Chapter Six

Potential Impacts of Well Stimulation on Human Health in California

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6.1. Abstract

This chapter addresses environmental public health and occupational health hazards that are directly attributable to well stimulation or indirectly associated with oil and gas development facilitated by well stimulation in California. Hazards that are directly attributable to well stimulation primarily consist of human exposures to well stimulation chemicals through inadvertent or intentional release to water, air, or soil followed by environmental fate and transport processes. Hazards that are indirectly associated with well-stimulation-enabled oil and gas development also include chemicals and environmental releases. Such hazards may not be directly related to well stimulation, but rather could result from expanded development that is enabled by well stimulation.

The risk factors directly attributable to well stimulation stem largely from the use of a very large number and quantity of stimulation chemicals. The number and toxicity of chemicals used in well stimulation fluids make it impossible to quantify risk to the environment and to human health. To gain insight on the potential of chemicals used in stimulation to harm human health, we used a ranking scheme that is based on toxic hazards of chemicals and reported quantities used in well stimulation operations. The ranking includes both acute and chronic toxicity. (Note that these same chemicals were ranked for aquatic toxicity in Volume II Chapter 2.)

Important pathways for human exposure to well stimulation chemicals and emissions include both water and air pathways. For water, possible pathways leading to exposure in California were identified in Volume II Chapter 2. These pathways include (1) the possibility of shallow hydraulic fractures intersecting protected groundwater, (2) the possibility of hydraulic fracturing intersecting other wells that could provide leakage paths, (3) the potential for spills and leaks of stimulation fluids, (4) injection of produced water, which could contain stimulation chemicals, into protected aquifers, (5) use of produced water that may contain stimulation chemicals in agriculture, (6) disposal of produced water that may contain stimulation chemicals in unlined sumps, and (7) the impact of strong acid use in recovered fluids and produced water. Wastewater generated from stimulated wells in California includes “recovered fluids” (flowback fluids collected into tanks following stimulation, but before the start of production) and “produced water” (water extracted with oil and gas during production). Air pathways that could result in human exposure to chemicals used in well stimulation include atmospheric dispersion of air pollutant emissions to communities near production sites. Studies have found human health risks attributable to emissions of petroleum-related compounds associated with oil and gas development in general. However, public health impacts associated with proximity to oil and gas production have not been measured in California. As such, detailed studies of the relationship between health risks and distance from oil and gas development sites are warranted. In the interim, increased application and enforcement of emission control technologies to limit air pollutant emissions and science-based minimum surface setbacks between oil and gas development and human populations could help to reduce these risks.

Our assessment of the scientific literature for community and occupational exposures and health outcomes indicates that there are a number of potential human health hazards associated with well-stimulation-enabled oil and gas development, but that California-specific peer-reviewed studies are critically scarce, and that air, water, and human health monitoring data have not been adequately collected, analyzed, verified, or reported.

6.2. Introduction

This chapter addresses environmental public health and occupational health hazards that are directly attributable to well stimulation or indirectly associated with oil and gas development facilitated by well stimulation in California.

Hazards that are directly attributable to well stimulation primarily consist of human exposures to well stimulation chemicals through inadvertent or intentional release to water, air, or soil followed by environmental fate and transport processes. Hazards that are indirectly associated with well-stimulation-enabled oil and gas development also include chemicals and environmental releases. Such hazards may not be directly related to well stimulation, but rather result from expanded development that is enabled by well stimulation. A number of potential contaminant release mechanisms and transport pathways have been described in Volume II, Chapters 2 and 3. In this chapter, we extend the previous discussion of environmental release and environmental transport mechanisms to include potential human exposure pathways, and summarize the hazards in the context of community and occupational health.

Hydraulic fracturing enables some oil and gas development that would not occur without this technology, but any oil and gas development presents hazards to human health through exposure to chemicals. Thus, to the extent that stimulation increases oil and gas development, hazards associated with development will also be increased. For example, additional emissions of toxic air contaminants (TACs) that are directly or indirectly attributable to well stimulation might be small relative to other regional sources (see Volume II, Chapter 3), but might have a higher local health impact near to the point of release. In addition, air pollution associated with the entire operation of oil and gas production can create significant human exposures. Therefore, we extend the discussion of indirect air pollution and emissions from Chapter 3 to consider potential human exposure pathways, and summarize the indirect hazards in the context of community and occupation health.

California-specific data on the impacts of well-stimulation-enabled oil and gas development is insufficient to provide a conclusive understanding of potential hazards and risks associated with well stimulation. Studies conducted outside of California consider health impacts near oil and gas development that are enabled by hydraulic fracturing, but do not differentiate the association of observed health risks between hydraulic fracturing stimulation and oil and gas development in general. Thus, the same health impacts that have been found near oil development enabled by hydraulic fracturing may exist in any oil and gas development.

The approach we take to assess human health hazards follows the general recommendations of the National Research Council (NRC, 1983; 1994; 1996; 2009) to compile, analyze, and communicate the state of the science on the human health hazards associated with well stimulation.

We begin with a summary of all hazards that have been described in earlier chapters of this volume, with an emphasis on human health aspects and risk factors. This provides a single comprehensive list of human health risk factors and hazards for well stimulation activities in California, with reference to the specific locations in the report where each hazard is discussed. We then carry out a detailed assessment of human-health-relevant hazards from chemicals, and from water and air pollution.

Because it is extremely difficult to identify specific causal relationships for a given hazard and health outcome, we employ two alternative approaches to explore hazards associated with a given activity, a bottom-up and top-down approach. The bottom-up approach follows the standard risk assessment framework. In this approach, we characterize the composition of well stimulation fluids and toxic air contaminants associated with well stimulation activities, and then identify chemical-specific human-health-relevant toxicity data, where available, and rank the chemical hazards based on a combined hazard metric that includes frequency of use, mass used, and toxicity. Our second approach, the top-down assessment, evaluates chemical and physical hazards associated with well stimulation activity by starting with population health outcomes and working backwards to evaluate potential associations between health outcomes and well stimulation activity (or oil and gas development activity, more broadly). To apply the top down approach, we draw from the peer-reviewed literature, where individual outcomes and potential hazards are studied, and findings provide evidence of possible associations between public health hazards and risks. We conclude with a review of occupational-health-relevant regulations and studies and a discussion of noise- and light-pollution health hazards. We identify potential mitigation strategies that, if properly deployed and enforced, may reduce occupational and community health impacts. Finally, we discuss well-stimulation information gaps related to environment protection in California.

As explained in Volume II, Chapter 1, there are both direct and indirect impacts of well-stimulation-enabled oil and gas development that influence public health risks. Based on available evidence, public health risks associated with direct impacts (which are the incremental impacts of oil and gas development attributable to the stimulation process itself and activities directly supporting the stimulation) appear to be small relative to the indirect impacts. To say it another way, the majority of public health risks associated with well stimulation are likely to be indirect, in that they arise from the additional oil and gas development that is enabled by well stimulation. All forms of oil and gas development, not just that enabled by well stimulation, may cause similar public health risks.

As an example, Volume II, Chapter 3 (air) found that benzene and formaldehyde emissions from oil and gas development is a significant fraction of stationary source emissions and may result in elevated atmospheric concentrations in places where people live, work, play, and learn. The current scientific literature has established that benzene is emitted from nearly all oil and gas development (Pétron et al., 2012; Pétron et al., 2014; Helmig et al., 2014). Studies show elevated health risks near hydraulic-fracturing-enabled oil and gas development attributable to benzene (McKenzie et al., 2012). Benzene and formaldehyde are not intentionally added to hydraulic fracturing or other well stimulation fluids, but may be a component of some of the petroleum-based mixtures used in hydraulic fracturing fluids. Overall, the health risks associated with benzene and formaldehyde occur because oil and gas is co-produced—and co-emitted—with these compounds. If public health investigations of benzene exposure were to be conducted only for those exposures near *stimulated* wells, then such investigations would result in a very poor understanding of both the extent of these risks and potentially effective mitigation measures that could protect public health. Concern about the health effects from benzene, formaldehyde, and many other health risks associated with oil and gas development should be approached through studies of oil and gas development from all types of reservoirs, not just those that are stimulated.

6.2.1. Framing the Hazard and Risk Assessment Process

The terms *hazard*, *risk*, and *impact* are often used interchangeably in everyday conversation, whereas in a regulatory context they represent distinctly different concepts with regard to the formal practice of risk assessment. A hazard is defined as any biological, chemical, mechanical, environmental, or physical stressor that is reasonably likely to cause harm or damage to humans, other organisms, or the environment in the absence of its control (Sperber, 2001). Risk is the *probability* that a given hazard will cause a particular harm, loss, or damage as a result of exposure (NRC, 2009). Impact is the particular harm, loss, or damage that is experienced if the risk occurs. Hazard can be considered an intrinsic property of a stressor that can be assessed through some biological or chemical assay. For example, a pH meter can measure acidity, disintegration counters can detect ionizing radiation, cell or whole animal assays, etc. can detect biological disease potency. These types of tests allow us to declare that a substance is acidic, radioactive, a mutagen, a carcinogen, or other hazard. However, defining the probability of harm requires a receptor (e.g., human population) to be exposed to the hazard, and often depends on the vulnerability of the population based on age, gender, and other factors. As a result, risk is extrinsic and requires detailed knowledge about how a stressor agent (hazard) is handled, released, and transported to the receptor populations.

In its widely cited 1983 report, the National Research Council (NRC) first laid out the now-standard risk framework consisting of research, risk assessment, and risk management as illustrated in Figure 6.2-1 (NRC, 1983). The NRC proposed this framework to organize and evaluate existing scientific information for the purpose of decision making. In 2009, the NRC issued an updated version its risk assessment guidance titled “Science and Decisions: Advancing Risk Assessment” (NRC, 2009). This report reiterated the value of the framework illustrated in Figure 6.2-1, but expanded it to include a solutions-based format that integrates planning and decision making with the risk characterization process. The NRC risk framework illustrates the parallel activities that take place during risk assessment and the reliance of all activities on existing research. These activities combine through the risk characterization process to support risk management.

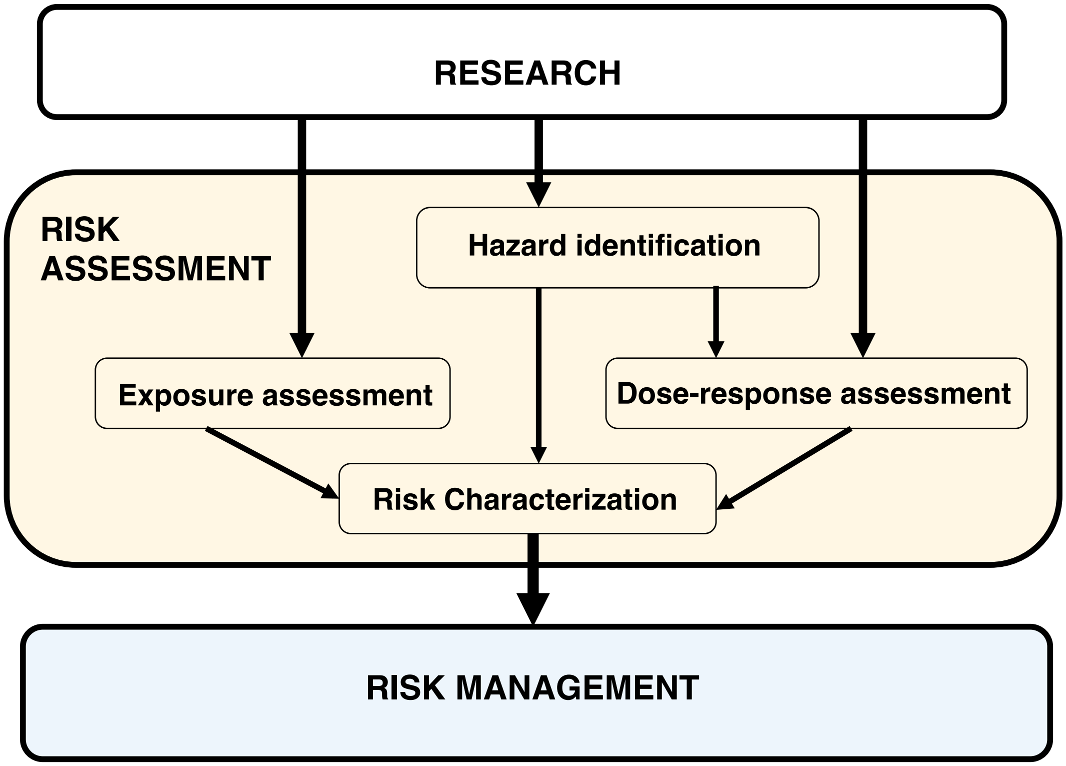

Figure 6.2-1. The NRC (1983) Risk Analysis Framework.

In using the framework in Figure 6.2-1, the first task in the risk analysis process is to identify any feature, event, or process associated with an activity that could cause harm. These are called "hazards." Any given hazard may or may not be a problem. It depends on the answers for two additional questions. First, is the hazardous condition likely to result in a population being exposed to the hazard? Second, what will be the impact if the hazardous exposure does occur (dose-response)? If we know the magnitude of a specific hazard exposure and the relationship between the magnitude of exposure and response or harm, then we can estimate the risk associated with that hazard. In cases where the hazardous condition is unlikely or where, even if it did occur, the harm is insignificant, then the risk is low. Risk is only high when the hazardous condition is both likely to occur and would cause significant harm if it did occur. Of course, there are many combinations of likelihood and harm possible.

Formal risk analysis presents difficulties, because we often lack:

- Data on all the possible hazards;
- Information on the likelihood and magnitude of exposure; and
- Data to support an understanding the relationship between exposure (dose) and harm (response).

If a hazard has not been identified, then it is difficult to develop steps to mitigate potential harm. In this case, a useful approach is to avoid the problem where possible, for example by choosing chemicals that are better understood, less toxic, or more controllable rather than choosing ones for which there is little toxicity information or poor understanding of the relationship between the hazard and risk to the environment and/or to public health. These options for both known and unknown hazards are discussed further in the mitigation section of this chapter as well as in Volume II, Chapter 2, Section 2.4 and in the Summary Report Conclusions.

Although one can attempt to identify *all* hazards associated with well-stimulation-enabled oil and gas development in California, it is important to note that this does not mean that all hazards that are identified present risks. A formal risk assessment is required to estimate risk associated with any given hazard. Although operators can make use of chemicals identified "acceptable" by programs such as the U.S. Environmental Protection Agency (U.S. EPA) Design for Environment Program or the North Sea Gold Ban list, uncertainties about exposure and impact can remain. A formal risk assessment is a significant undertaking that is beyond what was possible in this report. Among the goals of this chapter are to identify community and occupational hazards and highlight those where additional study may be warranted in the context of developing and implementing policies for well stimulation operations.

6.2.2. Scope of Community and Occupational Health Assessment

We consider and include both intentional and unintentional releases of chemical hazards to surface water, groundwater, and air as a direct and indirect result of well stimulation activities. These activities include the transport of equipment and materials to and from the well pad; mixing, handling, and injection of chemicals; and management of recovered fluids/produced water, drill cuttings, and other waste products (NRC, 2014; Shonkoff et al., 2014). In addition, we consider chemical hazards that are produced and/or released during support activities for well stimulation and from stimulated wells, such as: reaction products and mobilized chemical and/or radioactive hazards from the stimulated wells; emissions from generators, compressors, and other equipment during and after stimulation activity; leakage from transfer lines and infrastructure; and accidental spills. Finally, we consider other physical hazards related to well stimulation activity, including elevated noise and light. These hazards are relevant to both community and occupational health.

We exclude hazards associated with the manufacturing of materials, supplies, or equipment that are used in well stimulation activity; hazards from transport of oil and gas to refineries; hazards related to refining; or hazards from the combustion of hydrocarbons as fuel. These hazards, though important, are far removed both temporally and geographically from activities related to the well-stimulation-enabled oil and gas development process. We also exclude economic and psychosocial hazards that may be related to oil and gas development activities and may be important considerations in specific areas, but are beyond the scope of this chapter.

We focus primarily on hazards identified in relevant California-specific datasets and/or in the peer-reviewed literature that is specific to California. We augment this information with hazards identified in peer-reviewed studies conducted outside of California. As pointed out in Volume I and in other chapters in Volume II, geologic conditions and current practice with well stimulation in California can be different from that performed in other states, so not all hazards associated with well-stimulation-enabled oil and gas development outside of California are generally applicable to the California context.

6.2.3. Overview of Approach and Chapter Organization

The objective of this chapter is to catalogue and highlight important *community and occupational health hazards* associated with well stimulation activity in California. This is in contrast to earlier chapters of this volume that focused on environmental hazards in general and specifically those with water, air, and ecological pathways. There is significant overlap among the water, air, and ecological hazards described in earlier chapters and human-health-relevant hazards discussed in this chapter. Therefore, we begin in Section 6.2.4 with a summary of all hazards that have been described in earlier chapters of this volume, with an emphasis on human health aspects and risk factors, and we merge these with hazards that are identified and described in subsequent sections of this chapter. This provides a single list of human-health-relevant risk factors and hazards for well-stimulation-enabled oil and gas development activities in California, with reference to the specific locations in the report where each hazard is discussed. We also link the identified human health hazards to the case studies in Volume III of this report, where some of these hazards are illustrated and/or assessed in specific geographic places. Following the table of human-health-relevant hazards, we provide additional details on each risk factor/hazard combination from the list as well as other hazard/risk factors that are not listed (e.g., coccidiomycosis from exposure to San Joaquin Valley dust) along with recommendations for mitigating of risk.

After reporting and reviewing all human-health-relevant hazards in Section 6.2.4, we conduct a more detailed assessment of human-health-relevant hazards. The remainder of this chapter follows the issues summarized in the table, with the human health hazards (both community and occupational) defined and grouped into the following categories (and the section in which they are discussed):

- *Well stimulation chemicals* (Section 6.3)—includes both hydraulic fracturing and acidization chemicals intentionally injected to stimulate the reservoir or to improve oil and gas production. These chemicals are known and reported by industry on a mostly voluntary basis and more recently under Senate Bill 4 (SB 4, 2014) on a compulsory basis.

- *Recovered fluids and produced water* (Section 6.4)—includes some fraction of the well stimulation chemicals but can also include mobilized chemical compounds, naturally occurring toxic materials (such as radionuclides), and degradation and synergistic by-products from well stimulation chemicals, naturally occurring chemical constituents, and hydrocarbons.

- *Air pollutant emissions associated with well stimulation-enabled oil and gas development* (Section 6.5)—includes combustion products and/or chemical emissions from pumps, generators, compressors and equipment; venting and flaring emissions; dust from well stimulation and land-clearing activities; leaks from transfer lines and/or well heads; longer-term leakage of oil and gas from stimulated wells. (This category does not include emissions from refining and use of the hydrocarbon products.)

- *Occupational Health* (Section 6.6) —includes hazards such as exposure to respirable silica, volatile organic compounds (VOCs), and acids.

- *Other* (Section 6.7)—includes physical hazards such as light and noise and heavy equipment activity, industrial accidents (e.g., loss of well control, explosions), biological hazards such as valley fever in areas where surface soil is disturbed by well stimulation activity, spills from trucks transporting chemicals that can contaminate private wells.

We use the above categories to differentiate hazards that have similar release mechanisms and time of release, such that all chemicals in a given category are likely to be released into the environment by the same mechanism or activity and in the same location. These categories enable us to group hazards identified in this report that are relevant to human and occupational health risk in the summary table below (Table 6.2-1). The specific hazards are listed in terms of the four categories above, along with California-specific factors or conditions (risk factors) that are expected to increase or decrease the human health risk associated with the hazards. All of these risk factors identified in the summary table are applicable to the San Joaquin Valley (SJV), where more than 85% of the well stimulation events in California occur. Some factors also apply to other oil and gas producing regions where well stimulation is used.

In the sections that follow the summary table, we expand on the specific human health hazard categories identified above. In general, when evaluating population-level human-health impacts, it is extremely difficult to identify specific causal relationships for a given health hazard and impact. As a result, risk assessors consider alternative approaches to assess the likelihood of harm. The first approach, sometimes referred to as "bottom-up," starts with a cause, such as chemical hazard, and attempts to track emissions and exposure pathways along with dose-response modeling to characterize population impact. This approach often must confront uncertainties identifying exposures and actual health impacts. The second approach, sometimes referred to as "top-down," starts with an impact—for example disease incidence—and attempts to track it back to some source chemical or activity. For the "top-down" approach, uncertainty arises from the lack of statistical power in making associations with low disease rates, as well as from the considerable lag times between exposure and occurrence of diseases (e.g., cancer). Because of their significant but different types of limitations, it is useful to consider both approaches. These alternate ways of exploring hazard are illustrated in Figure 6.2-2. In this chapter, we use both approaches.

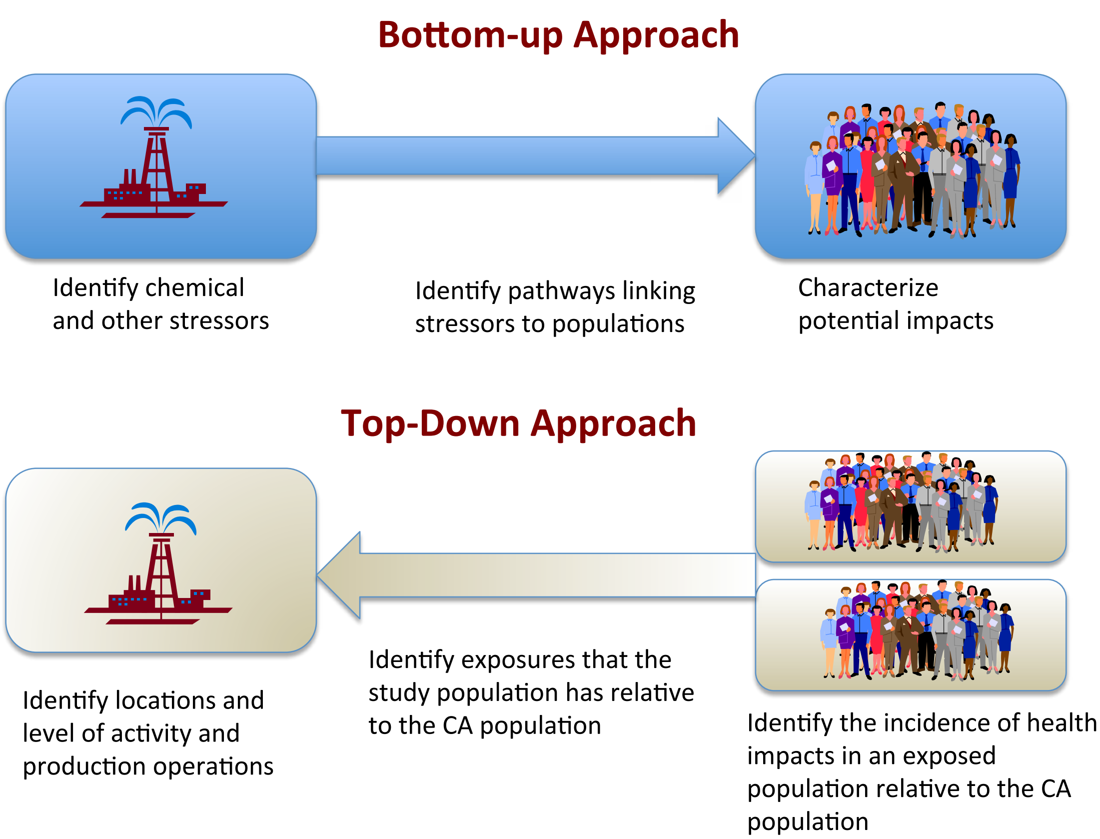

Figure 6.2-2. Illustration of two approaches used to identify human health hazards associated with an activity.

We conduct a bottom-up assessment in Section 6.3, 6.4, and 6.5 where we evaluate chemical and physical hazards associated with well stimulation chemicals and potential contamination pathways. We build on the discussions in Volume II Chapters 2 and 3 that characterize the composition of well stimulation fluids and toxic air contaminants associated with well stimulation activity. We extend this data by identifying chemical-specific human-health-relevant dose-response information where available, and rank the chemical hazards based on a combined hazard metric that includes frequency of use, mass used, and toxicity. We also discuss potential exposure factors to further extend the bottom-up assessment.

The most relevant approach for top-down hazard assessment would be to conduct a formal epidemiological study that attempts to pull out specific cause-effect relationships within a population. However, these studies require that the "effect" already be expressed (and measured) in the population, and that the effect is both unique and common enough to identify. A more general top-down approach draws from the peer-reviewed literature, where individual outcomes and potential hazards are studied, and findings provide evidence of possible associations between hazard and public health risk. We include a top-down hazard assessment in support of each section focusing primarily on California and health-outcome studies and, where studies from outside of California are relevant, we review and summarize the evidence for hazards based on experience and observations from outside California. A detailed summary compilation of the literature is provided in Appendix 6.A for public health, Appendix 6.D for occupational health and Appendix 6.F for noise.

We wrap up the chapter with a summary of critical data gaps (in addition to those identified in earlier chapters) and then with conclusions and recommendations for community and occupation health.

6.2.4. Summary of Environmental Public Health Hazards and Risk Factors

The geology and history of hydrocarbon development, along with current practices and current regulatory framework for well stimulation-enabled oil and gas development in California, give rise to the potential public health risks associated with well stimulation activities. Table 6.2-1 summarizes all human health relevant hazards identified in this chapter and in previous chapters of this volume. We also provide reference to the location in this volume where each risk factor and hazard is discussed in more detail. Although we include possible mitigation strategies in Table 6.2-1, data on the *adequacy and effectiveness* of regulations to achieve these goals is often not available, requires more study, and/or is beyond the scope of this report.

Table 6.2-1. Summary of human health hazards and risk factors in California substantiated with California-specific data.

Risk Factor	Hazard	Description of the issue	How the risk factor is expected to influence public health risks	Possible mitigation	Volume and Section in this Report
Number and toxicity of chemicals in well stimulation fluids	Well stimulation chemicals	Operators have few restrictions on the types of chemicals they can use for hydraulic fracturing and acid stimulation. In California, oil and gas operators have reported the use of over 300 chemical additives. About 1/3 have not been assessed for toxicity. Of the chemicals for which there is basic environmental and health information, only a few are known to be highly toxic, but many are moderately toxic. There is incomplete information on which of the chemicals used have the potential to persist or bio-accumulate in the environment and may present risks from chronic low-level exposure.	If these chemicals are not released into usable water, including agricultural water and to the atmosphere then the risk is minimal. However, if there are leakage and emission pathways then it is nearly impossible to assess the risk because of the large number of chemicals, incomplete knowledge about which chemicals are present, how long these compounds persist and what their environmental and human health impacts are. Researchers and the public need access to sufficient levels of information on all chemicals involved in well stimulation, to begin an assessment of the toxicity, environmental profiles, and human health hazards associated with hydraulic fracturing and acidizing stimulation fluids.	Invoke Green Chemistry principles to reduce risk, that is, use smaller numbers and amounts of less toxic chemicals, and avoid chemicals with unknown impacts. Mitigate exposure pathways. Limit the chemical use in hydraulic fracturing to those on an approved list that would consist only of those chemicals with known and acceptable toxicity profiles.	Vol. II Ch. 2 S. 2.4 & Summary Report S. 3.1
Disposal of water in unlined sumps	Recovered fluids & produced water	The disposal of contaminated water in unlined pits is banned in nearly all other states because such fluids can migrate out of sumps into groundwater and move along with this water to wells or surface water where contamination can be a serious problem. Nearly 60% of wastewater from stimulated wells in California was disposed in unlined sumps.	Well stimulation and naturally occurring chemical constituents can evaporate from these ponds to the atmosphere as air pollutants, leak into aquifers, or migrate through the soil which could lead to food chain exposure to biota and humans. Chemicals in recovered fluids and produced water may be toxic, persistent, or bioaccumulative.	Test and appropriately treat water going in to unlined pits, or phase out the use of unlined sumps in the SJV for wastewater disposal.	Summary Report S. 3.2 & Vol. II Ch. 2 S. 2.6.2.1 & Vol. III Ch. 5

Risk Factor	Hazard	Description of the issue	How the risk factor is expected to influence public health risks	Possible mitigation	Volume and Section in this Report
Beneficial use of produced water	Recovered fluids & produced water	California is a water-short state and California's oil reservoirs produce about 10 times more water than oil. Produced water is sometimes reused, for example to irrigate crops. If this produced water comes from stimulated wells or oil wells producing from a reservoir where stimulation was used, stimulation chemicals could be present in the produced water.	Well stimulation chemicals and their reaction products may be toxic, persistent or bioaccumulative. Current water district requirements for testing such waters before they are used for irrigation are not sufficient to guarantee that stimulation chemicals are removed, although some local treatment plants do use adequate protocols. If produced water used in irrigation water contains well stimulation and other chemicals, this would provide a possible exposure pathway for farmworker and animals and could lead to exposure through the food chain. Currently, more than 60% of the fruits and vegetables consumed domestically come from the Central Valley.	Water districts in the SJV should explicitly disallow the use for irrigation of produced water from wells that have been hydraulically fractured, or demonstrate that their monitoring and treatment methods ensure that hydraulic fracturing chemicals and other contaminants are not present in water destined for irrigation.	Vol. II Ch. 2 S. 2.6.2.3 & Summary Report S. 3.2
Shallow hydraulic fracturing	Well stimulation chemicals	The majority of hydraulic fracturing in California is conducted from shallow vertical wells. These operations present a larger probability of fractures intersecting near-surface groundwater compared to high volume fracturing from deep long-reach horizontal wells commonly used elsewhere.	The groundwater in the vicinity of some shallow fracturing is protected. Contamination of usable groundwater presents environmental public health risks. Groundwater monitoring requirements are likely insufficient to determine whether water has been contaminated by well stimulation-enabled oil and gas development or not. The groundwater in the vicinity of much of the shallow hydraulic fracturing operations in California has high salinity and has no beneficial uses that might constitute environmental exposure pathways to humans.	The focus of regulations should be on preventing contamination of aquifers, not just monitoring for it. Operators should be required to demonstrate that stimulations could not intersect usable groundwater to receive a permit. A higher level of scrutiny should be applied to shallow stimulations. Groundwater monitoring plans should be adapted as part of the corrective action, to improve the monitoring system and specifically look for contamination in close proximity to possible fracture extensions into groundwater.	Vol. I Ch. 3 S. 3.2.3.3 & Vol. II Ch. 2 S. 2.6.2.5

Risk Factor	Hazard	Description of the issue	How the risk factor is expected to influence public health risks	Possible mitigation	Volume and Section in this Report
Hydraulic fracturing in reservoirs with long history of oil and gas production	Well stimulation chemicals Recovered fluids & produced water Air and other pollutant emissions associated with well-stimulation-enabled oil development Other	Many of the issues faced by other states arise because hydraulic fracturing has opened up oil and gas development in regions that previously had little or no experience with production. When the US Energy Information Agency issued a report indicating that a large amount of such development was also possible in California from the Monterey Formation (subsequently revised dramatically downward), many were concerned about the development of oil and gas in new geographies. This assessment finds that the most likely future use of hydraulic fracturing is in and around the reservoirs where it is currently being used.	New production in developed fields can use the existing roads, platforms and infrastructure already in place. As a result, the impacts caused by construction and traffic are much less than in new, previously undeveloped regions.	Existing infrastructure reduces the need for new pads pipelines and other stationary infrastructure. Existing infrastructure can often transport fluids to and from the pad, reducing the need for truck trips. This reduces traffic accidents and the emission of diesel particulates and other health-damaging air pollutants	Vol. II, Ch.. 3
			Old reservoirs have many existing wells. If hydraulic fractures intersect or come near these old wells, the wells could form leakage pathways for stimulation fluids. Older existing infrastructure (e.g. pipelines, storage tanks) may increase the likelihood of failures or leakage.	Locate and seal old wells in the vicinity of hydraulic fracturing if they would provide leakage paths to air and usable groundwater. Regulations should explicitly require an assessment of the integrity and leakage risk of existing wells that might be encountered by a hydraulic fracture, and remediation of wells which create a high risk of leakage into water less than 10,000 milligrams/liter total dissolved solids.	Vol. II Ch. 2 S. 2.6.2.6 & Vol. III Ch. 5 and Ch.2, Table 2.6-1.
Injection of recovered fluids and produced water into aquifers used for drinking, agriculture, and other direct and indirect uses by humans	Well stimulation chemicals Recovered fluids & produced water	Produced water from stimulated fields has been injected into aquifers that are suitable for drinking water, irrigation, and other beneficial uses.	If water from contaminated aquifers is used, it could expose humans to unsafe concentrations of toxic compounds.	Prevent injection of well stimulation chemicals to usable groundwater in the future. In the process, of reviewing, analyzing and remediating the potential impacts of wastewater injection into protected groundwater, consider the possibility that stimulation chemicals may have been present in these wastewaters.	Vol. II Ch. 2 S. 2.6.2.2 & Vol. III Ch. 5

Risk Factor	Hazard	Description of the issue	How the risk factor is expected to influence public health risks	Possible mitigation	Volume and Section in this Report
Spills and leaks	Well stimulation chemicals Recovered fluids & produced water	Surface spills and leaks are common occurrences in the oil and gas industry and must be reported and cleaned up.	Information recorded on spills and leaks is insufficient to determine whether stimulation chemicals could be involved.	Require public reporting about whether the source of the leak could contain well stimulation chemicals.	Vol. II Ch. 2 S 2.6.2.9
Oil and gas development near human populations	Well stimulation chemicals Recovered fluids & produced water Air and other pollutant emissions associated with hydraulic fracturing-enabled development Other	California has large oil reserves located under densely populated areas primarily in the San Joaquin and Los Angeles Basins. In Los Angeles, oil and gas production developed simultaneously with the growth of the city. The Los Angeles Basin has world-class oil reservoirs, with the most concentrated oil in the world. Los Angeles is also a global megacity.	Proximity to production increases exposures to air pollutant emissions and other results of oil and gas development activities (e.g., dust, chemicals, noise, light). Households that use groundwater from private drinking water wells in close proximity to oil and gas development may be at increased risk of exposure to potential water contamination.	Identify and apply appropriate measures to limit exposure by residents and sensitive receptors such as schools, daycare facilities and elderly care facilities such as scientifically based setback requirements.	Vol. II Ch. 6S. 6.8.1 & Vol. III Ch. 4.3 & Summary Report S. 3.2
Acid use	Well stimulation chemical	Operators in California commonly use mixtures of hydrochloric acid and hydrofluoric acid with other sources of fluoride anions as the most economical reagent for cleaning out wells or enhancing geological formation permeability. Reported use of hydrofluoric acid in the SCAQMD data lists the concentration as percent mass in the ingredient as 1%-3%.	Spills and leaks of undiluted acids may present an acute toxicity and corrosivity hazard. The use of acid can also mobilize naturally occurring heavy metals and other compounds that are known to be health hazards and these compounds could therefore be present in recovered fluids and produced water which humans could be exposed to if treatment and disposal is not sufficiently undertaken.	Evaluate the chemistry of recovered fluids and produced water for wells that have used acids and the potential consequences for the environment. Require reporting of significant chemical use for oil and gas development based on these results.	Vol. II Ch. 2 Ss. 2.4.3.2, 2.6.2.9 & Summary Report S. 3.2

6.3. Public Health Hazards of Unrestricted Well Stimulation Chemical Use

Previous chapters have considered environmental and ecological hazards. In this section, we examine the potential impact of well stimulation chemicals on human health, based on reported use information (frequency and quantity) and on published toxicity information.

The majority of important potential direct impacts of well stimulation result from the use of chemicals. Operators have few restrictions on the types of chemicals they use for hydraulic fracturing and acid treatments. In California, oil and gas operators have reported, on voluntary and mandated bases, the use of over 300 chemical additives (see Volume II, Chapter 2 for detailed description of chemicals). Although SB 4 (2014) now mandates reporting of chemical use by operators, the data are not subject to independent verification, and chemicals can be reported as “trade secrets,” meaning they need not be fully identified. The many chemicals used in well stimulation makes it very difficult to judge the public health risks posed by releases of stimulation fluids.

In addition to the sheer number of known and unknown (trade-secret) chemical additives used, we often lack information on potential release mechanisms and important physical and chemical properties needed to characterize environmental fate and exposure pathways, and toxicological characteristics (acute and chronic) needed to fully understand chemical hazards.

The most common toxicity information about chemicals is from standardized mammalian acute toxicity tests that measure the short-term (minutes to hours) exposure concentration or one-time dose of a chemical required to induce a well-defined response (death, narcosis, paralysis, respiratory failure, etc.) of a test animal, most commonly rats and mice. Such tests are used to assess toxicity of inhalation, ingestion, and/or uptake through the skin. Acute toxicity tests measure extreme outcomes, but the tests are useful for ranking chemicals against each other and identifying chemicals that are clearly dangerous if taken into the body.

More useful but less commonly available tests for health impacts are chronic toxicity tests. These are long-term studies (often lifetime or multi-generation studies) with small mammals to observe any increases in chronic disease incidence—including tumors and cancer, reproductive/developmental changes, neurological damage, respiratory damage, life shortening. Animal-based chronic toxicity results are used for assessing the hazards and risks to communities and workers from long-term (up to lifetime) exposures to relatively low concentrations or doses of chemicals. In addition to toxicity tests with animals, some chemicals have occupational or community epidemiological studies that provide useful information on chronic toxicity. Because these studies are the result of accidents or from improperly regulated chemicals or air contaminants, there are limited numbers of chemicals that have human-based chronic health data. Approximately two-thirds of the reported chemicals used in well stimulation have publically available results from acute mammalian toxicity tests (excluding material safety data sheets (MSDS) data), and only about one-fifth of the reported chemicals have associated chronic toxicity information.

Of the chemicals for which there is basic environmental and health information, only a few are known to be highly toxic, but many are moderately toxic. For most substances we consider, there is lack of toxicological testing for long-term chronic exposure at very low levels. There is also a lack of testing on mixtures. Some of the chemicals used may have the potential to persist or bio-accumulate in the environment and present risks from chronic low-level exposure. Because the toxicology for multiple routes of exposure—inhalation, ingestion, skin contact, etc.—is rarely reported, cumulative exposure assessment is beyond the scope of our analysis.

In this section, we develop and apply a semi-quantitative ranking system for chemical hazards associated with well stimulation activity. The ranking system is not a substitute for field observations or a full risk assessment, but provides an initial focus on which chemicals are of highest concern and which are of lower priority. Section 6.3.1 describes the approach, followed by results for hydraulic fracturing chemicals, acidization chemicals, and toxic air contaminants in Section 6.3.2, finishing with a summary of relevant literature in Section 6.3.3.

6.3.1. Approach for Human Health Hazard Ranking of Well Stimulation Chemicals

Chemical hazards include both hydraulic fracturing and acidization chemicals that are intentionally injected to stimulate the reservoir or to improve oil and gas production (see Volume I, Chapter 2 for the engineering purpose of these chemicals) and unintentional releases from spills or leaks. Chemicals are used in the drilling and well stimulation processes for a variety of purposes, including as corrosion inhibitors, biocides, surfactants, friction reducers, viscosity control, and scale inhibitors (Southwest Energy, 2012; Stringfellow et al., 2014) (Section 2.4.4.1). Hydraulic fracturing uses fluids or gels that contain organic and inorganic chemical compounds, a number of which are known to be health damaging (Aminto and Olson, 2012).

In this section, we provide a bottom-up assessment to develop hazard priorities for chemicals that are used in well stimulation. The ranking is based on reported information about the specific chemical identity, the quantity and frequency of use, and available information on both acute and chronic toxicity.

6.3.1.1. Chemical Hazard Ranking Approach

Well stimulation (e.g., hydraulic fracturing and acidization) includes processes that use, generate, and release (intentionally and unintentionally) a wide range of chemical, physical, and, in some cases, biological stressors. To organize the large and diverse number of potential stressors, we use a hazard-ranking scheme that begins with a list of all identifiable stressors, and then records for each stressor our attempts to characterize potential outcomes, using measures of toxicity combined with information representing the frequency and magnitude of use. Sections 6.4 and 6.5 describe potential exposure pathways that would bring chemicals to a human population through water supply or air.

The hazard-ranking scheme used here gives weight to three factors— the number of times a chemical is reported in the database (a surrogate for frequency of use), mass or mass fraction (concentration) used, and toxic hazard screening criterion. So it is not the most toxic substances that always rank high, because weight is also given to substances of intermediate toxicity (or even relatively low toxicity) that are used frequently and/or in large quantities. Even with high mass and frequent use of compounds with elevated toxicity, an exposure pathway is required to bring the compound into contact with the human receptor for an adverse effect to be realized.

The disclosed mass and frequency of chemical use (as described in Section 2.4.3 for hydraulic fracturing and in Section 6.3.2.2 for acidization) provides a surrogate for potential chemical release and exposure, but this is only part of the hazard picture. It is also important to consider the impact of exposure to a chemical. Impacts considered in this assessment include both acute and chronic toxicity outcomes for individual chemicals. As noted above in Section 6.3, toxicity can be characterized as acute (short-term consequences from a single exposure or multiple exposures over a short period) or chronic (long-term consequences from continuous or repeated exposures over a longer period). It is not possible to evaluate potential synergistic hazards with multiple pollutants at this time.

For acute toxicity, we use a screening hazard criterion based on the Global Harmonization Score (GHS) that combines all acute toxicity information into a single screening value (UN, 2011). For chronic toxicity, we use published regulatory reference levels that consider information reported for different routes of exposure (inhalation, ingestion, dermal) and different health outcomes.

The ultimate goal of the hazard ranking is to combine the different elements that relate to increasing hazard. In considering specific chemical stressors, we used the information on frequency of use, mass or mass fraction used per treatment, and acute and/or chronic health hazard criteria, to develop a potential hazard score that could be used to assign a rank for each substance. In cases where all three pieces of information are available, the hazard score is calculated as an Estimated Hazard Metric (EHM) given by:

$$\text{EHM} = (\text{frequency of use}) \times (\text{mass or mass fraction used})/(\text{toxicity criterion})$$

The calculated EHM are used to rank all substances from highest estimated hazard to lowest. For chemicals that lack sufficient information to calculate an EHM, we ranked from most toxic to least toxic, and when toxicity information is lacking we rank from most to least reported use. The resulting sorted list provides an indication of level of concern for each compound.

The development of acute and chronic toxicity criteria used for calculating the EHM are discussed in Sections 6.3.1.2 and 6.3.1.3, respectively, with the hazard ranking results for hydraulic fracturing and acidization presented in Sections 6.3.2.1 and 6.3.2.2, respectively.

6.3.1.2. Acute Toxicity Hazard Screening Criterion

Human hazards associated with acute or short-term exposures are inferred from laboratory studies that examine the acute toxicity of an individual compound or chemical formulations through standardized testing procedures using mammals—typically mice, rats, and rabbits. In these studies, the test animals are exposed to high concentrations of the test chemical and the response of the animals as a function of the exposure is determined, with the metric being the concentration at which some significant fraction of the animals have a measurable outcome (05%, 10%, 50%). These effective concentrations (EC) or effective doses (ED) are reported as respectively EC05 (EC05), EC10 (ED10), and EC50 (ED50).

We collected acute toxicity data for the chemicals that have been disclosed in well stimulation fluid in California that were definitively identified by their Chemical Abstract Service Registration Numbers (CASRN). Toxicity data were gathered from publicly available sources as described in Volume II, Chapter 2 and from MSDS. Acute toxicity data is available for a number of exposure routes and a range of effects. To merge this diverse data set into a single health-screening criterion, we used the United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS). The GHS is a system for categorizing chemicals based upon their LD50 (lethal dose) or EC50 values (UN, 2011). In the GHS system, lower numbers indicate more toxicity, with a designation of "1" indicating the most toxic compounds. Chemicals for which the LD50 or EC50 exceeded the highest GHS category were assigned a value of 6 and classified as non-toxic. Chemicals that lack data on acute effects were assigned a GHS value of zero.

We also reviewed material safety data sheets (MSDS) for each chemical and recorded GHS values for a range of outcomes, including acute dermal, skin irritation, eye effects, respiratory sensitization, and skin sensitization. The GHS values from publicly available sources (oral and inhalation) were assessed separately from the GHS scores reported in MSDS.

Because the GHS is reported on a scale of 1 to 5, we found it to be ineffective for sorting out highly toxic chemicals. To address this issue for human health impacts, we converted the GHS category scores back to the midpoint exposure concentration for animal oral toxicity in milligrams per kilogram (mg/kg) for the given category, based on the definitions provided for GHS categories (Table 3.3-1 in UN, 2011). GHS categories 1, 2, 3, 4, and 5 were assigned equivalent toxicity criteria of 2.5, 25, 200, 1,150, and 3,500 mg/kg, respectively. We refer to this as the GHS-surrogate-concentration or "GHS-sc."

Most stimulation chemicals are used at fairly low concentrations, usually less than 0.1%. These concentrations can be well below concentrations that would cause test animals to have a measureable acute response. However, most chemicals that have been assessed for toxicity are assessed with acute toxicity tests. Low-concentration responses are difficult to measure but highly relevant to efforts to protect human health. Public health actions are intended to prevent harm before it happens, rather than provide methods to monitor harm as it happens. This goal reflects the need for chronic hazard screening as a key supplement to acute hazard screening.

6.3.1.3. Chronic Toxicity Hazard Screening Criterion

Chronic toxicity values are typically expressed using a long-term average intake that is considered a “safe” or no-effect dose, expressed in mg/kg (body weight) per day. For example, the state of California issues reference exposure levels (RELs) in milligrams per kilogram per day (mg/kg/d) for a number of non-cancer chemicals. Acceptable chronic exposure levels for cancer-causing chemicals are selected to assure a minimum cancer risk, such as below 1 in 100,000. In developing a screening criterion for chronic toxicity, we select a single chronic screening score (CSS), which reflects the lowest acceptable chronic exposure in mg/kg/d across a broad range of chronic outcomes. Chronic health hazard screening values for hydraulic fracturing and acidizing fluid-treatment chemicals were developed from several sources of chronic toxicity information compiled by California and federal health agencies. These values indicate the likelihood of an adverse health outcome from repeated or continuous exposure over the long term.

Chronic toxicity screening criteria were developed separately for inhalation and oral exposure. Details on the compilation of chronic screening scores (CSS) for well stimulation chemicals are provided for the inhalation and oral routes of exposure in the following sections.

6.3.1.3.1. Chronic Screen Scores for the Inhalation Route

The following sources were used to identify screening values for the inhalation route of exposure.

1. Office of Environmental Health Hazard Assessment-derived (OEHHA) Reference Exposure Levels (RELs) for non-carcinogenic toxicants, and inhalation Unit Risk values (URs) for carcinogens (OEHHA, 2008; 2014a);

2. U.S. EPA toxicity criteria, which are similar to the OEHHA criteria in both form and method of derivation. U.S. EPA develops Reference Concentrations (RfCs) for non-carcinogens and Unit Risk Estimates (UREs) for carcinogens1 (U.S. EPA, 2014a; 2014b);

3. Agency for Toxic Substances and Disease Registry (ATSDR) Minimal Risk Levels (MRLs) for non-carcinogens, also similar to the OEHHA REL values (ATSDR, 2014).

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1. U.S. EPA’s Integrated Risk Information System (IRIS) was used as the primary source of information from U.S. EPA. In some cases, additional values were based on Provisional Peer Reviewed Toxicity Values (PPRTVs) derived by U.S. EPA’s Superfund Health Risk Technical Support Center, or U.S. EPA’s Health Effects Assessment Summary Tables.

For purposes of comparison, the available dose-response values were converted into a consistent scale of measurement, namely, a reference concentration in units of milligrams per cubic meter (mg/m3). Details and assumptions for calculating screening level dose-response values for chronic inhalation exposure are provided in Appendix 6.B. The reference concentrations were then converted to mg/kg/d equivalent dose, assuming a 20 m^3(5,283 gallons)/day inhalation rate and 70 kg (154 lbs) body weight. This value is meant only for ranking hazards across different routes of exposure; the original regulatory reference concentrations should be used in any subsequent assessment of risk.

6.3.1.3.2. Screening Values for the Oral Route

The following sources of toxicity information were used to identify hazard-screening values for the oral route of exposure:

1. OEHHA-derived values: Public Health Goals (PHGs) and Maximum Contaminant Levels (MCLs) for drinking water, “No Significant Risk Levels” (NSRLs), and Maximum Allowable Dose Levels (MADLs) for carcinogens and reproductive toxicants listed under Proposition 65 (OEHHA, 2014a; 2014b);

2. U.S. EPA: oral Reference Doses (RfDs) and cancer Slope Factors (SFs) (U.S. EPA, 2014a; 2014b);

3. ATSDR MRLs for oral exposure (ATSDR, 2014).

Oral route toxicity screening values are presented as mg/kg/d of oral intake. For details on derivation of chronic toxicity screening value for oral dose in this report, see Appendix 6.B.

6.3.2. Results of Human-Health Hazard Ranking of Stimulation Chemicals

This section provides results ranking hazards for chemical additives in hydraulic fracturing fluids (Section 6.3.2.1) and in acidization fluids (Section 6.3.2.2). In addition, we review hazards for chemicals released during well stimulation activity that are not directly added to the well (Section 6.3.2.3).

6.3.2.1. Hazard Ranking of Chemicals Added to Hydraulic Fracturing Fluids

The hazard ranking for hydraulic fracturing fluids is derived for all substances reported to be used in hydraulic fracturing that were definitely identified by CASRN. Additives without CASRN identification could not be assessed for toxicity screening values and thus were not included in the hazard ranking analysis. However, the absence of definitive identification for a chemical should not be interpreted as an indication that the specific additive is not hazardous.

For each disclosed additive, we use the available information on frequency of use in well stimulation (Section 2.4.3.1), quantity used (median concentration used across all well stimulation events) (Section 2.4.3.2), along with the GHS-based toxicity screening criterion for acute mammalian toxicity (normalized to exposure concentration as described in Section 6.3.1.2), and chronic screening values normalized to dose as derived from published values and regulatory values. We rank the acute and chronic hazards separately, and we include separate chronic rankings to reflect intake by inhalation or oral routes. For the acute toxicity information, we often had to rely on information that was only on material safety data sheets (MSDS), which is not always reliable but often the only toxicity information for specific health outcomes (e.g., eye irritation or sensitization). In cases where toxicity information from other published sources is available, we include separate hazard rankings using for results from material safety data sheets (MSDS) and from published sources. We base the ranking on the minimum, or most conservative, acute hazard value for each hazard ranking (i.e., with and without using MSDS data).

Out of 320 substances identified in the chemical disclosures (Table 2.A-1), 227 were definitively identified. We identified acute hazard screening values for 176 substances and chronic screening values for 56. The acute screening values are reported in Appendix 6.C Table 6.C-1. The chronic screening values are reported in Appendix 6.C Table 6.C-2. Four of the 56 compounds with chronic screening values did not have acute screening values, so we had a total of 176 compounds out of 320 (55%) for which we could develop a complete hazard ranking. There are an additional 23 compounds reported for which we have CASRN, but no information on frequency of use or mass used. Of these 23, we have an acute and/or chronic hazard screening value for 17. There are 121 substances for which we have generic descriptors ("trade secrets") and frequency of use information, but no CASRN identifications or toxicity information (note that chemicals without CASRN were not reviewed for toxicity). In Table 6.3-1 below, we summarize our findings regarding the different combinations of known versus unknown factors for reported hydraulic fracturing chemical additives.

Table 6.3-1. Available and unavailable information for characterizing the hazard of stimulation chemicals used in hydraulic fracturing.

Number of chemicals	Proportion of all chemicals	Identified by unique CASRN	Impact or toxicity	Quantity of use or emissions
176	55%	Available	Available	Available
17	5%	Available	Available	Unavailable
6	2%	Available	Unavailable	Available
121	38%	Unavailable	Unavailable	Available

Following the approach described above, we used information on frequency of use, quantity used, and health hazard screening criterion to derive an estimated acute hazard metric (EHM_{acute}) score for each of the 176 substances used in hydraulic fracturing that had sufficient information to make this calculation. All 176 EHM_{acute} scores are provided in

Table 6.C-1. The scores range over six orders of magnitude from 0.003 to 4,000. These are relative scores with higher values associated with higher concern. We used these scores to sort the substances from high to low. Table 6.3.2 lists the 12 substances with the highest EHM_{acute} values and identifies what factor(s) contribute most to this score—frequency of use, quantity used, and/or toxicity. The footnote to Table 6.3-2 indicates the acute toxicity and source of information for each chemical. Substances that did not have sufficient information to calculate EHM_{acute} values are sorted from low to high on a toxicity criterion; then for chemicals that lack a toxicity criterion, we sorted from high to low on frequency of use, then mass used, and finally the last chemicals are simply sorted alphabetically in Table 6.C-1.

Table 6.3-2. A list of the 12 substances used in hydraulic fracturing with the highest acute Estimated Hazard Metric (EHM_{acute}) values along with an indication of what factor(s) contribute most to their ranking (from high to low).

Chemical Name	**Reported frequency of use**	**Reported median mass fraction per WST (mg/kg)**	**Acute Toxicity**
Distillates, petroleum, hydrotreated light paraffinic	✔	✔	
Isotridecanol, ethoxylated	✔		✔[1]
Hydrochloric acid		✔	✔[2]
Polyethylene-polypropylene glycol	✔		✔[3]
Sodium hydroxide			✔[4]
Glyoxal		✔	✔[5]
Potassium carbonate	✔	✔	
Glutaraldehyde			✔[6]
Ammonium Persulfate	✔		✔[7]
Hydrofluoric acid		✔	✔[8]
Sodium tetraborate decahydrate	✔	✔	
5-Chloro-2-methyl-3(2H)-isothiazolone	✔		✔[9]

[1] Skin corrosion/irritation GHS = 1 per MSDS; [2] Skin sensitization and eye effects GHS = 1 per MSDS; [3] Inhalation LC50 for rats of 45 ppm equivalent to GHS 1 from published data; [4] Skin corrosion/irritation GHS = 1 per MSDS; [5] Eye effects GHS = 1 per MSDS; [6] Inhalation equivalent to GHS 1 per published values and Eye effects GHS = 1 per MSDS; [7] Respiratory sensitization GHS = 1 per MSDS; [8] Inhalation equivalent to GHS 2 per published values and dermal, skin corrosion/irritation and eye effects per MSDS; [9] Inhalation equivalent to GHS 1 per published values

In developing a chronic hazard metric ($EHM_{chronic}$) score, we again make use of frequency of use, mass used per treatment, and health-hazard screening criterion for each of 55 substances used in hydraulic fracturing that had sufficient information to make this calculation. All 55 $EHM_{chronic}$ scores are provided in Table 6.C-2. The scores range over nine orders of magnitude from 200 to 400,000,000,000 and tend to be higher for the inhalation route compared to the oral route. These are relative scores with higher values associated with higher concern. We used these scores to sort the substances from the highest to lowest estimated $EHM_{chronic}$ sorted on the average rank across inhalation and oral routes. The median chronic score is around 1 million. The top 12 substances for chronic hazard all have $EHM_{chronic}$ values over 1 million. Table 6.3-3 lists the 12 substances with the highest $EHM_{chronic}$ values and identifies what factor(s) contribute most to this score—frequency of use, quantity used, or toxicity. Substances with neither an EHM_{acute} or $EHM_{chronic}$ value are listed in Table 6.C-1, but not repeated in Table 6.C-3.

Table 6.3-3. A list of the 12 substances used in hydraulic fracturing with the highest chronic Estimated Hazard Metric ($EHM_{chronic}$) values along with an indication of what factor(s) contribute most to their ranking (from high to low).

Chemical Name	Reported frequency of use	Reported median conc. per WST (mg/kg)	Chronic[8] Toxicity
Proppant material[1]		✔	✔[1]
Glutaraldehyde	✔	✔	✔
Zirconium oxychloride	✔	✔	✔[2]
Bromic acid, sodium salt (1:1)		✔	✔[3]
Hydrochloric acid	✔	✔	✔
Boron sodium oxide	✔	✔	✔[4]
Ethylbenzene		✔	✔
Naphthalene	✔		✔
Sodium tetraborate decahydrate	✔	✔	✔[5]
Boric acid, dipotassium salt		✔	✔[6]
Aluminum oxide		✔	✔[7]
Diethanolamine		✔	✔[6]

[1] Proppant materials reported that might include Crystalline silica impurity (Mullite, Kyanite, Silicon dioxide) use Crystalline silica impurity as reference chemical for hazard screening (inhalation); [2] Soluble Zirconium compounds used as reference chemical for hazard screening (oral); [3] Boric Acid and Bromate used as reference compound for hazard screening (oral) and (inhalation) respectively; [4] Boric acid used as reference chemical for hazard screening (oral); [5] Boric Acid used as reference compound for hazard screening (oral); [6] Boric acid used as reference chemical for hazard screening (oral); [7] The toxicity value used is only for non-fibrous forms of aluminum oxide, and does not apply to fibrous forms; [8] Screening toxicity values for aluminum oxide, titanium oxide, propargyl alcohol, glyoxal, butyl glycidyl ether, hydrogen peroxide, and ethanol are available for occupational health criteria but screening values are not provided because for each of these substances, there was an indication in the literature of possible mutagenicity or carcinogenicity such that the available occupational health criteria might not be sufficiently health protective of workers and the general population.

6.3.2.2. Hazard Ranking of Acidization Chemicals

The data used to characterize hydraulic fracturing fluids did not include disclosed acidization events. However, the South Coast Air Quality Management District (SCAQMD) rule 1148.2 mandates that operators disclose the chemicals used in oil and gas development activities that include acidization. Acidization events are defined for the purpose of this review as events that include hydrochloric acid (HCl) and/or hydrofluoric acid (HF). The data that meets the definition of an acidization event were exported from data entered into the SCAQMD database between July 2013 and May 2014. The data include 243 events in 243 wells with a total of 8,549 entries for individual chemicals or "trade secrets" (listed by chemical family). The actual date of each event is not listed, but it appears that most of the data was entered into the database between March and May of 2014.

As with the hydraulic fracturing fluid disclosures, not all additives in the acidization events were clearly identified. Between 3 and 21 lines (ingredients in the acidization event) for each event are reported as trade secret, with no information provided on mass, composition, or definitive chemical identification. A total of 87 definitively identified chemicals are listed for the acidization events with 33 chemicals unique to acidization (i.e., not used in hydraulic fracturing). The remaining 54 chemicals are used in both acidization (per SCAQMD disclosures) and hydraulic fracturing (per FracFocus disclosures). It is unclear which if any disclosures for specific events are included in both databases.

Twenty-six chemicals were listed more than 50 times in the acidization notices, with methanol (n = 532), hydrochloric acid (n = 436) and propargyl alcohol (n = 272) being the most commonly reported chemicals used in acidization events (excluding water). There are 45 chemicals listed fewer than five times. Data are not available to assess the coverage of the SCAQMD disclosures relative to all acidization treatments in California, but clearly the data provided in the SCAQMD database are specific for activity in the South Coast Air Basin which includes Orange County and the non-desert regions of Los Angeles and Los Angeles County, San Bernardino County, and Riverside County.

Twelve chemicals are reported with median application rate greater than 200 kg per event, but several of these are either base fluid or proppant material. The reporting of proppant indicates that there may be some overlap between acidization treatments and fracturing treatments in the SCAQMD database. The remaining high-use chemicals in the list include primarily acids and buffering compounds. For chemicals that are used in both hydraulic fracturing and in acidization treatments, a comparison of the reported mass used indicates that there is no correlation ($r^2 = 0.01$) between median mass reported for specific compound used in the SCAQMD acidization treatments and the FracFocus/DOGGR (Division of Oil, Gas and Geothermal Resources) hydraulic fracturing treatments.

In order to develop a hazard ranking for acidizing fluids, we follow the procedure outlined above for hydraulic fracturing fluids to compile a list of all substances for which we had CASRN and provided, for each chemical, any available information on frequency of use in well stimulation, quantity used in each well stimulation, the GHS screen criterion for acute toxicity, and available chronic screening criteria. The frequency used and quantity used are specific to the acidization treatments and differ from values reported for the same chemical in the assessment of hazard for stimulation chemicals used in hydraulic fracturing (previous section). The data used to assess acidization did not provide information that would allow the calculation of mass fraction or concentration as used in the hydraulic fracturing assessment above, so the media mass (kg) used across all events was used as a surrogate for quantity. The acute screening values for acidization chemicals are reported in Appendix 6.C, Table 6.C-3. The chronic screening values are reported in Appendix 6.C, Table 6.C-4. Out of 165 uniquely identified additives (or products), 78 compounds were identified with CASRN, 48 had both quantity and toxicity information, and 39 had only quantity information. In Table 6.3-4 below, we summarize our findings regarding these different combinations of known versus unknown factors.

Table 6.3-4. Available and unavailable information for characterizing the hazard of stimulation chemicals use in acidizing.

Number of chemicals	Proportion of all chemicals	Identified by unique CASRN	Impact or toxicity	Quantity of use or emissions
48	29%	Available	Available	Available
0	0%	Available	Available	Unavailable
39	24%	Available	Unavailable	Available
78	47%	Unavailable	Unavailable	Unavailable

Following the approach described above and used for hydraulic fracturing chemicals, we used the information on frequency of use, quantity used, and toxicity screening criterion to derive an estimated acute hazard metric (EHM_{acute}) score for each of the 48 substances used in acidization that had sufficient information to make this calculation. All 48 EHM_{acute} scores are provided in Table 6.C-3 along with information for other substances for which the score could not be determined. The scores range over eight orders of magnitude from 0.002 to 150,000. These are relative scores with higher values associated with higher concern. We used these scores to sort the substances from high to low on the average EHM between results, including MSDS data and results based on published toxicity data. The median score is around 1. Table 6.3-5 lists the 10 substances with the highest EHM_{acute} values and identifies what factor(s) contribute most to this score—frequency of use, quantity used, or toxicity. Substances with no EHM_{acute} are sorted by decreasing concentration.

In developing a chronic hazard metric ($EHM_{chronic}$) score for acidization chemicals, we again make use of frequency of use, mass used per treatment, and health hazard screening values for each of 17 substances used in acidization that had sufficient information to make this calculation. All 17 $EHM_{chronic}$ scores, along with toxicity and use-frequency data for substances that did have reported mass used, are provided in Table 6.C-6. The scores range over eight orders of magnitude from 10 to 800,000,000, and tend to be higher for the inhalation route than the oral route. These are relative scores with higher values associated with higher concern. We used these scores to rank the substances from 1 to 17, with 1 being the greatest estimated hazard rank. The median chronic score is around 10,000. Table 6.3-6 lists the 10 substances with the highest $EHM_{chronic}$ values and identifies what factor(s) contribute most to this score—frequency of use, quantity used, or toxicity.

Table 6.3-5. A list of the 10 substances used in acidization with the highest acute Estimated Hazard Metric (EHM_{acute}) values, along with an indication of what factor(s) contribute most to their ranking (from high to low).

Chemical Name	Reported frequency of use	Reported median mass per WST (kg)	Acute Toxicity
Hydrochloric acid	✔		✔[1]
Hydrofluoric acid	✔		✔[2]
Potassium chloride		✔	
Ammonium Chloride	✔	✔	✔[3]
Citrus Terpenes			✔[4]
2-Butoxyethanol (Ethylene glycol butyl ether)	✔		✔[5]
Propargyl alcohol	✔		✔[6]
Acetic Acid			✔[7]
Crystalline silica quartz		✔	
Citric acid	✔	✔	✔[8]

[1] Skin sensitization and eye effects GHS = 1 per MSDS; [2] Inhalation equivalent to GHS 2 per published values and dermal, skin corrosion/irritation and eye effects per MSDS; [3] Eye effects GHS = 2 per MSDS; [4] Skin corrosion/irritation GHS = 1 and eye effects GHS = 2 per MSDS; [5] Inhalation effects GHS 2 from published data and eye effects GHS = 2 per MSDS; [6] Oral effects GHS 2 from published data and numerous effects with GHS = 1 or 2 per MSDS; [7] Skin corrosion/irritation GHS = 1 and eye effects GHS = 1 per MSDS; [8] Eye effects GHS = 2 per MSDS

Table 6.3-6. A list of the 10 substances used in acidization with the highest chronic Estimated Hazard Metric ($EHM_{chronic}$) values along with an indication of what factor(s) contribute most to their ranking (from high to low).

Chemical Name	Reported frequency of use	Reported median mass per WST (kg)	Chronic Toxicity
Hydrochloric acid	✔		✔
Propargyl alcohol			✔
Crystalline silica quartz		✔	✔
Ethylbenzene			✔
Ammonium Chloride		✔	✔
Hydrofluoric acid			✔
2-Butoxyethanol (Ethylene glycol butyl ether)			✔
Acetic Acid		✔	
Methanol	✔		
Phosphoric acid, calcium salt (2:3)			✔

6.3.2.3. Hazard Summary of Air Pollutants that are Related to Well Stimulation Fluid

There are fifteen chemicals listed in Tables 6.C.1– 6.C.4 for hydraulic fracturing and acidization activity that are also listed on the California Air Resources Board (CARB) Toxic Air Contaminant (TAC) Identification List (CARB, 2015). These compounds are listed in Table 6.3-7, along with an indication of the well stimulation activity that they are reportedly used in. Five of the compounds listed on the TACs list are already identified in the previous tables, but all compounds listed as TACs should be considered hazardous and included in subsequent risk assessments. The California TACs list (CARB, 2015) includes all Hazardous Air Pollutants (HAPs) listed by the U.S. EPA and are heavily regulated compounds.

Table 6.3-7. The substances used in hydraulic fracturing and acidization that are also listed on the California TAC Identification List (http://www.arb.ca.gov/toxics/id/taclist.htm).

Chemical Name	CASRN	Used in Hydraulic Fracturing	Used in Acidization
Hydrochloric acid	7647-01-0	✔	✔
Methanol	67-56-1	✔	✔
Toluene	108-88-3		✔
Acetophenone	98-86-2		✔
Ethylene Glycol	107-21-1	✔	✔
Formaldehyde	50-00-0	✔	✔
Naphthalene	91-20-3	✔	✔
Diethanolamine	111-42-2	✔	
Benzyl Chloride	100-44-7	✔	
Acrylamide	79-06-1	✔	

Volume III, Chapter 3 summarizes a list of all CARB-reported TACs air emissions associated with all oil-well production activities including well stimulation fluids (Chapter 3, Section 3.3.2.2). We noted that not all of the TACs listed above are reported emissions—likely as a result of different requirements for reported use versus reported emissions. It is not possible at this point to allocate the CARB-reported emissions specifically to the use well stimulation fluids. In addition to chemicals added to well stimulation fluids, there a number of TACs released during well stimulation activities that are not added directly to the well. As TACs, these substances have all been identified as posing human health hazards, with the actual health risk dependent on the magnitude and duration of exposure. Among this substance list are combustion products and/or chemical emissions from pumps, generators, compressors, and equipment; venting and flaring; dust from well stimulation activity; leaks from transfer lines and/or well heads; and emissions related to leakage of oil and gas from stimulated wells (this category does not include emissions from refining and use of the hydrocarbon products). A variety of mobile sources relevant to oil and gas (and presumably to well stimulation) activities are tracked by CARB in its emissions inventories (See Chapter 3, Section 3.3.2.2), especially for off-road diesel equipment. However, it is not clear how to apportion these activities between conventional oil production and well stimulation activities without a much more detailed study.

Several criteria pollutants (particulate matter, carbon monoxide, nitrogen oxides, and sulfur dioxide) as well as reactive organic gases are associated with well stimulation activities (see Section 3.3.2.2 for details on emissions estimates). Criteria pollutants are heavily regulated and should be included in any hazard or risk assessment associated with well stimulation. Given the known and accepted hazards associated with criteria pollutants, no further hazard assessment is provided for these compounds in this chapter.

6.3.3. Literature Summary of Human Health Hazards Specific to Well Stimulation

In the sections above, we made bottom-up characterizations and rankings of chemicals used and/or emitted during well stimulation operations in California. This section reviews and analyzes the chemical hazards of well stimulation chemicals based primarily on published source categories related to well stimulation activities and associated equipment. Much of the literature discussed below is associated with activities outside of California, but offers insights on what is or could be done in California.

Colborn et al. (2011) used Chemical Abstract Service (CAS) numbers and systematic searches in the National Library of Medicine, Toxicology Data Network (TOXNET) and other databases to determine that (a) 75% of the identified compounds from fracturing fluids in samples from Colorado are known to negatively impact sensory organs, the gastrointestinal system, and/or the liver; (b) 52% of the identified chemicals have the potential to adversely affect the nervous system; and (c) 37% are candidate endocrine disrupting chemicals (EDCs). EDCs present unique hazards compared to other toxins, because their effects at higher doses do not always predict their effects at lower doses (Vandenberg et al., 2012). They are particularly hazardous during fetal and early childhood growth and development (Diamanti-Kandarakis et al., 2009), can impact the reproductive system, and have epigenetic mechanisms that may lead to pathology decades after exposure (Zoeller et al., 2012).

In addition to the chemicals used in well stimulation, the major constituents of well acidization fluid are hydrochloric acid and hydrofluoric acid. Hydrochloric acid is used frequently in oil and gas wells in California and elsewhere as an additive to well-injection fluids during matrix acidizing, wellbore cleanout, and other forms of acid treatments of oil and gas wells (Colborn et al., 2011; Stringfellow et al., 2014) (also see Volume I for more details). Hydrochloric acid is corrosive to the skin, eyes, and mucous membranes, and is associated with a number of acute health effects (ATSDR, 2002). Oral exposure may result in the corrosion of mucous membranes, the esophagus, and the stomach. Symptoms may include nausea, vomiting, and diarrhea (U.S. EPA, 2000a). Dermal exposure may result in severe burns, ulceration, and scarring. Chronic exposures in occupational settings are associated with gastritis, chronic bronchitis, dermatitis, and photosensitization (U.S. EPA, 2000a). As discussed in the occupational health section below, we note that exposure to acid vapors resulting in acid-vapor inhalation is a hazard for any unprotected individuals close to the location of acid use or transfer.

Hydrofluoric acid is also used as an additive to well injection during matrix acidizing, wellbore cleanout, and other forms of acid treatments of oil and gas wells (Colborn et al., 2011; Stringfellow et al., 2014) (See Volume I). Acute exposure to hydrofluoric acid in liquid and gaseous form causes irritation of the eyes and nose, and can result in severe respiratory damage (Centers for Disease Control and Prevention (CDC), 2014). In high doses, exposure to hydrofluoric acid can lead to convulsions, cardiac arrhythmias, or death from cardiac or respiratory failure (U.S. EPA, 2000b). Chronic exposure to elevated concentrations of hydrofluoric acid is associated with adverse pulmonary effects, renal injury, thyroid injury, anemia, hypersensitivity, and dermatological reactions (U.S. EPA, 2000b). When inhaled at low concentrations, hydrofluoric acid can result in nose, throat, and bronchial irritation and congestion (ATSDR, 1993; CDC, 2014). To date, no studies on the public health dimensions of hydrofluoric and hydrochloric acid have been conducted in the upstream oil and gas context.

6.4. Water Contamination Hazards and Potential Human Exposures

This section reviews the transport mechanisms that could cause human exposures to stimulation chemicals through water contamination. Section 6.4.1 briefly reviews the pathways identified in Volume II, Chapter 2, and summarized in Table 6.2-1, and discusses implications for human health. This is followed by Section 6.4.2, which provides a literature survey of health issues attributed to water contamination due to stimulation.

A direct impact of concern from chemical use for well stimulation is the potential for water contamination and subsequent human exposure from accidental releases related to the handling of the well stimulation fluids and the management of produced water that may contain stimulation chemicals. Similarly, potential subsurface leakage pathways into protected groundwater present a potential impact of contamination by the petroleum constituents in the reservoir. This risk may be exacerbated by the presence of chemicals used in hydraulic fracturing. If chemicals contained in well stimulation fluids are well managed and not released into usable water, including agricultural water, then the public health risks would be reduced. Acid use increases the probability that naturally occurring heavy metals and other pollutants from the oil-bearing formation will be dissolved and mobilized. Assessment of the environmental public health risks posed by acid use along with commonly associated chemicals, such as corrosion inhibitors, cannot be undertaken without a more complete disclosure of chemical use, and a better understanding of the chemistry of treatment fluids and produced water returning to the surface, in order to understand the risks these fluids may pose. Risk assessment would also require better knowledge of potential transport mechanisms and pathways that could lead to human exposure, as well as how treatment chemicals are altered during transport.

6.4.1. Summary of Risk Issues Related to Water Contamination Pathways

The potential for surface and groundwater contamination from well stimulation activities (contamination with stimulation chemicals, recovered fluids and produced water, residual oil, methane and other compounds) was evaluated in great detail in Chapter 2 of this volume. Release mechanisms and environmental transport pathways associated with well stimulation and production that are relevant to California include spills and leaks, percolation of wastewater from unlined pits, siting of disposal wells near abandoned wells or into protected groundwater, reuse or disposal of inadequately treated wastewater; loss of wellbore integrity; subsurface leakage and migration through abandoned wells, migration though faults, fractures, or permeable regions, and illegal waste discharge

(Section 2.6.2). Some of these release mechanisms are primarily relevant to California, and are uncommon elsewhere, such as disposal of wastewater in unlined percolation pits, which has been banned in many states, and potential siting of disposal wells into protected groundwater. However, many of the release mechanisms have also been noted in other parts of the country. Below, we briefly summarize the main findings from Chapter 2 with regard to release mechanisms and transport pathways of concern for human health impacts.

Stimulation fluids can move through the environment and come into contact with human populations in a number of ways, including surface spills, accidental releases (Rozell and Reaven, 2012), loss of zonal isolation in wellbores (Chilingar and Endres, 2005; Darrah et al., 2014), venting and flaring of gases (Roy et al., 2013; Warneke et al., 2014), and transportation and disposal of wastes (Rozell and Reaven, 2012; Warner et al., 2012; Warner et al., 2013a; Fontenot et al., 2013).

6.4.1.1. Disposal of Produced Water in Unlined Pits

As noted in Volume II, Chapter 2, the most commonly reported recovered fluids and produced water disposal method for stimulated wells in California is by evaporation and percolation in unlined surface impoundments, also referred to as unlined sumps or pits. Operators report that nearly 60% of the produced water from stimulated wells was disposed of in unlined sumps during the first full month after stimulation. There is no testing required, or thresholds specified, for the contaminants found in well stimulation fluids or other naturally occurring chemical constituents in produced water, such as benzene, heavy metals, and naturally occurring radioactive materials (NORMs). The primary intent of unlined pits is to percolate water into the ground, and as a result, this practice provides a potentially direct subsurface pathway for the transport of produced water constituents, including returned stimulation fluids, into groundwater aquifers that are or may be used for human consumption and agricultural use. Where groundwater intercepts rivers and streams, surface water resources could also be affected. If protected water were contaminated and if plants (including food crops), humans, fish, and wildlife use this water, it could introduce contaminants into the food web and expose human populations to known and potentially unknown toxic substances.

6.4.1.2. Public Health Hazards of Produced Water Use for Irrigation of Agriculture

As noted in Volume II, Chapter 2, large volumes of water of various salinities and qualities are produced along with oil. Most produced water is re-injected into the oil and gas reservoirs to help produce more oil, maintain reservoir pressure, and prevent subsidence. But some of this produced water is not highly saline, and small quantities of it are now being used by farmers for irrigation. As discussed in Chapter 2 of this volume, concerns arise that stimulation chemicals could be mixed with produced water and thus end up in irrigation water. Because of the growing pressures on water resources in the state, there is increasing interest in whether produced water could be used for a range of beneficial purposes such as groundwater recharge, wildlife habitat, surface waterways, irrigation, and other uses. If produced water comes from an oil field where well stimulation has been used, stimulation chemicals could also be present in the produced water and would not necessarily be detected by current testing. The presence of stimulation chemicals and other naturally occurring constituents, such as heavy metals that could be mobilized by stimulation chemicals makes it far more difficult to determine if the produced water can be safely reused. The presence of stimulation chemicals also makes it more difficult to determine the amount and type of water treatment required to make the water safe for beneficial use in agriculture from a public health perspective.

6.4.1.3. Public Health Hazards of Shallow Hydraulic Fracturing

Deep fracturing operations are unlikely to produce fractures and conduits that intersect fresh water aquifers far above them (See Volume I of this study for more details). However, in California, about three quarters of the hydraulic fracturing takes place in shallow wells less than 600 m deep. Where drinking water aquifers exist above shallow fracturing operations, there is an inherent risk that hydraulic fractures could intersect aquifers used for drinking, agriculture, and other uses and contaminate them, thus introducing human exposure pathways and public health risks. To the extent that human populations are drinking, washing, or using water that has been contaminated via this environmental exposure pathway, there exists a public health risk (See Chapter 2 of this volume for me details water exposure pathways).

6.4.1.4. Leakage Through Wells

One of the problems faced in a number of other states is oil and gas development in regions that have not previously had intensive oil and gas development. California's experience with well stimulation is the opposite: most well stimulation is occurring in reservoirs where oil and gas has been produced for a long time. This means the operations are taking place where many wells have previously been drilled, plugged, abandoned, and orphaned. Leakage can occur if a hydraulic fracture intersects another well (offset well). Offset wells can also act as a conduit through which emissions to air and water resources can occur. If protected water is contaminated and if plants (including food crops), humans, fish, and wildlife use this water, it could introduce contaminants into the food web and expose human populations to known and potentially unknown toxic substances. Because geologic conditions in California result in almost no coal mining, we did not consider leakage facilitated by abandoned coal mines, which is a problem in other states.

6.4.1.5. Injection Into Usable Aquifers

In June 2014, the U.S. EPA expressed concerns to the state of California regarding an EPA evaluation of injection wells in California used to dispose of oil-field waste, primarily recovered fluids and produced water that returns to the wellhead along with oil (U.S. EPA, 2014c). The EPA found that some wells inappropriately allowed injection of waste into protected groundwater. The California Division of Oil, Gas and Geothermal Resources (DOGGR) has shut down some of these wells and is reviewing many more for possible violations. Some chemicals that are used in well-stimulation operations are known to be toxic, but more than 50% of reported well stimulation chemicals in California have unknown environmental and health profiles. Some of the naturally occurring constituents in produced water are also toxic. Introduction of recovered fluids or produced water into protected groundwater presents a risk to the health of human populations that may drink, bathe, or irrigate with these water supplies.

6.4.2. Literature on Water Contamination from Well Stimulation

6.4.2.1. Exposure to Water Pollutants

We identified original research, including modeling studies on the potential for exposures to water quality impairment associated with oil and gas development enabled by well stimulation. We excluded studies that explored only evaluative methodology or baseline assessments, as well as papers that simply comment on or review previous studies. Papers on the potential for exposure to well-stimulation-associated contaminated water (a) rely on empirical field measurements, (b) explore plausibility of mechanisms for contamination, or (c) use modeled data to determine hazard and risk associated with potential water exposure pathways. Some of these studies explore only one aspect of shale gas development, such as the well-stimulation process of hydraulic fracturing. These studies do not indicate whether well-stimulation-enabled oil and gas development as a whole is associated with water contamination and are therefore limited in their utility for gauging water quality impacts. We are only concerned with actual findings in the field or modeling studies that specifically identify hazard, or actually document the occurrence or non-occurrence of water contamination.

Surface and groundwater contamination from well-stimulation-enabled oil and gas development is extensively documented in Chapter 2 of this volume. But the question of potential health risks remains, especially given the dearth of investigations and monitoring on this issue in California. Some association studies have reported that well stimulation contributes to higher levels of methane in drinking-water wells within 1 km of active gas development sites (Darrah et al., 2014; Jackson et al., 2013; Osbourne et al., 2012). Other studies found no association and have suggested that methane contamination of shallow groundwater from oil and gas production may be less likely to occur in certain shale formations, owing in part to regional geological variations, including the presence of intermediate gas-bearing formations above target formations (e.g., in the Pennsylvania area of the Marcellus Shale region), but not others (e.g., in the Fayetteville shale region) (Warner et al., 2013b). The most recent study on fugitive gas contamination of drinking-water wells used noble gas data to implicate faulty well production casings in water contamination rather than upward migration of methane through geological strata triggered by hydraulic fracturing (Darrah et al., 2014). While methane is not considered to be toxic, these studies suggest that there are subsurface pathways through which gases and liquids, some of which may contain hazardous compounds, may be present. Methane—particularly thermogenic methane (Stolper et al., 2014)—can migrate and mix with protected water through natural seepages (Dusseault et al., 2014; Dusseault and Jackson, 2014). Such seepages are common in California. Investigations of aquifer contamination attributable to oil and gas development have not been conducted in California. There is a need for these investigations, including studies to determine the effect of natural seepages in methane migration.

Other studies that evaluated water quality in private drinking-water wells near natural gas operations found higher levels of arsenic, selenium, strontium, and total dissolved solids in water wells located within 3 km of active gas wells (Fontenot et al., 2013). While this study used historical data from the region as a baseline to link the water contamination to natural gas development, the specific mechanism responsible for contamination was not determined.

Water contamination events associated with well stimulation have been documented in geographically diverse parts of the country. In Colorado, an analysis of 77 reported surface spills (~0.5% of active wells) within Weld County and groundwater monitoring data revealed BTEX (benzene, toluene, ethylbenzene, xylene) contamination in groundwater (Gross et al., 2013). Another study in Colorado measured estrogen and androgen receptor activity in surface and groundwater samples, using reporter gene assays in human cell lines from drilling-dense areas in the Piceance basin (Kassotis et al., 2013). Water samples collected from the more intensive areas of natural gas extraction exhibited statistically significantly more estrogenic, antiestrogenic, or antiandrogenic activity than reference sites. Notably, the concentrations of chemicals detected by Kassotis and colleagues (2013) were high enough to potentially interfere with the response of human cells to male sex hormones and estrogen.

In August 2014, the Pennsylvania Department of Environmental Protection (PA DEP) announced that 243 cases of water contamination attributable to oil and gas development in the region had occurred since 2008, and as of 4 March 2015, the number of confirmed water contamination cases was 254 (PA DEP, 2014). While this database makes clear that these cases of water contamination were caused by oil and gas development, it is not clear which mechanisms were most prominent. However, the presence of methane and other VOCs in the aquifers suggests that loss of wellbore integrity was a likely mechanism among the many of the cases. The majority of the events occurred in the northeastern region of the state; however, reasons for this geographic trend are still unknown and are currently being investigated. More research is needed to determine if wellbore integrity is associated with these events and if that integrity is affected by hydraulic fracturing.

6.4.2.2. Oil and Gas Recovered and Produced Water

Well stimulation generates recovered fluids and produced water. Evidence indicates that approximately 35% of the initial fracturing fluid volume injected underground returns to the surface as recovered fluids and produced waters, although estimates range from 9% to

80% (U.S. EPA, 2004, 2010; Horn, 2009). Recovered fluids and produced water contain chemical compounds added to fracturing fluids as well as naturally occurring compounds that are mobilized from target geological features (Alley et al., 2011; Thurman et al., 2014; Warner, 2013a). Compounds hazardous to human health identified in produced waters include chlorides, heavy metals, and metalloids (e.g., cadmium, lead, arsenic), volatile organics (e.g., benzene, toluene, ethylbenzene, and xylene), bromide, barium, and, depending upon the geochemistry of the target reservoir, naturally occurring radioactive materials (e.g., radium-226 and radon) and other compounds (Alley et al., 2011; Maguire-Boyle and Barron, 2014; Nelson et al., 2014). Many of these naturally occurring compounds have moderate to high toxicity and can induce health effects when exposure is sufficiently elevated (Balaba and Smart, 2012; Haluszczak et al., 2013). It should be noted that no studies to date have analyzed the chemical constituents of recovered fluids and produced water from well-stimulation-enabled oil wells in California.

Recovered fluid and produced water are sometimes treated at publicly owned treatment works (POTWs) and then discharged into surface waters (Ferrar et al., 2013). This practice is currently applied to a subset of recovered fluid/produced water in California (DOGGR, 2014) (also see Chapter 2 on impacts to water resources). Warner et al. (2013a) examined water quality and isotopic compositions of discharged effluents, surface waters, and stream sediments associated with a Marcellus wastewater treatment facility site. This study reported that treated recovered fluid and produced water still contained some elevated concentrations of contaminants associated with shale gas development. The researchers also found elevated levels of chloride and bromide downstream, along with radium-226 levels in stream sediments at the point of discharge that were approximately 200 times greater than upstream and in background sediments, and well above regulatory standards (Warner et al., 2013a). The study did not differentiate what amounts of these elevated concentrations were directly attributable to hydraulic fracturing. Some papers have noted that these types of emissions to water supplies could increase the health risks of residents who rely on these surface and hydrologically contiguous groundwater sources for drinking, bathing, recreation (Wilson and VanBriesen, 2012), and sources of food (i.e., fish protein) (Papoulias and Velasco, 2013).

6.5. Air Emissions Hazards and Potential Human Exposures

In addition to the potential direct impacts of water contamination, there is the possibility of direct public health risks of exposures to stimulation chemicals that are known toxic air contaminants (TACs). In Volume II Chapter 3, we analyzed the SCAQMD mandatory oil and gas reporting database and noted TACs have been reported as used in hydraulic fracturing and acidizing fluids. All of these TACs are hazardous to human health, yet none of them have known emission factors. This makes it difficult to assess the extent to which populations may be exposed and at what concentrations. Section 6.5 below expands this topic. This section reviews the potential human health impact of air emissions associated with well stimulation in two parts. Section 6.5.1 reviews what is known about air emissions from the assessment in Chapter 3 and elsewhere. Section 6.5.2 reviews the literature on human health impacts.

6.5.1. Emissions Characterized in Chapter 3

As discussed in Chapter 3 of this volume, air emissions from oil and gas development can come from a variety of sources, including, but not limited to drilling, production processing, well completions, servicing, and transportation. Among *known* air contaminants, compounds of particular concern that are known to be emitted during the well-stimulation-enabled oil and gas development process (and from oil and gas development in general) are BTEX compounds (benzene, toluene, ethylbenzene, and xylene), formaldehyde; hydrogen sulfide; particulate matter (PM); nitrogen oxides (NO_x); sulfur dioxide (SO_2); polycyclic aromatic, aliphatic, and aromatic hydrocarbons; and volatile organic compounds (VOCs) that can contribute to tropospheric ozone formation.

Also discussed in Chapter 3 of this volume are methane emissions, which are currently assessed as greenhouse gases but can also be used as a predictor of many VOC emissions. Some VOCs are directly health damaging (e.g., benzene), and many others are precursors to regional tropospheric ozone, a strong respiratory irritant. In the San Joaquin Valley Unified Air Pollution Control District (APCD), 2012 oil and gas associated reactive organic gas (ROG) emissions were approximately 8% of total regional ROG emissions (see Chapter 3). In a field-based study in the San Joaquin Valley of California, Gentner et al. (2014) found that at least 22% of all anthropogenic VOC emissions are attributable to oil development.

The quantity of specific chemicals emitted to the atmosphere per unit of injected well stimulation fluid is completely lacking from the existing literature. Compounds noted in the previous paragraph can be emitted or released prior to use during transport, transfer, blending, and injection by accidental release, intentional release or by fugitive emission pathways. After injection of fluid into the well-bore, the release pathways and emission rates become even more uncertain, because of a lack of knowledge about the recovered fraction of well stimulation fluid and changes in composition of recovered fluid and produced water at stimulated wells. There are a number of potential release pathways to air for the stimulation fluids recovered from a treated well, including both intentional (evaporation ponds, agricultural use, re-injection) and accidental (spills, transportation, disposal and fugitive emissions). None of these potential emission pathways for down-hole TACs is sufficiently characterized beyond the frequency and total mass estimates derived in Chapter 2.

Emission rates for TACs that are indirectly related to well stimulation activity are based on activity-specific emission factors that report the quantity of a pollutant released to the atmosphere relative to an activity associated with the release of that pollutant. Emission factors are provided by regulatory agencies such as the U.S. EPA. Generic or generalizable emission rates are not available at the wellhead scale. Estimating emission rates depends on the combination of site-specific activities and equipment (e.g., number of stationary and mobile source, leakiness of transfer lines and connections). However, all TACs by definition are hazardous, so they should be included in any thorough risk assessment for well stimulation activity using case-specific conditions and emission factors to determine ultimate exposures and quantify risk.

6.5.2. Potential Health-Relevant Exposure Pathways Identified in the Current Literature

6.5.2.1. Air Emissions Exposure Potential

Based on the potential harm of a number of VOCs (i.e., benzene, toluene, ethylbenzene, xylene, etc.) and the role of VOCs in the production of tropospheric ozone, we considered studies that address methane *and* non-methane volatile organic compounds (VOC) emissions. We considered papers that specifically address human exposures from well stimulation (i.e., unconventional oil and gas development) at either a local or regional scale. These include local and regional measurements of non-methane volatile organic compounds and tropospheric ozone.

As discussed in Chapter 3 of this volume, emissions from oil and gas development can come from a variety of sources including, but not limited to, drilling, processing, well completions, servicing, and transportation. Of particular concern are BTEX compounds (benzene, toluene, ethylbenzene, and xylene), other VOCs; formaldehyde; hydrogen sulfide; methylene chloride; particulate matter (PM); nitrogen oxides (NO_x); sulfur dioxide (SO_x); polyaromatic, aliphatic, and aromatic hydrocarbons; and tropospheric ozone.

An issue of potential concern in California is tropospheric (ground-level) ozone, which is formed through the interaction of VOCs, and NO_x in the presence of sunlight (Jerrett et al., 2009; U.S. EPA, 2013). Tropospheric ozone is a strong respiratory irritant associated with increased respiratory and cardiovascular morbidity and mortality (Jerrett et al., 2009; UNEP, 2011). However, as noted in Chapter 3 of this volume, the oil and gas industry is currently not a major contributor to tropospheric precursors in California air basis. There is some research on tropospheric ozone production associated with oil and gas development operations in other states. Modeling studies in the Haynesville and Barnett shale plays have predicted substantially increased atmospheric ozone concentrations associated with oil and gas development in Texas (Kemball-Cook et al., 2010; Olaguer, 2012; Gilman et al., 2013). Some observations in oil and gas producing basins in the western U.S. have found high levels of ozone in the winter, often in excess of air quality standards (Edwards et al., 2014). Nevertheless, as discussed in Volume II Chapter 3 and in contrast to the studies noted above, the ozone levels in California air basins are mostly dependent on an abundance of ozone precursors from outside of oil production.

As discussed in Chapter 3 of this volume, methane emissions, which are currently assessed as greenhouse gases, can be used as a predictor of many VOC emissions. Some VOCs are directly health damaging (e.g., benzene), and many others are precursors to regional tropospheric ozone. In a field-based study in the San Joaquin Valley of California, Gentner et al. (2014) found that at least 22% of all anthropogenic VOC emissions are attributable to oil development.

Local human exposures to emissions from oil and gas development have not been well-characterized, but modeling and preliminary studies have indicated that intermittent spikes in emissions to the atmosphere may pose increased risks to local human populations through air pollution concentrations at the regional scale (Brown et al., 2014; Colborn et al., 2014). Few studies to date have investigated the frequency and magnitude of air pollution emission spikes from oil and gas development, but available studies document their occurrence and their potential frequency and magnitude (Allen et al., 2013; Macey et al., 2014; Helmig et al. 2014).

6.5.2.2. Emissions and Potential Exposures from Equipment and Infrastructure

Oil and gas development relies on a variety of ancillary infrastructure throughout the well stimulation and oil and gas production process. This equipment includes, but is not limited to, diesel-powered trucks, generators, and pumps, separator tanks, condensate tanks, pipelines, flaring/venting operations, and gas compressor stations. The deployment and use of each of these pieces of equipment act as emissions sources that can present risks through exposure to chemicals, air emissions, and physical stressors. Specific to well stimulation operations is the need for heavy truck traffic to transport water, proppant, chemicals, and equipment to and from the well pad. 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.

The pollutants of primary health concern identified in the scientific literature and attributable to transportation and other heavy machinery associated with well stimulation are emissions of dust, diesel particular matter (dPM), nitrogen oxides (NO_x), sulfur dioxide and secondary sulfate particles (SO_x), volatile organic compounds (VOCs), and secondarily tropospheric ozone (Roy et al., 2013; Kemball-Cook et al., 2010). A pollutant of primary health concern emitted from the transportation component of shale gas development is dPM with aerodynamic diameter less than 2.5 microns ($PM_{2.5}$). dPM is a California TAC and a well-studied health-damaging pollutant that contributes to cardiovascular illnesses, respiratory diseases (e.g., lung cancer) (Garshick et al., 2008), atherosclerosis, and premature death (Pope, 2002; Pope et al., 2004). A study by the California Air Resources Board indicates that for each 10 $\mu g/m^3$ increase in $PM_{2.5}$ exposure in California, there is an expected 10% (uncertainty interval: 3%, 20%) increase in the number of premature deaths (Tran et al., 2008). Particulate matter can also contain concentrated associated products of incomplete combustion (PICs), and when particle diameter is $< 2.5\ \mu m$, they can act as a delivery system of these compounds to the alveoli of the human lung (Smith et al., 2009). In addition to dPM, NO_x and VOCs, other pollutants prevalent in diesel emissions react in the presence of sunlight and high day-time temperatures to produce tropospheric (ground-level) ozone. Tropospheric ozone is a well-established respiratory irritant associated with increased respiratory and cardiovascular morbidity and mortality (Jerrett et al., 2009). It should be noted that most of the places where well stimulation is known to take place in California—The San Joaquin Valley and the Los Angeles Basin—are also the regions that are consistently out of attainment for atmospheric concentrations of tropospheric ozone. As such, oil and gas developments in these regions are a potentially significant factor (Gentner et al., 2013) of cumulative environmental public health risks for populations in these areas.

Formaldehyde is a volatile compound with well-established health impacts that is produced all along the oil and gas production chain. Notably, it is formed by incomplete combustion emitted by natural gas-fired reciprocating engines at oil and gas compressor stations, as well as being a component of diesel combustion. It is a suspected human carcinogen, but it has also been associated with acute and chronic health effects (U.S. EPA, 2013). One community-based exploratory monitoring study determined that levels of formaldehyde exceeded health-based risk levels near compressor stations with gas developed from wells enabled by hydraulic fracturing in Arkansas, Pennsylvania, and Wyoming oil/gas production sites (Macey et al., 2014). It should be noted that formaldehyde is not added to stimulation fluids, but rather is a product of combustion associated with oil and gas development activity, including well stimulation activity.

6.5.3. Public Health Studies of Toxic Air Contaminants

Oil and gas development—including that enabled by well stimulation—creates the risk of exposing human populations to a broad range of toxic air contaminants (TACs). Data suggest that these TACs are likely more elevated close to compared to far from active oil and gas development, and that emissions of TACs in areas of high population density (e.g., the Los Angeles Basin) result in larger population exposures than when population density is lower (See Chapter 3 of this Volume for more details).

Many of the constituents used in and emitted by oil and gas development are known to be damaging to health, and place disproportionate risks on sensitive populations, including children, the elderly, those with pre-existing respiratory and cardiovascular conditions, and those exposed to multiple environmental stressors. Oil and gas development poses more elevated population health risks when conducted in areas of high population density, such as the Los Angeles Basin, because it results in larger population exposures to TACs (see Los Angeles Basin Case Study in Volume III for more details).

California has large developed oil reserves located in densely populated areas. For example, the Los Angeles Basin has the highest concentrations of oil in the world, but Los Angeles is also a global megacity, and oil and gas development occurs in close proximity to human populations. In the San Joaquin Valley, there are a number of communities that live, work, and play near oil and gas development. Approximately half a million people live within one mile of a stimulated well, and many more live near oil and gas development of any type. In addition, large numbers schools, elderly facilities, and daycare facilities are sited within a mile of a stimulated well. The closer citizens are to these industrial facilities, the more potentially elevated their exposure to TACs. Volume II, Chapter 3 indicates that stationary source oil and gas facilities in the San Joaquin Valley are responsible for over 70% of H2S emissions, and 2-5.5% of benzene, formaldehyde, hexane, and xylene emissions. In the South Coast region, stationary oil and gas sources are responsible for less than 0.25% of all ten indicator TACs studied. While these fractions are in many cases not large as a fraction of regional impacts, they can still have important health impacts on nearby populations.

Studies from out of state indicate that community public health risks of exposures to toxic air contaminants, such as benzene and aliphatic hydrocarbons, are most significant within 800 meters (½ mile) from active oil and gas development (McKenzie et al., 2012). Atmospheric data on dilution of conserved TACs indicate that potentially harmful community exposures can occur out to ~3 km (almost 2 miles) from the source. There are no studies from inside California that have measured the relationship between health impacts and the distance from active oil and gas development. The Los Angeles County Department of Public Health conducted a peer-reviewed public health outcome study near the Inglewood Oil Field in Los Angeles County (Rangan and Tayour, 2011). This study did not find any health effects in populations relative to proximity to oil and gas development. However, the study was not designed to see long-term outcomes with incidence rates below ~ 1%. Therefore, significant questions remain about the health effects of proximity to oil and gas production that should be the subject of further study.

6.5.3.1. Methods for Peer Review of Scientific Literature

We conducted a review of the peer-reviewed scientific literature on the environmental public health and occupational health dimensions of well stimulation. In contrast to the bottom-up approach based on moving from hazard to exposure to outcome, most of the public health-relevant literature focuses on known links between population health risks and environmental pollution that arises from the well-stimulation-enabled oil and gas development. The best information for evaluation of the public health and occupational health impacts of oil and gas development, including that enabled by well stimulation in California, should be from verified California-specific datasets and peer-reviewed scientific studies conducted in California. However, we found California-specific information on public health risks to be extremely limited in quantity, quality, and scope. As a result, we also assessed the relevance of environmental public health-relevant studies from outside of California.

We included papers that consider the question of public health in the broad context of shale gas development. Of course, research findings in other categories such as air quality and water quality are relevant to public health, but in this subsection we only include those studies that directly consider the health of individuals and human populations. We only consider research to be original if it measures health outcomes or complaints (i.e., not health research that only attempts to determine opinion or methods for future research agendas).

We organized this literature review in a framework that tracks pathways from community health to various well stimulation types, in order to investigate what is known about any associations between sources of environmental pollution, potential exposures, and human health hazards related to well stimulation. We restricted the boundaries of our literature review to upstream oil and gas development processes prior to hydrocarbons being sent to market. We also only included physical health outcomes. Although some of the literature suggests that social, psychological, and economic impacts of well stimulation are possibly important for community health, these studies are beyond the scope of this review.

The source-to-outcome pathway is commonly used to describe associations between pollutant sources and health effects. This approach addresses in sequence the emissions, environmental concentrations of pollutants, pollutant exposure pathways (ambient air, water, etc.), and dose (e.g., micrograms of pollutant ingested, inhaled or absorbed per unit body weight per day) (Figure 6.5-1) (ATSDR, 2005). Potential sources of health-relevant environmental pollution are present throughout the well stimulation and oil and gas production process. Sources of environmental pollution include hydrocarbon production and processing activities (e.g., drilling, well stimulation, hydrocarbon processing and production, and wastewater disposal) and the transportation of water, sand, chemicals, and wastewater before, during, and after well stimulation (Shonkoff et al., 2014).

As noted above, the best information for evaluation of the public health and occupational health impacts of oil and gas development, including that enabled by well stimulation in California, should be from verified California-specific datasets and peer-reviewed scientific studies. However, we found this California-specific information to be limited in quantity, quality, and scope. With the exception of the Inglewood study (Rangan and Tayour, 2011), which had limited scope and statistical power, there have been no comprehensive health outcome studies that focus directly on the health impacts of stimulated wells. As a result, we also assessed the relevance of environmental public-health studies and experience from outside of California. Since 2007, the rapid growth of hydrocarbon development in shale and other low-permeability (aka, “tight”) formations across the U.S. has been accompanied by an increase in scientific investigations of the environmental and public health dimensions of oil and gas development, including that enabled by well stimulation, especially hydraulic fracturing. For example, approximately 70% of the peer-reviewed journal papers that are pertinent to the public health dimensions of onshore well-stimulation-enabled oil and gas development have been published between January 2009 and December 2014 (PSE Healthy Energy, 2014)[2]. This body of literature is still relatively new; many uncertainties and data gaps on the human health impacts persist on the national scale, and especially with application to California.

2. For a near-exhaustive collection of peer-reviewed scientific literature on the subject of shale gas and well-stimulation-enabled oil and gas development please see the PSE Healthy Energy Peer Reviewed Literature Database at http://psehealthyenergy.org/site/view/1180.

Some studies of well stimulation in other parts of the country, including Pennsylvania, Colorado, Utah, North Dakota, and Texas, may be relevant to California. There are notable differences between direct and indirect impacts of oil and gas development practices in California compared to those in other states, due to differences in geology, variability and tectonics, well-stimulation and drilling techniques, and oil production and transmission infrastructure, such as pipelines to transport fresh water, recovered fluids, and produced water (see Volume I).

However, in many cases, there are similarities between the *types* of hazards noted in other states and those in California, although the magnitude of risks associated with these hazards are not clear. For example, studies of oil and gas development with relevance to public health in Colorado, Utah, and Wyoming assess oil and gas development at the regional scale (Pétron et al., 2012; Pétron et al., 2014; Darrah et al., 2014; Thompson et al., 2014; Helmig et al. 2014) in the context of shale and source rock formations, but also of hydraulic-fracturing-enabled migrated oil development, much like the majority of production in California.

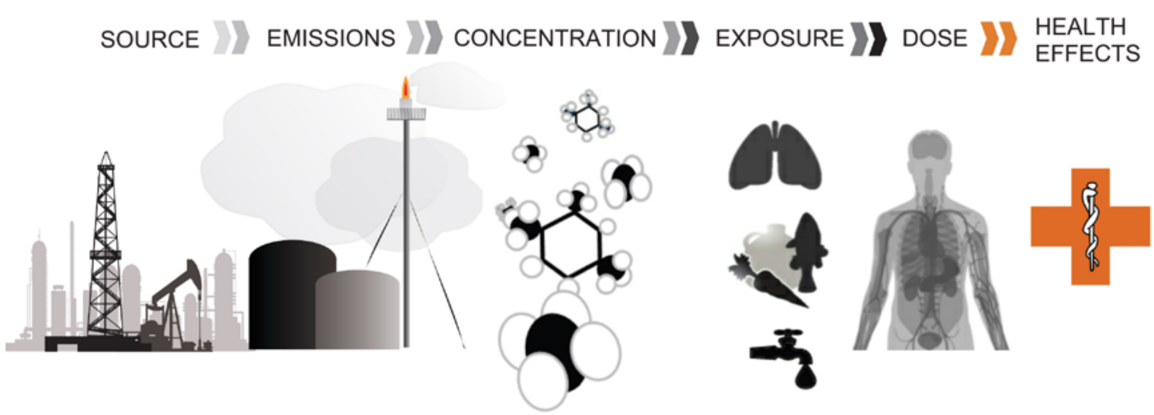

Figure 6.5-1. Simplified environmental exposure framework. Source: Shonkoff et al. (2014).

6.5.3.2. Results from the Environmental Public Health Literature Review

We divide the results for our literature review into three sections. The first section provides an overview of the peer-reviewed literature on well-stimulation-enabled shale and tight gas, and discusses the relevance of the current literature to well-stimulation-enabled oil and gas development in California. While the development of tight-gas resources is not a perfect proxy for the resources developed by means of well stimulation in California, the peer-reviewed literature between 1 January 2009 and 31 December 2014 (the time range we accessed) has a strong focus on tight-gas resources and provides useful but not necessarily relevant insight. We note, however, that there are fundamental differences between the production of tight gas and what is going on in California. Many of the volatile organic compounds found in tight gas are also produced from and emitted by California oil and gas development, but the relative concentrations of these compounds between different types of oil and gas development can differ widely, based on geology, geography, and hydrocarbon type. In the second section, we review epidemiologic and population health studies, and identify what these studies tell us about any potential impacts on public health. The third section examines what the wider literature says about health issues due to potential exposures to water and air emissions from well-stimulation-enabled oil and gas development.

6.5.3.3. Public Health Outcome Studies

Within California, we could only identify one public health outcome study that has relevance to well-stimulation-enabled oil production. This is the Inglewood study carried out by Los Angeles County (Rangan and Tayour, 2011), which is discussed below. Outside of California, health outcome studies and epidemiologic investigations continue to be particularly limited, and most of the peer-reviewed papers to date are commentaries and reviews of the environmental literature pertinent to environmental public health risks.

A cursory public health outcome study was conducted by the Los Angeles County Department of Public Health near the Inglewood Oil Field in Los Angeles County. This study compared incidence of a variety of health endpoints including all-cause mortality, low birth weight, birth defects, and all cancer among populations nearby the Inglewood Oil Field and Los Angeles County as a whole. The study found no statistically significant difference in these endpoints between the population near the Inglewood field and the overall county population. While this may seem to indicate that there is no health impact from oil and gas development, as the study notes, the epidemiological methods employed in this study do not allow it to pick up changes in "rare events" such as cancer and birth defects in small sample sizes, as is the case in this study (Rangan and Tayour, 2011). In addition, lacking statistical power, the Inglewood Oil Field Study is a cluster investigation with exposure assigned at the group level (i.e., an ecological study). It also appears that only crude incidence ratios were calculated. This type of study design is insufficient for establishing causality and has many major limitations, including exposure misclassification and confounding, which may have obscured associations between exposure to environmental stressors from oil and gas development and health outcomes.

Health assessments have been confounded by the dearth of well-designed human-population studies that measure both human exposure and impacts. While a number of studies have found environmental and exposure pathways and health-damaging compounds in environmental concentrations sufficiently elevated to induce health effects, epidemiological studies aimed to assess and quantify the population health burden (i.e., impact severity) of oil and gas production remain in their infancy.

In a study that analyzed air samples from locations in five different states using a community-based monitoring approach, it was found that levels for eight volatile chemicals, including benzene, formaldehyde, hexane, and hydrogen sulfide, exceeded federal guidelines (ATSDR minimal risk levels (MRLs) (ATSDR, 2014) and EPA Integrated Risk Information System (IRIS) cancer risk levels) in a number of instances (Macey et al., 2014). Notably, the residents who collected the grab samples reported a number of common health symptoms, including "headaches, dizziness or light-headedness, irritated, burning, or running nose, nausea, and sore or irritated throat" (Macey et al., 2014). We note that this was not a formal outcomes-based study, and the authors did not attempt to associate the reported health effects with the chemicals measured in the samples. But the study suggests that concentrations of hazardous air pollutants near well-stimulation-enabled oil and gas operations can be elevated to levels where health impacts could occur. We further note that such elevated levels may not be due to well stimulation itself, but to existing petroleum production combined with enhanced petroleum production.

There have been health complaints associated with oil and gas development documented in the peer-reviewed literature. These studies have limitations because they are mainly provide self-reported outcomes and are based on convenience samples, which are collected for other purposes or easily collected by or from local populations. However, many of the reported health outcomes are consistent with what would be expected from exposure to some of the known contaminants associated with oil and gas development, and are consistent across geographic space. In a 2012 survey of Pennsylvania citizens, more than half of the participants surveyed who live in close proximity to well-stimulation-enabled oil and gas development reported increased fatigue, nasal irritation, throat irritation, sinus problems, burning eyes, shortness of breath, joint pain, feeling weak and tired, severe headaches, and sleep disturbance (Steinzor et al., 2013). The survey also found that the number of reported health problems decreased with distance from facilities.

Some research has attempted to assess human-health risks related to air pollutant emissions associated with hydraulic-fracturing-enabled oil and natural gas development. Using U.S. EPA guidance to estimate chronic and subchronic non-cancer hazard indices (HIs) as well as excess lifetime cancer risks, a study in Colorado suggested that those living in closer geographical proximity to active oil and gas wells ($\leq$ 0.8 km [0.5 mile]) were at an increased risk of acute and sub-chronic respiratory, neurological, and reproductive health effects, driven primarily by exposure to trimethyl-benzenes, xylenes, and aliphatic hydrocarbons. It also suggested that slightly elevated excess lifetime cancer risk estimates were driven by exposure to benzene and aliphatic hydrocarbons (McKenzie et al., 2012). The findings of this study are corroborated with atmospheric dilution data of conserved pollutants; for instance, a U.S. EPA report on dilution of conserved toxic air contaminants indicates that the dilution at 800 m (0.5 mile) is on the order of 0.1 mg/m^3 per g/s (U.S. EPA, 1992). Going out to 2,000 m increases this dilution to 0.015 mg/m^3 per g/s, and going out to 3,000 m increases dilution to 0.007 mg/m^3 per g/s. Given that, for benzene, there is increased risk at a dilution of 0.1, it is not clear that concentrations out to 2,000 m (1.25 miles) and 3,000 m (1.86 miles) can necessarily be considered as presenting acceptable risk. However, beyond 3,000 m (1.86 miles), where concentrations fall more than two orders of magnitude via dilution relative to the ½ mile radius, there is likely to be a sufficient margin of safety. Nevertheless, these results indicated that any potentially harmful community exposures could occur at 2,000 meters (1.25 miles) and as much as almost ~3,000 meters (~2 miles) from the source. In considering these dilution assessments, we note that—based on wind, topography, and inversion layers--dilution can increase or decrease, and that increasing density of oil and gas development will require greater dilution to attain the same level of risk as lower density.

In contrast, an oil and gas industry study in Texas compared VOC concentration data from seven air monitors at six locations in the Barnett Shale with federal and state health-based air concentration values (HBACVs) to determine possible acute and chronic health effects (Bunch et al., 2014). The study found that shale gas activities did not result in community-wide exposures to concentrations of VOCs at levels that would pose a health concern. The key distinction between McKenzie et al. (2012) and Bunch et al. (2014) is that Bunch et al. (2014) used air quality data generated from monitors focused on regional atmospheric concentrations of pollutants in Texas, while McKenzie et al. (2012) included samples at the community level. Finer geographically scaled samples can often capture local atmospheric concentrations that are more relevant to human exposure (Shonkoff et al., 2014).

This geographical correlation has been observed in random sampling efforts as well. In a recent study in Pennsylvania, researchers evaluated the relationship between household proximity to natural gas wells and reported health symptoms for 492 people in 180 randomly selected homes with ground-fed wells in an area of active drilling (Rabinowitz et al., 2014). The results suggest that close proximity to gas development is associated with prevalence of dermal and respiratory health symptoms.

In addition to population health hazards in varying distances from active oil and gas development, other studies have assessed the effect of the *density* of oil and gas development on health outcomes. In a retrospective cohort study in Colorado, McKenzie et al. (2014) examined associations between maternal residential location and density of oil and gas development. The researchers found a positive dose-response association between the prevalence of some adverse birth outcomes, including congenital heart defects and possibly neural tube defects and increasing density of development (McKenzie et al., 2014). For instance, the observed risk of congenital heart defects in neonates was 30% (OR = 1.3 (95% CI: 1.2, 1.5)) greater among those born to mothers who lived in the highest density of oil and gas development (> 125 wells per mile), compared to those neonates born to mothers who lived with no oil and gas wells within a 16 km (10-mile) radius. Similarly, the data suggest that neonates born to mothers in the highest density of oil and gas development were twice as likely (OR = 2.0, 95% CI: 1.0, 3.9) to be born with neural tube defects than those born to mothers living with no wells in a 10-mile radius (McKenzie et al., 2014). The study, however, showed no positive association between the density and proximity of wells and maternal residence for oral clefts, preterm birth, or term low birth weight. We also note that these indirect effects, by definition, cannot be directly linked to stimulation technology, but to existing and well-stimulation-enhanced petroleum production.

6.5.4. Summary of Public Health Outcome Studies

There have been few epidemiological studies that measure health effects associated with oil and gas development, whether enabled by well stimulation or not. The studies that have been published have been heavily focused on exposures to toxic air contaminants (hazardous air pollutants), while fewer studies have evaluated associations between oil and gas development and water contamination.

Each of the studies discussed above have limitations to their study designs, their geographic focus, and their statistical power to evaluate associations. These studies suggests that health concerns about oil and gas development may not be **direct** effects specific to the well stimulation process, but rather are associated with **indirect** effects of oil and gas development. For example, the studies in Colorado (McKenzie et al., 2012; McKenzie et al., 2014) found that the most likely driver of poor health outcomes were aliphatic hydrocarbons and benzene. Neither of these compounds is added to stimulation fluids, but rather are mobilized in the subsurface and co-produced (and co-emitted) with oil and gas production, processing, transmission, and consumption.

6.6. Occupational Health-Hazard Assessment Studies

Due to their proximity to hazards, workers directly involved in well stimulation processes may have exposure to chemical and physical hazards larger than those of the surrounding communities, and therefore have the greatest likelihood of any resulting acute and/or chronic health effects. The expansion of well stimulation in California has the potential to expose workers in this industry to a range of existing hazards related to oil and gas development, and additional hazards specific to well stimulation such as elevated VOC exposures during injection and flowback operations (Esswein et al., 2014) and the use of proppant, which has been noted to subject workers to elevated silica exposure (Esswein et al., 2013). Silica exposure is a major risk factor for the development of the lung disease silicosis.

An adequate understanding of occupational health hazards requires information about the quantities and composition of materials used, handling protocols, and emissions factors of operations in addition to information about the tasks, protocols, and exposure reduction control measures for activity on well pads, in and around trucks and machinery, and in other locations throughout the oil development process related to well stimulation. Employers can and often do implement comprehensive worker protection programs that substantially reduce worker exposure and likelihood of illness and injury. Employers in the oil and gas industry are required to comply with existing California occupational safety and health regulations, and follow best practices to significantly reduce and/or eliminate illness and injury risk to their employees (California Occupational Safety and Health Act of 1973 and Title 8 of the California Code of Regulations). In following these standards and best practices in protecting workers from chemical exposures while they are involved in well stimulation operations, employers in this industry may also reduce the likelihood of chemical exposure to the surrounding community.

There is a large California workforce engaged in the oil development and production industry. We reviewed available literature and the scope of this occupation group (and the hazards they face). Although data are available on health risks faced by this work population, little data is available on the hazards directly associated with well stimulation activities.

6.6.1. Scope of Industry and Workforce in California

Employment numbers and occupations involved in well stimulation are impossible to ascertain with precision, as companies engaged in drilling and support activities in well stimulation are also involved with overall oil and gas development in California. Any workers engaged in well stimulation are typically part of the broader oil and gas well development/production industry. This is an industry where workers can be exposed to a range of hazards in addition to those directly associated with well stimulation. Table 6.6-1 provides a summary of the employment in the oil and gas extraction industry in California.

Table 6.6-1. Employment in oil and gas extraction – California 2014.

Industry Title	Establishments	Average Monthly Employment
2111111 Crude Petroleum and natural gas extraction	179	9,669
2111112 Natural Gas Liquid Extraction	10	193
213111 Drilling Oil and Gas Wells	91	3,419
213112 Support Activities, Oil/Gas Operations	240	9,162
Total	**520**	**22,443**

Source: http://www.labormarketinfo.edd.ca.gov/

A review of all data on occupational health for the oil and gas extraction industry indicates that this industry has a high rate of worker injury and death relative to other industries, but does not collect publicly available data on the fraction of oil and gas development that is enabled by well stimulation (NIOSH, 2015a; 2015b; 2015c; 2015d). According to NIOSH (2015d), the oil and gas extraction industry had an annual occupational fatality rate of 27.5 per 100,000 workers (2003-2009)—more than seven times higher than the rate for all U.S. workers. The annual occupational fatality rate is highly variable, and correlates with the level of drilling activity. For example, the numbers of fatalities increased by 23% between 2011 and 2012 to the largest number of deaths of oil and gas workers since 2003. Appendix 6.D provides details on occupational health data we compiled for the U.S. oil and gas extraction industry. In the sections below, we summarize studies that address the direct impacts of well stimulation within the oil and gas industry. This is U.S. data, which is relevant to California operations, but not necessary fully representative of current or future California well stimulation activities.

6.6.2. Processes and Work Practices

In seeking insight on occupational hazards from well stimulation, we identified two review papers useful for describing occupational exposures in oil and gas development (Mulloy, 2013; Witter, 2014), but these papers do not include job or process descriptions. We identified two additional peer-reviewed papers describing the work processes in oil and gas extraction that evaluate occupational exposure for silica and VOCs attributable directly to well stimulation (Esswein et al., 2013; 2014). The Esswein et al. papers (2013; 2014) report results from the National Institute for Occupational Safety and Health study that collected 111 personal-breathing-zone samples at 11 sites in five states during four seasons, for investigation of crystalline silica exposure and personal and environmental measurements at six sites in two states, for investigation of chemical exposures. We found no other publicly available data sources that include job titles or work activities during oil and gas extraction or well stimulation.

In the first of these two papers, Esswein et al. (2013) describe the processes of hydraulic fracturing, in terms of the workers involved and their typical roles as:

> *At a typical site, 10 to 12 driver/operators position and set up equipment, configure and connect piping, pressure test, then operate the equipment (e.g., sand movers, blender, and chemical trucks) required for hydraulic fracturing. Other employees operate water tanks and water transport systems, and several control on-site traffic, including sand delivery trucks and other vehicles. An additional crew includes well liners (typically 3–5) who configure and assemble well casing perforation tools and operate cranes to move tools and equipment into and out of the well. … Moving proppant along transfer belts, pneumatically filling and operating sand movers, involves displacement of hundreds of thousands of pounds of sand per stage, which creates airborne dusts at the work site (Esswein et al., 2013).*

Similarly, in the second paper, Esswein et al. (2014) describe flowback operations and the associated exposures to VOCs from these operations as:

> *Typical flowback operations have two to four flowback personnel performing flowback tasks; these were the typical number of workers at each of the sites visited. Air sampling, typically collected over two days, included workers with the following job titles and descriptions:*

- *Flowback lead: recorded well pressures and temperatures, monitored separators and other equipment*
- *Flowback tech: gauged flowback tanks 1–4 times per hr., recorded volumes, assisted in tank pumping and fluid transfers to trucks*
- *Production watch lead: monitored rate and volume of natural gas and liquid hydrocarbons*
- *Production watch technician: gauged production tanks*
- *Water management operator: gauged water tanks, ran pumps*

Workers access the tanks through hatches located on the tops of tanks. Periodically, recovered liquid hydrocarbons/condensate is pumped to production tanks or to trucks, which collect and transport process fluids off the well pad; natural gas is typically piped to gas gathering operations. Tank gauging and other tasks required during flowback can present exposure risks for workers from alkane and aromatic hydrocarbons produced by the well and diluted treatment chemicals used during hydraulic fracturing (typically a combination of acid, pH adjusters, surfactant, biocides, scale and corrosion inhibitors, and, in some cases, gels, gel demulsifiers, and cross-linking agents) (Esswein et al., 2014).

6.6.3. Acid Used in Oil and Gas Wells

The oil and gas industry commonly uses strong acids along with other toxic substances, such as corrosion inhibitors, for both routine maintenance and well stimulation (see Volume I, Chapter 2 and 3 & Volume I). These acids pose occupational hazards relevant to well stimulation. Well acidizing requires the use of hydrochloric (HCl) and hydrofluoric (HF) acid. In many cases, HF is created at the oilfield by mixing hydrochloric acid with ammonium fluoride and immediately injecting the mix down the well (Collier, 2013). Creating the HF on site may be safer than offsite production, because it reduces the risk of transport accidents. In all uses of HF, there is the potential for worker exposure to acid gases. According to industry protocols, safety precautions for those on site during an acid treatment concern detection of leaks and proper handling of acid (SPE, 2015; API, 1985). As also reported in Volume II Chapter 2, due to the absence of state-wide mandatory reporting on chemical use in the oil and gas industry, it is not known how much acid is used for oil and gas development throughout California.

Well-established procedures exist for mixing and handling acids (NACE, 2007). The parent acids do not generally migrate long distances from the well, but acids formed through a complex series of reactions during acidization can migrate deeper into the formation (Weidner, 2011). If the acidization fluids are introduced into the well in the right proportions and order, and sufficient time and conditions allowed for reactions to proceed, then the original acids are used up during the acidization process (Shuchart, 1995). The reaction of strong acids with the rock minerals, corrosion products, petroleum, and other injected chemicals can also release contaminants of concern, such as hydrogen sulfide from acid reaction with iron sulfides, that have not been characterized or quantified. These chemicals may be present in recovered fluids and produced water (NACE, 2007). We do not have data to determine how much strong acid, including hydrochloric and hydrofluoric acid, is used in oil and gas development in California. DOGGR has only recently required reporting of all acid use that will result in a better understanding in the future. Hydraulic fracturing operations have only infrequently incorporated acid use (11 voluntarily reported applications between January 2011 and May 2014). Industry has voluntarily reported approximately twenty matrix-acidizing treatments per month throughout California, but has not revealed detailed chemical information. The South Coast Air Quality District requires reporting on the use of all chemicals by the oil and gas industry. Their data suggest widespread and common use of acid for many applications in the industry.

Environmental public health exposures to strong acids are only likely to occur at the surface, given that migration of acids in the subsurface are limited by relatively rapid reactions. The most likely human exposures to strong acids are to workers. The opportunities for exposure are predominantly the following: (1) handling and mixing of acids prior to well injection, (2) during flowback following an acid treatment, and (3) during accidents and spills.

State and federal agencies regulate spills of acids and other hazardous chemicals, and existing industry standards dictate standard safety protocols for handling acids (see Section 6.6.3.4). The Office of Emergency Services (OES) between January 2009 and December 2014 reported nine spills of acid that can be attributed to oil and gas development in California. Reports indicate the spills did not involve any injuries or deaths. These acid spill reports represents less than 1% of all reported spills of any kind attributed to the oil and gas development sector in the same period, and suggest that spills of acid associated with oil and gas development are infrequent. Given the lack of Occupational Safety and Health Administration (OSHA) reporting of worker exposures to acids, to the extent that this reporting is comprehensive, it appears that industry protocols for handling acids likely are protecting workers from such acute exposures.

Chapter 2 of this volume reports chemical spills in California oil fields, including spills of hydrochloric, hydrofluoric, and sulfuric acids. Of the 31 spills reported between January 2009 and December 2014, nine were acid spills. Among these was a storage tank at a soft water treatment plant containing 20 m^3(5,500 gallons) of hydrochloric acid in the Midway-Sunset Oil Field in Kern County that ruptured violently, releasing the acid beyond a secondary containment wall. No injuries or deaths were associated with this or any other acid spill.

Work processes and health hazards associated with well stimulation are summarized in Table 6.6-2.

The physical hazard associated with a chemical used on the job is most often characterized by evaluating a standard selection of properties associated with the individual chemical or chemical mixture. These properties include inflammability, corrosivity, and reactivity.

There are a number of different systems for classifying the hazardous properties of chemicals. The American Coatings Association, Inc. developed the Hazardous Materials Identification System (HMIS) (ACS, 2015) to aid its members in the implementation of an effective Hazard Communication Program as required by law. Another system developed by the National Fire Protection Association (NFPA) is directed at communicating potential hazards during emergency situations (NFPA, 2013.) Both systems have a “0 to 4” ranking system with a chemical ranked “4” having a severe hazard, “3” representing a serious hazard, “2” representing a moderate hazard, and “1” a slight hazard. Materials ranked “0” are of minimal or no hazard for the category ranked.

All of the chemicals reportedly in well stimulation in California (see Chapter 2, Appendix 2.A, Tables 2.A-3 and 2.A-5) were evaluated for this report using both the HMIS and the NFPA systems. Approximately 20% to 30% of the additives were not categorized under either the HMIS or NFPA systems for different hazards. Overall, only approximately 5% of the well stimulation fluid additives were considered flammable or fire hazard, and only a few compounds were ranked as physical or reactivity hazards (Figure 6.6-1).

Well stimulation fluid additives categorized as severe (4) or serious hazards (3) are listed in Chapter 2, Appendix 2.A, Table 2.A-8 (Chapter 2). Since chemical hazards and fire hazards are integral to both conventional and unconventional oil and gas extraction, the well stimulation additives illustrated in Figure 6.6-1 are not likely to pose new or unusual hazards that are specific to unconventional oil and gas production. However, the additives should be considered in evaluation of occupational exposure and in assessment of the risks associated with oil and gas production.

Table 6.6-2. Work processes and health hazards associated with well stimulation.

Work processes	Health hazards	Fed OSHA Standards
Mixing and injecting of chemicals and dusts - i.e., proppants, acids, pH adjustment agents, biocides etc.	Irritation and burns to skin and eyes Acute and chronic respiratory disease (COPD, asthma, silicosis, lung cancer) Low pH recovered fluid	Hazard Communication, Safety Data Sheets - 29 CFR 1910.1200(g) Personal Protective Equipment - 29 CFR Subpart I Specifications for Accident Prevention Signs and Tags -29 CFR 1910.145 Toxic and Hazardous Substances - 29 CFR 1910 Subpart Z Hazard Communication - 29 CFR 1910.1200 Emergency Response Program to Hazardous Substance Releases - 29 CFR 1910.120(q) Medical Services and First Aid - 29 CFR 1910.151(c)
Pressure pumping	Explosions Acute and chronic inhalation exposure due to high pressure from uncontrolled releases, use of flammable fluids, gases, and materials	Personal Protective Equipment, General Requirements - 29 CFR 1910.132
Recovered fluids	Explosions Acute and chronic inhalation exposure due to high pressure from uncontrolled releases, use of flammable fluids, gases and materials	Personal Protective Equipment - 29 CFR 1910 Subpart I Portable Fire Extinguishers - 29 CFR 1910.157 Welding, Cutting, and Brazing - 29 CFR Subpart Q, 29 CFR 1910.252, General Requirements
Multiple operations: hydrogen sulfide, volatile organic compounds (VOCs), combustion products and elevated noise	Asphyxia Nervous system, liver and kidney damage Cancer (blood)	Respiratory Protection, General Requirements - 29 CFR 1910.134(d)(iii) Air contaminants - 29 CFR 1910.1000
Transport, Rig-Up, and Rig-Down	Injuries and fatalities (struck-by, caught-in, crushing hazards, and musculoskeletal injuries) from off-site and on-site vehicle and machinery traffic or movement; heavy equipment, mechanical material handling, manual lifting, and ergonomic hazards (these are mostly indirect hazards with respect to well stimulation)	Electrical - 29 CFR 1910.307 – Hazardous (Classified) Locations Powered Industrial Trucks - 29 CFR 1910.178 Crawler, Locomotive, and Truck Cranes - 29 CFR 1910.180 Slings - 29 CFR 1910.184(c)(9) Walking-Working Surfaces - 29 CFR 1910 Subpart D Permit-Required Confined Spaces - 29 CFR 1910.146 Occupational Noise Exposure - 29 CFR 1910.95 Electrical: Selection and Use of Work Practices - 29 CFR 1910.33

Source: Adapted from U.S. OSHA (2014) and Esswein et al. (2013; 2014)

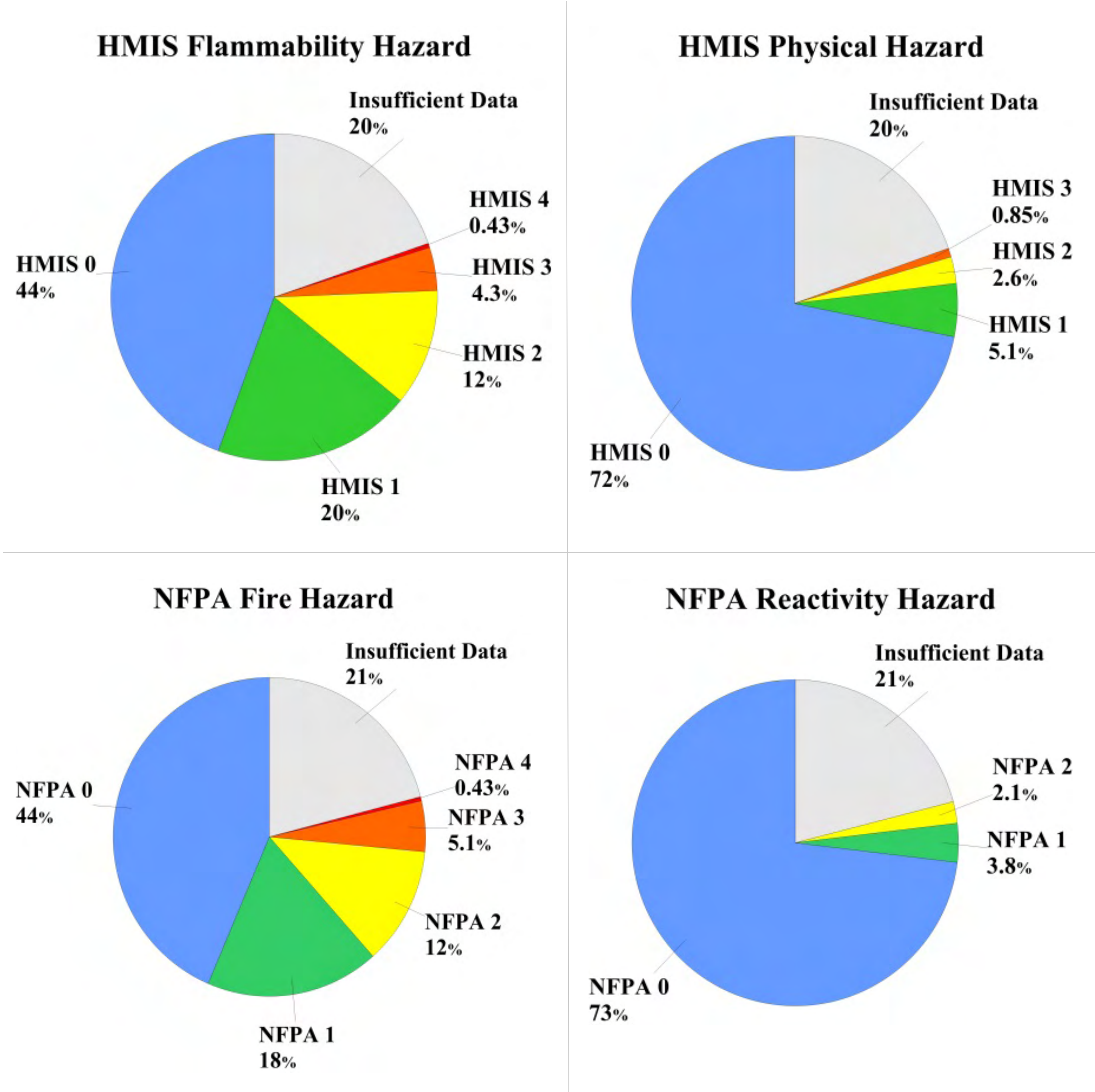

Figure 6.6-1. Evaluation of the flammability, reactivity, and physical hazards of chemical additives reported for hydraulic fracturing in California using the Hazardous Materials Identification System (HMIS) and the National Fire Protection Association (NFPA) classification system.

6.6.3.1. Occupational Health Outcomes Associated With Well Stimulation-Enabled Oil and Gas Development

There are few peer-reviewed health outcomes studies among workers in the oil and gas development industry that are specific to well-stimulation-enabled oil and gas development. For well stimulation, there are effectively no health outcome studies and only two studies addressing health risks (Esswein et al., 2013; 2014). The results of these two studies are summarized above.

6.6.3.2. Worker Protection Standards, Enforcement, and Guidelines for Well Stimulation Activities

The U.S. Occupational Safety and Health Administration (OSHA) has identified multiple hazards and enforces numerous standards for oil and gas extraction (OSHA, 2015a; 2015b). There are several specific OSHA exemptions for the oil and gas development industry, including:

- Process safety management (PSM) of highly hazardous and explosive chemicals (29 CFR 1910.119). The PSM standard requires affected facilities to implement a systematic program to identify, evaluate, prevent, and respond to releases of hazardous chemicals in the workplace. The PSM standard exempts oil and gas well drilling and servicing operations (OSHA, 2015c)

- Comprehensive General Industry Benzene Standard (29 CFR 1910.1028). Under the Comprehensive Standard, the limit for workers' exposure is 1 part per million (ppm)—the occupational exposure limit is the same. The exemption allows worker exposures up to 10 ppm in oil and gas. The exemption also eliminates requirements for medical monitoring, exposure assessments, and training (OSHA, 2015d).

- Hearing Conservation Standard (29 CFR 1910.95). This standard, designed to protect general industry employees, establishes permissible noise exposure limits and outlines requirements for controls, hearing protection, training, and annual audiograms for workers. Many sections of the standard do not apply to employers engaged in oil and gas well drilling and servicing operations (OSHA, 2015e).

- Control of Hazardous Energy Sources, or "Lockout/Tagout" (29 CFR 1910.147). The standard requires specific practices and procedures to safeguard employees from the unexpected energization or startup of machinery and equipment, or the release of hazardous energy during service or maintenance activities. The standard does not cover the oil and gas well drilling and servicing industry (OSHA, 2015f).

The U.S. OSHA has issued an alert on the hazards of silica exposure (OSHA, 2015g) and guidance to employers on other safety and health hazards during hydraulic fracturing and fluid recovery (OSHA, 2015h). The National Institute for Occupational Safety and

Health (NIOSH) has identified exposure to silica dust and volatile organic compounds as significant health hazards during oil and gas extraction (NIOSH, 2015a; 2015b; 2015c), and recommends additional quantification of exposure to diesel particulate and exhaust gases from equipment, high or low temperature extremes, noise, hydrocarbons, hydrogen sulfide, heavy metal exposure, and naturally occurring radioactive material (NIOSH, 2015d).

The California Division of Occupational Safety and Health (CalOSHA) has specific enforceable regulations pertaining to petroleum drilling and production (CalOSHA, 2015a; 2015b). For the ten-year period January 1, 2004–December 31, 2013, there were 281 inspections in oil and gas extraction: 77 inspections in NAICS 211, 98 inspections in NAICS 213111, and 106 inspections in NAICS 213112 (OSHA, 2015i). Of the 281 inspections, 153 (54%) were in response to an accident, 47 (17%) were planned, and 36 (13%) were due to complaints. Cal/OSHA is required to investigate all work-related amputations, hospitalizations for greater than 24 hours, and traumatic fatalities. There are 104 cases in which a detailed narrative is available regarding these incidents, including 16 work-related fatalities (Appendix 6.E).

The American Petroleum Institute has also published comprehensive safety and health guidelines for oil and gas well drilling and servicing operations, and includes recommended best practices from the American Conference of Governmental Industrial Hygienists and American National Standards Institute (API, 2007).

The American Petroleum Institute (API) and the Society of Petroleum Engineers have established protocols and safety precautions for those on site during an acid treatment (SPE, 2015; API, 1985). These guidelines state that (a) pressure tests with water or brine are used to ensure the absence of leaks in pressure piping, tubing, and packer; (b) anyone around acid tanks or pressure connections should wear safety goggles for eye protection; (c) those handling chemicals and valves should wear protective gauntlet-type, acid-resistant gloves; (d) water and spray washing equipment should be available at the job site; (e) when potential hydrogen sulfide gas hazards exist, workers need contained, full-face, fresh-air masks; (f) testing equipment and appropriate safety equipment should be on hand to monitor the working area and protect personnel in the area; and (g) special scrubbing equipment may be required for removal of toxic gases.

6.7. Other Hazards

Oil and gas development, including those enabled by well stimulation, creates a number of physical stressors, including noise and light pollution. Although noise pollution and light pollution are often thought of as mere nuisances, data suggest that these physical stressors can be detrimental to human health. Noise pollution is associated with truck traffic, drilling, pumps, flaring of gases, and other processes associated with well stimulation-enabled oil and gas development and oil and gas development in general.

6.7.1. Noise Pollution

While no peer-reviewed studies to date examine the public health implications of communities exposed to elevated noise from oil and gas development in California, numerous large-scale epidemiological studies have found positive associations between elevated environmental noise and adverse health outcomes. (See Noise Literature Review in Appendix 6.F.) Noise is a biological stressor that modifies the function of the human organs and nervous systems, and can contribute to the development and aggravation of medical conditions related to stress, most notably hypertension and cardiovascular diseases (Munzel et al., 2014). The World Health Organization (WHO, 2014) has noise thresholds, measured in decibels (dB), and their effect on population health, with noise levels above 55 dB considered dangerous for the general population (Table 6.7-1). A number of activities associated with drilling and production activity (Table 6.7-2), some of which could also be associated with well stimulation, generate noise levels greater than those considered dangerous to public health. Dose-response data indicate that noise during well stimulation in California and elsewhere is associated with sleep disturbance and cardiovascular disease (McCawley, 2013). These findings are corroborated by estimates from the New York State Department of Environmental Conservation on the development of shale gas (NYSDEC, 2011).

Table 6.7-1. WHO thresholds levels for effects of night noise on population health.

Average night noise level over a year $L_{night,outside}$	Health effects observed in the population
Up to 30 dB	Although individual sensitivities and circumstances may differ, it appears that up to this level no substantial biological effects are observed. $L_{night,outside}$ of 30 dB is equivalent to the no-observed-effect level (NOEL) for night noise.
30 to 40 dB	A number of effects on sleep are observed from this range: body movements, awakening, self-reported sleep disturbance, and arousals. The intensity of the effect depends on the nature of the source and the number of events. Vulnerable groups (for example children, the chronically ill and the elderly) are more susceptible. However, even in the worst cases the effects seem modest. $L_{night,outside}$ of 40 dB is equivalent to the lowest-observed-adverse-effect level (LOAEL) for night noise.
40 to 55 dB	Adverse health effects are observed among the exposed population. Many people have to adapt their lives to cope with the noise at night. Vulnerable groups are more severely affected.
Above 55 dB	The situation is considered increasingly dangerous for public health. Adverse health effects occur frequently, a sizeable proportion of the population is highly annoyed and sleep-disturbed. There is evidence that the risk of cardiovascular disease increases.

Source: Adapted from the WHO (2014)

Table 6.7-2. Equipment Noise Levels for Drilling and Production in Hermosa Beach, California.

Work Stage	Equipment	Sound Power Level† (dBA)
Drilling (30 month scheduled duration)	Hydraulic Power Unit	110.7
	Mud Pump	105.4
	Drill Rig	93.3
	Shaker	75.3
	Pipe Handling (Quiet Mode)	107.5
Production (at rate of 800 barrels per day)	Well Pumps	97.7
	Produced Oil Pump	77.7
	Produced Water Pump	86.7
	Shipping Pump	92.8
	Water Booster Pump	86.7
	Water Injection Pumps (2)	102.8
	Vapor Recovery Compressor	88.6
	Vapor Recovery Unit Cooler	90.2
	1st Stage Compressor (2)	96.2
	2nd Stage Compressor (2)	96.2
	Compressor Cooler	102.0
	Amine Cooler	102.1
	DEA Charge Pump	77.7
	Regenerator Reflux Pump	77.7
	Chiller	85.0
	Glycol Regenerator	92.4
	Micro-turbines (5)	92.9
	Variable Frequency Drives	83.3

Source: Adapted from Hermosa (2014) based on field measurements and identified as Source Noise Levels (measured in decibels (dBA)) used in modeling noise contour maps.

While noise mitigation measures are undertaken in some California oil fields, including Hermosa Beach (Hermosa, 2014) and Inglewood (Cardno ENTRIX, 2012), there are no data available as to their effectiveness and adherence. The City of Hermosa Beach allows noise levels in the 40-60 dB range (Appendix 6.F, Table 6.F-8a and Table 6.F-9).

6.7.2. Light Pollution

Light pollution is reported as a nuisance in communities undergoing well stimulation, because activities occur during both daytime and nighttime hours (Witter et al., 2013). While little research has been conducted on the public health implications of exposures to light pollution from oil and gas development, some epidemiologic studies of light pollution from other sources suggests a positive association between indoor artificial light and poor health outcomes (Chepesiuk, 2009). Further, other studies suggest that night-time light exposure can disrupt circadian and neuroendocrine physiology (Chepesiuk, 2009; Davis and Mirick, 2006). Hurley et al. (2014) found that women living in areas with high levels of artificial ambient light at night may be at an increased risk of breast cancer, although how these findings translate to the levels of night-time light exposure to oil and gas development remains understudied.

6.7.3. Biological Hazards

Coccidioides immitis (*C. immitis*) is a soil fungus that causes Valley Fever and is endemic to the soils of the southwest. The San Joaquin Valley is an area where the fungal spores live in the top 2”-12” of soil. Soil disturbance associated with developing and maintaining oil field infrastructure may generate airborne *C. immitis* and expose workers and nearby residents. Cases of Valley Fever are not uncommon among workers in the oil fields of Kern County (Hirshmann, 2007).

While over 60% of people exposed to *C. immitis* never have symptoms, symptomatic infection can result in those who are exposed to the spores through inhalation. Symptoms range from mild, influenza-like illness to systemic fungal infection and severe disease, particularly in those who are immune-compromised. Coccidioidomycosis is considered an occupational hazard in endemic regions, particularly for workers who are exposed to spores through earth-moving activities or who are exposed to dusty conditions (Friedlander, 2014). In California, Cal/OSHA issued a fact sheet to employers to outline the health hazards of Valley Fever and preventative measures, focusing on worker education, adopting site plans to reduce exposure, and protecting workers against exposure with NIOSH-approved respiratory protection filters (Friedlander, 2014).

While the health hazards of Valley Fever have been outlined, no data have been published on the rates of infection among workers specifically in the oil and gas industry in California. Valley Fever remains an important occupational health hazard, as much of the well-stimulation-enabled oil and gas extraction activities take place in California’s Central Valley.

6.8. Community and Occupational Health Hazard Mitigation Strategies

A number of strategies exist to reduce potential public health hazards and risks associated with well-stimulation-enabled oil and gas development activities. Most hazards have not been observed or measured in California, rendering it difficult to determine which hazards present risks at any given site in California. The most important hazards will not be identified until California-based studies document chemical compositions and release mechanisms, emission intensities, and potential for human exposure. As site-specific information becomes available, hazard mitigation strategies can be considered.

The following sections catalogue several potential community health and occupational hazard mitigation strategies. The strategies noted below highlight those among the more detailed mitigation recommendations provided above in this chapter as well as in Volume

II, Chapters 2 and 3. These strategies are to be considered in addition to employment of best practices in well-stimulation-enabled oil and gas development, which are employed to avoid exposure to a given hazard in the first place. It should be noted that mitigation and "best practices" should be systematically evaluated for effectiveness in the field, and even those mitigation practices with high efficacy are not effective if they are not properly executed and enforced.

6.8.1. Community Health Mitigation Practices

6.8.1.1. Setbacks

Exposures to environmental pollution and physical hazards such as light and noise falls off with distance from the source. The literature on oil and gas production suggests that the closer a population is to active oil and gas development, the more elevated the exposure, primarily to air pollutants but also to water pollutants, if a community relies on local aquifers for their drinking water, and zonal isolation of gases and fluids from aquifers is not achieved (see Section 6.4.1 above). While some California counties and municipalities have minimum surface setback requirements between oil and gas development and residences, schools, and other sensitive receptors, there are no such regulations at the state level. Further, the scientific literature is clear that certain sensitive and vulnerable populations (e.g., children, asthmatics, those with pre-existing cardiovascular or respiratory conditions, and populations already disproportionately exposed to elevated air pollution) are more susceptible to health effects from exposures to environmental pollutants known to be associated with oil and gas development (e.g., benzene) than others. The determination of sufficient setback distances should consider these sensitive populations.

Setback requirements have been instituted in some locales to decrease exposures to air pollutants, especially to VOCs that are known to be health damaging (e.g., benzene). The Dallas-Fort Worth area recently instituted a 460 meters (1,500 foot) minimum setback requirement between oil and gas wells and residences, schools, and other sensitive receptors. In summary, the scientific literature supports the recommendation for setbacks (City of Dallas, 2015). The distance of a setback would depend on factors such as the presence of sensitive receptors, such as schools, daycare centers, and residential elderly care facilities. The need for setbacks applies to all oil and gas wells, not just those that are stimulated.

6.8.1.2. Reduced Emission Completions and Other Air Pollutant Emission Reduction Technological Retrofits

As discussed in Volume II, Chapter 3, reductions of air pollutant emissions from well completions and other components of ancillary infrastructure have been demonstrated to reduce emission of methane, non-methane hydrocarbons, and VOCs during the oil and gas development process. Many of the non-methane VOCs contribute to background and regional tropospheric ozone concentrations and some are directly health damaging (e.g., benzene, toluene, ethylbenzene, xylene, formaldehyde, and hydrogen sulfide). Therefore, a reduction in emissions could decrease exposure of populations, especially at the local level, to harmful air pollutants. For a more complete discussion of these types of air pollutant emission mitigation technologies, please refer to Volume II, Chapter 3.

The deployment of mitigation technologies that have a demonstrated ability to reduce emissions in the laboratory or in small studies in the field do not necessary translate to actual reductions in air pollutants at scale if the sources of pollution increase. For example, Thompson et al. (2014) found that although regulations that strengthen rules about emission-reducing technologies in Colorado are much more stringent today than in 2008, emissions of VOCs have increased because of expansion of oil and gas development.

6.8.1.3. Use of Produced Water for Agricultural Irrigation

As noted in Chapter 2 of this volume, at least seven cases were identified that allow produced water to be used in agricultural irrigation in the San Joaquin Valley, with testing and treatment protocols that are insufficient to guarantee that well stimulation and other chemical constituents are at sufficiently low concentrations not to pose public health and occupational (farm worker) risks. To reduce public health risks that are potentially associated with the use of produced water for irrigation, prior to authorization to use produced water for irrigation, California should develop and implement testing and treatment protocols which account for stimulation chemicals and the other possible chemicals mobilized in the subsurface, prior to approving beneficial reuse of water produced from fields with well stimulation (and logically any produced water).

6.8.1.4. Water Source Switching

As noted in Chapter 2 of this volume, subsurface disposal of recovered fluid and produced water (Class II Underground Injection Control (UIC) wells) has been conducted in aquifers that are suitable for drinking water and other beneficial uses. The majority of Californians do not source their drinking water from such wells, and there has been no groundwater monitoring in the state to determine the number or the extent to which drinking water aquifers may be contaminated by well-stimulation-enabled oil development. Concerned households can eliminate their potential exposure by being provided with alternative drinking water sources that are known to be safe. It should be noted that water source switching is not be an alternative to the protection of drinking water resources.

6.8.2. Occupational Health Mitigation Practices

6.8.2.1. Personal Protective Equipment

The research is limited on the use of personal protective equipment (PPE) in the oil and gas extraction industry. A study on worker health and safety during flowback noted the routine use of PPE by workers at all sites, depending on work task (Esswein et al., 2014).

The PPE observed in use included flame-retardant clothing, steel toe boots, safety glasses, hard hats, and occasional use of fall protection, riggers gloves, and hearing protection. None of the workers observed in this study who experienced the highest exposure to silica sand and chemicals (flowback technicians, production watch technicians, or water management technicians) was observed wearing respirators, nor were they clean-shaven, which is necessary for proper respirator protection. Workers who wore half mask respirators during mixing of crystalline silica proppant were also not sufficiently protected, indicating that a similar study to this NIOSH assessment should be performed in California to assess worker exposure on the well pad.

6.8.2.2. Reducing Occupational Exposure to Silica

Mulloy (2014) identified opportunities for reducing silica exposure, including: elimination; substitution of ceramic or alternative proppants; proper engineering controls that minimize respiratory exposure; administrative control that limit worker time on site; and personal protection. Other recommendations included conducting workplace exposure assessments to characterize exposures to respirable crystalline silica; controlling exposures to the lowest concentrations achievable (and lower than the OSHA PEL or NIOSH REL); and ensuring that an effective respiratory protection program is in place that meets the OSHA Respiratory Protection Standards (Esswein et al., 2013).

6.9. Data Gaps

We need four types of information to assess environmental public health hazards:

1. The source and identity of the chemical substances (or stressor such as noise, traffic, etc.) of concern

2. A qualitative or quantitative measure of the outcome of the stressor, such as an acute or chronic toxicity factor,

3. Quantification of an emissions factor to air and/or water or a reporting of the quantity used.

4. Information about the number and plausibility of human exposure pathways associated either with emissions or quantities used. This factor is useful for hazard assessments and essential for risk assessments.

In preparing this hazard assessment, we have found that only for a minority of cases do we have information for items (1) identity, (2) outcome measure, (3) quantity/emission, and (4) exposure pathways. It is more common that we have (1) but not (2) or (3); (1) and (3) but not (2); or (1) and (2) and not (3). In some cases, for example some of the unidentified or ambiguously described components for the well treatment mixtures, we lack information on (1), (2) and (3). To add to our uncertainty, we find that even in cases where we have information about identity, toxicity, and/or quantity/emissions, there are significant concerns about the accuracy of the information.

6.10. Conclusions

The majority of important potential direct impacts of well stimulation result from the use of well stimulation chemicals. The large number of chemicals used in well stimulation makes it very difficult to judge the risks posed by accidental releases of stimulation fluids, such as those related to surface spills or unexpected subsurface pathways. Of the chemicals used, many are not sufficiently characterized to allow a full risk analysis.

There is a lack of information related to human exposure pathways for well-stimulation-enabled oil and gas development in California. For example, it is known that some produced water is diverted for agricultural use (see Chapter 2 in this volume); however, information regarding the composition of the fluids at the point of release and the environmental persistence, toxicity, and bioavailability of specific compounds in agricultural systems has not been studied. There is also a need to design and/or expand monitoring studies to better evaluate time activity patterns and personal exposure on and off-site for well-stimulation-enabled oil and gas development activities. Finally, it is important to extend the characterization of some on-site (occupational) exposures to off-site (community) exposures, i.e., for airborne silica proppant.

California-specific studies on the epidemiology of exposures to stimulation chemicals and stressors remain, by and large, non-existent. Although air and water quality studies suggest public health hazards exist, many data gaps remain, and more research is needed to clarify the magnitude of human-health risks and potential existing and future morbidity and mortality burdens associated with these concerns. It is clear that environmental public health science is playing catch up with well stimulation-enabled oil and gas development—and oil and gas development in general—across the country, and this is particularly notable in California.

Most of the studies included in this review of the literature were conducted in geographically and geologically diverse areas of the U.S., and may or may not be directly generalizable to the California context. Furthermore, much of the research on health risks has been conducted on the development of hydrocarbons from shale. While there are many similarities between the processes involved in the development of shale across the country and in the development of diatomite and other oil reservoirs in California, there are also a number of differences that increase and decrease public health hazards and potential public health risks (See Volume I).

There is no data on work-related fatalities related specifically to oil and gas development enabled by well stimulation, but the types of hazardous work activities during well stimulation are similar to those seen in general oil and gas extraction operations. Work-related fatality rates are significantly higher in the oil and gas development industry compared to the general industry average.

Work processes in oil and gas development, including that enabled by well stimulation, should be fully characterized to determine the specific risk factors for work-related injury and illness relative to risk factors for oil and gas production in general. Health effects among oil and gas development workers engaged in well stimulation should be monitored and evaluated to determine specific occupational health risk factors and harm-mitigation strategies to reduce the risk of deaths and serious injuries.

The current scientific literature and well stimulation chemical data available in California reveals that many of the well-stimulation-associated hazards have not been adequately characterized, nor have the associated environmental public health or occupational health risks been adequately analyzed—an observation that has been made by others (Adgate et al., 2014; Law et al., 2014; Kovats et al., 2014; New York Department of Health, 2014; NRC, 2014; Shonkoff et al., 2014). Studies of public health risk have failed to make clear whether the impact is caused by well stimulation or by oil development that is enabled by stimulation. Studies of health risks that differentiate the cause of the hazard would remedy this.

One of the most prominent key findings from our efforts to assess hazards is the significance of data gaps and the uncertainty that arises from these gaps in our confidence about characterizing human health risks for California.

This scientific literature review and hazard assessment, as well as other chapters in this volume, indicates that there are a number of potential human health hazards associated with well-stimulation-enabled oil and gas development in California with regards to air quality, water quality, and environmental exposure pathways. Our review also found that California-specific scientific assessments and datasets more generally on air, water, and human health are sparse. Additionally, human health monitoring data have not been adequately collected, let alone pursued. The hazard assessment of California-specific datasets on well stimulation chemistry indicates that more than half of the chemical constituents of stimulation fluids in California do not have any toxicity and/or use frequency or quantity information available, rendering it challenging to conclusively assess the magnitude of human health hazards associated with these processes. The emission of criteria and hazardous air pollutants have also only been monitored on the regional scale, and even in cases when these air pollutant emission factors are known, it is not possible, with the data available, to determine local emissions, community exposures, and subsequent population health risks.

We identified mitigation options that may reduce the magnitude of public health risks associated with well-stimulation-enabled oil and gas development in California; however, proper monitoring and enforcement are important components of sound mitigation that are often overlooked. Moreover, the data gaps that we identified create challenges in producing an adequately detailed assessment to provide clear guidance on the protection of public health, in the context of well-stimulation-enabled oil and gas development in California.

6.11. Recommendations

This chapter provides findings about what can and cannot be determined about potential impacts of well stimulation technology on human health, based on currently available information. One of the challenges that arise in efforts to study health risks for well-stimulation-enabled oil and gas development is the lack information available to carry out a standard hazard assessment and a broader risk characterization that requires information on exposure and dose-response. Here, we provide recommendations to address these information gaps.

6.11.1. Recommendation Regarding Chemical Use

The majority of important potential direct impacts of well stimulation result from the use of well stimulation chemicals. The large number of chemicals used in well stimulation makes it very difficult to judge the risks posed by accidental releases of stimulation fluids, such as those related to surface spills or unexpected subsurface pathways. Of the chemicals used, many are not sufficiently characterized to allow a full risk analysis.

Recommendation: *Operators should report the unique CASRN identification for all chemicals used in hydraulic fracturing and acid stimulation and the use of chemicals with unknown environmental profiles should be disallowed. The overall number of different chemicals should be reduced, and the use of more hazardous chemicals and chemicals with poor environmental profiles should be reduced, avoided or disallowed. The chemicals used in hydraulic fracturing could be limited to those on an approved list that would consist only of those chemicals with known and acceptable environmental hazard profiles. Operators should apply Green Chemistry principles to the formulation of hydraulic fracturing fluids.*

6.11.2. Recommendation Regarding Exposure and Health-Risk Information Gaps

This chapter identifies information gaps on hazards of substances used, the quantities and, in some cases, the identity of chemicals used for acidization and hydraulic fracturing, the magnitude of air emissions of well stimulation chemicals and fugitive emissions of oil and gas constituents, exposure pathways, and availability of acute and (in particular) chronic dose-response information.

Recommendation: *Conduct integrated research that cuts across multiple scientific disciplines and policy interests at relevant temporal and spatial scales in California, to answer key questions about the community and occupational impacts of oil and gas production enabled by well stimulation. Provide verification and validation of reported chemical use data, and conduct research to characterize the fate and transport of both intentional and unintentional chemical releases during well stimulation activities.*

6.11.3. Recommendation on Community Health

Oil and gas development—including that enabled by well stimulation—creates the risk of exposing human populations to a broad range of potentially hazardous substances (chemical and biological) or physical hazards (e.g., light and noise). For many of these hazards, we conclude that regional impacts associated with well stimulation activity are likely to be low, but exposures that can occur near well stimulation activity and enabled oil and gas development may result in elevated community health risks.

Recommendation: *Initiate studies in California to assess public health as a function of proximity to all oil and gas development, not just stimulated wells, and develop policies, for example science-based surface setbacks, to limit exposures.*

6.11.4. Recommendation on Occupational Health

Workers who are involved in oil and gas operations are exposed to chemical and physical hazards, some of which are specific to well stimulation activities, and many of which are general to the industry. Our review identified studies confirming occupational hazards related to well stimulation in states outside of California. There have been two peer-reviewed studies of occupational exposures attributable to hydraulic fracturing conducted by the National Institute for Occupational Safety and Health (NIOSH) across multiple states (not including California) and times of year. One of the studies found that respirable silica (silica sand is used as a proppant to hold open fractures formed in hydraulic fracturing) was in concentrations well in excess of occupational health and safety standards, in this case permissible exposure limits (PELs), by factors of as much as ten. Exposures exceeded PELs even when workers reported use of personal protective equipment. The second study found exposure to VOCs, especially benzene, above recommended occupational levels. The NIOSH studies are relevant for identifying hazards that could be significant for California workers, but no study to date has addressed occupational hazards associated with hydraulic fracturing and other forms of well stimulation in California.

Employers in the oil and gas industry must comply with existing California occupational safety and health regulations, and follow best practices to reduce and eliminate illness and injury risk to their employees. Employers can and often do implement comprehensive worker-protection programs that substantially reduce worker exposure and likelihood of illness and injury, but the effectiveness of these programs in California has not been evaluated. Engineering controls that reduce emissions could protect workers involved in well stimulation operations from chemical exposures and potentially reduce the likelihood of chemical exposure to the surrounding community.

Recommendation: *Design and execute California-based studies focused on silica and volatile organic compound exposures to workers engaged in hydraulic-fracturing-enabled oil and gas development processes, based on the NIOSH occupational health findings and protocols.*

6.12. References

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