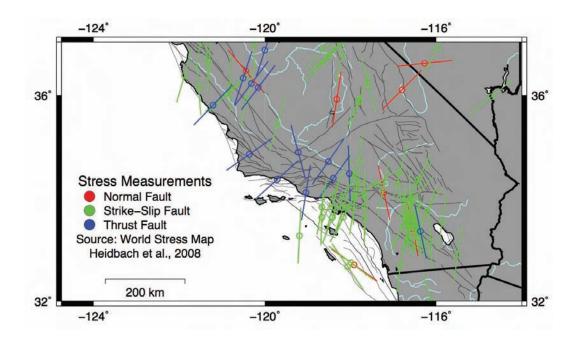


Figure 5-8. Highest quality stress measurements for California from the World Stress Map (Heidbach et al., 2008), plotted with mapped faults from UCERF3 FM 3.1 (Field et al., 2014). Stress measurements show orientation of the maximum horizontal compressive stress direction, color-coded according to stress regime.

5.3.6.2 Naturally-Occurring and Induced Seismicity in California

The generally low-magnitude detection threshold in California discussed in Section 5.3.3.1 means that Californian earthquake catalogs provide a relatively high-resolution picture of seismicity in the state as a whole. Figure 5-9 shows high-precision, relocated epicenters (Hauksson et al., 2012;) of southern California earthquakes recorded between 1981 and 2011, contained in the Southern California Earthquake Data Center catalog (SCEDC, 2013). Intense seismicity occurs along the major fault systems like the San Andreas and Eastern California Shear Zone, and includes relatively frequent (10s to 100s of years), large ($\rm M_w > 6$) earthquakes. Large events accompanied by aftershock sequences have also occurred during this 30-year time period along the western slopes of the Central Valley near Coalinga (1983), near Northridge north of Los Angeles (1994), and along the coast near San Simeon (2003). Elsewhere, lower-magnitude seismicity is generally more diffuse.

In addition to the Los Angeles basin, areas of the southern San Joaquin, Ventura, Santa Clarita and Santa Maria basins, where active water disposal wells are concentrated at present (Figure 5-10), have relatively high rates of seismicity in the 2-5 magnitude range. While undoubtedly most of these earthquakes are naturally-occurring, detailed study of the seismicity in relation to fluid injection will be needed to assess the likelihood that a

proportion of the events in these areas are induced. There are numerous published studies of induced seismicity associated with production from geothermal fields in California (e.g. Eberhart-Phillips and Oppenheimer, 1984; Majer et al., 2007; Kaven et al., 2014; Brodsky and Lajoie, 2013). However, while microseismic monitoring is routinely used to monitor hydraulic fracturing operations (e.g. Murer et al., 2012), no systematic study to examine possible correlations of significant (M>2) seismicity with well stimulation or other fluid injection operations at oil and gas fields in California has yet been completed or published.

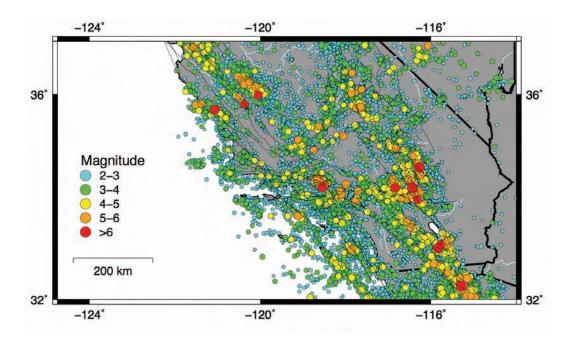


Figure 5-9. High-precision earthquake locations 1981-2011 from Hauksson et al. (2011). Faults as in Figure 5-8.

To our knowledge, in only one published paper (Kanamori and Hauksson, 1992) was a California earthquake greater than magnitude 2 linked to oilfield fluid injection. In that case, the authors attributed the occurrence of a very shallow M_L3.5 slow-slip event to hydraulic fracture injection at the Orcutt oilfield in the Santa Maria basin. This event was anomalous in that it radiated much lower energy at much lower dominant frequencies than normal earthquakes of similar size. One reason for the lack of progress on this front to date is that unlike stable plate interiors, where identification of anthropogenic seismicity is relatively easy, one of the major challenges in tectonically-active regions is the problem mentioned previously of discriminating between induced and naturally-occurring events (e.g. Brodsky and Lajoie, 2013). The University of Southern California Induced Seismicity Consortium is currently carrying out a study of spatial and temporal variations in seismicity statistics in relation to active oilfields in the southern San Joaquin basin. Preliminary results reported by Aminzadeh and Gobel (2013) suggest that systematic differences in earthquake frequency-magnitude distributions and other characteristics may be a promising tool for identifying induced seismicity.

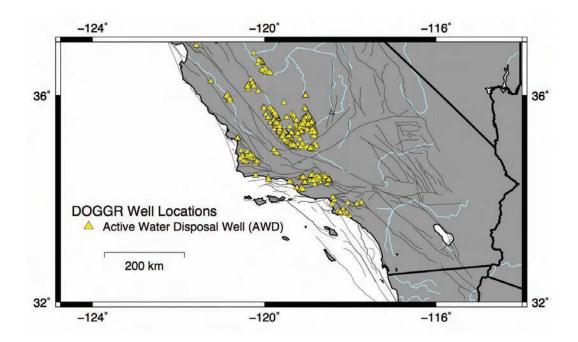


Figure 5-10. Locations of 1509 active water disposal wells from DOGGR (2014b). Faults as in Figure 5-8.

5.3.6.3 Wastewater Disposal Activity in California

With the exception of the San Joaquin Valley, presently active wastewater disposal wells shown in Figure 5-10 are in general situated within a few km of mapped Quaternary active surface faults. Wells along the western margin of the southern San Joaquin Valley are more than 10 km (~6 mi.) away from the San Andreas fault, but several of the southernmost wells are within a few km of the historically active (M_w7.3) White Wolf fault. The crystalline basement under the western margin is 10-12 km deep. The basement surface slopes upward to outcrop at the Sierra front, and in the vicinity of Bakersfield it is at a depth of about 2-3 km, much closer to reservoir depths. In this respect the setting towards the eastern Valley margin appears more similar to that in the midcontinent than in other oil-producing basins in California, although, as discussed previously, the shallow basement may not be capable of nucleating large (M>6) tectonic earthquakes. Within and on the margins of other currently producing basins the structure is generally much more complex, and basement depths are highly variable. Injection depths are available for roughly twenty percent (20%) of the ~1500 active water disposal wells in the DOGGR (2014b) database. Of these, 21 wells in their current configurations have the deepest injection interval at a depth greater than 1.8 km (6,000 ft) (DOGGR, 2014c).

Currently, the total disposal volume per well in California is generally less than in other regions where well stimulation is taking place. According to DOGGR (2010) (the most recent annual report available), total annual wastewater disposed in 2009 for Kern County was approximately 79.4 million m³ (2.1 billion gal) into 611 active wells. This indicates an average disposal rate of about 360 m³ (95,000 gallons) per well per day. This is one-fourth of the average 2008 water disposal rate per well of 1,430 m³ (378,000 gallons) per day in Tarrant and Johnson Counties, Texas, where the Dallas-Fort Worth events occurred (Frohlich et al., 2010).

In-depth analyses are required to examine relationships, in any, of past and current wastewater disposal to seismicity and possible surface and basement fault sources. The results of the analyses will provide a foundation for assessing the potential for induced seismicity as a result of disposing of substantially larger volumes of wastewater, and perhaps also from carrying out hydraulic fracturing in the significantly deeper Monterey source formations. This assessment will form the basis for quantitative seismic hazard analyses at basin scale utilizing the approaches outlined below. In other areas in the US where stimulation-related induced seismicity has occurred, access to accurate, finely sampled (volume per day) injection rate data was a critical piece of information required to demonstrate a causal link.

5.3.7 Induced Seismic Hazard and Risk Assessment

Seismic hazard is defined as the annual probability that a specific level of ground shaking will occur at a particular location. Seismic risk is the probability of a consequence, such as deaths and injuries or a particular degree of building damage, resulting from the shaking. Risk, therefore, combines the hazard with the vulnerability of the population and built infrastructure to shaking, so that for the same hazard the risk is higher in densely populated areas. Seismic hazard maps are developed for California by the USGS and California Geological survey as part of the National Seismic Hazards Mapping Project (http://earthquake.usgs.gov/hazards/index.php). Of the areas in which water disposal wells are currently active (Figure 5-10), seismic hazard from naturally-occurring earthquakes is high in the Los Angeles and Ventura Basins and the Santa Clarita Valley, moderate in the Santa Maria Basin and moderate to high along the western and southern flanks of the southern San Joaquin Valley. The hazard decreases towards the center of the Valley and is relatively low in the Bakersfield area.

Rigorous assessment of the incremental hazard and risk from induced seismicity will be needed both for regulatory purposes and, in the worst-case scenario, for determining liability. In addition to the probability of damage and casualties dealt with in conventional seismic risk analysis, the risk of public nuisance from small, shallow events that occur relatively frequently has also to be considered. Approaches to assess induced seismicity risk can be developed by adapting standard probabilistic seismic hazard assessment (PSHA) and probabilistic seismic risk assessment (PSRA) methods, such as that used by the USGS and CGS. The standard methods cannot be applied directly, however, because

(except on a few of the best-characterized fault segments of the San Andreas system) conventional PSHA is based only on mean long-term (100s to 1000s of years) earthquake occurrence rates; i.e. earthquake occurrence is assumed to be time-independent. Induced seismicity, on the other hand, is strongly time- and space-dependent because it is driven by the evolution of the pore pressure field, which must therefore be built in to the calculation of earthquake frequencies and spatial distributions. There is also the problem of discriminating induced from naturally-occurring events.

Developing a rigorous PSHA method for short- and long-term hazards from induced seismicity presents a significant challenge. In particular, no satisfactory method of calculating the hazard in the planning and regulatory phases of a project is available at the present time. This is largely because, whereas in conventional PSHA earthquake frequency-magnitude statistics for a given region are derived from the record of past earthquakes, obviously no such record can exist prior to injection. Using seismicity observed at an assumed "analog" site as a proxy (e.g. Cladouhos, 2012) would not appear to be a satisfactory approach because induced seismicity is in general highly dependent on site-specific subsurface structure and rock properties. Physics-based approaches to generate simulated catalogs of induced seismicity at a given site for prescribed sets of injection parameters are under development (e.g. Foxall et al., 2013). Such approaches rely on adequate characterization of the site geology, hydrogeology, stress and material properties, which are inevitably subject to significant uncertainties (see Chapter 4, Section 5.3 and Section 5.3.6). However, large uncertainties in input parameters are inherent in PSHA in general, and techniques for propagating them to provide rigorous estimates of the uncertainty in the final hazard have been developed.

There has been more progress in developing methods for short-term hazard forecasting based on automated, near real-time empirical analysis of microseismicity recorded by a locally-deployed seismic network once injection is underway (e.g. Bachmann et al., 2011; Mena et al., 2013; Shapiro et al., 2007). Continuously-updated hazard assessments can form the input to a real-time mitigation procedure (Bachmann et al., 2011; Mena et al., 2013), as outlined in the following section (5.3.7.1). Using two different time-dependent empirical models, Bachmann et al. (2011) and Mena et al. (2013) were able to obtain acceptable overall fits of forecast to observed seismicity rates induced by the 2006 EGS injection in Basel, Switzerland over time periods ranging from 6 hours to 2 weeks. However, the forecast occurrence probability of the largest event (M_L3.4), which occurred after well shut-in, was only 15%, and the probability of exceeding the maximum observed ground motion was calculated as 5%. The performance of the method could probably be improved by incorporating a more physically-based dependence on injection rate or pressure (C. Bachmann, personal communication, 2014).

5.3.7.1 Protocols for Evaluating and Reducing the Risk from Induced Seismicity

The issue of induced seismicity is not new or unique to the oil and gas industry. The geothermal industry has had projects not only delayed, but cancelled due to induced seismicity (Majer et al 2007). In 2004 the US DOE and the IEA started an effort to develop

protocols and best practices to guide all stakeholders (operators, public, regulators, policy makers) to aid the geothermal industry to advance in a cost effective and safe manner. These protocols/best practices (Majer et al., 2009, 2012, Majer et al., 2014) were jointly developed by researchers, industry and geotechnical engineers. They were not intended to be a universally applicable approach to induced seismicity management, but rather a suggested methodology to observe, evaluate, understand and manage induced seismicity at a geothermal project. It is not a "one size fits all" approach, and stakeholders should tailor their actions to project-specific needs and circumstances.

The oil and gas industry outside of California, especially in the midcontinent, is now facing the same issues with induced seismicity that the geothermal industry faced in the early 2000's, including public resistance, felt seismicity that is being attributed (rightly or wrongly) to oil and gas operations, and potential regulatory requirements. Therefore, based on the experiences in the geothermal industry, similar protocols and best practices are beginning to be developed by oil and gas companies (mainly in the midcontinent) to implement practices and tools for dealing with induced seismicity issues. Two examples of such protocols are the ones being developed by the Oklahoma Geological Survey and also by an industry consortium of companies in the American Exploration and Production Council (AXPC), a national trade association representing 34 of America's independent natural gas and oil exploration companies (personal communication, Austin Holland, Oklahoma Geological Survey; Hal McCartney AXPC). Another example of a "protocol" that resembles the geothermal protocol is Zoback (2012), which describes similar steps and could also be used as a guide for oil and gas companies.

Most protocols are a "common sense" approach but guided by the best available science. They are not regulatory documents; consequently the protocols are intended to be living documents and evolve as needed. As new knowledge and experience is gained the protocols should be updated and refined to match "accepted" practices. In the geothermal and other protocols, there is series of recommended steps to address the hazard and risks associated with induced seismicity. Not all steps may be needed and the order of steps may vary. How the protocol is implemented will depend upon such factors as project location, past seismicity, community acceptance needs, current monitoring of seismicity, geologic conditions, past experiences with induced seismicity, and proximity to sensitive facilities. As an example, the geothermal protocol has the following steps for addressing induced seismicity issues as they relate to the whole project. All of the protocols have varying degrees of the following steps. (For details of the protocols, refer to the published editions referenced above.)

 Perform a preliminary screening evaluation. (Does the project pass basic hazard criteria, i.e. proximity to known active faults, past induced seismicity, near population centers, amount of injection and time of injection, public acceptance issues etc.)

- Implement an outreach and communication program. (Keep the community informed and educated on anticipated hazards and risk. An important step is gaining acceptance by non-industry stakeholders and promoting safety, the protocols outline the suggested steps a developer should follow to address induced seismicity issues)
- 3. Review and select criteria for ground vibration and noise. (Which communities, types of structures, etc. will be affected by any induced seismicity; this will inform criteria for setting maximum event sizes)
- 4. Establish seismic monitoring. (What has been the past seismicity in the area. Also allow data to be collected to develop an understanding of the origin (in space and in time) of any seismicity in the area and help determine if it is induced or natural)
- 5. Quantify the hazard from natural and induced seismic events. (How big an event is expected and what are the seismicity rates and magnitude distributions. For induced seismicity this may be difficult with a limited amount of geologic and site condition knowledge)
- 6. Characterize the risk of induced seismic events. (Given information in steps 3,4, and 5) perform a risk analysis. As discussed in Section 5.4.7 this is a challenging problem for induced seismicity, but at least bounds on risk should be estimated.)
- 7. Develop risk-based mitigation plan. (Such as a stop light procedure as described below, appropriate insurance coverage, etc.)

Figure 5-11 shows an example implementation strategy for the oil and gas induced seismicity protocol that the AXPC is considering. This step-wise approach will depend on specifics of the site and activity. This is a proposed draft that was shown at the KCC/KGS/KDHE Induced Seismicity State Task Force Meeting in Wichita, KS April 16, 2013.

The success of developing specific induced seismicity protocols for WST has yet to be evaluated in the midcontinent, let alone California. In terms of how such risk-reduction protocols may be defined and implemented for WST in California, one would expect a strong similarity to the response of the California geothermal industry. Many geothermal operators in the western US are successfully implementing either all or parts of the geothermal protocol. In addition, the BLM is using the geothermal protocol to develop its own criteria for geothermal permitting on BLM land in the U.S. as a whole.

Current real-time induced seismicity monitoring and mitigation strategies used by most enhanced geothermal system (EGS) operators employ a traffic light system (see Step 7 in the sample protocol above), originally developed for the Berlin geothermal project in El Salavador (Bommer et al., 2006). The traffic light system may incorporate up to four stages of response to seismicity as it occurs, and is generally based on some combination of maximum observed magnitude, measured peak ground velocity and public response.

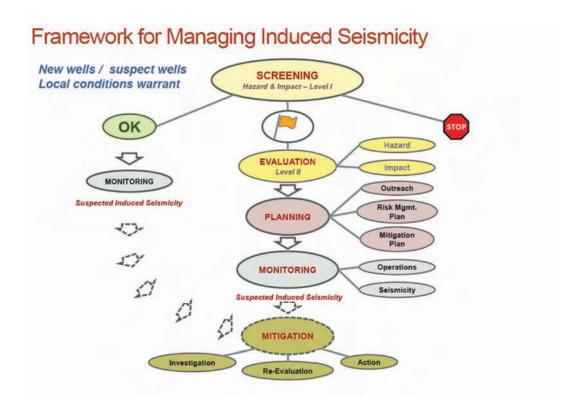


Figure 5-11. This example represents the collective thoughts of subject matter experts drawn from AXPC member companies and other Oil and Gas Industry companies. The subject matter experts include geologists, geophysicists, hydrologists, and regulatory specialists. This is a proposed draft that was shown at the KCC/KGS/KDHE Induced Seismicity State Task Force Meeting in Wichita, KS April 16, 2013. This presentation does not represent the views of any specific trade association or company.

Based on these criteria the injection will be either: 1) continued as planned (green); 2) continued but without increasing the rate (yellow); 3) stopped and pressure bleed-off initiated (orange); or 4) stopped with bleed-off to minimum wellhead pressure (red). Exact definition of these criteria is usually somewhat ad hoc and depends on the project scenario. The traffic light procedure implemented at the Basel EGS project was not successful in preventing the occurrence of the M_L 3.4 earthquake on the same day that shut down the project, even though the orange stage was triggered after an M_L 2.7 and the well eventually shut down. The traffic light system implemented at the St Gallen, Switzerland EGS project was also unsuccessful in preventing a strongly-felt earthquake that caused minor damage, but the circumstances in that case were highly unusual. The EGS community is currently beginning development of traffic light methods that employ near-real time hazard updating like that reported by Bachmann et al. (2011) and Mena et al. (2013). These will provide input for truly predictive, risk-based decision making based on the evolving seismicity and state of the reservoir.

5.3.8 Summary of Induced Seismicity Hazard Assessment

The severity of ground shaking generated by an earthquake depends on it's magnitude, the proximity of the surface site to the earthquake source, the geology along the seismic wave propagation path, and the local soil or rock conditions. For example, an m³ earthquake that would likely not be felt if it occurred at a normal seismogenic depth for California would most likely be strongly felt if it occurred nearby at the relatively shallow depths at which most fluid injections take place.

The underlying general mechanism for how well stimulation activities induce seismic events is fairly well understood. However, applying this knowledge in a predictive sense to assess seismic hazard is difficult because of complexities in geology, subsurface fluid flow and well stimulation technology. Advances in coupled hydro-geomechanical modeling and simulation of fluid injection and hydraulic fracturing are beginning to explain how they affect fracture propagation and fault rupture (e.g. Rutqvist et al., 2013). Assessing the seismic hazard in a local area due to, for example fluid injection, requires knowledge of pre-existing faults, the state of stress on those faults, the evolving subsurface pressure field, and fault and rock properties, but many of these parameters will be known only with large uncertainties. However, seismic hazard assessment in general is invariably subject to considerable uncertainty, and an important and mature part of the analysis procedure is to properly characterize the uncertainties in the input parameter and then propagate them through the calculation to provide rigorous uncertainty bounds on the final hazard estimates.

To date, the maximum observed magnitude caused by hydraulic fracturing is $\rm M_L 3.6$ (BC Oil and Gas Commission, 2012). The largest earthquake suspected of being related to wastewater disposal is $\rm M_w 5.7$ (Keranen et al., 2013; Sumy et al., 2014), but the causal mechanism of this event is still the subject of active research and the possibility that it was a natural tectonic earthquake cannot, at present, confidently be ruled out. Overall, the likelihood of such an event occurring in the US as a whole is extremely low, given the current scale of well stimulation activities and the small handful of cases of significant induced seismicity experienced to date.

Hydraulic fracturing as it is carried out at the present time in California is not considered to pose a high seismic hazard. Apart from one highly anomalous event reported by Kanamori and Hauksson (1992), there have been no other published reports of felt seismicity related to either hydraulic fracturing or wastewater disposal in California. However, in many areas of California discriminating small induced events in the 2-4 magnitude range from frequently occurring natural events poses a significant challenge, and systematic studies have begun only recently. The duration and extent of the pressure disturbance from hydraulic fracturing in general are relatively small and, based on experience elsewhere, appear unlikely to generate larger felt or damaging events. The lack of reported felt seismicity for hydraulic fracturing in California is consistent with the relatively shallow injection depths (Section 5.2.3.2.1) and small injection volumes

(Section 3.2.3) currently employed in California operations. A shift to deeper stimulation, particularly if combined with increased injection volumes, could increase the seismic hazard to some degree.

The total volume of wastewater injected in California is much larger than the volume used for well stimulation. However, because present injection volumes are relatively small and injection intervals are shallow compared to other areas of the United States, the seismic hazard related to current wastewater injection is also likely to be relatively low. For example, California's disposed water volume per wastewater-injection well is about four times less and 1.5–2.7 km (4,700–7,700 ft) shallower than disposal into the wells in the vicinity of the Barnett Shale where induced events have occurred (Frohlich et al., 2010). However, further studies of the relationship, if any, between wastewater injection, seismicity and faulting in California will be need to establish this with confidence and to provide a better idea of incremental hazard levels due to induced seismicity.

The results from these studies can then be used as the initial basis for assessing the hazard that would result from increase well stimulation activity. WST applied at the scale presently employed in other regions of the US currently requires the disposal of much larger volumes of both flowback water from the stimulations themselves and produced water resulting from increased and expanded production, which could increase the hazard. Given the high rate of tectonic activity and the large number of active and potentially active faults in most of the areas that might be considered for unconventional recovery, it will be very important to carry out formal, probabilistic assessments of the potential incremental hazard and risk that could result from induced seismicity in those areas.

5.4 Other Potential Impacts

This section briefly addresses miscellaneous other possible impacts of WST.

5.4.1 Wildlife and Vegetation

While the impacts of oil and gas production on wildlife and vegetation are well-documented, the direct impacts of well stimulation are not. It is difficult to parse out direct and indirect impacts from the extant literature. This report outlines the most well-documented impacts of oil and gas production on wildlife and vegetation, examines the aspects that are most likely to be exacerbated by well stimulation, and discusses the native species in California most likely to be impacted by well stimulation.

5.4.1.1 General Effects of Oil and Gas Production on Wildlife and Vegetation

Oil and gas production has been shown to have numerous negative effects on wild animal and plant populations (for a review of unconventional oil and gas production impacts on wildlife impacts, see Northrup and Wittemyer, 2013). The footprint of well pads and support infrastructure such as upgrading facilities, roads, seismic lines, and power lines

cause habitat loss (Jones and Pejchar 2013). Unpermitted activities can also cause habitat loss, as in one case in Pennsylvania when a company illegally constructed a wastewater pit in a wetland, important habitat for native wildlife (Department of Environmental Protection, Commonwealth of Pennsylvania). However, the area directly occupied by oil and gas production infrastructure is small compared to the area that is fragmented by the web of seismic lines, power lines, and roads that connect well pads (McDonald et al., 2009). Habitat fragmentation associated with oil and gas development impacts wildlife populations in a number of ways. It can reduce the size of home ranges for territorial animals and force them to travel longer distances to avoid interaction with human-built features (Webb et al., 2011a; 2011b), reduce patch sizes below what is needed by an animal that requires a large area for foraging (Linke et al., 2005), and act as barriers to dispersal (Dyer et al., 2002). Fragmentation also increases the proportion of disturbed edge habitat to interior habitat; some species are more vulnerable to predation or to be killed by humans along edge habitat (Moseley et al., 2009; Nielsen et al., 2006). In addition to habitat loss and fragmentation, noise pollution from oil and gas production have been shown to cause changes in the behavior of local wildlife that contribute to population declines (Bayne et al., 2008; Blickley et al., 2012; Francis et al., 2012). Vehicle collisions kill animals (Nielsen et al., 2006). Organisms sometimes die after drinking from or immersing themselves in wastewater (Ramirez 2010; Timoney and Ronconi 2010). Accidental spills of oil or wastewater can also cause mortality of plants and animals (Brody et al., 2012). In one case, an intentional application of wastewater following hydraulic fracturing caused tree mortality in an eastern forest (Adams 2011). The disturbances caused by oil and gas production promotes colonization by invasive species (Bergquist et al., 2007, Fiehler and Cypher 2011). Organisms that specialize in habitat near human disturbances are often invasive species that can inhabit a wide array of habitats, tolerate human disturbance, and displace native species (Coffin 2007; Belnap 2003; Jones et al., 2014).

All of the above impacts have been specifically documented in areas where well stimulation is commonly applied. However, to our knowledge, no study has attempted to parse out the direct impacts of well stimulation from the impacts of activities that precede and follow well stimulation. As a result, it is not possible to say what proportion of impacts on wildlife and vegetation are directly attributable to the process of well stimulation as opposed to the indirect impacts associated with all oil and gas production activities.

5.4.1.2 Potential Direct Effects of Well Stimulation on Wildlife and Vegetation

This section of the report focuses on wildlife and vegetation impacts of hydraulic fracturing, as it is the most commonly documented form of well stimulation in California. Hydraulic fracturing can affect wildlife and vegetation via direct and indirect pathways. Important direct factors are the possibility of increased toxicity of wastewater, water resource depletion, truck traffic, and noise. Indirectly, hydraulic fracturing can affect biota by increasing the intensity of oil and gas production in existing fields, or, probably to a lesser extent in California, by extending the range of oil and gas production into new areas. However, indirect impacts are beyond the scope of this report.

As mentioned above, the authors of this report could not find any studies that isolated the impacts of well stimulation from the effects of oil and gas production in general. Nonetheless, it is reasonable to infer that certain activities that are associated with well stimulation have the potential to exacerbate the known impacts of oil and gas production on wildlife and vegetation.

5.4.1.2.1 Wastewater Toxicity

One report found that nine chemicals used in hydraulic fracturing are regulated under the Safe Drinking Water Act for their risks to human health (United States House of Representatives Committee on Energy and Commerce 2011); however, the toxicity, concentrations of these chemicals in flowback and produced water, and the likelihood of releases to the environment are unknown (US EPA, 2012). Potential routes of environmental exposure to hydraulic fracturing chemicals include surface spills (discussed in Section 5.1.3.1.1 of this report) and wildlife drinking from or immersing themselves in surface storage ponds (Ramirez 2010; Timoney and Ronconi 2010). Bamberger and Oswald (2012) document a number of observations of harm to livestock, domestic animals, and wildlife that correlated with surface spills or intentional surface applications of wastewater from hydraulically fractured wells; however, these case studies were not controlled, replicated experiments, nor did they distinguish hydraulic fracturing flowback from produced water, so they cannot be taken as definitive evidence of direct harm from hydraulic fracturing operations. As detailed in Section 5.1.3.1.4 of this report, under certain circumstances wastewater can legally be disposed of via unlined sumps or discharged to a stream. As a result it is possible for flora and fauna to come in contact with flowback either in sumps or surface waterways. No studies were found that document whether these practices are either benign or harmful. In sum, it is established that oil and gas production yields wastewater that can at times be fatal to plants and animals, and it is possible under current regulations for wildlife and vegetation to come in contact with flowback in California. However, additional research is necessary to determine the extent to which wastewater toxicity is altered by the inclusion of hydraulic fracturing chemicals.

5.4.1.2.2 Water Depletion

Water use for hydraulic fracturing is discussed in detail in Section 5.1.1 of this report. While the quantity of water used for hydraulic fracturing is a small proportion of freshwater used in the state, it could be an important fraction of water in a given area, especially during periods of drought. If water is sourced from local water districts, it will come out of the overall regional or statewide allotment of water for agriculture, industrial and domestic use in the state. However, unlike water used in other applications, water injected for oil and gas production can effectively leave the water cycle if it is disposed of in a Class II well. Water for oil and gas production can also be sourced from local wells. To date, hydraulic fracturing notices state they are using fresh water from local water districts, with well water as a backup water source. Rapid withdrawal from aquifers can lower the water table, diminish stream recharge, and affect groundwater quality (US EPA, 2011).

5.4.1.2.3 Truck Traffic

Vehicles impact natural habitats by striking and killing animals (Fahrig and Rytwinski 2009), acting as vectors for invasive species (Ansong and Pickering 2013), and causing noise (Blickley et al., 2012; Forman and Deblinger 2014). Road mortality is noted as a major factor affecting the conservation status of three state and federally listed special status species in California: the San Joaquin kit fox, the blunt-nosed leopard lizard, and the California tiger salamander (Williams et al., 1998; Bolster 2010). The San Joaquin kit fox and blunt-nosed leopard lizard ranges overlap with oil fields in the San Joaquin Valley (Williams et al., 1998), while California tiger salamanders can be found in oil fields in Santa Barbara County (US Fish and Wildlife Service (FWS) 2000).

The proppant, and occasionally water, required for hydraulic fracturing is transported via trucks. Section 5.4.2 of this report discusses the amount of truck traffic associated with hydraulic fracturing in the state. However, there is insufficient data to quantify the impact to wildlife and plant populations caused by truck transport associated specifically with hydraulic fracturing.

5.4.1.2.4 Noise from Well Stimulation

As discussed in Section 5.4.2 of this report, there is only one reported measurement of noise during hydraulic fracturing in California. Noise levels of 68.9 and 68.4 decibels (dBA) were measured 1.8 m (5 ft) above the ground 33m (100 ft) and 66 m (200 ft) away from a high-volume hydraulic fracturing operation in the Inglewood Field (Cardno ENTRIX, 2012). These levels are substantially lower than those found to disturb wildlife and ecosystem processes in Blickley et al., 2012 and Francis et al., 2012, but difficult to compare to the noise levels measured in Bayne et al., 2008, which were noted as averaging 48 db(A) (SD 6) at an average distance of 242 m (SD 86). Regardless of the noise levels, well stimulation would increase the duration of noise generation at a well site. Unfortunately, there is insufficient data on typical noise levels associated with well stimulation in California and the behavioral responses of local species to reach any conclusions on how noise from well stimulation affects native fauna in the state.

5.4.1.3 Wildlife and Vegetation Most Likely to be Affected by Well Stimulation

A substantial number of native organisms, including endangered and threatened species, live on existing oil fields in California (Table 5-9), where they could be impacted by the direct effects of well stimulation.

It has been documented that species specializing in saltbush scrub habitat such as Le Conte's thrashers, San Joaquin antelope squirrel, short-nosed kangaroo rats, and San Joaquin kit foxes occur in oil and gas fields with a low density of well pads and a corresponding low level of human disturbance (fewer than 50 wells in a 36 hectare area, and less than 70% of area disturbed) (Fiehler and Cypher 2011). In plots with higher levels of disturbance, none of these specialist species was found.

Table 5-9. List of special status species inhabiting oil fields in California. Key: CT = listed as threatened by the state of California, CE = listed as endangered by the state of California, FT = listed as threatened by the United States federal government, FE = listed as endangered by the United States federal government. The year the species was listed is given in parenthesis.

Species	Status	Reference
Bakersfield cactus (Opuntia basilaris var. treleasei)	CE (1990) FE (1990)	Williams et al., 1998
Blunt-nosed leopard lizard (Gambelia silus)	CE (1971) FE (1967)	Williams et al., 1998
California Condor (Gymnogyps californianus)	SE (1971) FE (1967)	US FWS 2005
California Tiger Salamander (Ambystoma californiense) 3 Distinct Vertebrate Population Segments: Central CA	ST (2010) FT (2004 FE (2000) FE (2000)	US FWS 2000
Giant kangaroo rat (Dipodomys ingens)	CE (1980) FE (1987)	Williams et al., 1998
Kern mallow (Eremalche kernensis)	FE (1990)	Williams et al., 1998
San Joaquin antelope squirrel (Ammospermophilus nelsoni)	CT (1980)	Williams et al., 1998
San Joaquin kit fox (Vulpes macrotis mutica)	CT (1971) FE (1967)	Williams et al., 1998, Cypher et al., 2000, Fiehler and Cypher 2011
San Joaquin woollythreads (Monolopia congdonii)	FE (1990)	US FWS 2001

The California condor forages in the Sespe Oil Field in the Los Padres National Forest. Condors have died or been injured by landing on power poles and colliding with power lines (Mee et al., 2007a). Despite US Forest Service guidelines that well pads be maintained free of debris, oil operations are nonetheless potential sources of microtrash that can cause mortality in condors (Mee et al., 2007b). Power poles, power lines, and microtrash can increase with the intensity of oil production activities; however, they are not uniquely associated with well stimulation, but rather with oil and gas production activity as a whole.

5.4.2 Traffic and Noise

Well stimulation operations generate noise and lead to an increase in heavy truck traffic for transporting water, proppant, chemicals, and equipment. Well stimulation as practiced in California typically requires about a hundred to two hundred heavy truck trips per vertical well and two hundred to four hundred trips per horizontal well, counting two trips for each truck traveling to the site. This is one-third to three-quarters of the heavy truck traffic required for well pad construction and drilling. Noise generation during hydraulic fracturing could not be quantified because of the limited data and estimates, and disagreement between those that are available.

For vertical wells, NYDEC (2011) indicates light truck traffic increases about one-eighth due to hydraulic fracturing relative to that related to pad construction and drilling. Hydraulic fracturing in California is predominantly performed in vertical and near-vertical wells, as discussed in Section 3.2.3.

NYDEC (2011) assesses vehicle trips associated with gas-well development using hydraulic fracturing. Most of the heavy truck trips for hydraulic fracturing are for hauling water and proppant to the site and hauling flowback fluid away. The remaining trips are for equipment and chemical delivery. The analysis estimates one-fifth as many truck trips for produced water disposal as for water supply for a horizontal well, and one-half as many for a vertical well.

The typical tractor-trailer and bulk tanker has an 18.2 to 24.5 metric ton (20 to 27 short ton) capacity (Davis et al., 2013). Consequently, delivery of the average proppant mass of 100 metric tons for hydraulic fracturing in California discussed in Section 5.2.1.4.2 requires 4 to 6 truck trips (all trips are one-way in this discussion, so the values should be doubled to calculate trips to and from the site). Section 5.2.1.4.2 used an estimate of 662 m³ (175,000 gallons) of water per hydraulic fracturing treatment per well in California. This has a mass of 662 metric tons (728 short tons) and so requires 27 to 36 truck trips.

Flowback water volume may be higher in California than in New York, due to use of hydraulic fracturing in migrated oil reservoirs rather than shale gas reservoirs, as discussed in Section 5.1.2. Assuming the volume of flowback fluid is the same as water used in the hydraulic fracturing results in a total of 58 to 78 heavy truck trips per vertical well that is not near pipelines for water delivery and flowback removal.

For wells in fields with available pipelines, NYDEC (2011) estimated heavy truck traffic would be reduced by 72% for water delivery and 38% for flowback fluid disposal. Applying these reductions to the California case with equal water supply and flowback fluid volumes results in a total of 28 to 38 heavy truck trips per vertical well near pipelines for water and proppant delivery and flowback removal.

Hydraulic fracturing also entails heavy truck trips to transport fluid storage tanks, chemicals, and other equipment, such as the pumps. NYDEC (2011) indicates the number of trips for fluid storage tanks and chemicals is the same as for water and proppant supply for a vertical well far from pipelines. NYDEC (2011) estimates five trips for other equipment, resulting in 36 to 46 trips for fluid tanks, chemicals and other equipment in the California case.

For the California case of a vertical well far from water supply and disposal pipelines, the total of all the heavy truck trips is 94 to 124. For the case of a vertical well near such pipelines, the total is 64 to 84 trips.

NYDEC (2011) estimates 171 to 164 heavy truck trips related to pad construction and drilling of a vertical well far and near pipelines, respectively. The difference is due to fewer trucks for pad construction in the near pipeline case.

NYDEC (2011) does not state the well depth for this estimate, but maps the depth and thickness of the Marcellus Shale, the main unconventional gas resource considered. The top of the Marcellus shale resource is between 1,830 to 2,130 m (6,000 and 7,000 ft) in depth with a thickness less than 100 m (330 ft). The median depth appears to be shallower than the midpoint of this range. Consequently the depth of unconventional gas wells in the Marcellus may be similar to hydraulically fractured wells in California currently, as represented in Section 5.1.3.1. This suggests the drilling rig size may be similar in California, and so the estimated heavy truck traffic related to drilling may be similar.

The analysis above indicates that, on average, hydraulic fracturing increases heavy truck traffic relative to that related to pad construction and drilling by about one-third to one-half for vertical wells near water supply and disposal infrastructure, and one-half to three-quarters for wells far from pipelines.

NYDEC (2011) indicates heavy truck traffic for hydraulic fracturing of horizontal wells would be larger, by up to 2.5 times, than heavy truck traffic for other activities. However, this study assumed 18,000 m³ (5 million gallons) of water use. The average water volume used to fracture horizontal wells in California is smaller by an order of magnitude, and about two times the volume used above in the vertical well estimate. NYDEC (2011) indicates about twice the heavy truck trips related to pad construction and drilling for a horizontal versus a vertical well. This suggests that, on average, hydraulic fracturing of horizontal wells in California requires about twice the heavy truck trips as for vertical wells.

Only one set of measurements of noise at one site during hydraulic fracturing was identified. Noise levels of 68.9 and 68.4 decibels (dBA) were measured 1.8 m (5 ft) above the ground 33 m (100 ft) and 66 m (200 ft) away from a high-volume hydraulic fracturing operation in the Inglewood Field (Cardno ENTRIX, 2012). For comparison, this is nearly as loud as a typical home vacuum cleaner (Cardno ENTRIX, 2012). The measured noise level is substantially less than 85 to 90 dBA estimate at 76 m (250 ft) in NYDEC (2011). These levels are loud enough to potentially damage hearing. The reason for the difference in noise levels measured by ENTRIX (2012) and reported by NYDEC (2011) is not known. The Inglewood Field operates under an allowable noise limit set by local regulation due to the proximity of the surrounding urban land use (Cardno ENTRIX, 2012). This may have resulted in the deployment of noise mitigation measures that are not typical of other contexts. Consequently it is not clear how representative the identified measurements are with regard to hydraulic fracturing in other settings.

5.5 Conclusions

The main conclusions regarding the potential direct environmental effects from the use of well stimulation are given below. These are organized by technical subject matter. The relevant section numbers for each topic are provided.

Water Quantity and Sources (Section 5.1.1)

- 1. Water use for typical WST operations in California is much lower than for hydraulic fracturing in unconventional plays outside of California. Given the relatively low average volumes of water for each hydraulic fracturing event, the total water demand for hydraulic fracturing relative to total water supply or compared to other major water uses in the California economy is low in average water years, but can be sufficiently large locally in constrained years or specific watersheds to potentially have an impact.
- 2. Water use for hydraulic fracturing could substantially increase in California if operators switch from low-volume fracturing with gel to slickwater.

Water Quality: Injection-Fluid Composition and Toxicology (Sections 5.1.2.1 and 5.1.2.2)

- 3. A list of chemicals used for hydraulic fracturing in the United States and in California was developed from disclosures in FracFocus, but the list is incomplete, to an unknown degree, because of incomplete disclosure in that data source. For matrix acidization, a list of chemicals used was developed from stimulation notices, which did not indicate any undisclosed chemicals. Toxicological data were gathered from various sources for the chemicals on these lists, but such data were available for just a majority of chemicals for oral toxicity.
- 4. A number of stimulation-fluid constituents are known toxicants to mice and rats during single-component exposure, implying a general possibility of hazardous effects on humans. However, most of the chemicals applied in California for which toxicity information was available are considered to show low toxicity. In any case, the individual constituent concentrations in injection fluids, flowback and produced waters, as well as the specific exposure pathways, will ultimately determine effective doses and potential hazards.
- 5. In California, injection fluids applied to "general" hydraulic fracturing and matrix-acidizing jobs are different in their overall chemical composition, because of the unique technical needs for each type of application. However, a first, qualitative analysis of oral toxicity during single-component exposure in rats suggests that toxic effects of the chemicals used are fairly comparable between these fluids.

6. During this review, a series of data gaps have been identified in the literature regarding the potential toxicological impacts of fracturing/injection fluids. These include gaps in the following areas: (1) biological responses to acute exposure to many of the stimulation chemicals; (2) biological responses to chronic exposure to stimulation-fluid chemicals, such as carcinogens, endocrine disrupting compounds, and bioaccumulable materials; (3) eco-toxicological effects of fluid constituents on aquatic organisms; (4) overall toxicological effects of fluids as a mixture of compounds (compared to single-chemical exposure); and (5) potential time-dependent changes in toxicological impacts of fluid constituents, due to their potential degradation or transformation in the environment.

Water Quality: Flowback and Produced Water (Sections 5.2.2.3, 5.2.2.4, and 5.2.2.5)

- 7. Flowback and produced waters exhibit a range of compositions that depend on regional geology, fluids injected, and time at which samples were collected. In general, for oil-bearing shales such as the Monterey, flowback/produced waters would contain oil and gas, dissolved constituents from the formation (major cations/anions, trace elements, NORMs, organics), and potentially constituents of injection fluids and their reaction products.
- 8. The recovery of wastewaters from well stimulation varies widely, with values between 5 and 53% within the United States. In California, somewhat different recoveries compared to national averages may be expected, for the following two reasons: (1) targets in California differ from those in other states in terms of their local geology and rock types, with often higher permeability zones consisting of moderately brittle rocks; and (2) predominantly cross-linked gel is used for hydraulic fracturing in California as compared to a variety of fluids elsewhere.
- 9. Fracturing-fluid constituents typically evaluated for their residual concentrations in flowback or produced waters include friction reducers, surfactants, PCBs, biocides, alcohols, glycols and acids, such as acetic acid. Organic chemicals and biocides appear to be of particular concern.
- 10. While a detailed evaluation proves difficult, current literature suggests that the general composition of produced waters from well stimulation operations is similar to produced waters recovered during conventional oil and gas production.

Water Quality: Potential Impacts to Surface and Groundwater (Sections 5.1.3 and 5.1.4)

11. In California, flowback and produced waters from well stimulation are managed together. Current management practices in California allow for the disposal of oil and gas wastewater, including the co-mingled well stimulation fluids, into unlined pits in some areas and reuse for agriculture without prior treatment. A detailed assessment is needed to ascertain the wastewater disposal practices in the areas where well stimulation is occurring, to determine if they pose a risk to surface water and groundwater aquifers.

- 12. There are reports of surface water and groundwater contamination in regions where hydraulic fracturing activities are occurring in the United States. In California, there are documented cases of the intentional release of flowback fluids into unlined pits, as well as the accidental release of hazardous chemicals associated with well stimulation. Detailed assessments are not available as to whether these releases contaminated surface water and/or groundwater aquifers.
- 13. Potential contaminant of concern in flowback/produced waters include methane, TDS (salts), trace metals, NORMs, and some organics. However, at this time, it is not possible to evaluate whether this list of contaminants is relevant to California, since there is very limited information regarding the concentrations of these substances in flowback/produced waters from well stimulation operations in California. Some data may become available in 2014 as operators report the composition of waters recovered from well stimulation operations to DOGGR.
- 14. There are no recorded instances of subsurface release of hydraulic fracturing fluid into potable groundwater in California, but a lack of studies and consistent and transparent data collection and reporting makes it difficult to evaluate the extent to which this may have occurred. California needs to develop an accurate understanding about the location, depth, and quality of groundwater in oil and gas producing regions in order to evaluate the risks of WST operations to groundwater. This information on groundwater must be integrated with additional geophysical information to map the actual extent of hydraulic fractures to assess whether and where water contamination from WST activities have been or will be a problem.
- 15. Geomechanical modeling studies conducted for high-volume fracturing operations in the Barnett Shale have indicated that fracturing directly from shale formations into groundwater is unlikely for formations more than 600 m (1,970 ft) below the base of groundwater, but fracture connections to pre-existing permeable pathways (e.g., abandoned or degraded wells) have been discussed as possible migration mechanisms.
- 16. Most hydraulic fracturing occurs at a depth of less than 610 m (2,000 ft) in California. Much of this occurs in areas with poor groundwater quality, but tens of hydraulic fracturing operations per year in this depth range may occur in areas with higher quality groundwater. Data are not available to assess if changes to groundwater quality as a result of shallow hydraulic fracturing have occurred.
- 17. In general, monitoring efforts near well stimulation operations in the United States have not been extensive, and data on concentrations of potential contaminants in groundwater are sparse and not easily available to the public. A lack of baseline data on groundwater quality is a major impediment in identifying or clearly assessing the key water-related risks associated with hydraulic fracturing and other WST.

- 18. The few studies that have monitored groundwater near well stimulation operations in the United States have so far not observed significant impacts to water quality. Elevated levels of constituents detected in a few studies could not be definitively linked to the fracturing operations. For example, even though high levels of methane and TDS have been detected in groundwater near hydraulic fracturing operations outside of California, it has not been demonstrated whether this is solely due to hydraulic fracturing, natural processes, pre-existing pathways, or a combination of mechanisms. Further research is needed to understand the mechanisms by which contamination could occur.
- 19. Existing wells are often considered as the highest concern for subsurface migration of WST and subsurface fluids (including injection fluids, flowback/produced waters, formation brines and gas present in the target or other subsurface formations). Understanding this potential hazard is critical for the protection of groundwater resources. In particular, the locations and condition of preexisting wells near WST operations in California should be determined to assess potential hazards. Continued monitoring and data collection are warranted to avoid potential risks.
- 20. Proper well construction is critical for the protection of groundwater resources, and for preventing subsurface release or migration of reservoir or fracturing fluids. Well construction standards should be enforced for WST operations in California.

Air Quality (Section 5.2.1)

- 21. Estimated marginal emissions of NO_{x} , $\mathrm{PM}_{2.5}$, VOCs directly from activities directly related to WST appear small compared to oil and gas production emissions in total in the San Joaquin Valley where the vast majority of hydraulic fracturing takes place. However, the San Joaquin Valley is often out of compliance with respect to air quality standards and as a result, possible emission reductions remain relevant.
- 22. Three major sources of air pollutants include the use of diesel engines, flaring of gas and the volatilization of flowback water. The first, diesel engines (used for transport and pumping of estimated fluid volumes required for WST) emit a small portion of total emissions nitrogen oxides (NO_x), particulate matter (PM_{2.5}), and volatile organic compounds (VOC) associated with other oil and gas production operations as a whole.
- 23. Emissions from flaring in California are uncertain because of variability in flare combustion conditions and to a lack of information regarding the frequency of flare-use during WST operations. However, current California Air Resource Board inventories of pollutant emissions from all flaring suggest that flares as a whole emit less than 0.1% of the VOCs and are not a major regional air quality hazard.

- 24. Emissions from volatilization of flowback water constituents have not been measured but might be bracketed. The California Air Resource Board has conducted a "bottom-up" VOC emission inventory by adding up all known sources of emissions. It is unknown whether these sources included emissions from WST-related produced or flowback water. However, the sum of the emissions in the inventory matches well with "top-down" measurements taken from the air in the San Joaquin Valley (Gentner et al., 2014). This agreement between "bottom-up" and "top-down" estimates of VOC emissions from oil and gas production indicates California's inventory probably included all major sources.
- 25. The inventory indicates that VOC emissions from oil and gas evaporative sources, such from flowback water, might occur from stimulation fluids produced back after the application of WST, are small compared to other emission sources in the oil and gas development process. Data suggest that emissions from oil and gas production and upstream processing in general contribute to ~10% of anthropogenic VOC ozone precursor emissions in the San Joaquin Valley.
- 26. Some of the potential air-quality impacts can be addressed by regulation and largely avoided. Emissions from diesel equipment and diesel trucks can be controlled through use of the cleanest engines, such as US EPA classified tier 4 engines for off-road equipment or on-road truck engines that meet 2010 engine standards. Requiring reduced emission completions can control emissions from flaring and venting related to WST. Emissions from evaporative sources related to WST could be limited by requiring vapor controls on the temporary tanks to which flowback water is stored.
- 27. If practices in California were to change, for example if more fluid was used in WST or production was moved to remote locations, emissions from activities directly related to WST could become important if left uncontrolled.

Climate Impacts (Section 5.2.2)

- 28. Fugitive methane emissions from the direct application of WST to oil wells are likely to be small compared to the total greenhouse gas emissions from oil and gas production in California. This is because current California oil and gas operations are energy intensive. However, all greenhouse gas emissions are relevant under California's climate laws and many emissions sources can be addressed successfully with best available control technology and good practice.
- 29. Fugitive methane emissions for oil and gas production are uncertain and are currently an active area of scientific research. A number of measurement studies in California suggest higher methane emissions from oil and gas production activities than is listed in the State inventory. However, even if accepting the higher rate of emissions indicated by the measurement studies, methane emissions

- from oil and gas production are still likely to be small compared to direct CO_2 emissions associated with oil and gas production. Additionally, methane emissions directly related to WST are likely to account for only a small portion of total production related methane emissions.
- 30. Methane emissions related to WST can be addressed successfully with best controls, such as requiring reduced emission, or "green," completions and requiring vapor controls on temporary tanks in which flowback water is stored. We note that while green completions will be required nationally for gas wells starting in 2015, they will not be required for wells that produce oil or oil and gas, such as most of the wells in the San Joaquin Valley.
- 31. Other emissions such as CO₂ from diesel fuel used for pumping fluid or delivering supplies was found to be negligible.
- 32. While other regions are currently using WST for the production of petroleum (e.g., the Bakken formation of North Dakota) or gas (e.g., the Barnett shale of Texas), emissions from these regions may not be representative of emissions from California-specific application of WST. For example, the volume of fluid used for WST operations in California is typically lower than operations in other shale plays, potentially leading to lower evaporative emissions of methane from flow back fluid.

Induced Seismicity (Section 5.3)

- 33. The general underlying mechanism for inducing seismic events as a result of well stimulation technologies is well established (i.e., reduction in effective stress due to increased pore pressure) (NRC, 2013).
- 34. Hydraulic fracturing does not pose a high seismic hazard in California. The duration and extent of pressure increases from hydraulic fracturing is believed to be relatively small. In California in particular, most hydraulic fracturing is shallow and uses a small injection volume. A shift to deeper stimulation, particularly combined with a shift to larger volumes, would increase the hazard. Protocols and best practices developed for other water/wastewater injection activities to limit induced seismicity should be followed.
- 35. At present, the seismic hazard due to the disposal by injection of flowback water is relatively low in California. While the total volume of wastewater injected is about two orders of magnitude larger than the total volume used for stimulation in WST operation typical for California, the total wastewater injection volumes are generally smaller than in other parts of the country. In addition, injection is relatively shallow, and injection rates are relatively small. Disposal of produced water from oil and gas production in deep injection wells has caused felt seismic

events in several states. However, to date, no felt seismic events have been observed in this state as a result of produced water disposal from oil and gas production. If future WST practices in California result in expanded oil and gas production, the seismic hazard due to produced water disposal could increase, in particular when injecting larger volumes into deeper formations, and in areas of higher seismic risk.

Wildlife and Vegetation (Section 5.4.1)

- 36. No studies that specifically evaluated impacts of well stimulation on wildlife and vegetation were identified. One reason for this lack of information is that well stimulation occurs alongside other oil and gas production activities, and so its direct effects cannot be readily separated in the field from the overall effects of oil and gas production.
- 37. Co-management of flowback and produced water creates the possibility that wildlife could be exposed to stimulation-fluid constituents in waters discharged into pits for disposal or used for irrigation.
- 38.Increased truck traffic related to well stimulation can increase wildlife road mortality. For instance, road mortality is a major factor affecting the San Joaquin kit fox, blunt-nosed leopard lizard, and the California tiger salamander, whose ranges overlap with oil fields.

Traffic and Noise (Section 5.4.2)

- 39. Well stimulation as practiced in California typically requires about a hundred to two hundred heavy truck trips per vertical well and two hundred to four hundred trips per horizontal well, counting two trips for each truck traveling to the site. This is one-third to three-quarters of the heavy truck traffic required for well pad construction and drilling.
- 40. Noise generation during hydraulic fracturing could not be quantified because of the limited data and estimates, and disagreement between those that are available.

Indirect Impacts of WST-enabled Increases and Expansion in Production (Entire Section)

41. The primary impacts of WST on California's environment will be indirect impacts due to WST-enabled expansion in the footprint of oil and gas production by way of increased intensity of production in established fields, and potentially by expansion of oil and gas production into new areas. Impacts of WST-enabled production will vary depending on whether expanded production occurs in existing rural or urban fields or in green fields, as well as on the nature of the ecosystems, wildlife, geology, and groundwater in the vicinity.

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Summary

Authored by CCST Steering Committee

Hydraulic fracturing in a variety of forms has been widely applied over many decades in California. However, the practice of using well stimulation has mostly been different from the high-volume hydraulic fracturing (using long-reach horizontal wells) conducted elsewhere, such as in the Bakken formation in North Dakota or the Eagle Ford formation in Texas. In California, hydraulic fracturing tends to use less water, the hydraulic fracturing fluids tend to have higher chemical concentrations, the wells tend to be shallower and more vertical, and the target geologies present different challenges. This is because the majority of the oil produced from fields in California is not from oil source rocks (i.e., organic-rich shales in the Monterey Formation), but rather from porous sandstone and diatomite reservoirs, or from naturally fractured siliceous mudstones, porcelanites, and dolomitic mudstones, which contain oil that has migrated from source rocks. Consequently, the experiences in other states are largely not applicable to California.

As to the prospects for expanded oil production in California using hydraulic fracturing in the future, the likelihood of finding major new shale plays similar to what has occurred in other states is quite uncertain. However, about 5 to 16 billion barrels of oil from additional oil production, beyond reported reserves, could be produced through the application of currently used technology in existing oil fields of the San Joaquin and the Los Angeles Basins. Production from Monterey diatomite reservoirs the San Joaquin Basin depends in part on hydraulic fracturing. New production in and around these existing production sites would likely also be amenable to production with hydraulic fracturing. New production in and around existing fields that currently does not depend on well stimulation technologies (WST), such as in the Los Angeles Basin, could well continue to be produced without WST in the future.

Current water demand for well stimulation operations in California is a small fraction of statewide water use. Even so, it can contribute to local constraints on water availability, especially during extreme droughts, such as the drought California is currently experiencing. Most of the chemicals reported for hydraulic fracturing treatments in California are not considered to be acutely toxic, but a few reported chemicals do present concerns for acute toxicity. Groundwater contamination from hydraulic fracturing has not been observed in this state, but a lack of data about the location and quality of groundwater resources, lack of knowledge about existing wells which might provide leakage paths, and inconsistent monitoring of potential groundwater impacts, limit our ability to assess whether and where water contamination from hydraulic fracturing activities have been or will be a problem. In some cases, hydraulic fracturing is taking place in shallow wells, in regions where the quality and location of the groundwater is not specified. These situations lack the inherent safety provided by conducting hydraulic fracturing thousands of feet below potable groundwater resources, and thus deserve closer scrutiny.

Hydraulic fracturing as currently practiced in California does not present a risk for induced seismic events of significance. The duration and extent of pressure increases due to hydraulic fracturing is relatively small compared to what is normally required to produce a felt, let alone a damaging, earthquake. In contrast, disposal of produced water from oil and gas production in deep injection wells has caused felt seismic events across the United States. Protocols similar to those that have been developed for other types of injection wells, such as for geothermal injections, can be applied to limit this risk. The direct emissions of hydraulic fracturing are a small component of total air pollution and methane, but these emissions occur largely in the San Joaquin Valley, which is often out of compliance for air quality. Another consideration is that all greenhouse gas (GHG) emissions are relevant under California's climate laws.

This review focuses on direct environmental impacts of WST, including direct impacts to water supply, water quality, air quality, GHG emissions, seismicity, ecology, traffic and noise, while indirect impacts of WST-enabled oil and gas production receive only cursory treatment. Based on this limited assessment, there is evidence that if the future brings significantly increased production enabled by WST, the primary impacts of WST on California's environment will be indirect impacts, i.e. those due to increases and expansion in production, not the WST activity itself. Impacts of WST-enabled production will vary depending on whether this production occurs in existing rural or urban environments or in regions that have not previously been developed for oil and gas and the nature of the ecosystems, wildlife, geology and groundwater in the vicinity.

Acknowledgements for Overall Report

The authors wish to thank Helen Prieto (LBNL) and Neela Babu (CCST) for administrative support and Daniel Hawkes (LBNL) and M. Daniel DeCillis (CCST) for technical editing of this report.

Appendix A Statement of Work

Project: Independent Review of Scientific and Technical Information on Well Completion Techniques, including Hydraulic Fracturing, in California. Bureau of Land Management, California State Office

1. Scope of Work

The Bureau of Land Management (BLM) is seeking to obtain up-to-date scientific and independent technical assessment of well completion techniques associated with and primarily focused on hydraulic fracturing (HF), employed in California. This information will be used in future planning, leasing, and development decisions regarding oil and gas issues on the Federal mineral estate in California.

The purpose of the work is to produce a report that will synthesize and assess the available scientific and engineering information associated with HF in California. The report should include 1) a description of the process of well completion techniques, including HF, in California; (2) based on the underlying geology of California assess changes in the oil and gas potential that have been made possible by advanced well technology associated with HF; (3) an assessment of the environmental hazards associated with advanced well completion techniques, including HF, that have occurred in the past or might occur in the future in California. The focus of the assessment is to evaluate the changes in practice and environmental impacts that have occurred or might occur due to advanced technology rather than the process and environmental hazards of conventional oil and gas development as a whole.

Key questions for each of the report sections are identified in this Statement of Work, which will be a living document. The steering committee, in consultation with the BLM, will review, modify and select the key questions from the list below to be addressed at a level of detail commensurate with the available funding for the report.

Objectives and Key Questions

Since this information will be used in BLM's compliance with the National Environmental Policy Act (NEPA) for future oil and gas decisions, the report should be structured in a manner that will be easily transferable into a NEPA framework, and be written in plain language to the extent possible.

A. Characterization of Well Completion Techniques in CA, including HF. The objective of this part of the report is to provide a profile of advanced well completion techniques being employed in California including HF. A typical HF well profile(s), with cross sections, will also be included.

The synthesis on well completion techniques, including HF, in CA should seek to address the following key questions:

- 1. What are the basic elements of oil well construction using advanced techniques?
- 2. What are the steps in a hydraulic fracturing job?
- 3. What are the key differences in the process when fracturing for oil versus natural gas?
- 4. What advanced well completion techniques are commonly used in California?
- 5. Are most wells in CA typically vertical or horizontal? Has this changed in recent years? Are hydraulic fracturing jobs typically on vertical or horizontal wells?
- 6. How much water is typically used on HF projects in California, and what are the water sources and disposal methods?
- 7. Is recycling of water (returned, produced) practiced in California, and to what extent?
- 8. How does HF compare with other well completion techniques employed in CA?
- **B.** Underlying Geology and Oil and Gas Potential. The objective of this part of the report is to synthesize, assess and publish existing information on the geology and consequent geography of oil and gas basins in California that have or might become targets of development due to the availability of advanced well technology, including HF. This information will help target BLM's future oil and gas program administration to the areas where the issues are the most geographically relevant. Maps and geographic data and metadata should be produced to accompany the report in this section.

The synthesis on the underlying geology and oil and gas potential of California should seek to address the following key questions:

- 1. What are the historic development trends in California in terms of targeted horizons and technologies employed in oil and gas development?
- 2. What specific advanced technologies have been tried in California and why and what has been the experience with them?
- 3. Where have these advanced technologies been used in California? Which have been used in unconventional reservoirs? Are these technology applications judged to have been successful?

- 4. What major geologic regions of California could be produced using advanced technology including HF? Which of these represent new targets for production as a result of new technology?
- 5. How do these potential targets compare to oil and gas reservoirs in other parts of the US that are currently being produced with advanced technology including HF?
- 6. What are the ranges of target depths for advanced technologies in California? What are the target formations? What is the vertical separation between target formations and underground useable water? How does this vary by geographic area?
- 7. What aspects of the Monterey formation are relevant when considering the feasibility of HF in California (ex. age of the reservoir, depositional setting, diagenesis, structural setting/trap, source rocks, other factors)?
- 8. Based on the above, where can we expect future oil and gas development in California?

C. Environmental Hazards of Well Completion Techniques in CA, including HF.

The objective of this part of the report is to compile, synthesize and assess available scientific and engineering information on the environmental hazards of advanced well completion techniques in California, including HF.

The synthesis on the environmental hazards of well completion techniques, including HF, in CA should seek to address the following key questions:

- 1. What are the potential hazards to groundwater quality and supply in CA specific to HF?
- 2. What are the potential hazards to surface water quality and supply in CA specific to HF?
- 3. What are the potential releases of fugitive emissions in CA specific to HF?
- 4. What is the potential for induced seismicity from HF, including disposal of flowback fracturing fluids and subsequently produced water, given CA's underlying geology?
- 5. Are there hazards to other resources (air, noise, wildlife habitat, threatened and endangered species) that are particular to HF in CA compared to oil and gas development generally?
- 6. Are there differences in environmental hazards when fracturing for oil versus fracturing for gas?

- 7. Have Best Management Practices been developed to address the environmental impacts of hydraulic fracturing?
- 8. What are the environmental hazards for other well completion techniques commonly employed in California?

2. Performance Period

Team creation, literature review, and preparation of the synthesis report will take place over a 7-month period starting in September 2013.

3. Specific Tasks and Deliverables

Task 1: Establish Project Structure

The California Council on Science and Technology (CCST) will lead this independent review on the scientific and technical information on well completions, including hydraulic fracturing. As a 501(c)(3) with expertise in providing science and technology advice to governments, CCST has extensive experience in collaboration with government agencies and academic scientists. CCST is also an objective and unbiased external party, with expertise and particular focus on issues of importance to California.

As described in the associated Project Charter, CCST will:

- 1. Serve as the team lead and project manager for the overall project which includes a literature review, map-making, and document creation, convening and facilitating any meetings with team members. CCST will issue the final report.
- 2. Oversee a rigorous peer review process of the report according to established CCST guidelines and processes. This is necessary to ensure a high quality report that is both actually and perceived as being independent. This process will be similar to that used by the National Academy of Sciences and/or the Office of Management and Budget's Information Quality Bulletin for Peer Review.
- 3. Create a steering committee comprised of subject matter experts that will ensure quality and independence of the project.
- 4. Establish and coordinate a working group of agencies contributing information to the study, referred to below as "the team".
- 5. Monitor all deadlines identified in the Statement of Work and verify that work is of high quality.
- 6. Select additional team members, with feedback from participating organizations in this charter.

- 7. Conduct monthly briefings for the BLM to formally update project status.
- 8. Submit a draft report to the BLM.
- 9. Provide BLM with digital copies of all references, data sources, and metadata as received from team members.
- 10. Publish a final CCST report (digitally) once peer review is completed.

Participating team members assembling the report (referred to as "the team") are Lawrence Berkeley National Laboratory (LBNL), California Division of Oil, Gas, and Geothermal Resources (DOGGR), California Geological Survey (CGS). The US Geological Survey (USGS) will provide peer reviewers for the draft report. Team member roles and responsibilities are described in the associated Project Charter. Additional team members may be added in the future by signing on to the Project Charter, as additional needs for expertise arise.

Team members have subject matter expertise in petroleum geology, petroleum engineering, groundwater/surface water hydrology, air quality, and biology, with expertise particular to California. Scientists from agencies with expertise and/or jurisdiction on oil and gas issues will be requested. Scientists from academia will also be requested.

Task 2: Design the Scientific Synthesis and Literature Review

The team will develop a basic outline of the report to guide the literature review. The report will use a format that will be easily utilized when conveying the information into a NEPA document. Team members will conduct a literature review seeking to address the key guiding questions for the synthesis shown in the Scope of Work. The team will identify information missing from published literature and, under guidance from the steering committee, decide if it is possible to obtain this information independently, such as through interviews, under budget constraints and a priority to do so.

Task 3: Writing the Report

The team will prepare a report that characterizes the current state of science on well completion techniques, including HF, in CA, with focus on the key questions stated above. The report will be written using plain language, understandable to the public, to the extent possible.

Deliverable 1: Signed Project Charter and List of Steering Committee Members

Working Group (Team members assembling the report): CCST and BLM will collaborate with agency partners to formally initiate the start of work by signing the associated Project Charter.

Steering Committee: CCST will keep BLM up-to-date about the composition, affiliation, and qualifications of steering committee members.

Deliverable 2: Project Budget

CCST and LBNL will provide project budgets to the BLM detailing personnel, report preparation, and travel/logistical costs, at a minimum.

Deliverable 3: Initial Outline of the Report

CCST will provide a digital copy of the team's outline to the BLM for review and comments. CCST, the Steering Committee, and the BLM will communicate to prioritize key research questions to make best use of available funds and address the key questions that are most important for future BLM NEPA compliance.

Deliverable 4: Written Interim Progress Report

One written, interim progress report will be provided to the BLM when the team is 4 months in to the process. The report will discuss what the team has produced to date, what potential barriers to completion may exist, and a strategy to address those barriers and achieve completion of the project.

Deliverable 5: Monthly Briefings

CCST will provide formal monthly briefings to the Energy and Minerals Division of BLM California on the status of the project (what has been accomplished, is the timeline being met, any problems are coming up that affect the timeline, and any changes to the steering committee) and periodic informal communication on a more frequent, as-needed basis.

Deliverable 6: Draft Report to BLM

CCST will provide a draft report to the BLM prior to its release to the public. BLM will review the draft report, commenting on formatting, language clarity issues, needs for additional information or missed requirements from the scope of work, but not commenting on the scientific findings of the team

Deliverable 7: Draft Report to Peer Review

CCST will oversee a rigorous peer review process of the report according to established guidelines and processes necessary to ensure a high quality report that is both actually and perceived as being independent. This process will be similar to that used by the National Academy of Sciences and/or the Office of Management and Budget's Information Quality Bulletin for Peer Review.

USGS will serve as a peer reviewer, providing narrative comments to CCST and providing peer review on a pro-bono basis.

Deliverable 8: Digital Copies of References, Data Sources, and Metadata

Digital copies of all references, data, and metadata used in writing the report will be provided to the BLM upon completion of the project from CCST.

Team members will provide to CCST any references, data (geospatially referenced or non-geospatial) used or referenced in the report to support the science team's synthesis. In the case of geospatially referenced data, metadata must also be sent to CCST.

Deliverable 9: Final Report to BLM and Public

The final report will be provided to BLM and made public upon final BLM review.

Deliverable 10: Maps

Aggregation of geospatial data into maps will likely elucidate the responses to key study questions (such as- Based on the geology of oil and gas basins in CA, where are different well completion techniques likely to be employed?). In those cases, maps will be prepared or referenced by the science team and included in the report. In all cases, data and metadata accompanying the maps will be sent to the BLM for use in future analyses.

4. Schedule of Tasks and Deliverables

The draft report will be due to the BLM on February 18, 2014. The final report will be due on March 14, 2014. (Dates are subject to change, based on date of IA execution).

Appendix B CCST Steering Committee Members

Jane Long, Ph.D.

Principal Associate Director at Large, Lawrence Livermore National Laboratory, Retired

Dr. Long recently retired from Lawrence Livermore National Laboratory where she was the Principal Associate Director at Large, Fellow in the LLNL Center for Global Strategic Research and the Associate Director for Energy and Environment. She is currently a senior contributing scientist for the Environmental Defense Fund, Visiting Researcher at UC Berkeley, Co-chair of the Task Force on Geoengineering for the Bipartisan Policy Center and chairman of the California Council on Science and Technology's California's Energy Future committee. Her current work involves strategies for dealing with climate change including reinvention of the energy system, geoengineering and adaptation. Dr. Long was the Dean of the Mackay School of Mines, University of Nevada, Reno and Department Chair for the Energy Resources Technology and the Environmental Research Departments at Lawrence Berkeley National Lab. She holds a bachelor's degree in engineering from Brown University and Masters and PhD from U. C. Berkeley, Dr. Long is a fellow of the American Association for the Advancement of Science and was named Alum of the Year in 2012 by the Brown University School of Engineering. Dr. Long is an Associate of the National Academies of Science (NAS) and a Senior Fellow and council member of the California Council on Science and Technology (CCST) and the Breakthrough Institute. She serves on the board of directors for the Clean Air Task Force and the Center for Sustainable Shale Development.

Jens Birkholzer, Ph.D.

Deputy Director, Earth Sciences Division, Lawrence Berkeley National Laboratory

Dr. Birkholzer joined Lawrence Berkeley National Laboratory in 1994 as a post-doctoral fellow and has since been promoted to the second-highest scientist rank at this research facility. He currently serves as the deputy director of the Earth Sciences Division and as the program lead for the nuclear waste program, and also leads a research group working on environmental impacts related to geologic carbon sequestration and other subsurface activities. His area of expertise is subsurface hydrology with emphasis on understanding and modeling coupled fluid, gas, solute and heat transport in complex subsurface systems,

such as heterogeneous sediments or fractured rock. His recent research was mostly in the context of risk/performance assessment, e.g., for geologic disposal of radioactive wastes and for geologic CO₂ storage. Dr. Birkholzer has authored about 90 peer-reviewed journal articles and book chapters, and has over 230 conference publications and abstracts.

Adam Brandt, Ph.D.

Assistant Professor, Department of Energy Resources Engineering, Stanford University

Dr. Brandt is an Assistant Professor in the Department of Energy Resources Engineering, Stanford University. His research focuses on reducing the greenhouse gas impacts of energy production and consumption, with a focus on fossil energy systems. Research interests include life cycle assessment of transportation fuels, and the energy efficiency of energy extraction and refining systems. A particular interest is in unconventional fossil fuel resources such as oil shale, oil sands, and tight oil. He also leads research into computational optimization techniques as applied to the design and operation of ${\rm CO_2}$ capture and storage systems for mitigating greenhouse gas emissions from fossil energy consumption. Dr. Brandt received his PhD and MS degrees from the Energy and Resources Group, UC Berkeley.

Donald L. Gautier, Ph.D.

Consulting Petroleum Geologist, DonGautier L.L.C.

With a career spanning almost four decades, Dr. Donald L. Gautier is an internationally recognized leader and author in the theory and practice of petroleum resource analysis. As a principal architect of modern USGS assessment methodology, Gautier's accomplishments include leadership of the first comprehensive evaluation of undiscovered oil and gas resources north of the Arctic Circle, the first national assessment of United States petroleum resources to be fully documented in a digital environment, and the first development of performance-based methodology for assessment of unconventional petroleum resources such as shale gas or light, tight oil. He was lead scientist for the San Joaquin Basin and Los Angeles Basin Resource Assessment projects. His recent work has focused on the analysis of growth of reserves in existing fields and on the development of probabilistic resource/cost functions. Gautier is the author of more than 200 technical publications, most of which concern the evaluation of undiscovered and undeveloped petroleum resources. He holds a Ph.D. in geology from the University of Colorado.

Peter H. Gleick, Ph.D.

President, Pacific Institute

Dr. Peter H. Gleick is an internationally recognized environmental scientist and co-founder of the Pacific Institute in Oakland, California. His research addresses the critical connections between water and human health, the hydrologic impacts of climate change, sustainable water use, privatization and globalization, and international security and conflicts over water resources. Dr. Gleick was named a MacArthur "genius" Fellow in October 2003 for his work on water, climate, and security. In 2006 Dr. Gleick was elected to the U.S. National Academy of Sciences, Washington, D.C. Dr. Gleick's work has redefined water from the realm of engineers to the world of social justice, sustainability, human rights, and integrated thinking. His influence on the field of water has been long and deep: he developed one of the earliest assessments of the impacts of climate change on water resources, defined and explored the links between water and international security and local conflict, and developed a comprehensive argument in favor of basic human needs for water and the human right to water - work that has been used by the UN and in human rights court cases. He pioneered the concept of the "soft path for water," developed the idea of "peak water," and has written about the need for a "local water movement." Dr. Gleick received a B.S. in Engineering and Applied Science from Yale University and an M.S. and Ph.D. from the Energy and Resources Group of the University of California, Berkeley. He serves on the boards of numerous journals and organizations, and is the author of many scientific papers and ten books, including Bottled & Sold: The Story Behind Our Obsession with Bottled Water and the biennial water report, The World's Water, published by Island Press (Washington, D.C.).

Robert Harriss, Ph.D.

Senior Scientist, Lead Senior Scientist, Environmental Defense Fund

Robert Harriss is a Lead Senior Scientist at the Environmental Defense Fund, with a primary focus on characterizing and mitigating fugitive methane leakage from the United States natural gas system. He is also a Distinguished Fellow at the Houston Advanced Research Center and holds adjunct professorships at Texas A&M—Galveston and the Department of Earth & Atmospheric Sciences at the University of Houston. Other career positions have included Senior/Project Scientist at NASA Langley Research Center, Director of Earth Sciences at NASA Headquarters, Senior Scientist at the National Center for Atmospheric Research (NCAR), and senior faculty positions at Florida State University, University of New Hampshire, and Texas A&M. Dr. Harriss currently serves on a variety of volunteer scientific activities including the current NASA Science Definition Team for

the Arctic-Boreal Vulnerability Experiment, CCST Independent Review of Scientific and Technical Information on Advanced Well Stimulation Technologies in California, and as a Contributing Editor of Environment Magazine.

A. Daniel Hill, Ph.D.

Department Head, Professor and holder of the Noble Chair, Petroleum Engineering Department at Texas A&M University

Dr. A. D. Hill is Professor, holder of the Noble Endowed Chair, and Department Head of Petroleum Engineering at Texas A&M University. Previously, he taught for twentytwo years at The University of Texas at Austin after spending five years in industry. He holds a B. S. degree from Texas A&M University and M. S. and Ph. D. degrees from The University of Texas at Austin, all in chemical engineering. He is the author of the Society of Petroleum Engineering (SPE) monograph, Production Logging: Theoretical and Interpretive Elements, co-author of the textbook, Petroleum Production Systems (1st and 2nd editions), co-author of an SPE book, Multilateral Wells, and author of over 170 technical papers and five patents. He has been a Society of Petroleum Engineers (SPE) Distinguished Lecturer, has served on numerous SPE committees and was founding chairman of the Austin SPE Section. He was named a Distinguished Member of SPE in 1999 and received the SPE Production and Operations Award in 2008. In 2012, he was one of the two inaugural winners of the SPE Pipeline Award, which recognizes faculty, who have fostered petroleum engineering Ph.Ds. to enter academia. He currently serves on the SPE Editorial Review Committee, the SPE Global Training Committee, and the SPE Hydraulic Fracturing Technology Conference Program Committee. Professor Hill is an expert in the areas of production engineering, well completions, well stimulation, production logging, and complex well performance (horizontal and multilateral wells), and has presented lectures and courses and consulted on these topics throughout the world.

Amy Myers Jaffe

Executive Director, Energy and Sustainability, UC Davis

Amy Myers Jaffe is a leading expert on global energy policy, geopolitical risk, and energy and sustainability. Jaffe serves as executive director for Energy and Sustainability at University of California, Davis with a joint appointment to the Graduate School of Management and Institute of Transportation Studies (ITS). At ITS-Davis, Jaffe heads

the fossil fuel component of Next STEPS (Sustainable Transportation Energy Pathways). She is associate editor (North America) for the academic journal, Energy Strategy Reviews. Prior to joining UC Davis, Jaffe served as director of the Energy Forum and Wallace S. Wilson Fellow in Energy Studies at Rice University's James A. Baker III Institute for Public Policy. Jaffe's research focuses on oil and natural gas geopolitics, strategic energy policy, corporate investment strategies in the energy sector, and energy economics. She was formerly senior editor and Middle East analyst for Petroleum Intelligence Weekly. Jaffe is widely published, including as co-author of "Oil, Dollars, Debt and Crises: The Global Curse of Black Gold" (Cambridge University Press, January 2010 with Mahmoud El-Gamal). She served as co-editor of "Energy in the Caspian Region: Present and Future" (Palgrave, 2002) and "Natural Gas and Geopolitics: From 1970 to 2040" (Cambridge University Press, 2006). Jaffe was the honoree for Esquire's annual 100 Best and Brightest in the contribution to society category (2005) and Elle Magazine's Women for the Environment (2006) and holds the excellence in writing prize from the International Association for Energy Economics (1994).

Preston Jordan, P.G., C.E.G., C.HG. (see also Appendix C – Report Author Biosketches)

Geologist, Earth Science Division, Lawrence Berkeley National Laboratory

Preston Jordan is a Staff Research Associate in the Earth Sciences Division at Lawrence Berkeley National Laboratory (LBNL). He received his B.A. in Geology in 1988 and M.S. Eng. Sci. in Geotechnical Engineering in 1997, both from the University of California, Berkeley. He is a California Professional Geologist, Certified Hydrogeologist and Certified Engineering Geologist. Prior to joining LBNL, Jordan worked at a geotechnical engineering consultancy. Since joining LBNL, he has performed paleoseismic research, characterized the geology and hydrogeology of the lab for environmental remediation and conducted contaminant remediation pilot tests. Over the last decade his research focus has been geologic carbon storage with a particular emphasis on risk assessment. He has published on worker safety and well blowout and fault leakage risk, and participated in risk reviews of geologic carbon storage projects. His risk review of one of the world's few industrialscale geologic carbon storage projects led to reduction of injection pressures. He recently was the PI for a multi-year research project for the California Energy Commission regarding wide-scale pressure changes in response to historic oil and gas production in Kern County for the purpose of gaining insight into pressure changes in response to prospective geologic carbon storage. This involved dataset assembly and database construction using results of searches of California Department of Oil, Gas and Geothermal Resources records.

Larry Lake, Ph.D.

Professor, Department of Petroleum and Geosystems Engineering, University of Texas, Austin

Larry W. Lake is a professor of the Department of Petroleum and Geosystems Engineering at The University of Texas at Austin and director of the Center for Petroleum Asset Risk Management. He holds B.S.E and Ph.D. degrees in Chemical Engineering from Arizona State University and Rice University. Dr. Lake has published widely; he is the author or co-author of more than 100 technical papers, the editor of 3 bound volumes and author or co-author of four textbooks. He has been teaching at UT for 34 years before which he worked for Shell Development Company in Houston, Texas.

He was chairman of the PGE department twice, from 1989 to 1997 and from 2008-1010. He formerly held the Shell Distinguished Chair and the W.A. (Tex) Moncrief, Jr. Centennial Endowed Chair in Petroleum Engineering. He currently holds the W.A. (Monty) Moncrief Centennial Chair in Petroleum Engineering. Dr. Lake has served on the Board of Directors for the Society of Petroleum Engineers (SPE) as well as on several of its committees; he has twice been an SPE distinguished lecturer. Dr. Lake is a member of the US National Academy of Engineers and won the 1996 Anthony F. Lucas Gold Medal of the SPE. He won the 1999 Dad's Award for excellence in teaching undergraduates at The University of Texas and the 1999 Hocott Award in the College of Engineering for excellence in research. He also is a member of the 2001 Engineering Dream Team awarded by the Texas Society of Professional Engineers. He is an SPE Honorary Member.

Seth B. Shonkoff, Ph.D., MPH

Executive Director, Physicians Scientists & Engineers for Healthy Energy

Dr. Shonkoff is the executive director of the energy science and policy organization, Physicians Scientists & Engineers for Healthy Energy (PSE), and a visiting scholar in the Department of Environmental Science, Policy and Management at UC Berkeley. An environmental and public health scientist by training, he has many years of experience in water, air, climate, and population health research. Dr. Shonkoff completed his PhD in the Department of Environmental Science, Policy, and Management and his MPH in epidemiology at the School of Public Health from the University of California, Berkeley. He is a contributing author to Chapter 11, Human Health: Impacts, Adaptation, and Co-Benefits the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment report (AR5). He has worked and published on topics related to air and water quality and the environmental and public health dimensions of energy choices and climate change from

scientific and policy perspectives. Dr. Shonkoff has also researched interaction between the climate and human health dimensions of shorter-live climate forcing emissions (i.e., ozone, black carbon, sulphate particles, etc.) and on the development of more effective anthropogenic climate change mitigation policies that generate socioeconomic and health co-benefits. Dr. Shonkoff's current work focuses on the human health, environmental and climate dimensions of oil and gas development in the United States and abroad.

Sam Traina, Ph.D.

Vice Chancellor of Research, University of California, Merced

Dr. Traina is the Vice Chancellor for Research and Economic Development at the University of California, Merced where he holds the Falasco Chair in Earth Sciences and Geology. He serves as a Board Member of the California Council of Science and Technology. Prior to joining UC Merced in 2002 as a Founding Faculty member and the Founding Director of the Sierra Nevada Research Institute, Dr. Traina was a faculty member for 17 years at the Ohio State University, with concomitant appointments in the School of Natural Resources and the Environment, the department of Earth Science and Geology, Civil and Environmental Engineering, Microbiology and Chemistry. He has served on the National Research Council's Standing Committee on Earth Resources. In 1997-1998 he held the Cox Visiting Professorship in the School of Earth Sciences at Stanford University. Dr. Traina's past and current research has dealt with the fate, transformation and transport of contaminants in the soils and natural waters with an emphasis on radionuclides, heavy metals, and mining wastes. Dr. Traina holds a B.S. In soil resource management and Ph.D. in soil chemistry. He is a fellow of the Soil Science Society of American and of the American Association for the Advancement of Science as well as a recipient of the Clay Scientist Award of the Clay Minerals Society.

Appendix C Report Author Biosketches

Heather Cooley

Pacific Institute, Oakland, CA 94602 (510) 251-1600, Fax: (510) 251-2203 hcooley@pacinst.org

EDUCATION

1994-1998 University of California, Berkeley, CA.

B.S. in Molecular Environmental Biology.

2002-2004 University of California, Berkeley, CA.

M.S. in Energy and Resources.

RESEARCH AND PROFESSIONAL EXPERIENCE

Heather Cooley is Director of the Pacific Institute's Water Program. She conducts and oversees research on an array of water issues, such as the connections between water and energy, sustainable water use and management, and the hydrologic impacts of climate change. Ms. Cooley has authored numerous peer-reviewed scientific papers and co-authored five books, including The World's Water, A 21st Century US Water Policy, and The Water-Energy Nexus in the American West.

Ms. Cooley has received the US Environmental Protection Agency's Award for Outstanding Achievement (for her work on agricultural water conservation and efficiency) and her work was recognized when the Pacific Institute received the first US Water Prize in 2011. She has testified before the US Congress on the impacts of climate change for agriculture and on innovative approaches to solving water problems in the Sacramento-San Joaquin Delta. Ms. Cooley currently serves on the Board of the California Urban Water Conservation Council.

CURRENT AND PAST POSITIONS

Since 2004 Director, Water Program, Pacific Institute, Oakland, California

2000 – 2004 Lab Manager, Lawrence Berkeley National Laboratory,

Berkeley, California

1998 – 1999	Field and Laboratory Technician, Silver Laboratory, UC Berkeley, Berkeley, California
1996 – 1997	Field and Laboratory Assistant, Weston Laboratory, UC Berkeley, Berkeley, California

2010	Board Chair, California Urban Water Conservation Council
2009	Outstanding Achievement Award, US Environmental Protection Agency
2009	Nomination for Environmental Contribution of the Year, Global Water Intelligence
2006	Water Leader, Water Education Foundation

Patrick F. Dobson

Earth Sciences Division, MS 74-R316C Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 486-5373, Fax: (510) 486-5686 pfdobson@lbl.gov

EDUCATION

1977-1981	Williams College, Williamstown, MA, BA in Geology (magna cum laude)
1981-1984	Stanford University, Stanford, CA, M.S. in Geology
1984-1986	Stanford University, Stanford, CA, Ph.D. in Geology

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Dobson has been a research scientist in the Earth Sciences Division of LBNL since 2000. His expertise is in the study of water-rock interaction related to geothermal systems and high-level radioactive waste repositories. His most recent work has focused on radioactive waste disposal in shales, use of He isotopes in characterization of geothermal systems, and developing methodologies for assessing geothermal resources.

2010-present	Career Geological Staff Scientist, Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA
2007-2009	Deputy Program Manager, Geosciences Program, Office of Basic Energy Sciences, US Department of Energy, Germantown, MD (on detail from LBNL)
2003-2010	Career Geological Research Scientist, Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA
2000-2003	Geological Scientist, Earth Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA
1999-2001	Consultant, Empresa Nacional del Petroleo (ENAP), Santiago, Chile
1998-1999	Advising Geologist, Unocal Geothermal and Power Operations, Unocal Corporation, Santa Rosa, CA
1994-1998	Senior Geologist, Unocal Geothermal and Power Operations, Unocal Corporation, Santa Rosa, CA

1989-1994	Research Geologist, Unocal Science and Technology Division, Unocal Corporation, Brea, CA
1989	Postdoctoral Research Fellow, Department of Geological Sciences, University of California, Santa Barbara, CA
1986-1989	Postdoctoral Research Fellow, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA

2012	Geothermal Special Achievement Award, Geothermal Resources Council
2012	Fulbright Specialist Grant in Environmental Science, University of Chile
2009	Outstanding Contributions in Geosciences Research Award, DOE BES
2002, 2006	SPOT Awards (3), Lawrence Berkeley National Laboratory
1995, 1998	Special Recognition Awards (3), Unocal Corporation
1992	Fred L. Hartley Research Center Creativity Award, Unocal Corporation

Kristina Donnelly

654 13th St., Preservation Park Pacific Institute, Oakland, CA 94612 (510) 251-1600, Fax: (510) 251-2203

kdonnelly@pacinst.org

http://pacinst.org/about-us/staff-and-board/kristina-donnelly/

EDUCATION

2001-2005	American University, Washington, DC. B.S. in Mathematics, 2005.
2006-2008	University of Michigan, Ann Arbor, MI. M.S. in Natural Resources Management, 2008.

RESEARCH AND PROFESSIONAL EXPERIENCE

Ms. Donnelly has been a Research Associate with the Pacific Institute since 2011. Her research interests include: the social, economic, and policy aspects of water conservation and efficiency; conflict and conflict management over transboundary water resources; and US water policy and natural resources economics. During graduate school, Ms. Donnelly worked on a variety of projects, including modeling hypoxia development in the Gulf of Mexico, identifying water valuation strategies for international businesses, and analyzing water strategies for the Kingdom of Jordan.

CURRENT AND PAST POSITIONS

Since 2011	Research Associate, Pacific Institute, Oakland, California
2010-2011	Researcher and Program Coordinator, Arava Institute for Environmental Studies, Ketura, Israel
2008-2009	Sea Grant Fellow and Program Specialist, Great Lakes Commission, Ann Arbor, Michigan
2005-2006	Analyst, The Cadmus Group, Inc., Arlington, Virginia

2014	Water Education Foundation's Water Leaders Class
2008-2009	Great Lakes Commission-Sea Grant Fellowship
2008	International Economic Development Program, Ford School of Public Policy, University of Michigan

Laura C. Feinstein

California Council on Science and Technology 1130 K Street, Suite 280, Sacramento, CA 95814-3965 (530) 204-8325

laura.feinstein@ccst.us

EDUCATION

1994-1998	University of California at Berkeley, Berkeley, CA. B.A. in Anthropology, 1998.
2006-2012	University of California at Davis, Davis, CA. Ph.D. in Ecology, 2012.

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Feinstein has worked for the California Council on Science and Technology (CCST) since January 2014. She previously served as a CCST Science and Technology Fellow with the California Senate Committee on Environmental Quality. Her graduate student research focused on the ecology and genetics of an invasive plant species in the San Francisco Bay's tidal wetlands. She has worked on a diverse array of ecological problems, including restoration of coastal marshes, biogeochemical cycles in redwood forests, and the genetics of adaptation. Laura has published and presented at numerous conferences on ecological genetics and tidal wetland plant communities.

CURRENT AND PAST POSITIONS

Since 2014	Project Manager, Well Stimulation Technology in California, California Council on Science and Technology (CCST)
Since 2012	Postdoctoral researcher, restoration of San Francisco Bay tidal marshes, U.C. Davis
2012-2013	CCST Science and Technology Policy Fellow with the California Senate Committee on Environmental Quality
2006-2012	Ph.D. student, U.C. Davis

2007	CALFED Bay-Delta Science Fellow
2006	National Science Foundation Integrative Graduate Education and Research Traineeship on Invasive Species Research Award
2006	California Native Plant Society Research Award

Marc L. Fischer

Environmental Energy Technologies Division, MS90-2014 Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 486-5539, Fax: (510) 486-5928

mlfischer@lbl.gov
http://energy.lbl.gov/env/mlf/

EDUCATION

1978-1981	Massachusetts Institute of Technology, Pasadena, CA. B.S. Physics
1981-1982	University of Illinois, M.S., Physics
1979-1984	University of California, Berkeley, Ph.D. Physics.

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Marc Fischer is staff scientist in the Sustainable Energy Systems Group and Environmental Energy Technology Division at the Lawrence Berkeley National Laboratory (LBNL), and an associate researcher at the Air Quality Research Center at the University of California, Davis. Dr. Fischer's work focuses on quantifying and mitigating Earth radiative forcing due to greenhouse (GHG) gases and human habitation, and development of sustainable solutions for energy related environmental problems. As part of ongoing work, Fischer and colleagues are quantifying the sources of California's GHG emissions and identifying cost-effective options to mitigate emissions. Dr. Fischer has published more than 60 peer-reviewed publications

Since 1998	Staff Scientist, Environmental Energy Technology Divi		
	Lawrence Berkeley National Laboratory (LBNL)		
1991 – 1998	Postdoctoral Fellow and Research Associate,		
	University of California, Berkeley		

Bill Foxall

Earth Sciences Division, MS 74R316C Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 486-5082, Fax: (510) 486-5686 bfoxall@lbl.gov

EDUCATION

1966-1969	Queen Mary College, University of London, UK. B.Sc. in Physics, 1969.
1974-1976	University of Washington, WA. M.S. in Geophysics, 1976.
1986-1992	University of California, Berkeley, CA. Ph.D. in Geophysics, 1992.

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Foxall has lead induced seismicity research activities in the Earth Sciences Division Lawrence Berkeley National Laboratory since 2013. His expertise is in seismic source physics and wave propagation, seismic hazard analysis, and measurement and inversion of deformation in the Earth. Dr. Foxall most recent work has been on physics-based simulation approaches to seismic hazard assessment for induced seismicity related to ${\rm CO}_2$ sequestration and analysis of induced seismicity related to enhanced geothermal systems and unconventional oil and gas recovery. Other recent work was on inversion of ground surface deformation for imaging fluid flow in ${\rm CO}_2$, oil and geothermal reservoirs, and for characterization of underground facilities. He has also conducted research into joint inversion of seismic and acoustic data for determination of explosive yield. Dr. Foxall has authored and coauthored more than 30 peer-reviewed journal articles and conference publications.

Since 2013	Senior Geological Scientist, Earth Sciences Division, Lawrence Berkeley National Laboratory (LBNL)
1996 – 2013	Physicist, Lawrence Livermore National Laboratory (LLNL)
1996 – 1999	Visiting Research Geophysicist, University of California, Berkeley
1995 – 1996	Staff Scientist, Lawrence Berkeley National Laboratory
1992 – 1995	Postdoctoral Fellow, Lawrence Berkeley National Laboratory
1986 – 1992	Graduate Student Research Assistant, Lawrence Berkeley National Laboratory

1983 – 1992 Seismological Consultant

1976 – 1983 Staff to Senior Project Seismologist, Woodward-Clyde Consultants,

San Francisco, CA

HONORS AND AWARDS

1974 Fulbright Scholarship

Matthew G. Heberger

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http://www.pacinst.org/

EDUCATION

1992–1996	Cornell University, Ithaca, New York. B.S. in Agricultural and Biological Engineering, 1996.
2001–2003	Tufts University, Medford, Massachusetts. M.S. in Water Resources Engineering, 2003.

RESEARCH AND PROFESSIONAL EXPERIENCE

Mr. Heberger has been a research associate in the Water Program of the Pacific Institute since 2007. He is a water resource engineer and hydrologist specializing in hydraulic, hydrologic, and water quality analyses and modeling, the nexus between water and energy, and impacts of climate change on water resources. Prior to joining the institute Mr. Heberger worked as a consulting engineer at the consulting firm of Camp, Dresser, and McKee (CDM) where he was responsible for building and calibrating rainfall-runoff, hydraulic and water quality models for major waterways across the US.

Since 2007	Research Associate, Pacific Institute, Oakland, California
2003 – 2007	Water Resources Engineer, Camp Dresser & McKee, Cambridge, Massachusetts
2001 – 2003	Research Assistant, Department of Civil and Environmental Engineering, Tufts University, Medford, Massachusetts
1999 – 2001	Coordinator, International Network on Participatory Irrigation Management, Washington, DC
1996 – 1998	Water and Sanitation Extension Agent, United States Peace Corps, Mali, West Africa

2007	Registered Professional Engineer, Commonwealth of Massachusetts
2004	Certified Floodplain Manager, Association of State Floodplain Managers

James E. Houseworth

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jehouseworth@lbl.gov
http://esd.lbl.gov/about/staff/jameshouseworth/

EDUCATION

1973-1977	lifornia Institute of Technology, Pasadena, CA. S.in Environmental Engineering, 1977.	
1977-1978	California Institute of Technology, Pasadena, CA. M.S. in Environmental Engineering, 1978.	
1979-1984	California Institute of Technology, Pasadena, CA. Ph.D. in Environmental Engineering, 1984.	

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Houseworth has been a program manager in the Earth Sciences Division of Lawrence Berkeley National Laboratory (LBNL) since 2000. His expertise is in single and multiphase flow and solute transport in porous and fractured geologic media and has worked on applications to petroleum recovery, nuclear waste disposal, and geologic ${\rm CO}_2$ sequestration. His most recent work has centered on nuclear waste disposal in argillaceous rock, ${\rm CO}_2$ /brine leakage from geologic storage reservoirs, and risk assessments of petroleum recovery operations. Dr. Houseworth has authored over 30 peer-reviewed journal articles and conference publications.

Since 2000	Program Manager, Earth Sciences Division, Lawrence Berkeley National Laboratory (LBNL)
1997 – 2000	Technical Systems Manager II, Duke Engineering and Services, Las Vegas, Nevada
1992 – 1997	Senior Staff Consultant, INTERA Inc., Las Vegas, Nevada
1984 – 1992	Research Engineer, Chevron Oil Field Research Company, La Habra, California
1979 – 1980	Engineer, Bechtel Inc., San Francisco, California

HONORS AND AWARDS

2012	Director's Award for Exce	eptional Achievement	(TOUGH codes), by LBNL

2007, 2006 Outstanding Performance Award, by LBNL

1984 Ph.D. thesis - Richard Bruce Chapman Memorial Award

Preston D. Jordan

Earth Sciences Division, MS 74-R316C Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 486-6774, Fax: (510) 486-5686 PDJordan@lbl.gov

EDUCATION

1982-1987 University of California, Berkeley, B.A., Geology, 1988

1996-1997 University of California, Berkeley, M.S. in Eng. Sci., Geotechnical Engineering, 1997

LICENSES

California Professional Geologist (since 1998)

California Certified Hydrogeologist (since 2007)

California Certified Engineering Geologist (since 2012)

RESEARCH AND PROFESSIONAL EXPERIENCE

Mr. Jordan has been a geologist in the Earth Sciences Division at Lawrence Berkeley National Laboratory (LBNL) since 1990. His research over the last eight years has focused primarily on the risk of geologic carbon storage, with a focus on assessing leakage risk. His work on a risk assessment of one of the few industrial-scale geologic carbon storage projects in the world led the operator to reduce the injection pressure. Mr. Jordan has co-authored over 15 peer-reviewed journal articles and conference papers.

Since 1990	Staff Research Associate currently (after five promotions), Earth Science Division, Lawrence Berkeley National Laboratory
1988-1989	Staff Geologist, Harlan Tait Associates, San Francisco
1988	Field Geologist, Department of Geology and Geophysics, University of California, Berkeley
1987	Assistant Field Geologist, Department of Geology and Geophysics, University of California, Berkeley

HONORS AND AWARDS

2010 Outstanding Performance Award, by LBNL

1987 USGS/NAGT program nominee, by University of California, Berkeley

Nathaniel J. Lindsey

Earth Sciences Division, MS 74-R316C Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 486-5409, Fax: (510) 486-5686 njlindsey@lbl.gov

EDUCATION

2006-2010	University of Rochester, Rochester, NY. B.S. in Alternative Energy and Sustainable Engineering, 2010.
2011-2013	University of Edinburgh, Edinburgh, Scotland, M.Sc. in Geophysics, 2013

RESEARCH AND PROFESSIONAL EXPERIENCE

Mr. Lindsey has been a senior research associate in the Earth Sciences Division of Lawrence Berkeley National Laboratory (LBNL) since 2012. His research seeks to improve seismic methods that characterize earthquake hazard, and apply seismic and electromagnetic geophysics to image the high-temperature hydrothermal fluid processes within geothermal energy reservoirs. Recently, his work has centered on induced seismicity related to enhanced geothermal systems in the western US, and 3-D magnetotelluric (MT) numerical simulation of geothermal systems in Iceland, East Africa, New Zealand, and the United States.

Since 2012	Senior Research Associate, Earth Sciences Division, Lawrence Berkeley National Laboratory (LBNL)
2011 – 2012	US-UK Postgraduate Fulbright Scholar, School of GeoSciences, University of Edinburgh
2010 – 2011	Causal Employee, Dept. of Seismology, Geology, and Tectonophysics, Lamont-Doherty Earth Observatory, Columbia University
2010	NSF Research Experience for Undergraduates (REU) Intern, Summer of Applied Geophysical Experience Program, Los Alamos National Laboratory
2010	NSF REU Intern, Department of Physics, University of Rochester
2009	Summer Undergraduate Laboratory Intern, Earth Sciences Division, LBNL
2008	NSF REU Intern, Department of Chemistry, University of Rochester

2012	1st Place in International Geothermal Energy Contest, by Pacific Centre for Geothermal Energy, University of British Columbia
2012	Best Poster Award, School of GeoSciences Graduate Conference, University of Edinburgh
2011	US-UK Fulbright Scholarship (Edinburgh, Scotland)
2011	Honorable Mention for Best Poster at Annual Meeting, Society for Exploration Geophysics
2010	Dean's Prize for Undergraduate Research, University of Rochester
2009	Outstanding Commitment to Action for 'Net Metering Solar Energy in Uganda' (Undergraduate Thesis), by Clinton Global Initiative University

Dev E. Millstein

Environmental Energy Technologies Division, MS 90-R2002 Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 486-4556, Fax: (510) 486-5928

dmillstein@lbl.gov
http://eetd.lbl.gov/staff/dev-millstein

EDUCATION

1998-2002	Vassar College, Poughkeepsie, NY. B.A. in Economics, 2002.
2004-2005	University of California, Berkeley, CA. M.S. in Environmental Engineering, 2005.
2005-2009	University of California, Berkeley, CA. Ph.D. in Environmental Engineering, 2009.

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Millstein is a project scientist in the Environmental Energy Technologies Division of Lawrence Berkeley National Laboratory (LBNL). His expertise is in air quality and meteorological modeling as well as emissions inventory development. His most recent work has centered on evaluating the air quality benefits of integrating renewable energy into the US power grid. Other recent work has included co-developing a spatially explicit methane emissions inventory for oil and gas operations in California. Dr. Millstein has authored over 7 peer-reviewed journal articles and conference publications.

Since 2013	Project Scientist, Environmental Energy Technologies Division,
	Lawrence Berkeley National Laboratory (LBNL)
2010 - 2013	Postdoctoral Fellow, Environmental Energy Technologies Division,
	Lawrence Berkeley National Laboratory (LBNL)

Matthew T. Reagan

Earth Sciences Division, MS 74R316C Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 486-6517, Fax: (510) 486-5686 MTReagan@lbl.gov

EDUCATION

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, Cambridge, MA

PhD in Chemical Engineering, September 2000

UNIVERSITY OF PENNSYLVANIA, Philadelphia, PA

Bachelor of Science in Chemical Engineering, May 1994

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Reagan has performed research on the thermodynamics, transport, and chemistry of aqueous systems in the subsurface. His work has included research on the thermodynamics of gas hydrates, gas production from methane hydrate systems, the coupling of methane hydrates and global climate. He is a developer for the TOUGH+ and TOUGH2 series of codes. Additional work includes simulation of subsurface CO_2 injection, data reduction and uncertainty quantification using statistical methods, development of interactive tools for simulation pre- and post-processing, and the simulation of methane production from shales. His most recent work involves the simulation of methane and brine transport in fractured shale systems. Dr. Reagan has authored or co-authored over 30 peer-reviewed journal articles and over 25 conference papers and reports.

Since 2010	Geological Research Scientist, Earth Science Division, Lawrence Berkeley National Laboratory (LBNL)
2004-2010	Term Scientist, Earth Science Division, Lawrence Berkeley National Laboratory (LBNL)
2001-2004	Technical Staff, Combustion Research Facility, Sandia National Laboratories - California
1995-2000	Research Assistant, Massachusetts Institute of Technology

Ruth M. Tinnacher

Earth Sciences Division, MS 74-R316C Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 495 8231, Fax: (510) 486 5686 rmtinnacher@lbl.gov

EDUCATION

1993-1997	University of Leoben, Austria: CandIng. (Equiv. B.S.) Industrial Environmental Protection, Waste Disposal and Recycling.
1997-2000	University of Leoben, Austria: DiplIng. (Equiv. M.E.) Chemical Process Engineering in Industrial Environmental Protection. Mit Auszeichnung bestanden (Passed with distinction)
1999-2001	Colorado School of Mines, Golden, CO, USA: M.S. Environmental Science and Engineering. As part of the Dual-Degree Program with the University of Leoben, Austria
2001-2008	Colorado School of Mines, Golden, CO, USA: Ph.D. Environmental Science and Engineering.

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Tinnacher has been a Project Scientist in the Earth Sciences Division of Lawrence Berkeley National Laboratory (LBNL) since 2011. Her research focuses on environmental geochemistry problems driven by energy- and climate-related questions, such as the impacts of nuclear waste storage, geologic CO_2 sequestration and hydraulic fracturing on groundwater quality, and the effects of climate change on subsurface geochemistry. In particular, Dr. Tinnacher investigates parameters and processes that control the sorption, remobilization and transport behavior of metals and natural organic matter in the environment, including the role of colloids, sorption/desorption kinetics, and the influence of chemical solution conditions on transport rates. During past research, Dr. Tinnacher has also evaluated the (aquatic) toxicity of compounds. Dr. Tinnacher is the author of a number of peer-reviewed journal articles, conference proceedings and a book section, and holds a U.S. patent on a radiolabeling method for natural organic matter.

Since 2011	Project Scientist, Earth Sciences Division,
	Lawrence Berkeley National Laboratory (LBNL)
Since 2011	Visiting Scientist, Chemical Sciences Division,
	Lawrence Livermore National Laboratory (LLNL)

2008 – 2011 Postdoctoral Fellow, Chemical Sciences Division, Lawrence Livermore National Laboratory (LLNL)

2011	U.S. Patent (08039226): R.M. Tinnacher and B.D. Honeyman: Methods to Radiolabel Natural Organic Matter by Reduction with Hydrogen Labeled Reducing Agents
2009	LLNL Chemical Sciences Division Spot Award
2009	2008-2009 CH2MHill/ESE Outstanding Graduate Student Award (Ph.D. thesis)
2002-3	DOC Scholarship of the Austrian Academy of Sciences

William T. Stringfellow, Ph.D.

Earth Sciences Division, MS 84-173 Lawrence Berkeley National Laboratory, Berkeley, CA 94720 (510) 486-7903, Fax: (510) 486-5686 wstringfellow@lbl.gov

EDUCATION

1990-1994 Ph. D., Environmental Sciences and Engineering (supporting program: Microbial Physiology and Genetics), University of North Carolina at Chapel Hill.
 1982-1984 M. S., Microbiology (minor: Aquatic Ecology), Virginia Polytechnic Institute and State University, 1984.

1976-1980 B. S., Environmental Health, University of Georgia, 1980.

RESEARCH AND PROFESSIONAL EXPERIENCE

William T. Stringfellow is a Professor and Director of the Ecological Engineering Research Program in the School of Engineering and Computer Science at the University of the Pacific. He has a joint appointment as a Research Engineer at Lawrence Berkeley National Laboratory where he is the Director of the Environmental Measurements Laboratory. Dr. Stringfellow is an expert in water quality and industrial waste management. His recent research includes evaluations of the sustainability of biomass energy facilities treating agricultural wastes and investigating the water quality impacts of the Gulf of Mexico oil spill. He is currently investigating the use of water treatment chemicals in the energy industry, with an emphasis on understanding the environmental impacts of biocides. Dr. Stringfellow has over 30 publications in the field of water quality and industrial waste management.

CURRENT AND PAST POSITIONS

2004-present: University of the Pacific, Ecological Engineering Research Program,

School of Engineering and Computer Science, Stockton, CA,

Director, EERP and Professor

2003-present: Lawrence Berkeley National Laboratory, Environmental Measurements

Laboratory, Earth Sciences Division, Berkeley, CA, Director, EML

1996-present: Lawrence Berkeley National Laboratory, Earth Sciences Division,

Berkeley, CA, Environmental Engineer

1988-1989: Institut Pasteur, Departement d'Ecologie, Paris, France,

Stagiaire (Visiting Researcher)

1983-1988: Sybron Chemicals, Inc., Salem Research Facility, Salem, Virginia,

Senior Research Microbiologist

1980-1981: Ecology and Environment, Inc., Decatur, Georgia,

Hazardous Waste Site Investigator

HONORS AND AWARDS

2001 Outstanding Mentor Award, Lawrence Berkeley National Laboratory

2002 Outstanding Mentor Award, Department of Energy

Charuleka Varadharajan

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http://esd.lbl.gov/about/staff/charulekavaradharajan/

EDUCATION

2009	Doctor of Philosophy Civil and Environmental Engineering,
	Massachusetts Institute of Technology
2004	Master of Science Civil and Environmental Engineering,
2001	Massachusetts Institute of Technology
2001	Bachelor of Technology Civil and Environmental Engineering,
	Indian Institute of Technology, Chennai

RESEARCH AND PROFESSIONAL EXPERIENCE

Dr. Charuleka Vardharajan is a biogeochemist in the Earth Sciences Division at the Lawrence Berkeley National Laboratory (LBNL). Her research interests focus on understanding and predicting carbon fluxes in terrestrial and subsurface environments, and development of methods to monitor and mitigate contaminants and greenhouse gases. Recently, her postdoctoral work has involved an evaluation of trace metals that could be released due to potential leakage of carbon dioxide from sequestration sites into shallow overlying groundwaters, and the mechanisms for bio-remediation of chromium at the Hanford 100H site. Her doctoral dissertation work involved the study of the methane biogeochemical cycle in a freshwater lake. Her expertise spans across various techniques for data collection and analysis including geochemical laboratory experiments, X-ray synchrotron spectroscopy, sensor-based data collection, and the use of geoinformatics and statistical data processing to manage and analyze high spatial and temporal resolution data.

Current	Project Scientist, Earth Sciences Division, Geochemistry Department, Lawrence Berkeley National Laboratory
2010-2014	Postdoctoral Fellow, Earth Sciences Division, Geochemistry Department Lawrence Berkeley National Laboratory, Berkeley, CA
2004-2009:	Research Assistant, Parsons Laboratory, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA

2005-2008:		Teaching Assistant, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA Course: Introduction to Computers and Engineering Problem Solving				
2001-2005:		Research Assistant, Center for Educational Computing Initiatives, Department of Civil and Environmental Engineering Massachusetts Institute of Technology, Cambridge, MA				
2000-2001:		Research Assistant, Department of Civil and Environmental Engineering Indian Institute of Technology, Chennai, India				
Indian Institute of Technology, Chennai, India HONORS AND AWARDS 2011 Earth Sciences Division Spot Award, Lawrence Berkeley National Laboratory 2008-9 MIT Linden Earth System Fellow						
2011	Earth Sciences Division Spot Award, Lawrence Berkeley National Laboratory					
2008-9 MIT Linden Earth System Fellow						
2007	National Science Foundation Doctoral Dissertation Research Improvement Grant					
2007	Geolog	ological Society of America Graduate Student Research Grant				
2005-6 MIT Martin Family Society Fellow for Sustainability						
2005	MIT Department of Civil and Environmental Engineering, Trond Kaalstad Award for leadership, community building and academic excellence					
2001	Institute Blues for exceptional extra-curricular and organizational abilities, Indian Institute of Technology, Madras					
1995	95 National Talent Search Award for academic excellence, National Council					

of Educational Research and Training, Government of India

Appendix D Glossary

Acid fracturing – a form of hydraulic fracture stimulation of a formation performed by injecting the acid over the parting pressure of the rock and using the acid to etch channels in the fracture face.

Androgens – steroid hormones that promote the development and maintenance of male characteristics of the body.

Anti-androgens – a substance that can prevent the full expression of androgen.

Anti-estrogens – a substance that can prevent the full expression of estrogen.

Aquifer – a zone of saturated rock or soil through which water can easily move.

Bactericide – a product that kills bacteria in the water or on the surface of the pipe.

Basement faults – faults that occur in the undifferentiated assemblage of rock underlying the oldest stratified rocks in any region.

Basement rock – the undifferentiated assemblage of rock underlying the oldest stratified rocks in any region.

Bedding planes – surfaces that separate sedimentary layers in a rock. The beds are distinguished from each other by grain size and composition, such as in shale and sandstone. Subtle changes, such as beds richer in iron-oxide, help distinguish bedding. Most beds are deposited essentially horizontally.

Biogenic methane – methane produced as a direct consequence of bacterial activity.

Biomarkers – complex molecular fossils used to correlate crude oil and petroleum source rocks, provide information on the type of organic matter, and characterize the thermal maturity.

Borehole cuttings – the small chips and fines generated by drilling through a formation with a drill bit. Most of the cuttings are removed from the drilling mud as the fluid pass through the solids control equipment (e.g., shakers, screens, cyclones, etc.,) at the surface.

Brittle – a rock characteristic that implies mechanical failure in the form of a fracture created with little or no plastic deformation.

BTEX (benzene, toluene, ethylbenzene, and xylene) – volatile aromatic compounds typically found in petroleum products such as gasoline and diesel fuel.

Buffer – a chemical used to maintain the pH of a solution within a limited range.

Cations – positively charged ions.

Chemical Abstracts Service (CAS) number – a unique numeric identifier, designates only one substance, has no chemical significance, and is a link to a wealth of information about a specific chemical substance within the CAS registry.

Chimneys – vertically oriented geological structures that may have circular or subcircular in planform if associated with faults or may be more disperse laterally if not associated with faults. Chimneys form from gas migration processes and are often found in association with mud volcanoes.

Class II wells – used for injection/disposal of fluids associated with oil and natural gas production. Most of the injected fluid is salt water (brine), which is brought to the surface in the process of producing (extracting) oil and gas. In addition, brine and other fluids are injected to enhance (improve) oil and gas production.

Clay stabilizer – a chemical additive used to prevent clay destabilization that results in clay migration or swelling caused by a reaction to an aqueous fluid.

Conductor casing – generally, the first string of casing in a well. It may be lowered into a hole drilled into the formations near the surface and cemented in place, or it may be driven into the ground by a special pile driver. Its purpose is to prevent the soft formations near the surface from caving in and to conduct drilling mud from the bottom of the hole to the surface when drilling starts.

Conventional reservoir – reservoirs that may be produced commercially without altering the reservoir permeability or associated hydrocarbon viscosity.

Corrosion inhibitor – a chemical or mixture of chemicals that prevents or reduces corrosion.

Coulomb criterion – a criterion for rock failure as a function of the normal and shear stress conditions.

Cross-link gel fracturing fluid – is generally an aqueous fluid containing a gelling agent like guar or xanthan and a crosslinker. It has even greater viscosity than a gel fracturing fluid.

Crosslinker – A substance that promotes or regulates intermolecular covalent bonding between polymer chains, linking them together to create a larger structure.

Diagenetic –physical and chemical changes that affect sedimentary deposits during burial and may culminate in lithification, i.e., turning sediment into solid rock.

Diagenetic trap – a trap formed as a result of diagenetic alteration of rocks within a sedimentary basin, resulting in decreased permeability.

Diatomite – a fine, soft, siliceous sedimentary rock composed chiefly of the silica-rich remains of diatoms.

Dip – A measure of the angle between the flat horizon and the slope of a sedimentary layer, fault plane, metamorphic foliation, or other geologic structure.

Directional drilling – drilling the wellbore in a planned angle of deviation or trajectory other than vertical.

Dissolved Organic Carbon (DOC) – mass of organic carbon from a measured water sample that is dissolved or colloidal that can pass through a filter, typically a 0.4 to 0.7 micron filter

Dolomites – carbonate rocks made up of dolomite (CaMg(CaCO₃)₂).

Downdip – located down the dip of a sloping planar surface.

Drilling mud – the fluid, water, oil or gas based, circulated through the wellbore during rotary drilling and workover operations that is used to establish well control, transport cuttings to the surface, provide fluid loss control, lubricate the string and cool the bottom hole assembly.

Ductile – a rock characteristic that implies mechanical failure in the form of a fracture created with a large amount of plastic deformation.

Earthquake magnitude – a measure of the amount of energy released during an earthquake, such as the Richter scale.

Effective stress – the total stress minus the pore pressure.

Endocrine-disrupting compounds – chemicals that may interfere with the body's endocrine system and produce adverse developmental, reproductive, neurological, and immune effects in both humans and wildlife.

EPA maximum contaminant level (MCL) – threshold concentration of a contaminant above which water is not suitable for drinking.

Epicenter – a point, directly above the true center of disturbance at the earth's surface, from which the shock waves of an earthquake apparently radiate.

Estrogens – steroid hormones that promote the development and maintenance of female characteristics of the body.

Evaporative emissions – hydrocarbons released into the atmosphere through evaporation from equipment or storage facilities.

Fault – a fracture in the Earth in which one side has moved relative to the other.

Flaring – the combustion of unwanted gases produced by an oil well.

Flowback – fracturing fluid, perhaps mixed with formation water and traces of hydrocarbon, that flows back to the surface after the completion of hydraulic fracturing.

Foaming agent – a material that facilitates formation of foam.

Formation – a body of rock of considerable extent with distinctive characteristics that allow geologists to map, describe, and name it.

Fracture aperture – the distance between fracture faces.

Fracture height – the vertical extent of a fracture.

Fracture length – the horizontal extent of a fracture.

Fracture propagation – enlargement or extension of a crack in a solid material.

Friction reducer – a material, usually a polymer that reduces the friction of flowing fluid in a conduit.

Fugitive emissions – emissions of gases or vapors due to leaks and other unintended or irregular releases.

Gel fracturing fluid – is generally an aqueous fluid containing a gelling agent like guar or xanthan. It has an enhanced viscosity relative to slickwater fracturing fluids.

Globally Harmonized System of Classification and Labeling of Chemicals (GHS)

 a worldwide initiative to promote standard criteria for classifying chemicals according to their health, physical and environmental hazards.

Greenhouse gas emissions (GHG) – emissions of gases such as CO₂ and methane that trap heat in the atmosphere.

Horizontal drilling – a well drilled in a manner to reach an angle of 90 degrees relative to a level plane at its departure point at the surface. In practice, the horizontal section of most horizontal wells varies by several degrees.

Hybrid fracturing – hydraulic fracturing that utilizes more than one type of fracturing fluid for a given stage.

Hydraulic diffusivity coefficient – the ratio of the hydraulic conductivity to the volume of water that a unit volume of saturated soil or rock releases from storage per unit decline in hydraulic head. It is a parameter that combines transmission characteristics and the storage properties of a porous medium.

Hydraulic fracturing – an operation in which a specially blended liquid is pumped down a well and into a formation under pressure high enough to cause the formation to crack open, forming passages through which oil can flow into the wellbore.

Hydrostatic pressure – the pore pressure that results from the static weight of pore fluid above the point of interest.

Induced seismicity – earthquakes caused by human activities.

Intercalated turbiditic sandstones – sandstones deposited from a turbidity current (an underwater current flowing downslope owing to the weight of sediment it carries) that are alternately layered between other rock types.

Intermediate casing – the casing set in a well after the surface casing but before production casing to keep the hole from caving and to seal off formations.

Iron control agent – a chemical that controls the precipitation of iron from solution.

Kelly – the heavy square or hexagonal steel member suspended from the swivel through the rotary table and connected to the topmost joint of drill pipe to turn the drill stem as the rotary table turns.

Kerogen – solid, insoluble organic material in shale and other sedimentary rock that yields oil and/or gas upon heating.

Lithology – the physical characteristics (e.g., mineral content, grain size, texture and color) of a rock or stratigraphic unit.

Matrix acidizing – use of a mineral acid (typically hydrochloric acid (HCl) or HCl in combination with hydrofluoric acid (HF)) or an organic acid (typically acetic or formic) to remove damage or stimulate the permeability of a formation.

Maturation – the chemical transformation of kerogen into petroleum fluids.

Median lethal dose (LD $_{50}$) – the dose required to kill half the members of a tested population after a specified test duration.

Microearthquakes – an earthquake of low intensity with a magnitude of 2 or less on the Richter scale.

Microscanner log – a geophysical measurement record from a downhole instrument that consists of four orthogonal imaging pads containing microelectrodes in direct contact with the borehole wall. It is used for mapping of bedding planes, fractures, faults, foliations, and other formation structures and dip determination.

Microseismic monitoring – a method of tracking a fracture by listening for the sounds of shear fracturing in the formation during the hydraulic fracturing process.

Migrated oil – oil that has moved from source rock to reservoir rock.

Miocene – the geologic time ranging from about 23 to 5.3 million years ago.

MODFLOW - the USGS's three-dimensional (3D) finite-difference groundwater model.

Multi-stage hydraulic fracturing – is where hydraulic fracturing is conducted repeatedly in isolated segments along the length of the well's production interval.

Nanoparticles – a microscopic particle of matter that is measured on the nanoscale, usually less than 100 nanometers.

Normal stress – the internal forces per unit area that are exerted in a material object and are also perpendicular to the selected area.

Oil window - the temperature and pressure ranges under which the organic matter in organic-rich sedimentary rocks is transformed into petroleum fluids.

Opening mode fractures – a fracture that opens in response to tensile stress, i.e., a stress that acts to pull a material object apart.

Organic shales - organic-rich shales.

Overburden – the rock layers lying above a point of interest in the subsurface.

Oxides of nitrogen (NOx) – consist of nitric oxide (NO), nitrogen dioxide (NO₂) and nitrous oxide (N₂O).

Ozone precursors – chemical compounds, such as carbon monoxide, methane, non-methane hydrocarbons, and nitrogen oxides, which in the presence of solar radiation react with other chemical compounds to form ozone.

Particulate matter (PM) and PM_{2.5} – a complex mixture of extremely small particles and liquid droplets. PM_{2.5} consist of particles less than 2.5 microns in diameter.

Permeability – The ability of a rock or other material to allow fluid flow through its interconnected spaces.

pH adjuster – chemical agents to reduce, or to increase, the acidity of a solution.

Phosphatic shales – phosphate-rich shales.

Pipes – vertically-oriented geologic structures commonly circular or subcircular in planform that may have formed as a result of hydrothermal activity, overpressure, or dissolution processes.

Play – hydrocarbon reservoirs within the same region that have common sourcing and trapping mechanisms.

Pore pressure – the normal stress exerted by pore fluids on the porous medium.

Poromechanical effects – phenomena that occur in porous materials whose mechanical behavior is significantly influenced by the pore fluid.

Portland cement – a general class of hydraulic cements (cements that can harden under water) usually made by burning a mixture of limestone and clay in a kiln and pulverizing into a powder.

Precipitate – a solid substance formed from a liquid solution during a chemical process.

Produced water – water, ranging from fresh to salty, produced with the hydrocarbons as a result of pressure drawdown and flow through the petroleum reservoir.

Production casing – the last string of casing set in a well that straddles and isolates the producing interval, inside of which is usually suspended a tubing string.

Production liner – similar to casing pipe but does not extend back to the ground surface. Liners may or may not be cemented.

Propagation of water front – the movement of a constant water saturation level through a porous medium.

Proppant – well sorted and consistently sized sand or man-made materials that are injected with the fracturing fluid to hold the fracture faces apart after pressure is released.

Quaternary fault – a fault that formed sometime between the present and about 2.6 million years ago.

Radiogenic material – material produced by radioactive decay.

Redox conditions – a quantitative description of the environment in question with respect to be oxidizing or reducing.

Reservoir – a subsurface accumulation of hydrocarbon fluids that resides in rock pores and fractures.

Scale inhibitor – a chemical that prevents scale from forming in scale mineral saturated produced waters.

Sedimentary basin – a depression in the Earth's surface that collects sediment.

Seismic hazard – a phenomenon such as ground shaking, fault rupture, or soil liquefaction that is generated by an earthquake.

Seismic moment – a measure of the size of an earthquake based on the area of fault rupture, the average amount of slip, and the force that was required to overcome the friction sticking the rocks together that were offset by faulting.

Seismometer – an instrument for measuring the direction, intensity, and duration of earthquakes by measuring the actual movement of the ground.

Seismometer array – numerous seismometers placed at discrete points in a well-defined configuration.

Semi-volatile organic compounds (SVOC) – organic compound which has a boiling point higher than water and which may vaporize when exposed to temperatures above room temperature.

Shale – sedimentary rock derived from mud and commonly finely laminated (bedded). Particles in shale are commonly clay minerals mixed with tiny grains of quartz eroded from pre-existing rocks.

Shear failure – brittle or ductile damage that results from shear stress of sufficient magnitude.

Shear stress – the internal forces per unit area that are exerted in a material object and are also tangential to the selected area.

Siliceous – a rock rich in a silica phase, such as opal, cristobalite, or quartz.

Siliceous shales – silica-rich shales.

Slickwater fracturing fluid - a water base fracturing fluid with only a very small amount of a polymer added to give friction reduction benefit.

Solvent - a substance that will dissolve a solid. In the oil field, oil based solvents may range from xylene for asphaltenes and sludges, to kerosene and diesel/xylene mixtures for paraffins.

Source rock – a rock rich in organic matter from the original sediment deposition that can generate petroleum fluids under certain temperature and pressure conditions.

Specific conductance - the measure of a material to conduct an electric current.

Stable isotopes – two or more forms of a chemical element having different numbers of neutrons that do not have any measurable radioactive decay.

Static fractures – fractures that are not changing over time.

Steam cycling – a form of steam injection in which injection and production take place in the same well, which is accomplished by alternating steam injection with oil production.

Steam injection – a thermally-enhanced oil recovery method in which steam is forced into the reservoir by applying pressure; the thermal energy of the steam heats the reservoir which reduces the viscosity of heavy oil that are usually the target of thermal oil recovery methods.

Storage coefficient – the volume of water released from storage per unit surface area of a confined aquifer per unit decline in hydraulic head.

Stratigraphic trap – a trap formed as a result of variations in porosity and permeability of the stratigraphic sequence.

Stratigraphic zone – a body of strata that is distinguished on the basis of lithology, fossil content, age, or other rock property.

Stress – the internal forces per unit area that are exerted in a material object.

Strike – is a geometrical characteristic of a planar geologic surface and is defined by the line of intersection between the geologic surface and a horizontal plane.

Structural features – geologic features that result from tectonic, diapiric, gravitational and compactional processes.

Structural trap – a trap formed as a result of faulting or folding of the rock.

Supercritical CO₂ – a fluid state of carbon dioxide which displays characteristics of both liquid and gas that occurs at conditions above its critical temperature and critical pressure.

Surface casing – the casing following the conductor casing in a well that protects fresh water aquifers from contact with fluids moving through the well. It is always cemented across the water zone and the cement usually extends to the surface.

Surfactant – a chemical that is attracted to the surface of a fluid and modifies the properties such as surface tension.

Tectonic features – features that are a result of forces or conditions within the earth that cause movements of the crust.

Tectonic stress – stress that results from forces or conditions within the earth that cause movements of the crust.

Televiewer log – a record of the amplitude of high-frequency acoustic pulses reflected by the borehole wall; provides location and orientation of bedding, fractures, and cavities.

Thermogenic methane – methane created by the thermal decomposition of buried organic material.

Tiltmeter – an instrument used to measure slight changes in the inclination of the earth's surface resulting from subsidence or uplift, usually in connection with volcanology and earthquake seismology.

Total dissolved solids (TDS) – total amount of all inorganic and organic substances – including minerals, salts, metals, cations or anions – that are dissolved within a volume of water.

Total Organic Carbon (TOC) – total mass of organic carbon from a measured sample.

Total Suspended Solids (TSS) - total mass retained on a filter per unit volume of water, typically a 0.4 to 0.7 micron filter.

Toxicity – the degree to which a substance can harm humans or other living organisms.

Trace metals – metals that do not affect chemical or physical properties of the system as a whole to any significant extent, and have ideal solution behavior characteristic of very high dilution.

Trap – a configuration of geologic layers and/or structures that has a very low permeability and is suitable for blocking the upward movement of buoyant hydrocarbons.

Turbidity – the measure of relative clarity of a liquid. It is an optical characteristic of water and is an expression of the amount of light that is scattered by material in the water when a light is shined through the water sample.

Unconventional reservoir – oil and gas resources whose_porosity, permeability, fluid trapping mechanism, or other characteristics differ from conventional sandstone and_carbonate reservoirs, such as shale gas, shale oil, heavy and viscous oil, gas hydrates, tight gas, and coal bed methane resources.

Updip – located up the dip of a sloping planar surface.

Viscosity – a measurement of a fluid's internal resistance to flow, expressed as the ratio of shear stress to shear rate.

Vitrinite – a type of woody kerogen that is used to measure source rock maturity.

Vitrinite reflectance – a measure of source rock maturity based on the reflectance of vitrinite, measured as % Ro. The onset of oil generation typically occurs at around Ro = 0.6%, with gas formation occurring when Ro = 1.2 %.

Volatile organic compounds (VOC) –organic chemicals whose composition makes it possible for them to evaporate under normal indoor atmospheric conditions of temperature and pressure.

Water flooding – purposely injecting water below and/or into the reservoir to drive the oil towards the producing wellbore.

Well completion – the activities and methods of preparing a well for the production of oil and gas or for other purposes, such as injection; the method by which one or more flow paths for hydrocarbons are established between the reservoir and the surface.

Well stimulation technology – refers to well stimulation methods of hydraulic fracturing, acid fracturing, and matrix acidizing.

Zonal isolation – the exclusion of fluids such as water or gas in one zone from mixing with fluids in another zone along pathways outside of a well casing, accomplished through cement that seals the rock to the casing.

Appendix E Bibliography of Submitted Literature

Input was solicited by the CCST steering committee from external groups to identify documents that should be considered during the development of the report. 163 references were submitted; most of the input received was from the Natural Resourced Defense Council (NRDC) and the Center for Biological Diversity (CBD). A few additional on-line submissions were also received.

Protocol for referencing literature in the report

This report primarily relies on literature subject to systematic peer review and government data. However, a primary problem in conducting an assessment of well stimulation technology (WST) in California (and elsewhere) is a lack of credible data. Consequently, other literature - so-called "grey literature" - may be included if it meets certain criteria (categories 2-5 below), and adds important information to the assessment. When the report requires the use of grey literature as a primary source, the text also notes that the reference is not peer-reviewed literature. Literature deemed to be advocacy, policy or opinion-based material is not included in the assessment. When citing or using literature and data, authors will note any material caveats on the quality of the information.

Categories of literature that can be used as references in the WST report:

- 1. Published, peer-reviewed scientific papers.
- 2. Government data and reports.
- 3. Academic studies that are reviewed through a university process, textbooks, and papers from technical conferences.
- 4. Studies generated by non-government organizations that are based on data, and draw traceable conclusions clearly supported by the data.
- 5. Voluntary reporting from industry. This data is cited with the caveat that, as voluntary, there is no quality control on the accuracy or completeness of the data.

Submitted, admissible literature

The submitted references tabulated here were reviewed by the report team members and were determined to fall into one of the five usable categories of literature. While the literature below was reviewed by the authors it was not necessarily cited within the text of the report. The authors also reviewed many documents that are not included in the list below.

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Appendix F Water Chemistry Data Tables

Table AF-1. Typical Hydraulic Fracturing Fluid Components for Michigan (Wilson and Schwank, 2013).

Component	Concentration	Reason	Common Uses
Fresh Water	80.5%	Solvent or carrier	Drinking
Sand or ceramic	10-20%	Proppant – keeps fractures open to permit oil/gas f ow	Playground sand, drinking water filtration
Acids (usually HCl)	0.12%	Helps dissolve minerals, initiate fractures in rock	Swimming pool cleaner
Petroleum Distillates	0.088%	Dissolves polymers, reduces friction	Mineral Oil – laxative, makeup remover, candy
Isopropanol	0.081%	Viscosity increaser	Antiperspirant, glass cleaner, first aid antiseptic
Potassium chloride	0.06%	Creates brine carrier f uid	Low-sodium table salt substitute
Guar gum	0.056%	Water thickener for sand suspension	Thickener used in cosmetics, baked goods, ice cream
Ethylene Glycol	0.043%	Prevents scale deposits in pipe(s)	Automotive antifreeze, household cleansers, deicer, caulk.
Sodium or Potassium Carbonate	0.011%	Improves the effectiveness of other components such as cross-linkers	Washing detergents, soaps, water softeners, glass, ceramics
Sodium chloride	0.01%	Stabilizes gel polymer chains	Table salt
Polyacrylamide	0.009%	Minimizes friction between f uid and pipe	Water treatment, soil conditioner
Ammonium bisulfite	0.008%	Oxygen remover to prevent pipe corrosion	Cosmetics, food and beverage processing, water treatment
Borate salts	0.007%	Maintains f uid viscosity as T increases	Laundry detergents, hand soaps, cosmetics
Citric acid	0.004%	Prevents precipitation of metal oxides	Food additive, foods and beverages, lemon juice
N,N-dimethyl formamide	0.002%	Prevents pipe corrosion	Pharmaceuticals, acrylic fibers, plastics
Glutaraldehyde	0.001%	Eliminates bacteria from produced water	Disinfectant, sterilizer for medical or dental equipment

NOTE: Not all components may be used in every well

Table AF-2. Predominant chemicals in hydraulic fracturing fluids in California (>2% occurrence) with associated CAS numbers based on data from FracFocus, part 10f 3 (see text for details).

Chemical / ingredient name	CAS number	occurrence in hydraulic fracturing fluid	% Occurrence in fracturing fluid	Count of occurrence as additive	Average conc. in fracturing fluid (% mass)	Average additive conc. (% mass)	Oral toxicity (LD 50), rat (mg/kg)	Oral toxicity (LD ₅₀), mouse (mg/kg)	Oral toxicity (LD ₅₀), rabbit (mg/kg)
Quartz (SiO2)	14808-60-7	1384	6.66	4032	23.988	34.1	200	Not Found	Not Found
G uar gum	9000-30-0	1334	96.2	1339	0.198	55.0	6770	8100	7000
Water	7732-18-5	1209	87.2	2047	73.879	94.2	00006<	Not Found	Not Found
Diammonium peroxodis ulphate	7727-54-0	1182	85.3	1205	0.012	88.0	495-820	Not Found	Not Found
Sodium hydroxide	1310-73-2	1147	82.8	1148	0.010	10.8	140-340	Not Found	Not Found
Diatomaceous earth, calcined	91053-39-3	1068	77.1	1702	0.014	75.2	Not Found	Not Found	NotFound
Ethylene alvcol	107-21-1	1052	75.9	1049	0.029	28.1	4700	7500	Not Found
Cristobalite	14464-46-1	1022	73.7	1022	600'0	1.1	Not Found	Not Found	Not Found
Magnes ium nitrate	10377-60-3	1015	73.2	1015	0.000	9.8	5440	Not Found	Not Found
5-Chloro-2-methyl-3(2H)-is othia zolone	26172-55-4	1015	73.2	1015	0.000	9.8	481	Not Found	Not Found
2-Methyl-3(2H)-isothiazolone	2682-20-4	1015	73.2	1015	0.000	4.9	Not Found	Not Found	Not Found
Magnesium chloride	7786-30-3	1015	73.2	1015	0.000	4.9	2800	4700	Not Found
Is otridecanol, ethoxylated	9043-30-5	1014	73.2	626	0.016	5.0	Not Found	Not Found	Not Found
Distillates, petroleum, hydrotreated light	64742-47-8	1000	72.2	1003	0.097	30.2	>15000	Not Found	Not Found
Hemice llulase enzyme concentrate	9025-56-3	992	71.6	829	0.002	3.0	Not Found	Not Found	Not Found
Distillates, petroleum, hydrotreated light paraffinic	64742-55-8	973	70.2		0.098	30.4	>2000	Not Found	Not Found
2-butoxypropan-1-ol	15821-83-7	962	69.4		0.000		Not Found	Not Found	Not Found
1-butoxypropan-2-ol	5131-66-8	962	69.4	996	0.016	5.3	5.66mL/kg~4920mg/kg	Not Found	Not Found
1,2-E thanediaminium	138879-94-4	939	67.7	943	0.057	60.0	Not Found	Not Found	Not Found
Phos phonic acid	13598-36-2	680	49.1	680	0.000	1.0	1500-1895	1700-2172	Not Found
Boron sodium oxide	1330-43-4	929	48.8	677	0.030	27.6	2660	Not Found	Not Found
Wethanol	67-56-1	368	26.6	485	0.068	52.5	5628 - 6970	7300	14400
Borax	1303-96-4	364	26.3	364	0.033	25.3	2660	2000	Not Found
Carbonic acid, dipotassium salt	584-08-7	245	17.7	252	0.191	59.2	1870	2570	Not Found
S odium chloride	7647-14-5	223	16.1	92	0.005	6.3	3000	4000	Not Found
Potassium hydroxide	1310-58-3	201	14.5	179	0.015	0.6	273 - 1230	Not Found	Not Found
Phenol, polymer with formaldehyde	9003-35-4	197	14.2	199	0.529	3.1	>2000	Not Found	Not Found
Glycerin, natural	56-81-5	160	11.5	108	0.037	0.2	5570-12600	4100	27000
Acetic acid	64-19-7	157	11.3	101	0.008	49.8	3310-3530	4960	1200
Silica	7631-86-9	149	10.8	139	0.174	1.7	>20000	Not Found	Not Found
Isopropanol	67-63-0	148	10.7	150	0.072	18.3	4710-5840	3600-4475	5030-7990
Alcohols, C11-14-iso-, C13-rich, ethoxylated	78330-21-9	114	8.2	109	0.003	0.0	Not Found	Not Found	Not Found
Naphthalene	91-20-3	114	8.2	9/	0.001	0.8	490-2600	350 - 710	Not Found
Potassium chloride	/44/-40-/	113	8.2	111	0.003	100.0	0097	383	Not Found
Taic Taic Taic Taic Taic Taic Taic Taic	1480/-96-6	109	7.9	109	0.000	0.0	Not Found	Not Found	Not Found
l etrakis (nydroxymetnyi) phos phonium suirate	55566-30-8	109	7.9	109	0.003	0.0	248-333	Not Found	Not Found
Vinylide ne chloride/methyla cryla te copolymer	25038-72-6	105	7.6	105	0.004	0.0	Not Found	Not Found	Not Found
Alconois, C.7-9-180-, C.8-rich, ethoxylated	78330-19-5	103	7.4	103	0.050	10.2	Not Found	Not Found	Not Found
Ethoxylated C 4-1 5 alcohols	7-79-15689	999	7.1	99	0.018	18.9	Not Found	Not Found	Not Found
Zirconium oxychloride	/699-43-6	94	6.8	94	0.01/	0.1	2950-3500	122/	Not Found
G luta ra Ide hyde	111-30-8	91	9.9	80	0.008	35.3	134-1470	100	aqueous solution) ~843 ma/kg
Methenamine	100-97-0	06	6.5	92	0.118	9.0	Not Found	569-1853	Not Found
Quatemary a mmonium compounds, bis (hydrogenated	68953-58-2	06	6.5	4	0.015	0.1	0008<	Not Found	Not Found
Solvent naphtha, petroleum, heavy arom.	64742-94-5	83	6.0	98	0.010	8.9	7050	Not Found	Not Found
ماسات مات مات ما بالم	7 70 00 1	18	2.5	68	2100	1000	1700	L +- 4	

Chemical / ingredient name	CAS	Count of occurrence in hydraulic fracturing fluid	% Occurrence in fracturing fluid	Count of occurrence as additive	Average conc. in fracturing fluid (% mass)	Average additive conc. (% mass)	Oral toxicity (LD ₅₀), rat (mg/kg)	Oral toxicity (LD ₅₀), mouse (mg/kg)	Oral toxicity (LD 50), rabbit (mg/kg)
Poly(oxy-1,2-ethanediyl), alpha-hexyl-omega-hydroxy	31726-34-8	81	5.8	81	0.017	0.1	Not Found	Not Found	Not Found
Glyoxal	107-22-2	79	5.7	80	0.065	30.0	200-7070	400-1280	>3175
D-G lucitol	50-70-4	79	5.7	80	0.022	10.0	15900	17800	NotFound
Monoethanolamine borate (1:x)	26038-87-9	7.8	9.5	7,8	0.041	60.0	Not Found	Not Found	Not Found
2,2-Uistorno-3-nitrilopropionamide 2-Bromo-3-nitrilopropionamide	1113-55-9	77	0.0	77	0.004	5.00	Not Found	Not Found	NotFound
Triethanolamine	102-71-6	7.4	5. 4.	7.4	0.000	2.0	4200-11300 4200-11300	5400-7800	2200
Boric acid	10043-35-3	70	5.1	71	0.016	30.0	2660-4000	3450	Not Found
Diethylene alvcol	111-46-6	20	5.1	89	0.000	0.1	12565-16600	13300-26500	26900
Trimethyl borate	121-43-7	20	5.1	70	0.015	30.0	6140	1290	NotFound
S odium persulfate	7775-27-1	20	5.1	70	0.005	100.0	Not Found	Not Found	NotFound
2-ethylhexan-1-ol	104-76-7	69	5.0	69	0.000	0.0	2049-3730	2500	1180-1470
Oleic acid	112-80-1	69	5.0	69	0.000	0.0	25000-74000	28000	Not Found
P otas sium a ceta te	127-08-2	69	5.0	89	0.000	0.0	3250	NotFound	NotFound
Potas sium cis -9-octa decenoic acid	143-18-0	69	5.0	69	0.000	0.0	>2000	>2000	NotFound
Propylene glycol	57-55-6	69	5.0	69	0.000	0.0	20000-37000	22000-31800	18000-19000
B is (2-ethylhexyl) sodium sulfosuccinate	577-11-7	69	5.0	69	0.001	0.0	1900-4620	2640	NotFound
Dicoco dimethyl ammonium chloride	61789-77-3	69	5.0	69	0.001	0.0	096	Not Found	NotFound
Alcohols, C10-14, ethoxylated	66455-15-0	69	5.0	69	0.002	0.0	Not Found	Not Found	NotFound
Phenol, 4,4'-(1-methylethylidene)bis-, polymer with 2- (chloromethyl)oxirane 2-methyloxirane and oxirane	68123-18-2	69	5.0	69	0.007	0.0	Not Found	Not Found	NotFound
Poloxalene	9003-11-6	69	5.0	69	0.002	0.0	5700	3000-45000	NotFound
Calcium chloride anhydrous	10043-52-4	89	4.9	99	0.001	0.0	1000-4179	1940-2045	100-1000
2-Propenoic acid, polymer with sodium phosphinate	129898-01-7	99	4.8	99	0.011	0.1	Not Found	Not Found	Not Found
2-Butoxverhanol	111-76-2	62	4.5	32	0.028	40.9	470-3000	1200-1519	320
Acetyltriethyl citrate	77-89-4	59	4.3		0.024		7000	1150	NotFound
Citric acid	77-92-9	95	4.0	58	0.022	6.09	3000-6730	5040	7000
Boric acid, dipotas sium salt	1332-77-0	23	3.8	53	660'0	0.4	Not Found	Not Found	Not Found
Tryptones	73049-73-7	47	3.4	9	0.002	5.0	Not Found	Not Found	Not Found
Extract of yeast	08013-01-2	47	3.4	9	0.002	5.0	Not Found	Not Found	Not Found
Teflon	9002-84-0	47	3.4	47	0.000	0.0	Not Found	Not Found	NotFound
Polyethylene glycol	25322-68-3	44	3.2	44	0.001	0.0	600-51310	28915-36000	14000-76000
Formaldehyde, polymer with 4-nonylphenol and oxirane	30846-35-6	44	3.2	44	0.005	0.0	Not Found	Not Found	Not Found
Quatemary ammonium compounds, benzyl-C10- 16alkydimethyl, chlorides	68989-00-4	44	3.2	4	0.003	0.0	400-900	Not Found	NotFound
Alcohols, C9-11-iso-, C10-rich, ethoxylated	78330-20-8	44	3.2	44	0.006	0.0	Not Found	Not Found	Not Found
Cellulase	9012-54-8	44	3.2	58	0.008	21.2	Not Found	Not Found	Not Found
S odium s ulfate	7757-82-6	43	3.1		0.001		5989	193-6346	Not Found
Naphtha, petroleum, hydrotreated heavy	64/42-48-9	42	3.0	42	0.304	0.09	>15000	Not Found	Not Found
Marinanase, endo-1,4-beta-	60-53-7	117	0.0		0.001		1000 T 0000	15200	Not Found
Cellulose, microcrystalline	9004-34-6	41	3.0		0.001		>5000	Not Found	Not Found
E thanol	64-17-5	39	2.8	41	0.031	27.7	7060-10600	3450	63000
Hydrogen peroxide	7722-84-1	39	2.8	39	0.000	0.3	376-1617	2000	820
Decyldimethylamine	1120-24-7	38	2.7	38	0.000	0.0	Not Found	Not Found	Not Found
N,N-Dimethyldecylamine oxide	2605-79-0	38	2.7	38	0.020	0.1	Not Found	Not Found	Not Found
Ammonium chloride	12125-02-9	37	2.7	30	0.061	50.3	1650	1300	Not Found
S olvent naphtha, petroleum, light arom.	64742-95-6	33	2.4	33	0.012	16.8	3500-14000	Not Found	Not Found
Hydrogen chloride	7647-01-0	33	2.4	46	0.799	22.5	238-277	Not Found	900
_	_	3.1	2.3		0.003		Not Found	Not Found	Not Found
1.2.4-Trimethylbenzene	95-63-6	31	2.2	33	0.001	2.8	3280-6000	Not Found	Not Found
_	_	,		,		-			

Table AF-2. Continued, part 3 of 3.

Chemical / ingredient name	CAS	Count of occurrence in hydraulic fracturing fluid	b'	% Occurrence Count of in fracturing occurrence as fluid additive	Average conc. in fracturing fluid additive conc. (% mass)	Average additive conc. (% mass)	Oral toxicity (LD $_{50}$), (LD $_{50}$), (LD $_{50}$), mouse (LD $_{50}$), rabbit (mg/kg)	Oral toxicity (LD ₅₀), mouse (mg/kg)	Oral toxicity (LD ₅₀), rabbit (mg/kg)
Propargyl alcohol	107-19-7	29	2.1	31	0.001	7.7	20 -110	05	Not Found
Thiourea, polymer with formaldehyde and 1- phenylethanone	68527-49-1	29	2.1	20	0.003	19.5	Not Found	NotFound	Not Found

Oral Toxicity. LD₅₀ (mg. tenre.a/Kg.nimal)

Category 1: x<5
Category 2: 5<x<50
Category 3: 50<x<300
Category 4: 300<x<2000
Category 4: 300<x<5000
Category 5: x>5000

Table AF-3. Constituents without CAS numbers reported in hydraulic fracturing fluids in California (>2% occurrence) based on data from FracFocus (see text for details).

Chemical / ingredient name	Count of occurrence in hydraulic fracturing fluid	% Occurrence in fracturing fluid	Count of occurrence as additive	Average conc. in fracturing fluid (% mass)	Average additive conc. (% mass)
Amino Alkyl Phosphonic Acid	679	49.0	679	0.006	30.0
Contains non-hazardous ingredents which are listed in in the non-MS DS section of the report	253	18.3	182	0.068	100.0
No Hazardous Ingredients	135	9.7	136	0.048	100.0
Water (Including Mix Water Supplied by Client)	131	9.5	n/a	74.680	n/a
Petroleum Distillate Blend	127	9.2	127	0.549	70.0
Hemicellulase Enzyme	111	8.0	111	0.010	100.0
N.A.	89	6.4	89	0.069	100.0
Mixture of S urfactants	80	5.8	80	0.081	60.0
EDTA/Copper chelate	62	4.5	62	0.008	30.0
Carbohydrates	44	3.2	58	0.035	97.1
Non-hazardous Ingredients	41	3.0	41	0.067	100.0
Cured Acrylic Resin	38	2.7	n/a	0.001	n/a
Alkanes / Alkenes	33	2.4	33	0.291	45.0
Proprietary	33	2.4	33	0.030	61.2
S ulfonate	29	2.1	29	0.007	9.8
E thoxylated nonylphenol	28	2.0	38	0.104	35.8
Non-Hazardous Ingredient	28	2.0	31	0.040	100.0

 $Table\ AF-4.\ Chemicals\ listed\ on\ matrix\ acidizing\ notices\ in\ California,\ part\ 1\ of\ 2\ (see\ text\ for\ details).$

Chemical / ingredient name	CAS number	# of wells	% of wells	Oral toxicity (LD ₅₀), rat (mg/kg)	Oral toxicity (LD ₅₀), mouse (mg/kg)	Oral toxicity (LD ₅₀), rabbit (mg/kg)
2-E thyl hexanol	104-76-7	36	100%	2049-3730	2500	1180-1470
E thylene glycol	107-21-1	36	100%	4700	7500	Not Found
2-butoxyethanol	111-76-2	36	100%	470-3000	1200-1519	320
Dodecylbenzene sulfonic acid	27176-87-0	36	100%	500-2000	Not Found	Not Found
Methanol	67-56-1	36	100%	5628 - 6970	7300	14400
Isopropanol	67-63-0	36	100%	4710-5840	3600-4475	5030-7990
Hydrochloric Acid	7647-01-0	36	100%	238-277	Not Found	900
Water	7732-18-5	36	100%	>90000	Not Found	Not Found
Poly(oxy-1,2-ethanediyl), a lpha-hexyl-omega- hydroxy(C2H4O)n(C6H14O) or Polyethylene glycol monohexyl ether	31726-34-8	36	100%	Not Found	Not Found	Not Found
Acetic acid	64-19-7	29	81%	3310-3530	4960	1200
Benzaldehyde	100-52-7	19	53%	800-1600	28-1600	Not Found
Cinnamaldehyde	104-55-2	19	53%	2220-3400	200-3400	Not Found
Diethylene glycol	111-46-6	19	53%	12565-16600	13300-26500	26900
Ammonium bifluoride	1341-49-7	19	53%	130	Not Found	Not Found
Hydroxylamine hydrochloride	5470-11-1	19	53%	141	408	Not Found
Amine oxides, cocoalkyldimethyl	61788-90-7	19	53%	Not Found	Not Found	Not Found
Formic Acid	64-18-6	19	53%	1100	700	Not Found
E thoxylated hexanol	68439-45-2	19	53%	Not Found	Not Found	Not Found
Alcohols, C12-16, ethoxylated	68551-12-2	19	53%	Not Found	Not Found	Not Found
Copper dichloride	7447-39-4	19	53%	140-584	190-233	Not Found
E thylene oxide	75-21-8	19	53%	72-330	280-365	Not Found
S ilica, amorphous - fumed	7631-86-9	19	53%	>20000	Not Found	Not Found
S odium iodide	7681-82-5	19	53%	4340	1000	Not Found
Citric Acid	77-92-9	19	53%	3000-6730	5040	7000
Poly(oxy-1,2-ethandiyl), a-(nonylphenyl)-w- hydroxy-	9016-45-9	19	53%	1310-16000	>50000	Not Found
Magnesium nitrate	10377-60-3	17	47%	5440	Not Found	Not Found
Prop-2-yn-1-ol	107-19-7	17	47%	20 -110	50	Not Found
Oleic acid	112-80-1 123-01-3	17 17	47% 47%	25000-74000	28000	Not Found
Dodecylbenzene (impurity)	123-01-3	17	47%	>5000 Not Found	Not Found Not Found	Not Found Not Found
Linear/branched alcohol ethoxylate (11eo) Acetic acid, potassium salt	127-08-2	17	47%	3250	Not Found	Not Found
S odium hydroxide	1310-73-2	17	47%	140-340	Not Found	Not Found
Disodium ethylene diamine tetra acetate (impurity)	139-33-3	17	47%	2000-3700	400-2050	2300
Potassium oleate	143-18-0	17	47%	>5000	>5000	Not Found
Cristobalite	14464-46-1	17	47%	Not Found	Not Found	Not Found
Crystalline silica	14808-60-7	17	47%	500	Not Found	Not Found
Tris odium ethylenedia minetetra a ceta te (impurity)	150-38-9	17	47%	2150	2150	Not Found
Poly(oxy-1,2-ethanediyl)	25322-68-3	17	47%	600-51310	28915-36000	14000-76000
5-chloro-2-methyl-2h-is othiazolol-3-one	26172-55-4	17	47%	481	Not Found	Not Found
2-methyl-2h-is othiazol-3-one	2682-20-4	17	47%	Not Found	Not Found	Not Found
S odium glycolate (impurity)	2836-32-0	17	47%	7110	6700	Not Found
E thoxylated propoxylated 4-nonylphenol- formaldehyde resin	30846-35-6	17	47%	Not Found	Not Found	Not Found
Alcohol, C11 linear, ethoxylated	34398-01-1	17	47%	Not Found	Not Found	Not Found
Trisodium nitrilotriacetate (impurity)	5064-31-3	17	47%	1100-3500	681-3160	>3500
Glycerol	56-81-5	17	47%	5570-12600	4100	27000
Propylene glycol	57-55-6	17	47%	20000-37000	22000-31800	18000-19000
Dioctyl sulfosuccinate sodium salt Dicoco dimethyl quaternary ammonium chloride	577-11-7 61789-77-3	17 17	47% 47%	1900-4620 960	2640 Not Found	Not Found Not Found
Fatty acids, tall-oil	61790-12-3	17	47%	3200-74000	4600	Not Found
S odium erythorbate	6381-77-7	17	47%	>5000	Not Found	Not Found Not Found
Tetras odium ethylenedia minetetra a cetate	64-02-8	17	47%	1658-4500	20.5-30	Not Found
Heavy aromatic naphtha	64742-94-5	17	47%	7050	Not Found	Not Found
Alkenes, C>10 a-	64743-02-8	17	47%	Not Found	Not Found	Not Found
Alkyl (C10-C14) alcohols, ethoxylated	66455-15-0	17	47%	Not Found	Not Found	Not Found
Cross linked PO/E O-block polymer	68123-18-2	17	47%	Not Found	Not Found	Not Found
Coco-amido-propylamine oxide	68155-09-9	17	47%	Not Found	Not Found	Not Found
Alcohol, C9-C11, Ethoxylated	68439-46-3	17	47%	1378	Not Found	Not Found
Thiourea, polymer with formaldehyde and 1- phenylethanone	68527-49-1	17	47%	Not Found	Not Found	Not Found
Alcohols, C14-15, ethoxylated (7E O)	68951-67-7	17	47%	Not Found	Not Found	Not Found
			-			•

Table AF-4. Continued, part 2 of 2 (see text for details).

Chemical / ingredient name	CAS number	# of wells	% of wells	Oral toxicity (LD ₅₀), rat (mg/kg)	Oral toxicity (LD ₅₀), mouse (mg/kg)	Oral toxicity (LD ₅₀), rabbit (mg/kg)
Quaternary ammonium compounds chlorides derivatives	68989-00-4	17	47%	400-900	Not Found	Not Found
Hydrofluoric acid	7664-39-3	17	47%	Not Found	Not Found	Not Found
S ulfuric acid (impurity)	7664-93-9	17	47%	2140	Not Found	Not Found
Magnesium chloride	7786-30-3	17	47%	2800	4700	Not Found
Alcohol, C7-9-iso, C8, ethoxylated	78330-19-5	17	47%	Not Found	Not Found	Not Found
Alcohol, C9-11-iso, C10, ethoxylated	78330-20-8	17	47%	Not Found	Not Found	Not Found
Alcohol, C11-14, ethoxylated	78330-21-9	17	47%	Not Found	Not Found	Not Found
Methyl oxirane polymer with oxirane	9003-11-6	17	47%	2300-5700	1830-45000	35000
Diatomaceous earth, calcined	91053-39-3	17	47%	Not Found	Not Found	Not Found
Naphthalene (impurity)	91-20-3	17	47%	490-2600	350 - 710	Not Found
Ammonium chloride	12125-02-9	1	3%	1650	1300	Not Found

Oral Toxicity: LD ₅₀ (mg _{chemical} /kg _{animal})	
Category 1: x<5	
Category 2: 5 <x<50< td=""><td></td></x<50<>	
Category 3: 50 <x<300< td=""><td></td></x<300<>	
Category 4: 300 <x<2000< td=""><td></td></x<2000<>	
Category 5: 2000 <x<5000< td=""><td></td></x<5000<>	
Category >5: x>5000	

Appendix G Mammalian Toxicity

Acute mammalian toxicity is a measurement commonly made for many industrial chemicals that allows comparison of toxicity between chemicals (United Nations 2003). In an acute oral toxicity test, characteristics of chemicals are described in terms of the median lethal dose ($\rm LD_{50}$ value) after ingestion by mice, rats, or other animals. The $\rm LD_{50}$ value is the amount of a chemical required to kill half of the members of a tested population after a specified test duration. Toxicologists use the toxic effects observed in mice and rats as a surrogate for toxicological impacts on humans. In some cases oral toxicity in rabbits may be reported. Furthermore, rodent toxicity tests are highly standardized, affording a comparison between chemicals.

Values for the acute oral toxicity of hydraulic fracturing compounds, with reported CAS numbers and that occur in more than 2% of operations, are reported in Table AF-2. Acute oral toxicity values for matrix acidizing compounds are reported in Table AF-4. Acute oral toxicity information for rat, mouse, and rabbit was compiled from a number of data sources (National Library of Medicine, 2013 and 2014; European Chemicals Agency, 2000; Lewis and Sax, 1996; US EPA, 2013). In order to simplify interpretation of the results and allow comparison between compounds, the oral toxicity data were classified according to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), which has five levels or categories of toxicity (United Nations, 2003). In the GHS system, Category 1 chemicals have lowest LD₅₀ doses and so are the most toxic, and Category 5 compounds have the highest LD₅₀ doses and so are the least toxic (see footnote to Table 5-3 for toxicity ranges for GHS categories). For example (Table 5-3), 2,2-dibromo-3-nitrilopropionamide (DBNPA, CAS 10222-01-2) is a biocide with a reported rat oral LD₅₀ of between 178 and 235 mg/kg, which places it in GHS Category 3. In contrast, ethylene glycol (CAS 107-21-1) is a solvent, commonly used in anti-freeze, that has a reported rat oral LD₅₀ of 4,700 mg/kg, which places it in GHS Category 5. By most interpretations, in relation to potential oral toxicity, DBNPA would be of greater potential concern than ethylene glycol, however the actual hazards associated with the various chemicals depend on many other factors as well as acute oral toxicity.

Appendix H California Council on Science and Technology Study Process

The reports of the California Council on Science and Technology (CCST) are viewed as being valuable and credible because of the institution's reputation for providing independent, objective, and nonpartisan advice with high standards of scientific and technical quality. Checks and balances are applied at every step in the study process to protect the integrity of the reports and to maintain public confidence in them.

Study Process Overview—Ensuring Independent, Objective Advice

For over 25 years, CCST has been advising California on issues of science and technology by leveraging exceptional talent and expertise.

CCST can enlist the state's foremost scientists, engineers, health professionals, and other experts to address the scientific and technical aspects of society's most pressing problems. All serve without pay.

CCST studies are funded by state agencies, foundations and other private sponsors. CCST provides independent advice; external sponsors have no control over the conduct of a study once the statement of task and budget are finalized. Study committees gather information from many sources in public and private meetings but they carry out their deliberations in private in order to avoid political, special interest, and sponsor influence.

Stage 1: Defining the Study

Before the committee selection process begins, CCST staff and members work with sponsors to determine the specific set of questions to be addressed by the study in a formal "statement of task," as well as the duration and cost of the study. The statement of task defines and bounds the scope of the study, and it serves as the basis for determining the expertise and the balance of perspectives needed on the committee.

The statement of task, work plan, and budget must be approved by CCST's Board chair. This review often results in changes to the proposed task and work plan. On occasion, it results in turning down studies that CCST believes are inappropriately framed or not within its purview.

Stage 2: Committee Selection and Approval

Selection of appropriate committee members, individually and collectively, is essential for the success of a study. All committee members serve as individual experts, not as representatives of organizations or interest groups. Each member is expected to contribute to the project on the basis of his or her own expertise and good judgment. A committee is not finally approved until a thorough balance and conflict-of-interest discussion is held, and any issues raised in that discussion are investigated and addressed. Members of a committee are anonymous until this process is completed.

Careful steps are taken to convene committees that meet the following criteria:

An appropriate range of expertise for the task. The committee must include experts with the specific expertise and experience needed to address the study's statement of task. A major strength of CCST is the ability to bring together recognized experts from diverse disciplines and backgrounds who might not otherwise collaborate. These diverse groups are encouraged to conceive new ways of thinking about a problem.

A balance of perspectives. Having the right expertise is not sufficient for success. It is also essential to evaluate the overall composition of the committee in terms of different experiences and perspectives. The goal is to ensure that the relevant points of view are, in CCST's judgment, reasonably balanced so that the committee can carry out its charge objectively and credibly.

Screened for conflicts of interest. All provisional committee members are screened in writing and in a confidential group discussion about possible conflicts of interest. For this purpose, a "conflict of interest" means any financial or other interest which conflicts with the service of the individual because it could significantly impair the individual's objectivity or could create an unfair competitive advantage for any person or organization. The term "conflict of interest" means something more than individual bias. There must be an interest, ordinarily financial, which could be directly affected by the work of the committee. Except for those rare situations in which CCST determines that a conflict of interest is unavoidable and promptly and publicly disclose the conflict of interest, no individual can be appointed to serve (or continue to serve) on a committee of the institution used in the development of reports if the individual has a conflict of interest that is relevant to the functions to be performed.

Point of View is different from Conflict of Interest. A point of view or bias is not necessarily a conflict of interest. Committee members are expected to have points of view, and CCST attempts to balance these points of view in a way deemed appropriate for the task. Committee members are asked to consider respectfully the viewpoints of other members, to reflect their own views rather than be a representative of any organization, and to base their scientific findings and conclusions on the evidence. Each committee member has the right to issue a dissenting opinion to the report if he or she disagrees with the consensus of the other members.

Other considerations. Membership in CCST and previous involvement in CCST studies are taken into account in committee selection. The inclusion of women, minorities, and young professionals are additional considerations.

Specific steps in the committee selection and approval process are as follows:

Staff solicit an extensive number of suggestions for potential committee members from a wide range of sources, then recommend a slate of nominees. Nominees are reviewed and approved at several levels within CCST. A provisional slate is then approved by CCST's Board. The provisional committee members complete background information and conflict-of-interest disclosure forms. The committee balance and conflict-of-interest discussion is held at the first committee meeting. Any conflicts of interest or issues of committee balance and expertise are investigated; changes to the committee are proposed and finalized. Committee is formally approved. Committee members continue to be screened for conflict of interest throughout the life of the committee.

Stage 3: Committee Meetings, Information Gathering, Deliberations, and Drafting the Report

Study committees typically gather information through:

- 1) meetings;
- 2) submission of information by outside parties;
- 3) reviews of the scientific literature; and
- 4) investigations by the committee members and staff.

In all cases, efforts are made to solicit input from individuals who have been directly involved in, or who have special knowledge of, the problem under consideration.

The committee deliberates in meetings closed to the public in order to develop draft findings and recommendations free from outside influences. The public is provided with brief summaries of these meetings that include the list of committee members present. All analyses and drafts of the report remain confidential.

Stage 4: Report Review

As a final check on the quality and objectivity of the study, all CCST reports whether products of studies, summaries of workshop proceedings, or other documents must undergo a rigorous, independent external review by experts whose comments are provided anonymously to the committee members. CCST recruits independent experts with a range of views and perspectives to review and comment on the draft report prepared by the committee.

The review process is structured to ensure that each report addresses its approved study charge and does not go beyond it, that the findings are supported by the scientific evidence and arguments presented, that the exposition and organization are effective, and that the report is impartial and objective.

Each committee must respond to, but need not agree with, reviewer comments in a detailed "response to review" that is examined by one or two independent report review "monitors" responsible for ensuring that the report review criteria have been satisfied. While feedback from the peer reviewers and report monitors is reflected in the report, neither group approved the final report before publication. The steering committee and CCST take sole responsibility for the content of the report. After all committee members and appropriate CCST officials have signed off on the final report, it is transmitted to the sponsor of the study and is released to the public. Sponsors are not given an opportunity to suggest changes in reports. All reviewer comments remain confidential. The names and affiliations of the report reviewers are made public when the report is released.

The report steering committee wishes to thank the oversight committee and the peer reviewers for many thoughtful comments that improved this manuscript.

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